Electronic Supplementary Information

Chemoselective transfer hydrogenation of alkynoates enabled by Cu(I)-photosensitizer catalysis

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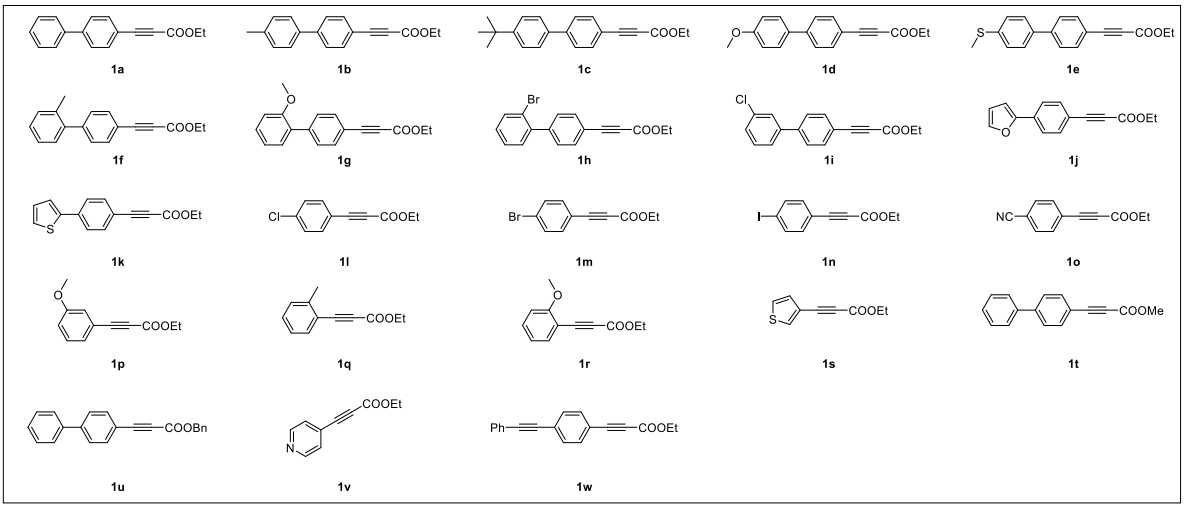
1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received. Flash column chromatography was performed on silica gel (100-200 mesh) with the indicated eluent solvents. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light or potassium permanganate indicator.

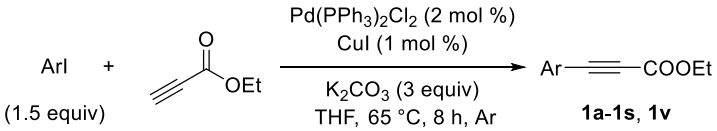
^{1}H NMR spectra were recorded on a spectrometer at 25 °C in $CDCl_3$ at 400 MHz, with TMS as internal standard. ^{13}C NMR spectra were recorded on a spectrometer at 25 °C in $CDCl_3$ at 101 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. The following abbreviations were used to identify the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), br (broad) and all combinations thereof can be explained by their integral parts. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal TMS signal at 0.0 ppm or chloroform signal at 7.26 ppm as a standard. ^{13}C NMR spectra were recorded on a Bruker 101 MHz spectrometer in chloroform-d. All signals are reported in ppm with chloroform signal at 77.16 ppm as a standard.

2. Preparation of Substrates and Photosensitizers



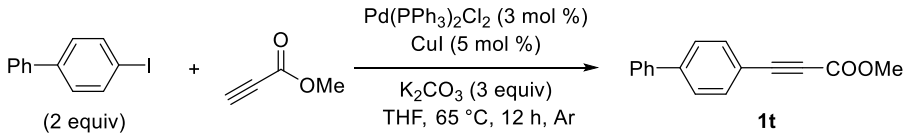
2.1 General procedure for the preparation of substrates

Substrates **1a**-**1s** and **1v** were prepared according to the procedure below.



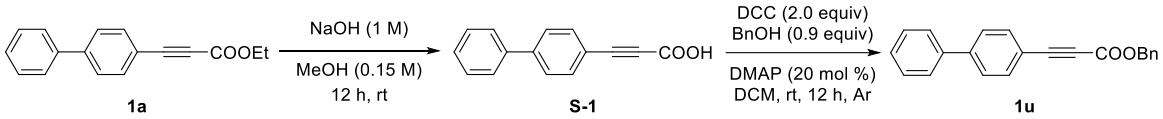
To a 50 mL of round bottom flask were sequentially added aryl iodide (7.5 mmol), ethyl propiolate (490 mg, 5 mmol), K_2CO_3 (2.07 g, 15 mmol), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol), CuI (9.5 mg, 0.05 mmol), and THF (15 mL) under an argon atmosphere. The resulting mixture was stirred at 65 ℃ for 8 h. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The filtrate was concentrated under vacuo, and the residue was purified by column chromatography on silica gel (eluent: PE/EA) to give substrates **1a**-**1s** and **1v**.[1-2]

Substrate **1t** was prepared according to the procedure below.



To a 50 mL of round bottom flask were sequentially added 4-iodo-1,1'-biphenyl (2.81 g, 10 mmol), methyl propiolate (420 mg, 5 mmol), K_2CO_3 (2.07 g, 15 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol), CuI (47.6 mg, 0.25 mmol), and THF (15 mL) under an argon atmosphere. The resulting mixture was stirred at 65 ℃ for 12 h. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was filtered through a short pad of silica gel and washed by ethyl acetate. The filtrate was concentrated under vacuo, and the residue was purified by column chromatography on silica gel (eluent: PE/EA = 60/1) to give substrate **1t** in 69% yield.[3]

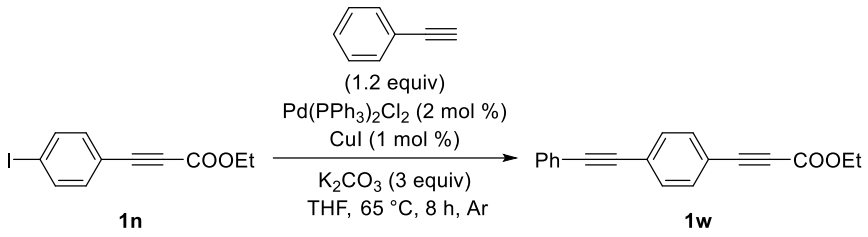
Substrate **1u** was prepared according to the procedure below.



To a 100 mL of round bottom flask were sequentially added **1a** (1.25 g, 5 mmol), methanol (33 mL), and aqueous sodium hydroxide solution (5 mL, 1 M). The resulting mixture was stirred at room temperature for 12 h. After completion of the reaction, the mixture was acidified to pH 1-2 by adding aqueous HCl (3 M). The organic layer was separated, and the aqueous layer was extracted with EA. The combined organic layers were dried over $MgSO_4$ and concentrated under vacuo to give **S-1** in 76% yield, which could be directly used in the next step without further purification.[4]

To a 25 mL of round bottom flask were sequentially added **S-1** (700 mg, 3 mmol), benzyl alcohol (0.28 mL, 0.9 mmol), DCC (1.24 g, 6 mmol), DMAP (77.1 mg, 0.6 mmol), and DCM (10 mL) under an argon atmosphere, then the resulting mixture was stirred at room temperature. After 12 h, the mixture was filtered through a short pad of silica gel and washed with DCM. The filtrate was concentrated under vacuo, and the residue was purified by column chromatography on silica gel (eluent: PE/EA = 30/1) to give substrate **1u** in 52% yield.[5-6]

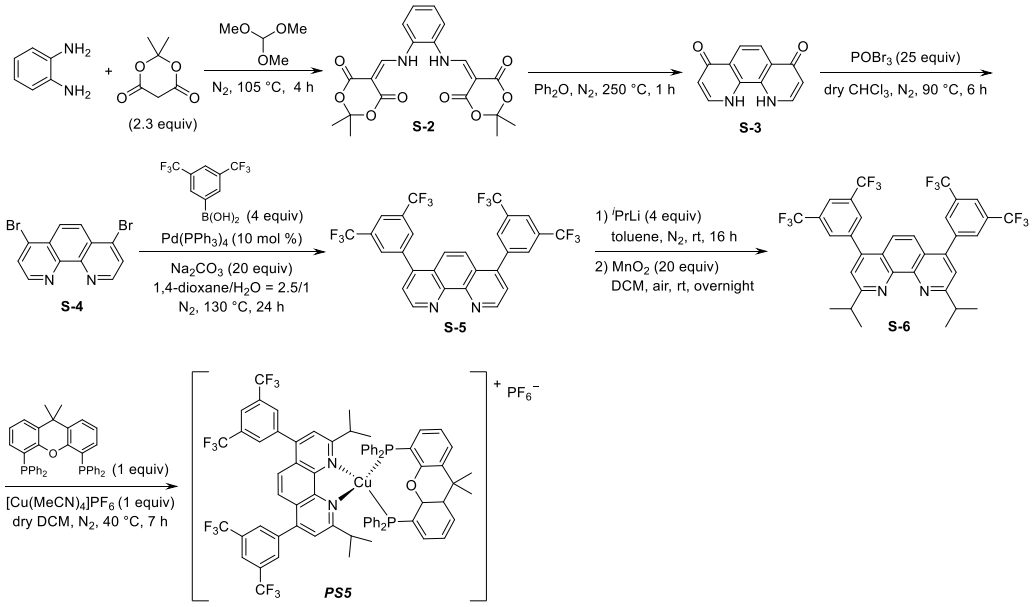
Substrate **1w** was prepared according to the procedure below.



1n **1w**

To a 50 mL of round bottom flask were sequentially added ethyl 3-(4-iodophenyl)propiolate (1.51 g, 5 mmol), ethynylbenzene (0.66 mL, 6 mmol), K_2CO_3 (2.07 g, 15 mmol), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol), CuI (9.52 mg, 0.05 mmol), and THF (15 mL) under an argon atmosphere. The resulting mixture was stirred at 65 ℃ for 8 h. After completion of the reaction, the mixture was filtered through a short pad of silica gel and washed with EA. The filtrate was concentrated under vacuo, and the residue was purified by column chromatography on silica gel (eluent: PE/EA = 30/1) to give substrate **1w** in 42% yield.

2.2 Synthesis of copper-based photosensitizer *PS5*



2,9-diisopropyl-4,7-di(3,5-bis(trifluoromethyl-phenyl))-1,10-phenanthroline (***PS5***) was synthesized according to the reported procedure.[7-9]

A mixture of cyclopropyl malonate (10.09 g, 70 mmol) and trimethyl orthoformate (124.73 mL) was stirred at reflux temperature at 105 °C under a nitrogen atmosphere. After 1

h, the reaction mixture was cooled to 80 °C before the addition of phenylenediamine (3.24 g, 30 mmol), and then the resulting mixture was stirred at 105 °C for an additional 4 h under a nitrogen atmosphere. After completion of the reaction, the mixture was cooled to room temperature, filtered, and washed with diethyl ether three times to afford **S-2** in 84% yield as a white solid.

A mixture of **S-2** (10 mmol) in diphenyl ether (120 mL) was stirred at 250 °C under a nitrogen atmosphere. After 1 h, the reaction mixture was cooled to 70 °C, filtered, washed sequentially with acetone (3 × 30 mL), *n*-hexane (3 × 30 mL), and diethyl ether (3 × 30mL), which gave **S-3** in 82% as a brown solid.

S-3 (5 mmol), $POBr_3$ (35.75 g, 125 mmol), and anhydrous chloroform (40 mL) were added to a dried flask, and then the reaction mixture was stirred at 90 °C for 6 h under a nitrogen atmosphere. After completion, the mixture was cooled to room temperature and slowly poured into 150 mL of ice-water. Afterward, the mixture was stirred at room temperature for an additional 1 h before chloroform (50 mL) was added. The pH of the system was adjusted to 13-14 using 50% aqueous sodium hydroxide solution, and the resulting mixture was stirred for 1 h, followed by extraction three times with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuo. The residue was purified by column chromatography on silica gel (eluent: DCM/MeOH = 50/1) to afford **S-4** in 45% as a white solid.

To a dried three-necked flask were added **S-4** (3 mmol), Na_2CO_3 (6.36 g, 60 mmol), $Pd(PPh_3)_4$ (0.34 g, 0.3 mmol), (3,5-bis(trifluoromethyl)phenyl)boronic acid (3.0 g, 12 mmol), and a mixed solvent of 1,4-dioxane (150 mL) and H_2O (60 mL). The resulting mixture was stirred at 130 °C for 36 h under a nitrogen atmosphere. After completion of the reaction, the mixture was concentrated under vacuo, and the crude product was extracted three times with DCM. The combined organic layers were dried over anhydrous Na_2SO_4. After concentration

under vacuo, the residue was purified by column chromatography on silica gel (eluent: DCM/MeOH = 100/1) to afford **S-5** in 48% yield as a white solid.

To a dried flask containing **S-5** (0.604 g, 1 mmol) and dry toluene (20 mL) was added isopropyl lithium (4 mL, 4 mmol) dropwise at 0 °C under a nitrogen atmosphere, and the resulting mixture was stirred at this temperature for 2 h, then warmed to room temperature and stirred for an additional 16 h. After completion of the reaction, the mixture was quenched with water, extracted three times with DCM, and then dried over anhydrous Na_2SO_4. The combined organic layers were concentrated under vacuum, and the residue was directly used in the next step without further purification. To a flask were added the above crude, activated manganese dioxide (1.74 g, 20 mmol), and dichloromethane (20 mL). The resulting mixture was stirred at room temperature in air for 6 h until the reaction was complete. Then, the mixture was filtered and washed with DCM. The filtrate was concentrated under vacuum, and the residue was purified by column chromatography on silica gel (eluent: PE/EA = 20/1) to afford **S-6** in 51% yield as a white solid.

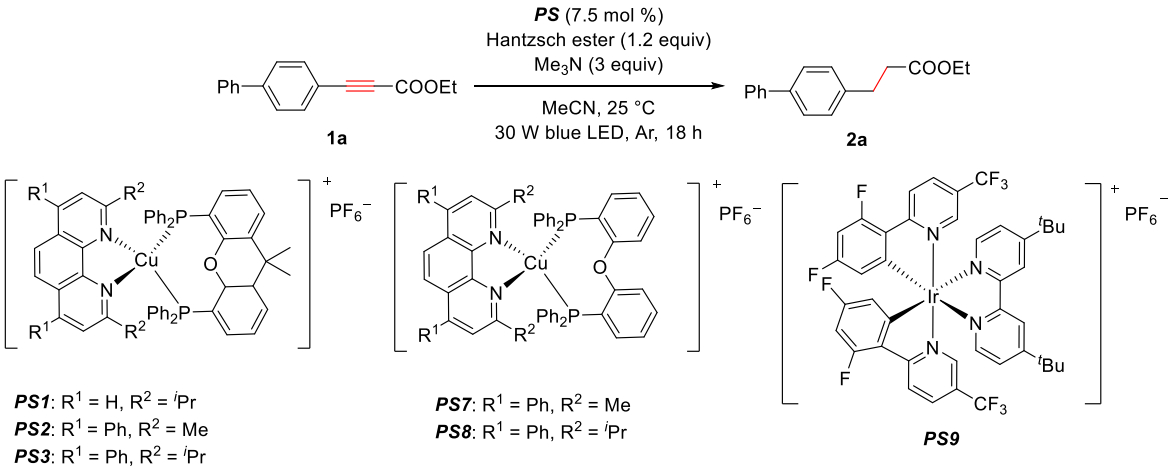
To an oven-dried flask were added $[Cu(MeCN)_4]PF_6$ (0.373 g, 1 mmol), Xantphos (0.579 g, 1 mmol), and dry DCM (20 mL). The resulting mixture was stirred at 40 °C for 4 h before the slow addition of a solution comprised of **S-6** (688 mg, 1 mmol) in DCM. After addition, the mixture was stirred for another 4 h, which was then cooled to room temperature, and the solvent was removed under vacuum. To the residue was added cyclohexane, and the mixture was triturated to precipitate the product. Direct filtration afforded ***PS5*** as a bright yellow solid.

Other Cu(I)-photosensitizers (***PS1-PS4***, ***PS6-PS8***) were synthesized according to the previously reported literature.[10-11] ***PS9*** and Rose Bengal are commercially available.

3. General Procedures for the Synthesis of Alkyl Carbonates

3.1 Optimization of reaction conditions

Table 1. Optimization of photosensitizers[a]



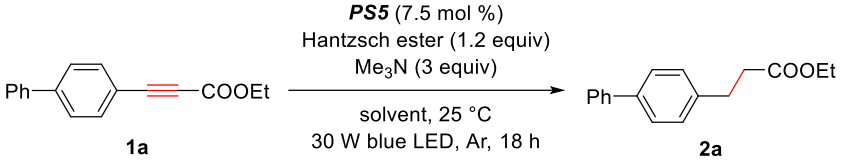
PS1: R^1 = H, R^2 = ^{i}Pr
PS2: R^1 = Ph, R^2 = Me
PS3: R^1 = Ph, R^2 = ^{i}Pr
PS4: R^1 = Ph, R^2 = ^{s}Bu
PS5: R^1 = 3,5-bis(trifluoromethyl)-phenyl, R^2 = ^{i}Pr
PS6: R^1 = 3,5-bis(trifluoromethyl)-phenyl, R^2 = ^{s}Bu
PS7: R^1 = Ph, R^2 = Me
PS8: R^1 = Ph, R^2 = ^{i}Pr

Entry	Photosensitizer	Yield of **2a** (%)[b]
1	***PS1***	<1
2	***PS2***	43
3	***PS3***	50
4	***PS4***	45
5	***PS5***	**67**
6	***PS6***	58
7	***PS7***	40
8	***PS8***	48
9	***PS9***	trace
10	Rose Bengal	<1

[a]Reaction conditions**: 1a** (0.2 mmol), ***PS*** (7.5 mol %), Hantzsch ester (0.24 mmol, 1.2 equiv), Me_3N (0.6 mmol, 3 equiv), MeCN (4 mL), irradiated with 30W blue LED at 25 ℃ under argon atmosphere for 18 h unless otherwise noted. [b] Isolated yield. Rose Bengal, 4,5,6,7-tetrachloro-

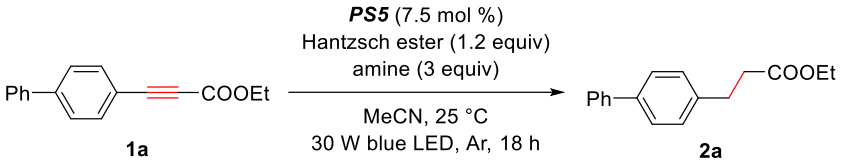
2',4',5',7'-tetraiodofluorescein disodium salt.

Table 2. Optimization of solvents[a]



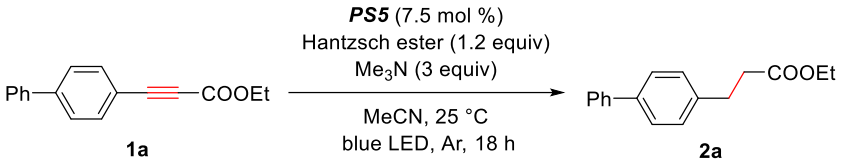
Entry	Solvent	Yield of **2a** (%)[b]
1	toluene	46
2	**MeCN**	**67**
3	THF	40
4	1,4-Dioxane	30
5	MeOH	55
6	DCM	47
7	DMF	56
8	DMSO	55

Table 3. Optimization of amines[a]



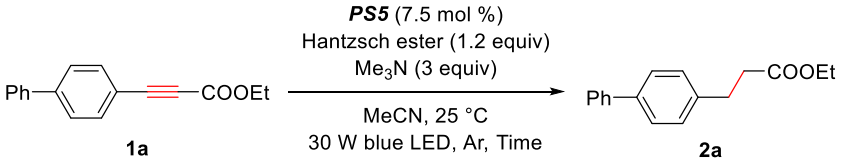
Entry	Amine	Yield of **2a** (%)[b]
1	**Me_3N**	**67**
2	$(^{n}Pr)_2NH$	41
3	$(^{i}Pr)_2NH$	43
4	Et_3N	58
5	DIPEA	40

Table 4. Optimization of the light source[a]



Entry	Light source	Yield of **2a** (%)[b]
1	15 W blue light	61
2	**30 W blue light**	**67**

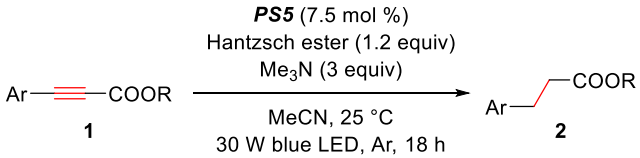
Table 5. Optimization of the reaction time[a]



Entry	Time (h)	Yield of 2a (%)[b]
1	12	62
2	**18**	**67**
3	24	67

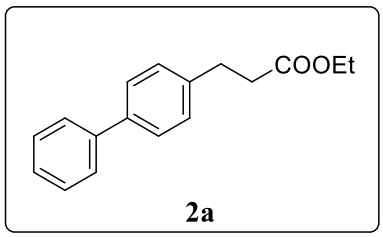
3.2 Experimental details and characterization of products

General procedure for the synthesis of alkyl carbonates



To a 25 mL flame-dried Schlenk tube were added ***PS5*** (20 mg, 0.015 mmol), **1** (0.2 mmol), and Hantzsch ester (61 mg, 0.24 mmol). The tube was evacuated and refilled with Ar three times. Me_3N (35 mg, 0.6 mmol, 4.2 mol/L in EtOH) and MeCN (4 mL) were added to the tube under an argon atmosphere, then the resulting mixture was irradiated at a distance of 3 cm with 30 W blue LED and stirred at 25 ℃ for 18 h. The reaction progress was monitored by TLC. After completion, the reaction mixture was concentrated under vacuum, and the residue was purified by column chromatography on silica gel (eluent: PE/EA) to give product **2**.

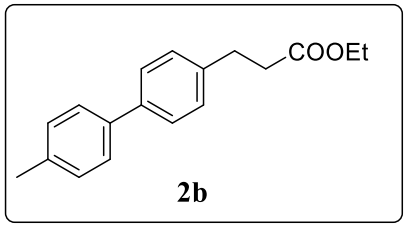
ethyl 3-([1,1'-biphenyl]-4-yl)propanoate (2a):



2a

Yellow oil. Yield: 67%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 141.1, 139.8, 139.3, 128.9, 127.4, 127.3, 127.2, 127.1, 60.6, 36.0, 30.7, 14.4. This compound is known and the spectroscopic data match those reported.[12]

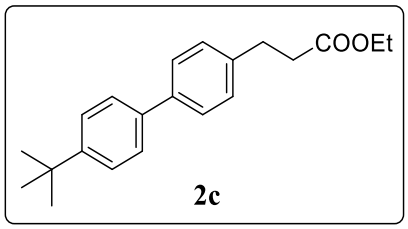
ethyl 3-(4'-methyl-[1,1'-biphenyl]-4-yl)propanoate (2b):



2b

Yellow oil. Yield: 66%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.18 – 7.09 (m, 4H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.8 Hz, 2H), 2.55 (t, *J* = 7.8 Hz, 2H), 2.28 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 139.5, 139.2, 138.2, 136.9, 129.6, 128.8, 127.1, 126.9, 60.5, 36.0, 30.7, 21.2, 14.3. **HR-MS** (ESI+) for $C_{18}H_{20}O_2Na$ $([M+Na])^+$: calcd. 291.1361, found. 291.1365.

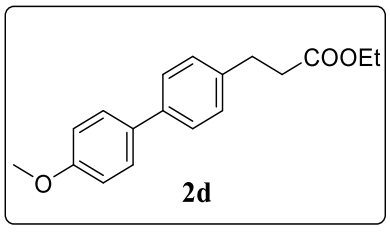
ethyl 3-(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)propanoate (2c):



2c

Yellow oil. Yield: 70%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 4H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 1.27 (s, 9H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 150.2, 139.5, 139.2, 138.2, 128.8, 127.2, 126.8, 125.8, 60.6, 36.0, 34.6, 31.5, 30.7, 14.4. **HR-MS** (ESI+) for $C_{21}H_{27}O_2$ $([M+H])^+$: calcd. 311.2011, found. 311.2015.

ethyl 3-(4'-methoxy-[1,1'-biphenyl]-4-yl)propanoate (2d):

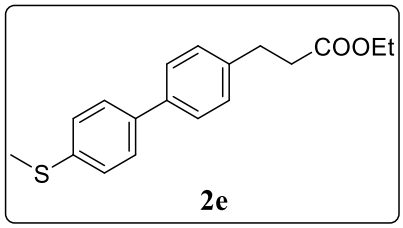


2d

Yellow oil. Yield: 68%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 4H), 7.16 (dd, *J* = 8.1, 1.8 Hz, 2H), 6.87 (dd, *J* = 8.7, 1.8 Hz, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 3.74 (s, 3H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 159.1, 139.1, 138.9, 133.6, 128.8, 128.1, 126.9,

114.3, 60.5, 55.4, 36.0, 30.7, 14.4. This compound is known and the spectroscopic data match those reported.[13]

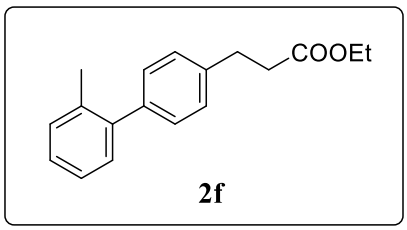
ethyl 3-(4'-(methylthio)-[1,1'-biphenyl]-4-yl)propanoate (2e):



2e

Yellow oil. Yield: 69%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 4H), 7.23 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.20 – 7.16 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.8 Hz, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.43 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 139.8, 138.6, 137.9, 137.5, 128.9, 127.4, 127.1, 127.0, 60.6, 36.0, 30.7, 16.1, 14.4. **HR-MS** (ESI+) for $C_{18}H_{20}O_2NaS$ $([M+Na])^+$: calcd. 323.1082, found. 323.1083.

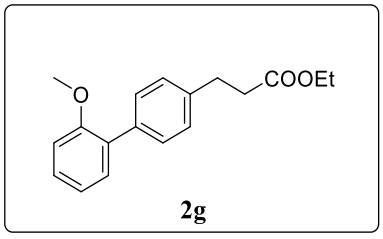
ethyl 3-(2'-methyl-[1,1'-biphenyl]-4-yl)propanoate (2f):



2f

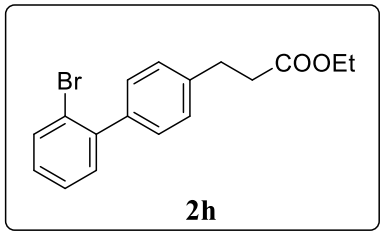
Yellow oil. Yield: 66%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 8H), 4.06 (q, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 7.9 Hz, 2H), 2.59 (t, *J* = 7.1 Hz, 2H), 2.18 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 141.8, 140.0, 139.1, 135.5, 130.4, 129.9, 129.4, 128.1, 127.3, 125.9, 60.5, 36.0, 30.8, 20.6, 14.4. **HR-MS** (ESI+) for $C_{18}H_{21}O_2$ $([M+H])^+$: calcd. 269.1542, found. 269.1542.

ethyl 3-(2'-methoxy-[1,1'-biphenyl]-4-yl)propanoate (2g):



2g

Yellow oil. Yield: 65%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.22 – 7.12 (m, 4H), 6.93 – 6.84 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 2.89 (t, *J* = 7.9 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 156.5, 139.2, 136.5, 130.8, 130.5, 129.7, 128.5, 128.0, 120.9, 111.2, 60.5, 55.5, 35.9, 30.8. 14.3. **HR-MS** (ESI+) for $C_{18}H_{21}O_3$ $([M+H])^+$: calcd. 285.1491, found. 285.1491.



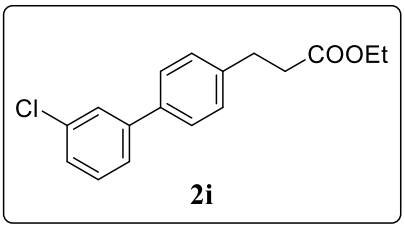
2h

ethyl 3-(2'-bromo-[1,1'-biphenyl]-4-yl)propanoate (2h):

Yellow oil. Yield: 70%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.22 (m, 4H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.09 – 7.03 (m, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ

172.9, 142.4, 140.0, 139.1, 133.2, 131.3, 129.5, 128.7, 128.0, 127.4, 122.7, 60.5, 35.8, 30.8, 14.3. **HR-MS** (ESI+) for $C_{17}H_{18}O_2Br$ $([M+H])^+$: calcd. 333.0490, found. 333.0494.

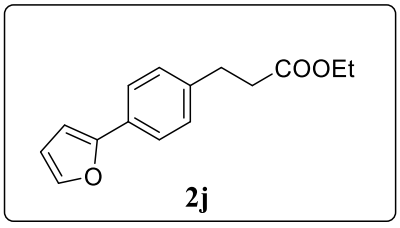
ethyl 3-(3'-chloro-[1,1'-biphenyl]-4-yl)propanoate (2i):



2i

Yellow oil. Yield: 72%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.5 Hz, 4H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.8 Hz, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 140.2, 139.5, 138.1, 133.3, 129.0, 128.3, 127.2, 60.6, 36.0, 30.7. 14.4. **HR-MS** (ESI+) for $C_{17}H_{18}O_2Cl$ $([M+H])^+$: calcd. 289.0995, found. 289.0992.

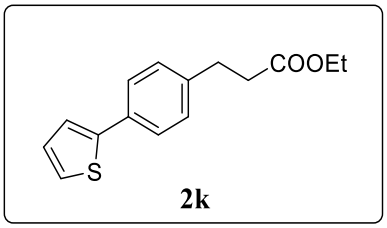
ethyl 3-(4-(furan-2-yl)phenyl)propanoate (2j):



2j

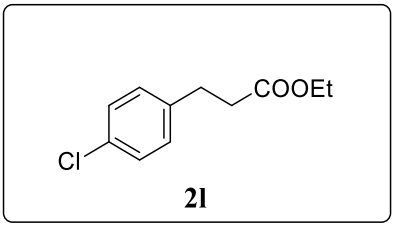
Yellow oil. Yield: 63%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.45 (s, 1H), 7.22 (d, J = 7.9 Hz, 2H), 6.60 (d, *J* = 3.3 Hz, 1H), 6.50 – 6.41 (m, 1H), 4.13 (q, *J* = 6.7 Hz, 2H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.23 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 154.1, 142.0, 139.9, 129.2, 128.8, 124.1, 111.7, 104.7, 60.6, 36.0, 30.9. 14.3. **HR-MS** (ESI+) for $C_{15}H_{17}O_3$ $([M+H])^+$: calcd. 245.1178, found. 245.1179.

ethyl 3-(4-(thiophen-2-yl)phenyl)propanoate (2k):



2k

Yellow oil. Yield: 65%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.10 (m, 4H), 6.96 (ddd, *J* = 5.0, 3.5, 1.2 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 2.87 (t, *J* = 7.8 Hz, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 1.14 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 144.4, 140.0, 132.6, 128.9, 128.0, 126.1, 124.6, 122.9, 60.6, 35.9, 30.7, 14.3. **HR-MS** (ESI+) for $C_{15}H_{17}O_2S$ $([M+H])^+$: calcd. 261.0949, found. 261.0951.

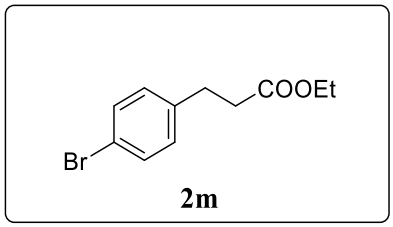


2l

ethyl 3-(4-chlorophenyl)propanoate (2l):

Yellow oil. Yield: 66%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 – 7.13 (m, 2H), 7.06 – 7.01 (m, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 139.1, 132.1, 129.8, 128.6, 60.5, 35.8, 30.3, 14.3. This compound is known and the spectroscopic data match those reported.[14]

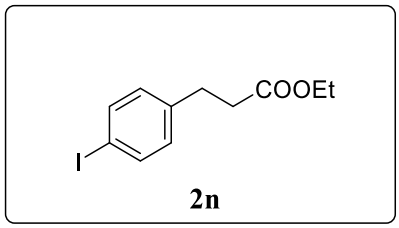
ethyl 3-(4-bromophenyl)propanoate (2m):



2m

Yellow oil. Yield: 64%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.10 – 7.04 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.7, 139.6, 131.6, 130.2, 120.1, 60.6, 35.7, 30.4, 14.3. This compound is known and the spectroscopic data match those reported.[15]

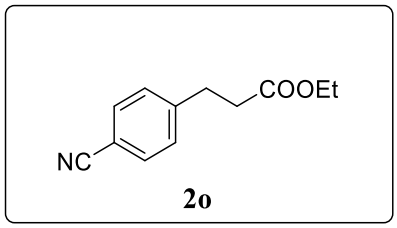
ethyl 3-(4-iodophenyl)propanoate (2n):



2n

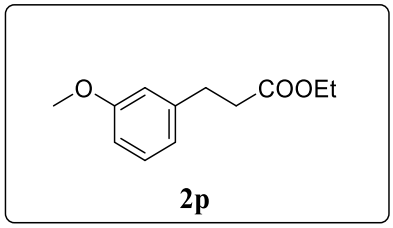
Yellow oil. Yield: 67%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.58 (t, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 140.3, 137.6, 130.5, 91.5, 60.6, 35.7, 30.5, 14.3. This compound is known and the spectroscopic data match those reported.[16]

ethyl 3-(4-cyanophenyl)propanoate (2o):



2o

Yellow oil. Yield: 70%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.24 (dd, *J* = 8.2, 1.4 Hz, 2H), 4.04 (q, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 146.2, 132.3, 129.3, 119.0, 110.3, 60.7, 35.1, 31.0, 14.3. This compound is known and the spectroscopic data match those reported.[17]

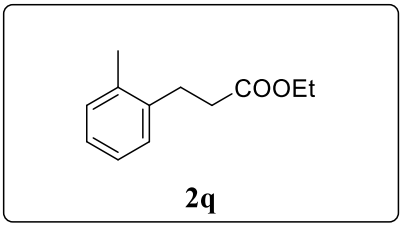


2p

ethyl 3-(3-methoxyphenyl)propanoate (2p):

Yellow oil. Yield: 62%. **^{1}H NMR**(400 MHz, $CDCl_3$) δ 7.09 (td, *J* = 7.5, 1.1 Hz, 1H), 6.70 – 6.61 (m, 3H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 3H), 2.82 (t, *J* = 7.9 Hz, 2H), 2.50 (t, *J* = 7.9 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8, 159.7, 142.2, 129.4, 120.6, 114.0, 111.6, 60.4, 55.1, 35.8, 31.0, 14.2. This compound is known and the spectroscopic data match those reported.[14]

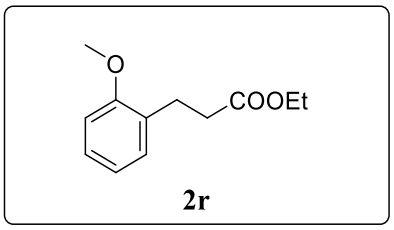
ethyl 3-(o-tolyl)propanoatel (2q):



2q

Yellow oil. Yield: 66%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 – 6.96 (m, 4H), 4.01 (q, *J* = 7.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.44 (t, *J* = 8.0 Hz, 2H), 2.20 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 138.6, 135.8, 130.2, 128.5, 126.3, 126.0, 60.3, 34.6, 28.3, 19.2, 14.2. This compound is known and the spectroscopic data match those reported.[18]

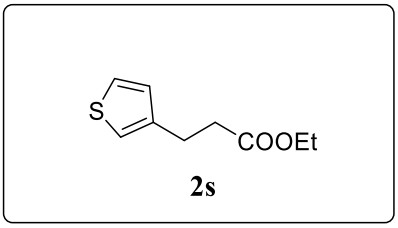
ethyl 3-(2-methoxyphenyl)propanoate (2r):



2r

Yellow oil. Yield: 64%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 – 7.03 (m, 2H), 6.79 – 6.72 (m, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 2.85 (t, *J* = 7.9 Hz, 2H), 2.50 (t, *J* = 7.8 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 157.5, 130.0, 128.9, 127.6, 120.4, 110.2, 60.3, 55.2, 34.3, 26.2, 14.3. This compound is known and the spectroscopic data match those reported.[14]

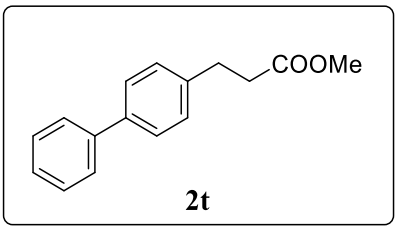
ethyl 3-(thiophen-3-yl)propanoate (2s):



2s

Yellow oil. Yield: 61%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 4.9, 2.9 Hz, 1H), 6.92 – 6.83 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 140.9, 128.1, 125.6, 120.6, 60.5, 35.3, 25.6, 14.3. This compound is known and the spectroscopic data match those reported.[19]

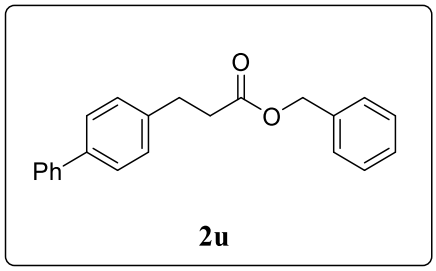
methyl 3-([1,1'-biphenyl]-4-yl)propanoate (2t):



2t

Yellow oil. Yield: 69%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.59 (s, 3H), 2.91 (t, *J* = 7.8 Hz, 2H), 2.58 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 141.0, 139.7, 139.4, 128.8(4), 128.8(1), 127.4, 127.2, 127.1, 51.7, 35.8, 30.7. This compound is known and the spectroscopic data match those reported.[20]

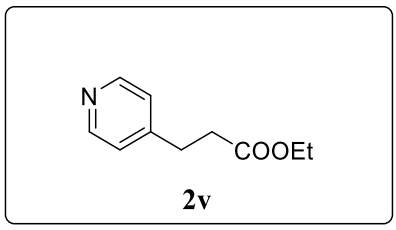
benzyl 3-([1,1'-biphenyl]-4-yl)propanoate (2u):



2u

Yellow oil. Yield: 65%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.44 – 7.40 (m, 2H), 7.36 – 7.31 (m, 2H), 7.25 – 7.23 (m, 3H), 7.22 – 7.11 (m, 3H), 7.10 – 7.06 (m, 2H), 5.04 (s, 2H), 2.93 (t, *J* = 7.7 Hz, 2H), 2.64 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8, 141.0, 139.6, 139.3, 136.0, 128.8, 128.7, 128.6, 128.3, 127.3(3), 127.3(1), 127.2, 127.1, 66.4, 35.9, 30.7. **HR-MS** (ESI+) for $C_{22}H_{20}O_2Na$ $([M+Na])^+$: calcd. 339.1361, found. 339.1351.

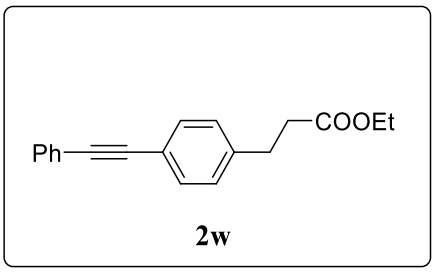
ethyl 3-(pyridin-4-yl)propanoate (2v):



2v

Yellow oil. Yield: 60%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 – 8.43 (m, 2H), 7.14 (d, *J* = 4.9 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 149.8, 149.7, 123.9, 60.8, 34.6, 30.2, 14.3. This compound is known and the spectroscopic data match those reported.[21]

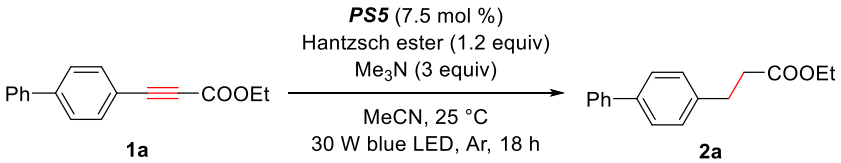
ethyl 3-(4-(phenylethynyl)phenyl)propanoate (2w):



2w

Yellow oil. Yield: 47%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 5.8, 2.1 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.36 – 7.31 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 2H), 4.13 (q, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 7.8 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.24 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8, 141.1, 131.9, 131.7, 128.5, 128.5, 128.3, 123.5, 121.3, 89.5, 89.2, 60.6, 35.8, 31.0, 14.4. **HR-MS** (ESI+) for $C_{19}H_{19}O_2$ $([M+H])^+$: calcd. 279.1385, found. 279.1386.

3.3 1.0 mmol-scale synthesis of 2a

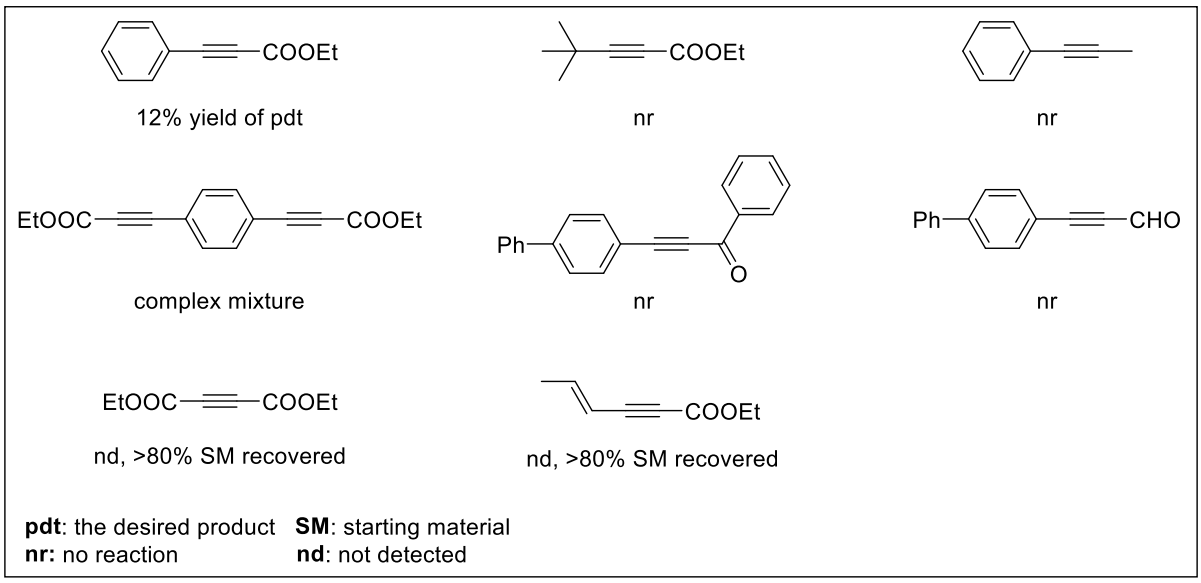


1a **2a**

To a 50 mL flame-dried Schlenk tube were added ***PS5*** (100 mg, 0.075 mmol), **1a** (250 mg, 1 mmol), and Hantzsch ester (305 mg, 1.2 mmol). The tube was evacuated and refilled

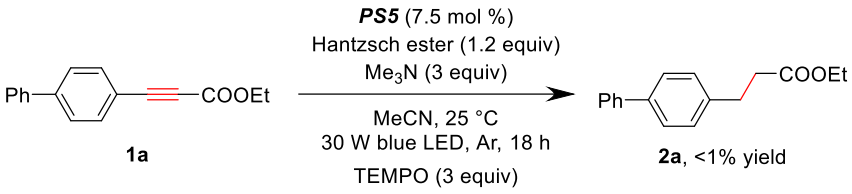
with Ar three times. Me_3N (175 mg, 3 mmol) and MeCN (20 mL) were added to the tube under an argon atmosphere. The resulting mixture was irradiated at a distance of 3 cm with 30 W blue LED and stirred at 25 ℃ for 18 h. The reaction progress was monitored by TLC. After completion, the reaction mixture was concentrated under vacuum, and the residue was purified by column chromatography on silica gel (eluent: PE/EA = 60/1) to give product **2a** in 57% yield (145 mg).

3.4 Challenging substrates



4. Mechanistic Studies

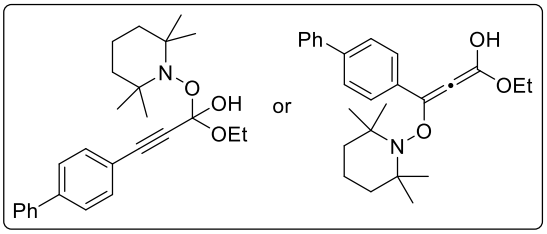
4.1 Radical scavenging experiment



To a 25 mL flame-dried Schlenk tube were added ***PS5*** (20 mg, 0.015 mmol), **1a** (50 mg, 0.2 mmol), Hantzsch ester (61 mg, 0.24 mmol), and TEMPO (94 mg, 3 equiv). The tube was evacuated and refilled with Ar three times. Me_3N (35 mg, 0.6 mmol) and MeCN (4 mL) were added to the tube under an argon atmosphere, then the resulting mixture was irradiated at a distance of 3 cm with blue LED and stirred at 25 ℃ for 18 h. The reaction mixture was analyzed by TLC, and the formation of **2a** was not detected.

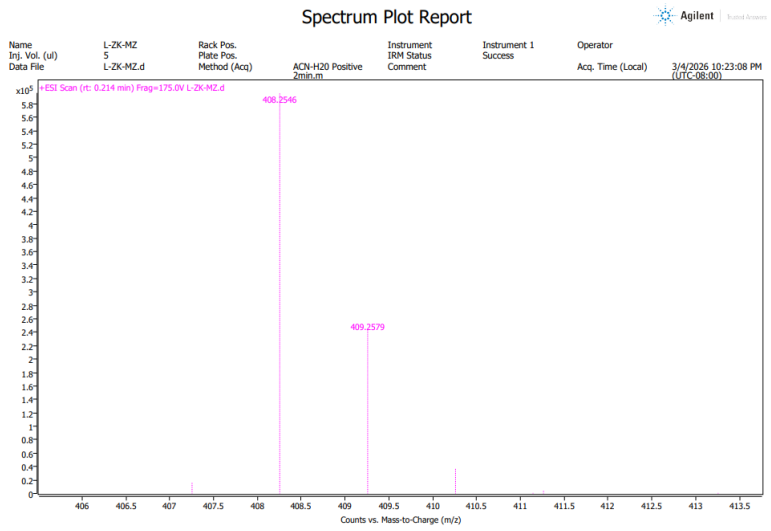
We took a sample from the crude solution and observed a TEMPO adduct via HR-MS, likely originating from the trapping of intermediate **C** or **D**.

Possible TEMPO adduct

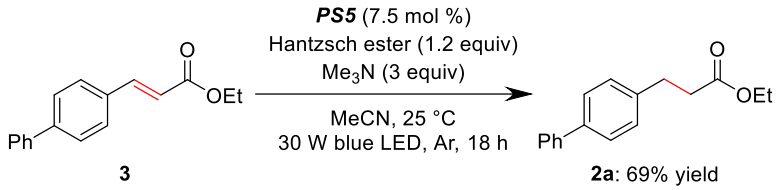


detected by **HR-MS**

HR-MS (ESI+) for $C_{26}H_{34}NO_3$ ($[M+H]^+$: calcd. 408.2533, found. 408.2546.

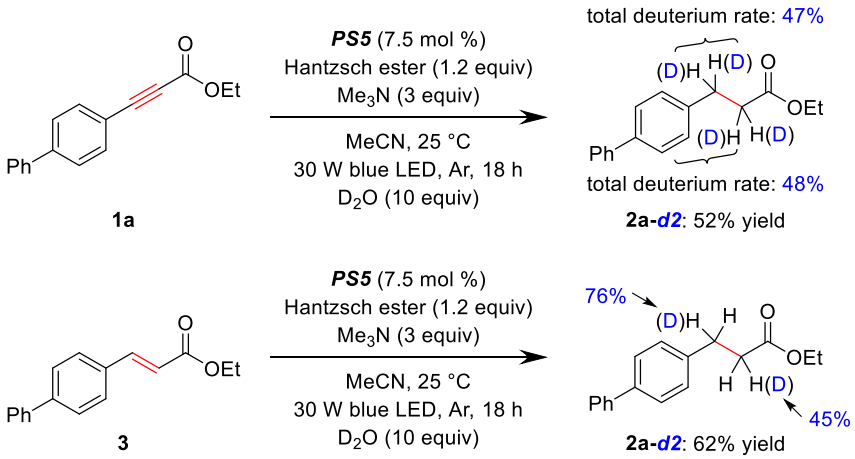


4.2 Intermediate investigation experiment



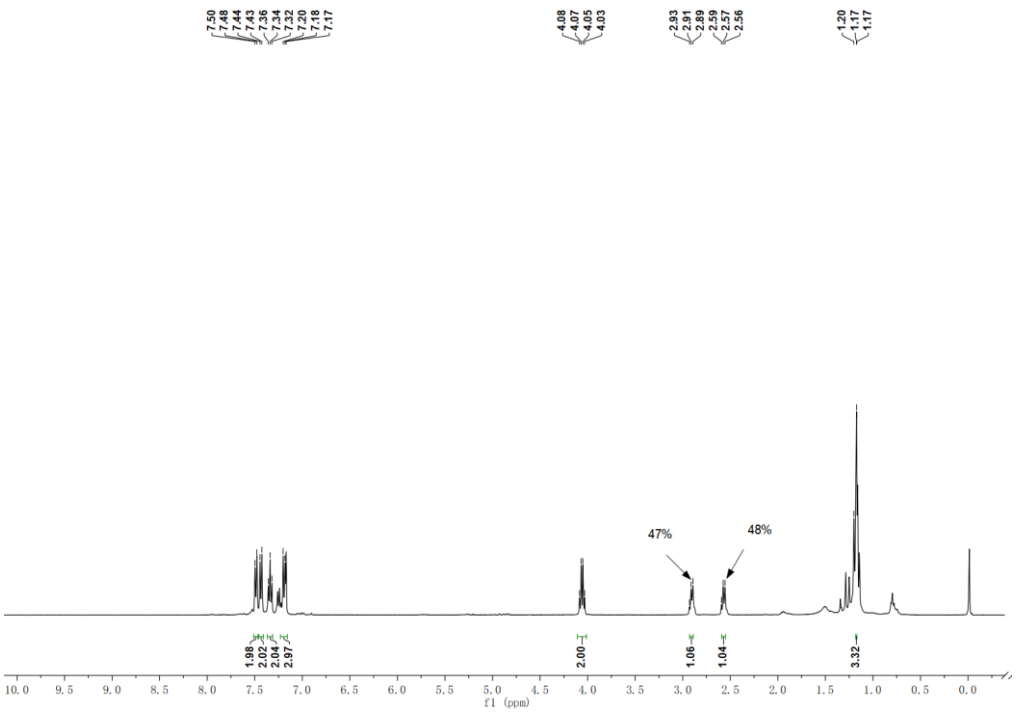
To a 25 mL flame-dried Schlenk tube were added ***PS5*** (20 mg, 0.015 mmol), **3** (50 mg, 0.2 mmol), and Hantzsch ester (61 mg, 0.24 mmol). The tube was evacuated and refilled with Ar three times. Me_3N (35 mg, 0.6 mmol) and MeCN (4 mL) were added to the tube under an argon atmosphere, then the reaction mixture was irradiated at a distance of 3 cm with blue LED and stirred at 25 ℃ for 18 h. The reaction progress was monitored by TLC. After completion, the reaction mixture was concentrated under vacuum, and the residue was purified by column chromatography on silica gel (eluent: PE/EA = 60/1) to give product **2a** in 69% yield.

4.3 Deuterium-labeling experiments

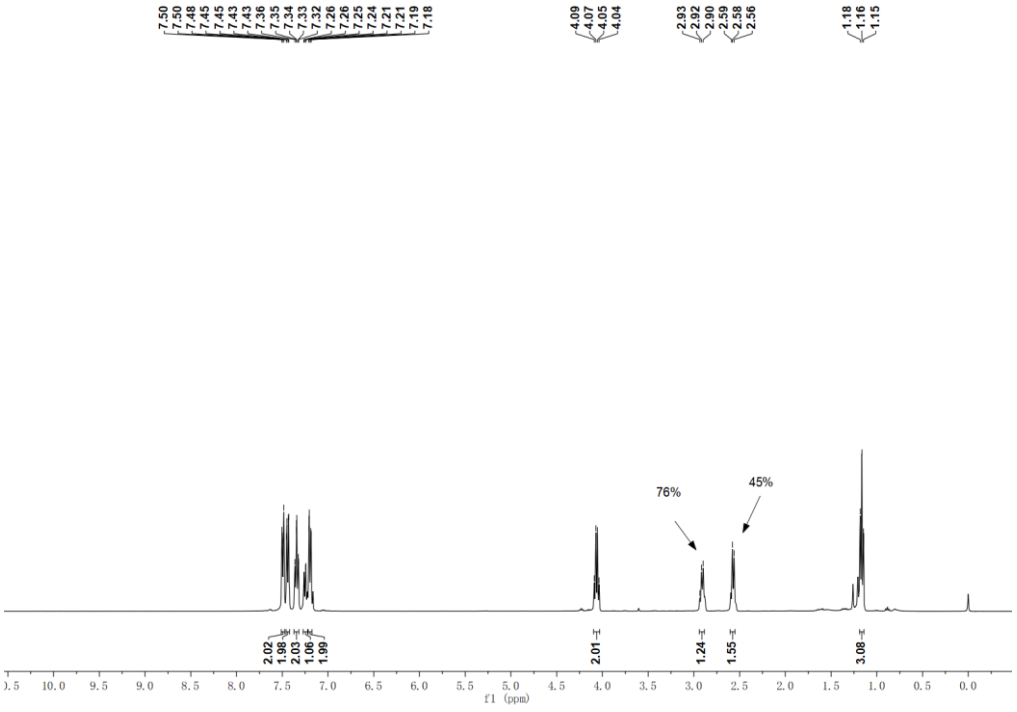


To a 25 mL flame-dried Schlenk tube were added ***PS5*** (20 mg, 0.015 mmol), **1a** (50 mg, 0.2 mmol), and Hantzsch ester (61 mg, 0.24 mmol). The tube was evacuated and refilled with Ar three times. Me_3N (35 mg, 0.6 mmol), MeCN (4 mL), and D_2O (10 equiv, D-enrichment of D_2O > 99.8%) were added to the tube under an argon atmosphere, then the resulting mixture was irradiated at a distance of 3 cm with blue LED and stirred at 25 ℃ for 18 h. After work-

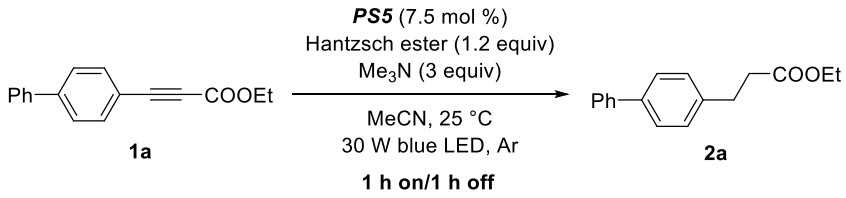
up and isolation, **2a-*d*$_2$** was obtained in 52% yield. The ^{1}H NMR spectrum of **2a-*d*$_2$** with the calculated D-incorporated rates is listed below:



The procedure is identical to that described above, using **3** instead of **1a** as the substrate. After work-up and isolation, **2a-*d*$_2$** was obtained in 62% yield. The ^{1}H NMR spectrum of **2a-*d*$_2$** with the calculated D-incorporated rates is listed below:



4.4 Light on/off experiment



To a 25 mL flame-dried Schlenk tube were added ***PS5*** (20 mg, 0.015 mmol), **1a** (50 mg, 0.2 mmol), and Hantzsch ester (61 mg, 0.24 mmol). The tube was evacuated and refilled with Ar three times. Me_3N (35 mg, 0.6 mmol, 4.2 mol/L in EtOH) and MeCN (4 mL) were added to the tube under an argon atmosphere, then the resulting mixture was irradiated at a distance of 3 cm with 30 W blue LED and stirred at 25 ℃ for 6 h. The light was turned on or off every 1 h, and the yield was determined by LC analysis.

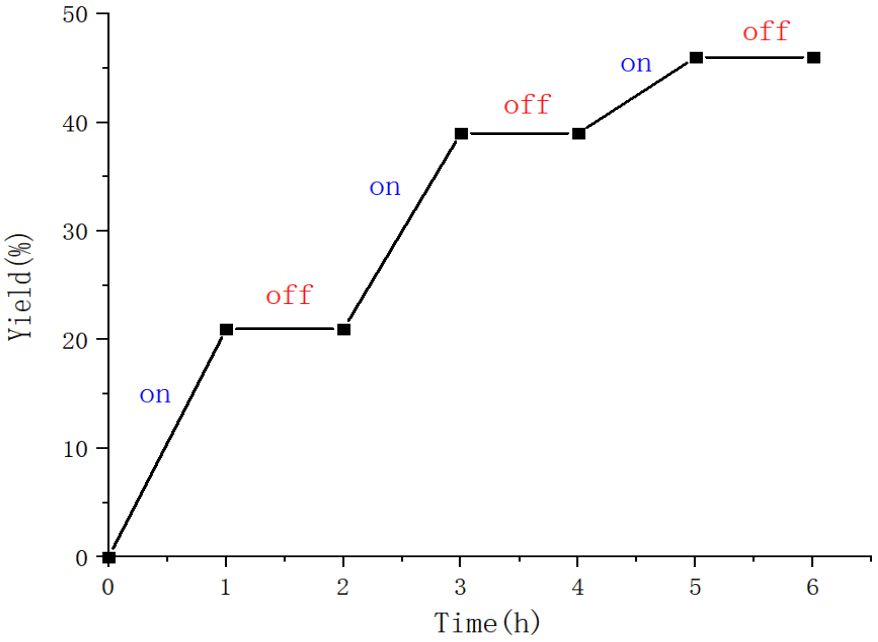


Figure S1. Yields of **2a** during on/off experiments.

4.5 Stern-Volmer experiments

Stern-Volmer experiments were carried out with a freshly prepared solution of 1×10^{-4} M ***PS5*** and different concentrations of trimethylamine in MeCN at room temperature under an Ar

atmosphere. The experimental results indicate that Me_3N can quench the copper-based photosensitizer ***PS5*** in acetonitrile.

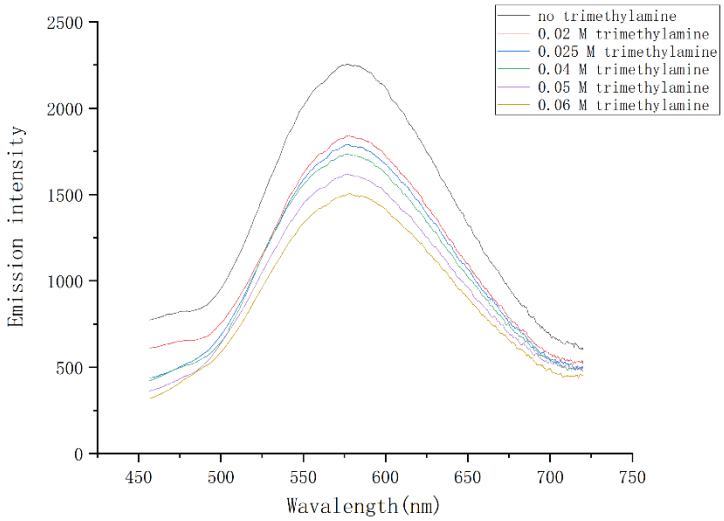
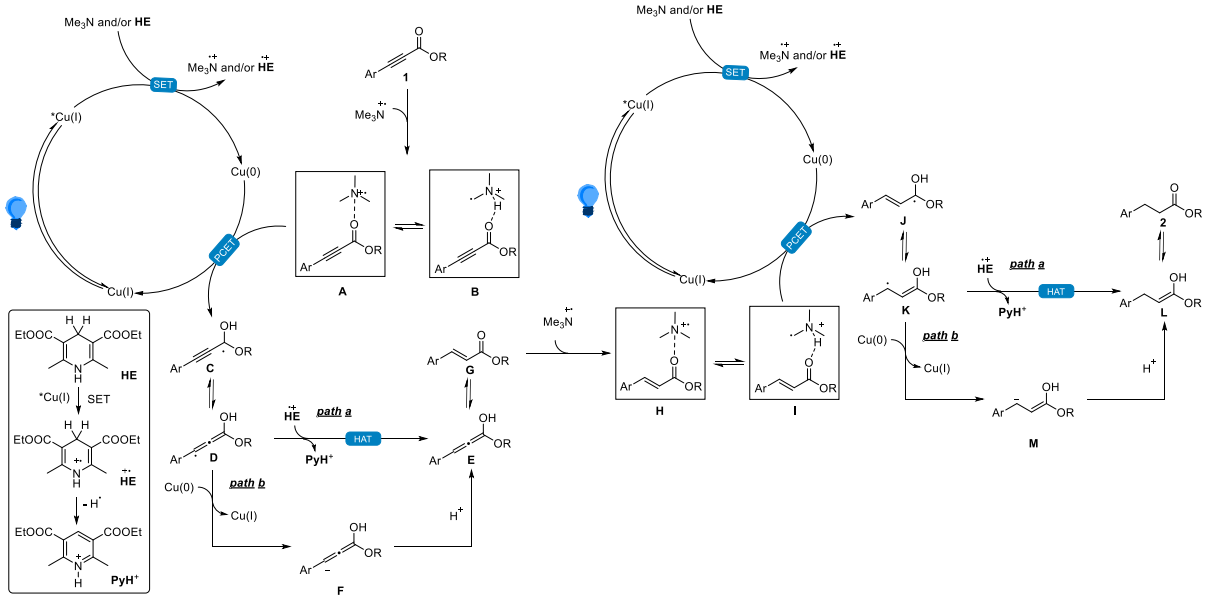


Figure S2. Stern-Volmer quenching experiment with varying concentrations of trimethylamine.

For details on Hantzsch ester as the quencher, see our previous work (*Chem. Commun.* **2025**, *61*, 5357).

4.6 Proposed mechanism



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6. Copies of ^{1}H and ^{13}C NMR Spectra

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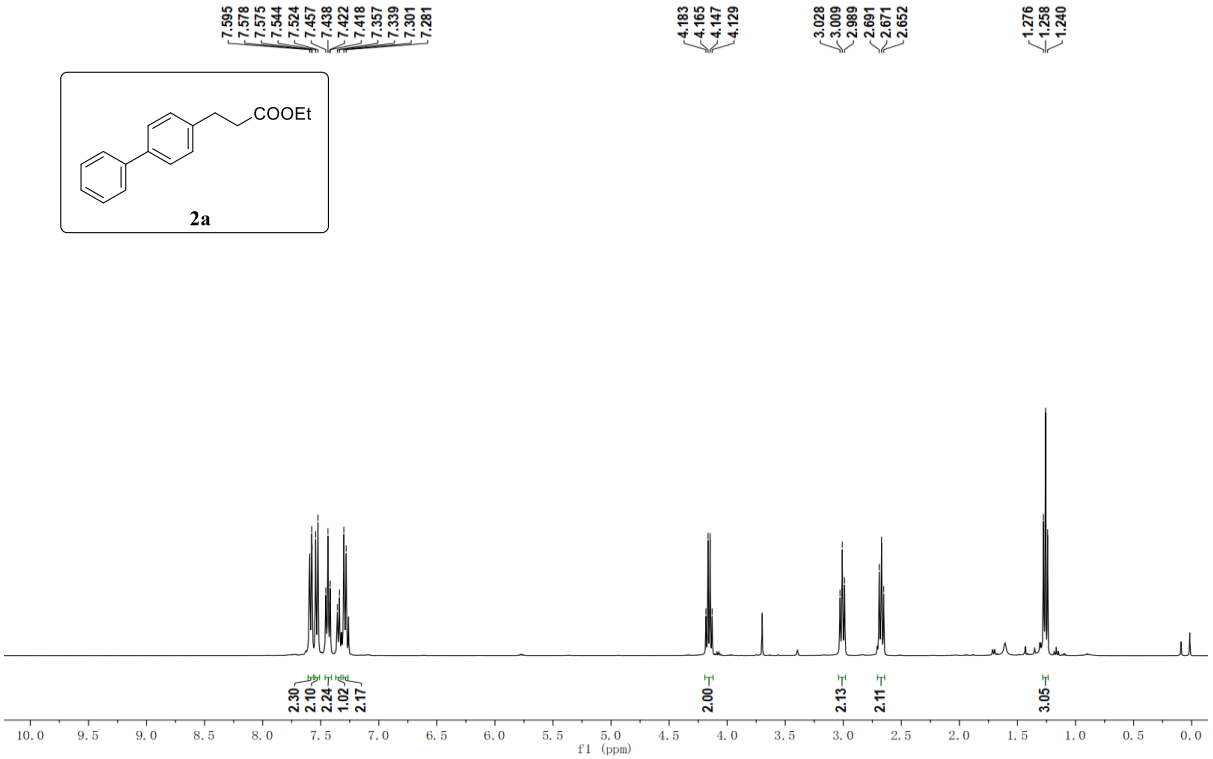
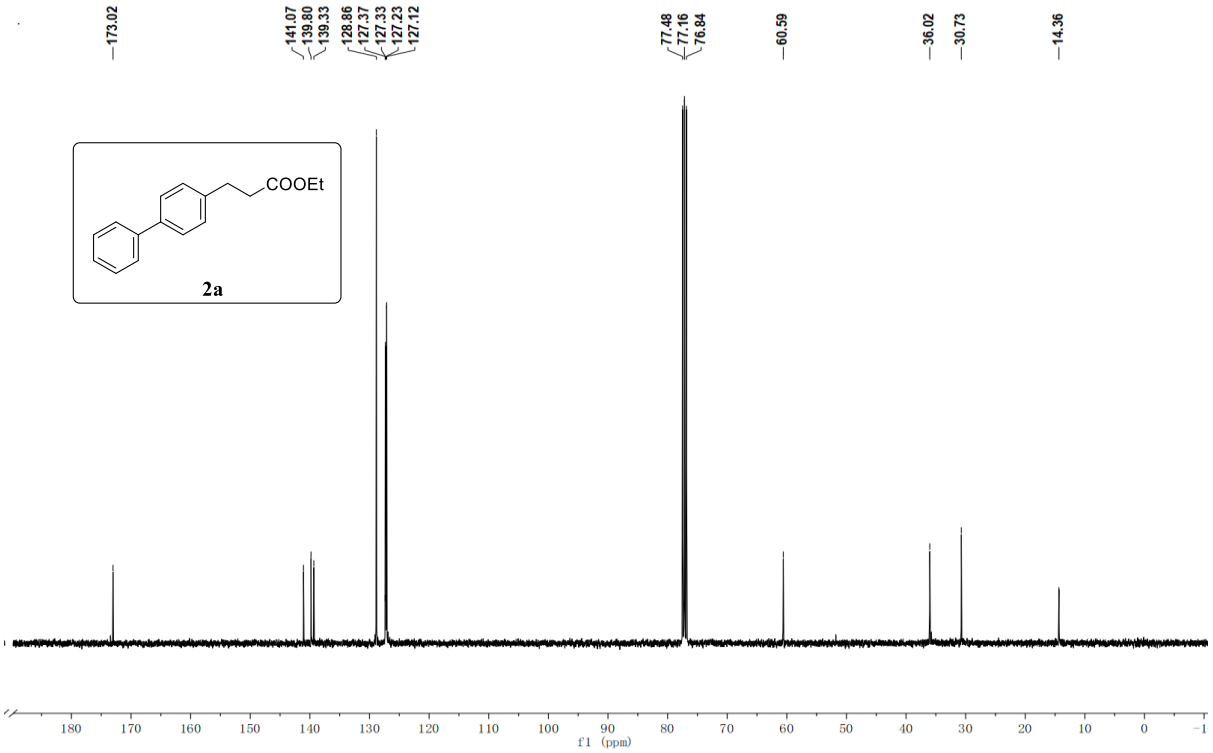
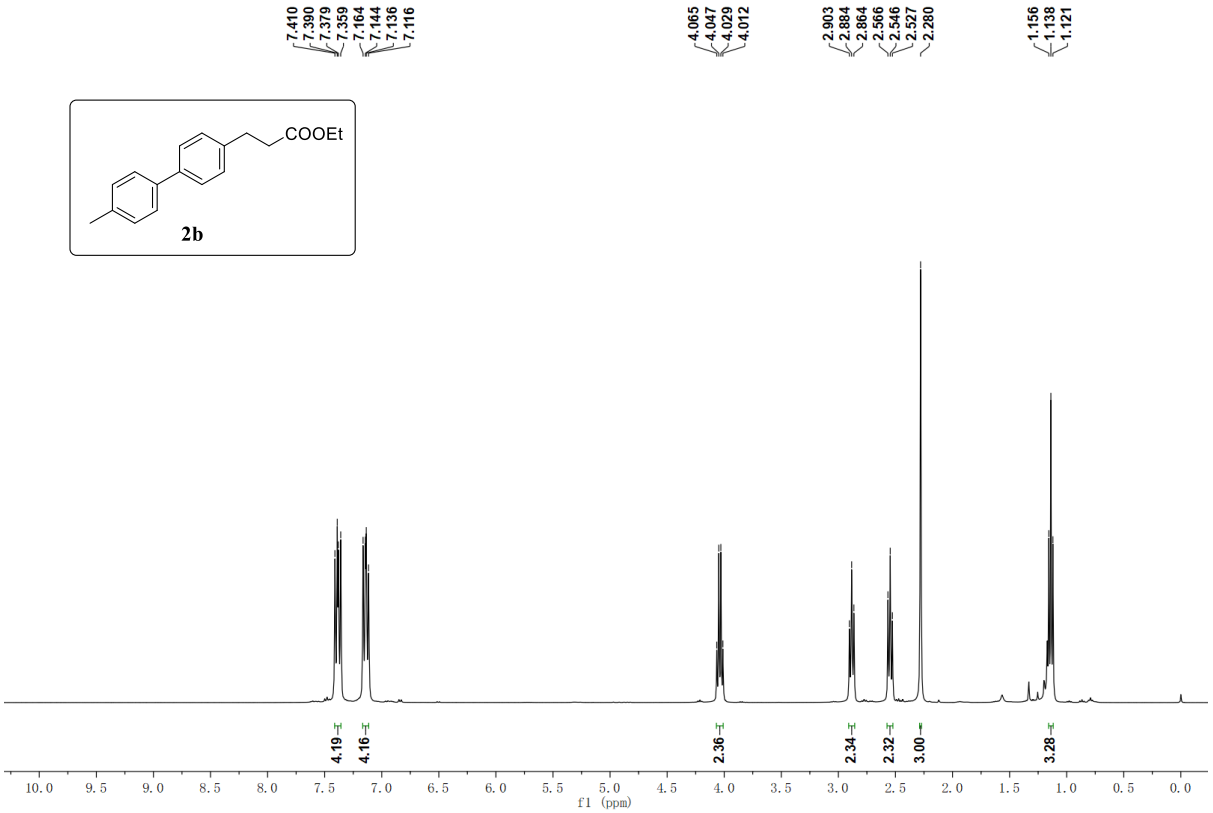


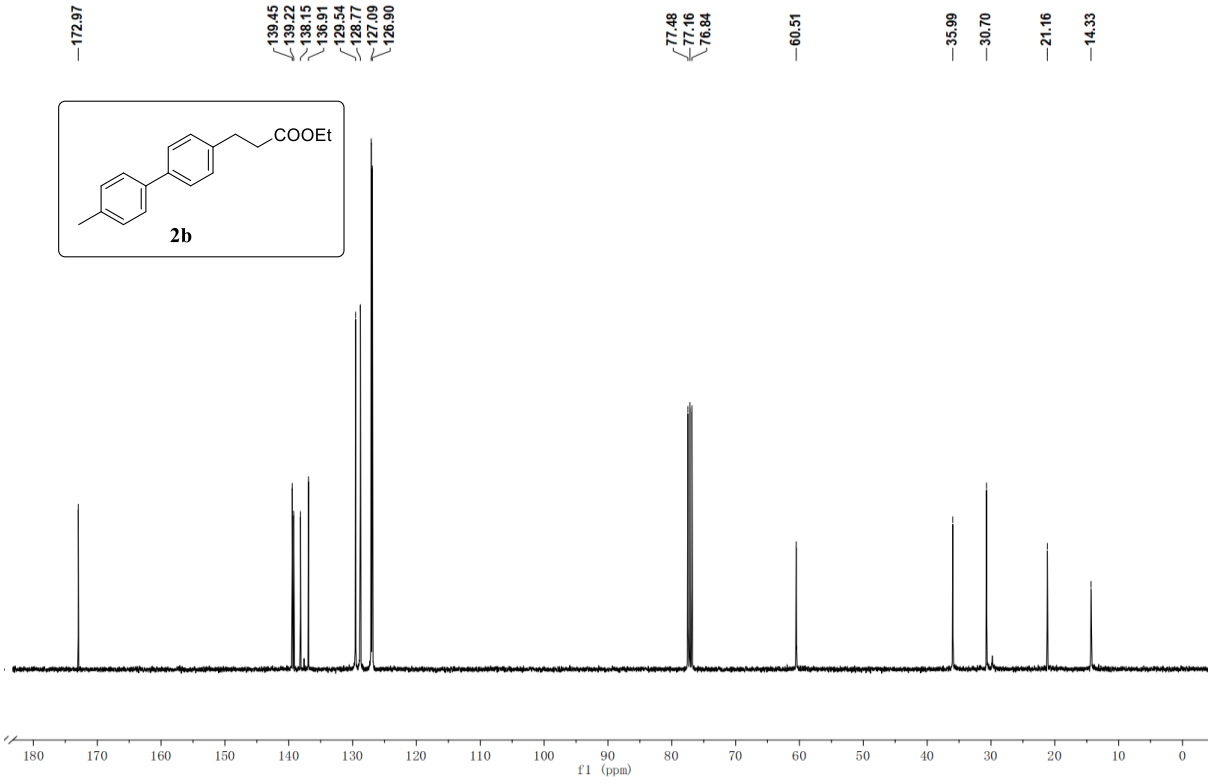
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2a



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2b



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2b



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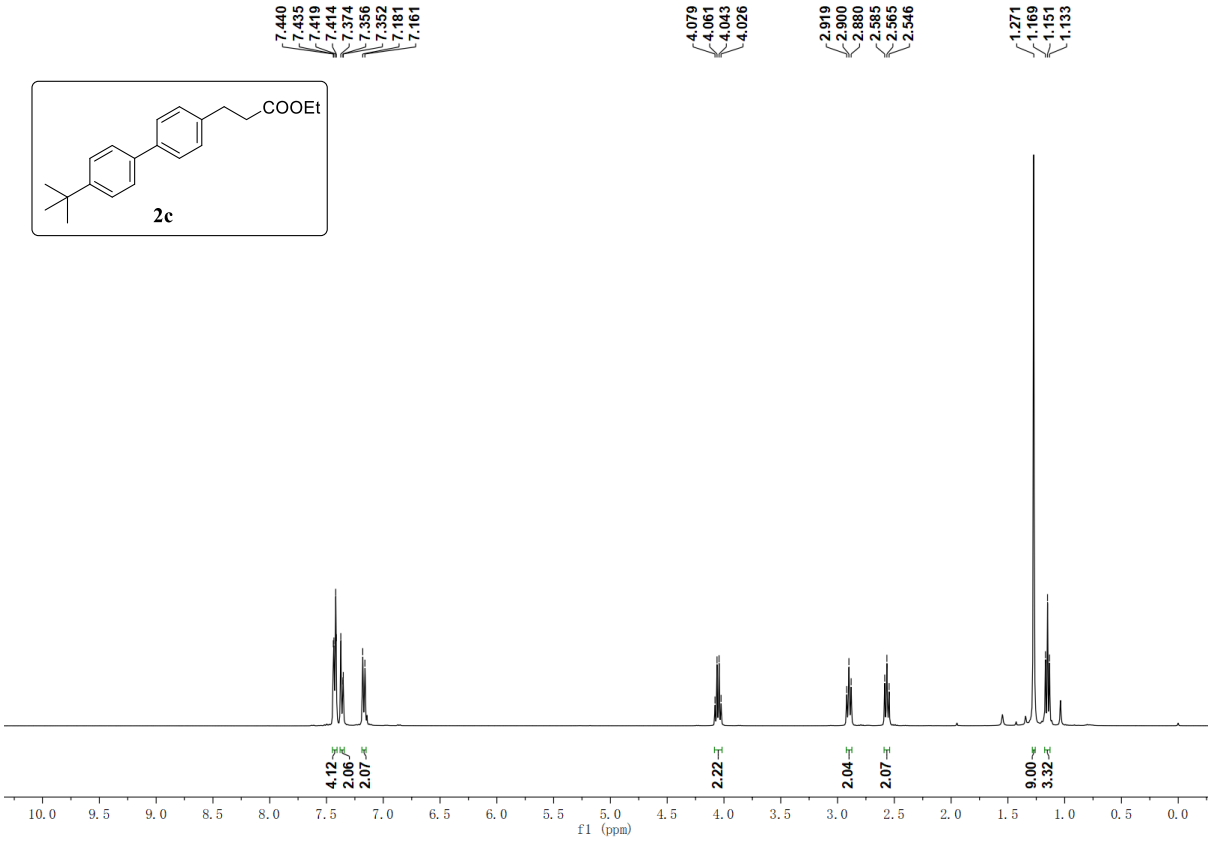

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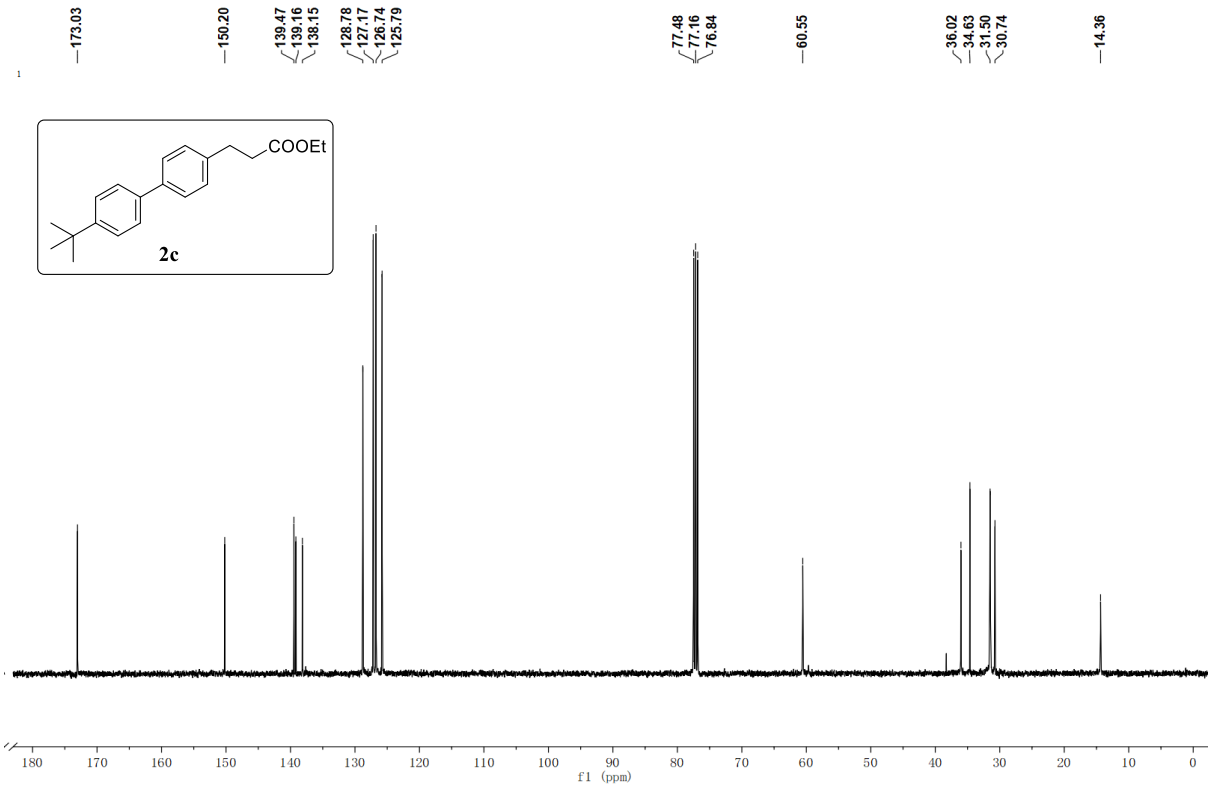

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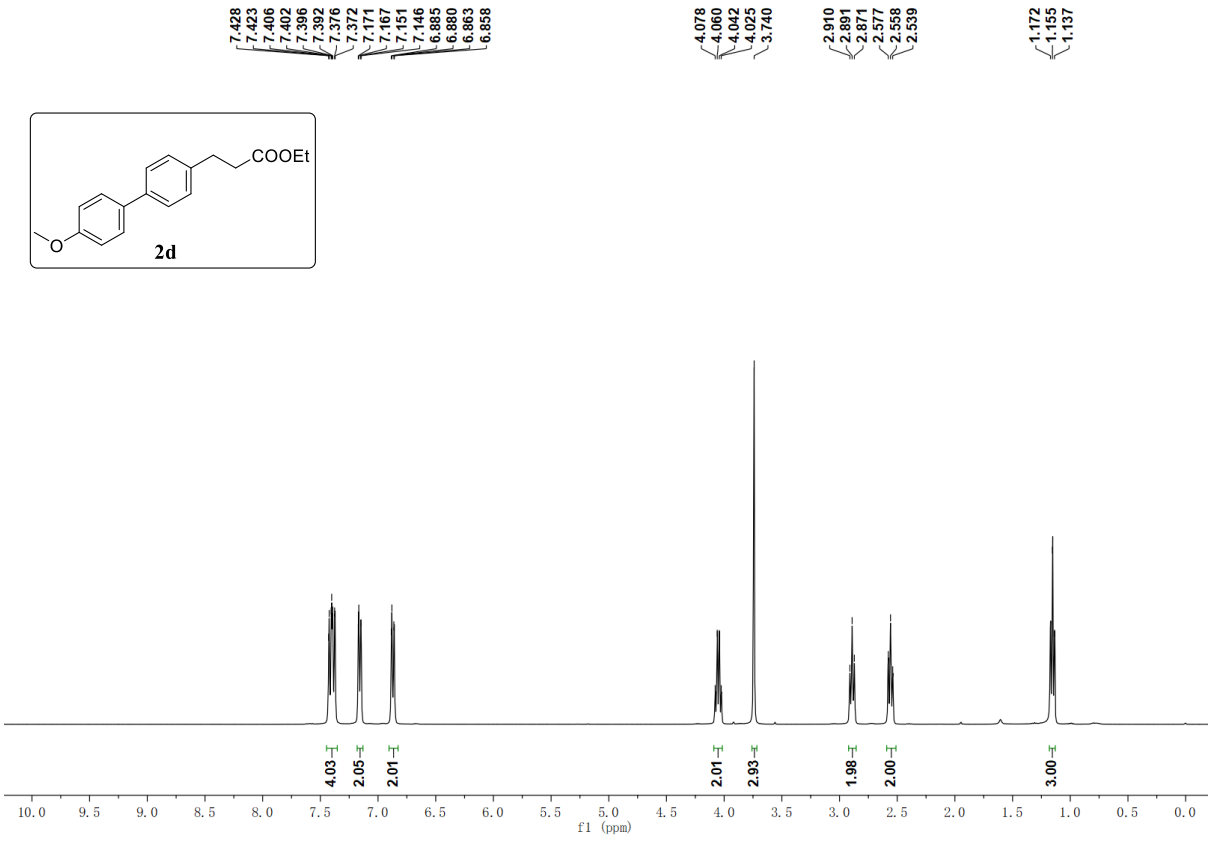

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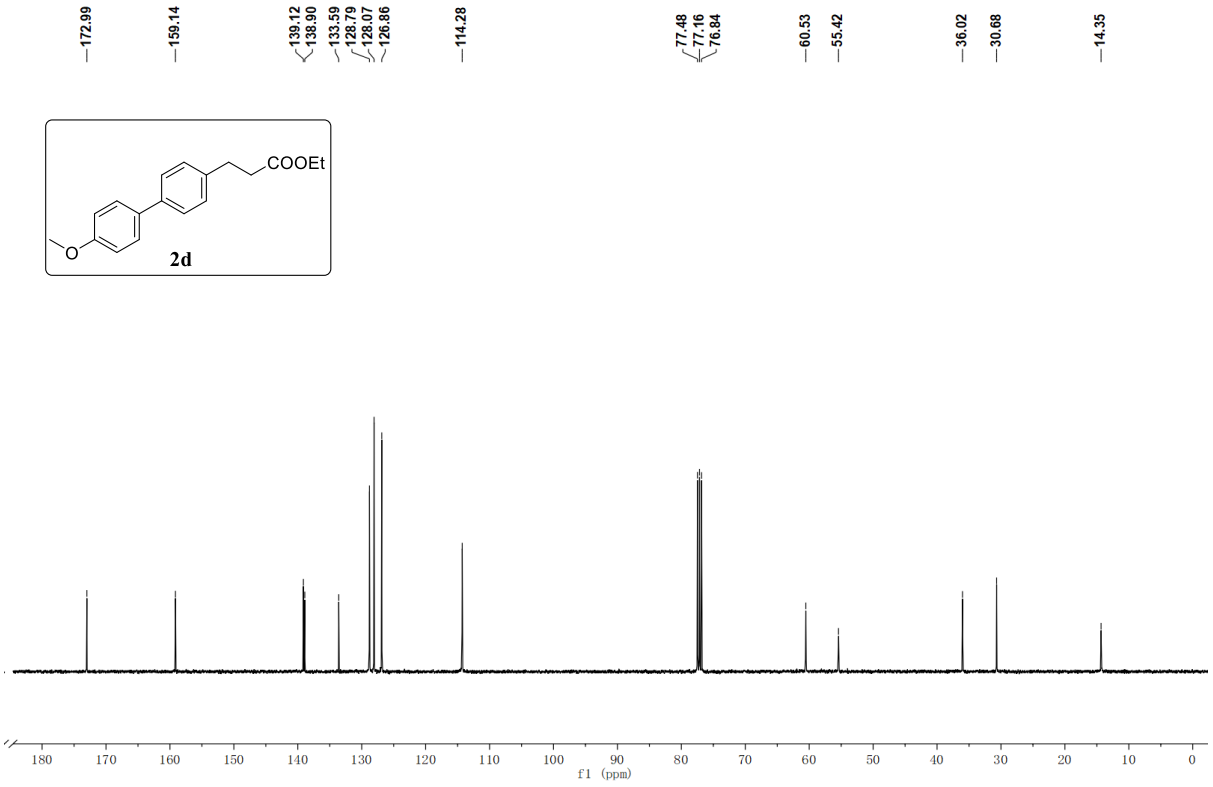

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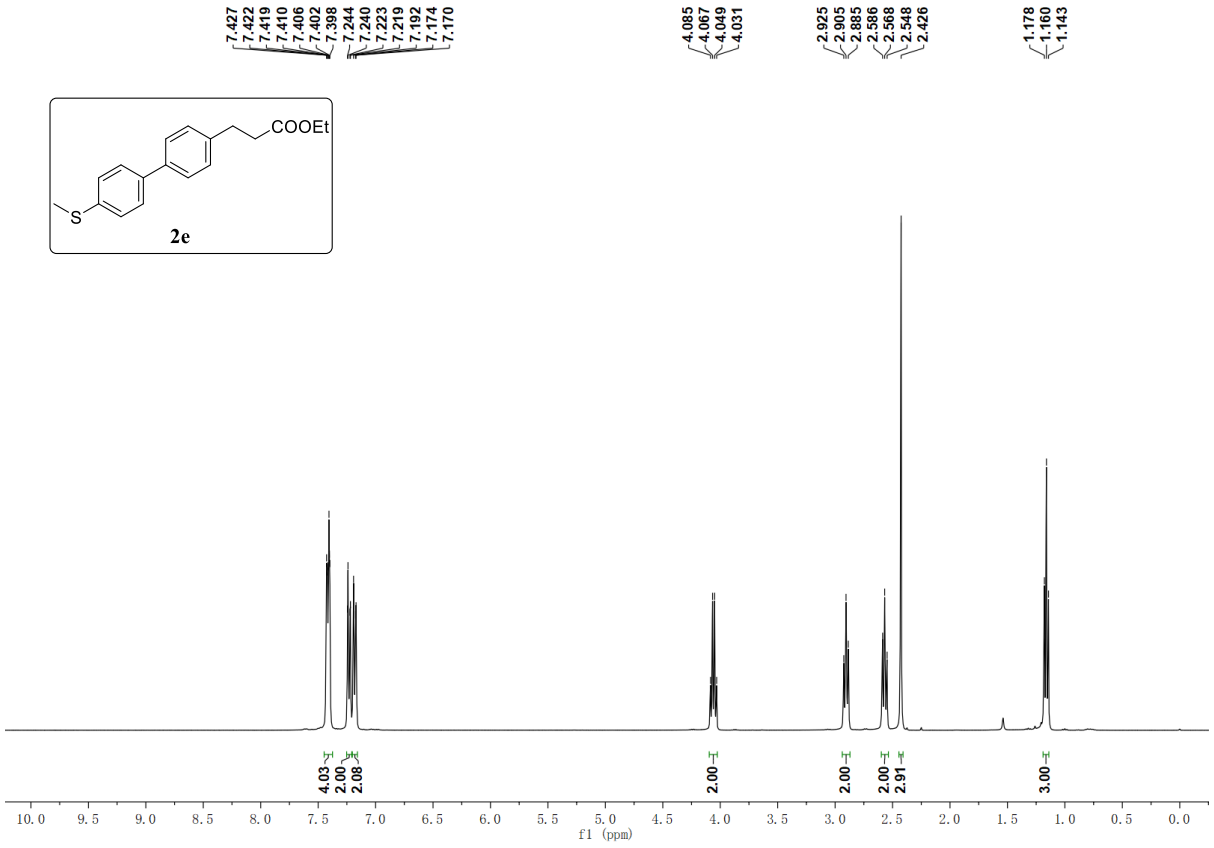

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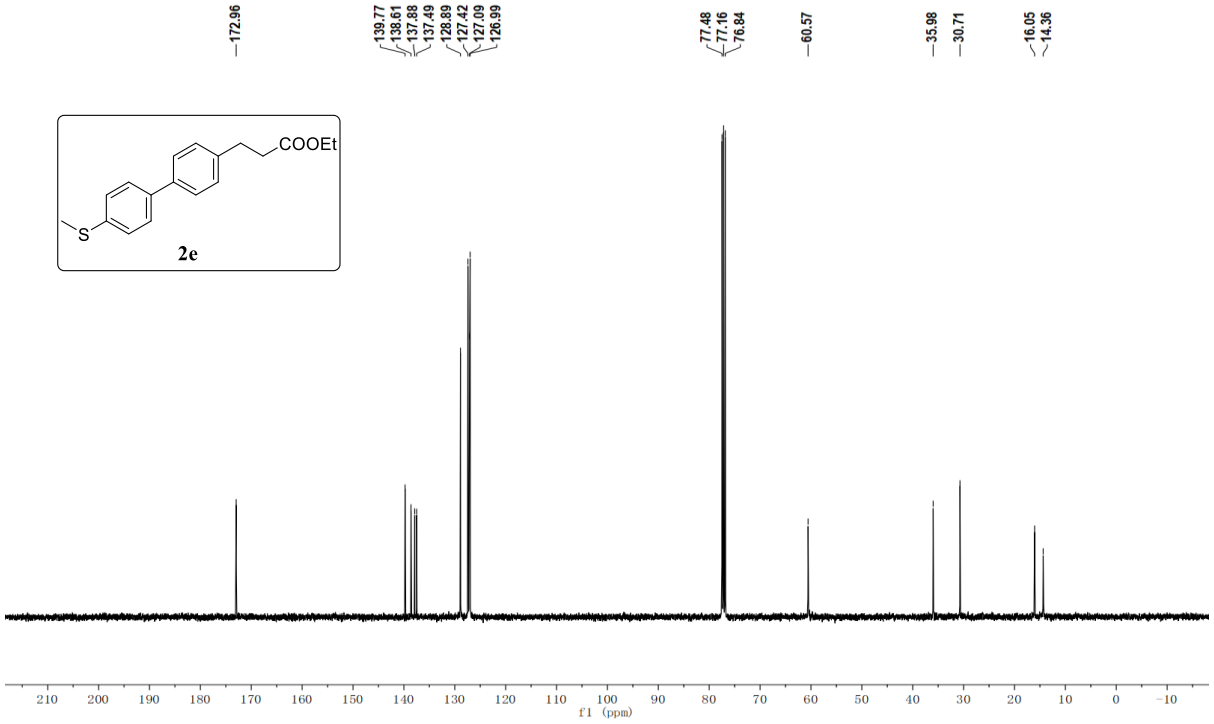

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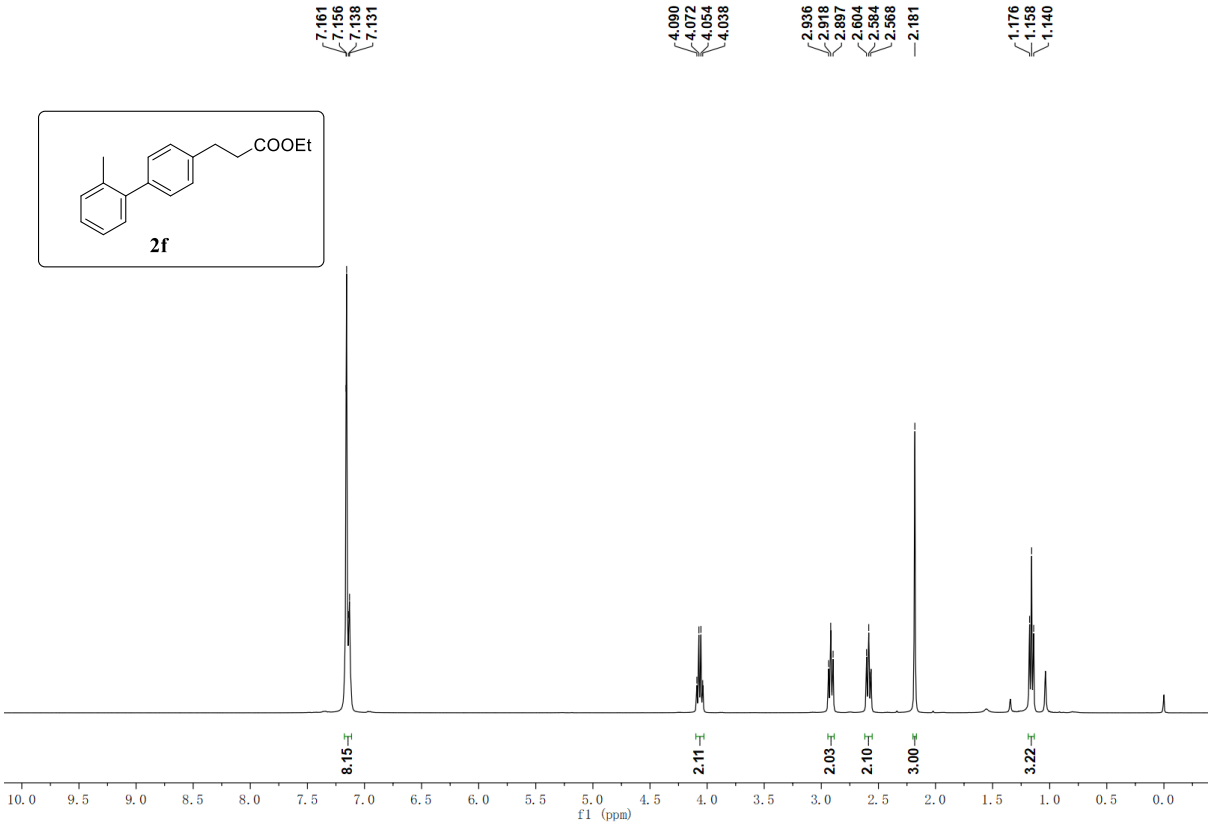

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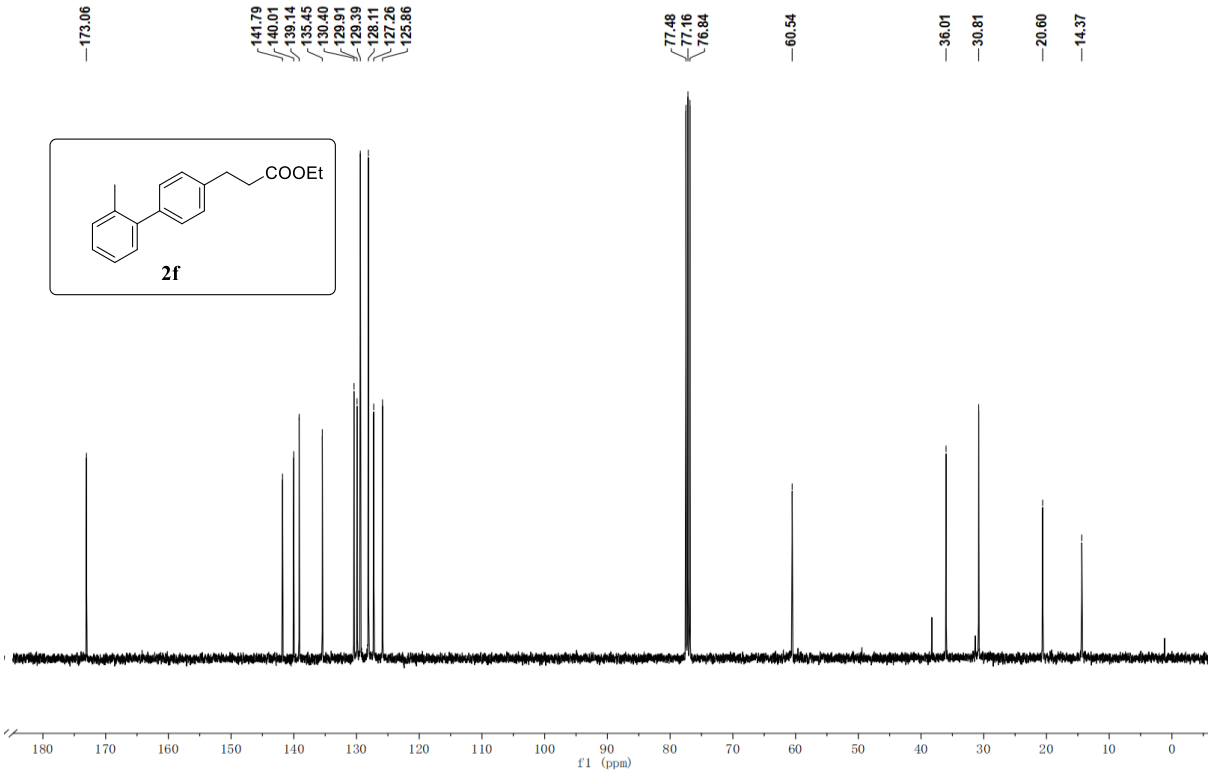

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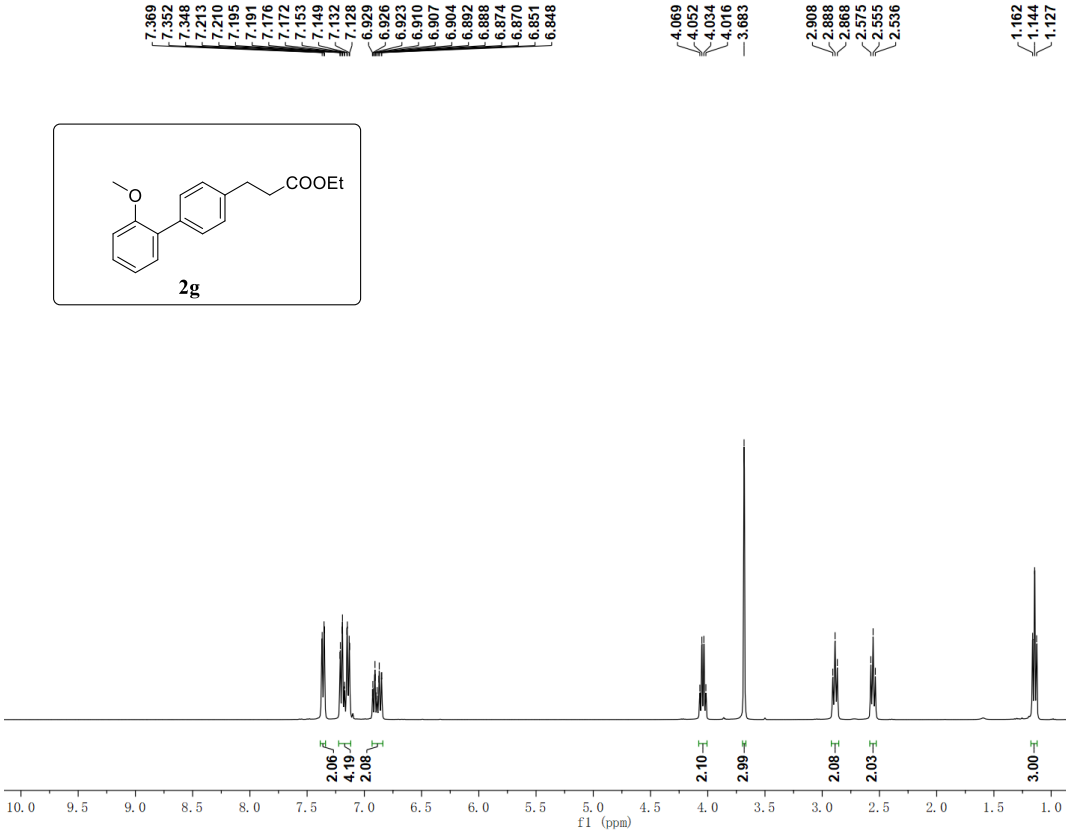

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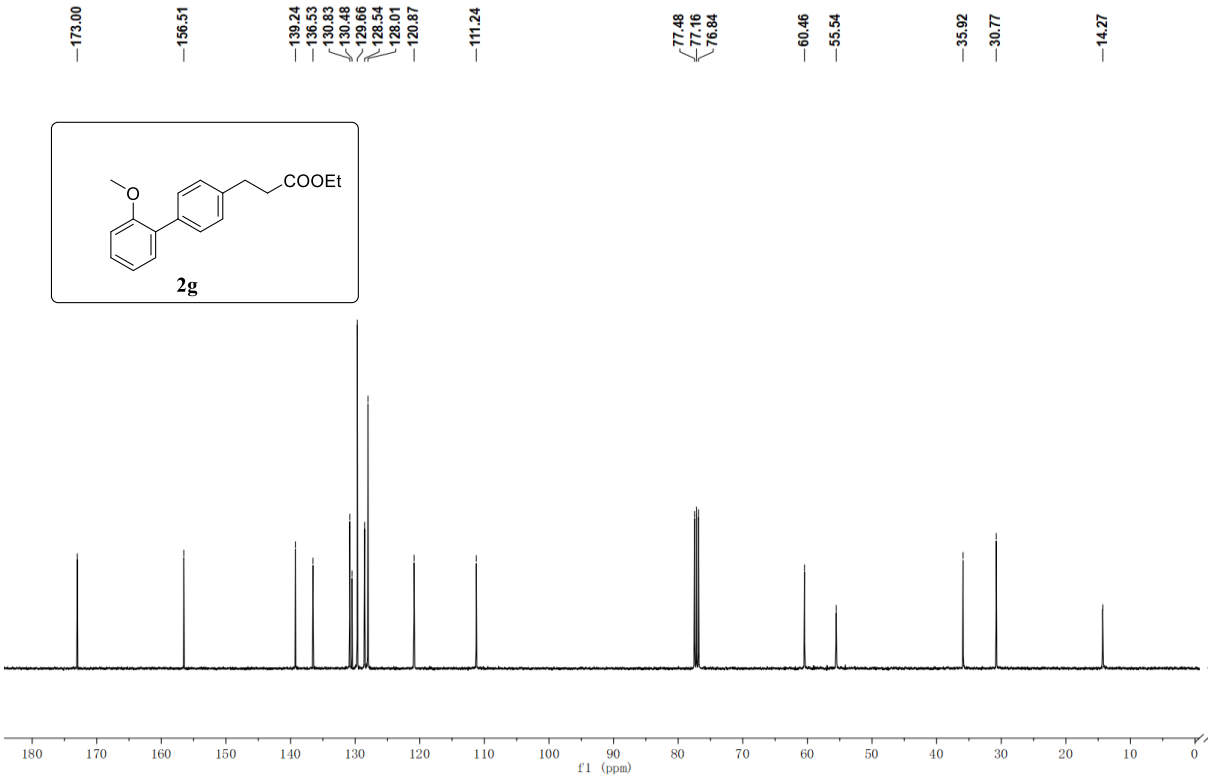

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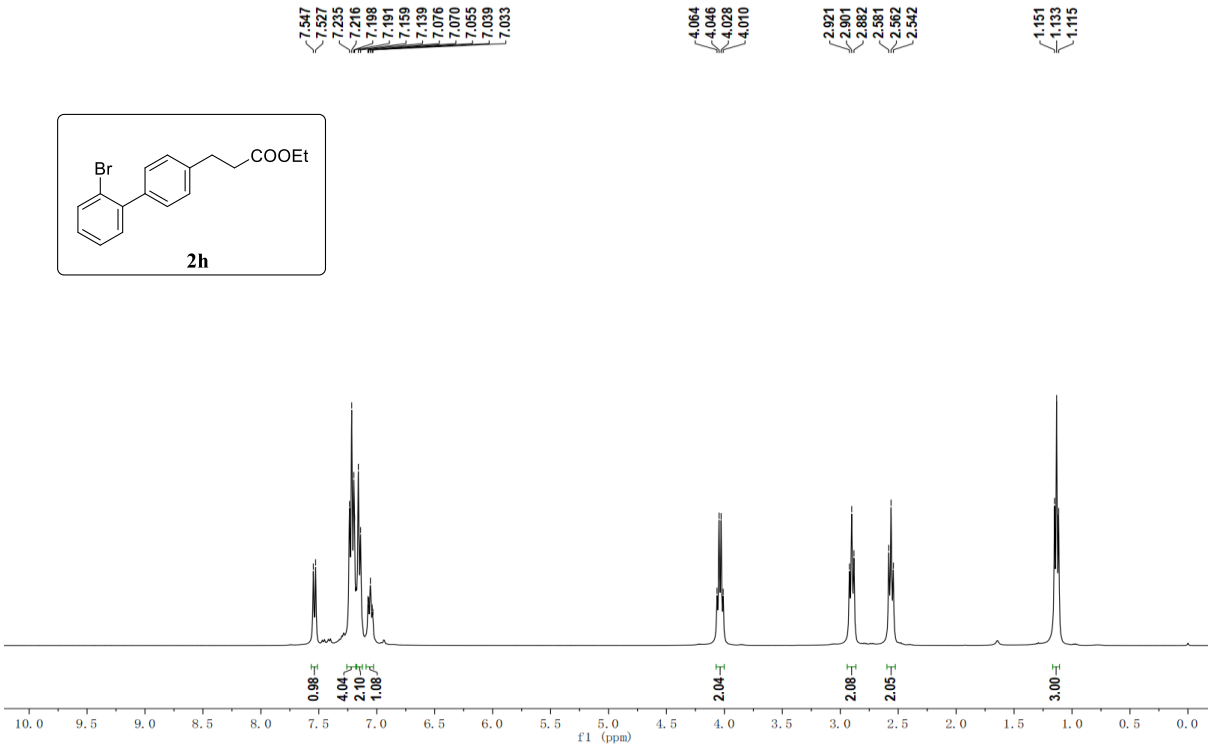
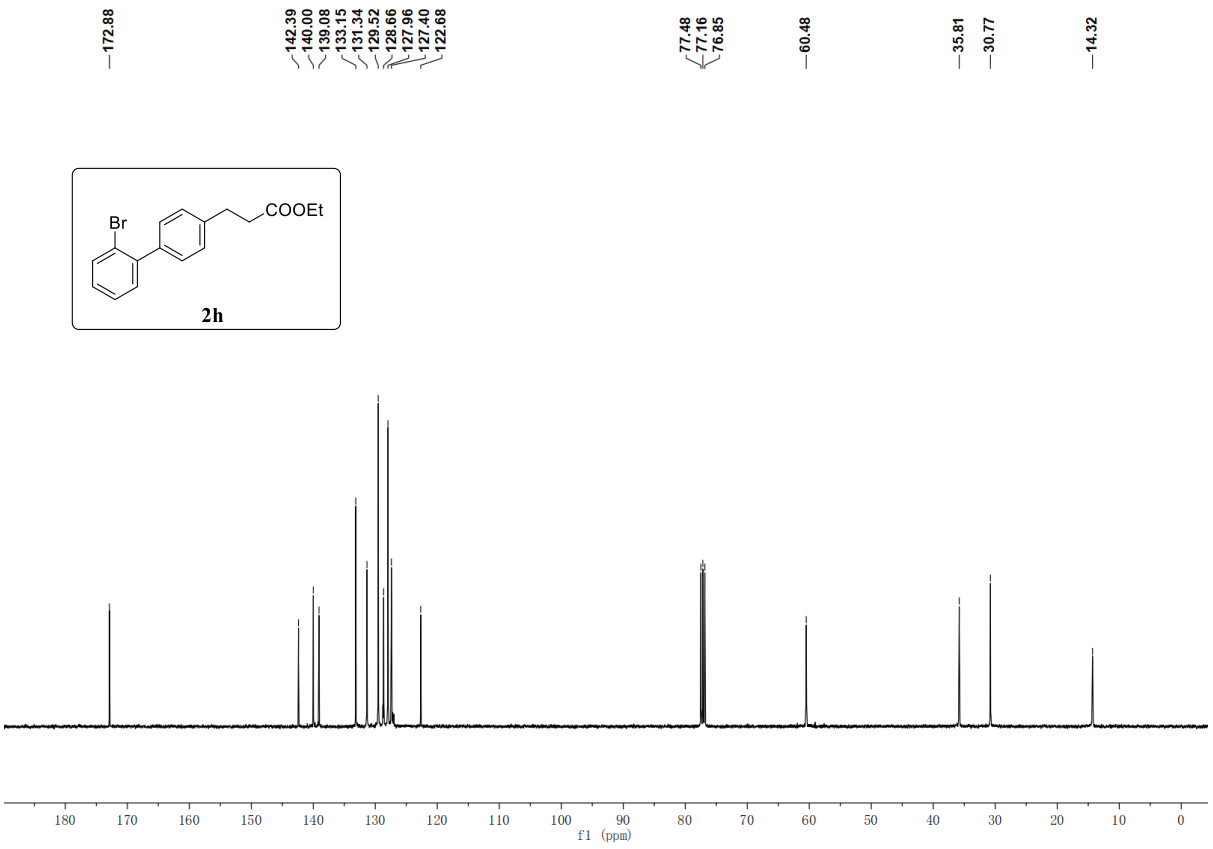
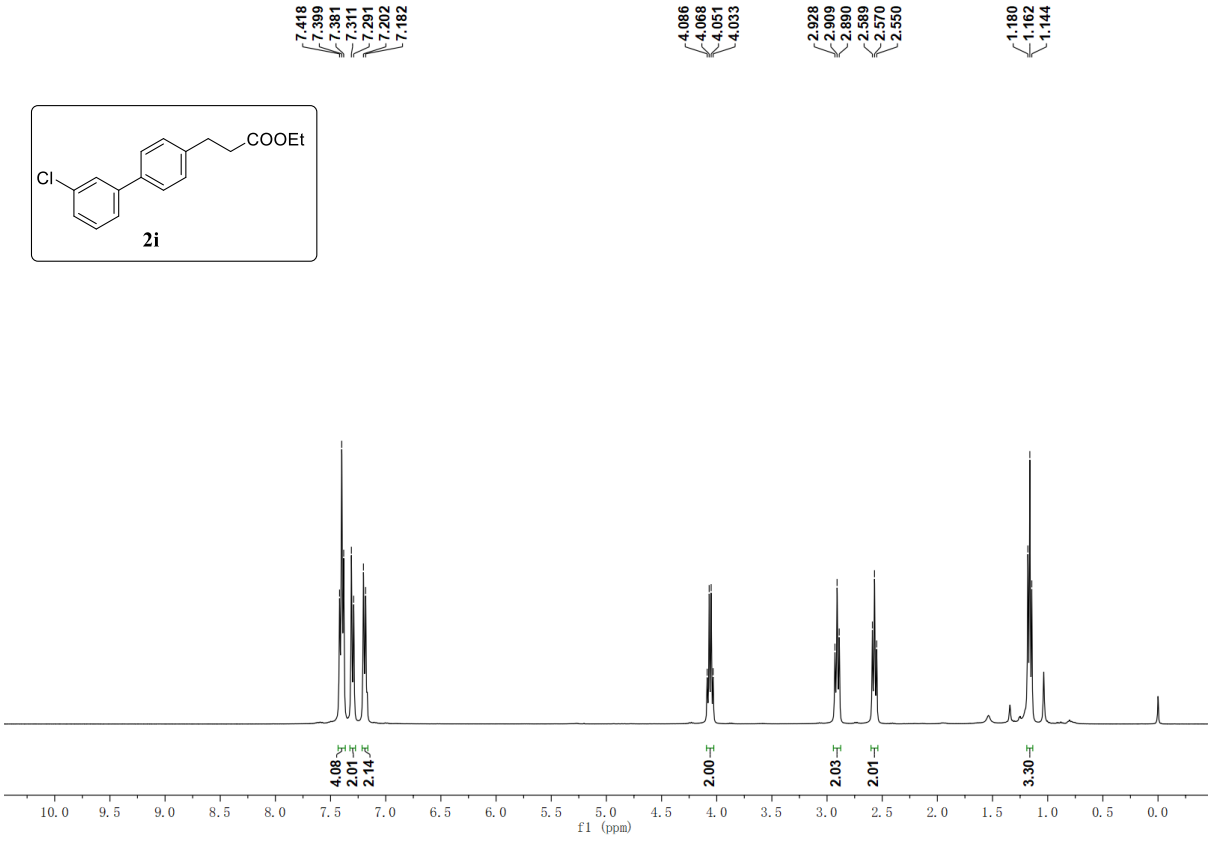


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2h



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2i



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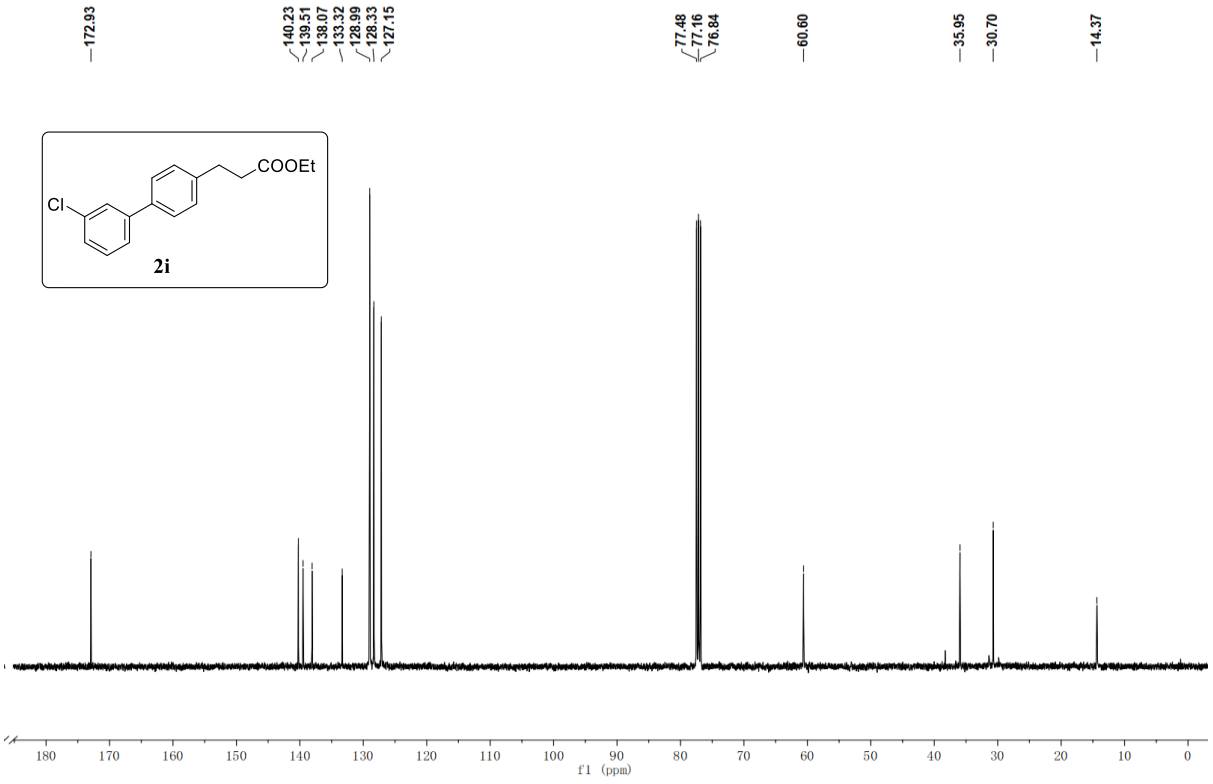

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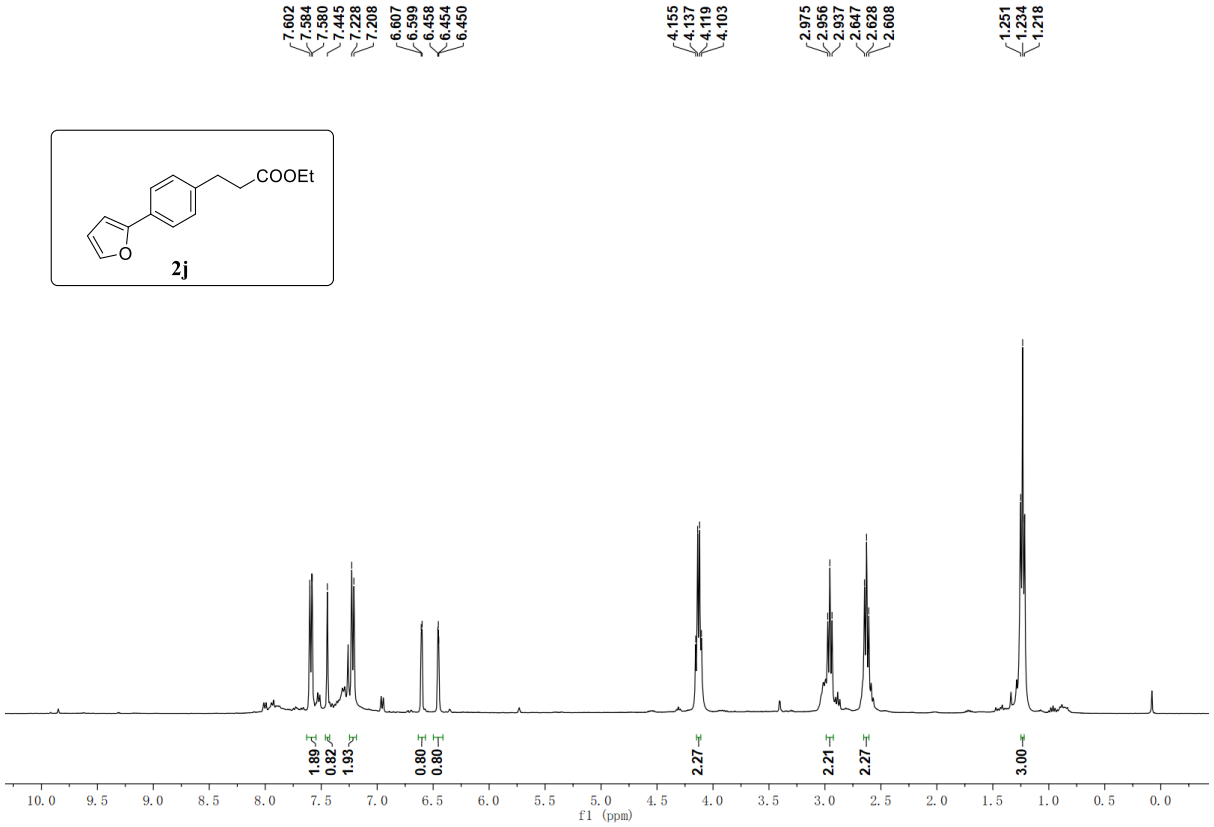

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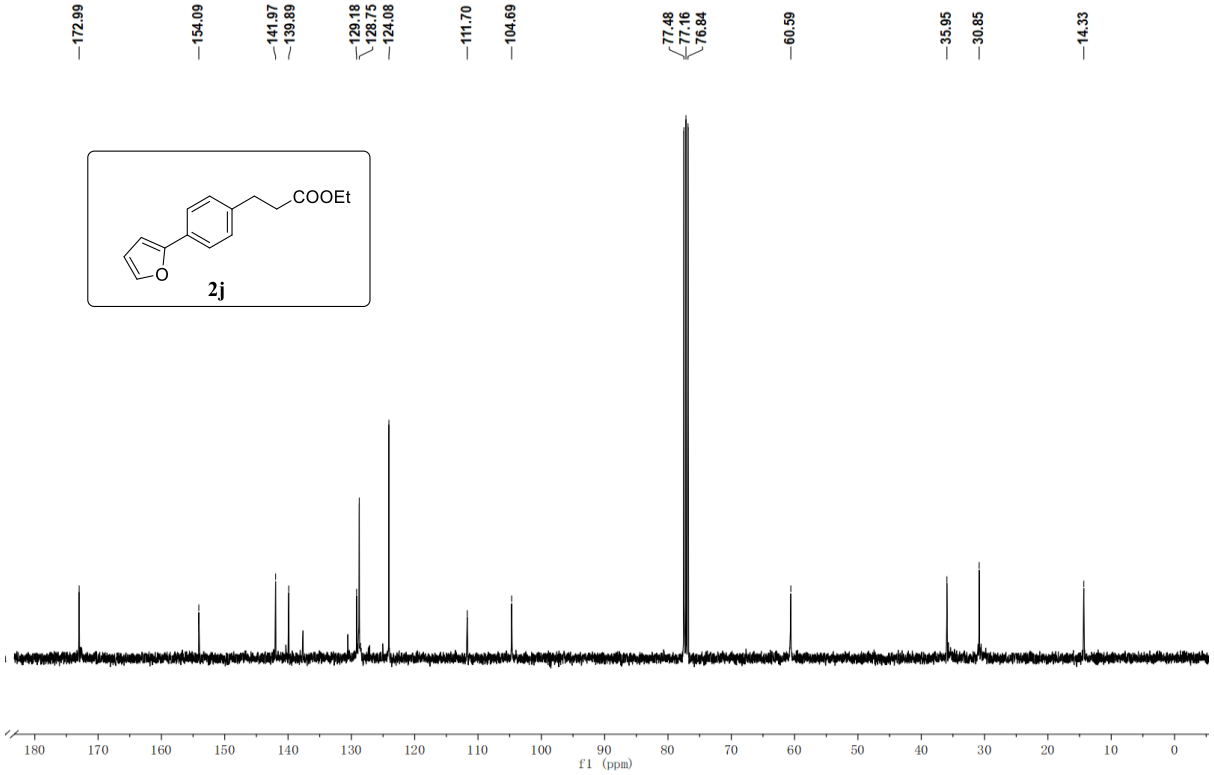

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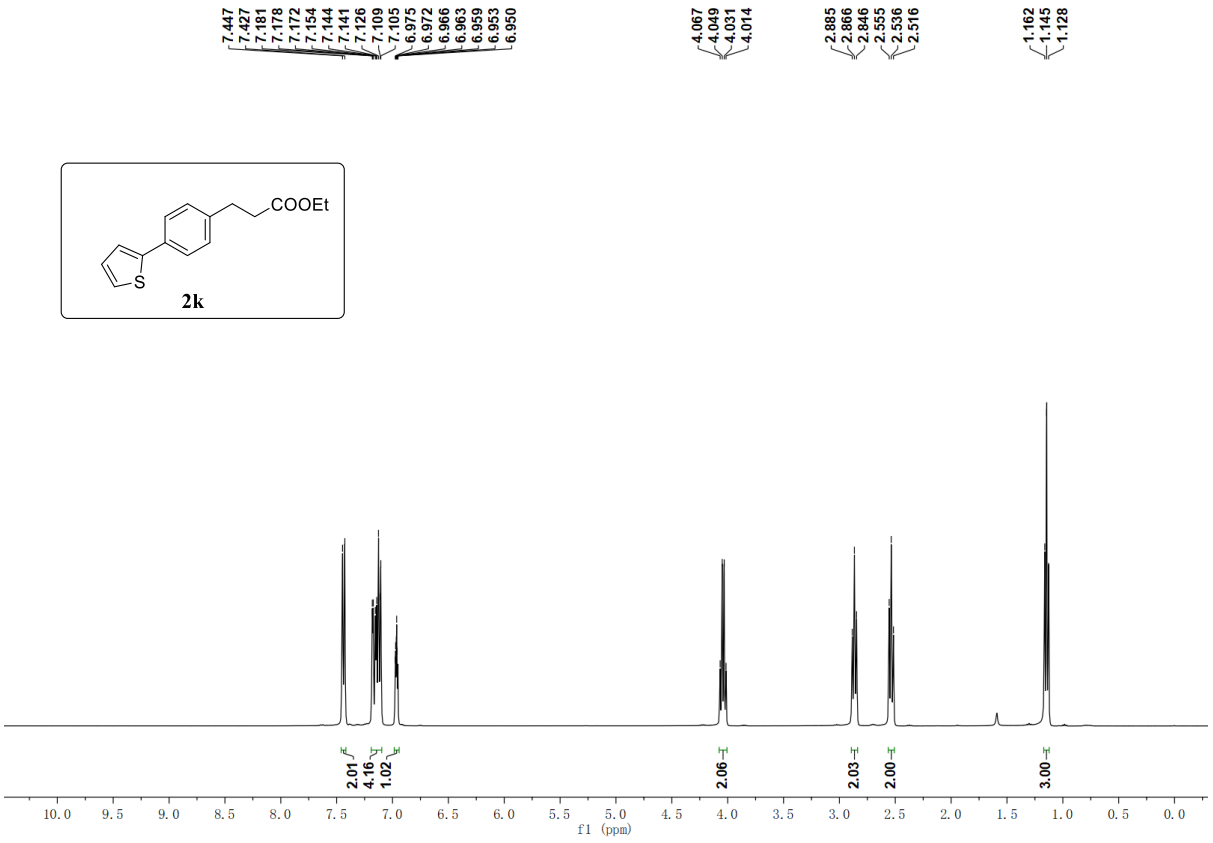

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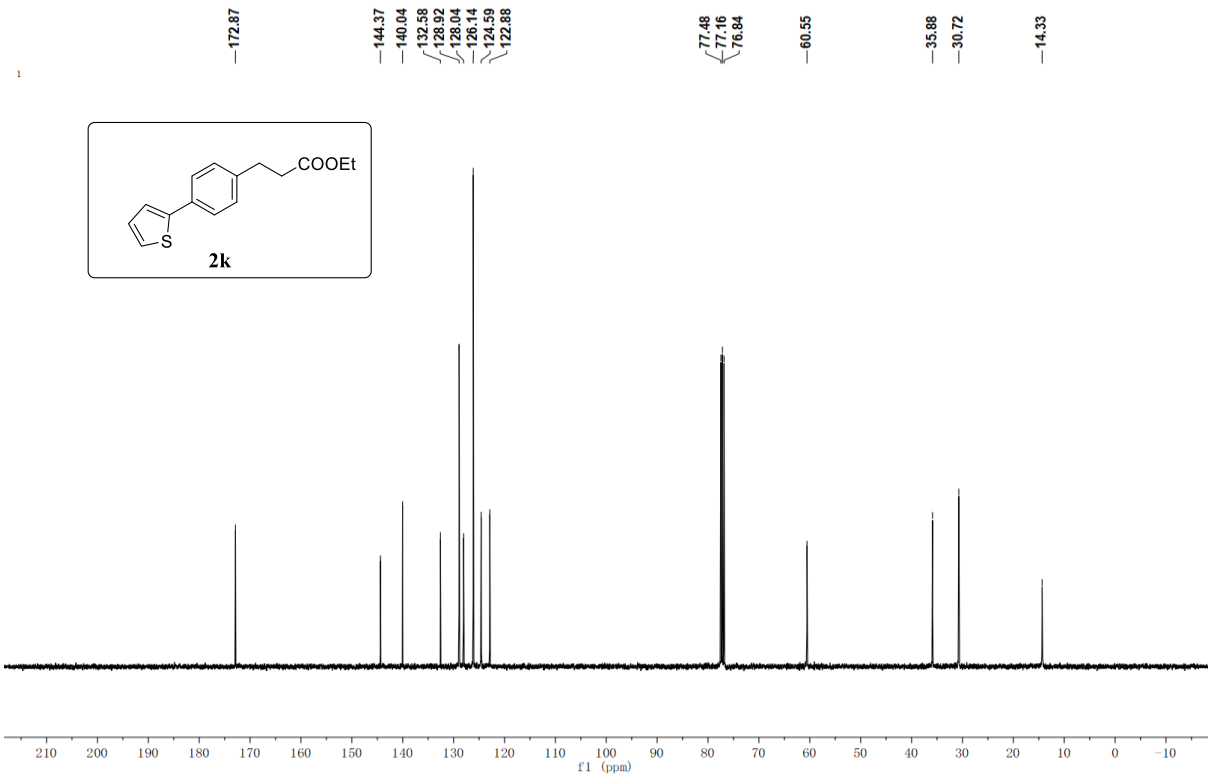

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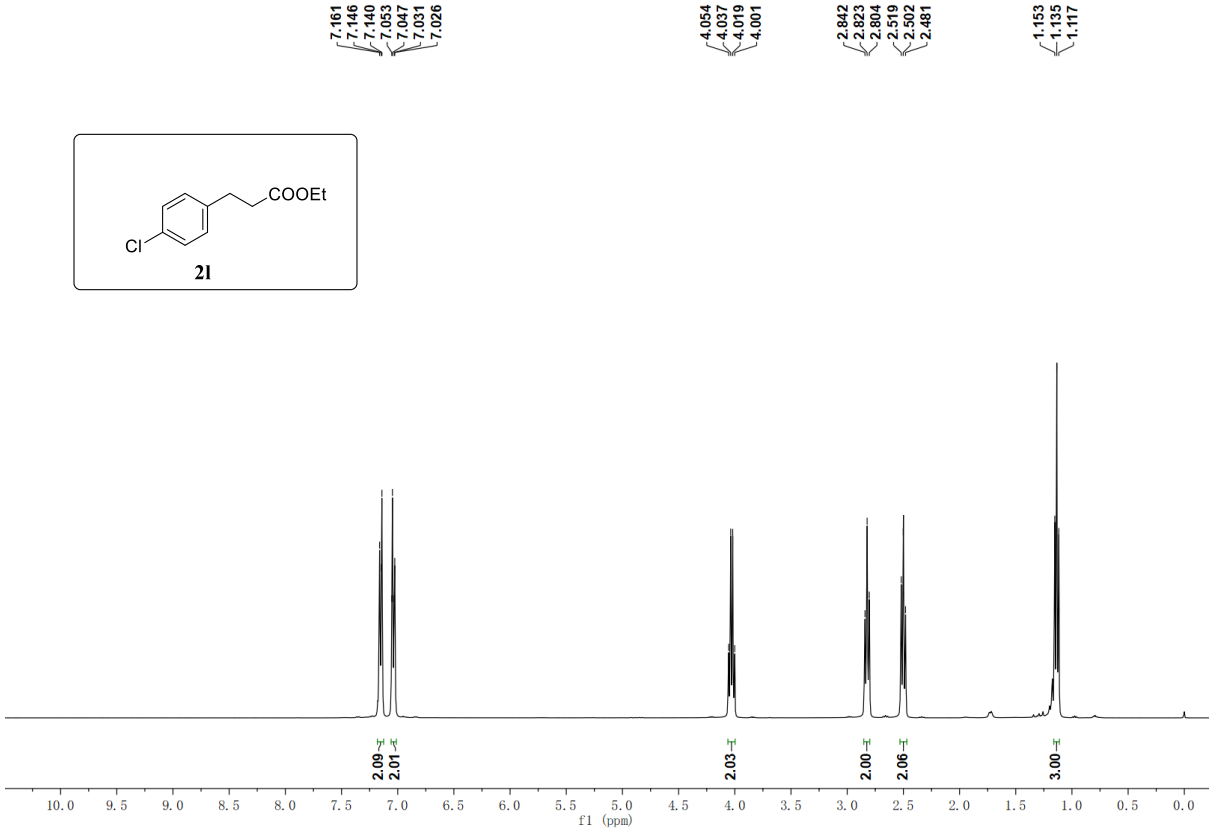

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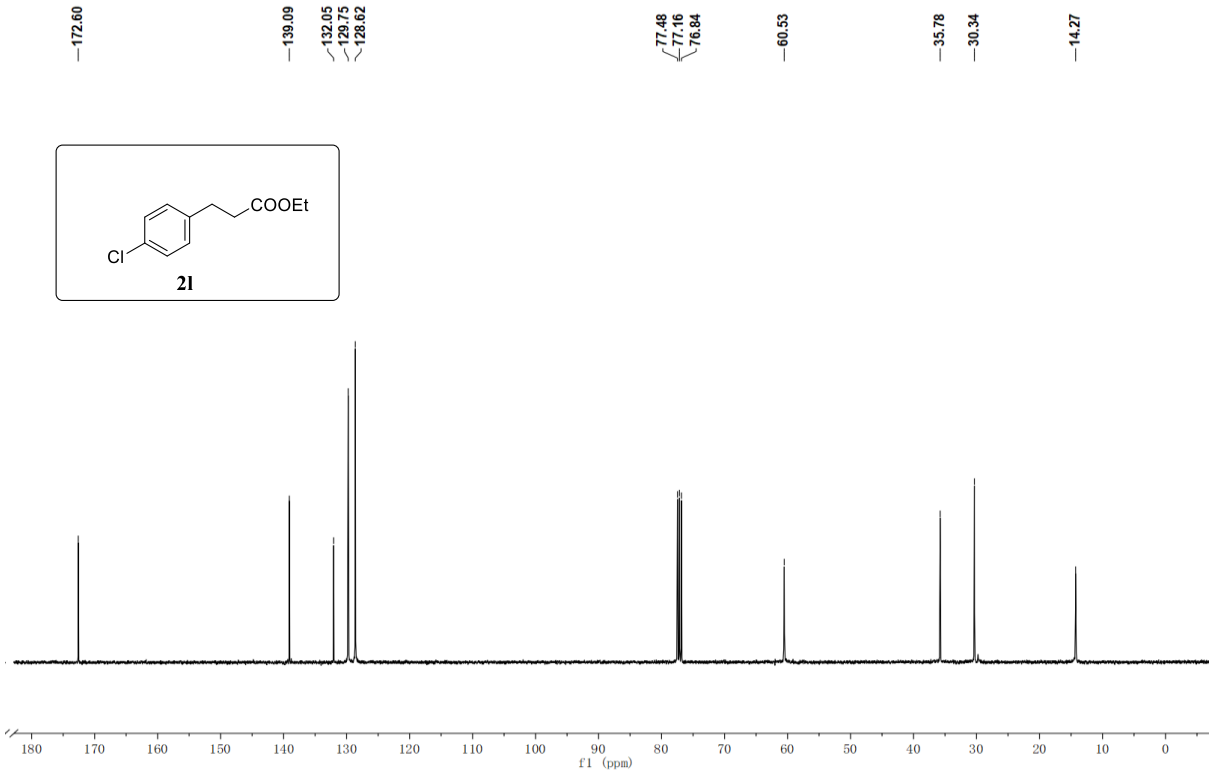

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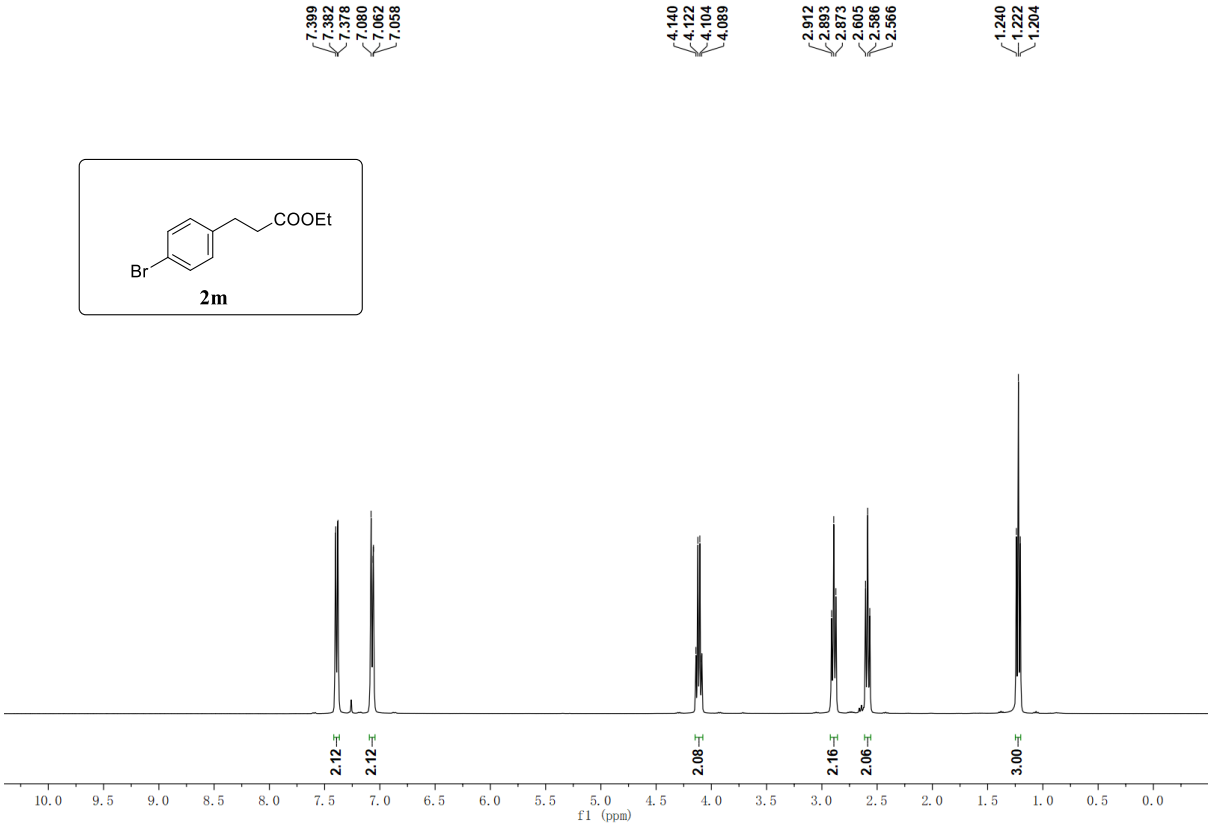

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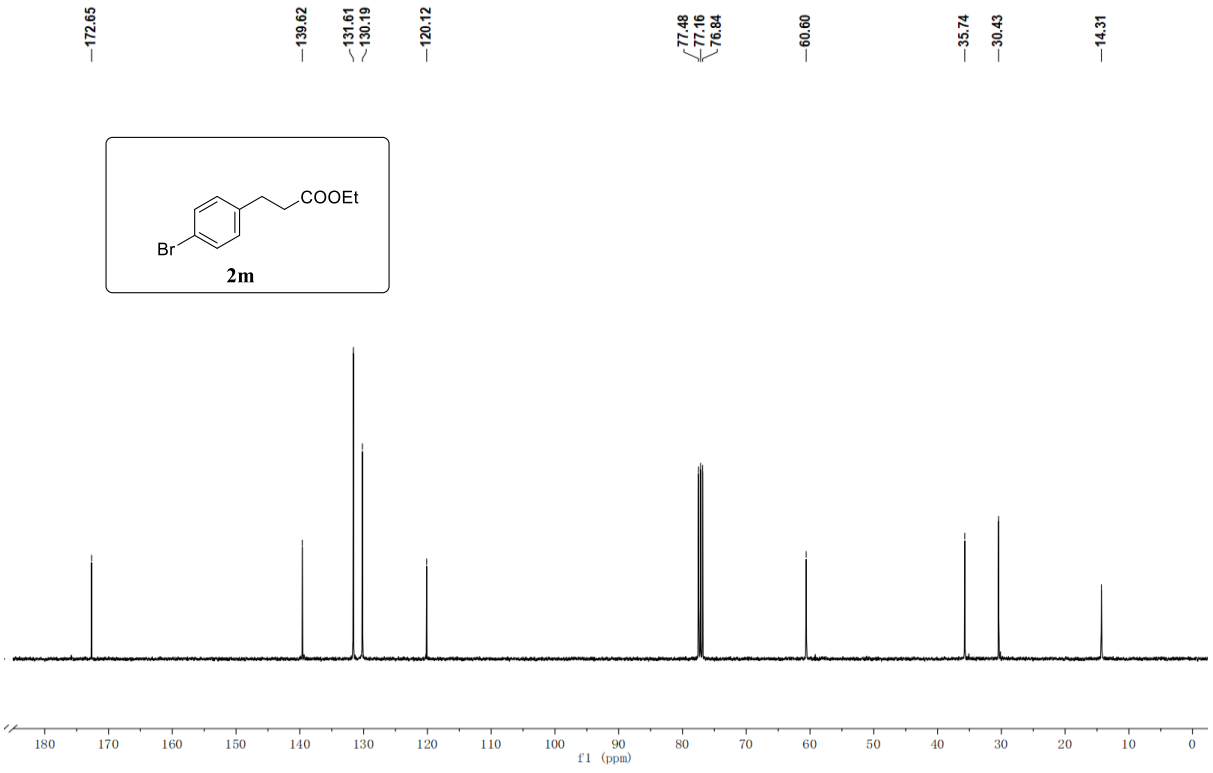

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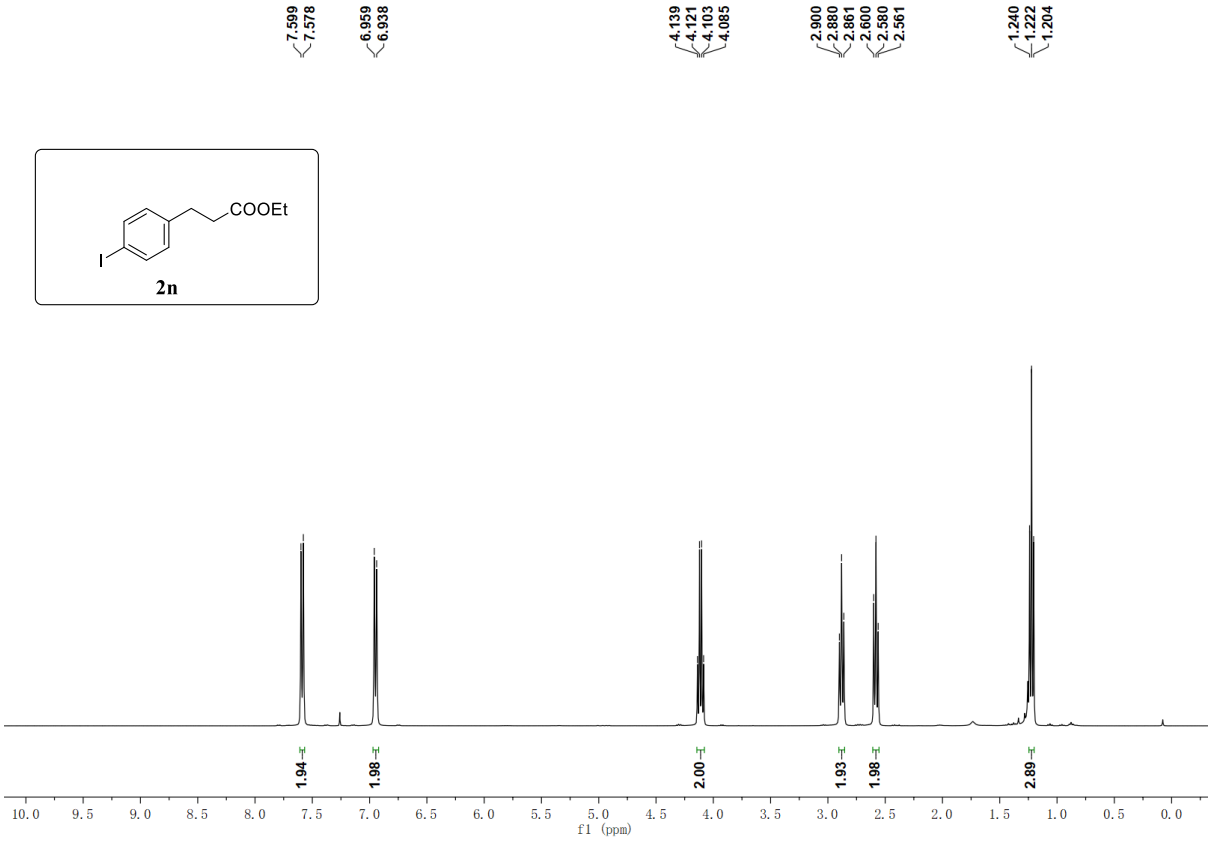
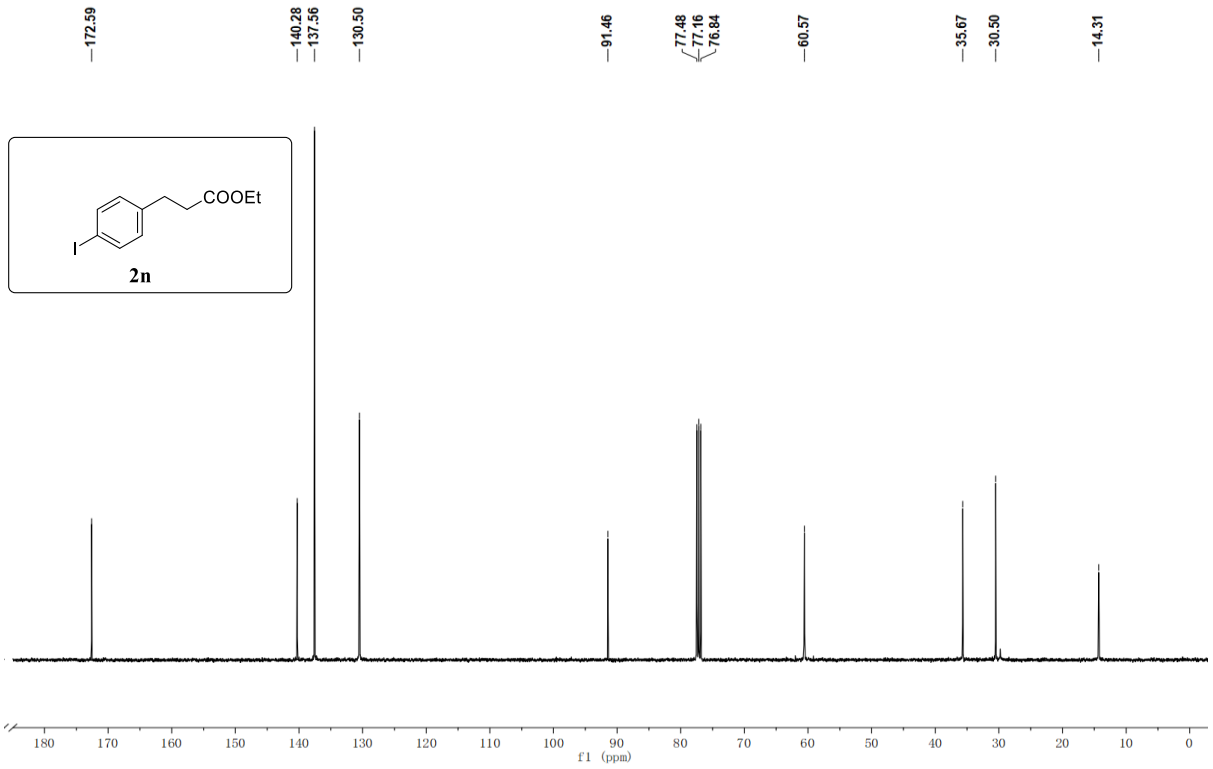
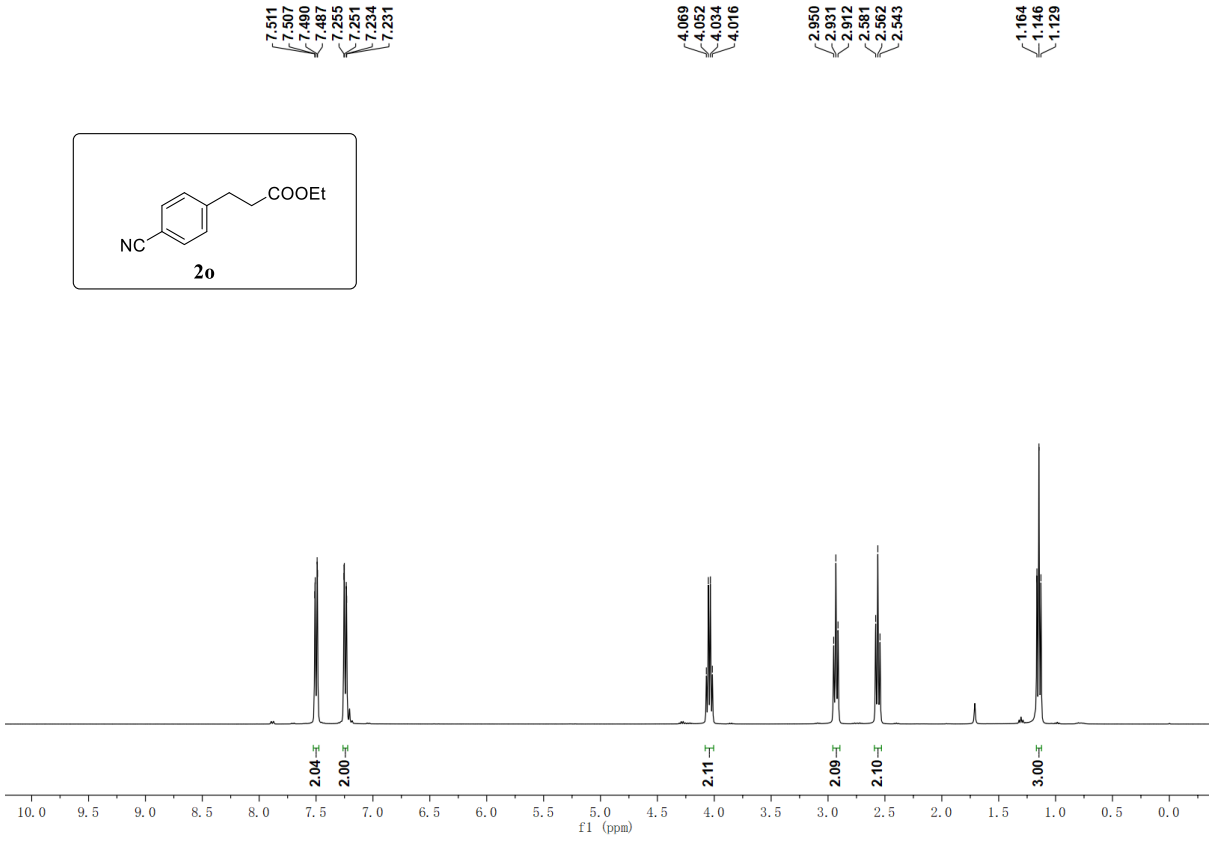


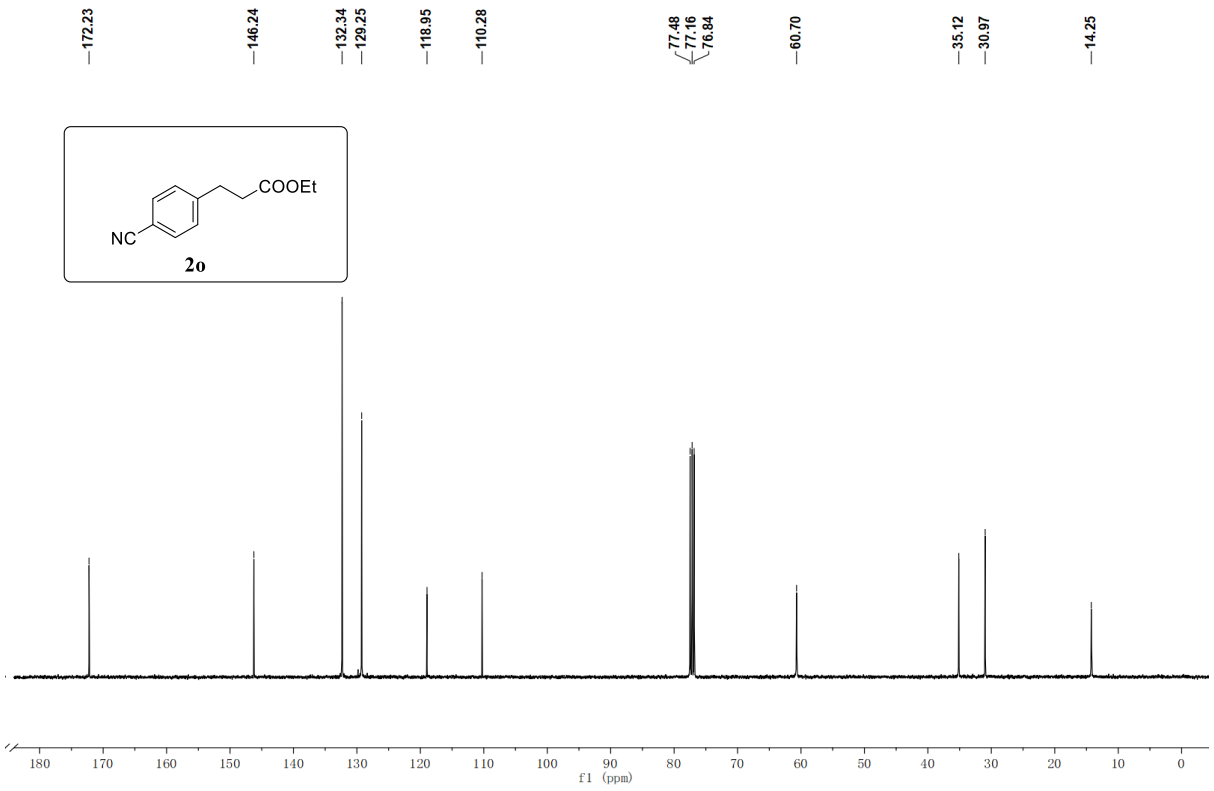
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2n



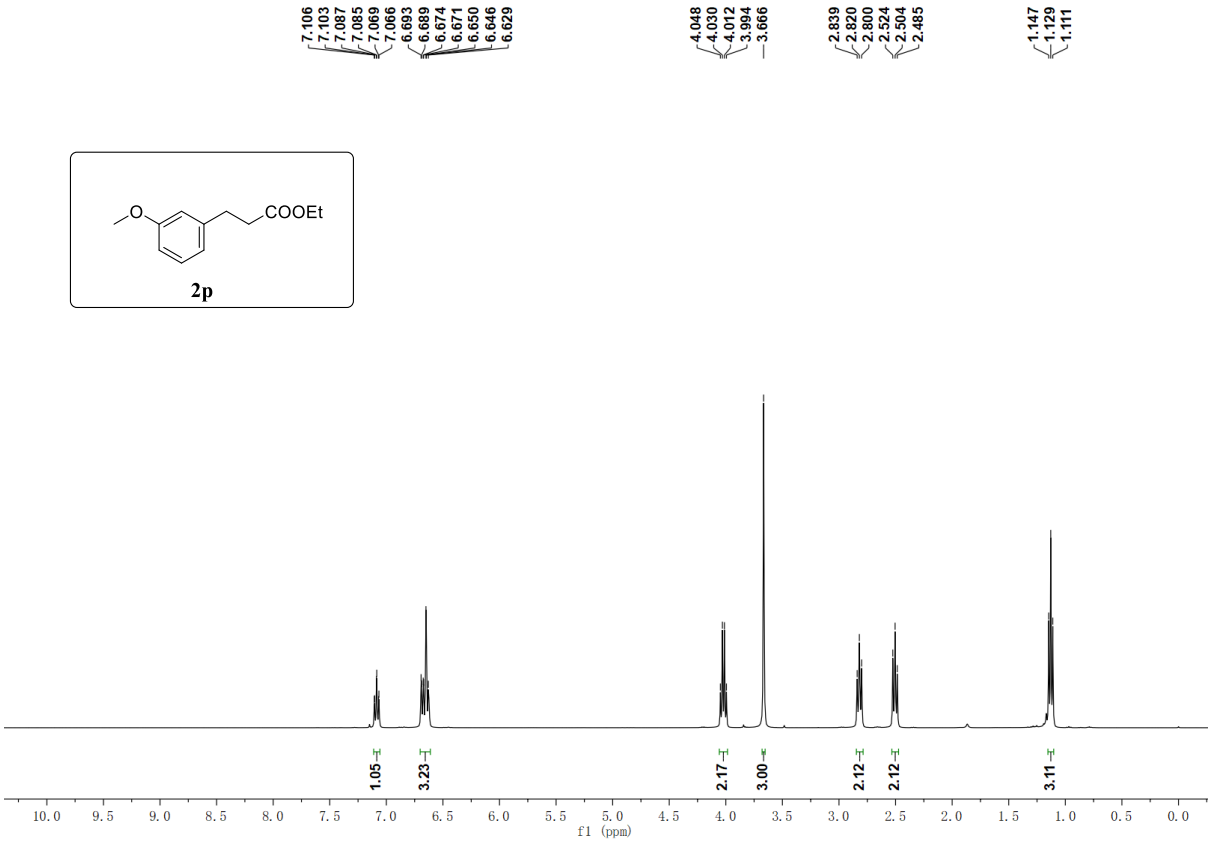
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2o



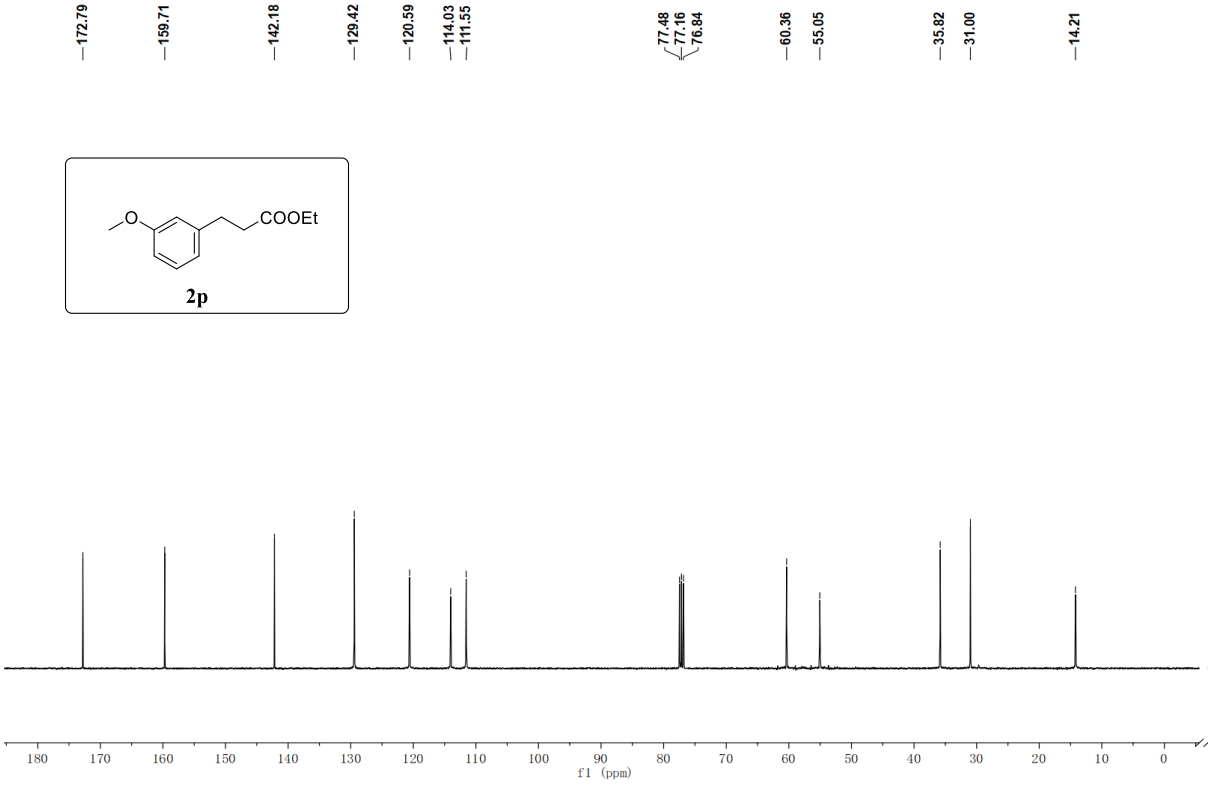
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2o



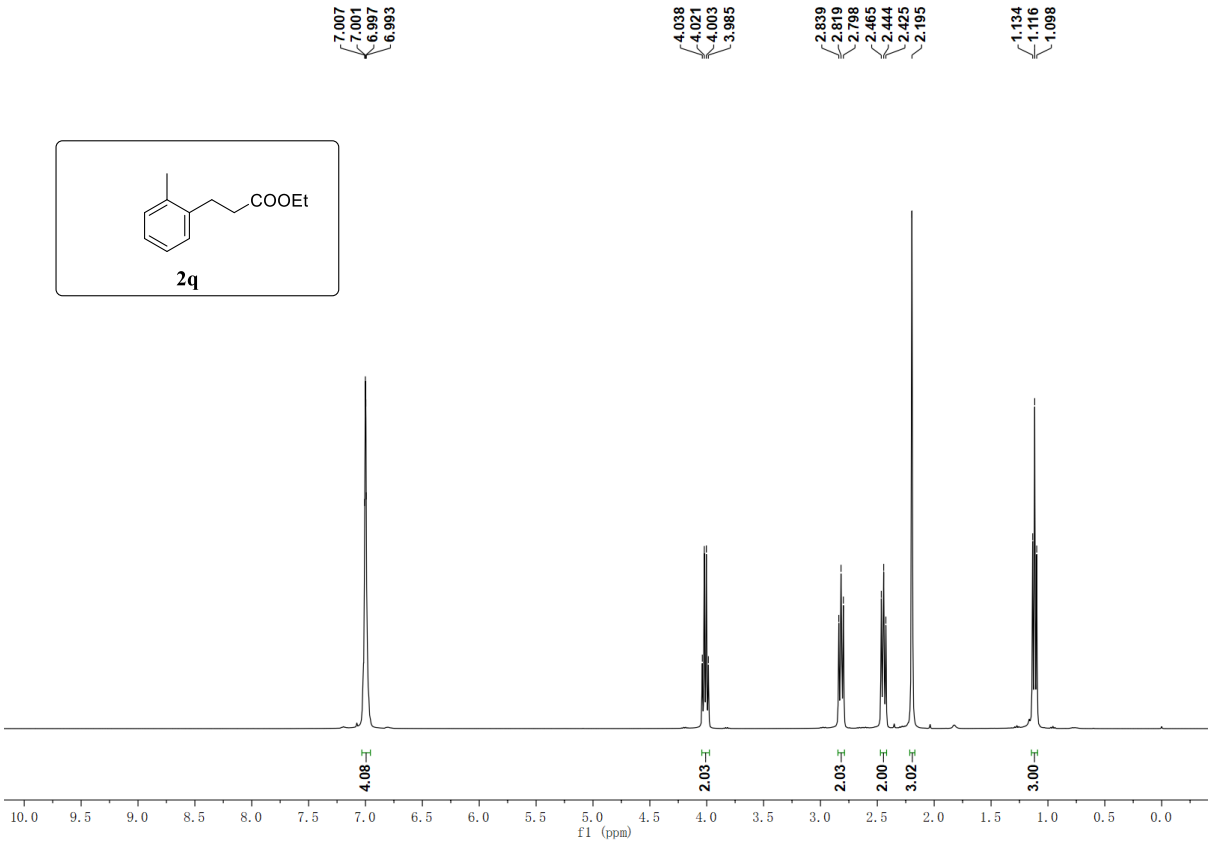
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2p



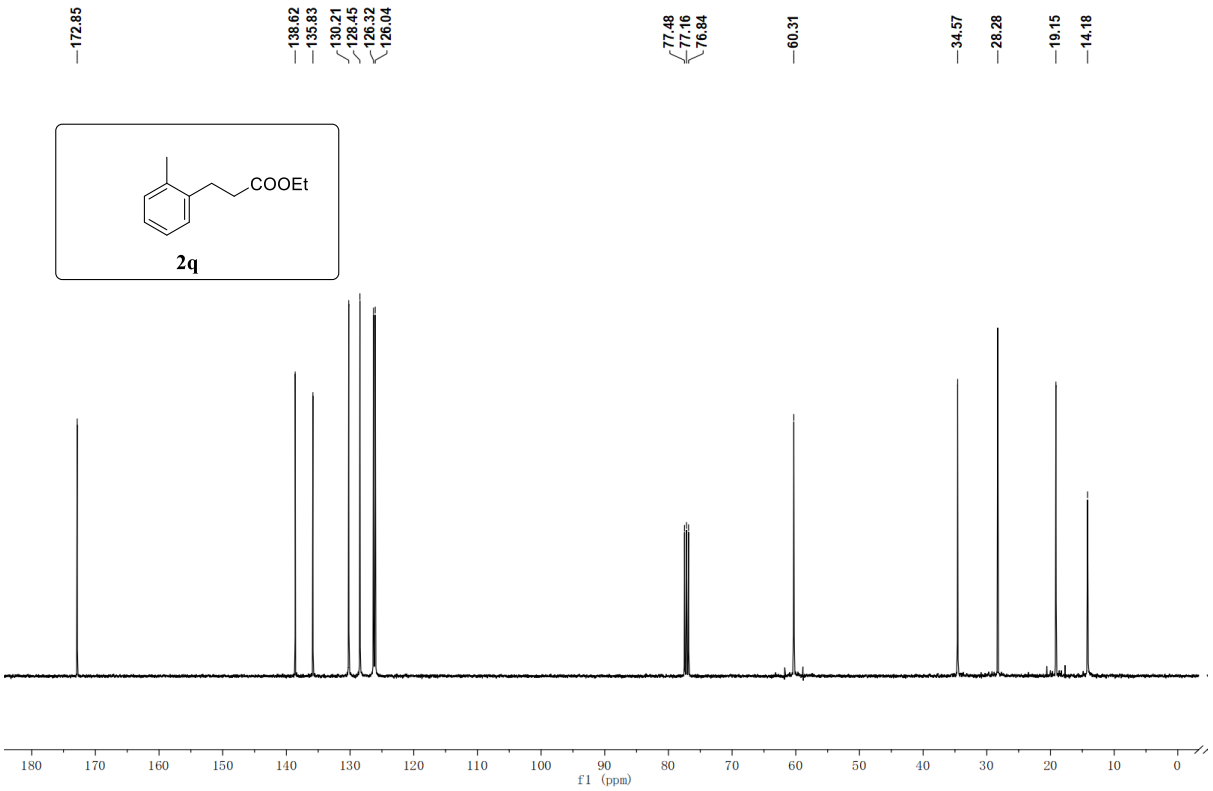
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2p



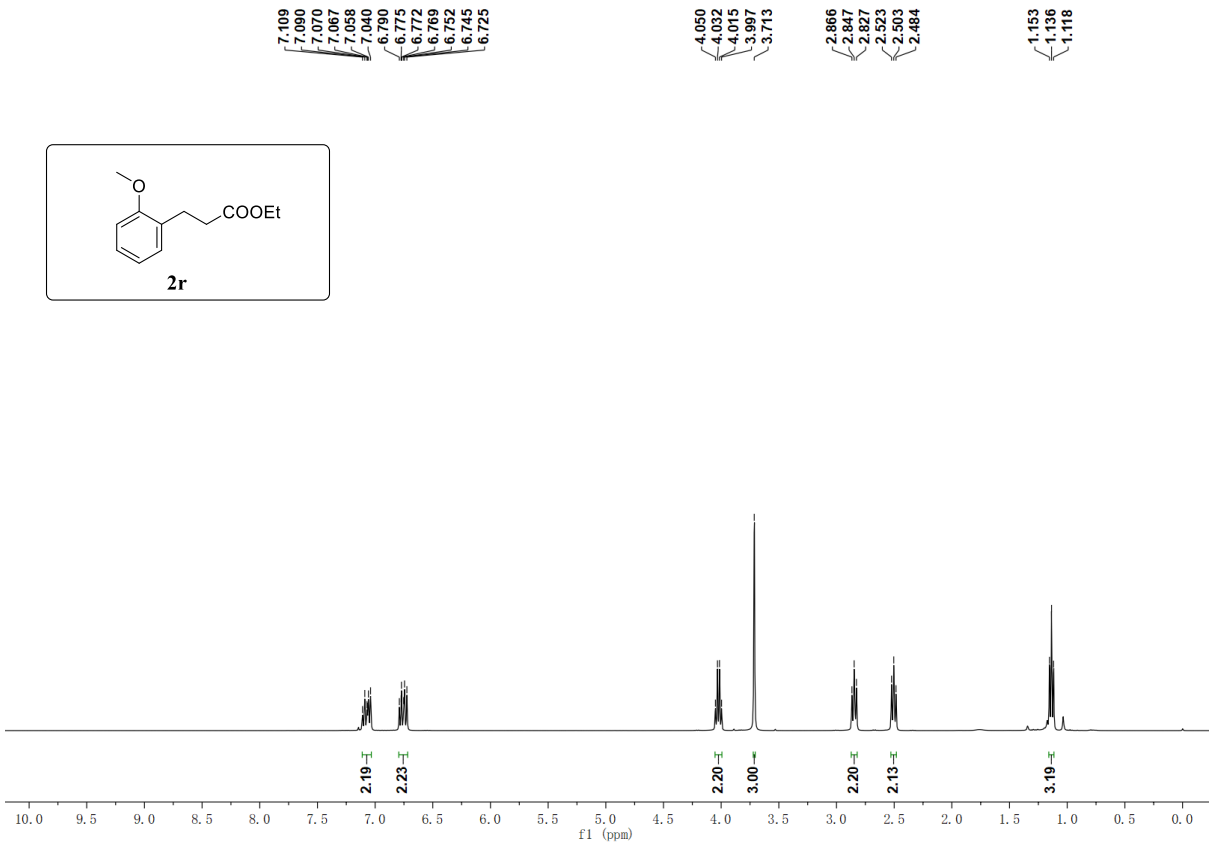
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2q



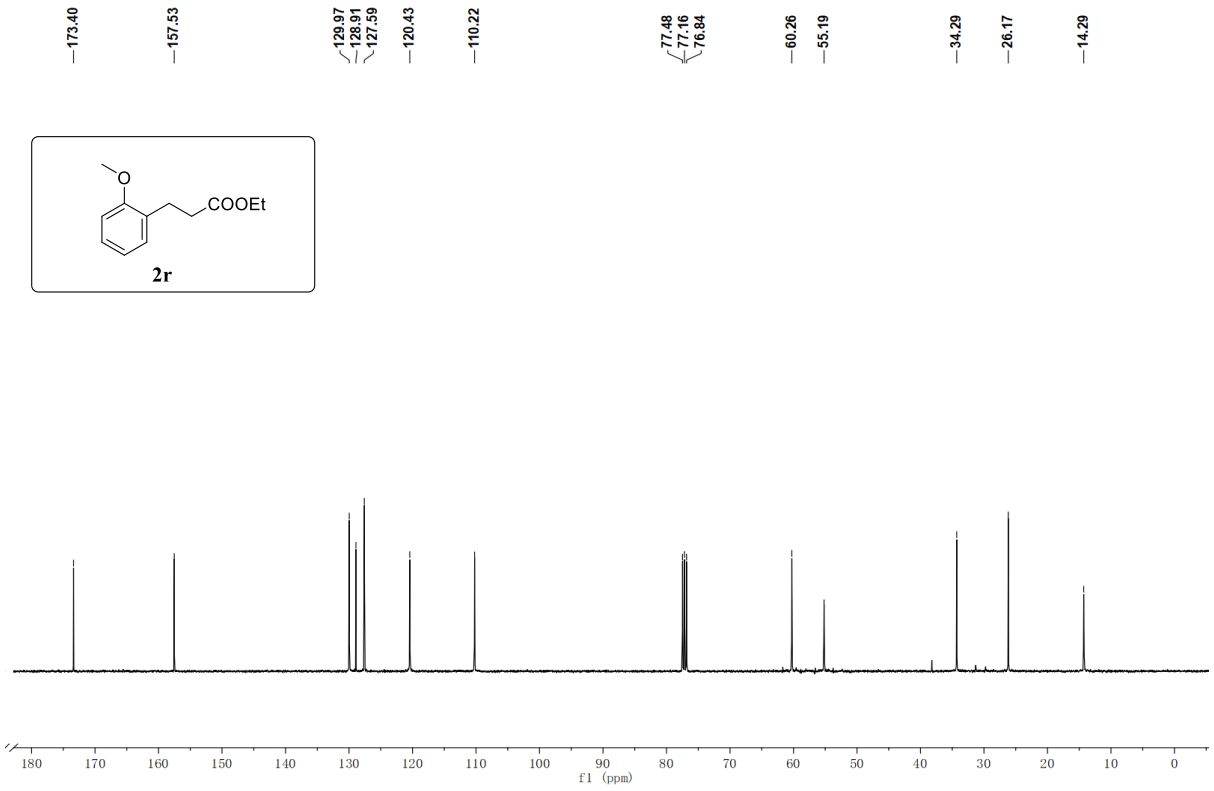
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2q



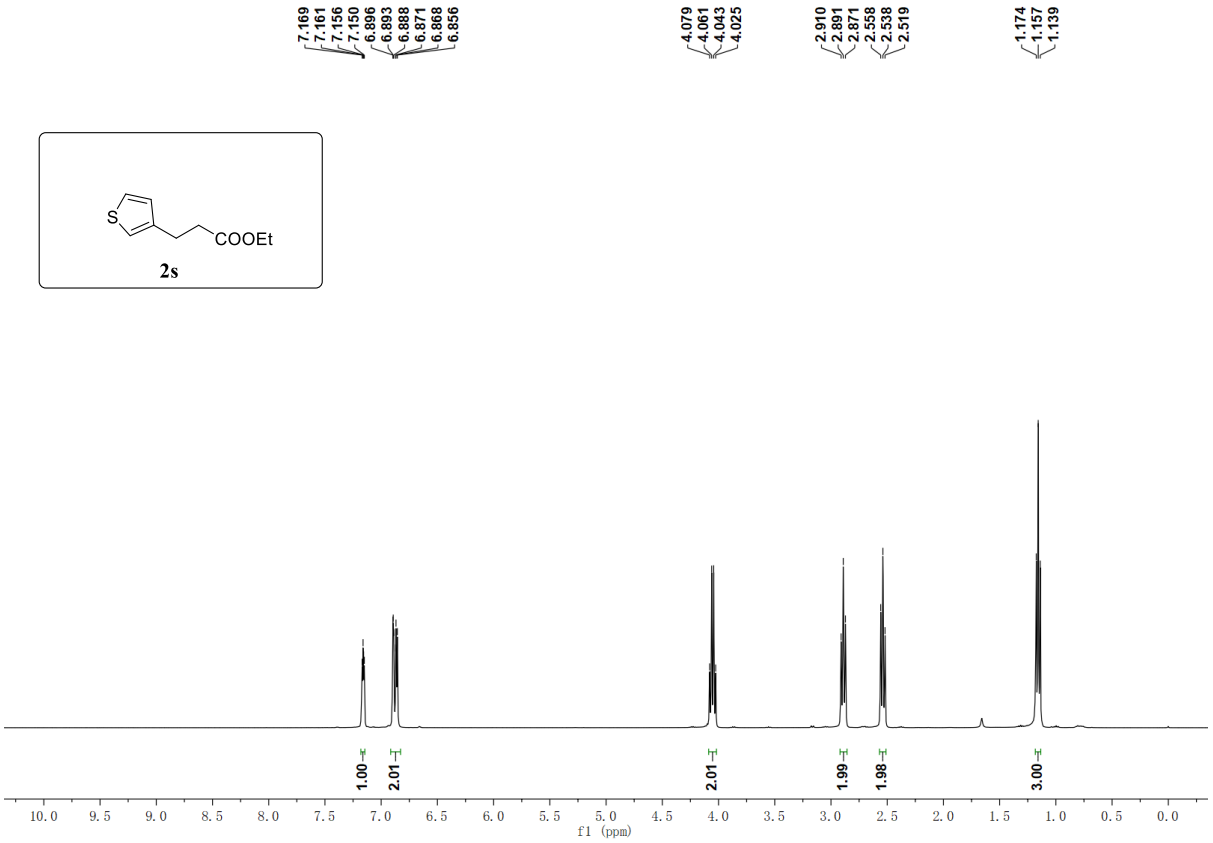
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2r



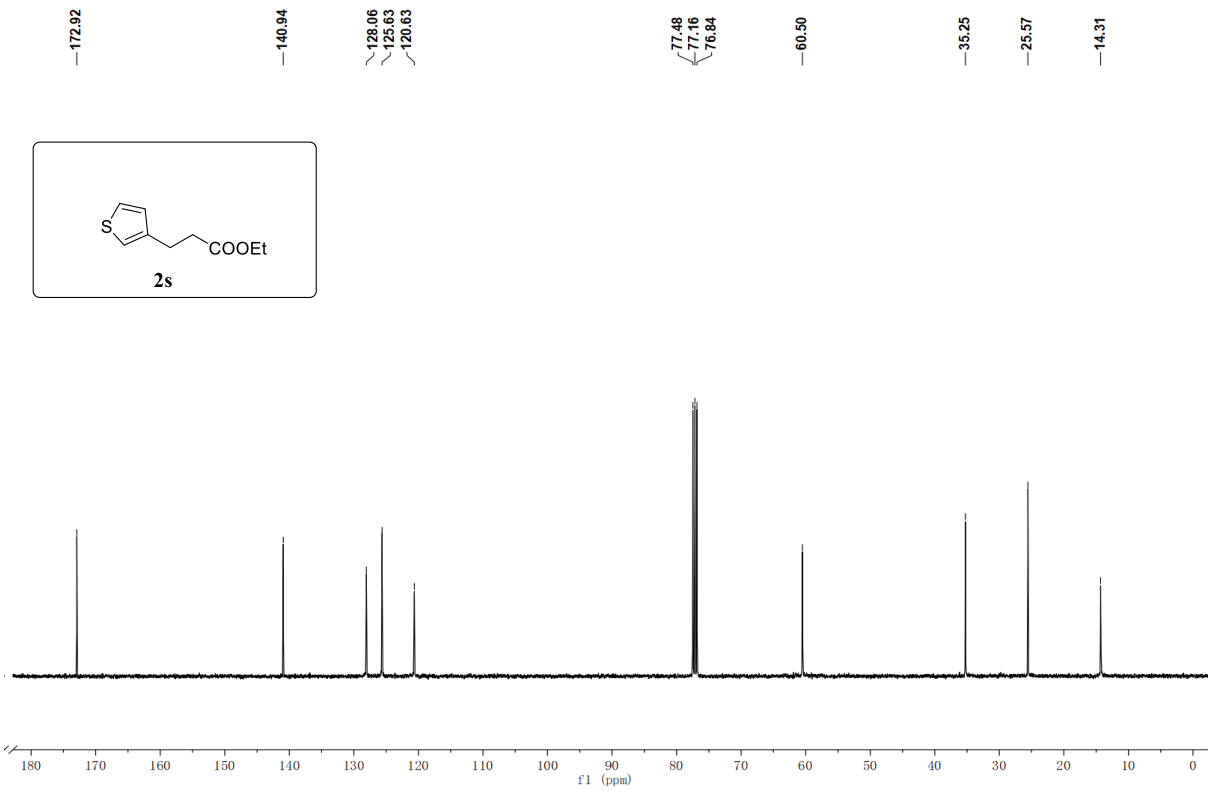
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2r



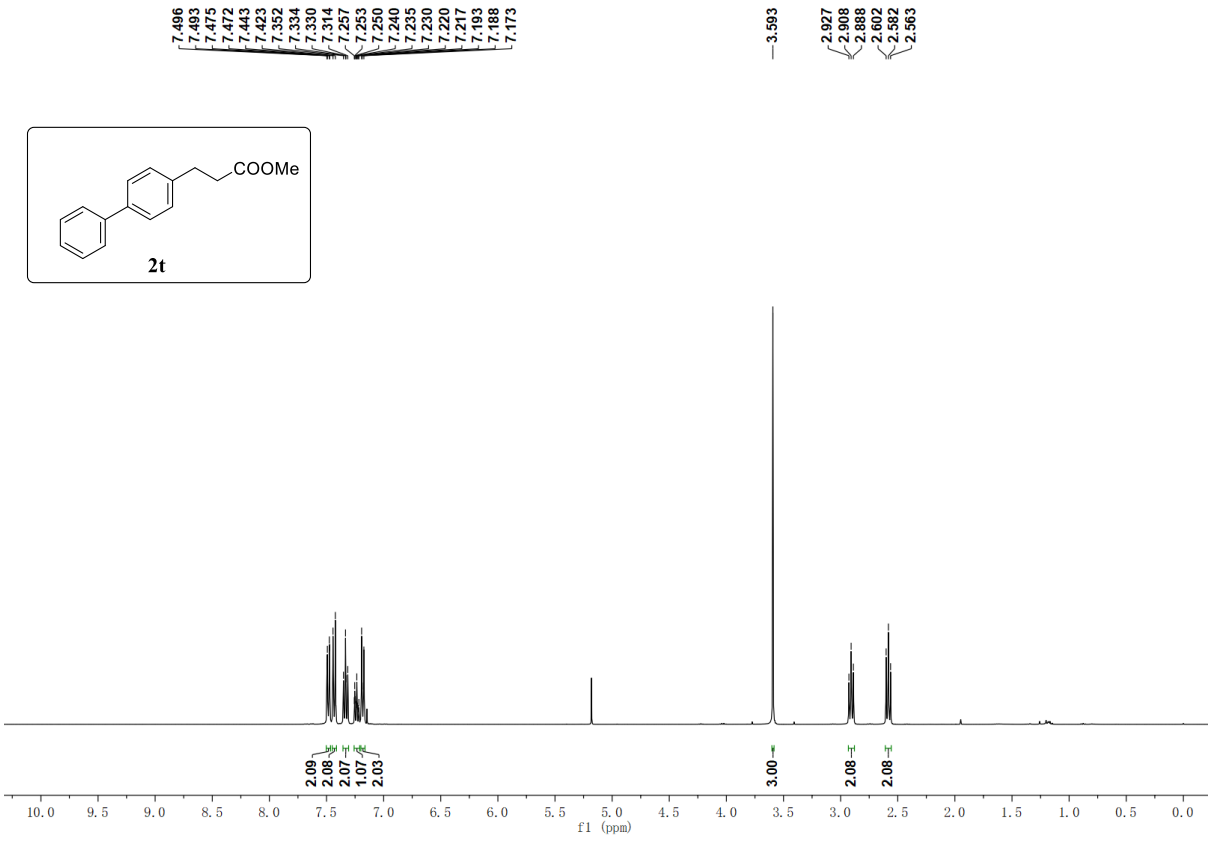
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2s



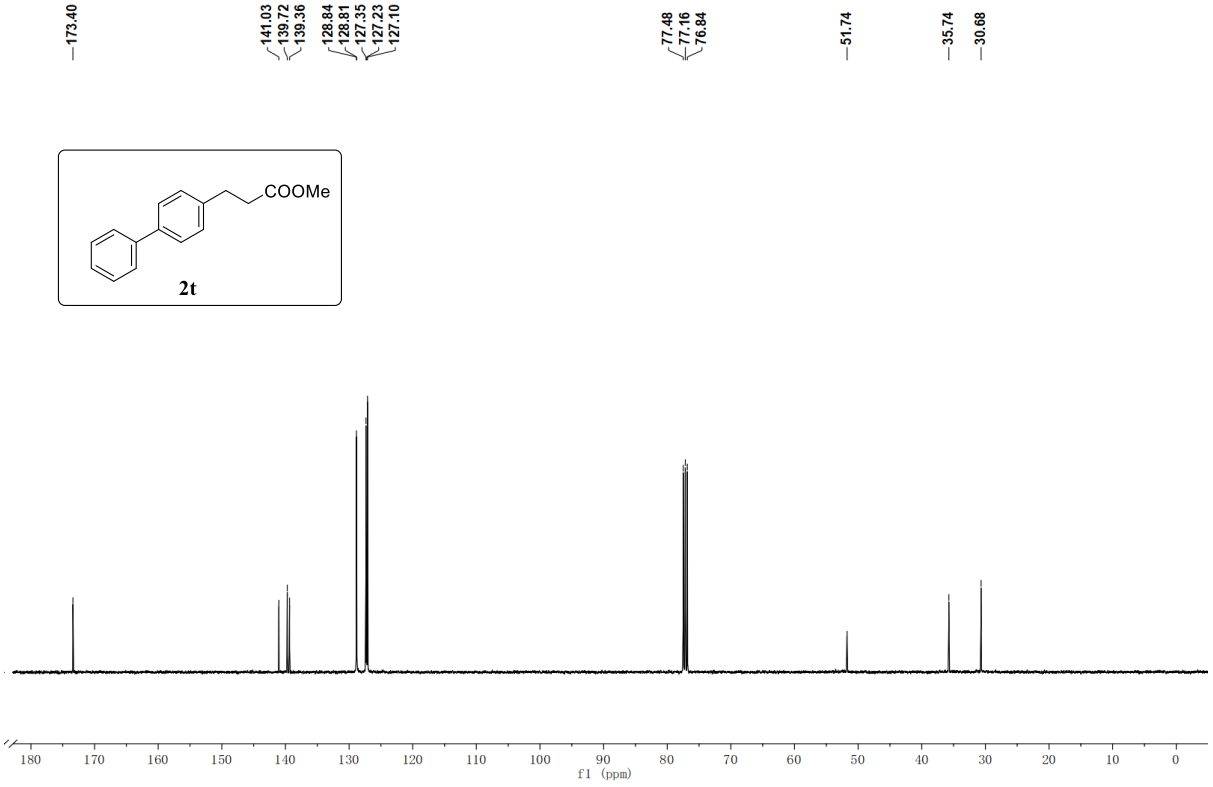
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2s



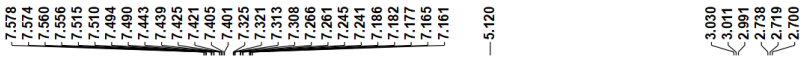
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2t

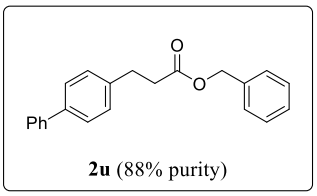


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2t

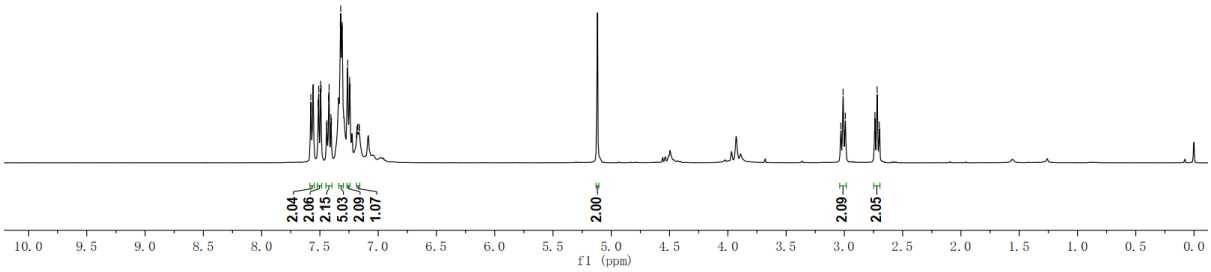


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2u

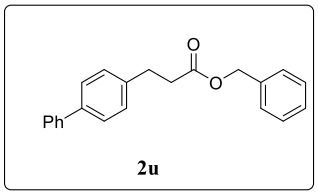




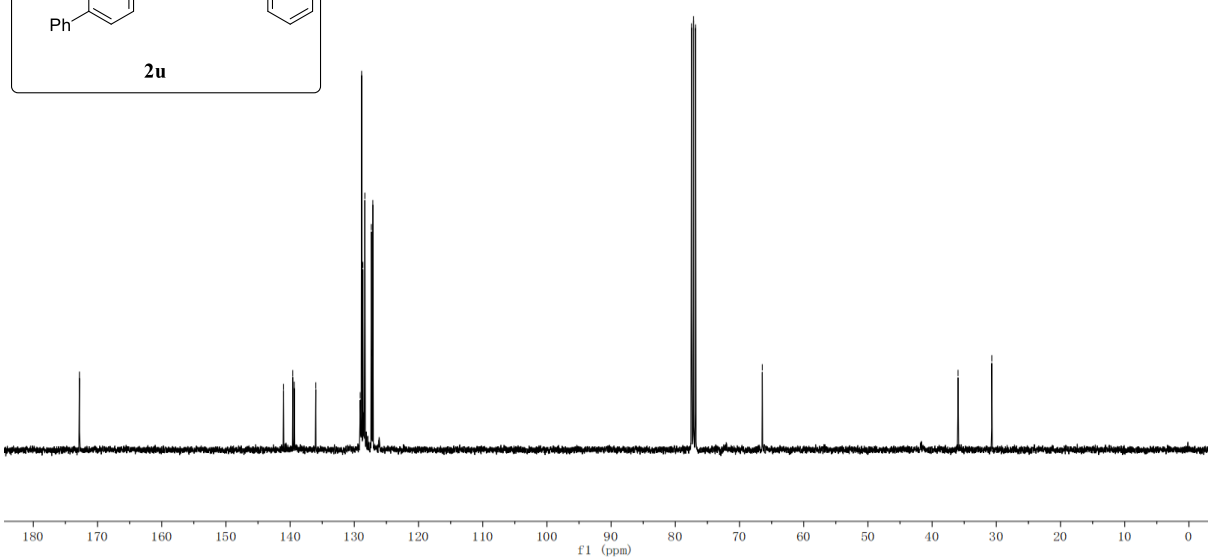
2u (88% purity)



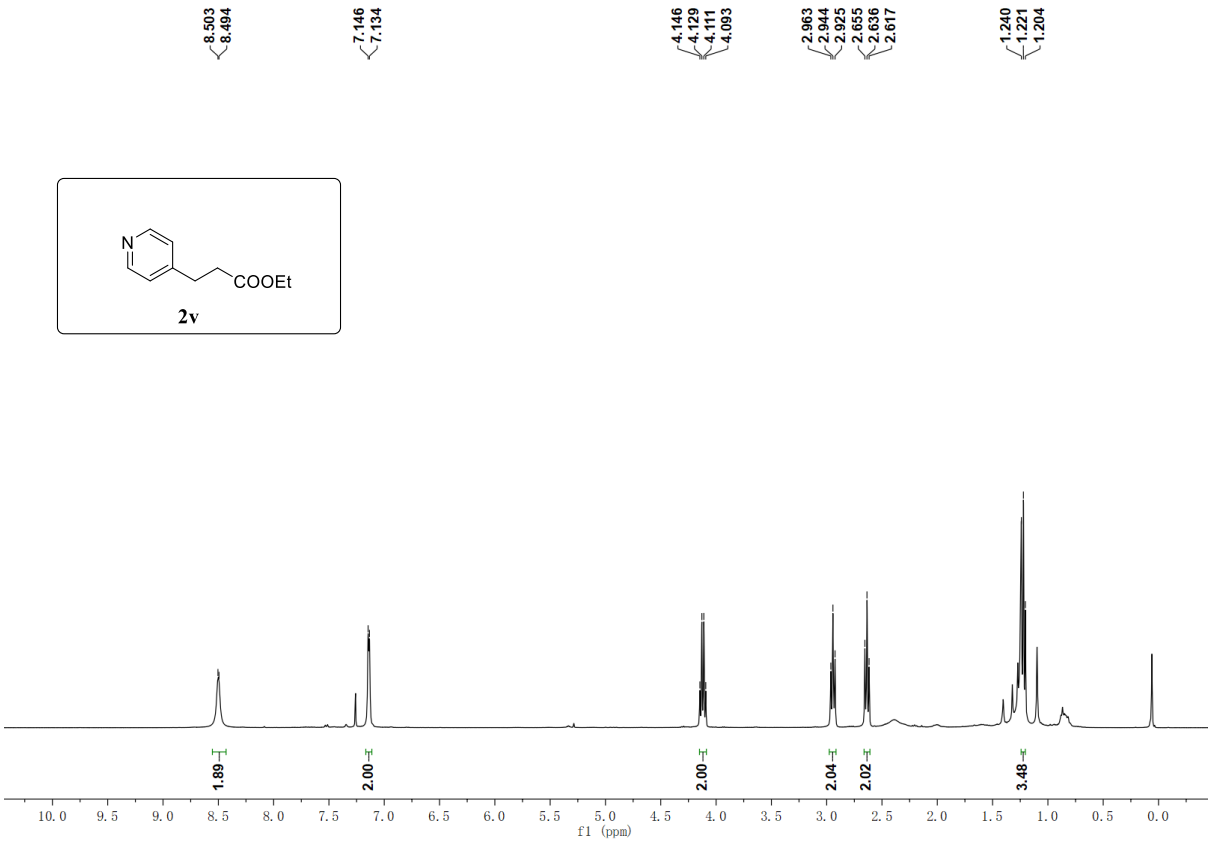
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2u



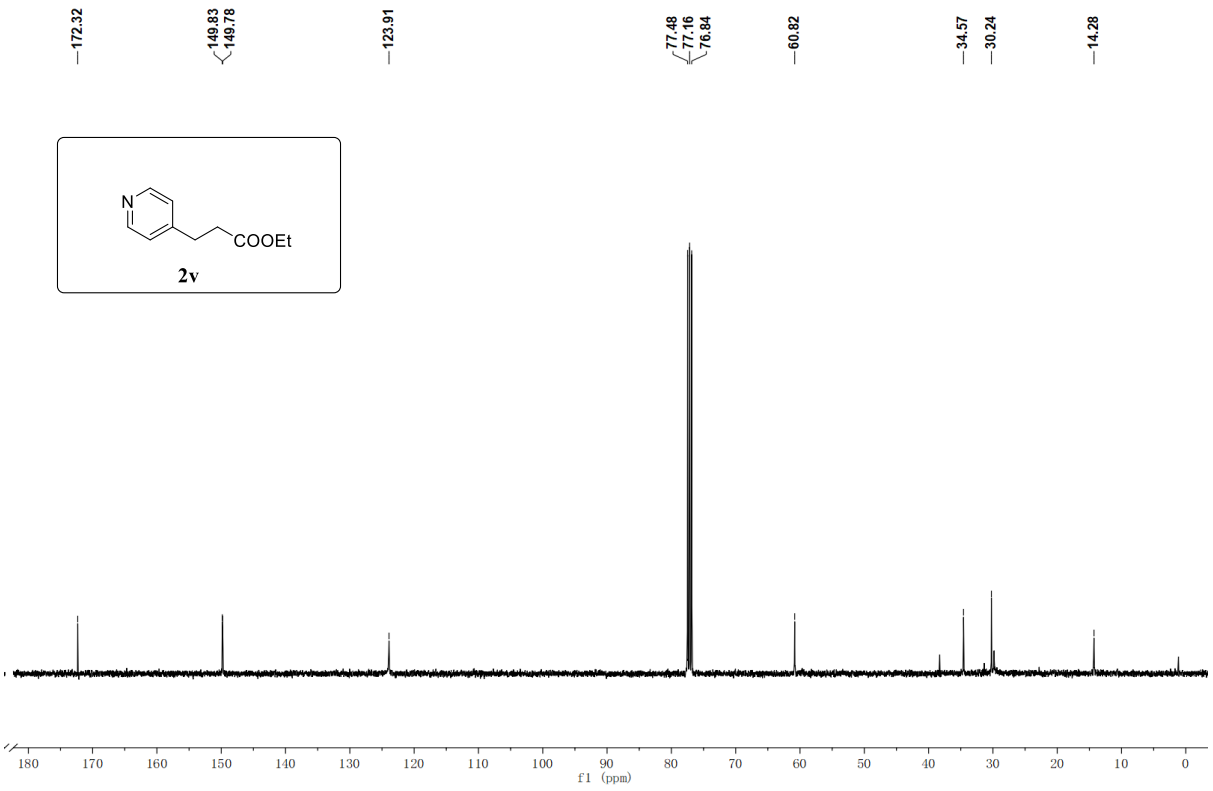
2u



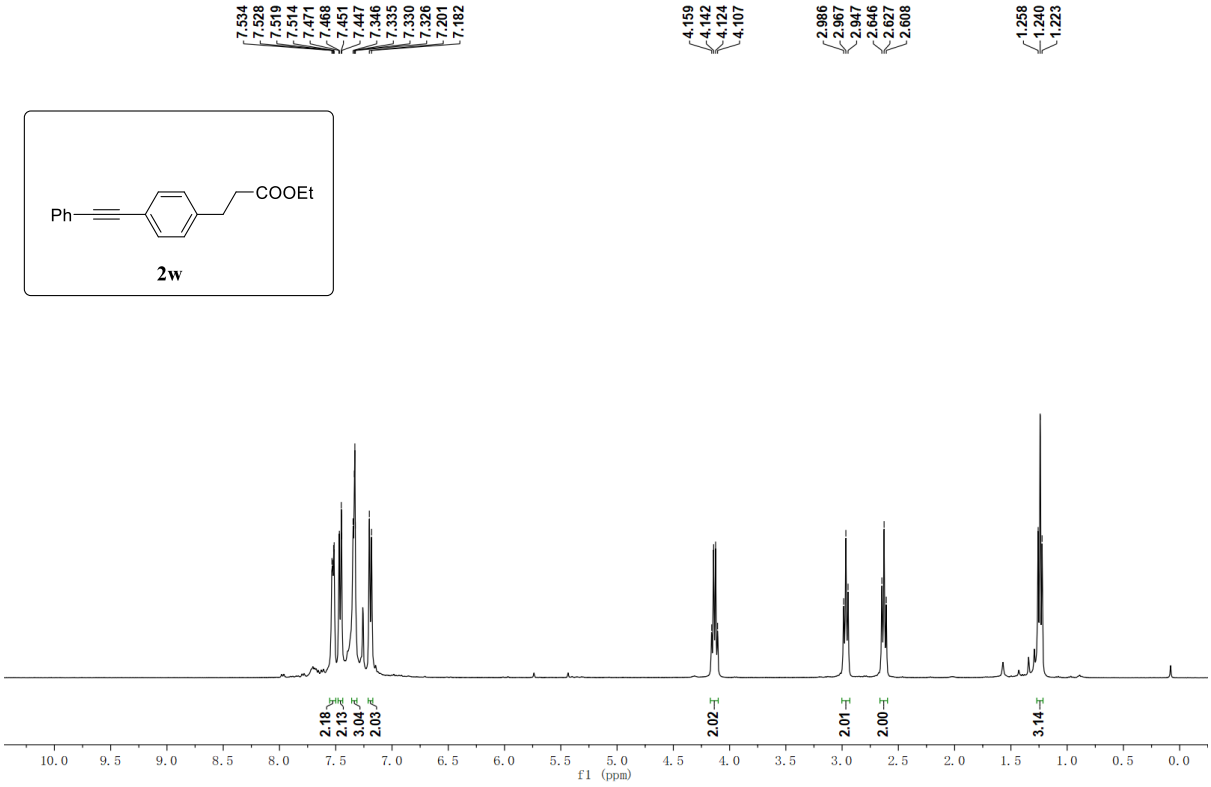
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2v



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2v



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2w



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 2w