# Supporting Information

## Visible-Light-Driven External-Photocatalyst-Free Alkylative Carboxylation of Alkenes With $CO_2$

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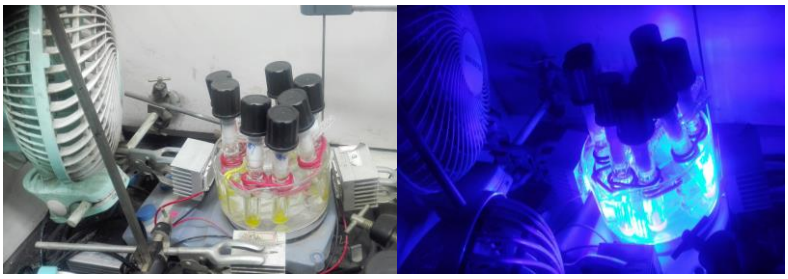
# 1. General considerations

All reactions were set up using standard Schlenk techniques and carried out under nitrogen or carbon dioxide atmosphere with anhydrous solvents, unless otherwise noted. Anhydrous solvents, including DMSO, DMA, DMF (99%+, Extra dry AcroSeal®), were purchased from Acros Organics and used as received. Commercially available chemicals were obtained from J&K, Across, TCI or Adamas and used as received unless otherwise stated. $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on a Brüker Advance 400 spectrometer ($^{1}H$: 400 MHz, $^{13}C$: 101 MHz and $^{19}F$ NMR: 376 MHz). Chemical shifts (δ) for $^{1}H$, $^{13}C$, and $^{19}F$ NMR spectra are given in ppm relative to TMS, the residual solvent signals were used as references for $^{1}H$ and $^{13}C$ NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$): δ H = 7.26 ppm, δ C = 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics MicroTOF-Q II. UPLC yields were recorded on waters ACQUITY UPLC M-Class. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2± 0.03 mm using UV light (254 nm) as a visualizing agent and phosphomolybdic acid in ethanol or iodine in silica gel as developing agents. Visible light irradiation was performed with a 30 W LED Light at $\lambda_{ir}$ = 450 ± 10 nm) for photocatalytic reactions.

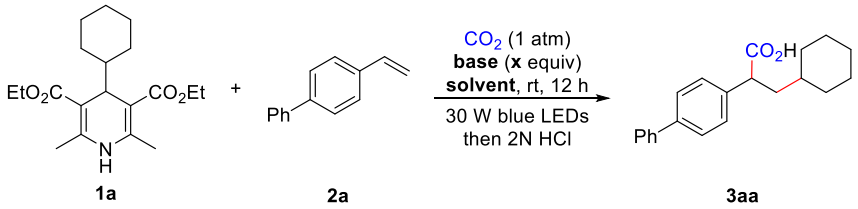
## 2. Optimization details

**Procedure for reaction optimization of diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate 1a with 4-vinyl-1,1'-biphenyl 2a:** The oven-dried Schlenk tube (25 mL) containing a stirring bar was charged with **1a** and **2a**, and transferred to glovebox to add base. The tube was then evacuated and back-filled with $CO_2$ for 3 times. Subsequently, solvent was added under $CO_2$. The reaction was stirred in water bath and irradiated with a 30 W blue LED lamp (3 cm away, with cooling fan to keep the reaction temperature at 25~30 °C) for a certain time. The resulting mixture was quenched by 2 mL of 2 N HCl (aq.), 4 mL of $H_2O$ and diluted with 4 mL of EtOAc and then stirred for 10 min and extracted by EtOAc for 4 times and the combined organic phases were concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography ($CH_2Cl_2$ as eluent) to give the pure desired product **3aa**.



**Blue LED reactors**

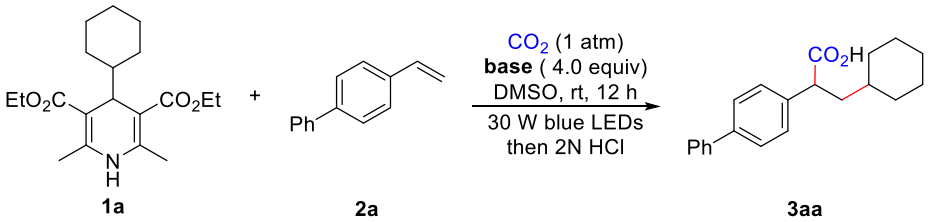
**Table S1: Screen of bases and solvents based on our previous report**[1]




| Entry | **base** | **x** | **solvent** | Yield of **3aa** (%)[a] |
|---|---|---|---|---|
| 1 | NaO$^t$Bu | 2.5 | NMP | 56 |
| 2 | LiO$^t$Bu | 2.5 | NMP | 75[b] |
| 3 | LiO$^t$Bu | 2.5 | DMSO | 72[b] |
| 4 | LiO$^t$Bu | 3.0 | DMSO | 79 |
| 5 | LiO$^t$Bu | 4.0 | DMSO | 88 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), **base** (**x** equiv), $CO_2$ (1 atm), **solvent** (3.0 mL), 30 W blue LEDs, room temperature (rt), 12 h, and isolated yields were given. NMP = *N*-Methyl-2-pyrrolidone, DMSO = dimethyl sulfoxide. [b]For Entry 2-3: NMP has a very high boiling point (202 ºC) results in trace solvent impurities in the product **3aa**, in contrast, DMSO (b.p. =189 ºC) can be completely evaporated by rotary evaporation. Despite the higher yield of NMP as the solvent, DMSO was chosen.

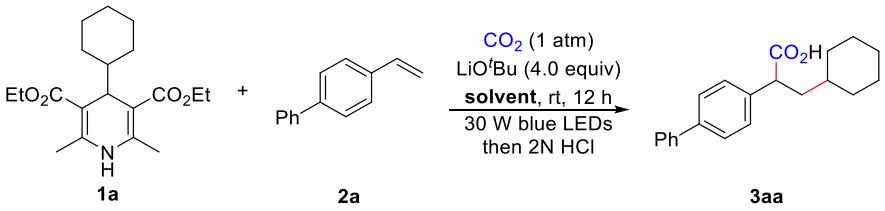
**Table S2: Screening of bases**




| Entry | **base** (4.0 equiv) | Yield of **3aa** (%)[a] |
|---|---|---|
| 1 | LiO$^t$Bu | 88 |
| 2 | KO$^t$Bu | 79 |
| 3 | NaO$^t$Bu | 70 |
| 4 | CsF | 82 |
| 5 | LiO$^t$Bu (3.0 equiv) | 79 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), **base** (4.0 equiv), $CO_2$ (1 atm), DMSO (3.0 mL), 30 W blue LEDs, rt, 12 h, and isolated yields were given. DMSO = imethyl sulfoxide.

**Table S3: Screening of solvents**

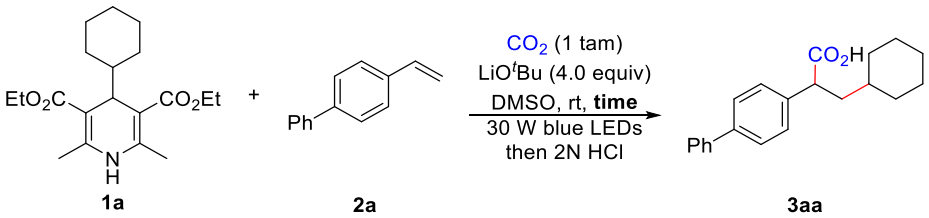



| Entry | **solvent** (3.0 mL) | Yield of **3aa** (%)[a] |
|---|---|---|
| 1 | DMSO | 88 |
| 2 | DMF | 67 |
| 3 | DMAc | 77 |
| 4 | DMSO (2.0 mL) | 80 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), LiO$^t$Bu (4.0 equiv), $CO_2$ (1 atm),

**solvent** (3.0 mL), 30 W blue LEDs, rt, 12 h, and isolated yields were given. DMSO = dimethyl sulfoxide, DMF = *N*,*N*-dimethylformamide, DMAc = *N*,*N*-dimethylacetamide.

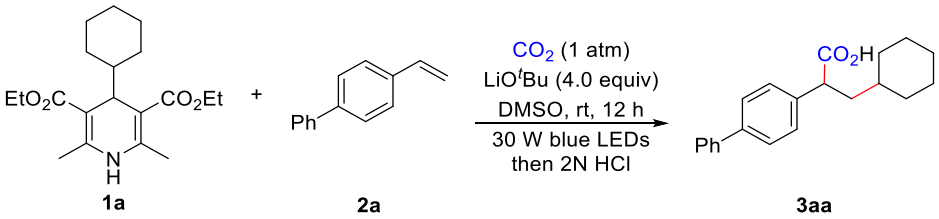
**Table S4: Screening of reaction time**




| Entry | **time** (h) | Yield of **3aa** (%)[a] |
|---|---|---|
| 1 | 3 | 60 |
| 2 | 6 | 72 |
| 3 | 9 | 85 |
| 4 | 12 | 88 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), LiO$^t$Bu (4.0 equiv), $CO_2$ (1 atm), DMSO (3.0 mL), 30 W blue LEDs, rt, **time** (h), and isolated yields were given. DMSO = dimethyl sulfoxide.

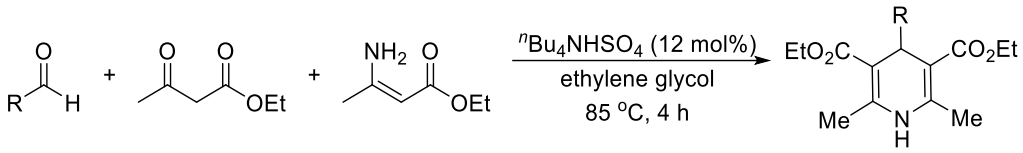
**Table S5: Control experiments**




| Entry | Variation from standard conditions | Yield of **3aa** (%)[a] |
|---|---|---|
| 1 | none | 88 |
| 2 | w/o light | N.D. |
| 3 | w/o LiO$^t$Bu | N.D. |
| 4 | $N_2$ instead of $CO_2$ | N.D. |
| 5 | 0.5 mol% *fac*-Ir(ppy)$_3$ as additive | 89 |
| 6 | 0.5 mol% 4CzIPN as additive | 92 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), LiO$^t$Bu (4.0 equiv), $CO_2$ (1 atm), DMSO (3.0 mL), 30 W blue LEDs, rt, 12 h, and isolated yields were given. w/o = without, N.D. = not detected. DMSO = dimethyl sulfoxide.

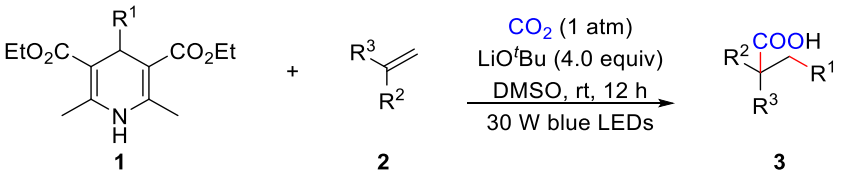
## 3. Synthesis of 4-alkyl-1,4-dihydropyridines




4-alkyl-1,4-dihydropyridines were synthesized according to literature report[2-5]. The spectral data is consistent with the literature data.

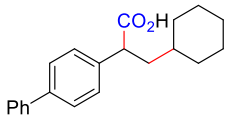
## 4. Experimental Procedures

**General Procedure A** (for reactions of 4-alkyl-DHPs **1** with alkenes **2**):



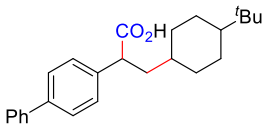

To an oven-dried Schlenk tube (25 mL) containing a stirring bar was charged with **1** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv, if solid) and transferred to glovebox to add Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv). The tube was then evacuated and back-filled with $CO_2$ for three times. Subsequently, **2** (if liquid) and DMSO (3.0 mL) were added under $CO_2$. The reaction was stirred in water bath and irradiated with a 30 W blue LED lamp (3 cm away, with cooling fan to keep the reaction temperature at 25~30 °C) for 12 hours. The resulting mixture was quenched by 2 mL of 2 N HCl (aq.), 4 mL of $H_2O$ and diluted with 4 mL of EtOAc and then stirred for 10 min and extracted by EtOAc for 4 times and the combined organic phases were concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography ($CH_2Cl_2$ as eluent) to give the pure desired product **3**.

The following compounds are new, tabulated $^1$H NMR, $^{13}$C NMR data and $^{19}$F NMR (if F-atom contained), HRMS data, NMR spectrum are provided.

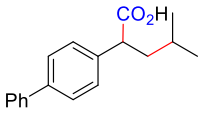



**2-([1,1'-biphenyl]-4-yl)-3-cyclohexylpropanoic acid (3aa):** According to the general

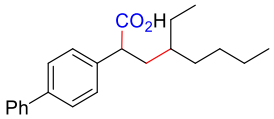
procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (54.2 mg, 0.176 mmol, 88%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.56 (ddt, *J* = 10.6, 8.6, 1.9 Hz, 4H), 7.46 – 7.36 (m, 4H), 7.36 – 7.30 (m, 1H), 3.75 (t, *J* = 7.8 Hz, 1H), 2.01 (dt, *J* = 13.7, 7.6 Hz, 1H), 1.80 – 1.56 (m, 6H), 1.27 – 1.12 (m, 4H), 0.92 (qd, *J* = 11.0, 2.6 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.02, 140.67, 140.30, 137.77, 128.74, 128.47, 127.37, 127.27, 127.06, 77.33, 77.01, 76.70, 48.26, 40.60, 35.09, 33.26, 32.92, 26.44, 26.05, 26.01; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{21}H_{23}O_2]^-$: 307.1704, found: 307.1710.



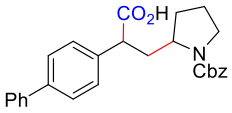

**2-([1,1'-biphenyl]-4-yl)-3-(4-(*tert*-butyl)cyclohexyl)propanoic acid (3ba):** According to the general procedure A, in $CO_2$ atmosphere **1b** (78.3 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (64.6 mg, 0.171 mmol, 86%). **$^1$H NMR** (400 MHz, $CDCl_3$) **(cis : trans = 2 : 3)**[6]: δ .64 – 7.48 (m, 4H), 7.46 – 7.26 (m, 5H), 3.74 (t, *J* = 7.8 Hz, 0.4H), 3.65 (t, *J* = 7.8 Hz, 0.6H), 2.17 (dt, *J* = 14.2, 7.5 Hz, 0.6H), 1.99 (dt, *J* = 14.7, 7.5 Hz, 0.4H), 1.85 (dd, *J* = 13.8, 7.1 Hz, 1H), 1.76 – 1.59 (m, 3H), 1.57 – 1.33 (m, 3H), 1.19 – 1.00 (m, 2H), 0.93 (d, *J* = 11.8 Hz, 2H), 0.81 (d, *J* = 6.1 Hz, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.45, 180.42, 140.67, 140.41, 140.32, 137.76, 137.60, 128.74, 128.59, 128.48, 127.40, 127.38, 127.29, 127.07, 127.06, 77.33, 77.01, 76.70, 49.23, 48.47, 48.07, 40.56, 35.21, 34.26, 33.71, 33.38, 32.55, 32.39, 30.57, 30.21, 29.87, 27.55, 27.50, 27.02, 21.68, 21.58; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{25}H_{31}O_2]^-$: 363.2330, found: 363.2330.



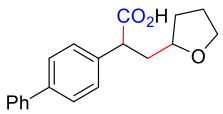

**2-([1,1'-biphenyl]-4-yl)-4-methylpentanoic acid (3ca):** According to the general procedure A, in $CO_2$ atmosphere **1c** (59.0 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (42.9 mg, 0.160 mmol, 80%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.62 – 7.50 (m, 4H), 7.47 – 7.38 (m, 4H), 7.38 – 7.29 (m, 1H), 3.71 (t, *J* = 7.8 Hz, 1H), 1.99 (dt, *J* = 13.6, 7.7 Hz, 1H), 1.73 (ddd, *J* = 14.0, 7.7, 6.7 Hz, 1H), 1.54 (dp, *J* = 13.5, 6.7 Hz, 1H), 0.93 (d, *J* = 6.6 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.12, 140.68, 140.37, 137.58, 128.73, 128.49, 127.37, 127.27, 127.05, 49.08, 41.98, 25.75, 22.59, 22.19.; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{18}H_{19}O_2]^-$: 267.1391, found: 267.1391.




**2-([1,1'-biphenyl]-4-yl)-4-ethyloctanoic acid (3da):** According to the general procedure A, in $CO_2$ atmosphere **1d** (70.0 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (51.2 mg, 0.158 mmol, 79%). **$^1$H NMR** (400 MHz, $CDCl_3$) **mixture of diastereomers**: δ 7.62 – 7.51 (m, 4H), 7.48 – 7.37 (m, 4H), 7.37 – 7.28 (m, 1H), 3.71 (td, *J* = 7.7, 1.6 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.76 (tdd, *J* = 10.5, 6.3, 2.7 Hz, 1H), 1.33 (ddt, *J* = 7.1, 5.4, 2.0 Hz, 2H), 1.30 – 1.18 (m, 7H), 0.93 – 0.76 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.55, 180.53, 140.70, 140.69, 140.33, 137.78, 137.72, 128.74, 128.54, 128.52, 127.36, 127.28, 127.06, 77.34, 77.02, 76.70, 48.92, 36.92, 36.83, 36.28, 36.20, 32.47, 32.29, 28.46, 28.29, 25.57, 25.39, 23.07, 23.02, 14.12, 14.11, 10.40, 10.26; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{22}H_{27}O_2]^-$: 323.2017, found: 323.2010. Diastereoisomers were determined by crude **$^1$H NMR** analysis as 1.0.

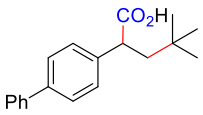



**2-([1,1'-biphenyl]-4-yl)-3-(1-((benzyloxy)carbonyl)pyrrolidin-2-yl)propanoic acid (3ea):** According to the general procedure A, in $CO_2$ atmosphere **1e** (91.2 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography (petroleum ether/EtOAc 10/1/0.1% HOAc) as a colorless oil (67.8 mg, 0.158 mmol, 79%). **$^1$H NMR** (400 MHz, $CDCl_3$) **mixture of diastereomers and rotamers:** δ 7.97 (b, 1H), 7.75 – 7.19 (m, 4H), 5.28 – 5.01 (m, 2H), 4.15 – 3.57 (m, 2H), 3.59 – 3.32 (m, 2H), 2.76 – 2.61 (m, 0.6H), 2.43 – 2.29 (m, 0.4H), 2.24 – 2.06 (m, 0.5H), 1.98 – 1.72 (m, 3.8H), 1.67 – 1.56 (m, 0.7H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) **mixture of diastereomers and rotamers**: δ 178.50, 178.32, 177.96, 155.21, 140.67, 140.43, 136.75, 128.78, 128.78, 128.76, 128.60, 128.51, 128.10, 127.85, 127.40, 127.07, 67.15, 66.97, 66.86, 56.42, 56.01, 55.14, 48.52, 48.35, 46.63, 46.38, 46.13, 38.08, 37.50, 36.98, 31.19, 30.73, 30.45, 23.72, 22.91; **HRMS (ESI+)** $[M+H]^+$ calculated m/z for $[C_{27}H_{28}NO_4]^+$: 430.2013, found: 430.2016. Diastereoisomers were determined by crude **$^1$H NMR** analysis as 1.1.

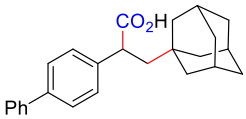



**2-([1,1'-biphenyl]-4-yl)-3-(tetrahydrofuran-2-yl)propanoic acid (3fa):** According to the general procedure A, in $CO_2$ atmosphere **1f** (64.6 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (47.9 mg, 0.162 mmol, 81%). **$^1$H NMR** (400 MHz, $CDCl_3$) **mixture of diastereomers**: δ 7.61 – 7.49 (m, 4H), 7.41 (t, $J$ = 7.8 Hz, 4H), 7.32 (t, $J$ = 7.3 Hz, 1H), 3.87 (dh, $J$ = 21.2, 7.0, 6.4 Hz, 2.5H), 3.72 (dq, $J$ = 13.7, 7.7 Hz, 1.5H), 2.39 – 2.24 (m, 1H), 2.04 – 1.77 (m, 4H), 1.53 – 1.44 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) **mixture of diastereomers:** δ 179.37, 178.84, 140.67,

140.66, 140.38, 140.35, 137.80, 137.21, 128.74, 128.72, 128.32, 127.45, 127.41, 127.28, 127.28, 127.06, 127.05, 77.35, 77.03, 76.88, 76.72, 76.30, 67.79, 67.57, 48.41, 48.03, 39.06, 38.83, 31.51, 31.41, 25.63, 25.60; **HRMS (ESI-)** $[M\text{-}CO_2\text{-}H]^-$ calculated m/z for $[C_{18}H_{19}O]^-$: 251.1441, found: 251.1443. Diastereoisomers were determined by crude **$^1$H NMR** analysis as 1.2.

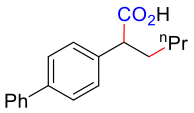



**2-([1,1'-biphenyl]-4-yl)-4,4-dimethylpentanoic acid** (**3ga**)**:** According to the general procedure A, in $CO_2$ atmosphere **1g** (61.8 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (36.1 mg, 0.128 mmol, 64%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.58 – 7.49 (m, 4H), 7.43 – 7.35 (m, 4H), 7.34 – 7.29 (m, 1H), 3.69 (dd, $J$ = 8.8, 4.2 Hz, 1H), 2.30 (dd, $J$ = 14.0, 8.7 Hz, 1H), 1.64 (dd, $J$ = 14.0, 4.1 Hz, 1H), 0.91 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 140.66, 140.22, 139.33, 128.72, 128.33, 127.39, 127.26, 127.04, 77.31, 77.00, 76.68, 47.57, 46.89, 31.10, 29.41; **HRMS (ESI-)** $[M\text{-}CO_2\text{-}H]^-$ calculated m/z for $[C_{18}H_{21}]^-$: 237.1649, found: 237.1655.

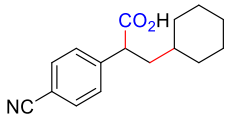



**2-([1,1'-biphenyl]-4-yl)-3-(adamantan-1-yl)propanoic acid** (**3ha**)**:** According to the general procedure A, in $CO_2$ atmosphere **1h** (77.5 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (55.5 mg, 0.154 mmol, 77%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.63 – 7.48 (m, 4H), 7.45 – 7.35 (m, 4H), 7.32 (t, $J$ = 7.3 Hz, 1H), 3.75 (dd, $J$ = 8.7, 4.0 Hz, 1H), 2.17 (dd, $J$ = 14.1, 8.8 Hz, 1H), 1.92 (s, 3H), 1.72 – 1.56 (m, 6H), 1.56 – 1.38 (m, 7H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.46, 140.67, 140.15, 139.53, 128.72, 128.35, 127.37, 127.25, 127.04, 77.32, 77.01, 76.69,

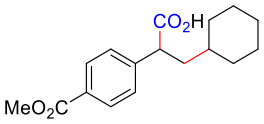
47.61, 45.69, 42.24, 36.90, 32.97, 28.53; **HRMS (ESI-)** [M-$CO_2$-H]$^-$ calculated m/z for [$C_{24}H_{27}$]$^-$: 315.2118, found: 315.2112.



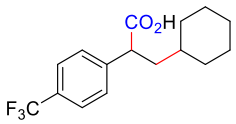

**2-([1,1'-biphenyl]-4-yl)hexanoic acid** (**3ia**)**:** According to the general procedure A, in $CO_2$ atmosphere **1i** (59 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (17.0 mg, 0.063mmol, 32%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 4H), 7.45 – 7.36 (m, 4H), 7.36 – 7.29 (m, 1H), 3.58 (t, *J* = 7.7 Hz, 1H), 2.17 – 2.00 (m, 1H), 1.88 – 1.72 (m, 1H), 1.36 – 1.26 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H).; **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 180.04, 140.67, 140.34, 137.58, 128.72, 128.44, 127.35, 127.26, 127.05, 51.19, 32.79, 29.63, 22.44, 13.87. **ESI-MS:** [M-H]$^-$ calculated m/z for [$C_{18}H_{19}O_2$]$^-$: 267.13, found: 267.45.



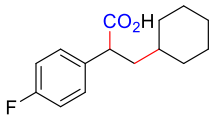

**2-(4-cyanophenyl)-3-cyclohexylpropanoic acid** (**3ab**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2b** (36.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (49.9 mg, 0.194 mmol, 97%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.63 – 7.54 (m, 2H), 7.44 – 7.37 (m, 2H), 3.73 (t, *J* = 7.8 Hz, 1H), 1.95 (dt, *J* = 13.8, 7.6 Hz, 1H), 1.75 – 1.54 (m, 6H), 1.09 (dtd, *J* = 14.6, 10.6, 6.0 Hz, 4H), 0.94 – 0.81 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 179.33, 143.91, 132.45, 128.99, 118.58, 111.38, 77.34, 77.03, 76.71, 48.78, 40.49, 35.06, 33.21, 32.70, 26.29, 25.96, 25.92; **HRMS (ESI-)** [M-H]$^-$ calculated m/z for [$C_{16}H_{18}NO_2$]$^-$: 256.1343, found: 256.1345.



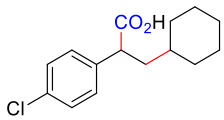

**3-cyclohexyl-2-(4-(methoxycarbonyl)phenyl)propanoic acid (3ac):** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2c** (48.6 mg, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (56.9 mg, 0.196 mmol, 98%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 3.88 (s, 3H), 3.74 (t, *J* = 7.8 Hz, 1H), 1.95 (dt, *J* = 14.6, 7.5 Hz, 1H), 1.74 – 1.55 (m, 6H), 1.10 (q, *J* = 8.2 Hz, 4H), 0.93 – 0.81 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 179.65, 166.87, 143.83, 129.93, 129.24, 128.18, 77.33, 77.01, 76.70, 52.14, 48.70, 40.49, 35.07, 33.25, 32.76, 26.36, 26.00, 25.96; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{17}H_{21}O_4]^-$: 289.1445, found: 289.1449.



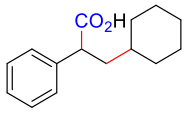

**3-cyclohexyl-2-(4-(trifluoromethyl)phenyl)propanoic acid (3ad):** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2d** (44.0 μL, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (54.6 mg, 0.182 mmol, 91%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 3.79 (t, *J* = 7.8 Hz, 1H), 2.01 (dt, *J* = 13.8, 7.5 Hz, 1H), 1.79 – 1.62 (m, 6H), 1.17 (pd, *J* = 8.0, 7.3, 3.9 Hz, 4H), 0.94 (qd, *J* = 12.2, 11.6, 3.4 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 179.83, 142.55, 130.18, 129.86, 129.54, 128.50, 128.09, 125.64, 125.60, 125.57, 125.53, 125.39, 122.68, 77.31, 76.99, 76.67, 48.53, 40.54, 35.02, 33.23, 32.75, 26.33, 25.97, 25.93; **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -62.57; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{16}H_{18}F_3O_2]^-$: 299.1264, found: 299.1266.




**3-cyclohexyl-2-(4-fluorophenyl)propanoic acid** (**3ae**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2e** (36.0 μL, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a yellow solid (35.5 mg, 0.142 mmol, 71%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.31 – 7.22 (m, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 3.66 (t, *J* = 7.8 Hz, 1H), 1.92 (dt, *J* = 13.7, 7.5 Hz, 1H), 1.74 – 1.50 (m, 6H), 1.11 (qd, *J* = 9.0, 7.2, 3.7 Hz, 4H), 0.95 – 0.80 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.44, 163.30, 160.85, 134.32, 134.29, 129.65, 129.57, 115.60, 115.38, 77.33, 77.01, 76.69, 47.86, 40.65, 34.99, 33.26, 32.77, 26.39, 26.03, 25.98; **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -115.22; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{15}H_{18}FO_2]^-$: 249.1296, found: 249.1295.

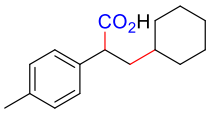



**2-(4-chlorophenyl)-3-cyclohexylpropanoic acid** (**3af**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2f** (36.0 μL, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a yellow oil (28.2 mg, 0.106 mmol, 53%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 2H), 3.65 (t, *J* = 7.8 Hz, 1H), 1.91 (dt, *J* = 13.8, 7.6 Hz, 1H), 1.73 – 1.55 (m, 6H), 1.18 – 1.05 (m, 4H), 0.89 (dd, *J* = 14.4, 9.9 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 179.47, 137.08, 133.25, 129.43, 128.79, 77.31, 76.99, 76.68, 47.92, 40.52, 34.99, 33.27, 32.74, 26.37, 26.01, 25.96; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{15}H_{18}ClO_2]^-$: 265.1001, found: 265.1001.

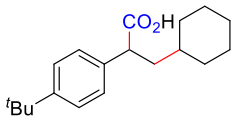



**3-cyclohexyl-2-phenylpropanoic acid** (**3ag**)**:** According to the general procedure A,

in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2g** (35.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (28.8 mg, 0.124 mmol, 62%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 4.4 Hz, 4H), 7.27 (dd, *J* = 8.1, 3.3 Hz, 1H), 3.69 (t, *J* = 7.8 Hz, 1H), 2.02 – 1.90 (m, 1H), 1.77 – 1.58 (m, 6H), 1.22 – 1.07 (m, 4H), 0.89 (q, *J* = 11.1 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.45, 138.72, 128.63, 128.07, 127.36, 77.33, 77.01, 76.69, 48.63, 40.57, 35.06, 33.24, 32.89, 26.44, 26.04, 26.00; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{15}H_{19}O_2]^-$: 231.1391, found: 231.1394.

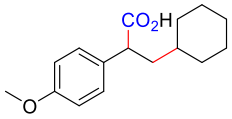



**3-cyclohexyl-2-(p-tolyl)propanoic acid (3ah):** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2h** (40.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (33.5 mg, 0.136 mmol, 68%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.64 (t, *J* = 7.8 Hz, 1H), 2.31 (s, 3H), 1.92 (dt, *J* = 13.7, 7.6 Hz, 1H), 1.74 – 1.56 (m, 6H), 1.13 (ddd, *J* = 14.9, 7.0, 3.7 Hz, 4H), 0.88 (tdt, *J* = 11.8, 8.1, 3.1 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.74, 137.05, 135.71, 129.34, 127.92, 77.34, 77.02, 76.71, 48.19, 40.51, 35.00, 33.27, 32.88, 26.46, 26.05, 26.00, 21.09; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{16}H_{21}O_2]^-$: 245.1547, found: 245.1546.

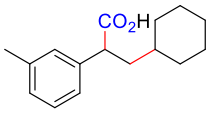



**2-(4-(*tert*-butyl)phenyl)-3-cyclohexylpropanoic acid (3ai):** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2i** (55.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography

($CH_2Cl_2$ as eluent) as a colorless oil (38.0 mg, 0.132 mmol, 66%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.34 – 7.29 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 3.69 – 3.63 (m, 1H), 1.97 (ddd, *J* = 13.9, 8.4, 6.9 Hz, 1H), 1.75 – 1.58 (m, 6H), 1.29 (s, 9H), 1.24 – 1.10 (m, 4H), 0.94 – 0.83 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.71, 150.15, 135.71, 127.61, 125.53, 77.32, 77.00, 76.69, 48.17, 40.65, 35.12, 34.43, 33.12, 33.07, 31.32, 26.46, 26.04, 26.01; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{19}H_{27}O_2]^-$: 287.2017, found: 287.2019.

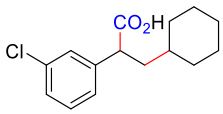



**3-cyclohexyl-2-(4-methoxyphenyl)propanoic acid** (**3aj**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2j** (40.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (32.5 mg, 0.124 mmol, 62%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 2H), 6.88 – 6.80 (m, 2H), 3.77 (s, 3H), 3.62 (t, *J* = 7.8 Hz, 1H), 1.90 (dt, *J* = 13.7, 7.6 Hz, 1H), 1.66 (dtt, *J* = 24.1, 14.7, 5.0 Hz, 6H), 1.23 – 1.05 (m, 4H), 0.87 (tdq, *J* = 15.5, 7.5, 3.9, 3.5 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.71, 158.80, 130.74, 129.06, 113.99, 77.33, 77.01, 76.69, 55.23, 47.74, 40.56, 34.99, 33.29, 32.84, 26.45, 26.06, 26.01; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{16}H_{21}O_3]^-$: 261.1496, found: 261.1497.

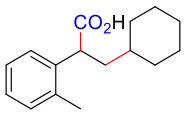



**3-cyclohexyl-2-(m-tolyl)propanoic acid** (**3ak**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2k** (40.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (29.5 mg, 0.120 mmol, 60%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 2H), 6.88 – 6.80 (m, 2H), 3.77 (s, 3H), 3.62 (t, *J* = 7.8 Hz, 1H), 1.90 (dt, *J* = 13.7, 7.6 Hz, 1H), 1.66 (dtt, *J* = 24.1, 14.7, 5.0 Hz, 6H), 1.23 – 1.05 (m, 4H),

0.87 (tdq, $J$ = 15.5, 7.5, 3.9, 3.5 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.71, 158.80, 130.74, 129.06, 113.99, 77.33, 77.01, 76.69, 55.23, 47.74, 40.56, 34.99, 33.29, 32.84, 26.45, 26.06, 26.01; **HRMS (ESI-)** [M-H]$^-$ calculated m/z for $[C_{16}H_{21}O_2]^-$: 245.1547, found: 256.1547.

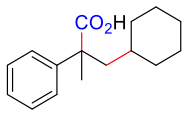



**2-(3-chlorophenyl)-3-cyclohexylpropanoic acid (3al):** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2l** (38.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a yellow oil (37.8 mg, 0.142 mmol, 71%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.31 (q, $J$ = 1.4 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.19 (hd, $J$ = 4.5, 2.3 Hz, 1H), 3.65 (t, $J$ = 7.8 Hz, 1H), 1.94 (dt, $J$ = 13.7, 7.6 Hz, 1H), 1.75 – 1.56 (m, 6H), 1.13 (qdt, $J$ = 13.1, 9.5, 4.9 Hz, 4H), 0.96 – 0.81 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.01, 140.58, 134.43, 129.85, 128.22, 127.63, 126.37, 77.32, 77.01, 76.69, 48.38, 40.50, 35.03, 33.20, 32.83, 26.38, 26.00, 25.96; **HRMS (ESI-)** [M-H]$^-$ calculated m/z for $[C_{15}H_{18}ClO_2]^-$: 265.1001, found: 265.1003.

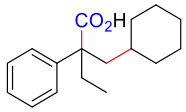



**3-cyclohexyl-2-(o-tolyl)propanoic acid (3am):** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2m** (39.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (29.5 mg, 0.120 mmol, 60%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.32 (dt, $J$ = 7.0, 1.5 Hz, 1H), 7.22 – 7.05 (m, 3H), 3.96 (dd, $J$ = 8.5, 6.5 Hz, 1H), 2.38 (s, 3H), 2.06 – 1.94 (m, 1H), 1.79 – 1.70 (m, 2H), 1.70 – 1.62 (m, 3H), 1.58 (dd, $J$ = 13.8, 6.8 Hz, 2H), 1.25 – 1.03 (m, 4H), 0.98 – 0.82 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.63, 137.39, 136.16, 130.52, 127.07, 126.89, 126.40, 77.33, 77.01, 76.70,

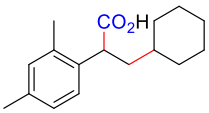
43.85, 40.32, 35.40, 33.37, 33.18, 26.45, 26.08, 26.06, 19.85; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{16}H_{21}O_2]^-$: 245.1547, found: 245.1549.



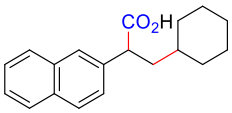

**3-cyclohexyl-2-methyl-2-phenylpropanoic acid** (**3an**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2m** (39.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (25.6 mg, 0.104 mmol, 52%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ7.44 – 7.35 (m, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.25 – 7.20 (m, 1H), 2.03 (dd, J = 14.0, 6.0 Hz, 1H), 1.80 (dd, J = 14.0, 5.1 Hz, 1H), 1.64 (d, J = 11.8 Hz, 2H), 1.58 (s, 3H), 1.43 (d, J = 13.9 Hz, 1H), 1.34 – 1.23 (m, 2H), 1.19 – 0.83 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 182.61, 143.64, 128.30, 126.84, 126.13, 77.32, 77.00, 76.68, 49.65, 46.12, 35.17, 34.57, 34.26, 26.40, 26.37, 26.18, 22.32; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{16}H_{21}O_2]^-$: 245.1547, found: 245.1547.



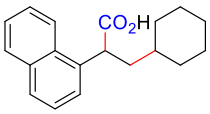

**2-(cyclohexylmethyl)-2-phenylbutanoic acid** (**3ao**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2o** (45.0 μL, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (25.5 mg, 0.098 mmol, 49%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ .36 – 7.25 (m, 4H), 7.22 (ddd, *J* = 8.4, 4.4, 2.5 Hz, 1H), 2.14 – 2.05 (m, 2H), 2.00 (dd, *J* = 14.2, 6.0 Hz, 1H), 1.91 (dd, *J* = 14.2, 5.2 Hz, 1H), 1.62 – 1.51 (m, 4H), 1.38 (d, *J* = 13.1 Hz, 1H), 1.23 – 1.05 (m, 4H), 1.00 – 0.86 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 182.72, 142.33, 128.21, 126.71, 126.65, 53.56, 40.91, 35.02, 34.21, 33.91, 27.28, 26.42, 26.39, 26.19, 8.61; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{17}H_{23}O_2]^-$: 259.1704, found: 259.1704.



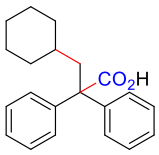

**3-cyclohexyl-2-(2,4-dimethylphenyl)propanoic acid** (**3ap**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2p** (44.0 μL, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a colorless oil (34.3 mg, 0.132 mmol, 66%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 6.8 Hz, 2H), 3.93 (dd, *J* = 8.4, 6.6 Hz, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.04 – 1.95 (m, 1H), 1.80 – 1.58 (m, 6H), 1.24 – 1.10 (m, 4H), 0.96 – 0.85 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.91, 136.65, 135.99, 134.38, 131.32, 127.09, 126.81, 43.55, 40.30, 35.35, 33.36, 33.22, 26.48, 26.08, 26.06, 20.95, 19.76; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{17}H_{23}O_2]^-$: 259.1704, found: 259.1702.



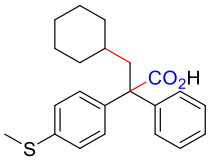

**3-cyclohexyl-2-(naphthalen-2-yl)propanoic acid** (**3aq**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2q** (46.3 mg, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (45.7 mg, 0.162 mmol, 81%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.36 – 7.25 (m, 4H), 7.22 (ddd, *J* = 8.4, 4.4, 2.5 Hz, 1H), 2.14 – 2.05 (m, 2H), 2.00 (dd, *J* = 14.2, 6.0 Hz, 1H), 1.91 (dd, *J* = 14.2, 5.2 Hz, 1H), 1.62 – 1.51 (m, 4H), 1.38 (d, *J* = 13.1 Hz, 1H), 1.23 – 1.05 (m, 4H), 1.00 – 0.86 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.45, 136.12, 133.38, 132.69, 128.37, 127.82, 127.61, 127.04, 126.15, 125.98, 125.88, 77.34, 77.02, 76.71, 48.78, 40.47, 35.05, 33.35, 32.84, 26.44, 26.04, 26.00; **HRMS (ESI-)** $[M-CO_2-H]^-$ calculated m/z for $[C_{18}H_{21}]^-$: 237.1649, found: 237.1632.



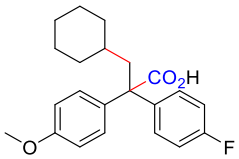

**3-cyclohexyl-2-(naphthalen-1-yl)propanoic acid** (**3ar**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2r** (46.3 mg, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (37.2 mg, 0.132 mmol, 66%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.39 (m, 4H), 4.54 (dd, *J* = 8.6, 6.3 Hz, 1H), 2.16 (ddd, *J* = 13.9, 8.6, 6.5 Hz, 1H), 1.91 – 1.56 (m, 6H), 1.31 (dtd, *J* = 14.7, 7.2, 3.7 Hz, 1H), 1.22 – 1.06 (m, 3H), 0.94 (qt, *J* = 11.7, 3.8 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.64, 135.02, 133.98, 131.55, 128.99, 127.90, 126.42, 125.63, 125.52, 125.01, 123.04, 43.59, 40.42, 35.58, 33.36, 33.15, 26.45, 26.08, 26.05; **HRMS (ESI-)** $[M\text{-}CO_2\text{-}H]^-$ calculated m/z for $[C_{18}H_{21}]^-$: 237.1649, found: 237.1640.



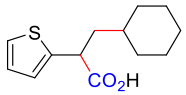

**3-cyclohexyl-2,2-diphenylpropanoic acid** (**3as**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2s** (53.0 μL, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (37.0 mg, 0.120 mmol, 60%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.38 – 7.32 (m, 4H), 7.31 – 7.23 (m, 6H), 2.29 (d, *J* = 5.1 Hz, 2H), 1.48 (dq, *J* = 8.5, 4.4, 3.5 Hz, 3H), 1.23 – 1.15 (m, 2H), 1.09 – 0.92 (m, 4H), 0.84 (q, *J* = 11.5, 11.0 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.74, 143.14, 129.13, 127.82, 126.86, 77.34, 77.02, 76.70, 59.86, 45.12, 34.63, 34.49, 26.37, 26.23; **HRMS (ESI-)** $[M\text{-}CO_2\text{-}H]^-$ calculated m/z for $[C_{20}H_{23}]^-$: 263.1805, found: 263.1802.



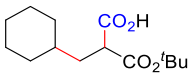

**3-cyclohexyl-2-(4-(methylthio)phenyl)-2-phenylpropanoic acid** (**3at**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2t** (67.8 mg, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (50.3 mg, 0.142 mmol, 71%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.33 – 7.24 (m, 7H), 7.18 – 7.14 (m, 2H), 2.46 (s, 3H), 2.26 (dd, *J* = 5.3, 1.7 Hz, 2H), 1.53 – 1.45 (m, 3H), 1.26 – 1.15 (m, 3H), 1.09 – 0.95 (m, 4H), 0.85 (tt, *J* = 13.7, 3.2 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.72, 143.03, 139.85, 137.03, 129.60, 129.00, 127.84, 126.88, 125.71, 59.42, 45.04, 34.59, 34.50, 34.45, 26.35, 26.21, 15.59; **HRMS (ESI+)** $[M+Na]^+$ calculated m/z for $[C_{22}H_{26}NaO_2S]^+$: 377.1546, found: 377.1532.



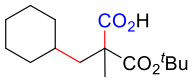

**3-cyclohexyl-2-(4-fluorophenyl)-2-(4-methoxyphenyl)propanoic acid** (**3au**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2u** (68.4 mg, 0.3 mmol, 1.5 equiv), Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a yellow oil (48.9 mg, 0.137 mmol, 67%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.31 – 7.22 (m, 4H), 6.99 – 6.91 (m, 2H), 6.86 – 6.78 (m, 2H), 3.79 (s, 3H), 2.28 (dd, J = 13.8, 5.3 Hz, 1H), 2.18 (dd, J = 13.8, 5.0 Hz, 1H), 1.50 (dd, J = 10.2, 3.7 Hz, 3H), 1.24 – 1.13 (m, 2H), 1.09 – 0.94 (m, 4H), 0.91 – 0.80 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 176.15, 158.00, 155.55, 153.68, 134.38, 134.34, 130.25, 126.02, 125.94, 125.28, 109.92, 109.70, 108.52, 53.85, 50.45, 40.59, 29.91, 29.79, 29.65, 21.66, 21.51, 21.35; **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -115.93. **HRMS (ESI-)** $[M-CO_2-H]^-$ calculated m/z for $[C_{21}H_{24}FO]^-$: 311.1817, found: 311.1792.




**3-cyclohexyl-2-(thiophen-2-yl)propanoic acid** (**3av**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2v** (33.1 mg, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a yellow oil (16.7 mg, 0.070 mmol, 35%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.20 (dd, *J* = 4.9, 1.5 Hz, 1H), 6.97 – 6.92 (m, 2H), 3.99 (t, *J* = 7.8 Hz, 1H), 1.96 (dt, *J* = 13.6, 7.5 Hz, 1H), 1.78 – 1.60 (m, 6H), 1.19 – 1.09 (m, 3H), 0.96 – 0.81 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 179.21, 141.03, 126.64, 125.60, 124.62, 43.91, 41.77, 35.04, 33.08, 32.81, 26.39, 26.02, 25.96; **HRMS (ESI+)** $[M+H]^+$ calculated m/z for $[C_{13}H_{19}O_2S]^+$: 239.1100, found: 239.1095.

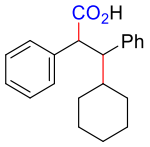



**3-(*tert*-butoxy)-2-(cyclohexylmethyl)-3-oxopropanoic acid** (**3aw**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2w** (44.0 μL, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a yellow oil (32.2 mg, 0.126 mmol, 63%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 3.38 (t, *J* = 7.6 Hz, 1H), 1.82 – 1.64 (m, 6H), 1.45 (s, 9H), 1.30 – 1.10 (m, 5H), 0.94 – 0.84 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 175.57, 169.10, 82.28, 77.31, 77.00, 76.68, 50.14, 36.36, 35.47, 32.92, 32.74, 27.84, 26.34, 26.05; **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{14}H_{23}O_4]^-$: 255.1602, found: 255.1601.

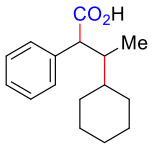



**3-(*tert*-butoxy)-2-(cyclohexylmethyl)-3-oxopropanoic acid** (**3ax**)**:** According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2x** (49.0

μL, 0.3 mmol, 1.5 equiv), LiO$^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a yellow oil (38.3 mg, 0.142 mmol, 71%). **$^1$H NMR** (400 MHz, $CDCl_3$): δ 1.83 (dd, *J* = 14.2, 6.0 Hz, 1H), 1.75 (dd, *J* = 14.2, 6.1 Hz, 1H), 1.65 – 1.59 (m, 4H), 1.44 (s, 9H), 1.40 (s, 3H), 1.32 – 1.05 (m, 5H), 0.93 (q, *J* = 10.7, 10.1 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 178.05, 173.12, 82.48, 77.32, 77.00, 76.68, 53.33, 42.97, 34.31, 34.18, 34.13, 27.71, 26.26, 26.23, 26.08, 21.35; **HRMS (ESI-)** [M-H]$^-$ calculated m/z for $[C_{15}H_{25}O_4]^-$: 269.1758, found: 269.1755.

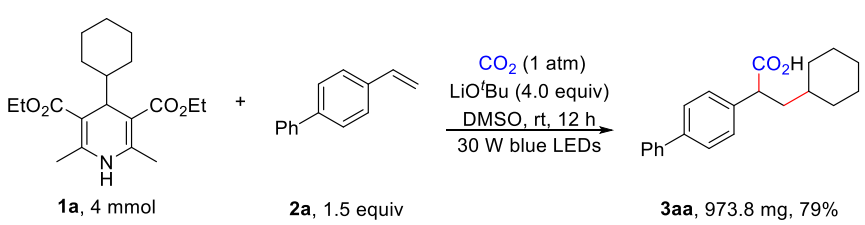



**3-cyclohexyl-2,3-diphenylpropanoic acid (3ay)**: According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2y** (54.0 mg, 0.3 mmol, 1.5 equiv), LiO$^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white soli (31.7 mg, 0.102 mmol, 51%).**$^1$H NMR** (400 MHz, $CDCl_3$) **mixture of diastereomers:** δ 7.46 (d, *J* = 6.9 Hz, 0.88H), 7.34 (dd, *J* = 14.5, 7.2 Hz, 1H), 7.28 – 7.16 (m, 4.37H), 7.11 – 6.97 (m, 6H), 6.92 (d, J = 6.8 Hz, 2H), 4.17 (dd, *J* = 16.4, 12.0 Hz, 1.41H), 3.41 (dd, *J* = 11.9, 4.0 Hz, 1H), 3.28 (dd, *J* = 12.2, 3.4 Hz, 0.45H), 1.85 (d, *J* = 12.7 Hz, 1.08H), 1.74 – 1.48 (m, 6.87H), 1.42 (dd, *J* = 11.7, 5.6 Hz, 1H), 1.32 – 1.10 (m, 4.91H), 1.01 – 0.67 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) **mixture of diastereomers:** δ 179.82, 178.53, 139.59, 138.65, 136.98, 129.04, 128.79, 128.59, 128.04, 127.68 (d, J = 10.0 Hz), 127.30, 127.00, 126.53, 125.94, 53.89, 53.78 (d, J = 2.6 Hz), 53.64, 41.43, 38.15, 32.53 (d, *J* = 7.3 Hz), 31.59, 29.70, 27.94, 26.90, 26.64, 26.51, 26.25 (d, *J* = 2.8 Hz), 26.14, 22.66, 14.14. **HRMS (ESI-)** [M-H]$^-$ calculated m/z for $[C_{21}H_{23}O_2]^-$: 307.1704, found: 307.1699. Diastereoisomers were determined by **$^1$H NMR** analysis as 2.2.




**3-cyclohexyl-2-phenylbutanoic acid (3az)**: According to the general procedure A, in $CO_2$ atmosphere **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2z** (35.45 mg, 0.3 mmol, 1.5 equiv), Li$O^tBu$ (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The product was isolated by flash column chromatography ($CH_2Cl_2$ as eluent) as a white solid (17.7 mg, 0.0718 mmol, 36%). **$^1$H NMR** (400 MHz, $CDCl_3$) **mixture of diastereomers:** δ 7.35 – 7.20 (m, 5.11H), 3.71 (q, *J* = 7.0 Hz, 0.18H), 3.43 (dd, *J* = 11.4, 3.5 Hz, 1H), 2.23 – 2.01 (m, 0.99H), 1.79 – 1.37 (m, 5.67H), 1.35 – 0.78 (m, 10H), 0.52 (d, *J* = 7.0 Hz, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) **mixture of diastereomers:**δ 180.26, 179.98, 56.22, 56.08, 41.16, 40.90, 40.52, 37.61, 32.17, 31.87, 26.87, 26.82, 26.70, 26.58, 26.52, 26.23, 26.11, 25.46, 13.09, 12.03. **HRMS (ESI-)** $[M-H]^-$ calculated m/z for $[C_{16}H_{21}O_2]^-$: 245.1547, found: 245.1549. Diastereoisomers were determined by **$^1$H NMR** analysis as 5.5.

## 5. Gram-scale reaction




**Blue LED reactors for gram scale reaction**

To an oven-dried Schlenk flask (500 mL) containing a stirring bar was charged with **1a** (1.34 g, 4.0 mmol), **2a** (1.08 g, 6.0 mmol, 1.5 equiv) and transferred to glovebox to add Li$O^tBu$ (1.28 g, 16.0 mmol, 4.0 equiv). The flask was then evacuated and back-filled with $CO_2$ for 3 times. Subsequently, DMSO (60 mL) were added under $CO_2$. The reaction was stirred in water bath and irradiated with four 30 W blue LED lamps (3 cm away, with cooling fan to keep the reaction temperature at 25~30 °C) for 12 hours. The resulting mixture was quenched by 20 mL of 2N HCl (aq.), 80 mL of $H_2O$ and diluted with 60 mL of EtOAc and then stirred for 10 min and extracted by EtOAc four times

and the combined organic phases were concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography ($CH_2Cl_2$ as eluent) to give the pure desired product **3aa** as a white solid (973.8 mg, 3.2 mmol, 79%).

# 6. UV-Vis absorption spectra

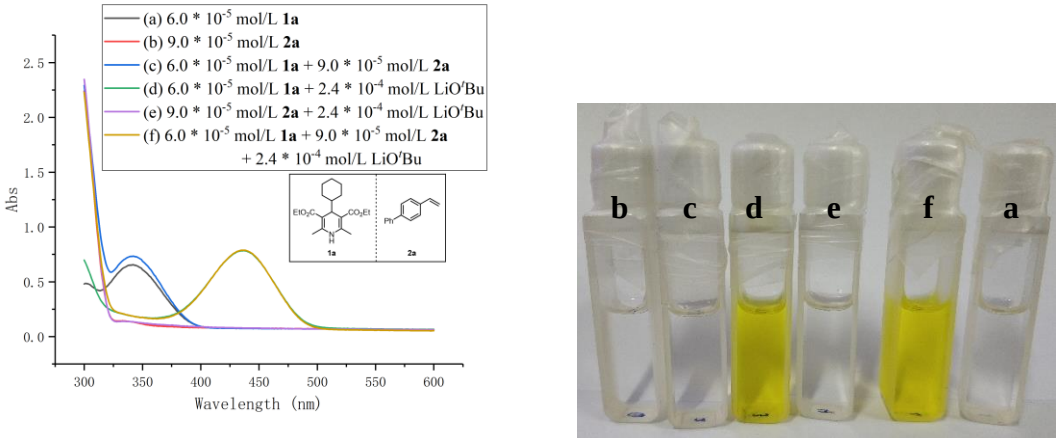



**Figure S1 UV-Vis absorption and their colors**

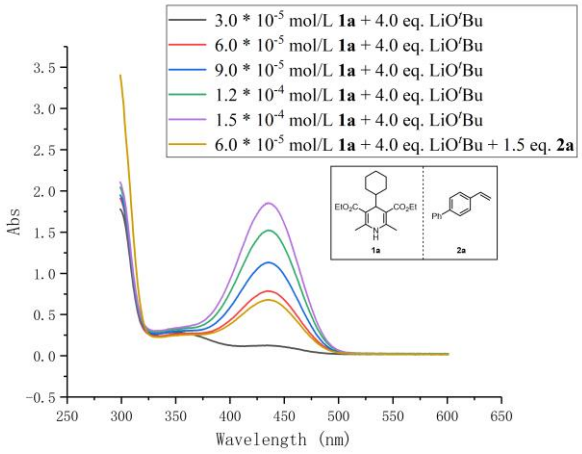



**Figure S2 concentration-absorption curve of 1a**

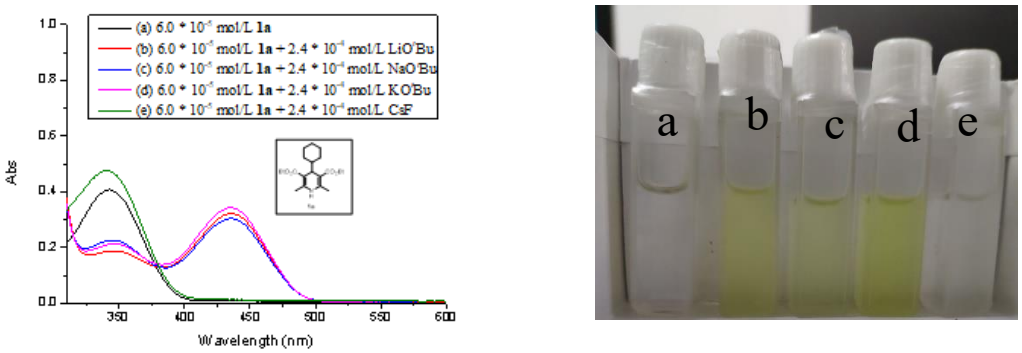
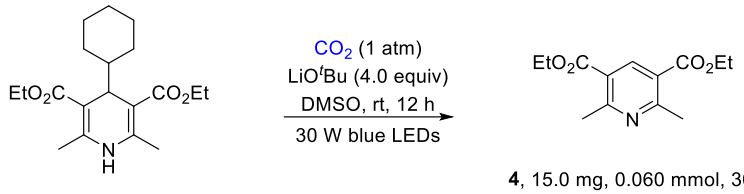



**Figure S3 UV-Vis absorption of 1a with base and their colors**

Optical absorption spectra of 4-Cy-DHP **1a** (6.0 * $10^{-6}$ M), 4-vinyl-1,1'-biphenyl **2a** (9.0 * $10^{-6}$ M), Li$O^t$Bu (2.4 * $10^{-5}$ M) and their conbinations in 2.0 mL anhydrous DMSO were recorded in 10 mm path quartz cuvettes equipped with a Teflon® septum under $N_2$ atmosphere (anhydrous DMSO as blank). The solutions were analyzed using a PUXI TU-1901 UV-Vis spectrophotometer. 1a has the absorption peak at 339 nm, upon mixing **1a** with Li$O^t$Bu, a red-shift spectrum was observed (Figure S1, line **d**, in green, $\lambda_{max}$ = 437 nm), and there is absorption even at 500 nm. However, upon mixing **1a**, **2a** with Li$O^t$Bu, compared with **1a** and Li$O^t$Bu, no new absorption band and no change in absorption intensity was observed in the wavelength longer than 350 nm (Figure S2, line **f**, in yellow), from this we did not prefer the possible existence of electron-donor-acceptor (EDA) complex. In addition, a concentration-absorption curve of **1a** was also measured (Figure S2).

We conducted UV/Vis spectroscopic experiment of **1a** in the presence of Li$O^t$Bu, Na$O^t$Bu, K$O^t$Bu and CsF, we could see from the picture below that 1a in the presence of both Na$O^t$Bu and K$O^t$Bu had an absorption peak at 339 nm, and a clear red-shift absorption (up to 500 nm), which also showed a yellow color and were similar the case with LiOtBu. But for CsF, no red-shift absorption was observed with a colorless solution. As all of the four bases promoted this reaction efficiently, we speculated that the red-shift absorption might not affect the reactivity of this reaction.

# 7. Direct irradiation of Cy-DHP under basic condition



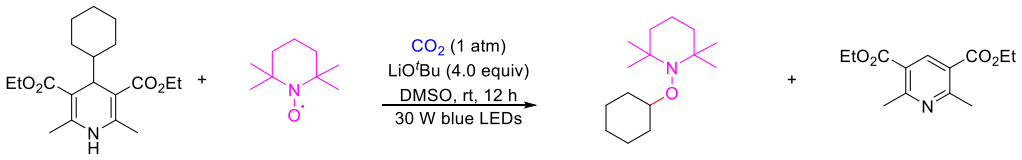

**1a**, 67.0 mg, 0.2 mmol

**4**, 15.0 mg, 0.060 mmol, 30%

recovery of **1a**: 39.5 mg, 0.118 mmol, 59%

To an oven-dried Schlenk tube (25 mL) containing a stirring bar was charged with **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), and transferred to glovebox to add LiO$^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv). The tube was then evacuated and back-filled with $CO_2$ for three times. Subsequently, DMSO (3.0 mL) were added under $CO_2$. The reaction was stirred in water bath and irradiated with a 30 W blue LED lamp (3 cm away, with cooling fan to keep the reaction temperature at 25~30 °C) for 12 hours. The resulting mixture was quenched by 2 mL of 2 N HCl (aq.), 4 mL of $H_2O$ and diluted with 4 mL of EtOAc and then stirred for 10 min and extracted by EtOAc for 4 times and the combined organic phases were concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc 20/1 to 10:1), pyridine product **4** was separated in 30% yield, and 59% of **1a** was recovered. This result indicated 4-Cy-DHP **1a** would decompose under base and blue LEDs. **Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate** (**4**): **$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 4.37 (q, $J$ = 7.1 Hz, 4H), 2.83 (s, 6H), 1.39 (t, $J$ = 7.1 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 165.96, 162.22, 140.91, 123.04, 77.31, 76.99, 76.68, 61.41, 24.96, 14.26; **HRMS (ESI+)** $[M+H]^+$ calculated m/z for $[C_{13}H_{18}NO_4]^+$: 252.1230, found: 252.1233.

# 8. Direct irradiation of Cy-DHP under basic condition in the presence of 2 equiv of TEMPO



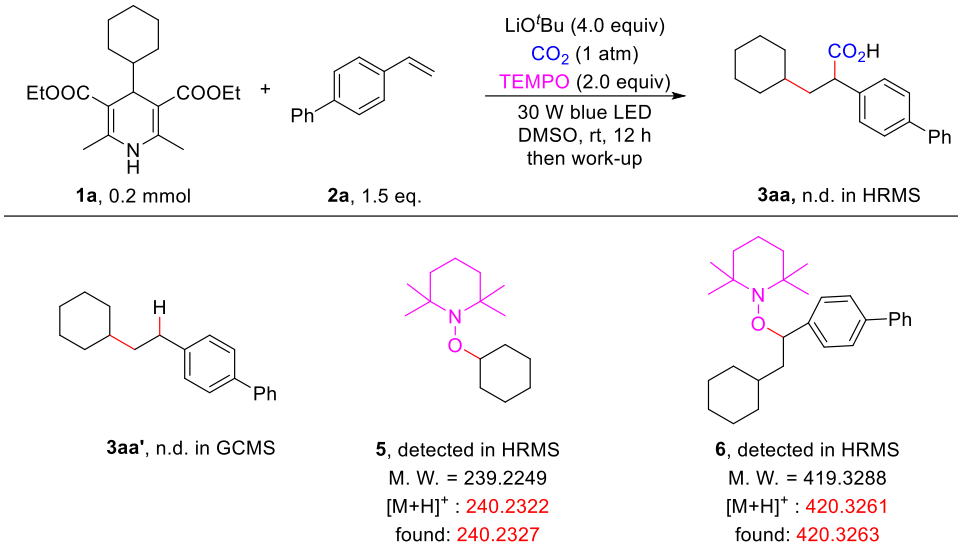

**1a**, 67.0 mg, 0.2 mmol TEMPO, 2.0 equiv **5**, 5.3 mg, 0.022 mmol, 11% **4**, 29.6 mg, 0.118 mmol, 59%

recovery of **1a**: 20.1 mg, 0.060 mmol, 30%

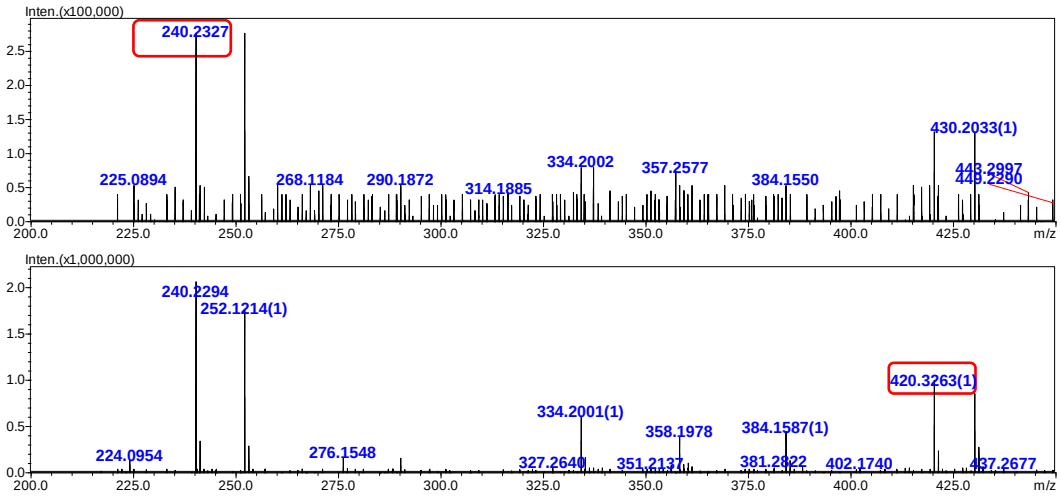
To an oven-dried Schlenk tube (25 mL) containing a stirring bar was charged with **1a** (67.0 mg, 0.2 mmol, 1.0 equiv) and TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv), and transferred to glovebox to add Li$O^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv). The tube was then evacuated and back-filled with $CO_2$ for three times. Subsequently, DMSO (3.0 mL) were added under $CO_2$. The reaction was stirred in water bath and irradiated with a 30 W blue LED lamp (3 cm away, with cooling fan to keep the reaction temperature at 25~30 °C) for 12 hours. The resulting mixture was quenched by 2 mL of 2 N HCl (aq.), 4 mL of $H_2O$ and diluted with 4 mL of EtOAc and then stirred for 10 min and extracted by EtOAc for 4 times and the combined organic phases were concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether to petroleum ether/EtOAc 10/1), TEMPO-cyclohexyl adduct **5** was separated in 11% yield, 53% of pyridine byproduct can be separated, and 30% of **1a** was recovered. The results of this experiment may indicate that the 4-Cy-DHP **1a** would decompose and produce cyclohexyl radical in the presence of base and blue LEDs.

**1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (5)**[7]: **$^1$H NMR** (400 MHz, $CDCl_3$): δ 3.58 (tt, *J* = 9.5, 4.0 Hz, 1H), 2.03 (tt, *J* = 13.4, 6.0 Hz, 2H), 1.78 – 1.69 (m, 2H), 1.57 – 1.39 (m, 6H), 1.26 – 1.03 (m, 18H).; **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 81.76, 59.63, 40.27, 34.43, 32.92, 25.95, 25.11, 17.33; **HRMS (ESI+)** $[M+H]^+$ calculated m/z for $[C_{15}H_{30}NO]^+$: 240.2322, found: 240.2327.

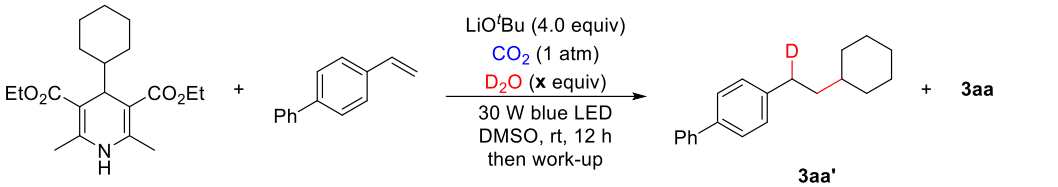
# 9. TEMPO radical capture experiment




Following the general procedure, **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), LiO$^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv) and 3.0 mL of DMSO were used and reacted for 12 h. Then the standard reaction was completely restrained, carbo-carboxylation product **3aa** and byproduct **3aa'** were not detected, TEMPO-adduct **5** and **6** were detected. This result might support the existence of cyclohexyl radical and benzyl radical. **HRMS** (**ESI+**) TEMPO-cyclohexyl adduct **5** $[M+H]^+$ calculated m/z for $[C_{15}H_{30}NO]^+$: 240.2322, found: 240.2327; TEMPO-benzyl adduct **6** $[M+H]^+$ calculated m/z for $[C_{29}H_{42}NO]^+$: 420.3261, found: 420.3263.



# 10. $D_2O$ labeling experiment

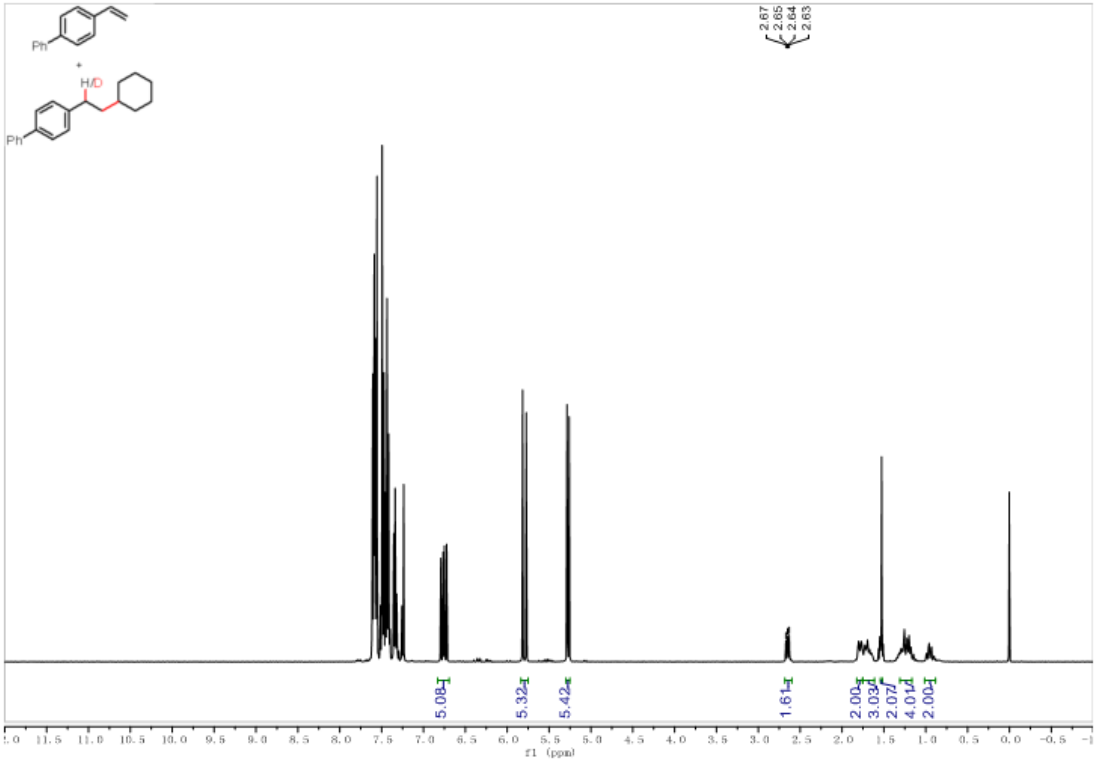



**1a**, 0.2 mmol　　**2a**, 1.5 equiv　　**3aa'**

**x** = 1.0, **3aa'**, 6% (39% D) + **3aa**, 74%

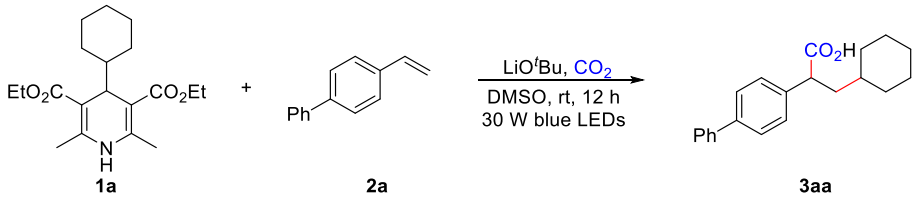
**x** = 3.0, **3aa'**: n.d. **3aa**: n.d. (without conversion of **1a**)

Following the general procedure, in $CO_2$ atmosphere, **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), LiO$^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv), $D_2O$ (3.6 μL, 0.2 mmol, 1.0 equiv or 10.8 μL, 0.6 mmol, 3.0 equiv) and DMSO (3.0 mL) were used and reacted for 12 h. The mixture of **3aa'** and **2a** was isolated by flash column chromatography (petroleum ether) as a white solid in 24.3 mg yield. 6% yield of **3aa'** with 39% deuterium incorporation can be derived from **$^1$H-NMR** spectrum below: signal at δ = 2.65 ppm corresponds to the hydrogen in the benzyl position, while 13 H-atoms at higher field represents cyclohexylmethyl structure[8], other peaks at lower field belongs to vinyl and aryl H-atoms. It can be calculated from the spectrum that the ratio between **3aa'** and **2a** was 1:5.27, This result indirectly confirmed the existence of benzylic carbanion.



## 11. Reaction under light for a certain time

Following the general procedure, a series of parallel reactions were conducted, in $CO_2$ atmosphere, **1a** (67.0 mg, 0.2 mmol, 1.0 equiv), **2a** (54.0 mg, 0.3 mmol, 1.5 equiv), LiO$^t$Bu (64.0 mg, 0.8 mmol, 4.0 equiv) and DMSO (3.0 mL) were used and reacted under light and without light for a certain time. From the experimental results, obviously we can see the reaction rate is very fast at the beginning of the reaction, but once the light stops during the reaction, the conversion of **1a** almost stops. It should be noted that for experiments 7 and 8, the further increase of reaction yield after stopping the light irradiation should be due to the decrease of $CO_2$ concentration in the reaction system at this time, which makes the nucleophilic attack of carbanion more difficult.



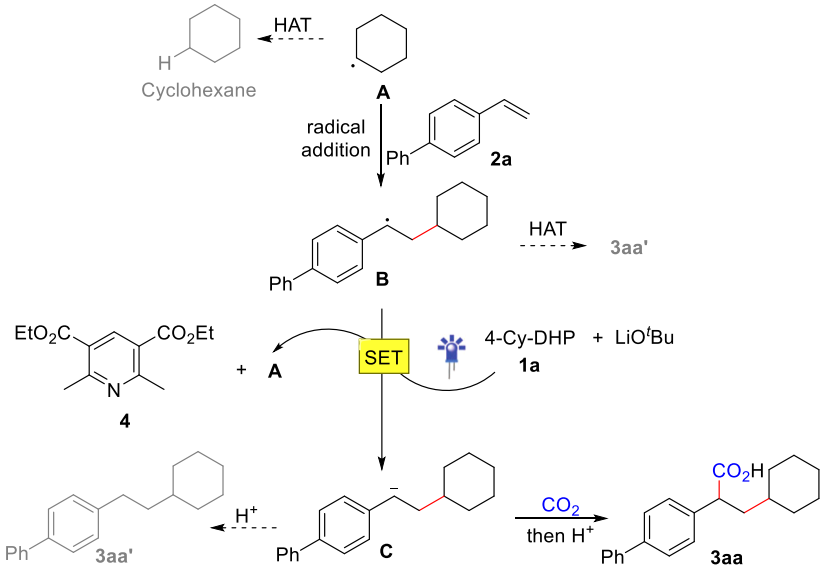

| | Reaction condition | yield of **3aa** | recovery of **1a** |
|---|---|---|---|
| 1 | 5 min light | 9% | 85% |
| 2 | 5 min light + 11 h 55 min dark | 9% | 84% |
| 3 | 10 min light | 19% | 73% |
| 4 | 10 min light + 11 h 50 min dark | 20% | 71% |
| 5 | 20 min light | 33% | 57% |
| 6 | 20 min light + 11 h 40 min dark | 35% | 53% |
| 7 | 1 h light | 57% | 22% |
| 8 | 1 h light + 11 h dark | 64% | 20% |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), LiO$^t$Bu (4.0 equiv), $CO_2$ (1 atm), DMSO (3.0 mL), with or without 30 W blue LEDs, room temperature (rt), total reaction time = 12 h, and isolated yields were given. DMSO = dimethyl sulfoxide.

## 12. Proposed mechanism

Based on the mechanistic studies and previous investigations, take the reaction between **1a** and **2a** as an example, the proposed the mechanism shown below (Scheme

S1), reaction was initiated by the decomposition of **1a** in the presence of blue LEDs and LiO$^t$Bu, then the generated cyclohexyl radical went through a giese-type radical addition with **2a** to produce a benzyl radical, subsequently a SET process from **1a** to benzyl radical under blue LEDs and LiO$^t$Bu to generate benzyl anion, and the oxidated **1a**$^{+\cdot}$ decomposed via C-C bond cleavage at C-4 position to regenerate cyclohexyl radical, the byproduct pyridine **4** was also generated. The reduced carbanion would attack $CO_2$ to get the carboxylate, with 2N HCl (aq.), the final product **1aa** was produced.




Scheme S1. Proposed mechanism

# 13. Reference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[3] Tewari N, Dwivedi N, Tripathi R. *Tetrahedron Lett*, 2004, 45: 9011-9014

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[5] Chen X, Ye F, Luo X, Liu X, Zhao J, Wang S, Zhou Q, Chen G, Wang P. *J Am Chem Soc*, 2019,

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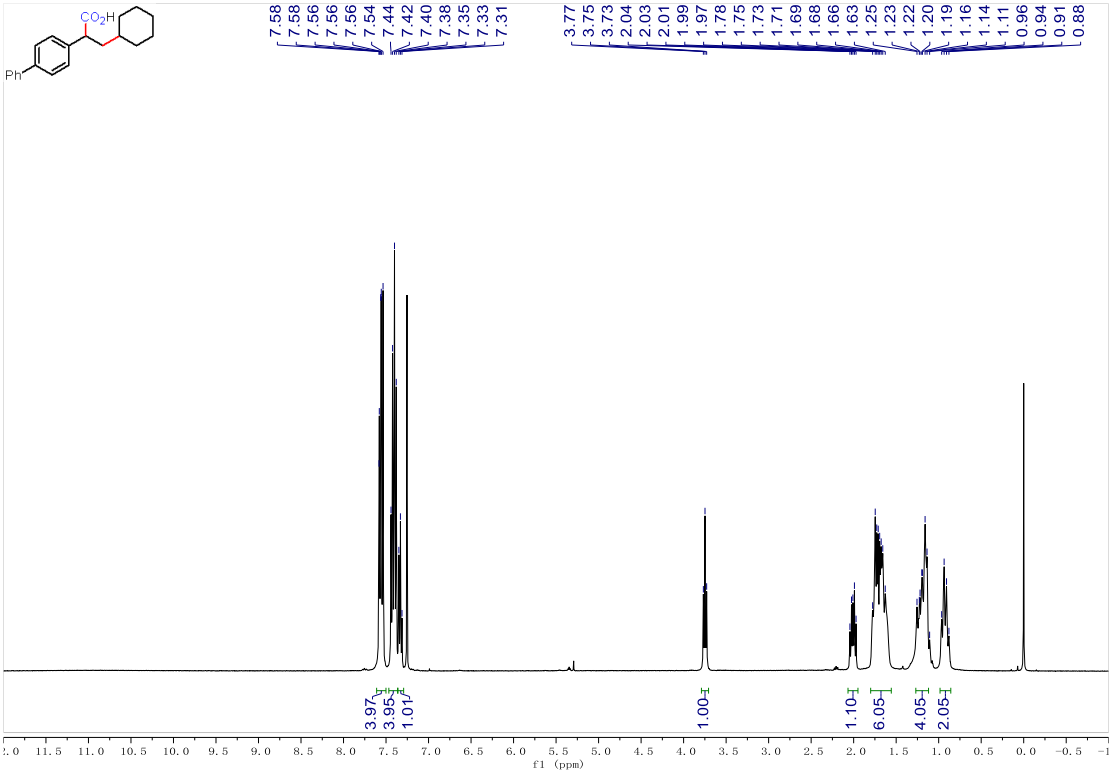
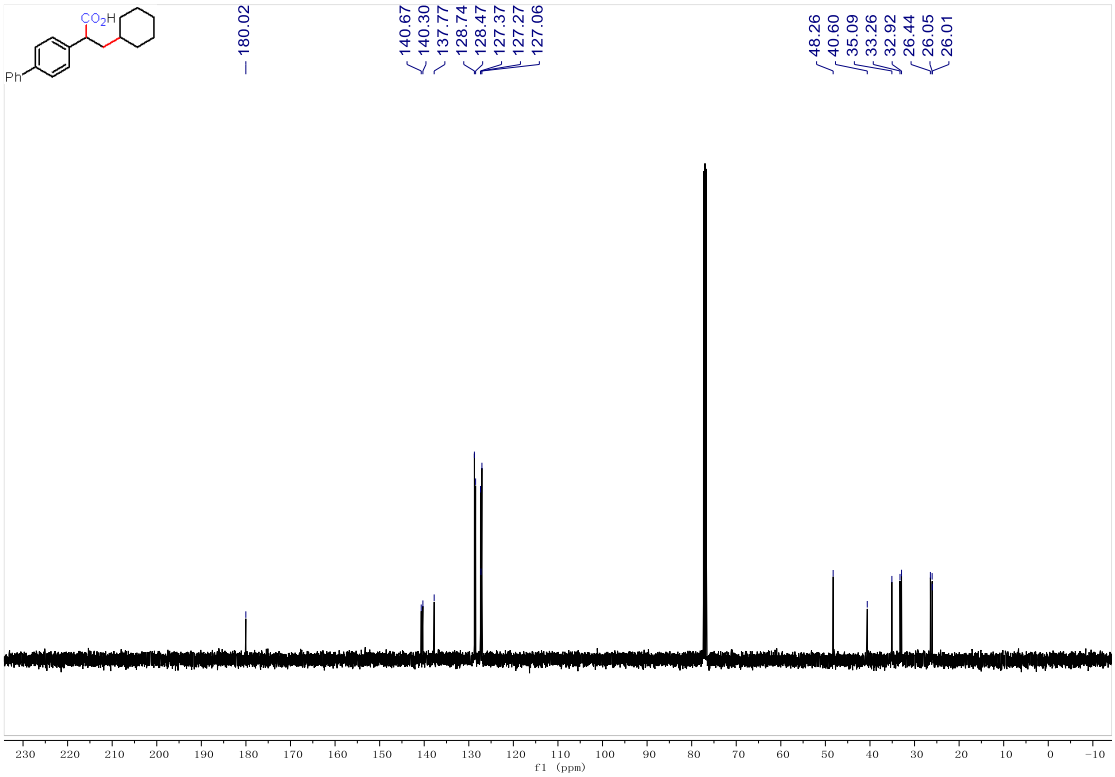
[8] Luo S, Yu DG, Zhu RY, Wang X, Wang L, Shi ZJ. *Chem Commun*, 2013, 49: 7794-7796

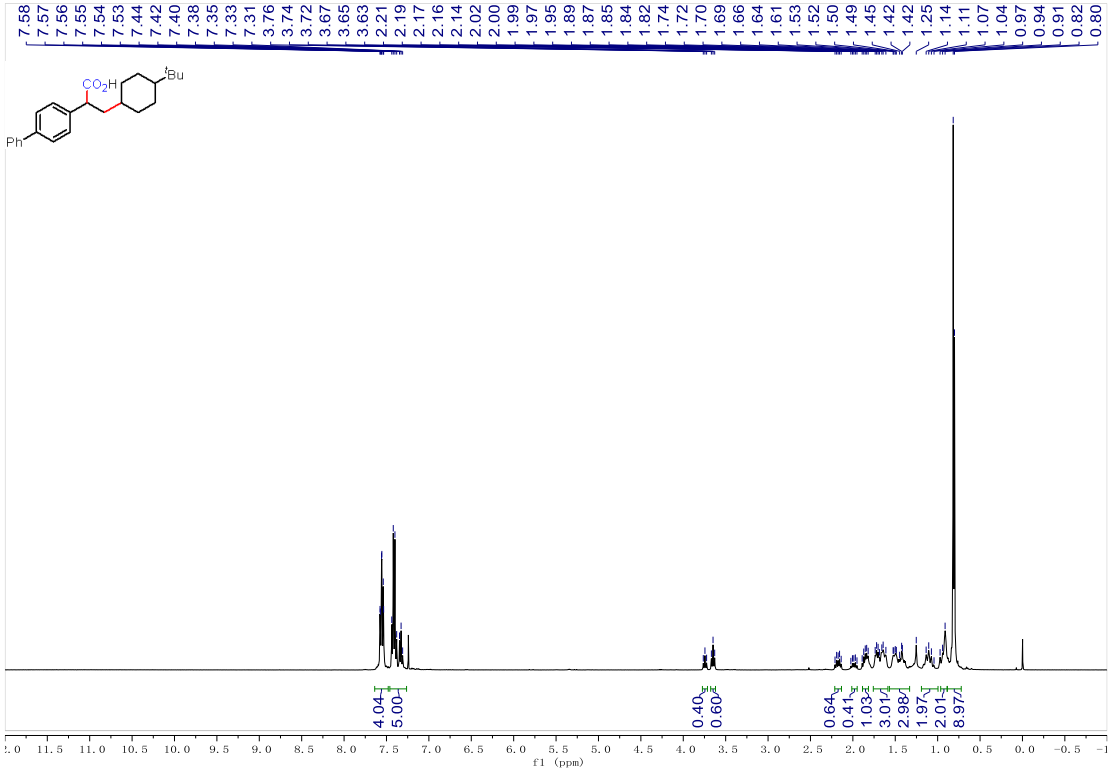
# 14. NMR copies

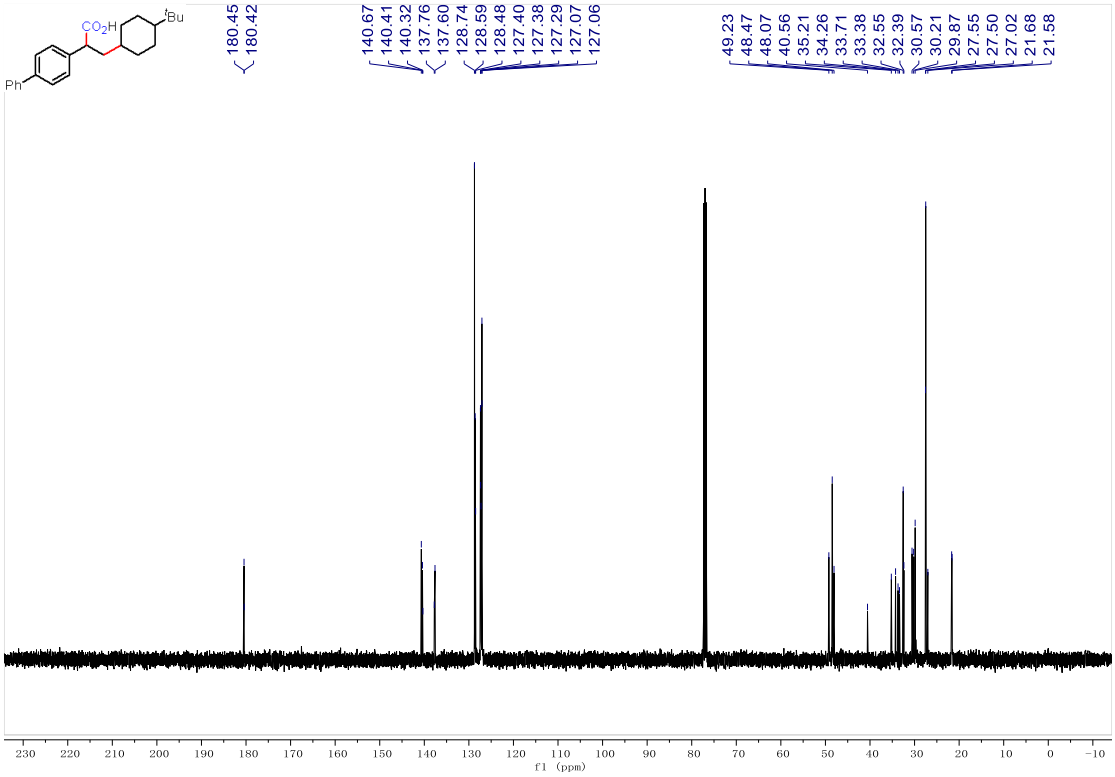
## 2-([1,1'-biphenyl]-4-yl)-3-cyclohexylpropanoic acid (3aa)



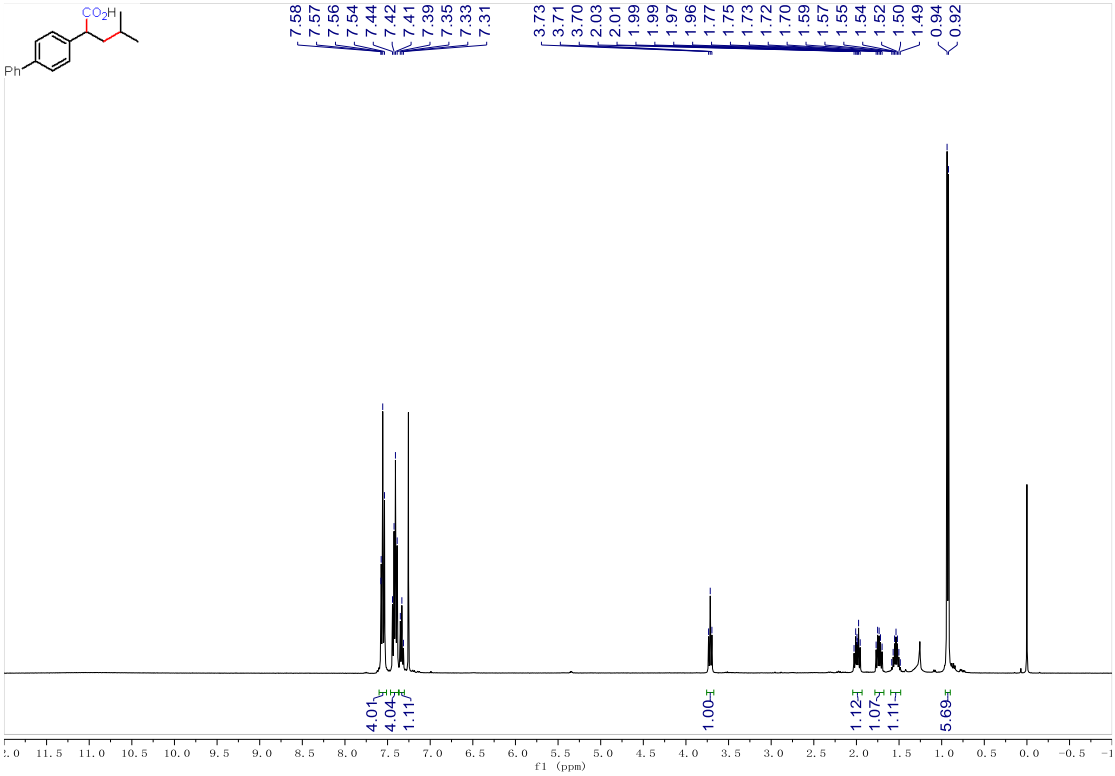



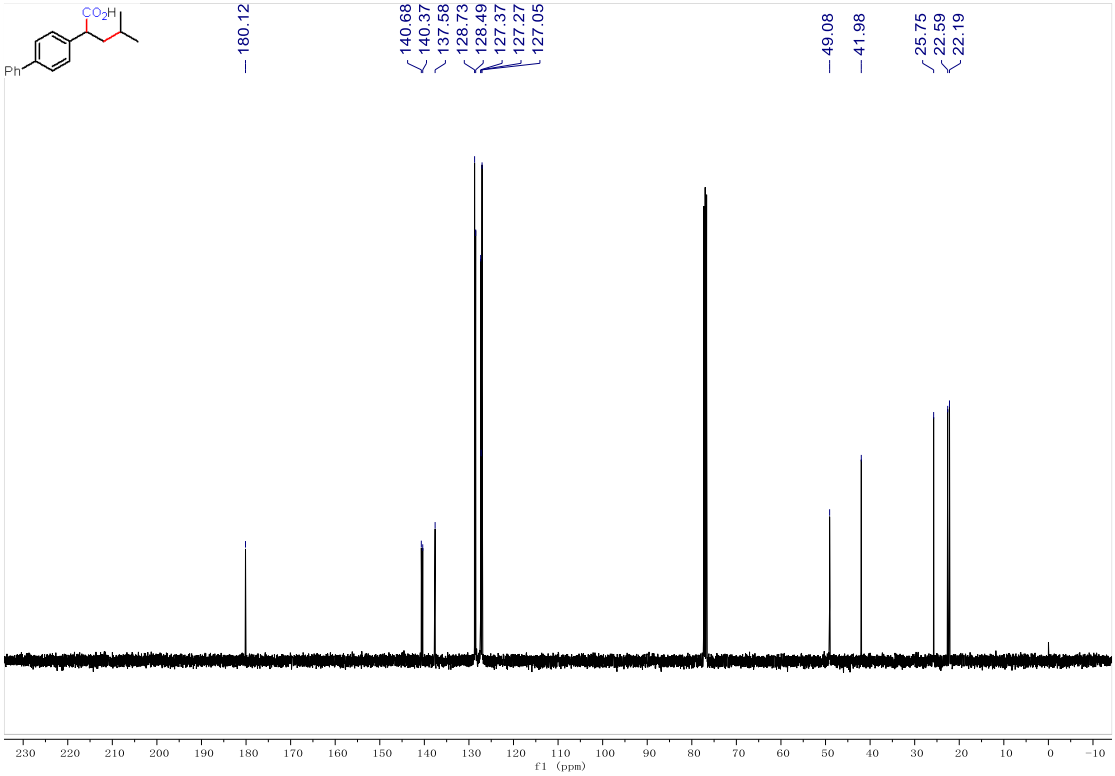
## 2-([1,1'-biphenyl]-4-yl)-3-(4-(*tert*-butyl)cyclohexyl)propanoic acid (3ba)



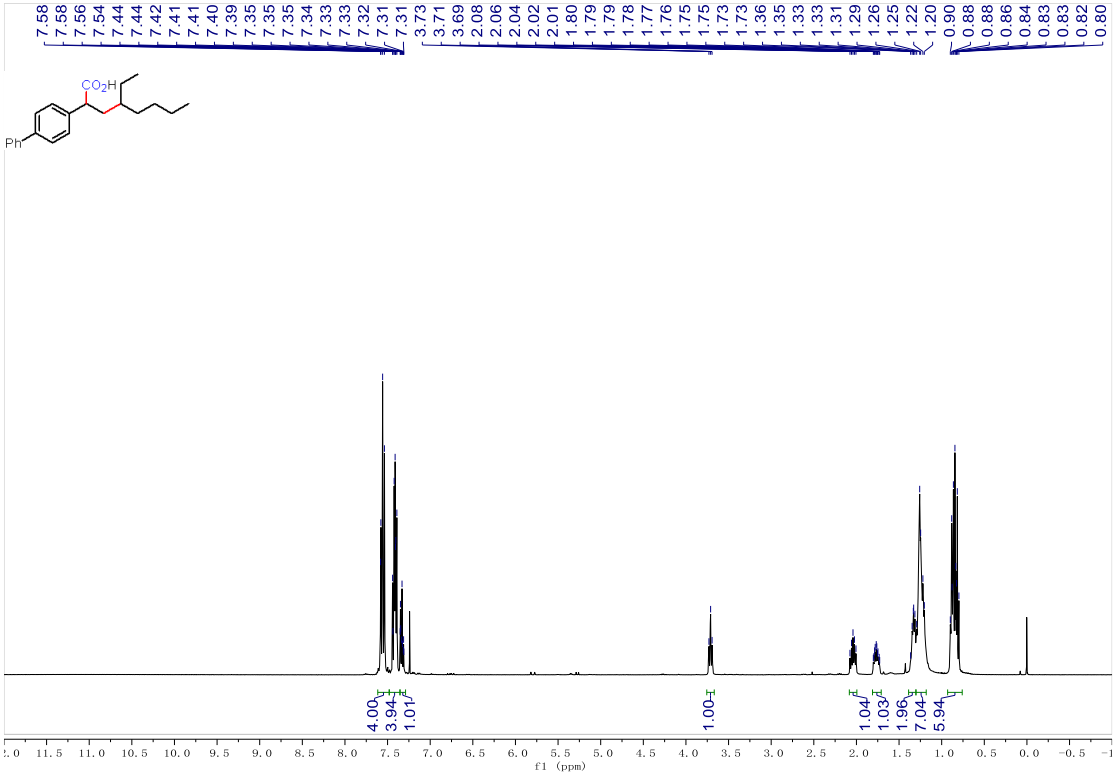



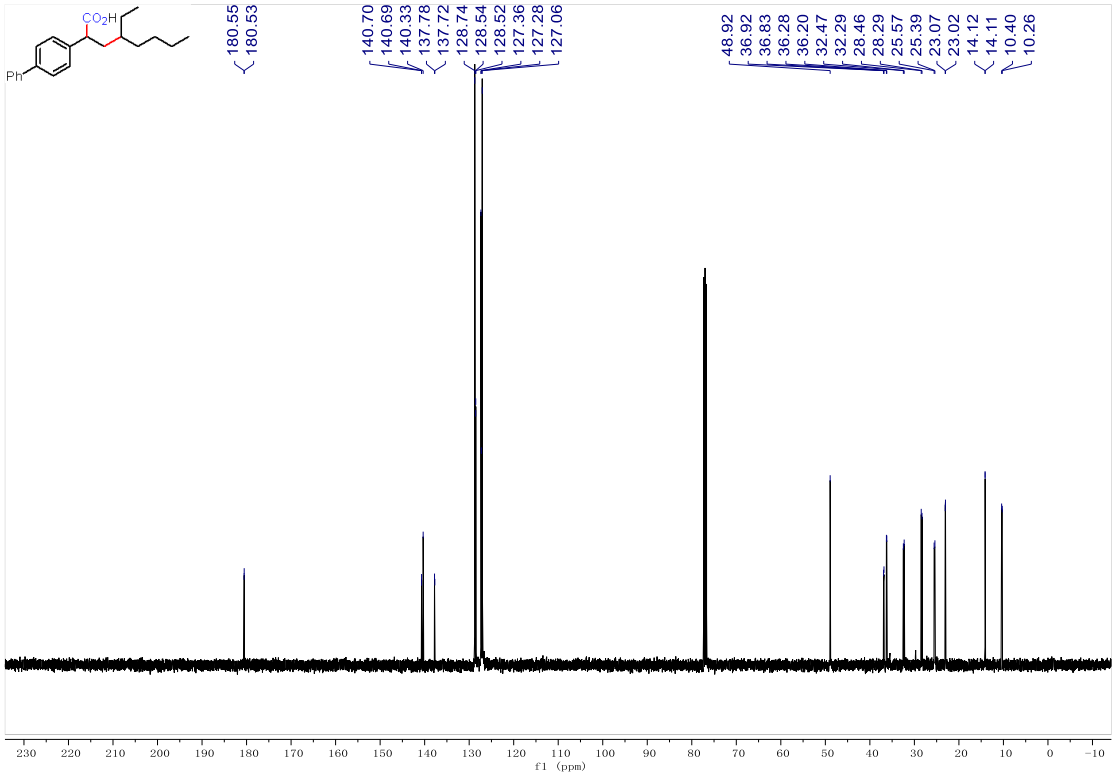
## 2-([1,1'-biphenyl]-4-yl)-4-methylpentanoic acid (3ca)



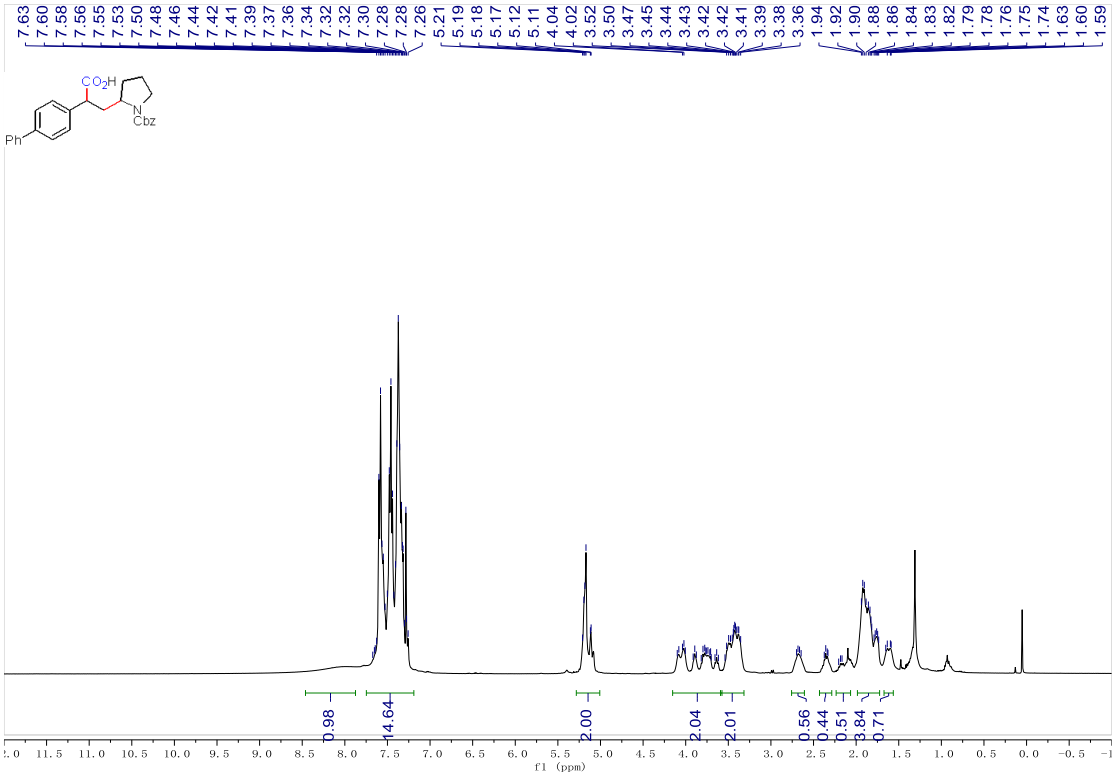



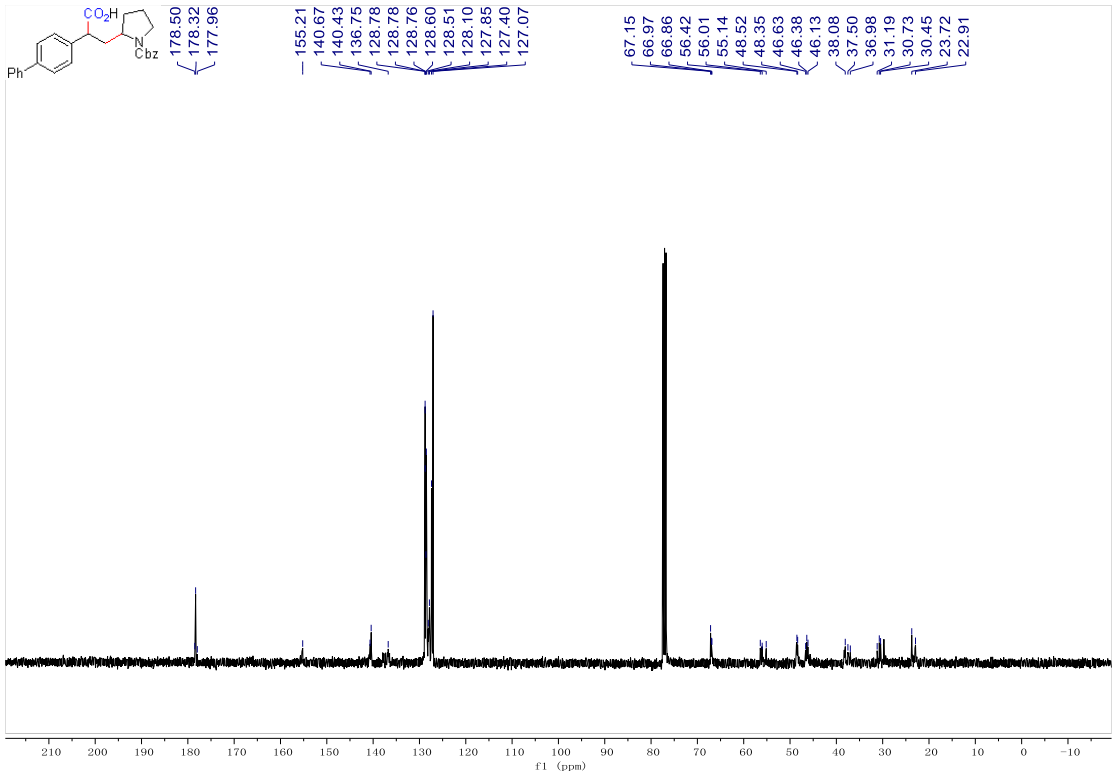
## 2-([1,1'-biphenyl]-4-yl)-4-ethyloctanoic acid (3da)



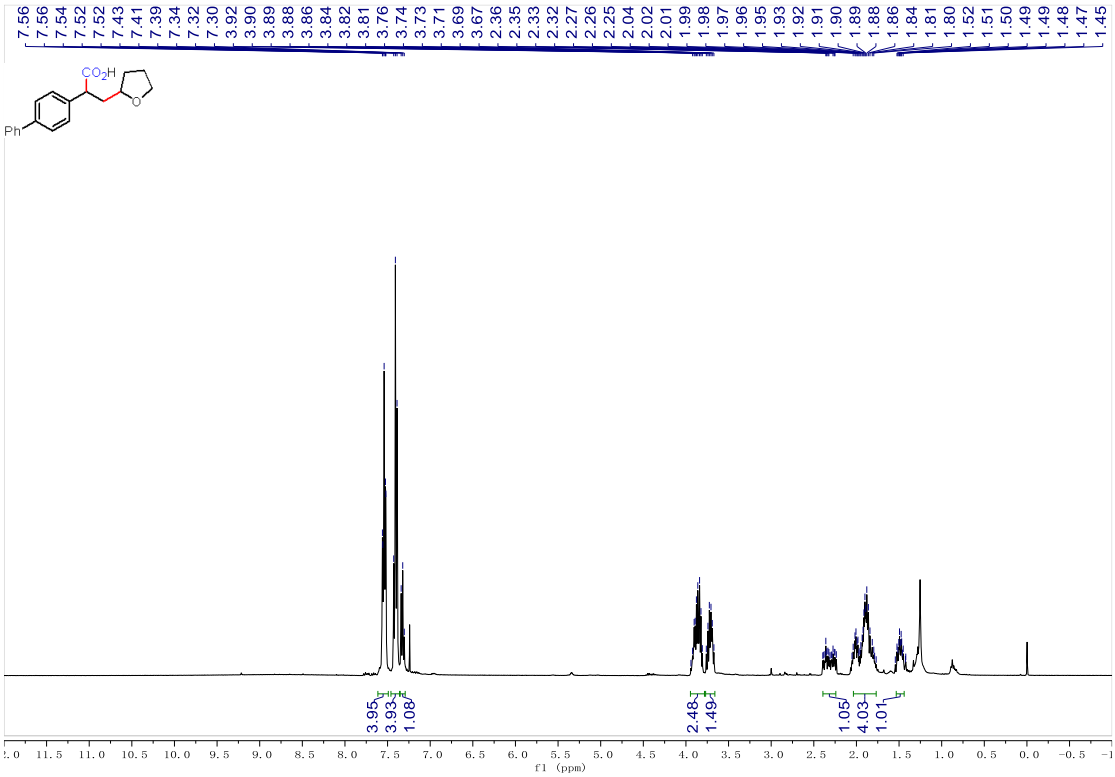



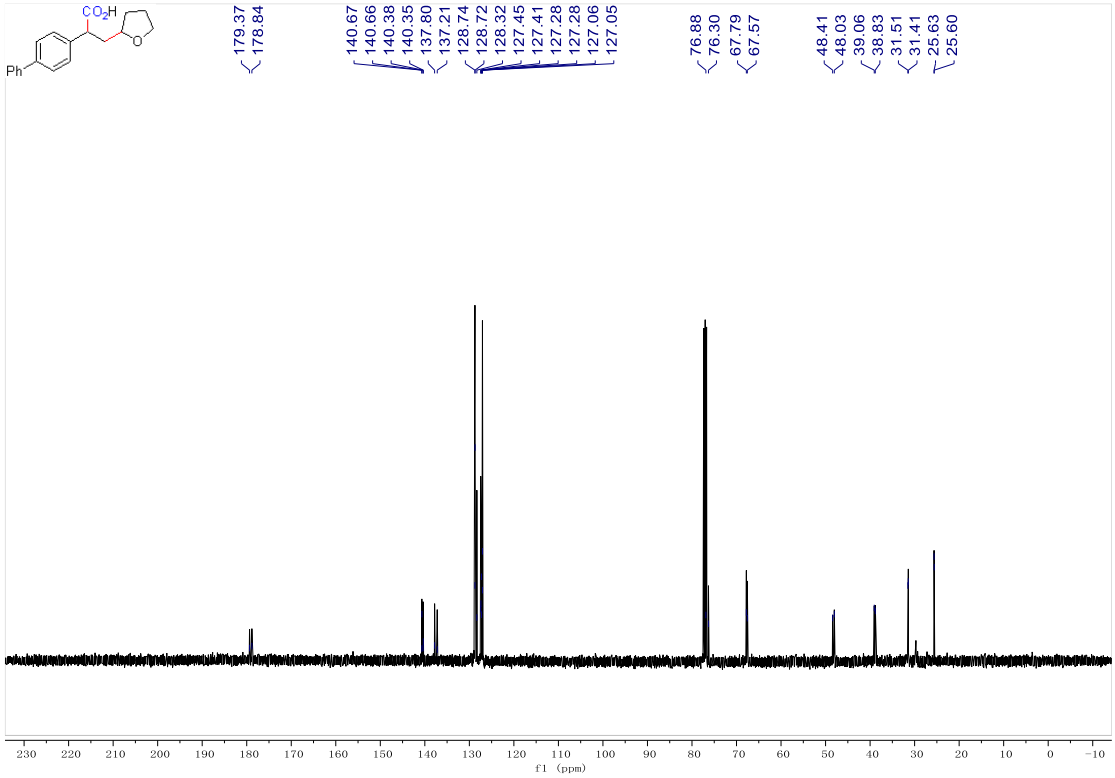
**2-([1,1'-biphenyl]-4-yl)-3-(1-((benzyloxy)carbonyl)pyrrolidin-2-yl)propanoic acid (3ea)**



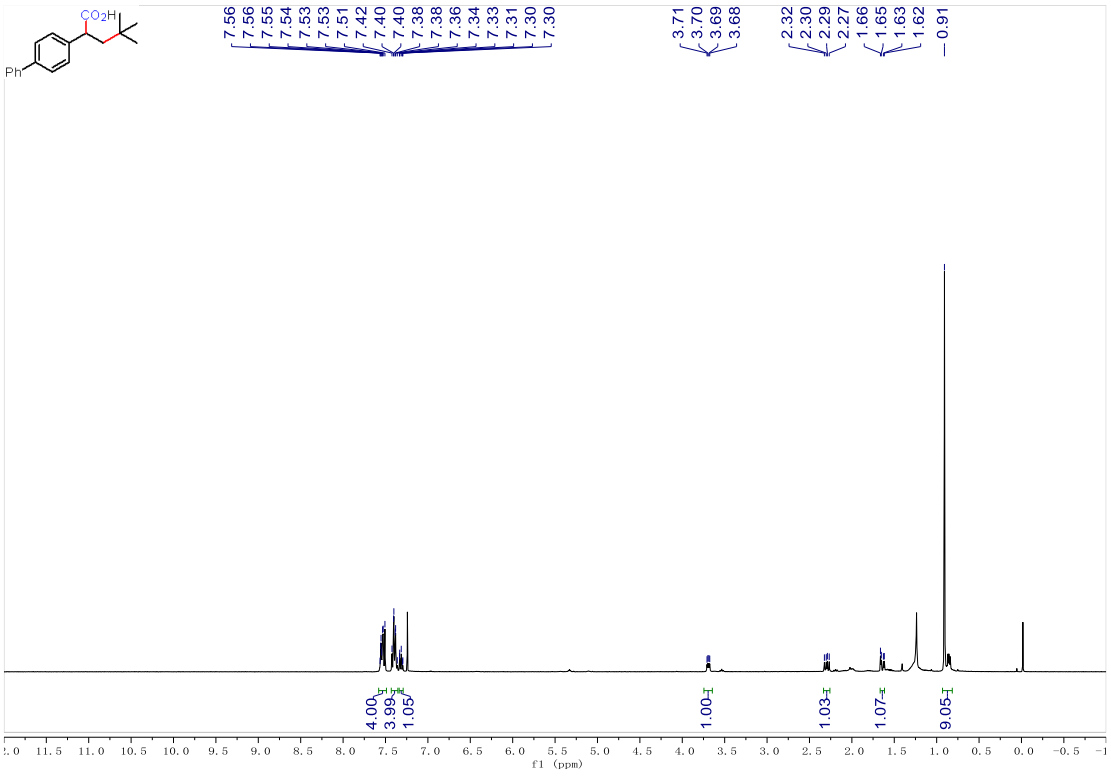



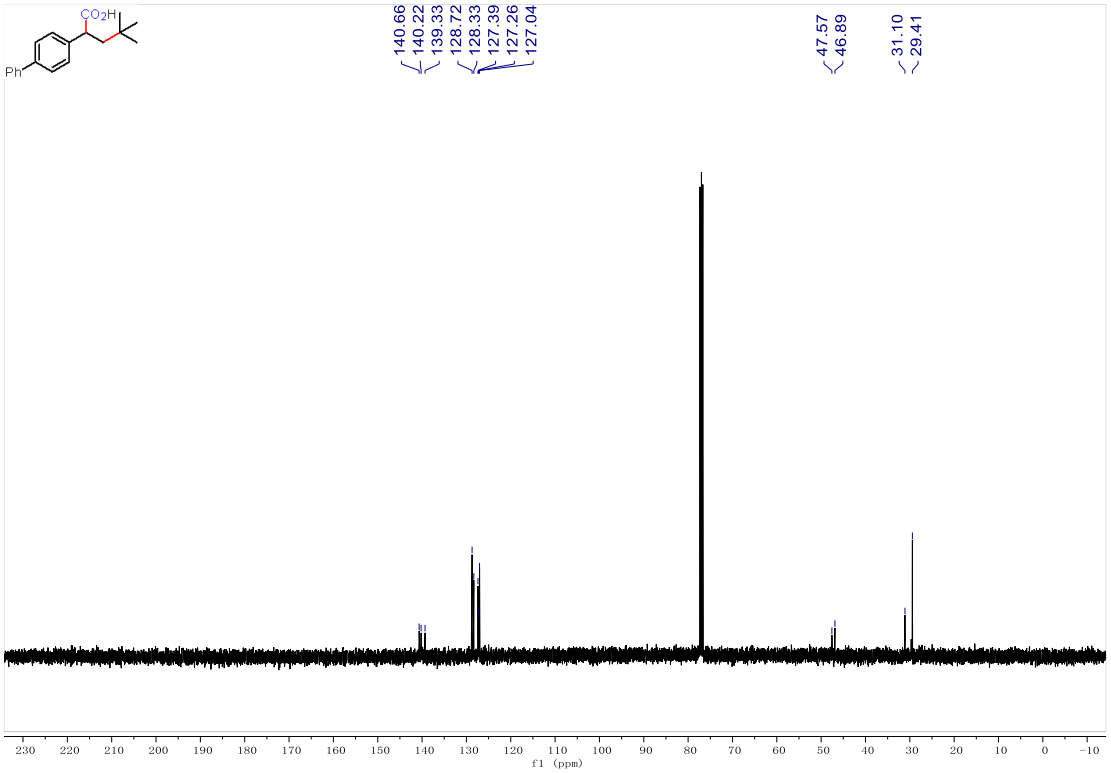
## 2-([1,1'-biphenyl]-4-yl)-3-(tetrahydrofuran-2-yl)propanoic acid (3fa)



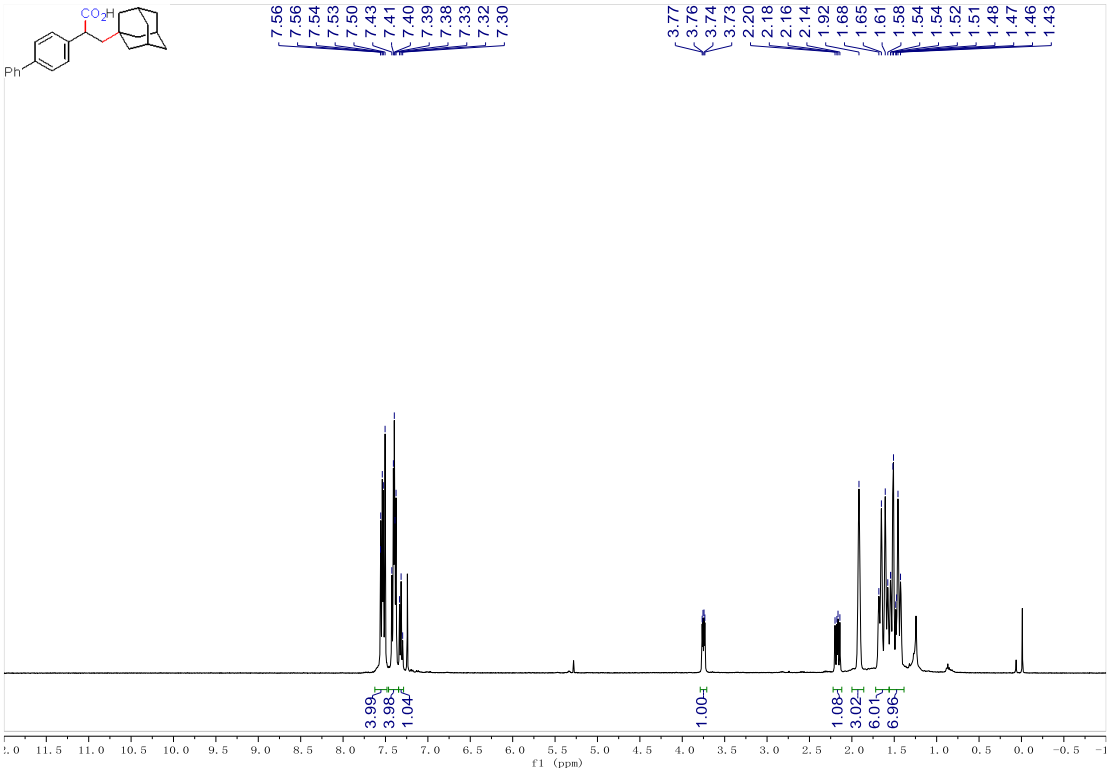



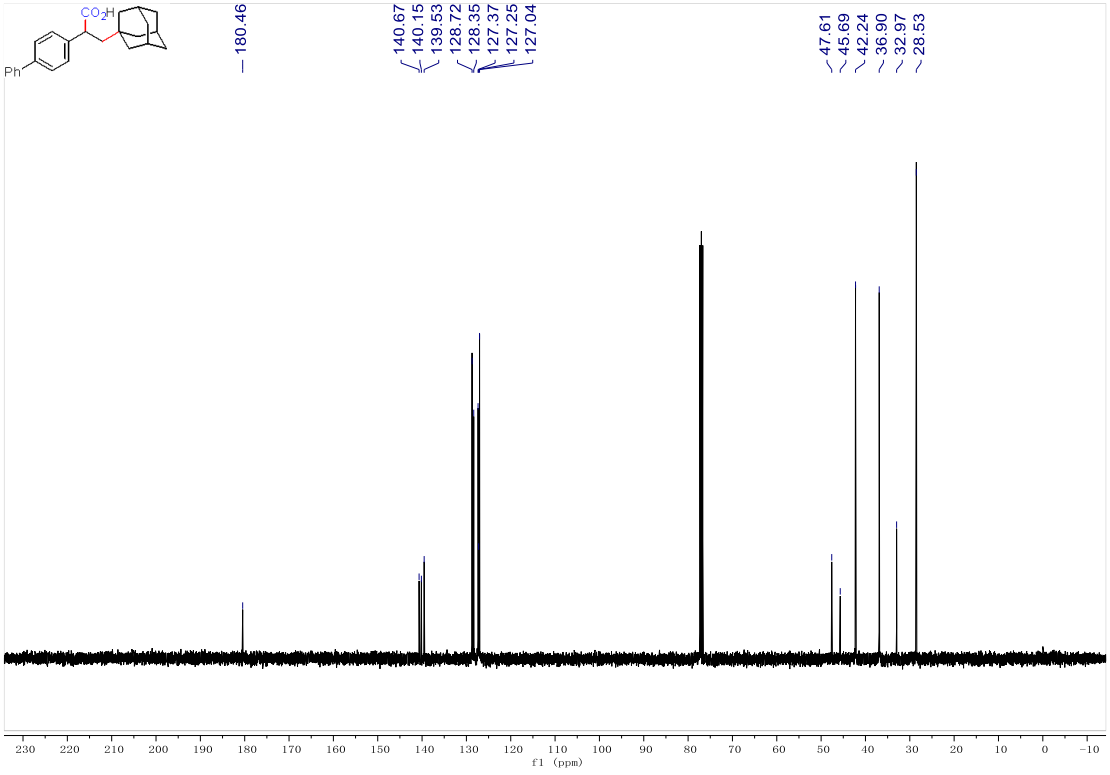
## 2-([1,1'-biphenyl]-4-yl)-4,4-dimethylpentanoic acid (3ga)



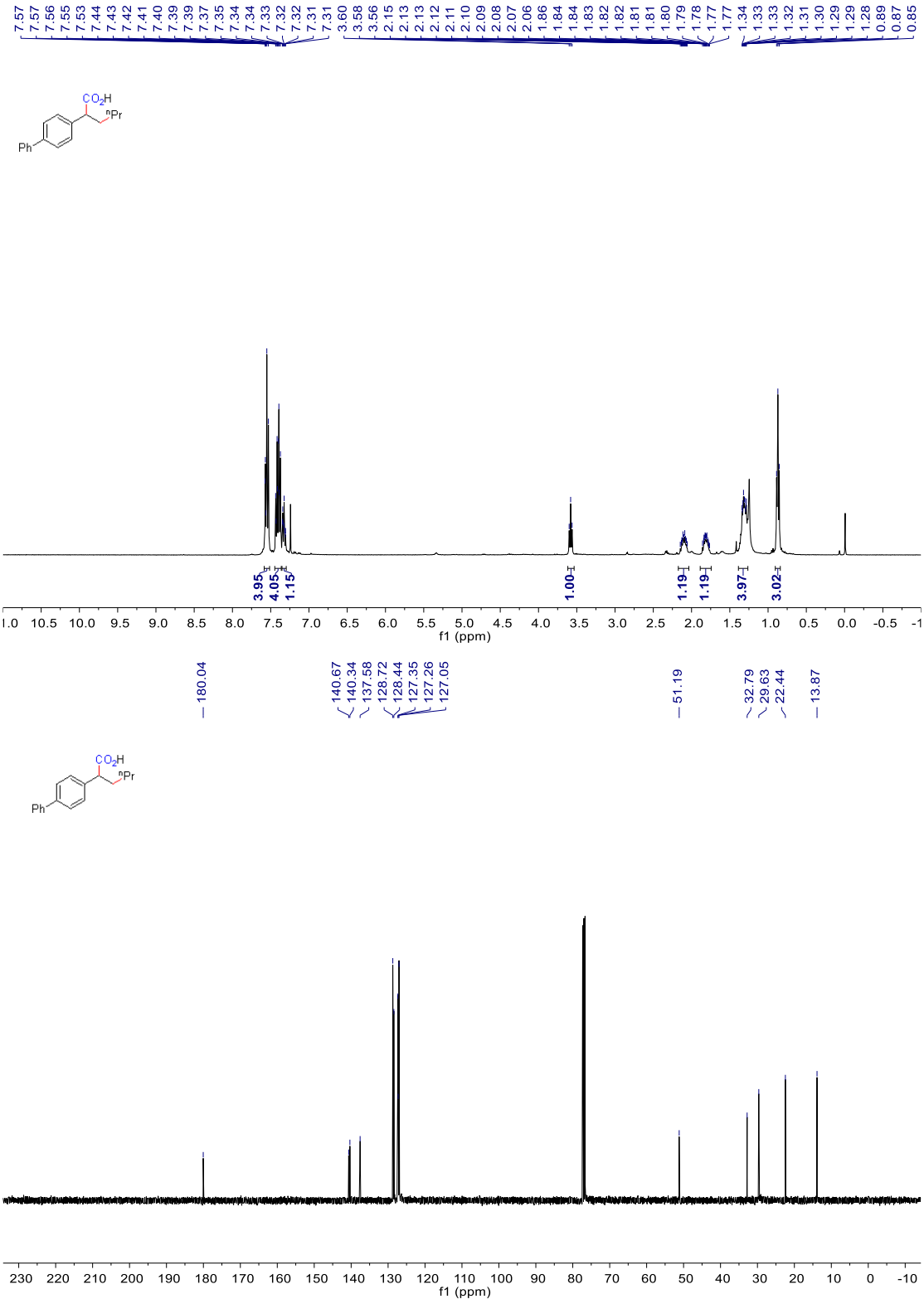



## 2-([1,1'-biphenyl]-4-yl)-3-(adamantan-1-yl)propanoic acid (3ha)

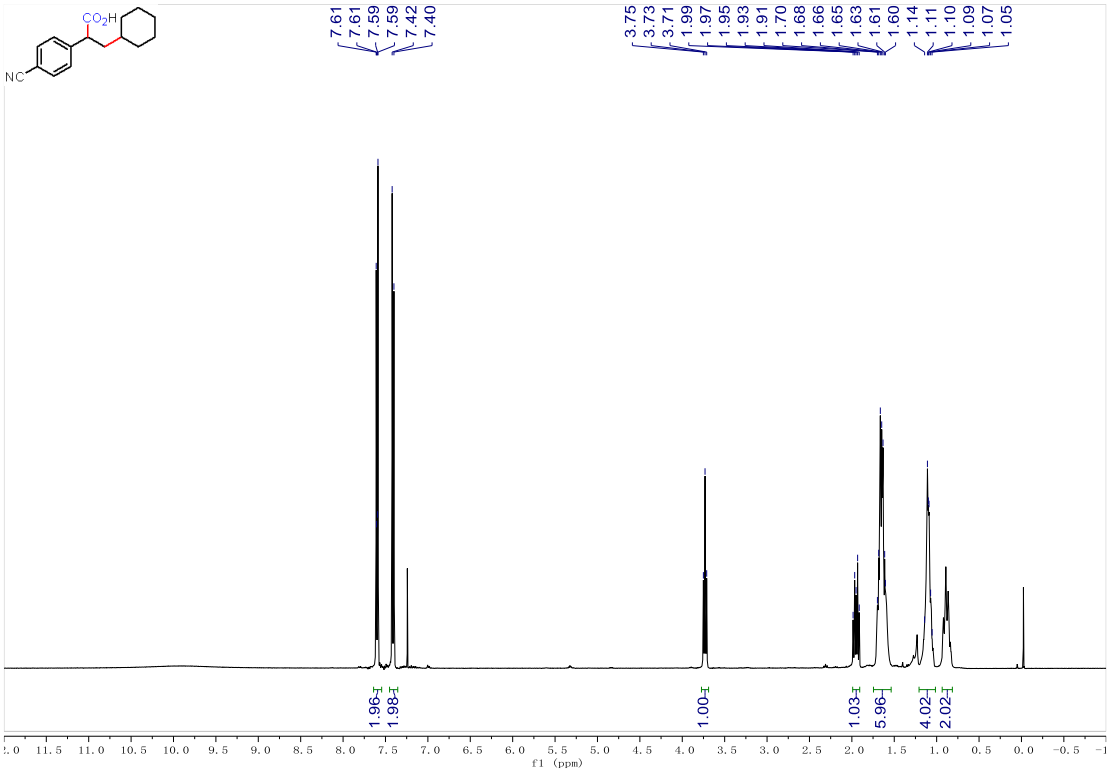


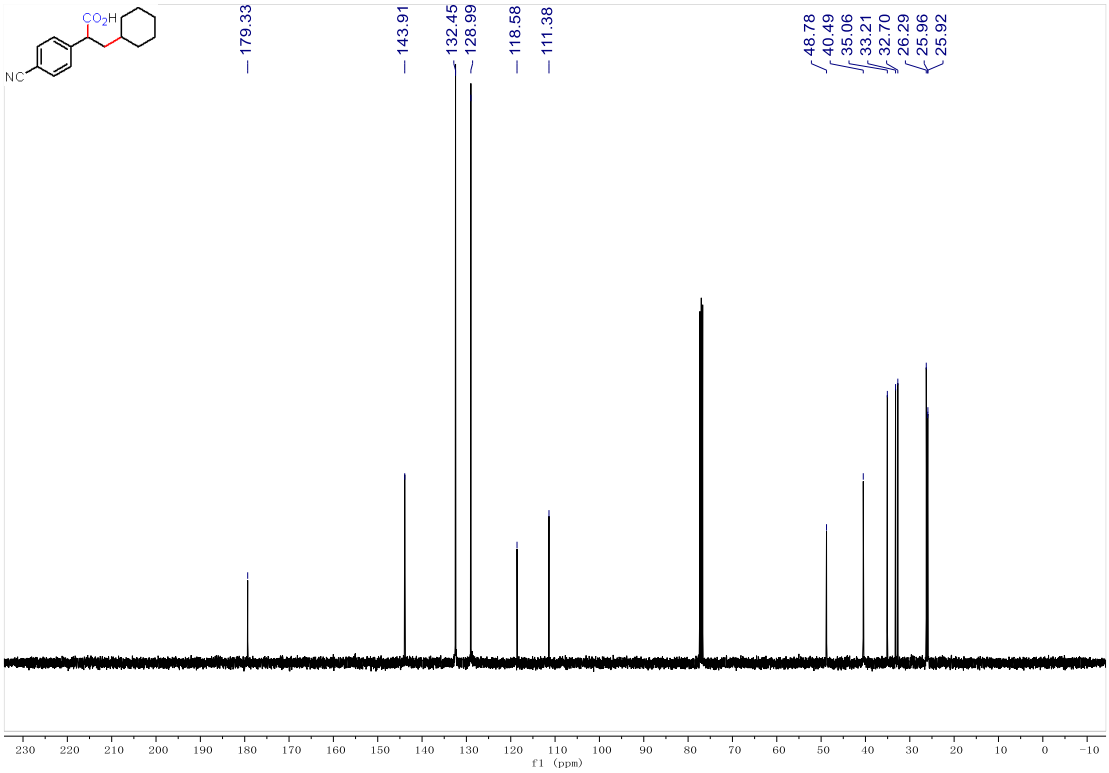



## 2-([1,1'-biphenyl]-4-yl)hexanoic acid (3ia)

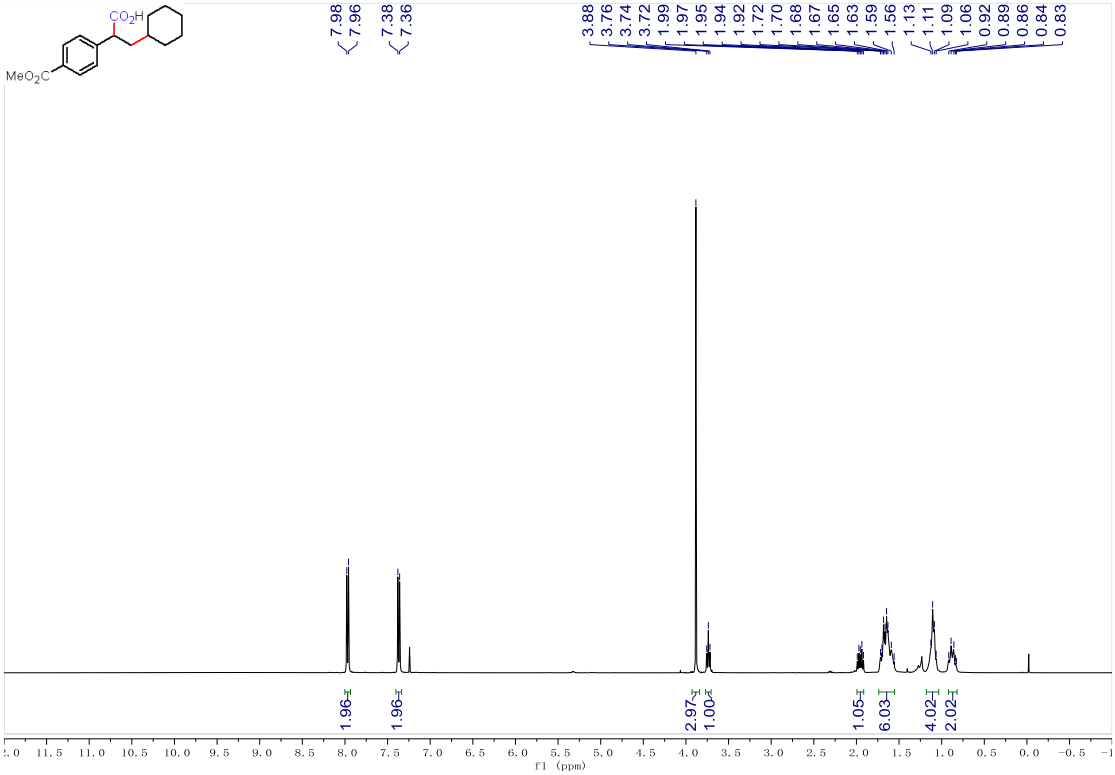


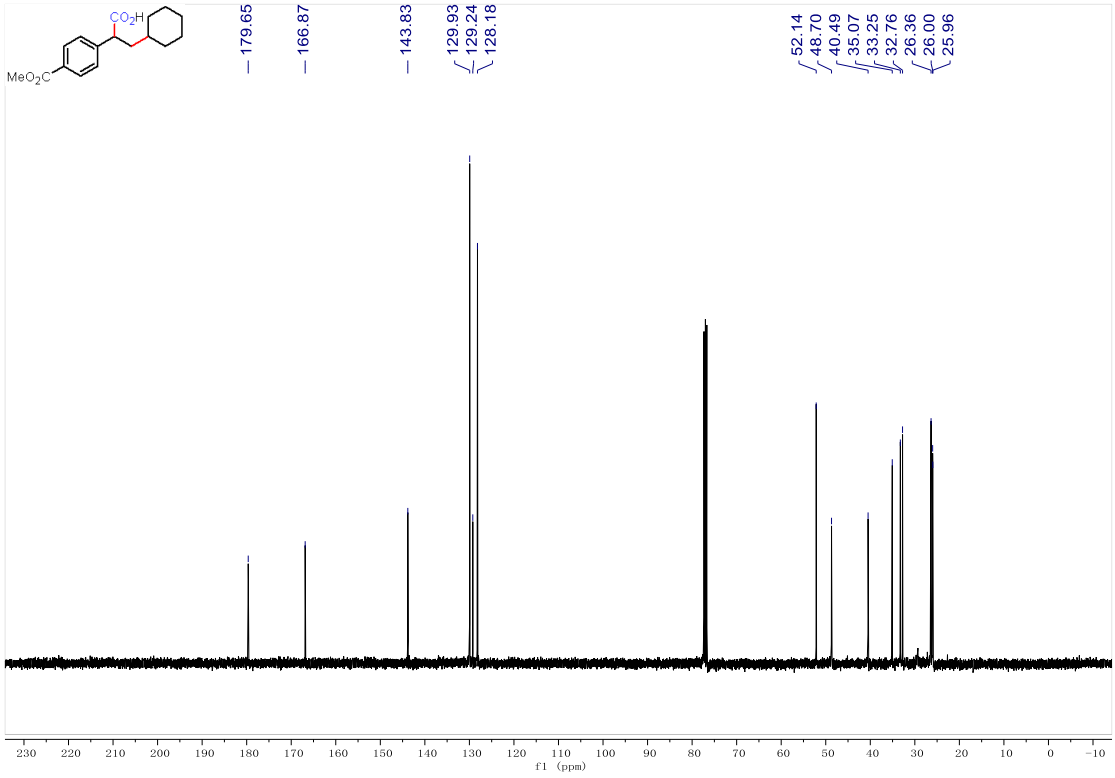
## 2-(4-cyanophenyl)-3-cyclohexylpropanoic acid (3ab)



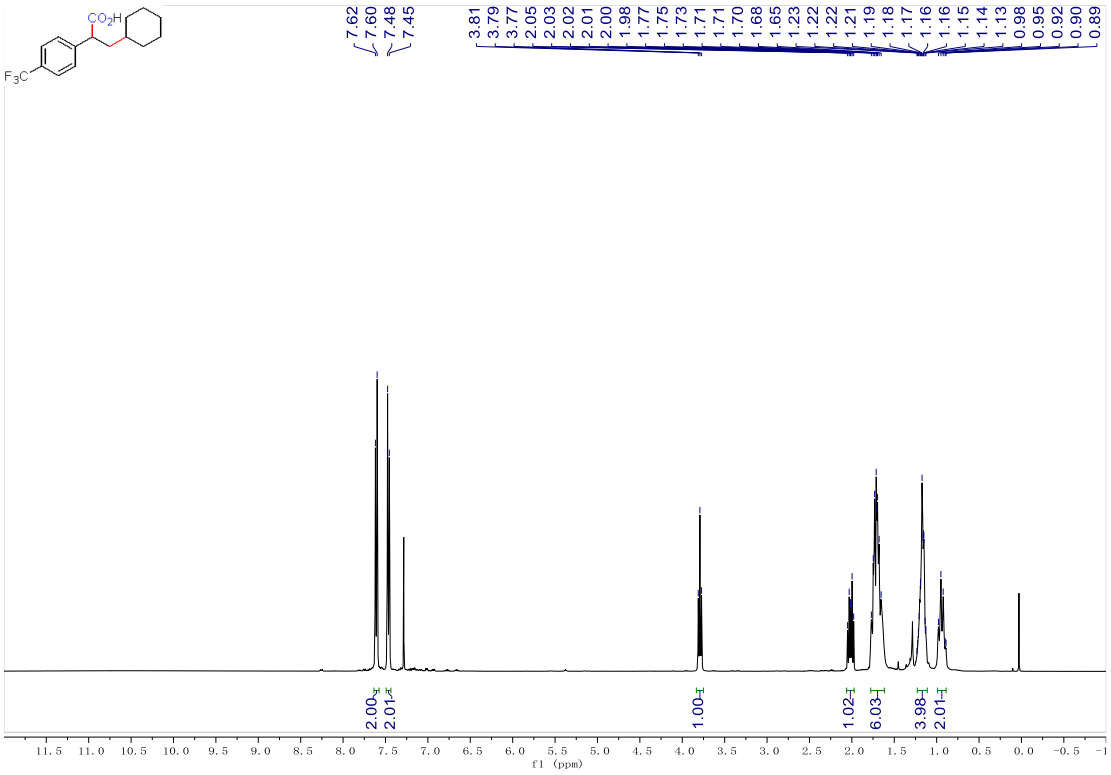



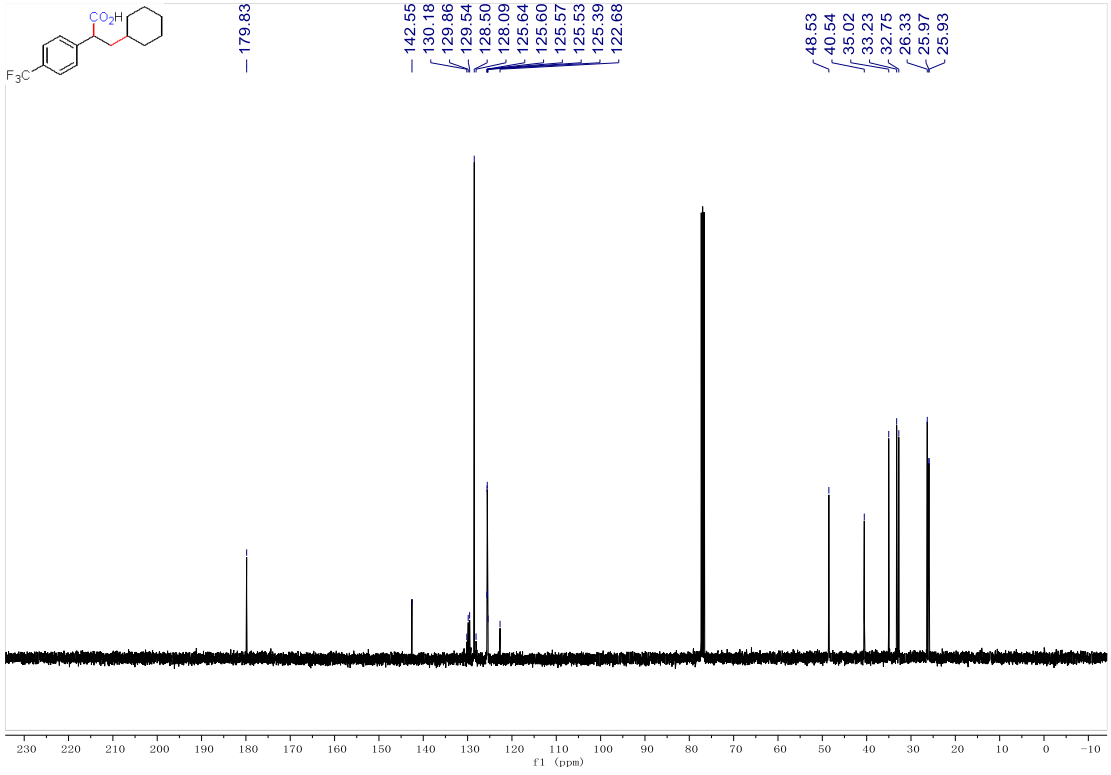
## 3-cyclohexyl-2-(4-(methoxycarbonyl)phenyl)propanoic acid (3ac)

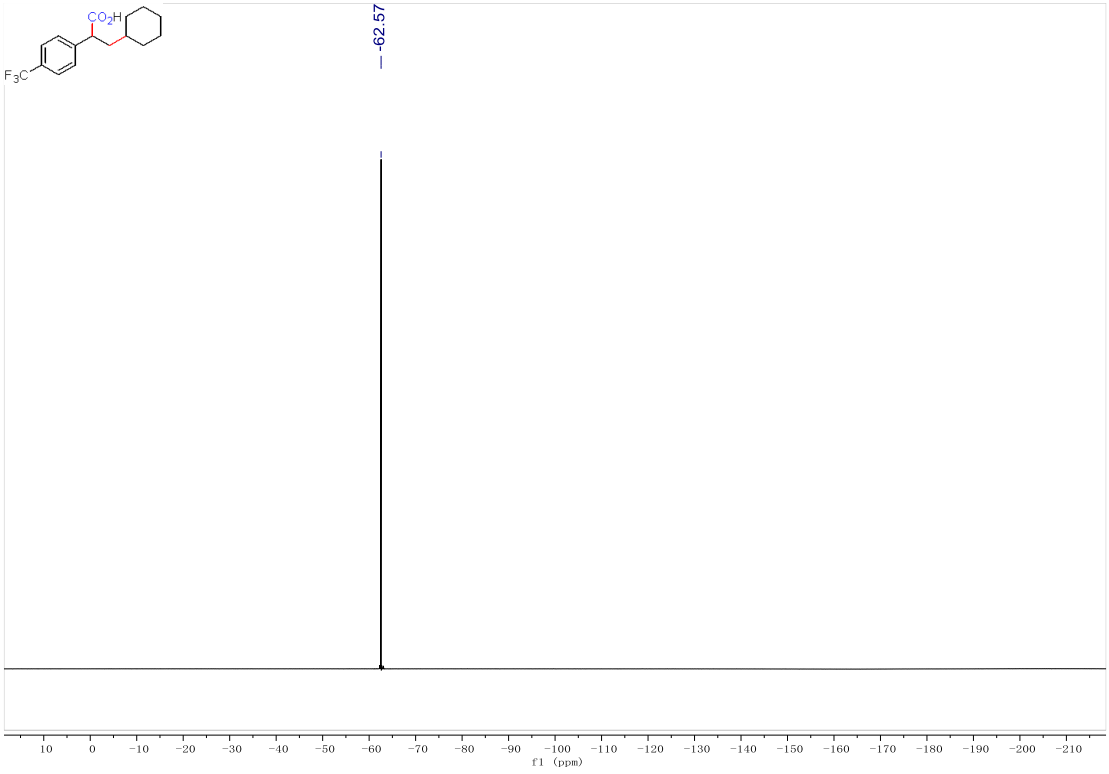


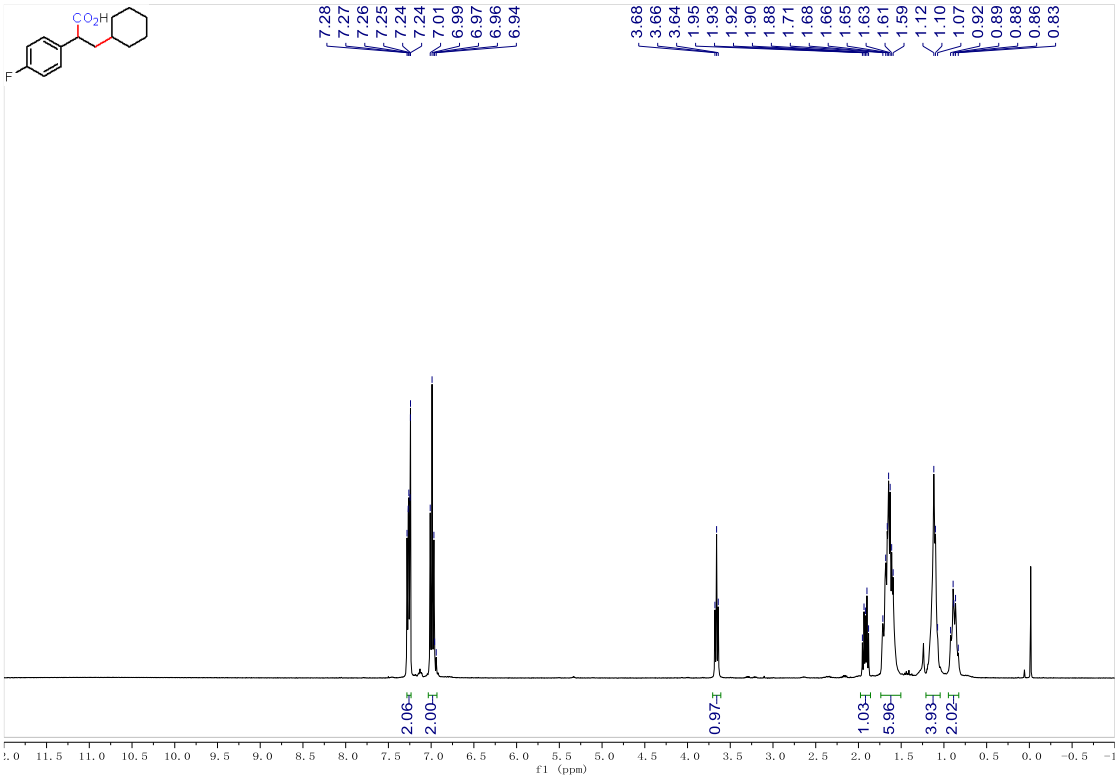
## 3-cyclohexyl-2-(4-(trifluoromethyl)phenyl)propanoic acid (3ad)

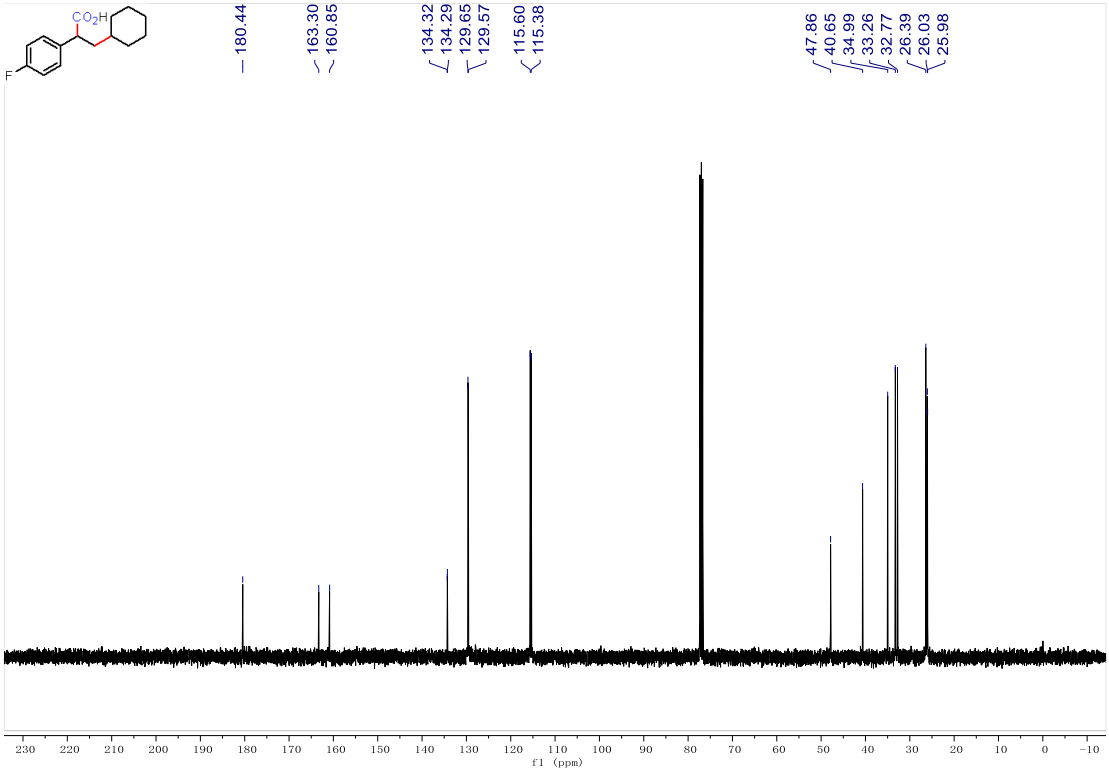


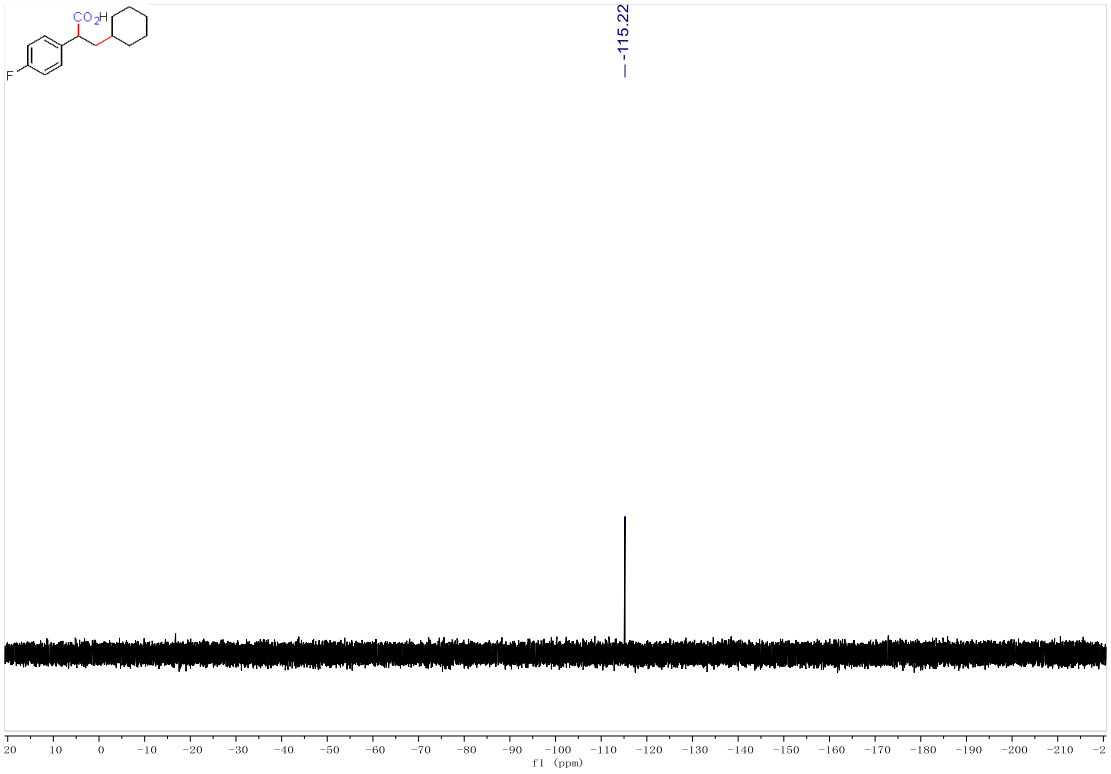




CO2H
F3C
-62.57
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

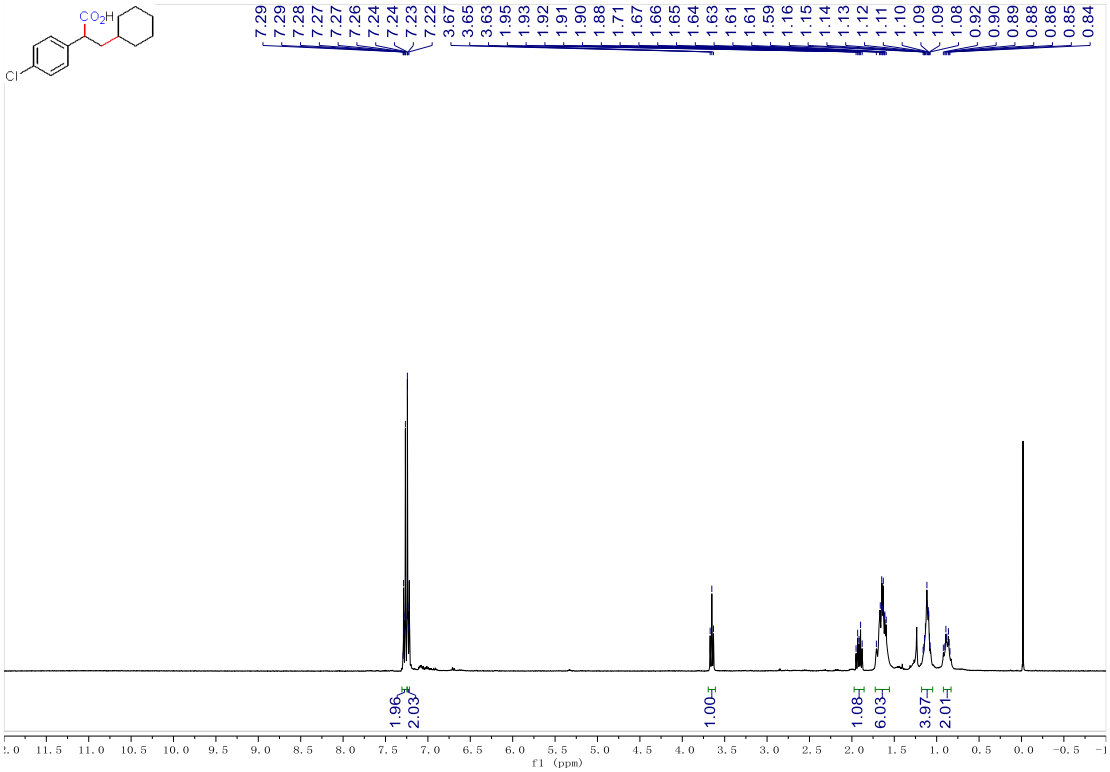
## 3-cyclohexyl-2-(4-fluorophenyl)propanoic acid (3ae)

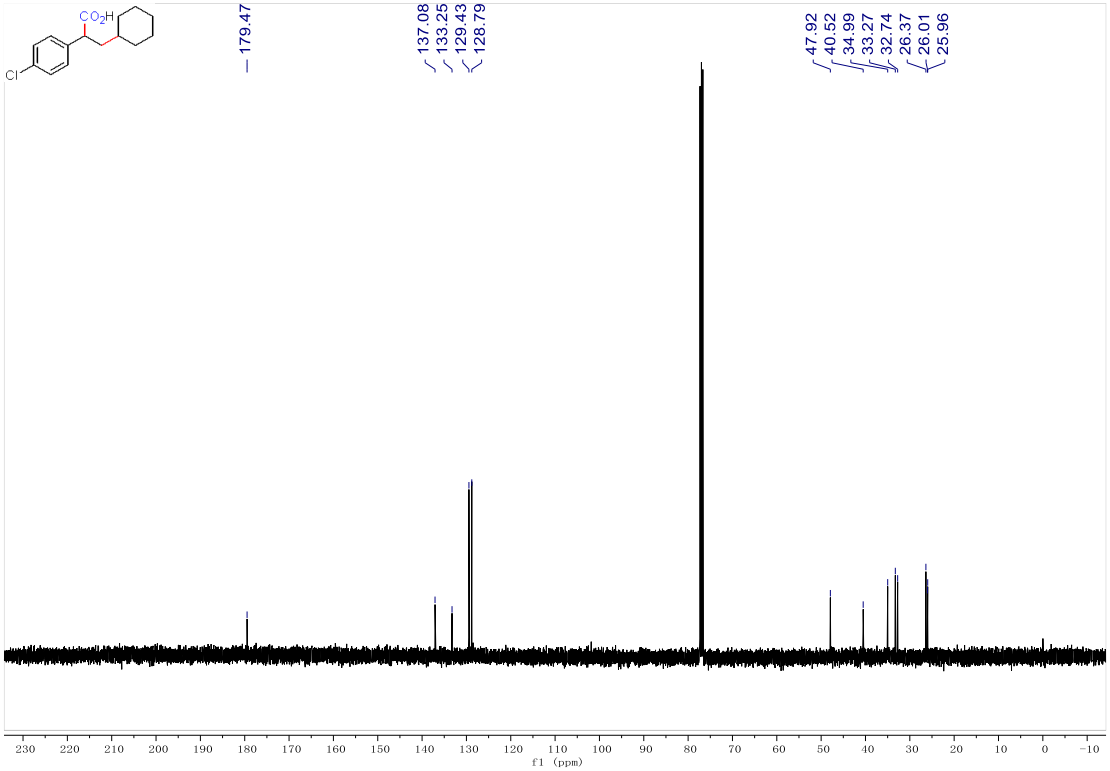



CO2H
F
180.44
163.30
160.85
134.32
134.29
129.65
129.57
115.60
115.38
47.86
40.65
34.99
33.26
32.77
26.39
26.03
25.98
f1 (ppm)

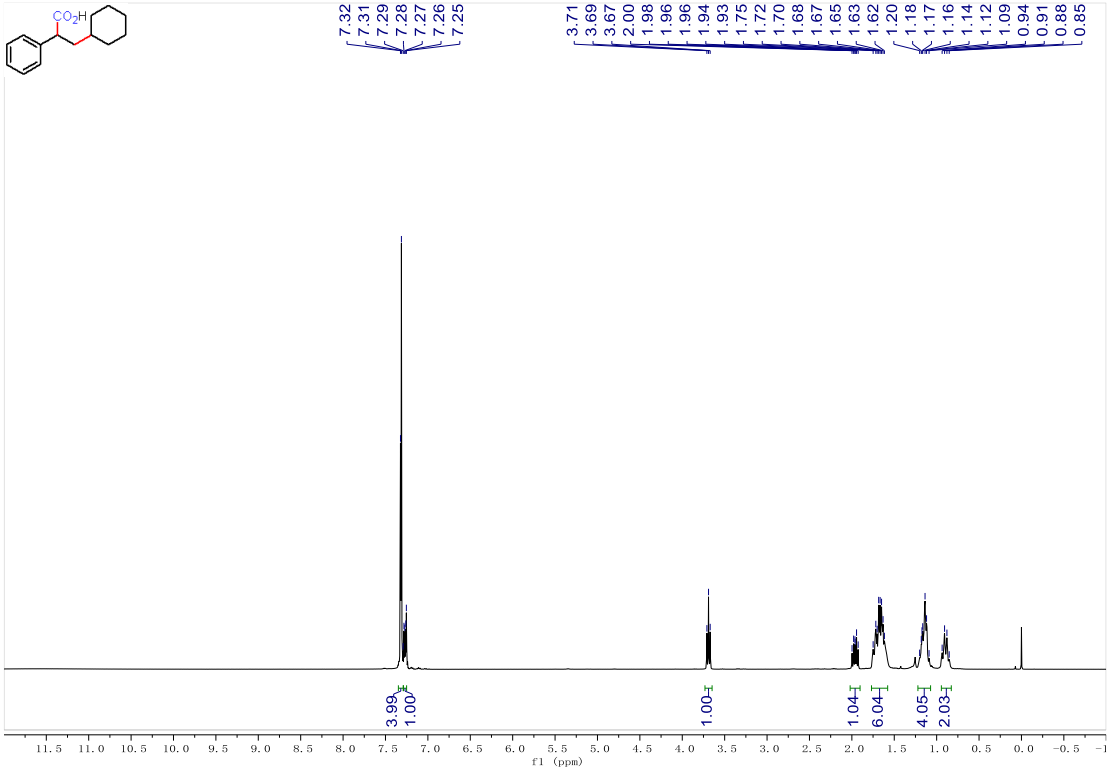

CO2H
F
-115.22
f1 (ppm)

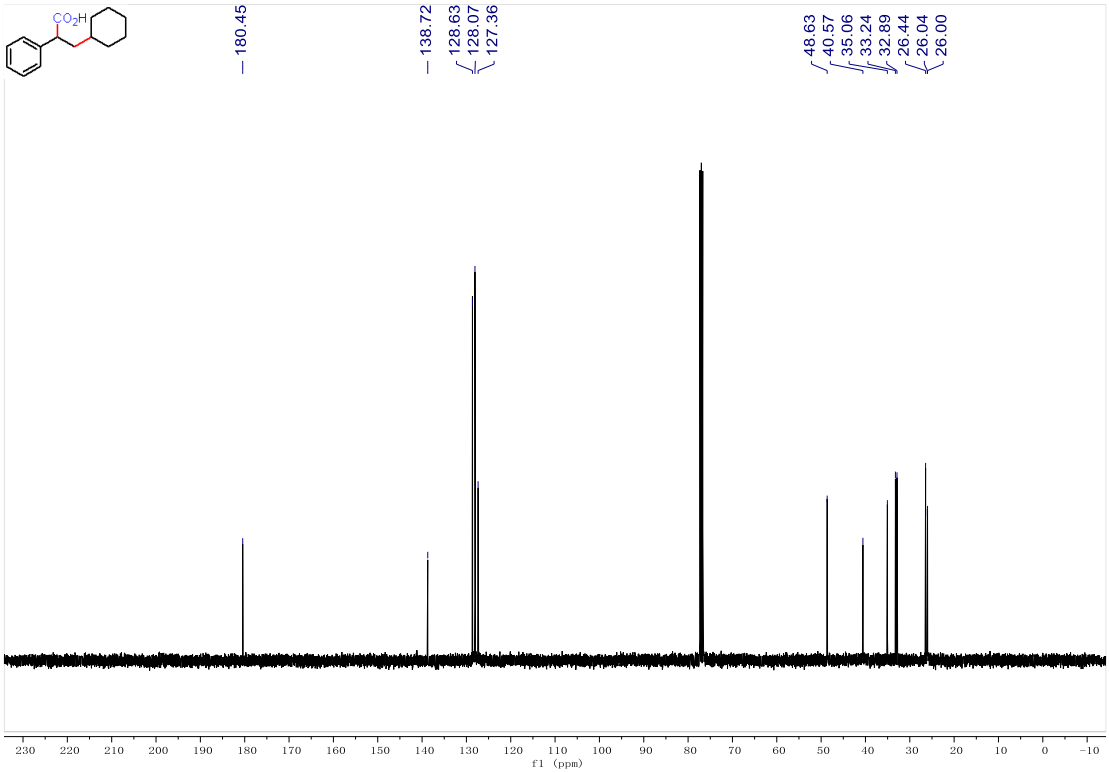
## 2-(4-chlorophenyl)-3-cyclohexylpropanoic acid (3af)



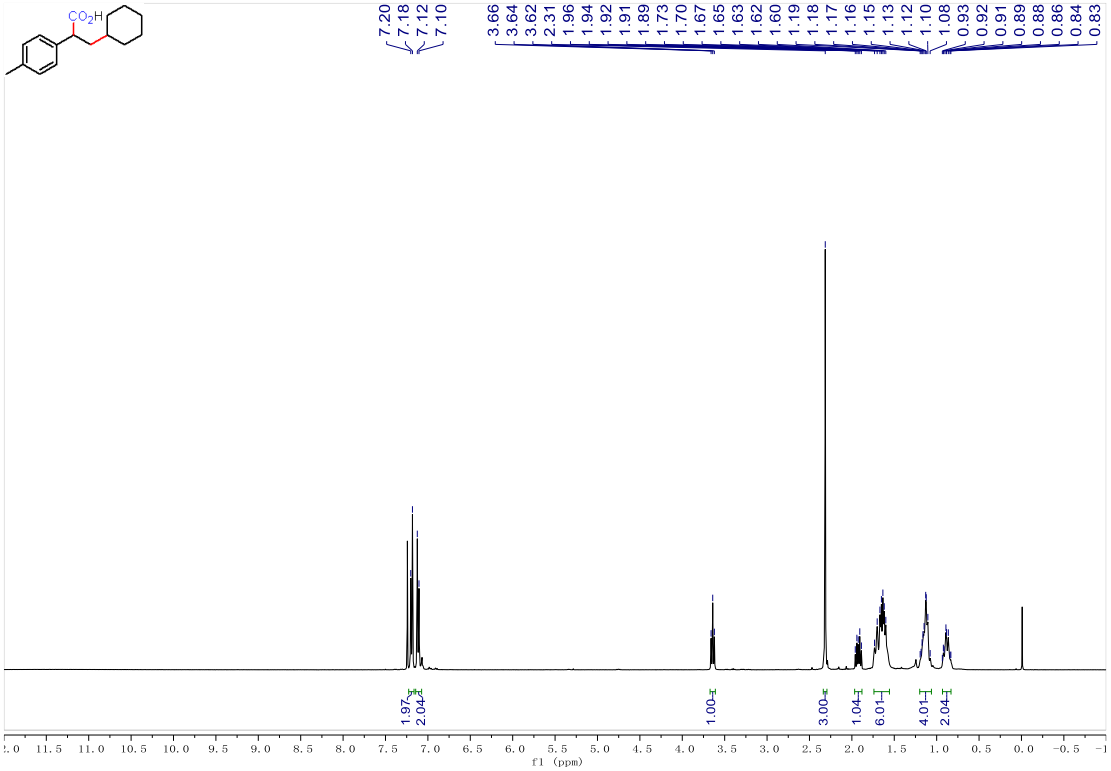



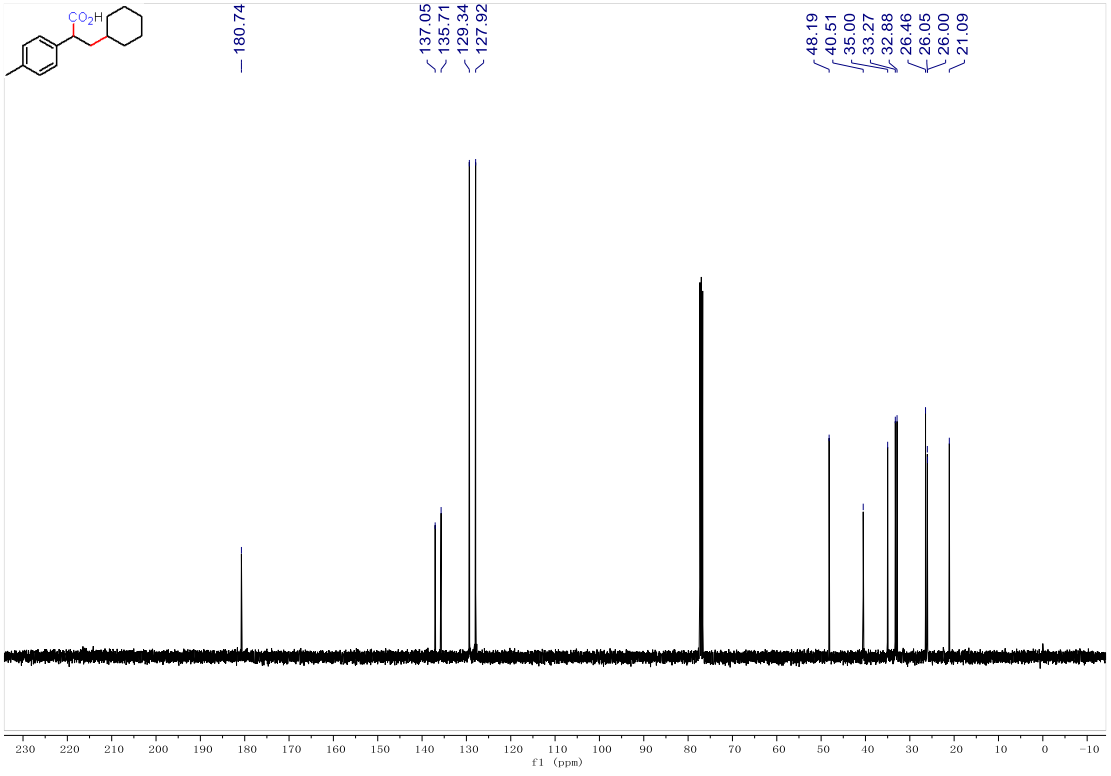
## 3-cyclohexyl-2-phenylpropanoic acid (3ag)



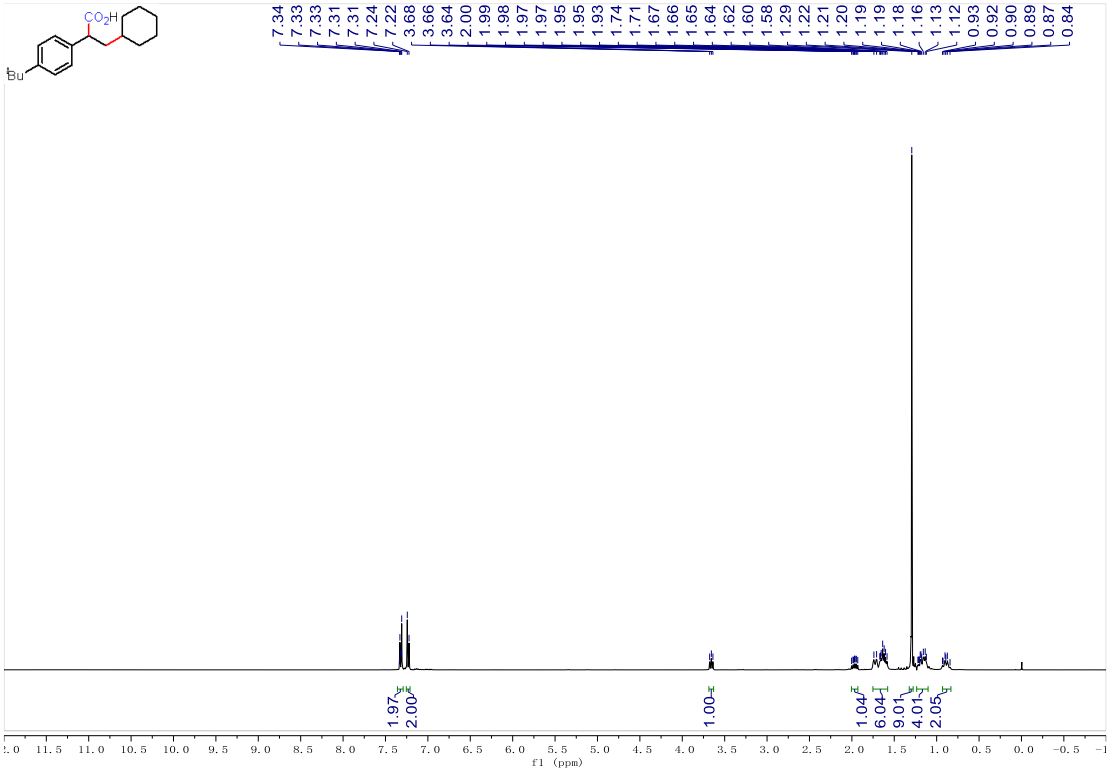



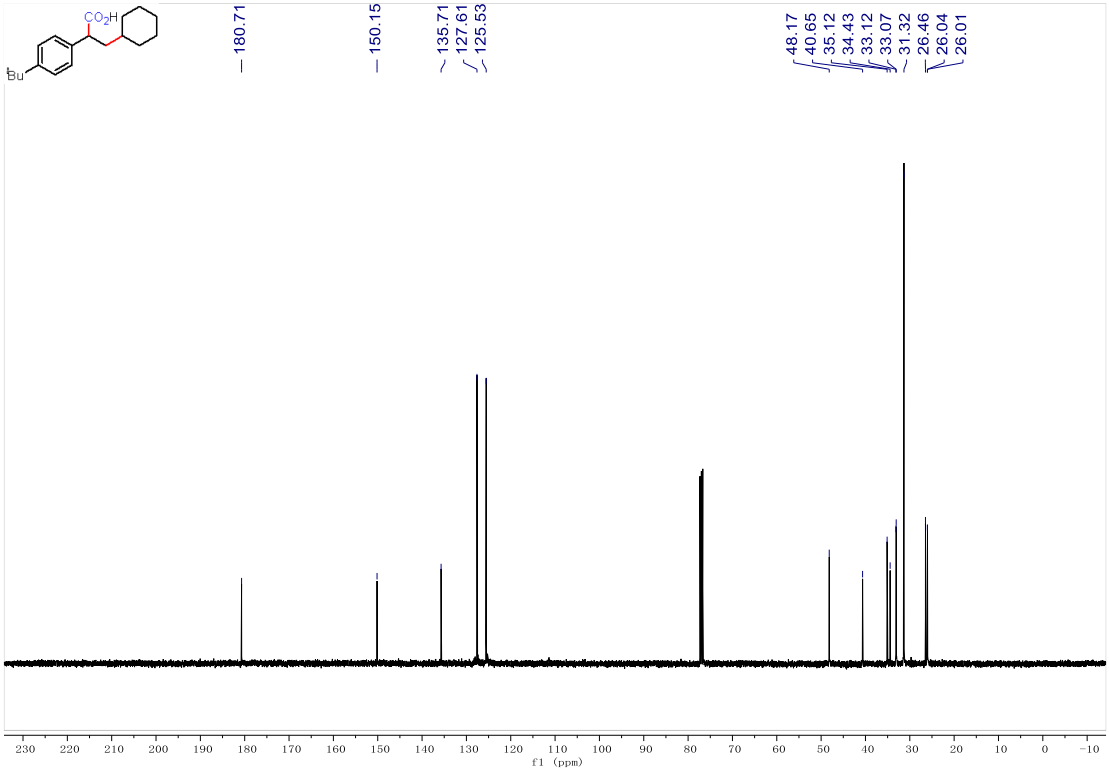
## 3-cyclohexyl-2-(p-tolyl)propanoic acid (3ah)



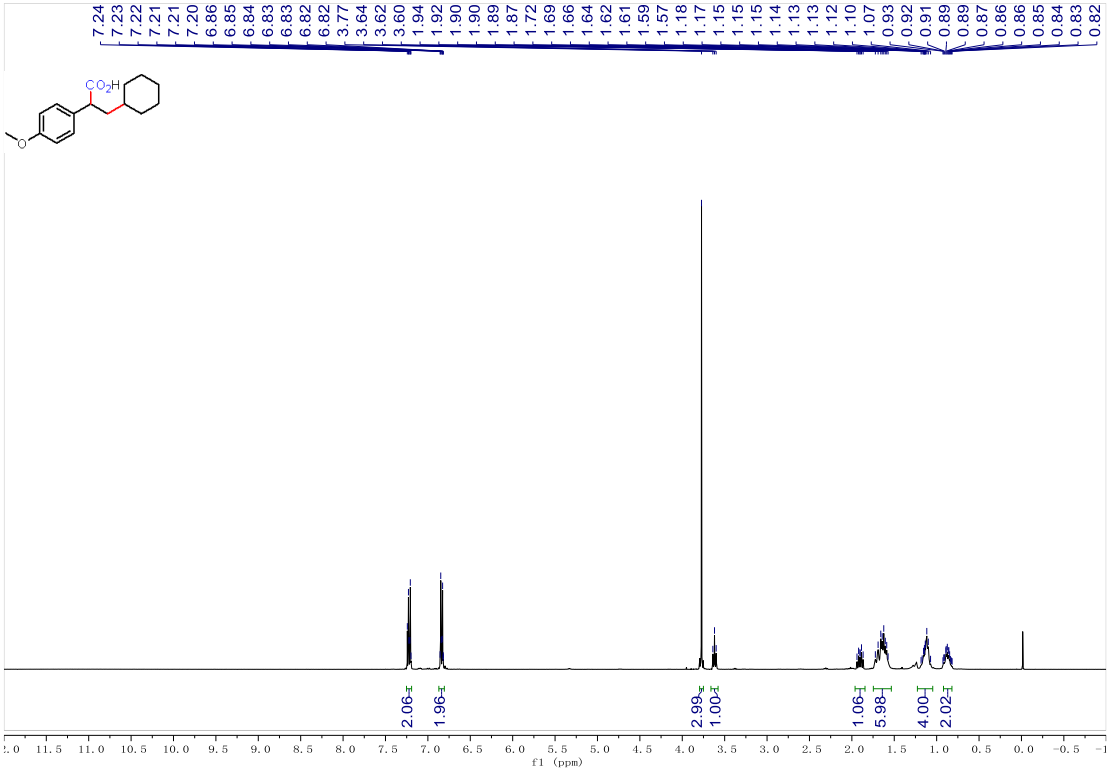



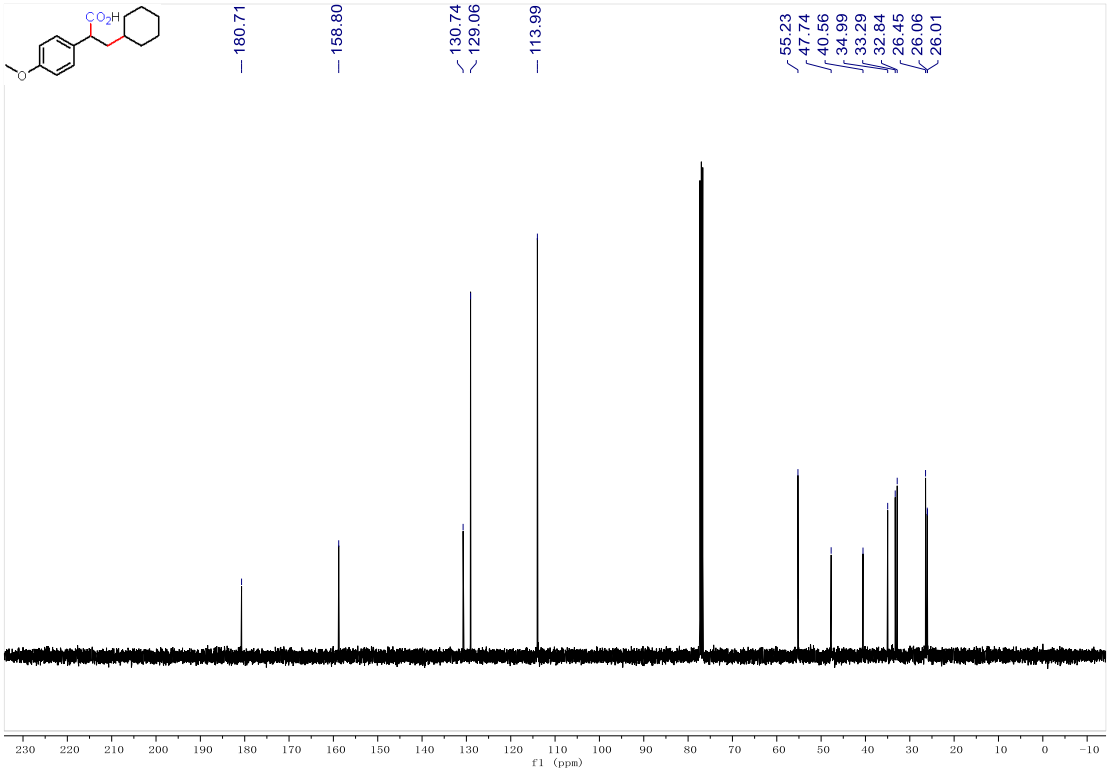
## 2-(4-(*tert*-butyl)phenyl)-3-cyclohexylpropanoic acid (3ai)



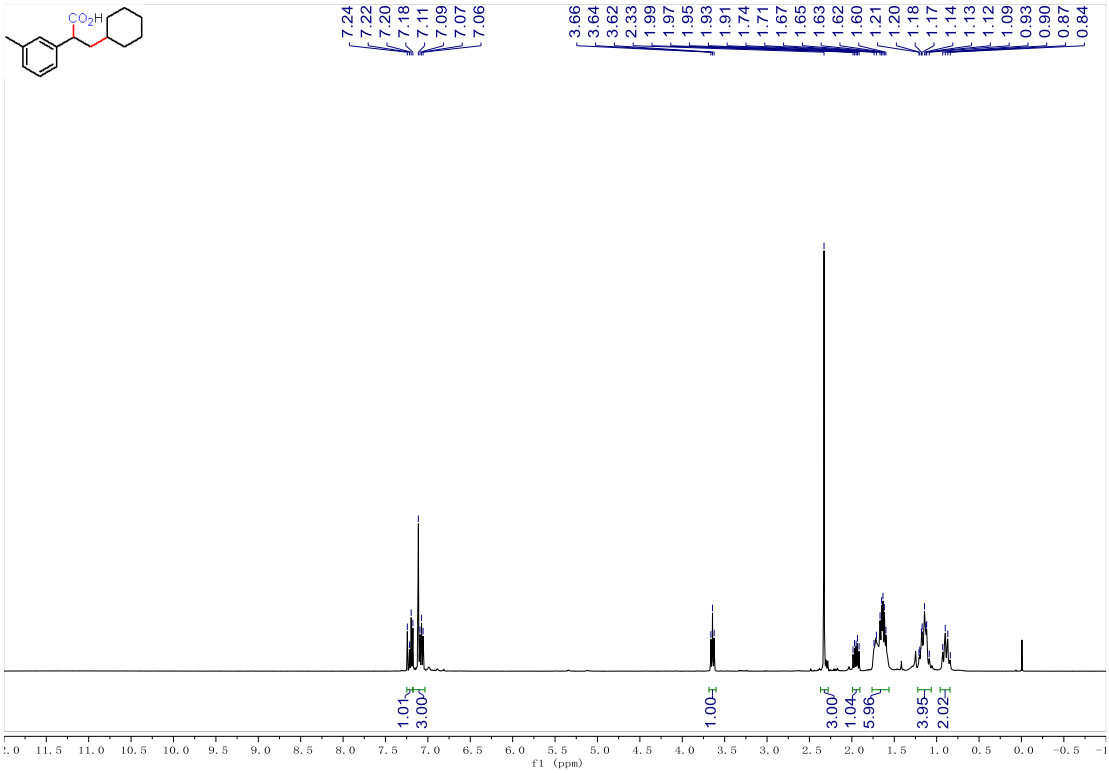



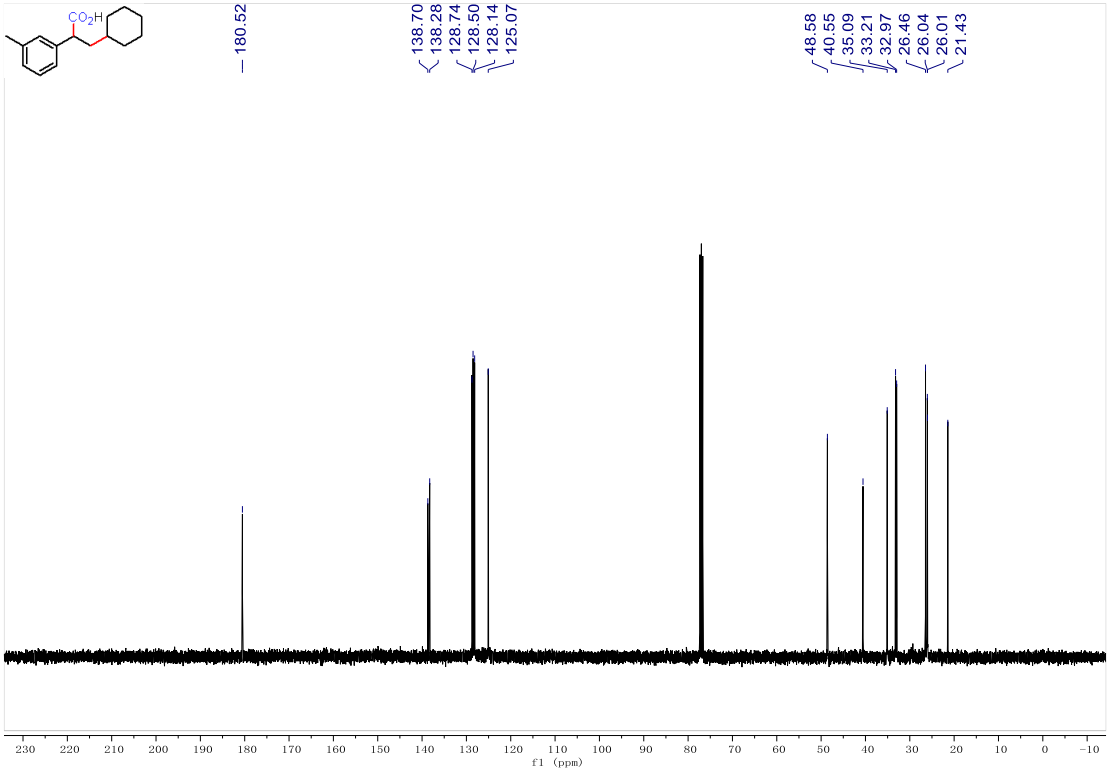
## 3-cyclohexyl-2-(4-methoxyphenyl)propanoic acid (3aj)



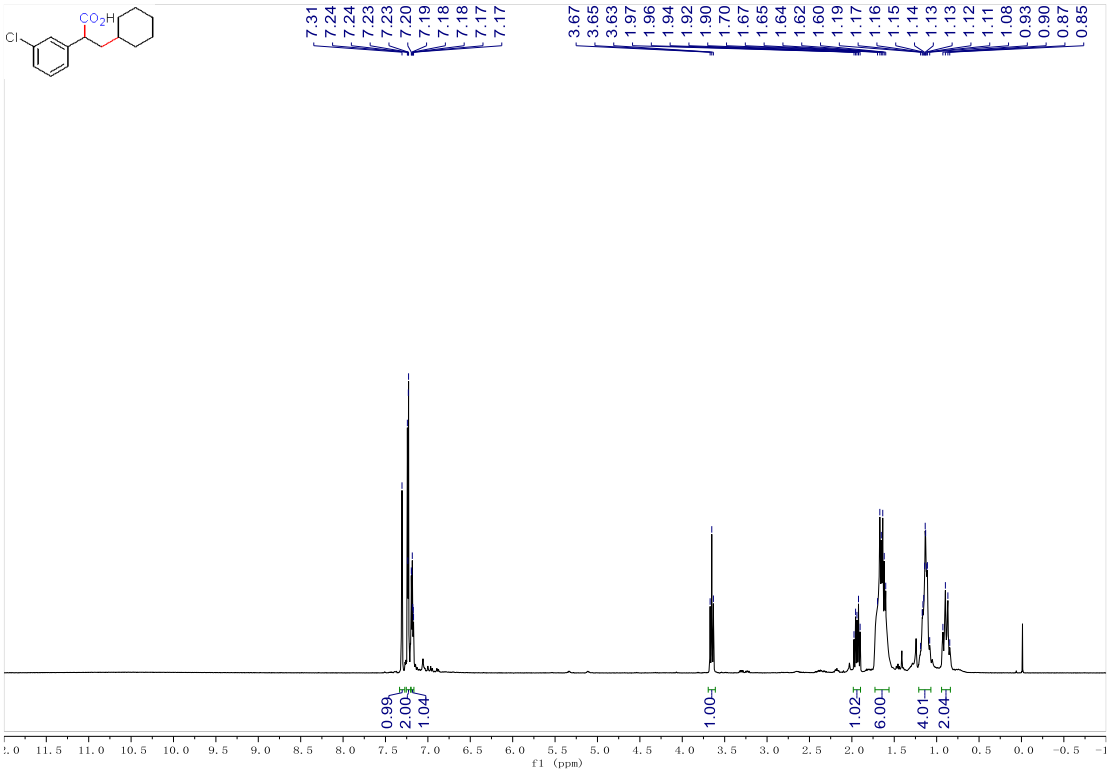



## 3-cyclohexyl-2-(m-tolyl)propanoic acid (3ak)

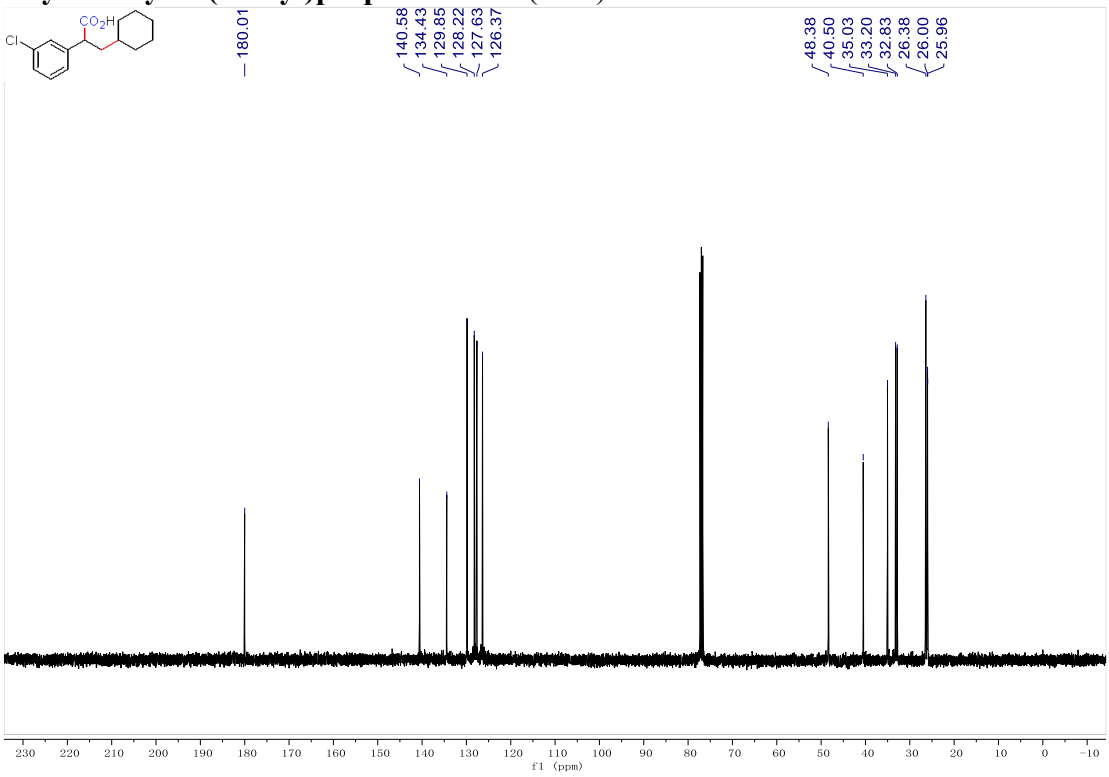


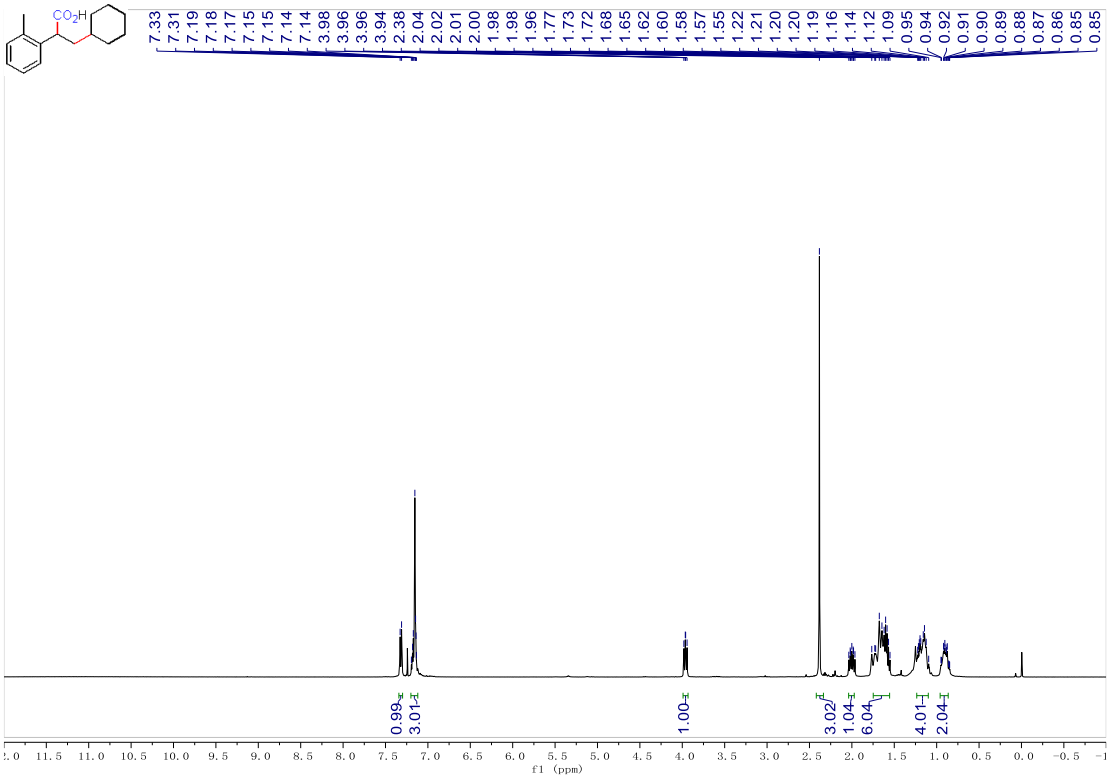



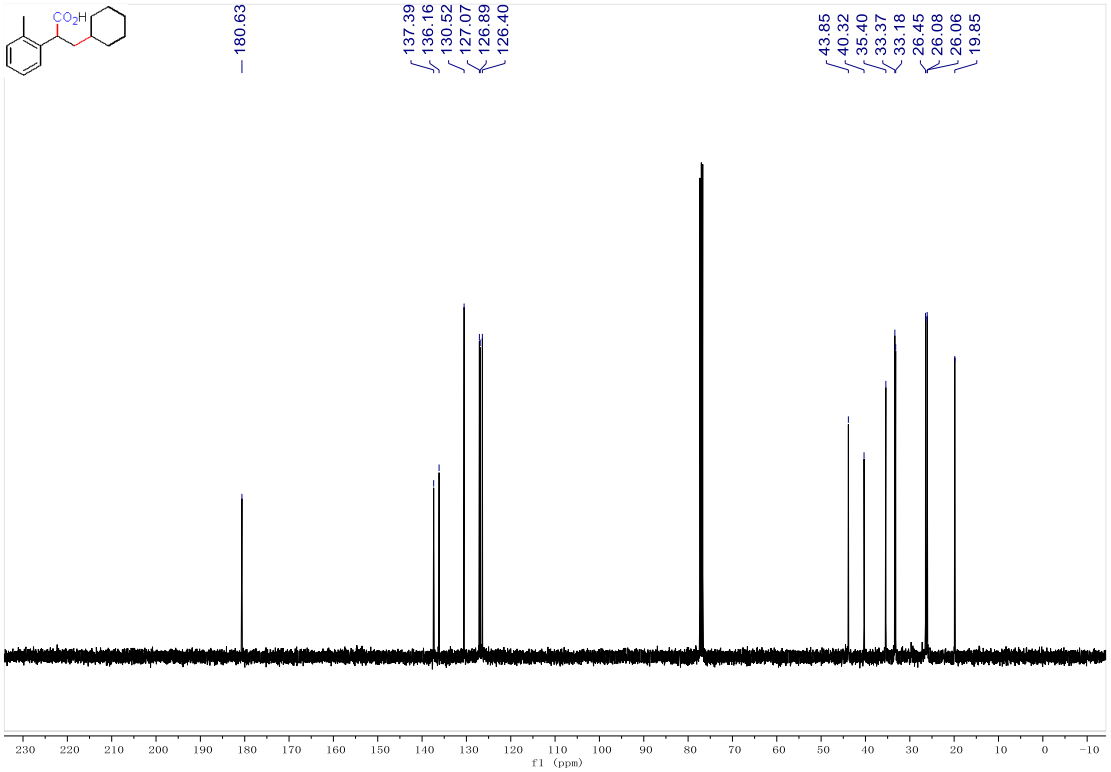
## 2-(3-chlorophenyl)-3-cyclohexylpropanoic acid (3al)



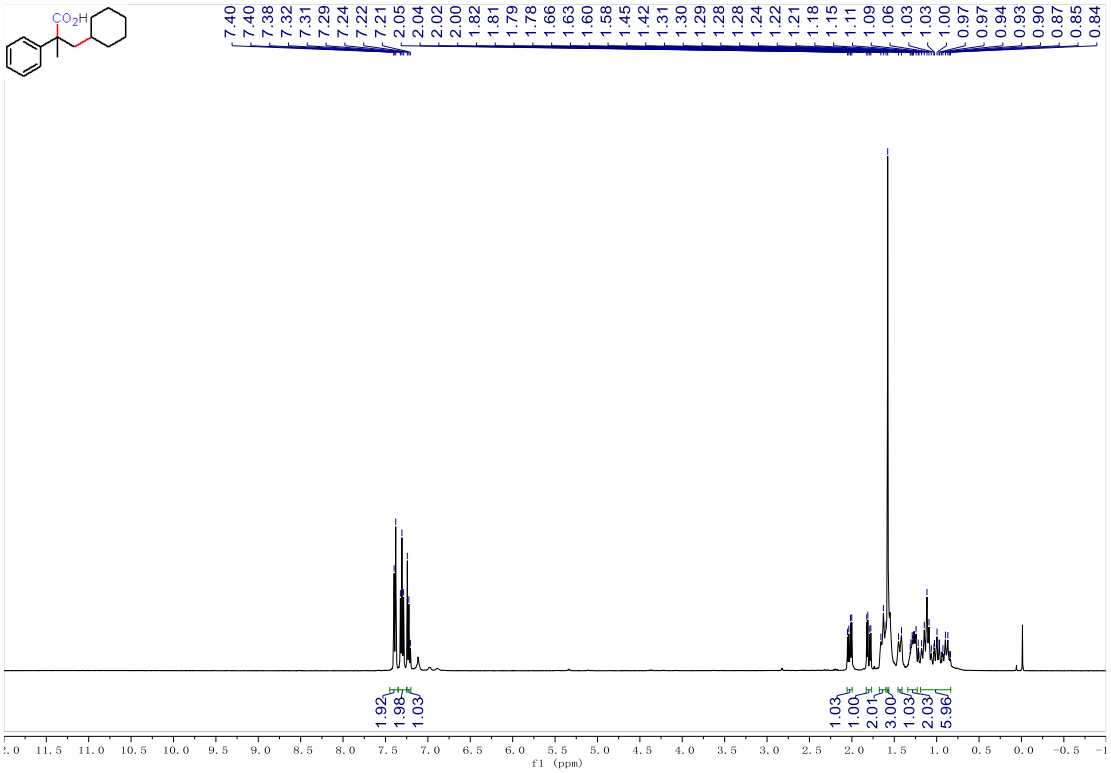

## 3-cyclohexyl-2-(o-tolyl)propanoic acid (3am)

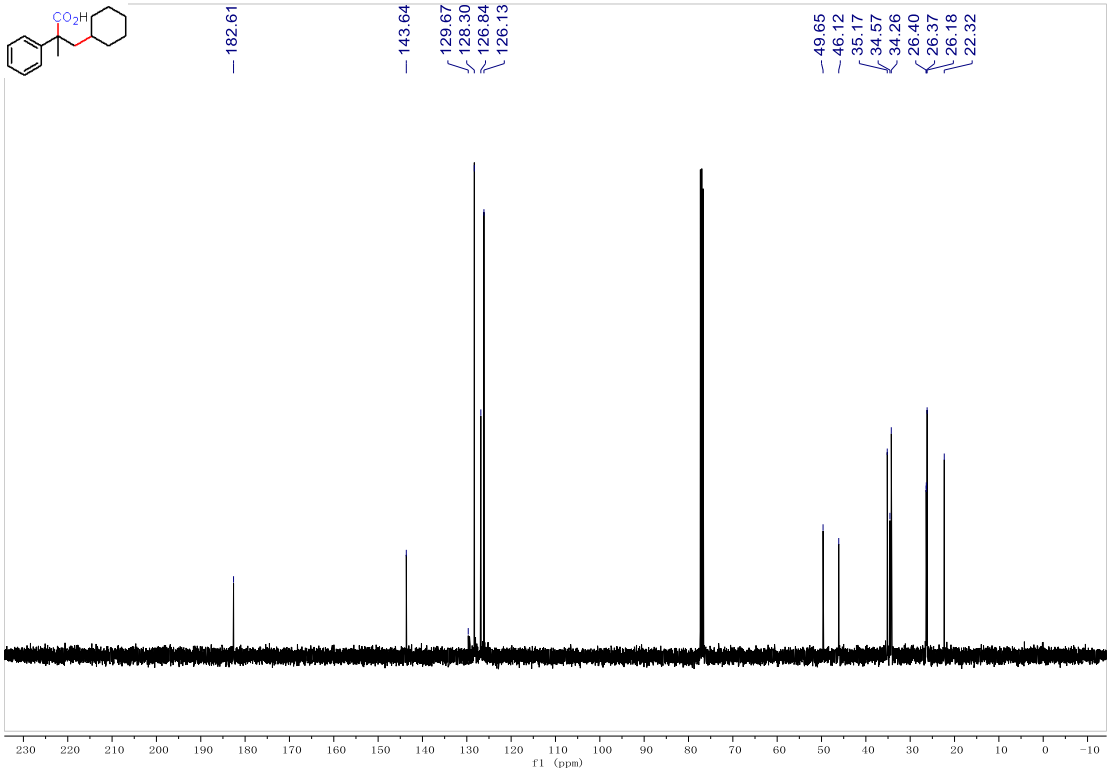



7.33
7.31
7.19
7.18
7.17
7.15
7.15
7.14
7.14
3.98
3.96
3.96
3.94
2.38
2.04
2.02
2.01
2.00
1.98
1.98
1.96
1.77
1.73
1.72
1.68
1.65
1.62
1.60
1.58
1.57
1.55
1.22
1.21
1.20
1.20
1.19
1.16
1.14
1.12
1.09
0.95
0.94
0.92
0.91
0.90
0.89
0.88
0.87
0.86
0.85
0.85
0.99
3.01
1.00
3.02
1.04
6.04
4.01
2.04
f1 (ppm)

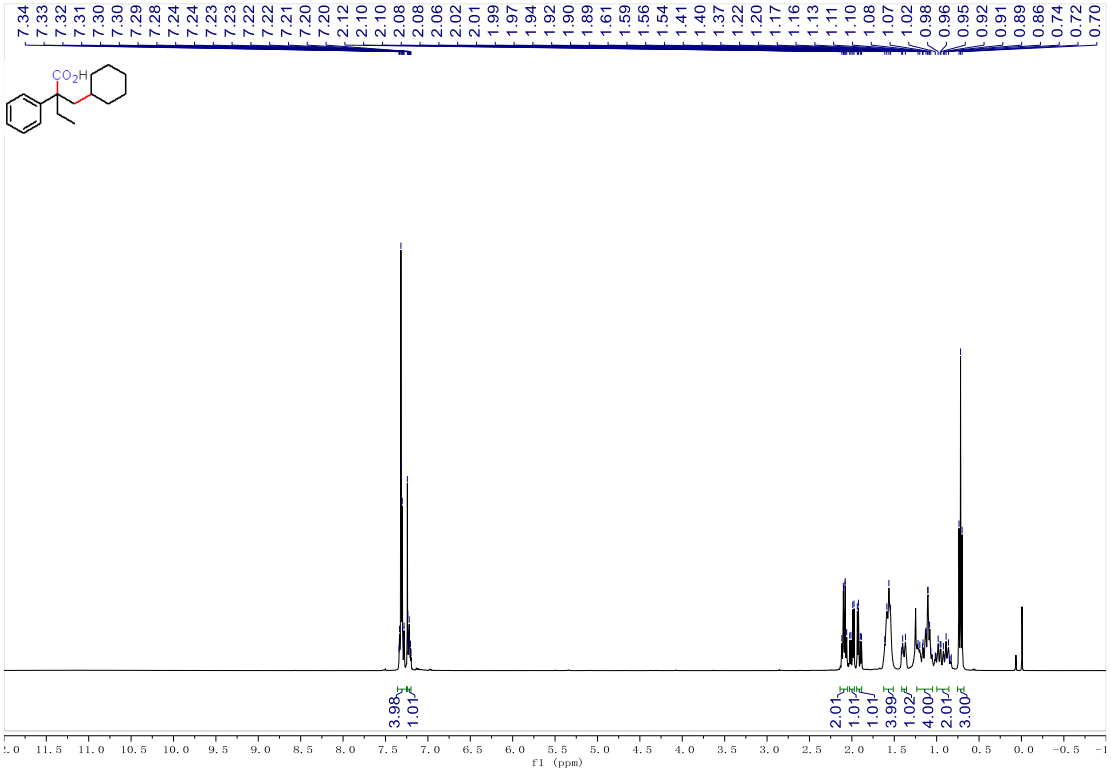

180.63
137.39
136.16
130.52
127.07
126.89
126.40
43.85
40.32
35.40
33.37
33.18
26.45
26.08
26.06
19.85
f1 (ppm)

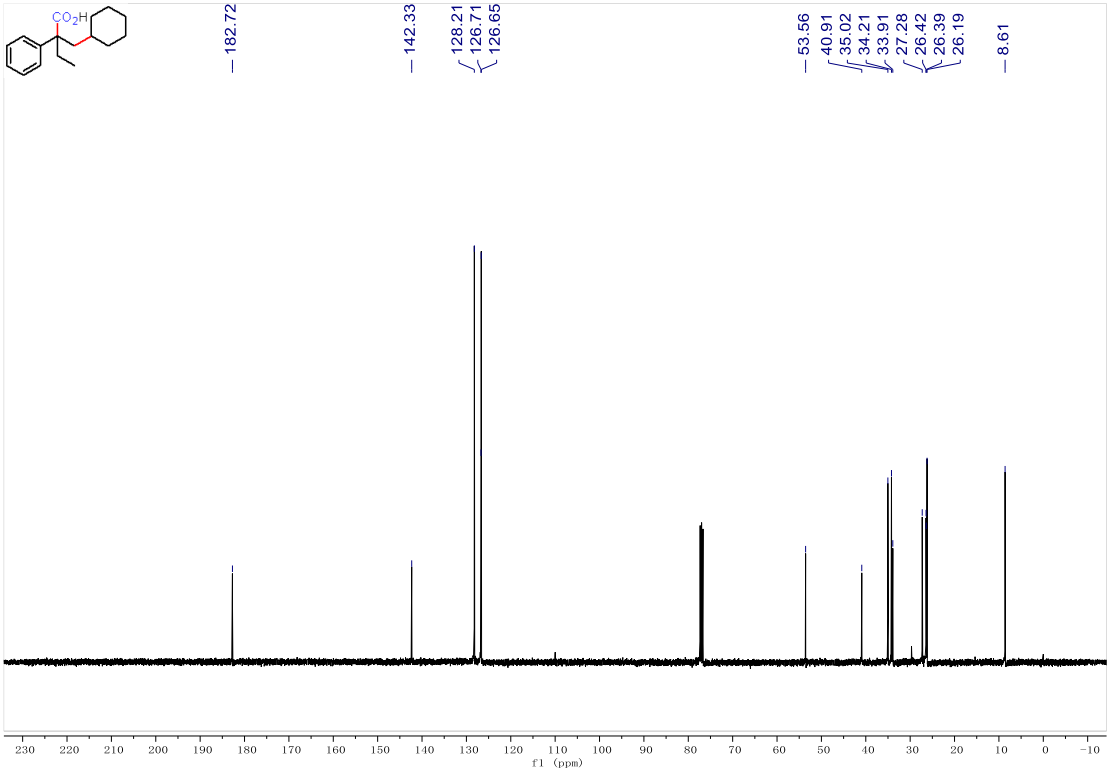
## 3-cyclohexyl-2-methyl-2-phenylpropanoic acid (3an)



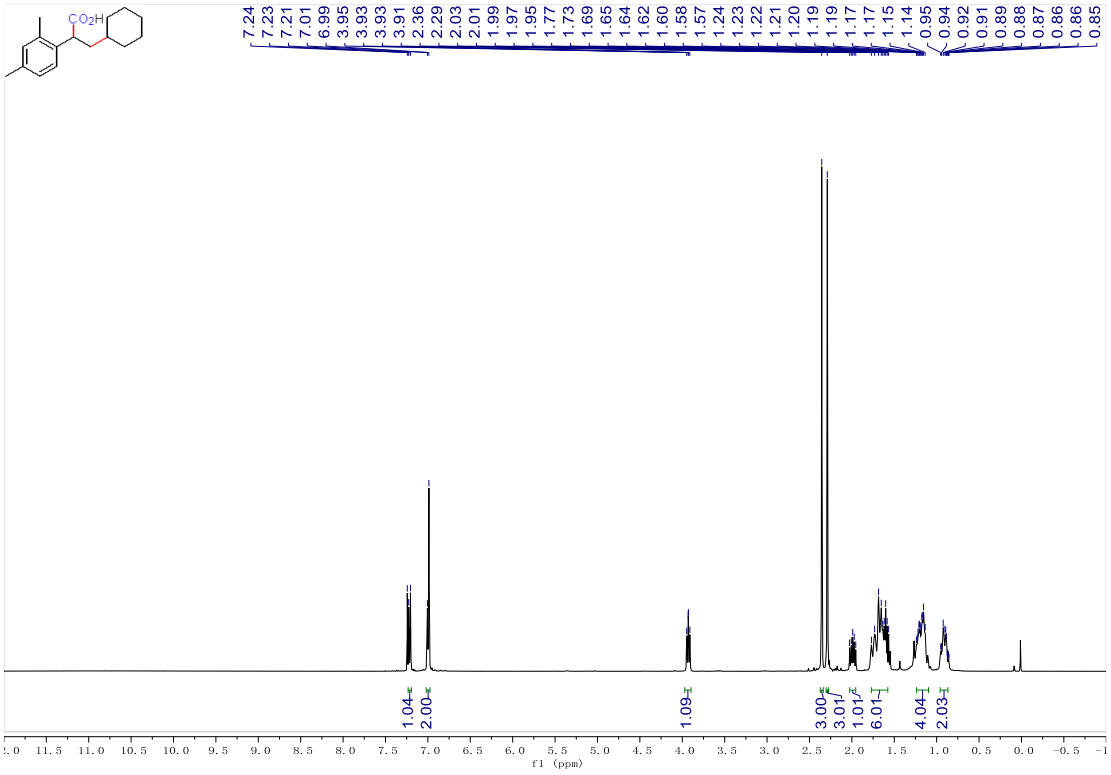



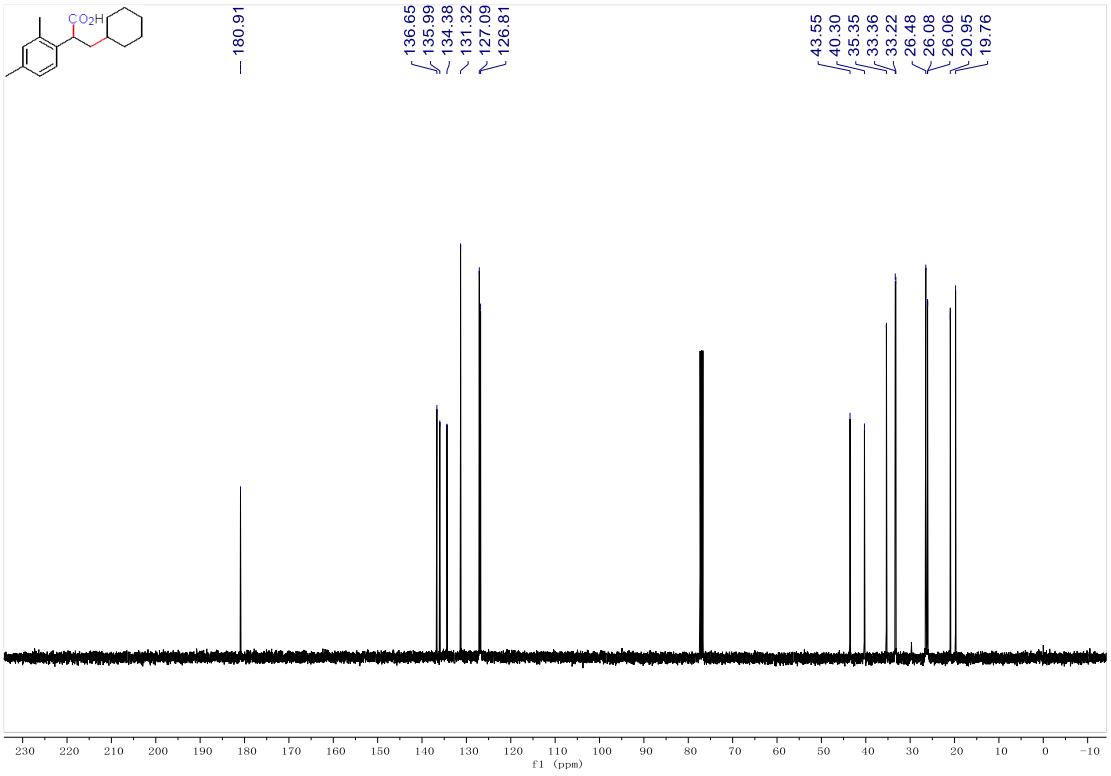
## 2-(cyclohexylmethyl)-2-phenylbutanoic acid (3ao)



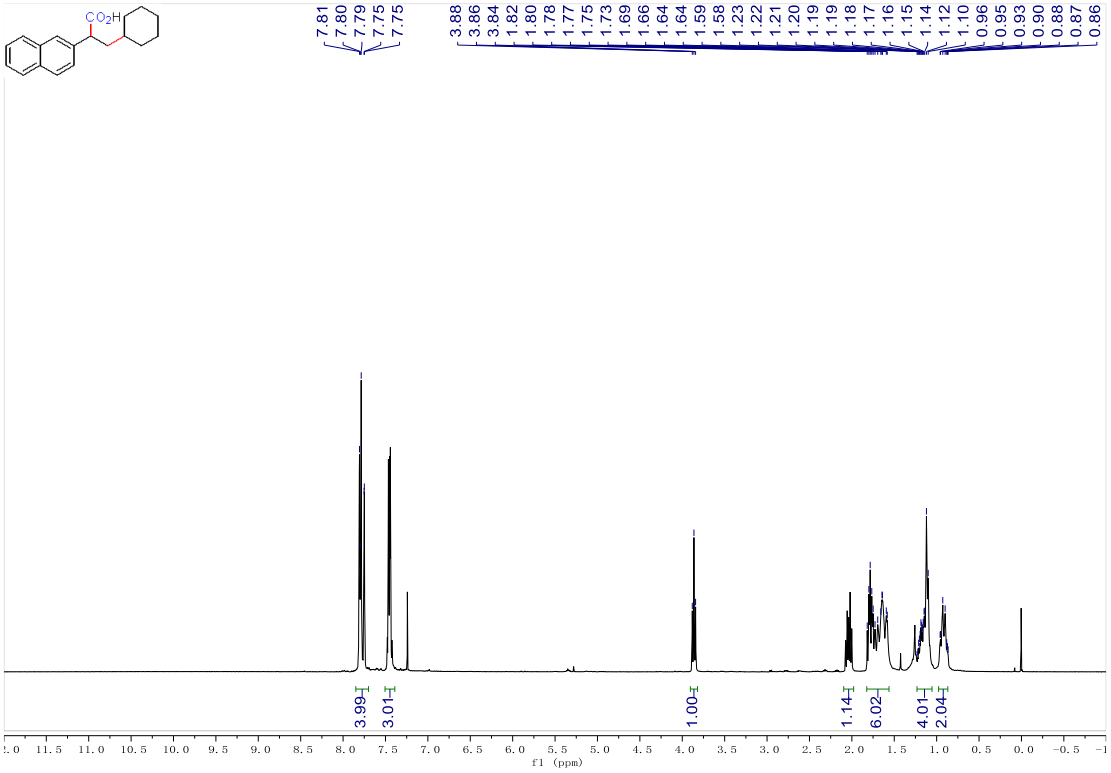



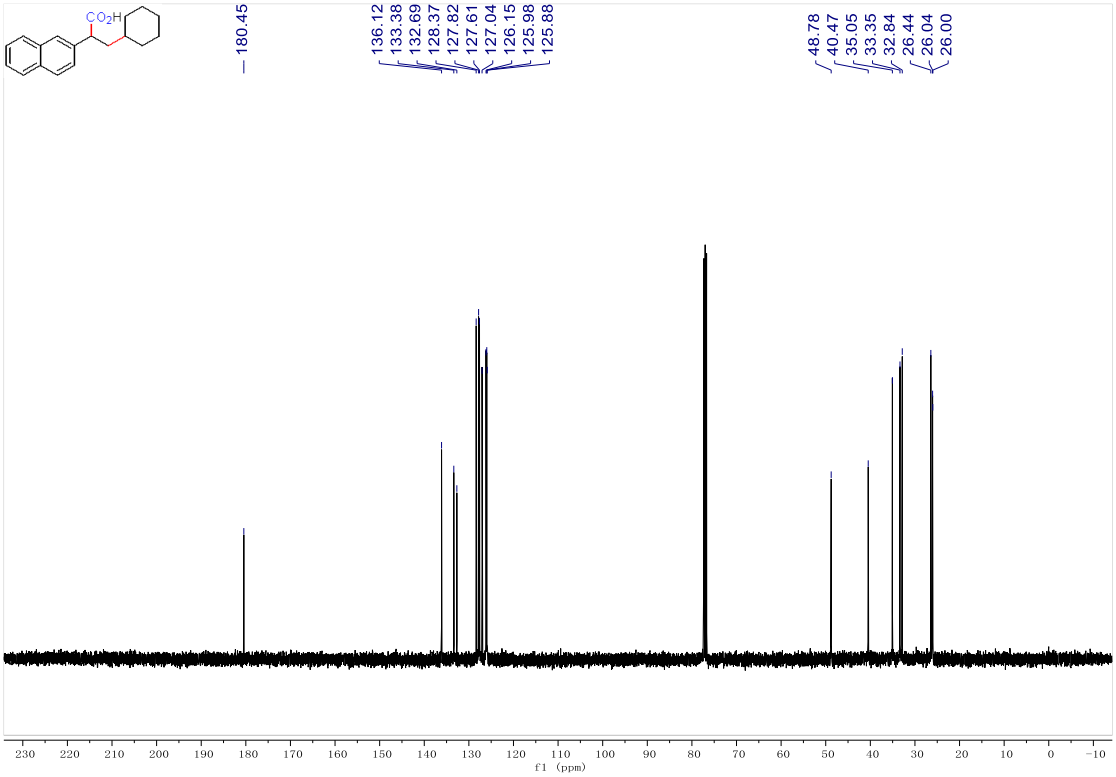
## 3-cyclohexyl-2-(2,4-dimethylphenyl)propanoic acid (3ap)



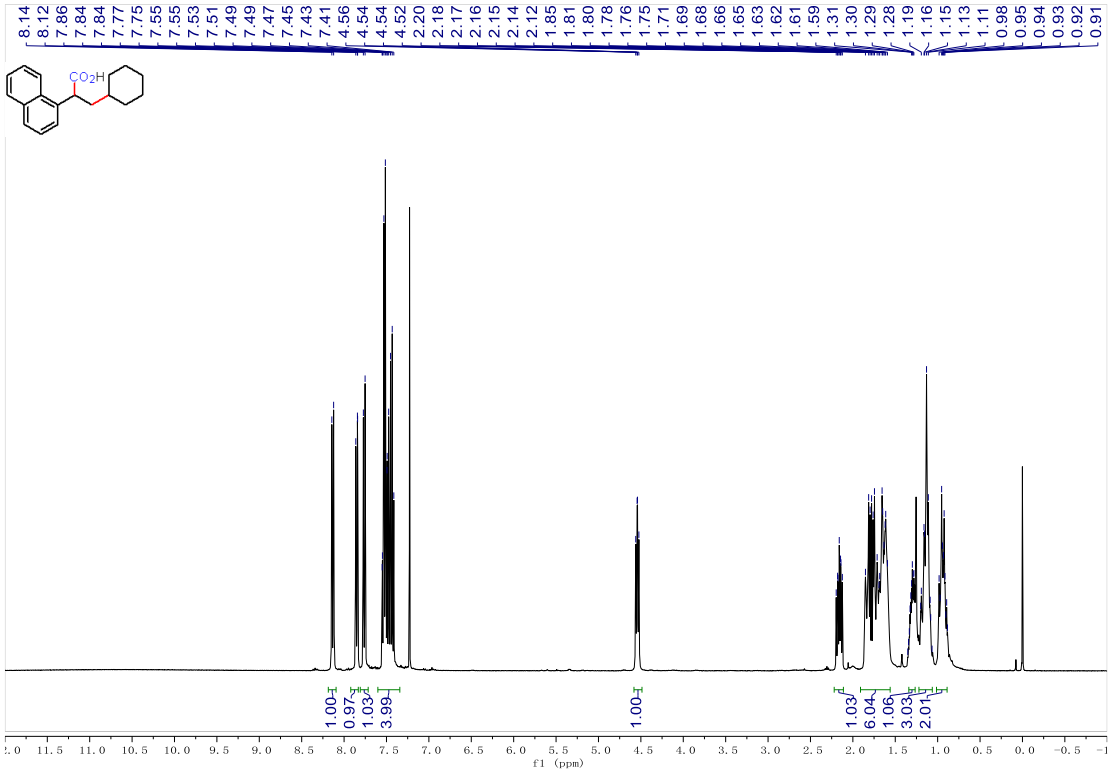



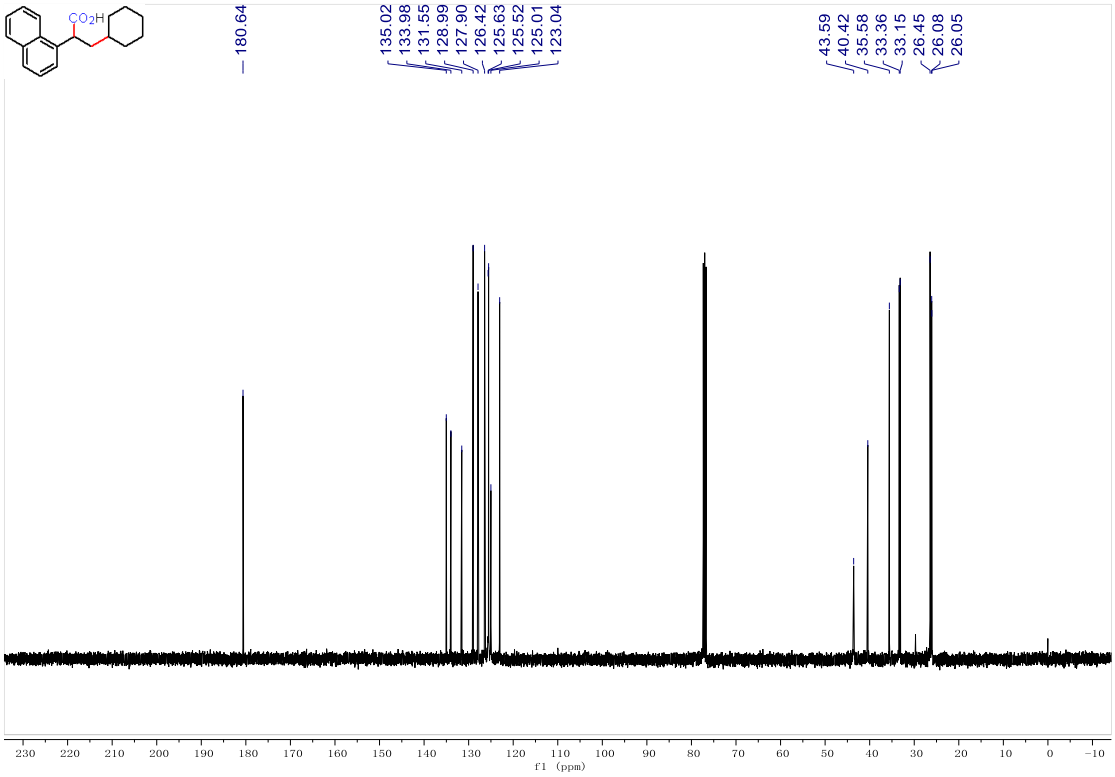
## 3-cyclohexyl-2-(naphthalen-2-yl)propanoic acid (3aq)



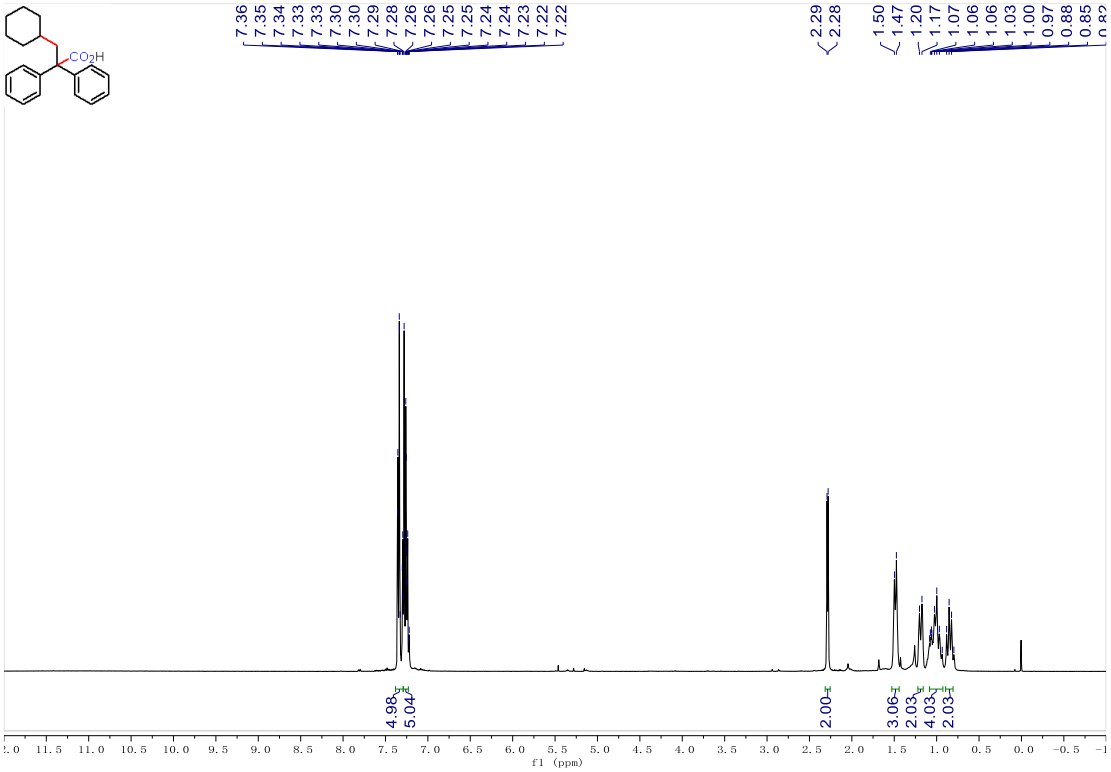



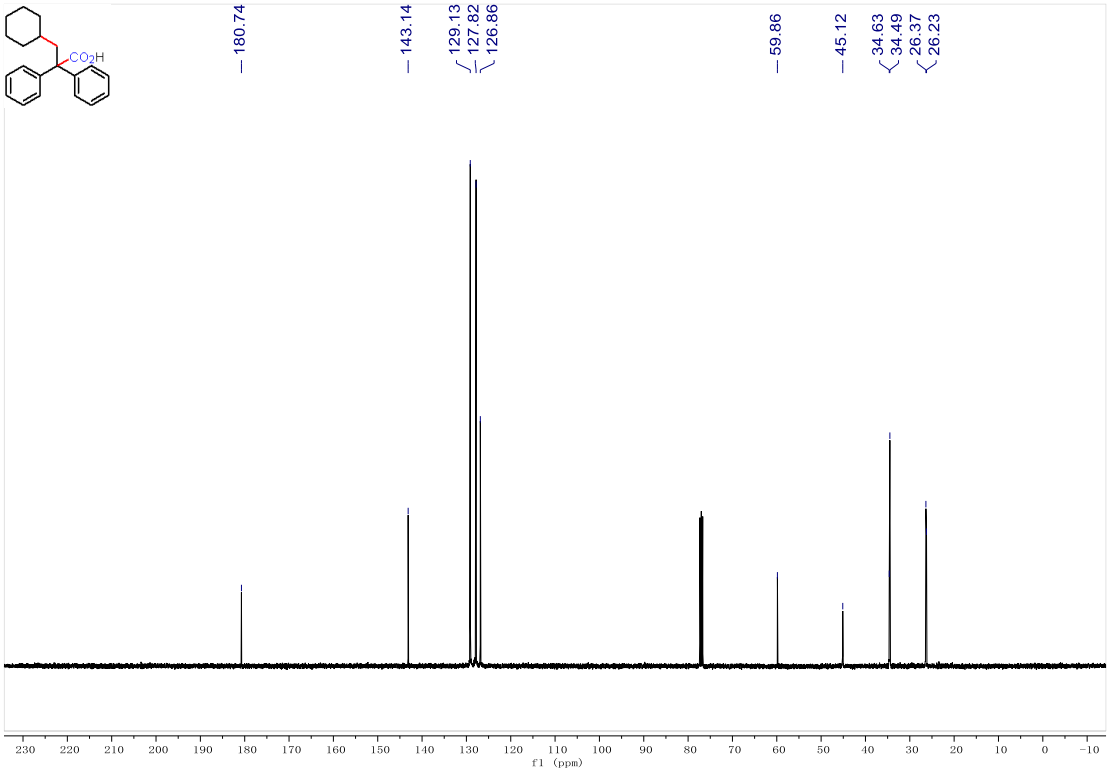
## 3-cyclohexyl-2-(naphthalen-1-yl)propanoic acid (3ar)



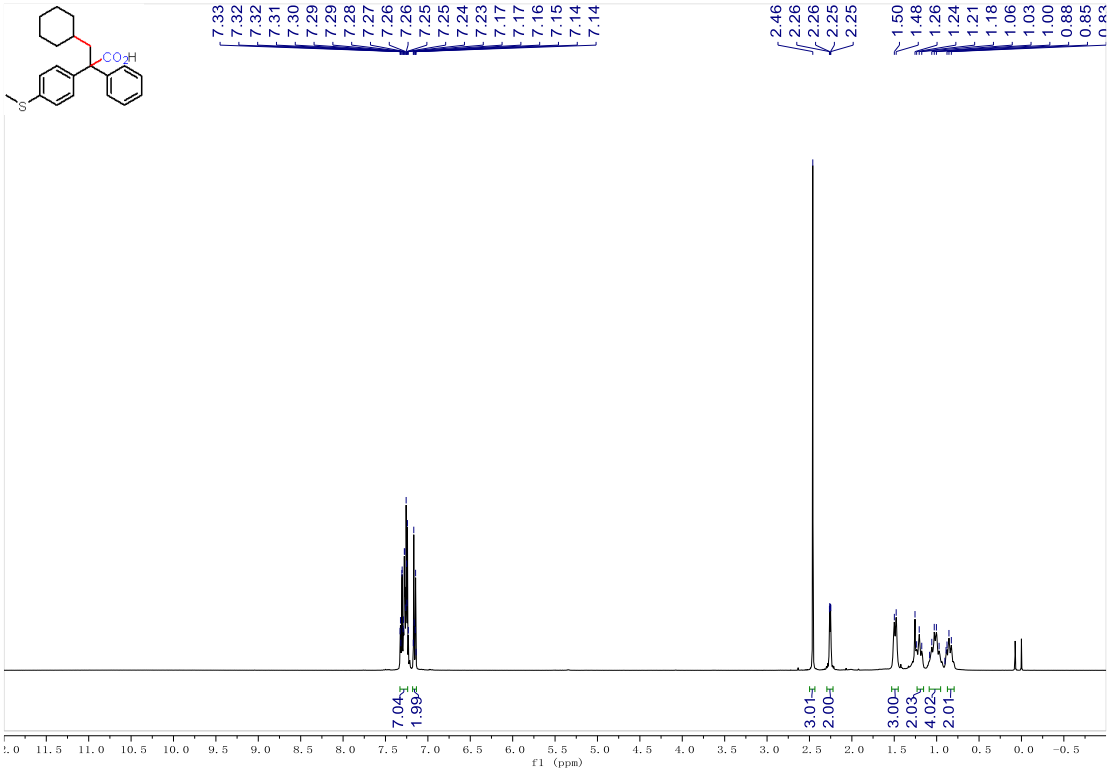



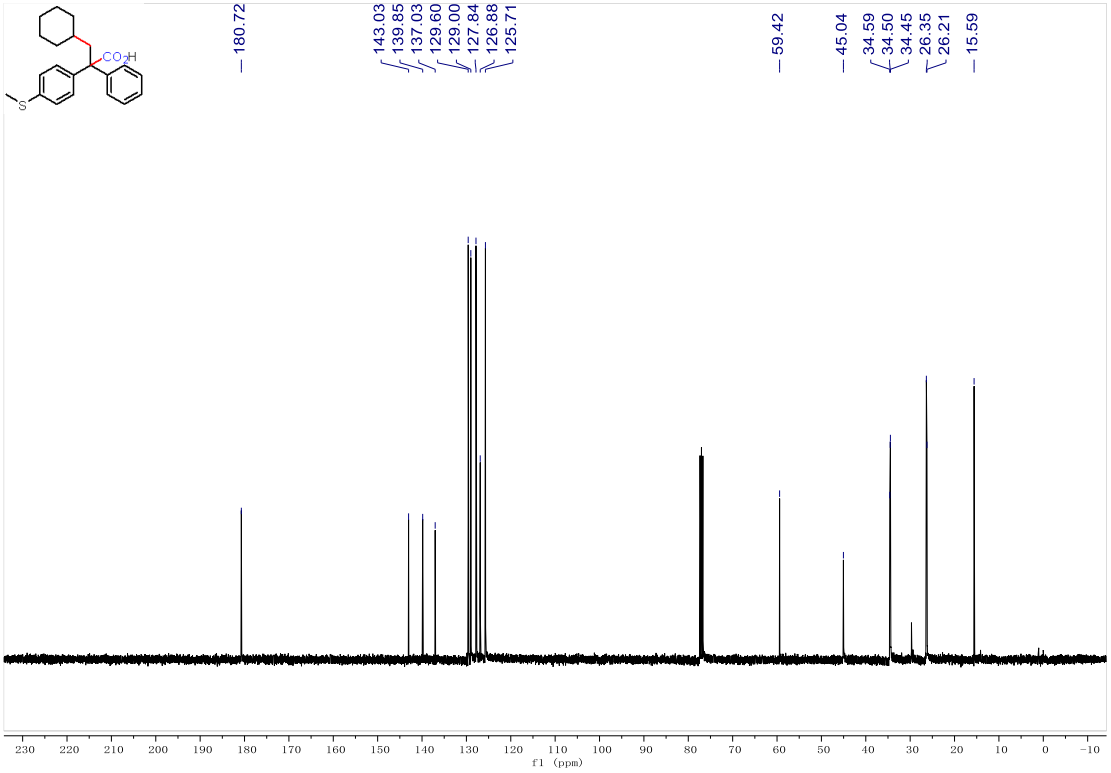
## 3-cyclohexyl-2,2-diphenylpropanoic acid (3as)



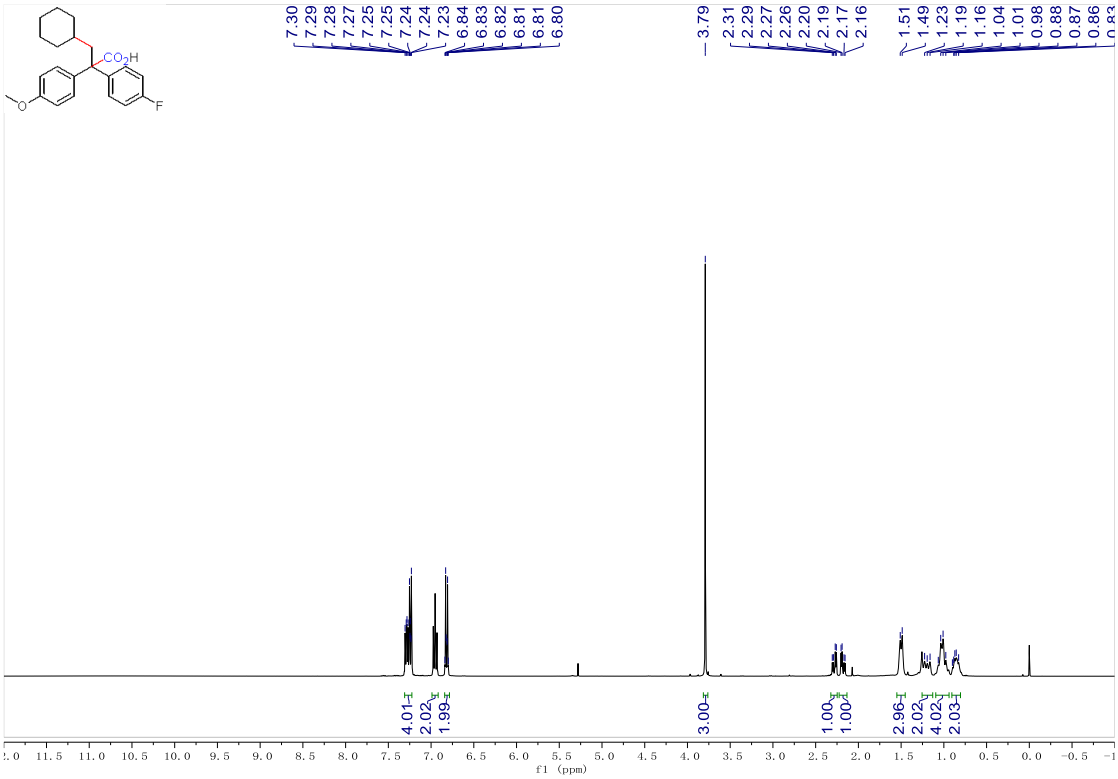



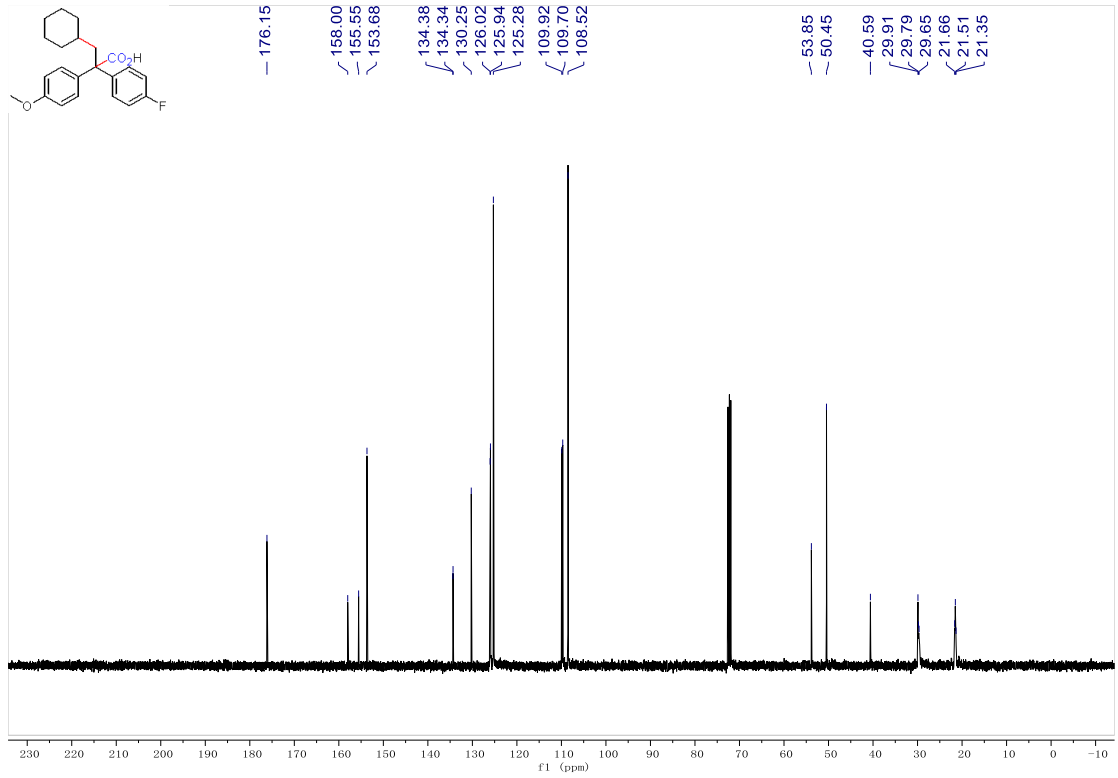
## 3-cyclohexyl-2-(4-(methylthio)phenyl)-2-phenylpropanoic acid (3at)

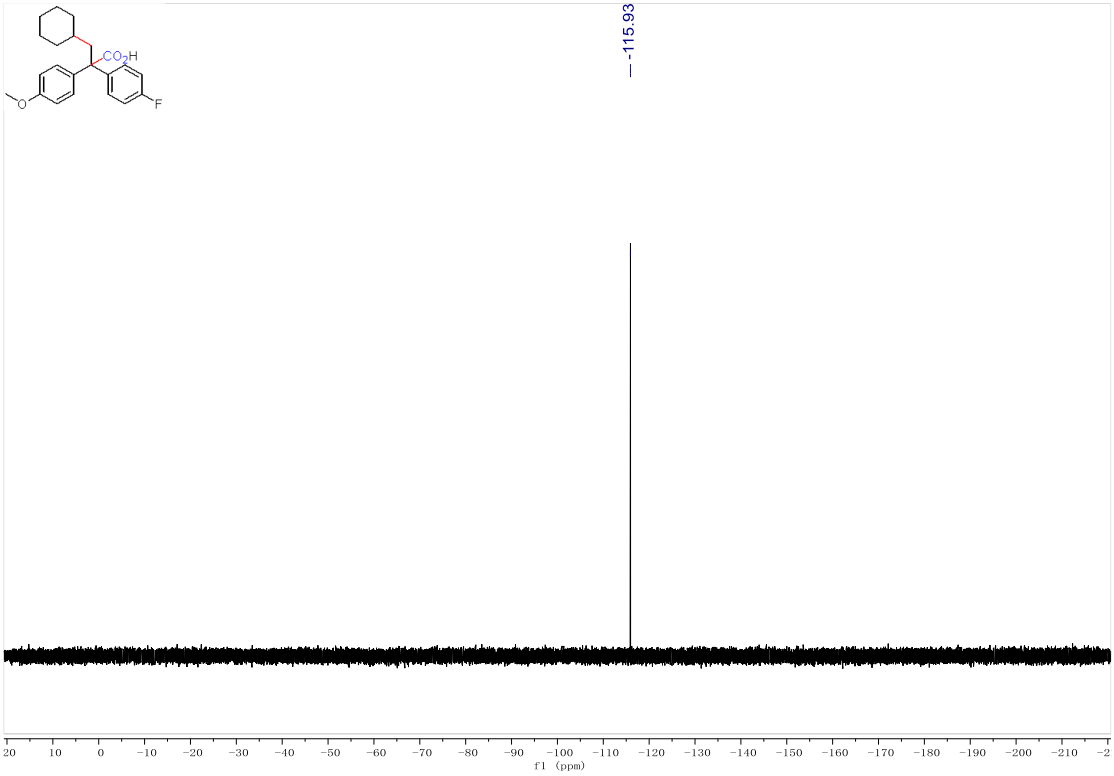


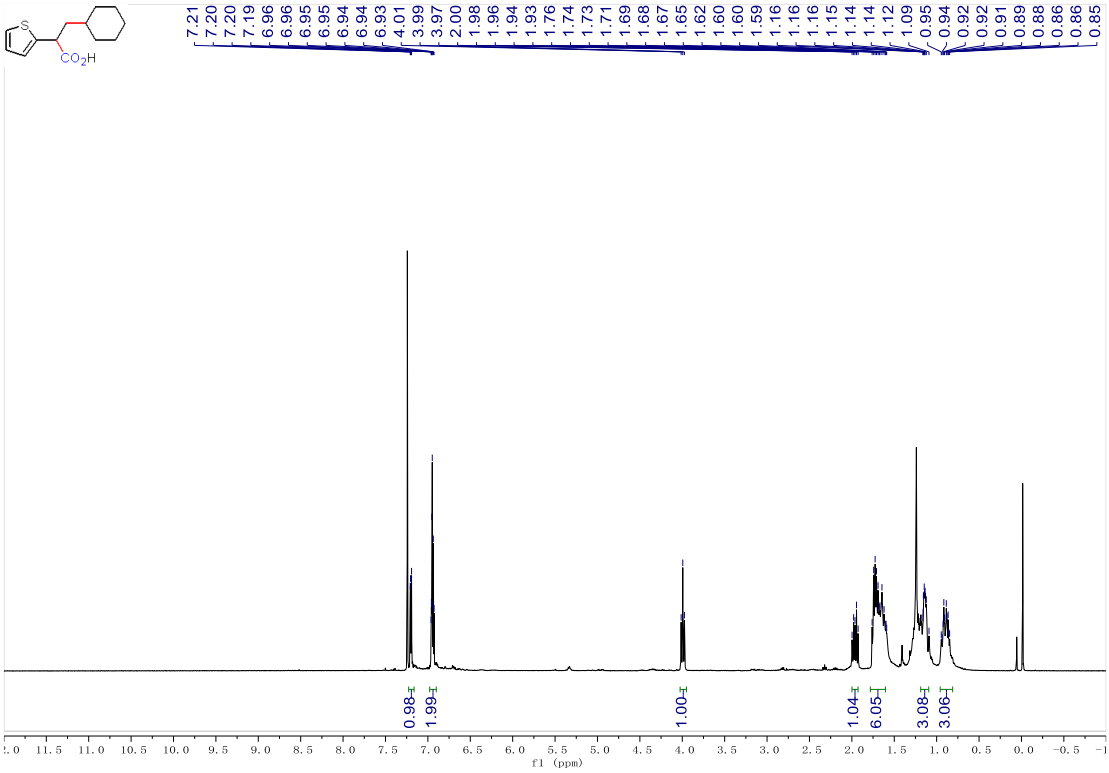
**3-cyclohexyl-2-(4-fluorophenyl)-2-(4-methoxyphenyl)propanoic acid (3au)**

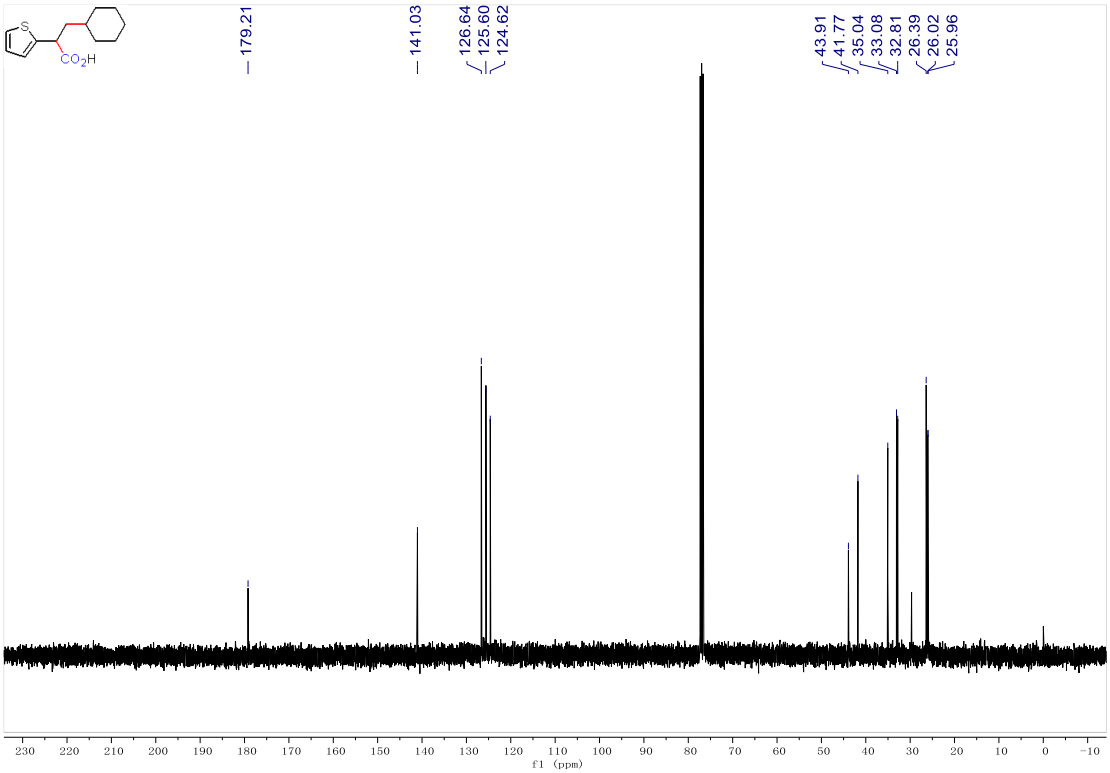


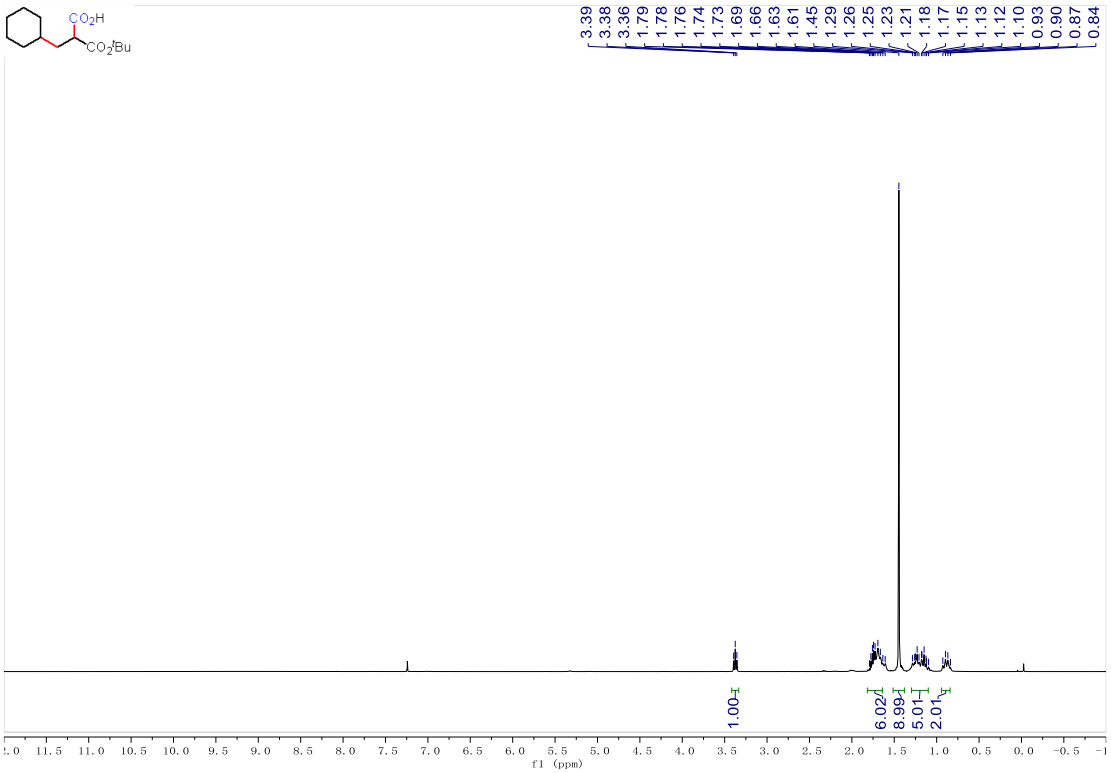

CO2H
O
F
-115.93
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

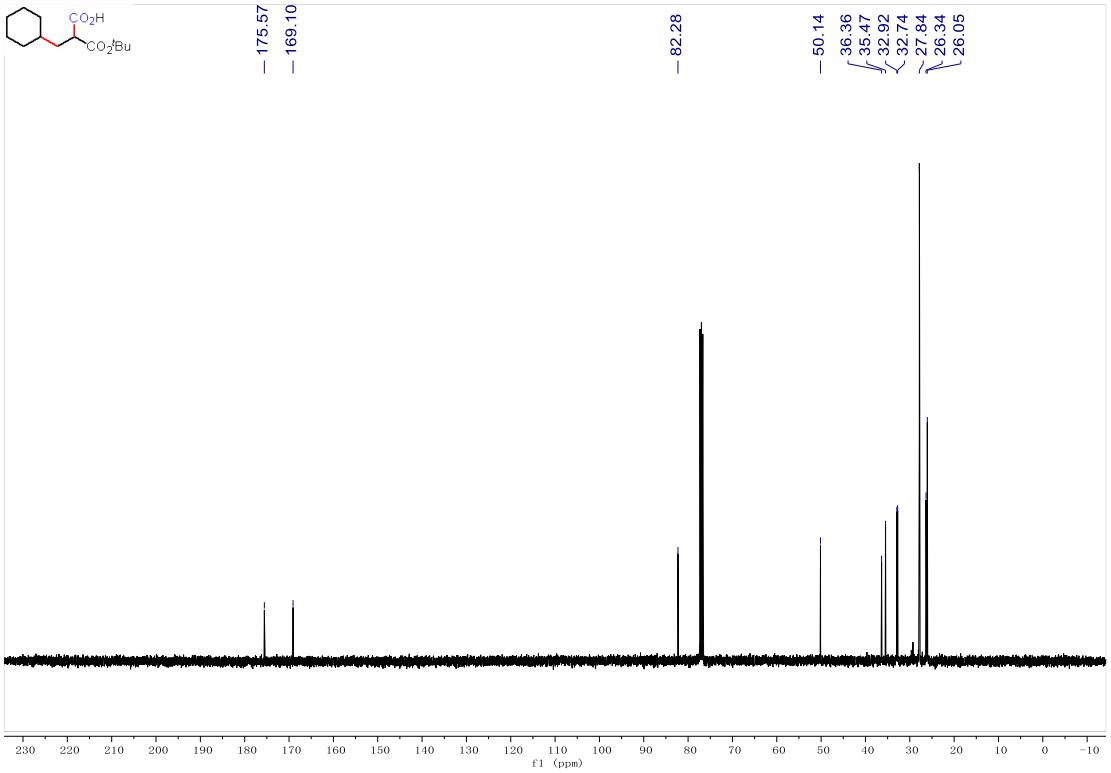
## 3-cyclohexyl-2-(thiophen-2-yl)propanoic acid (3av)



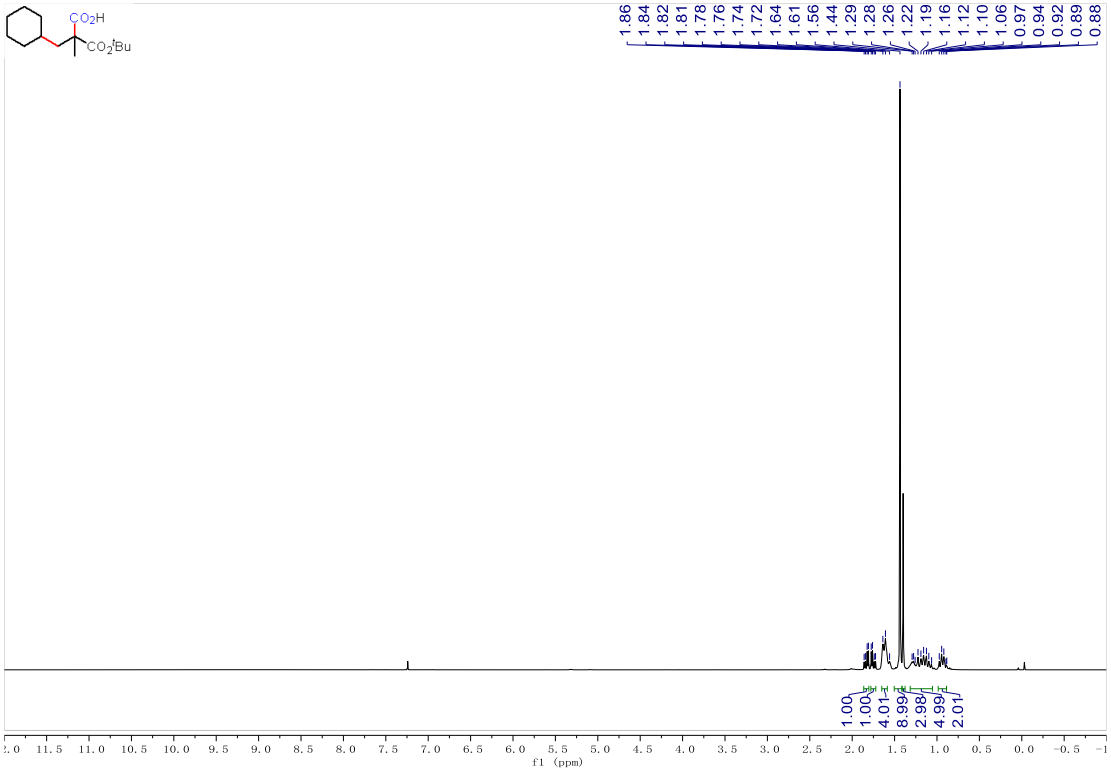



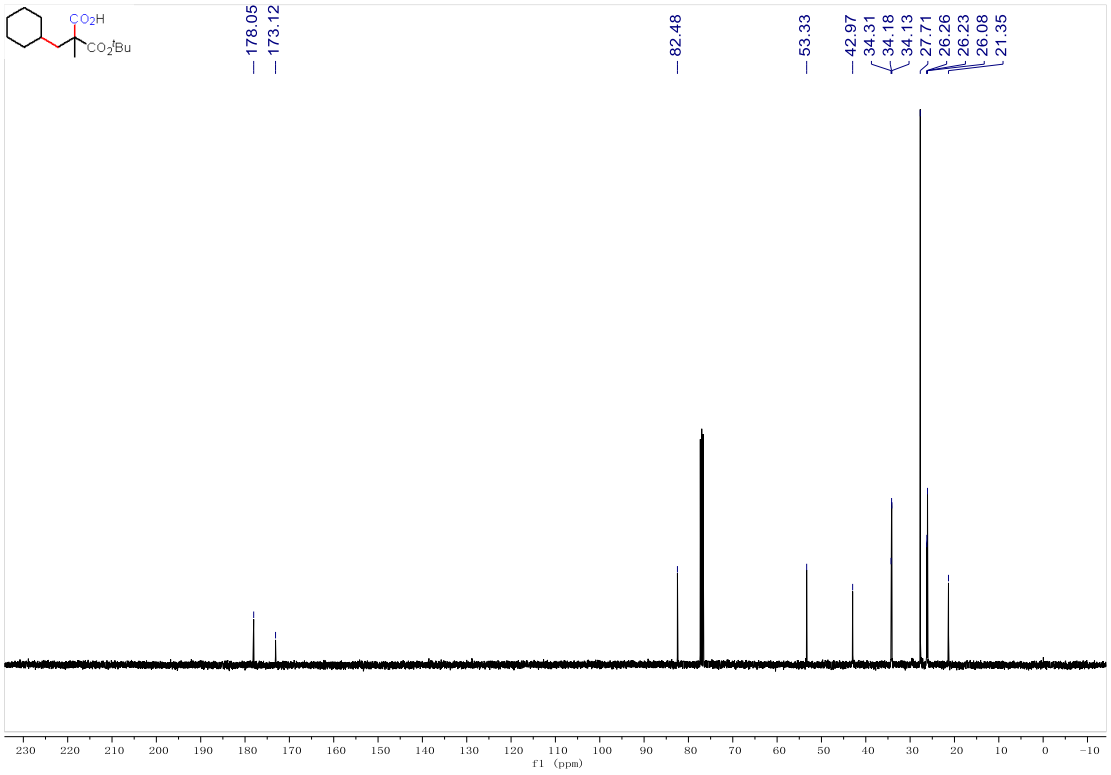
## 3-(*tert*-butoxy)-2-(cyclohexylmethyl)-3-oxopropanoic acid (3aw)



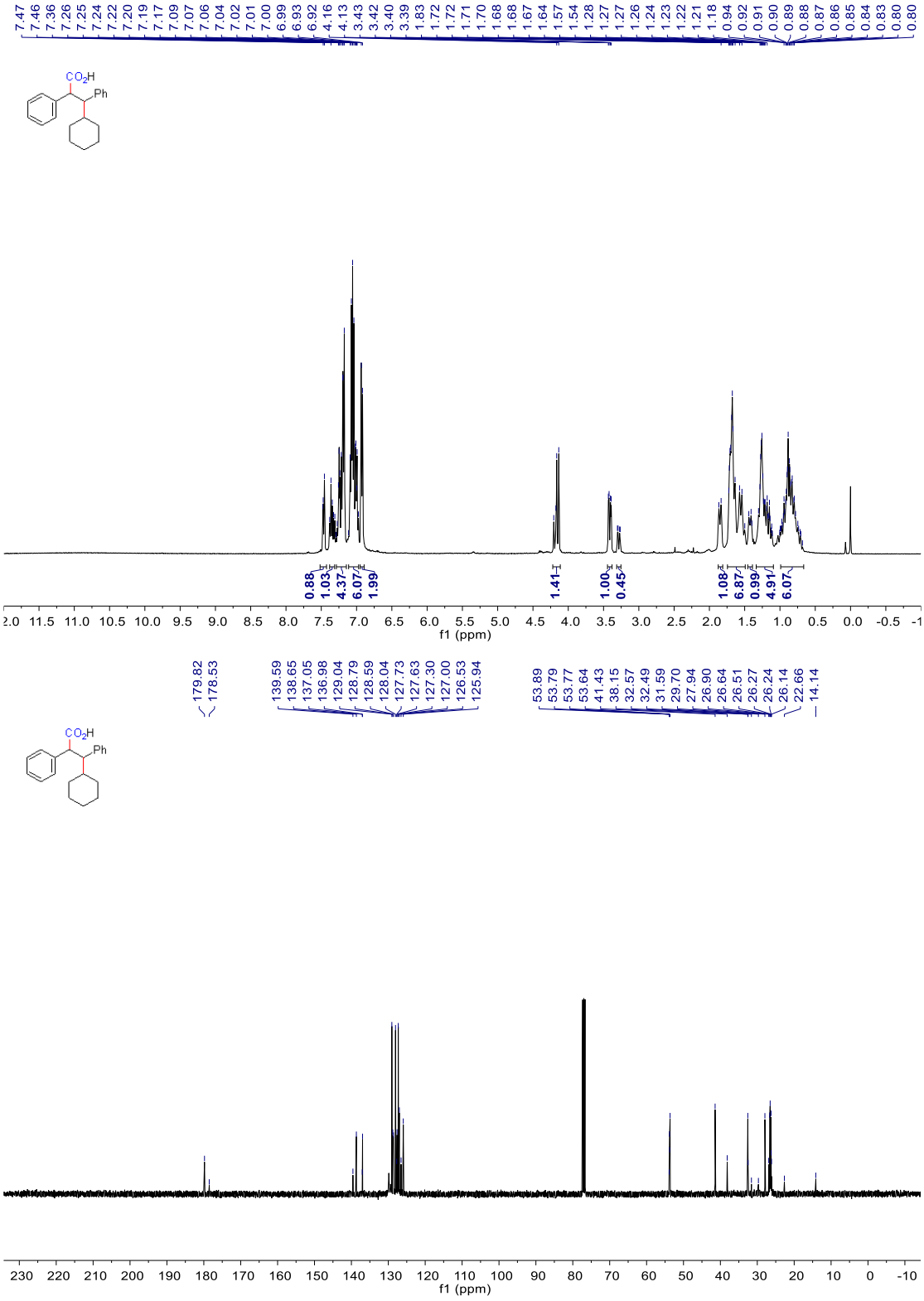



## 3-(*tert*-butoxy)-2-(cyclohexylmethyl)-3-oxopropanoic acid (3ax)

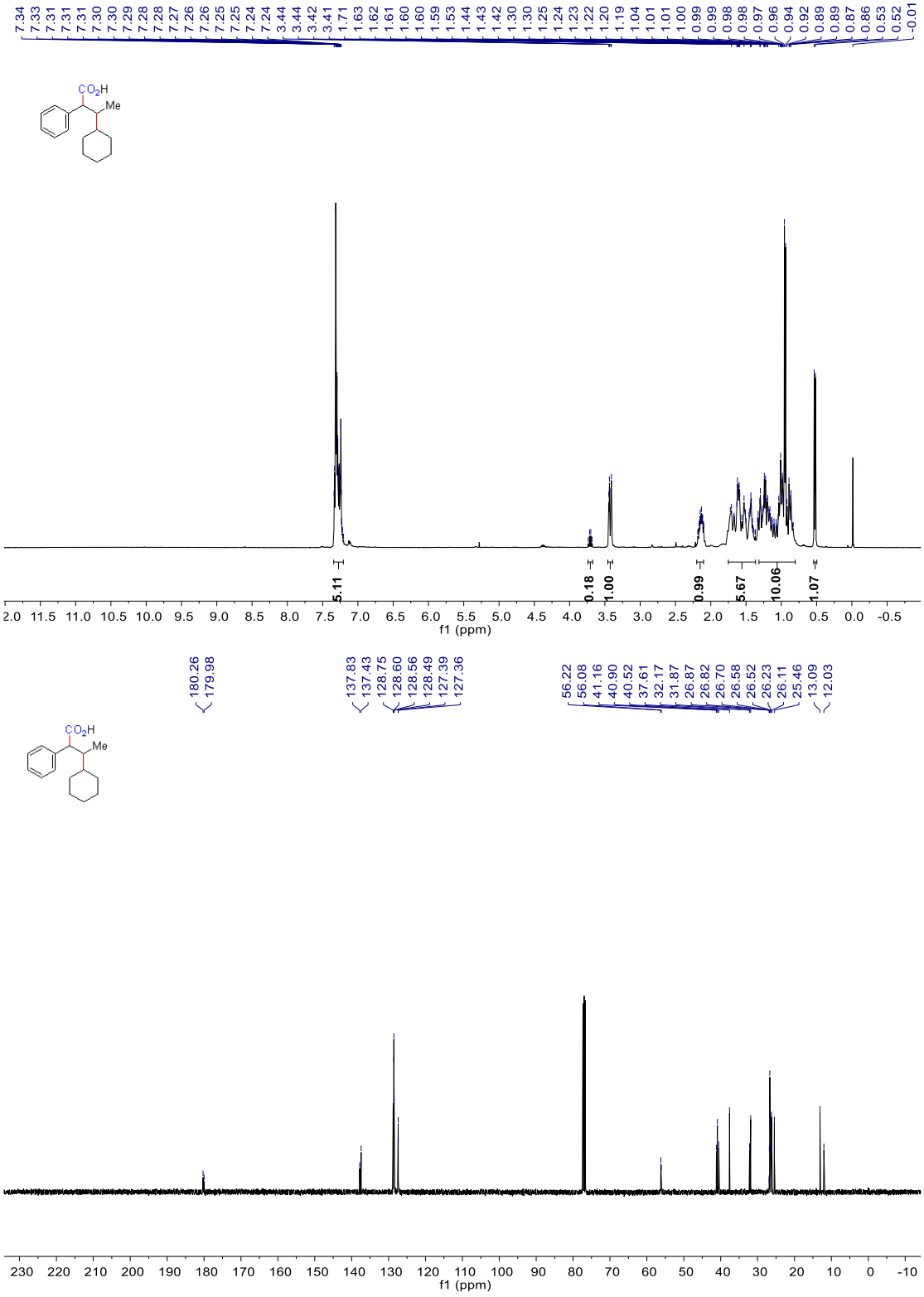


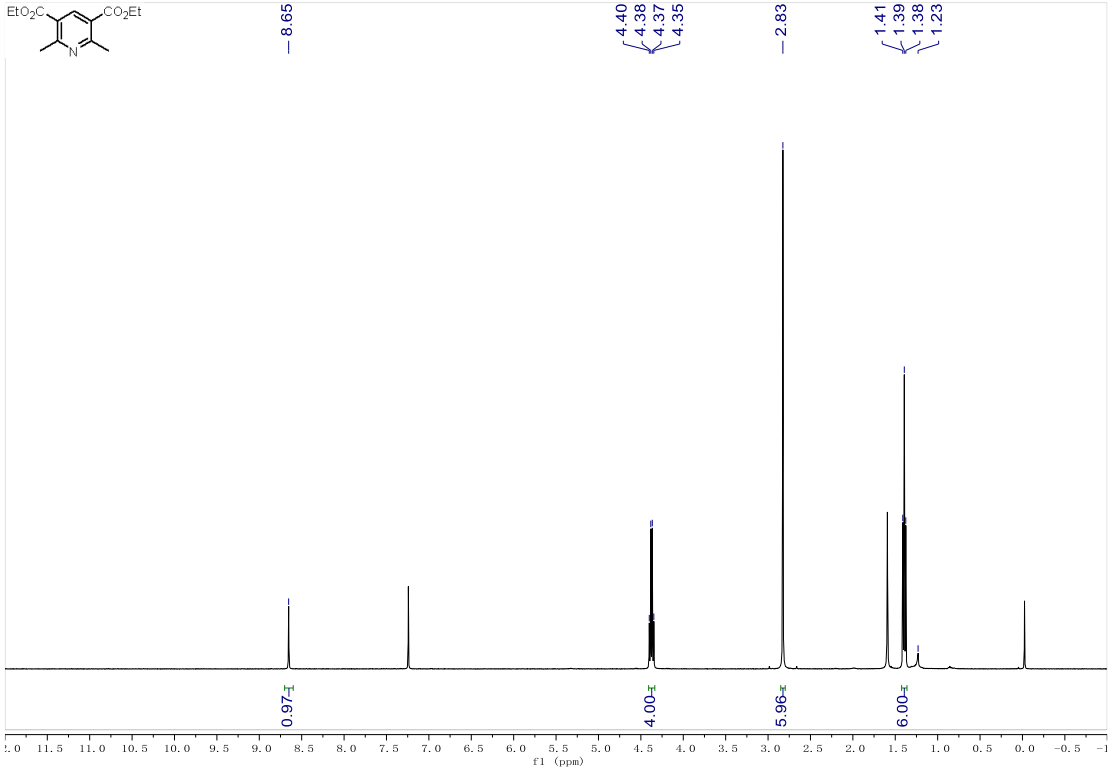
## 3-cyclohexyl-2,3-diphenylpropanoic acid (3ay)

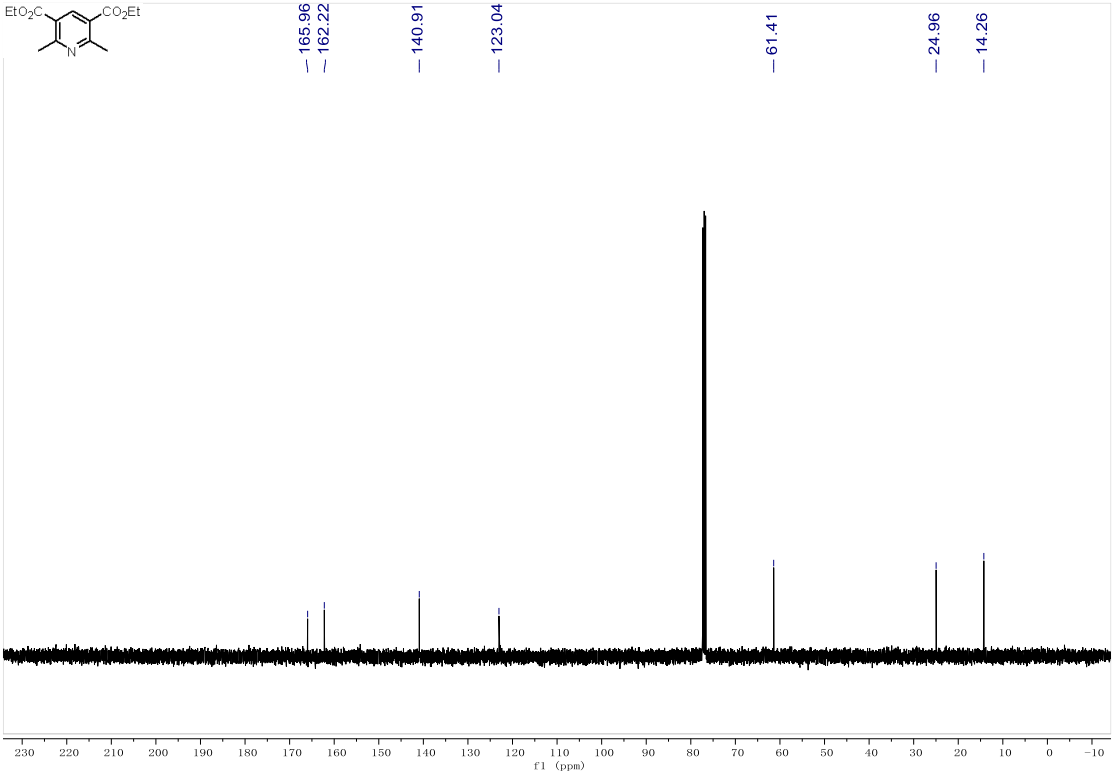


## 3-cyclohexyl-2-phenylbutanoic acid (3az)



**diethyl 2,6-dimethylpyridine-3,5-dicarboxylate** (pyridine byproduct **4**)



**1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine** (TEMPO-cyclohexyl adduct **5**)