Supporting Information

Synthesis of *β*-Amino Acid Derivatives via Photoredox-Catalyzed Radical Cross-Coupling of Anilines and Diazo Compounds

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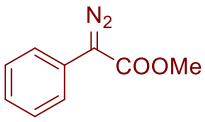
Table of Contents

1. General information

Commercial reagents were purchased from Aldrich Chemical, Alfa Aesar, TCI, Strem, Acros, Energy Chemical, J&K Chemical, Innochem and were used as received. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (376 MHz) were measured on a Bruker AVANCE III–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High Resolution Mass spectra were performed on Agilent 1260 Series (ESI Source). The blue LEDs were purchased from Kessil.

The diazoacetates (**1**)[1] and amines (**2**)[2] were prepared according to the literature procedure.

2. Numberings and structures of all compounds



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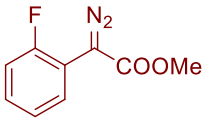

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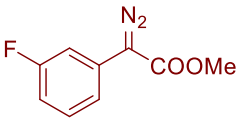

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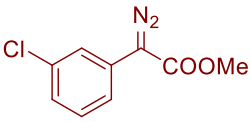

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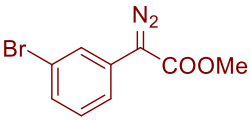

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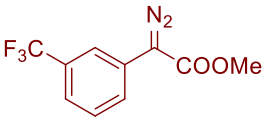

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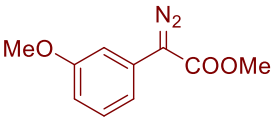

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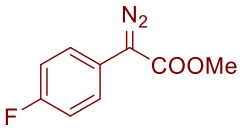

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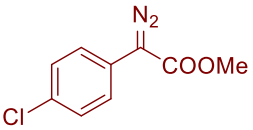

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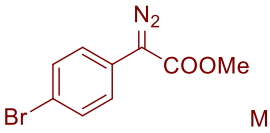

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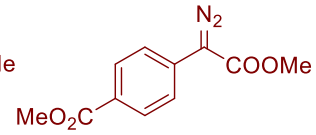

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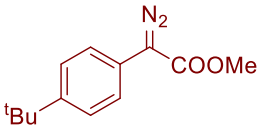

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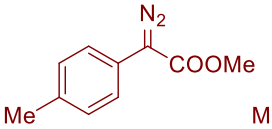

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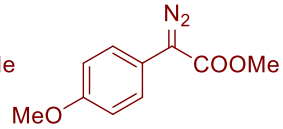

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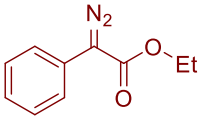

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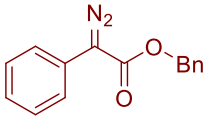

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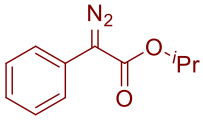

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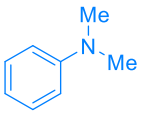

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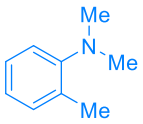

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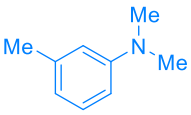

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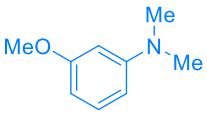

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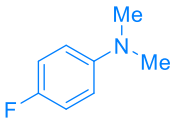

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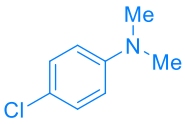

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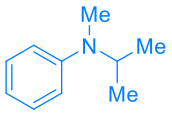

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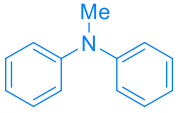

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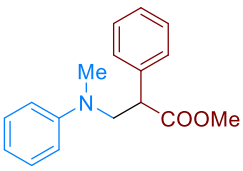

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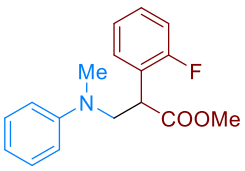

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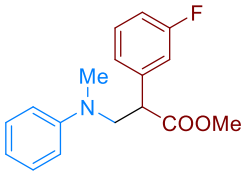

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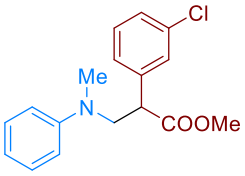

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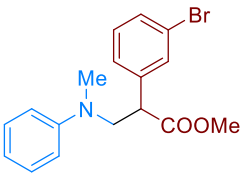

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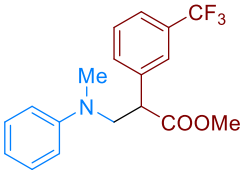

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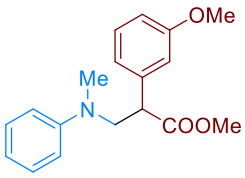

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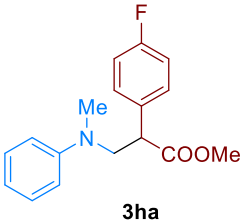

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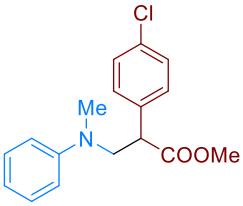

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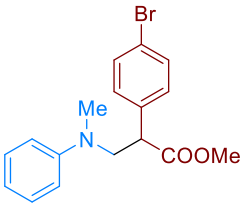

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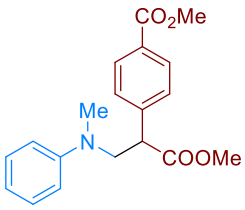

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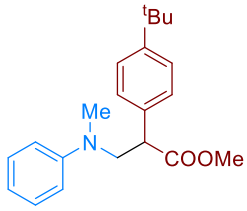

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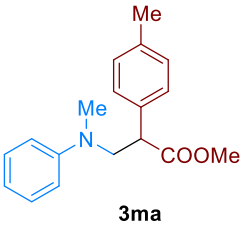

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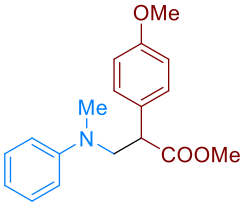

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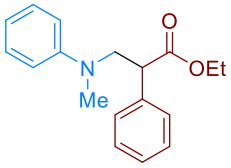

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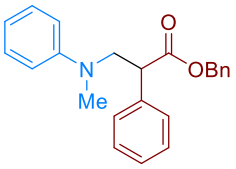

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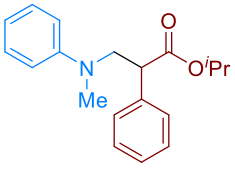

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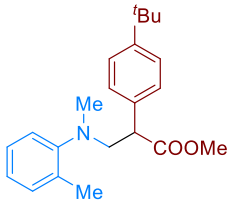

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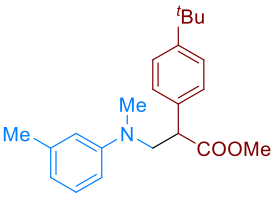

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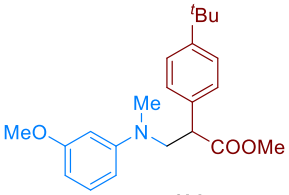

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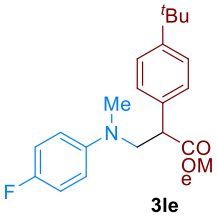

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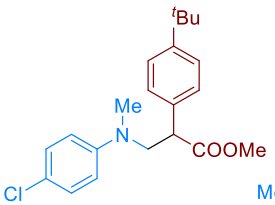

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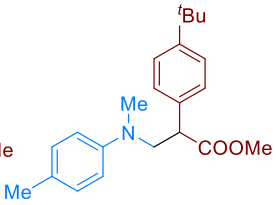

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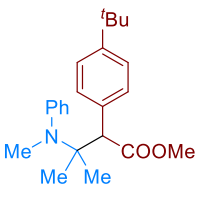

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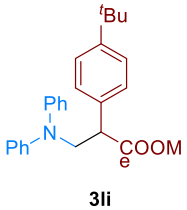

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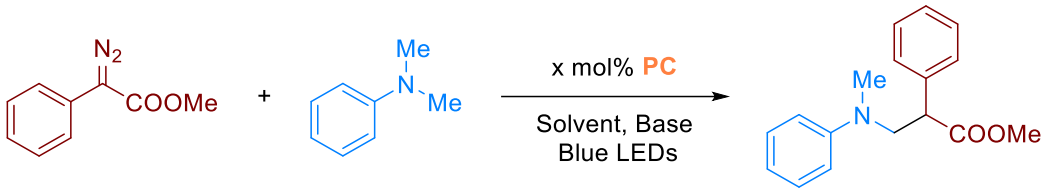
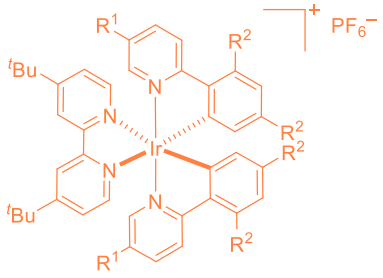
3. Condition optimizations for *β*-amino acid ester 3aa

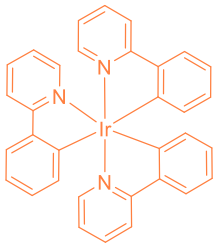
Table S1. Optimization of the conditions for 3aa[a]



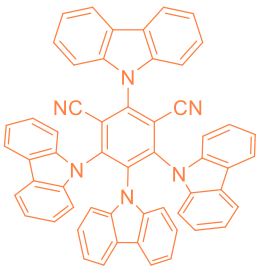
1a **2a** **3aa**



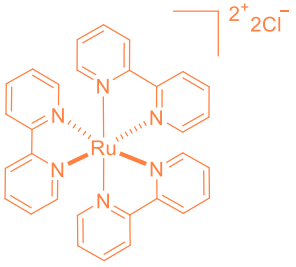
$R^1 = R^2$ =H, $Ir(ppy)_2(dtbbpy)PF_6$ (**I**)
$R^1 = CF_3$; R^2 = F, $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (**II**)



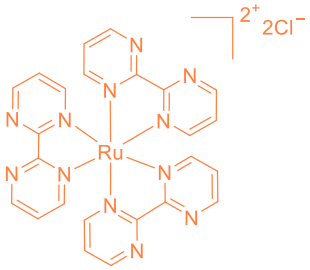
fac-$Ir(ppy)_3$ (**III**)



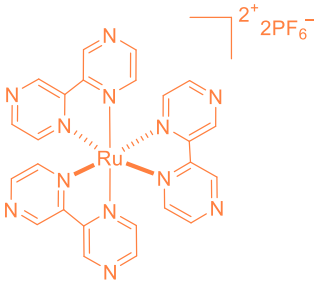
4CzIPN (**V**)



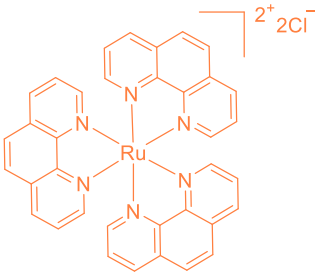
$Ru(bpy)_3Cl_2$ (**IV**)



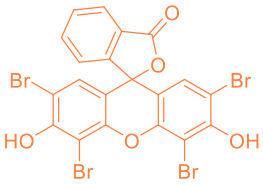
$Ru(bpm)_3Cl_2$ (**VI**)



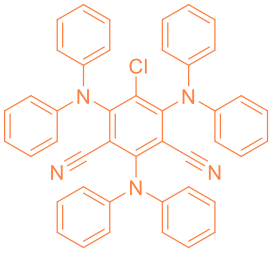
$Ru(bpz)_3[PF_6]_2$ (**VII**)



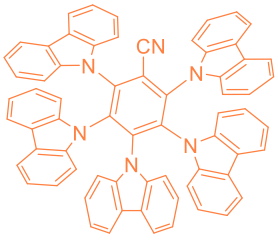
$Ru(phen)_3Cl_2$ (**VIII**)



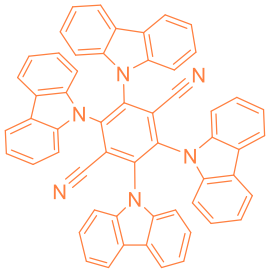
Eosin Y (**IX**)



3DPACIIPN (**X**)



5CzBN (**XI**)



4CzTPN (**XII**)

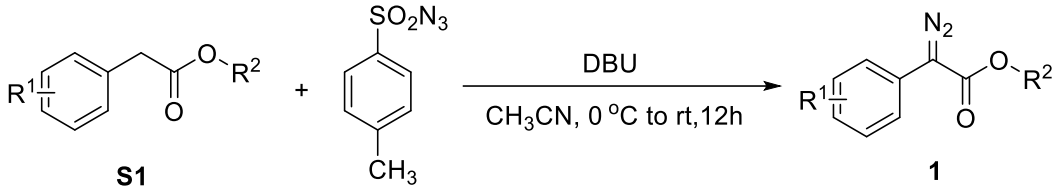
Entry	**PC**	Solvent (x mL)	**1a:2a**	Additives	Yield(%)[b]
1	**I**	CH_3CN (2.0 mL)	1.5:1	-	24
2	**II**	CH_3CN (2.0 mL)	1.5:1	-	11
3	**III**	CH_3CN (2.0 mL)	1.5:1	-	7
4	**IV**	CH_3CN (2.0 mL)	1.5:1	-	10
5	**V**	CH_3CN (2.0 mL)	1.5:1	-	15
6	**VI**	CH_3CN (2.0 mL)	1.5:1	-	9
7	**VII**	CH_3CN (2.0 mL)	1.5:1	-	6
8	**VIII**	CH_3CN (2.0 mL)	1.5:1	-	7
9	**IX**	CH_3CN (2.0 mL)	1.5:1	-	10
10	**X**	CH_3CN (2.0 mL)	1.5:1	-	10
11	**XI**	CH_3CN (2.0 mL)	1.5:1	-	14
12	**XII**	CH_3CN (2.0 mL)	1.5:1	-	12
13	**I**	DCM (2.0 mL)	1.5:1	-	trace
14	**I**	1,4-Dioxane (2.0 mL)	1.5:1	-	trace
15	**I**	EtOH (2.0 mL)	1.5:1	-	trace
16	**I**	EA (2.0 mL)	1.5:1	-	17
17	**I**	DMF (2.0 mL)	1.5:1	-	trace
18	**I**	DMSO (2.0 mL)	1.5:1	-	trace
19	**I**	CH_3CN (2.0 mL)	1.5:1	K_2CO_3	31
20	**I**	CH_3CN (2.0 mL)	1.5:1	$KHCO_3$	44
21	**I**	CH_3CN (2.0 mL)	1.5:1	K_2HPO_4	24
22	**I**	CH_3CN (2.0 mL)	1.5:1	KH_2PO_4	17
23	**I**	CH_3CN (2.0 mL)	1.5:1	Cs_2CO_3	4
24	**I**	CH_3CN (2.0 mL)	1.5:1	CsF	17
25	**I**	CH_3CN (2.0 mL)	1.5:1	K_3PO_4	7
26	**I**	CH_3CN (2.0 mL)	1:1.5	$KHCO_3$	26
27	**I**	CH_3CN (2.0 mL)	2.0:1	$KHCO_3$	47

28	**I**	CH_3CN (2.0 mL)	3.0:1	$KHCO_3$	56
29	**I**	CH_3CN (1.0 mL)	3.0:1	$KHCO_3$	70
30	-	CH_3CN (1.0 mL)	3.0:1	$KHCO_3$	N.R.
31[c]	**I**	CH_3CN (1.0 mL)	3.0:1	$KHCO_3$	N.R.
32	**I**	CH_3CN (1.0 mL)	3.0:1	AcOH	trace
33	**I**	CH_3CN (1.0 mL)	3.0:1	PhCOOH	trace
34	**I**	CH_3CN (1.0 mL)	3.0:1	TsOH	trace

[a]Unless indicated otherwise, the reaction was carried out in 0.2 mmol scale and catalyzed by **PC** (0.002 mmol, 1 mol %) in a solvent (x mL) with additive (0.30 mmol, 1.5 equiv) at 25 °C under the illumination of 45 W blue LEDs for 24 h. [b]Isolated yield. [c]No visible light irradiation.

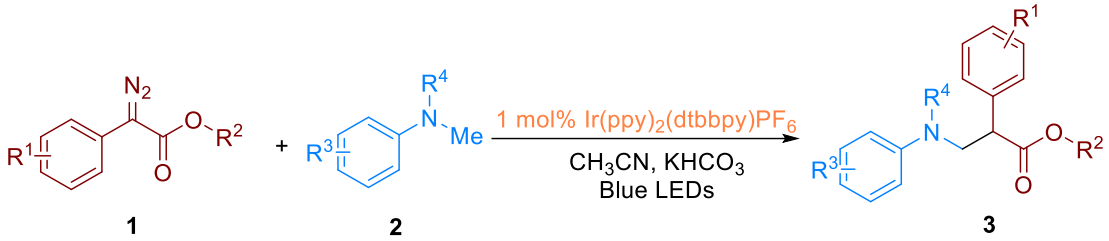
4. Synthetic procedures of substrates 1

General synthetic procedure for substrates 1: Substrates **1a-1s** are known compounds, and the synthetic procedure for these substrates was followed by the literature method.[1]



A solution of **S1** (5.00 mmol, 1.0 equiv) and *p*-toluenesulfonyl azide (6.00 mmol, 1.2 equiv.) in acetonitrile (20 mL) was treated with DBU (7.50 mmol, 1.5 equiv) at 0 °C and the mixture was stirred for overnight at room temperature. The resulting mixture was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate. Then, the organic layer was concentrated in vacuo to give a residue, which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford compound **1**.

5. Synthetic procedures and characterization data of products 3



In a nitrogen-filled glovebox, a 8 mL screw-cap test tube, equipped with a magnetic stir bar, then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (2.0 mg, 0.002 mmol, 1.0 mol%), $KHCO_3$ (30.1 mg, 0.15 mmol, 1.5 equiv), diazo compound **1** (0.6 mmol, 3.0 equiv), tertiary amine **2** (0.2 mmol, 1.0 equiv) and anhydrous CH_3CN (1.0 mL).The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LEDs at room temperature for 24 h. Next, the reaction mixture was transferred to a 50 mL round-bottom flask, diluted with 25 mL dichloromethane. The organic phase was concentrated under vacuum and purified through flash column chromatography (petroleum ether/ethyl acetate = 100/1) on silica gel to afford pure products **3**.

Reaction Setup

Medium-sized screw-cap test tubes (8 mL) were used for all 0.1 mmol scale reactions: Fisher13 x 100 mm tubes (Cat. No. 14-959-35C), Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No. 03378316)

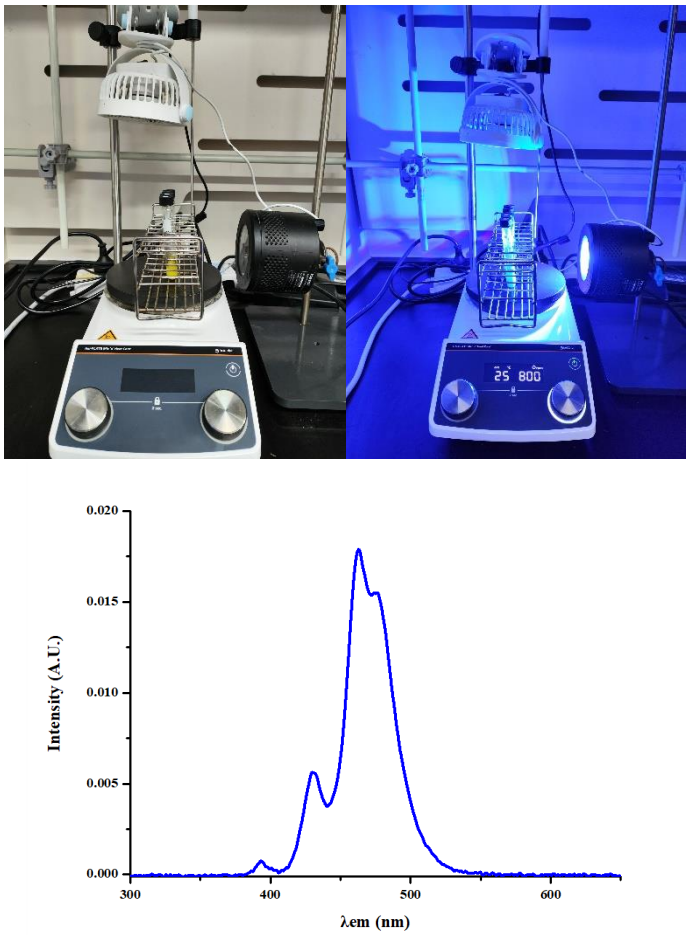
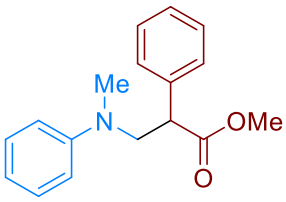


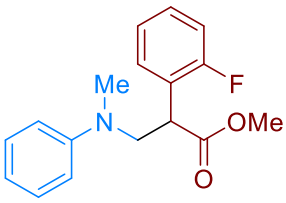
Figure S1. Photochemical reaction set up and spectrum of the blue LEDs.

methyl 3-(methyl(phenyl)amino)-2-phenylpropanoate (3aa)[3]:



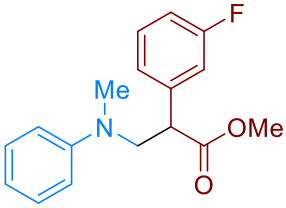
3aa was obtained as a colorless sticky oil (37.7 mg, 70%) from diazo compound **1a** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 7H), 6.73 – 6.65 (m, 3H), 4.08 (dd, *J* = 14.4, 8.6 Hz, 1H), 3.99 (dd, *J* = 8.7, 5.3 Hz, 1H), 3.61 (s, 3H), 3.57 (dd, *J* = 14.4, 5.3 Hz, 1H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 148.4, 137.1, 129.3, 128.9, 128.1, 127.7, 116.6, 112.2, 56.7, 52.2, 49.6, 39.3; ESI FTMS exact mass calcd for $(C_{17}H_{19}NO_2+H)^+$ requires m/z 270.1489, found m/z 270.1490.

methyl 2-(2-fluorophenyl)-3-(methyl(phenyl)amino)propanoate (3ba):



3ba was obtained as a colorless sticky oil (29.3 mg, 51%) from diazo compound **1b** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.22 (m, 2H), 7.14 – 7.05 (m, 2H), 6.76 – 6.69 (m, 3H), 4.36 (dd, *J* = 8.4, 5.9 Hz, 1H), 4.10 (dd, *J* = 14.8, 8.4 Hz, 1H), 3.66 (s, 3H), 3.62 (dd, *J* = 14.9, 6.0 Hz, 1H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 172.9, 160.6 (d, *J* = 244.7 Hz), 148.4, 129.56 (d, *J* = 3.8 Hz), 129.6, 129.3 (d, *J* = 8.1 Hz) 129.2, 124.5 (d, *J* = 3.6 Hz), 124.3 (d, *J* = 14.9 Hz), 116.7, 115.7 (d, *J* = 22.1 Hz), 112.2, 55.6, 52.3, 42.7, 39.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.50; ESI FTMS exact mass calcd for $(C_{17}H_{18}FNO_2+H)^+$ requires m/z 288.1394, found m/z 288.1391.

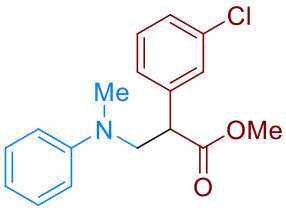
methyl 2-(3-fluorophenyl)-3-(methyl(phenyl)amino)propanoate (3ca):



3ca was obtained as a colorless sticky oil (31.0 mg, 54%) from diazo compound **1c** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.26 – 7.23 (m, 1H), 7.11 – 7.05 (m, 2H), 7.03 – 6.97 (m, 1H), 6.78 – 6.66 (m, 3H), 4.09 (dd, *J* = 14.2, 8.5 Hz, 1H), 4.02 (dd, *J* = 8.5, 5.2 Hz, 1H), 3.66 (s, 3H), 3.60 (dd, *J* = 14.2, 5.3 Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 162.9 (d, *J* = 245.2 Hz), 148.3, 139.4 (d, *J* = 7.4 Hz), 130.3 (d, *J* = 8.3 Hz), 129.3, 123.9 (d,

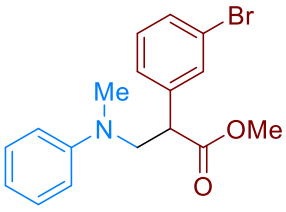
J = 3.0 Hz), 116.8, 115.1 (d, J = 21.8 Hz), 114.7 (d, J = 20.9 Hz), 112.3, 56.7, 52.3, 49.3, 39.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.33; ESI FTMS exact mass calcd for $(C_{17}H_{18}FNO_2+H)^+$ requires m/z 288.1394, found m/z 288.1396.

methyl 2-(3-chlorophenyl)-3-(methyl(phenyl)amino)propanoate (3da):



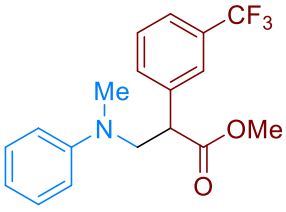
3da was obtained as a colorless sticky oil (35.1 mg, 58%) from diazo compound **1d** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.29 – 7.27 (m, 2H), 7.27 – 7.24 (m, 2H), 7.23 – 7.18 (m, 1H), 6.79 – 6.65 (m, 3H), 4.09 (dd, J = 14.5, 8.6 Hz, 1H), 3.99 (dd, J = 8.6, 5.4 Hz, 1H), 3.66 (s, 3H), 3.59 (dd, J = 14.5, 5.4 Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 148.2, 138.9, 134.7, 130.1, 129.4, 128.2, 127.9, 126.4, 116.8, 112.2, 56.7, 52.4, 49.2, 39.4. ESI FTMS exact mass calcd for $(C_{17}H_{18}ClNO_2+H)^+$ requires m/z 304.1099, found m/z 304.1096.

methyl 2-(3-bromophenyl)-3-(methyl(phenyl)amino)propanoate (3ea):



3ea was obtained as a colorless sticky oil (34.7 mg, 50%) from diazo compound **1e** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 1H), 7.46 – 7.41 (m, 1H), 7.29 – 7.26 (m, 2H), 7.25 – 7.24 (m, 1H), 7.23 – 7.19 (m, 1H), 6.78 – 6.67 (m, 3H), 4.08 (dd, J = 14.5, 8.6 Hz, 1H), 3.98 (dd, J = 8.6, 5.5 Hz, 1H), 3.66 (s, 3H), 3.59 (dd, J = 14.5, 5.5 Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 148.2, 139.2, 131.1, 130.9, 130.4, 129.4, 126.8, 122.9, 116.9, 112.3, 56.7, 52.4, 49.2, 39.4. ESI FTMS exact mass calcd for $(C_{17}H_{18}BrNO_2+H)^+$ requires m/z 348.0594, found m/z 348.0595.

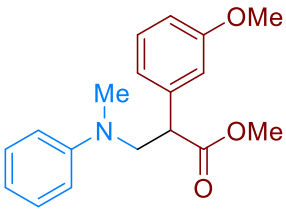
methyl 3-(methyl(phenyl)amino)-2-(3-(trifluoromethyl)phenyl)propanoate (3fa):



3fa was obtained as a colorless sticky oil (34.4 mg, 51%) from diazo compound **1f** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 3H), 7.49 – 7.44 (m, 1H), 7.28 – 7.24 (m, 2H),

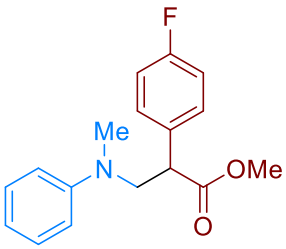
6.79 – 6.67 (m, 3H), 4.17 – 4.07 (m, 2H), 3.67 (s, 3H), 3.62 (dd, *J* = 13.0, 4.2 Hz, 1H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 148.2, 138.0, 131.6, 131.2 (q, *J* = 32.5 Hz), 129.4, 129.3, 124.9 (q, *J* = 3.9 Hz), 124.6 (q, *J* = 3.4 Hz), 123.9 (q, *J* = 272.7 Hz), 117.0, 112.3, 56.7, 52.4, 49.3, 39.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.60; ESI FTMS exact mass calcd for $(C_{18}H_{18}F_3NO_2+Na)^+$ requires m/z 360.1182, found m/z 360.1183.

methyl 2-(3-methoxyphenyl)-3-(methyl(phenyl)amino)propanoate (3ga):



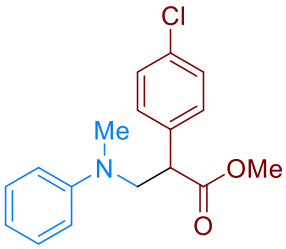
3ga was obtained as a colorless sticky oil (36.1 mg, 60%) from diazo compound **1g** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.26 – 7.24 (m, 2H), 6.93 – 6.90 (m, 1H), 6.89 – 6.87 (m, 1H), 6.86 – 6.83 (m, 1H), 6.77 – 6.69 (m, 3H), 4.10 (dd, *J* = 14.5, 8.7 Hz, 1H), 3.99 (dd, *J* = 8.7, 5.2 Hz, 1H), 3.81 (s, 3H), 3.65 (s, 3H), 3.61 (dd, *J* = 14.5, 5.3 Hz, 1H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 159.9, 148.4, 138.5, 129.9, 129.3, 120.4, 116.6, 113.8, 113.0, 112.2, 56.6, 55.3, 52.2, 49.6, 39.3. ESI FTMS exact mass calcd for $(C_{18}H_{21}NO_3+H)^+$ requires m/z 300.1594, found m/z 300.1595.

methyl 2-(4-fluorophenyl)-3-(methyl(phenyl)amino)propanoate (3ha):



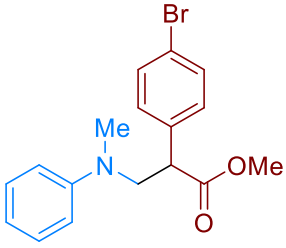
3ha was obtained as a colorless sticky oil (30.8 mg, 54%) from diazo compound **1h** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.28 – 7.23 (m, 2H), 7.07 – 7.00 (m, 2H), 6.77 – 6.66 (m, 3H), 4.09 (dd, *J* = 14.2, 8.4 Hz, 1H), 4.02 (dd, *J* = 8.4, 5.5 Hz, 1H), 3.66 (s, 3H), 3.57 (dd, *J* = 14.2, 5.5 Hz, 1H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 162.3 (d, *J* = 244.8 Hz), 148.3, 132.8 (d, *J* = 3.2 Hz), 129.7 (d, *J* = 8.0 Hz), 129.3, 116.7, 115.7 (d, *J* = 21.3 Hz), 112.2, 56.8, 52.3, 48.7, 39.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.72; ESI FTMS exact mass calcd for $(C_{17}H_{18}FNO_2+H)^+$ requires m/z 288.1394, found m/z 288.1394.

methyl 2-(4-chlorophenyl)-3-(methyl(phenyl)amino)propanoate (3ia):



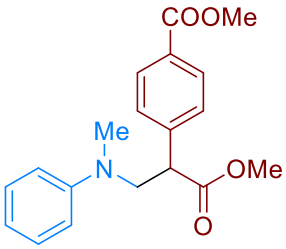
3ia was obtained as a colorless sticky oil (31.5 mg, 52%) from diazo compound **1i** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.27 – 7.25 (m, 2H), 7.25 – 7.21 (m, 2H), 6.78 – 6.62 (m, 3H), 4.08 (dd, *J* = 14.4, 8.3 Hz, 1H), 3.99 (dd, *J* = 8.3, 5.7 Hz, 1H), 3.64 (s, 3H), 3.56 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 148.2, 135.5, 133.6, 129.5, 129.3, 129.0, 116.8, 112.2, 56.7, 52.3, 48.9, 39.4.; ESI FTMS exact mass calcd for $(C_{17}H_{18}ClNO_2+H)^+$ requires m/z 304.1099, found m/z 304.1097.

methyl 2-(4-bromophenyl)-3-(methyl(phenyl)amino)propanoate (3ja)[4]:



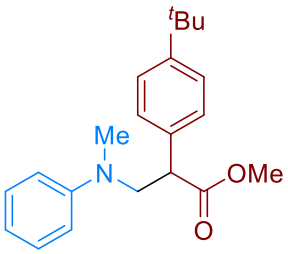
3ja was obtained as a colorless sticky oil (32.5 mg, 47%) from diazo compound **1j** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.29 – 7.24 (m, 2H), 7.24 – 7.20 (m, 2H), 6.77 – 6.66 (m, 3H), 4.09 (dd, *J* = 14.5, 8.3 Hz, 1H), 3.99 (dd, *J* = 8.3, 5.8 Hz, 1H), 3.65 (s, 3H), 3.57 (dd, *J* = 14.6, 5.7 Hz, 1H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 148.2, 136.0, 132.0, 129.8, 129.3, 121.7, 116.8, 112.2, 56.6, 52.3, 49.0, 39.4; ESI FTMS exact mass calcd for $(C_{17}H_{18}BrNO_2+H)^+$ requires m/z 348.0594, found m/z 348.0592.

methyl 4-(1-methoxy-3-(methyl(phenyl)amino)-1-oxopropan-2-yl)benzoate (3ka):



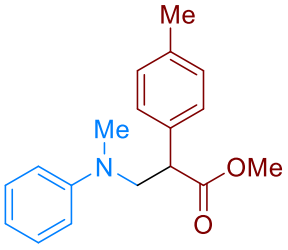
3ka was obtained as a colorless sticky oil (41.9 mg, 64%) from diazo compound **1k** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.43 – 7.37 (m, 2H), 7.28 – 7.24 (m, 2H), 6.78 – 6.65 (m, 3H), 4.17 – 4.07 (m, 2H), 3.92 (s, 3H), 3.66 (s, 3H), 3.61 (dd, *J* = 13.2, 4.5 Hz, 1H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 166.8, 148.2, 142.2, 130.1, 129.5, 129.4, 128.2, 116.9, 112.2, 56.6, 52.4, 52.2, 49.5, 39.4.; ESI FTMS exact mass calcd for $(C_{19}H_{21}NO_4+H)^+$ requires m/z 328.1543, found m/z 328.1542.

methyl 2-(4-(*tert*-butyl)phenyl)-3-(methyl(phenyl)amino)propanoate (3la):



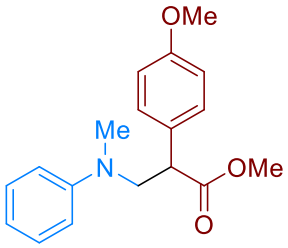
3la was obtained as a colorless sticky oil (62.2 mg, 96%) from diazo compound **1l** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.29 – 7.26 (m, 2H), 7.26 – 7.23 (m, 2H), 6.76 – 6.68 (m, 3H), 4.09 (dd, *J* = 14.4, 9.1 Hz, 1H), 4.00 (dd, *J* = 9.1, 4.7 Hz, 1H), 3.64 (s, 3H), 3.59 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.86 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 150.6, 148.5, 133.9, 129.2, 128.9, 127.6, 125.8, 116.5, 112.2, 56.7, 52.1, 49.2, 39.2, 34.5, 31.3; ESI FTMS exact mass calcd for $(C_{21}H_{27}NO_2+H)^+$ requires m/z 326.2115, found m/z 326.2111.

methyl 3-(methyl(phenyl)amino)-2-(*p*-tolyl)propanoate (3ma):



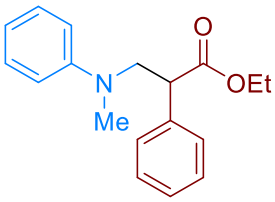
3ma was obtained as a colorless sticky oil (44.1 mg, 78%) from diazo compound **1m** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.22 – 7.19 (m, 2H), 7.16 – 7.12 (m, 2H), 6.75 – 6.65 (m, 3H), 4.08 (dd, *J* = 14.5, 8.7 Hz, 1H), 3.97 (dd, *J* = 8.8, 5.3 Hz, 1H), 3.62 (s, 3H), 3.56 (dd, *J* = 14.4, 5.3 Hz, 1H), 2.82 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 148.4, 137.4, 134.0, 129.6, 129.3, 127.9, 116.5, 112.2, 56.7, 52.2, 49.2, 39.3, 21.2; ESI FTMS exact mass calcd for $(C_{18}H_{21}NO_2+H)^+$ requires m/z 284.1645, found m/z 284.1643.

methyl 2-(4-methoxyphenyl)-3-(methyl(phenyl)amino)propanoate (3na):



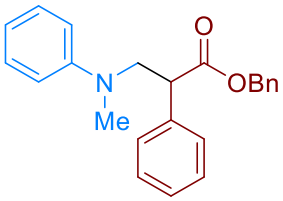
3na was obtained as a colorless sticky oil (29.9 mg, 50%) from diazo compound **1n** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 1H), 7.28 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 6.92 – 6.88 (m, 2H), 6.78 – 6.69 (m, 3H), 4.10 (dd, *J* = 14.5, 8.6 Hz, 1H), 3.99 (dd, *J* = 8.6, 5.5 Hz, 1H), 3.82 (s, 3H), 3.66 (s, 3H), 3.58 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 159.1, 148.4, 130.3, 129.3, 129.2, 129.1, 116.5, 114.2, 114.0, 112.2, 56.8, 55.3, 52.2, 48.7, 39.3; ESI FTMS exact mass calcd for $(C_{18}H_{21}NO_3+H)^+$ requires m/z 300.1594, found m/z 300.1592.

ethyl 3-(methyl(phenyl)amino)-2-phenylpropanoate (3oa)[5]:



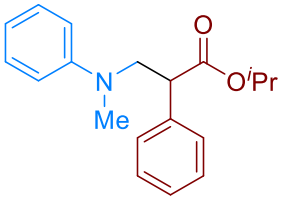
3oa was obtained as a colorless sticky oil (31.7 mg, 56%) from diazo compound **1o** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.32 – 7.26 (m, 2H), 7.25 – 7.23 (m, 1H), 6.76 – 6.67 (m, 3H), 4.16 – 4.09 (m, 2H), 4.09 – 4.04 (m, 1H), 4.00 (dd, *J* = 8.7, 5.2 Hz, 1H), 3.59 (dd, *J* = 14.5, 5.3 Hz, 1H), 2.84 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 148.5, 137.3, 129.3, 128.8, 128.0, 127.6, 116.6, 113.5, 112.2, 61.0, 56.7, 49.8, 39.2, 14.1; ESI FTMS exact mass calcd for $(C_{18}H_{21}NO_2+H)^+$ requires m/z 284.1645, found m/z 284.1642.

benzyl 3-(methyl(phenyl)amino)-2-phenylpropanoate (3pa):



3pa was obtained as a colorless sticky oil (37.3 mg, 54%) from diazo compound **1p** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.34 – 7.31 (m, 3H), 7.31 – 7.28 (m, 3H), 7.27 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 7.23 – 7.21 (m, 1H), 7.21 – 7.19 (m, 1H), 6.78 – 6.66 (m, 3H), 5.13 (d, *J* = 12.4 Hz, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 4.15 – 4.06 (m, 2H), 3.62 (dd, *J* = 12.8, 3.6 Hz, 1H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 148.4, 136.9, 135.7, 129.3, 128.9, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 116.6, 112.3, 66.7, 56.7, 49.8, 39.3; ESI FTMS exact mass calcd for $(C_{23}H_{23}NO_2+H)^+$ requires m/z 346.1802, found m/z 346.1800.

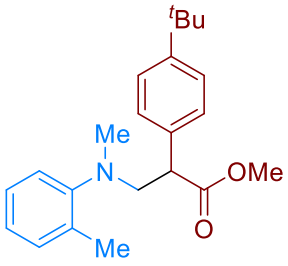
isopropyl 3-(methyl(phenyl)amino)-2-phenylpropanoate (3qa):



3qa was obtained as a colorless sticky oil (38.8 mg, 65%) from diazo compound **1q** and tertiary amine **2a**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.36 – 7.35 (m, 2H), 7.34 – 7.31 (m, 1H), 7.31 – 7.29 (m, 1H), 7.27 – 7.25 (m, 1H), 6.78 – 6.70 (m, 3H), 5.01 (p, *J* = 6.3 Hz, 1H), 4.11 (dd, *J* = 14.6, 8.8 Hz, 1H), 3.98 (dd, *J* = 8.8, 5.3 Hz, 1H), 3.60 (dd, *J* = 14.6, 5.3 Hz, 1H), 2.86 (s, 3H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 148.5,

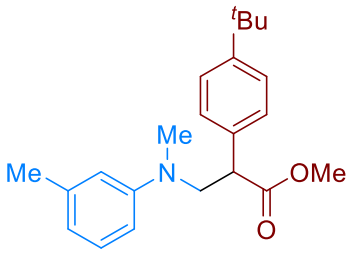
137.4, 129.3, 128.8, 128.0, 127.5, 116.5, 112.2, 68.4, 56.7, 50.1, 39.3, 21.7, 21.5; ESI FTMS exact mass calcd for $(C_{19}H_{23}NO_2+H)^+$ requires m/z 298.1802, found m/z 298.1801.

methyl 2-(4-(*tert*-butyl)phenyl)-3-(methyl(*o*-tolyl)amino)propanoate (3lb):



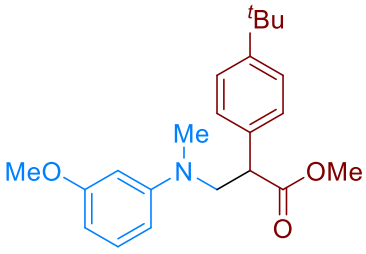
3lb was obtained as a colorless sticky oil (40.8 mg, 60%) from diazo compound **1l** and tertiary amine **2b**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 7.10 – 7.05 (m, 1H), 7.03 – 6.97 (m, 1H), 3.80 (dd, *J* = 10.3, 4.9 Hz, 1H), 3.72 – 3.66 (m, 1H), 3.62 (s, 3H), 3.27 (dd, *J* = 12.5, 4.9 Hz, 1H), 2.68 (s, 3H), 2.17 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 151.2, 150.3, 134.3, 134.1, 131.1, 127.7, 126.4, 125.5, 123.7, 120.9, 59.0, 51.9, 49.9, 43.4, 34.5, 31.3, 17.8; ESI FTMS exact mass calcd for $(C_{22}H_{29}NO_2+H)^+$ requires m/z 340.2271, found m/z 340.2267.

methyl 2-(4-(*tert*-butyl)phenyl)-3-(methyl(*m*-tolyl)amino)propanoate (3lc):



3lc was obtained as a colorless sticky oil (49.8 mg, 73%) from diazo compound **1l** and tertiary amine **2c**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.28 – 7.25 (m, 2H), 7.17 – 7.11 (m, 1H), 6.58 – 6.50 (m, 3H), 4.06 (dd, *J* = 13.9, 9.1 Hz, 1H), 4.00 (dd, *J* = 9.1, 4.2 Hz, 1H), 3.64 (s, 3H), 3.59 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.86 (s, 3H), 2.32 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 150.5, 148.6, 138.9, 134.0, 129.1, 127.6, 125.8, 117.5, 113.0, 109.4, 56.8, 52.1, 49.2, 39.3, 34.5, 31.3, 22.0; ESI FTMS exact mass calcd for $(C_{22}H_{29}NO_2+H)^+$ requires m/z 340.2271, found m/z 340.2269.

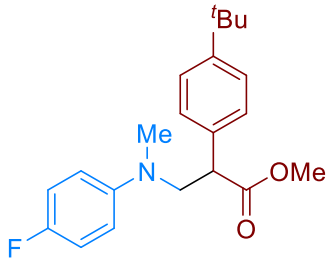
methyl 2-(4-(*tert*-butyl)phenyl)-3-((3-methoxyphenyl)(methyl)amino)propanoate (3ld):



3ld was obtained as a colorless sticky oil (46.9 mg, 66%) from diazo compound **1l** and tertiary amine **2d**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.09 (t, *J* = 8.1 Hz, 1H), 6.36 – 6.24 (m, 3H),

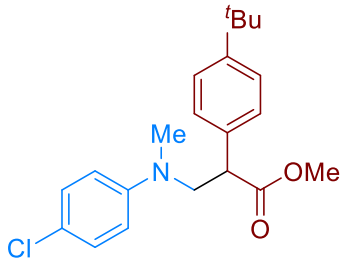
4.09 – 4.00 (m, 2H), 3.75 (s, 3H), 3.61 (s, 3H), 3.57 (dd, *J* = 11.9, 2.7 Hz, 1H), 2.84 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 174.0, 161.9, 151.2, 151.0, 135.2, 130.6, 128.6, 126.5, 106.1, 102.7, 99.5, 57.5, 55.2, 52.3, 49.9, 39.5, 35.0, 31.6; ESI FTMS exact mass calcd for $(C_{22}H_{29}NO_3+H)^+$ requires m/z 356.2220, found m/z 356.2220.

methyl 2-(4-(*tert*-butyl)phenyl)-3-((4-fluorophenyl)(methyl)amino)propanoate (3le):



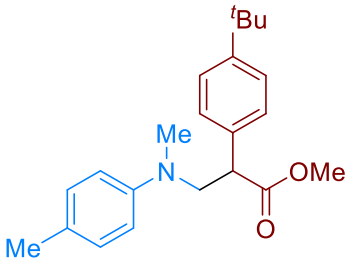
3le was obtained as a colorless sticky oil (54.9 mg, 80%) from diazo compound **1l** and tertiary amine **2e**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.26 – 7.23 (m, 2H), 6.97 – 6.91 (m, 2H), 6.68 – 6.61 (m, 2H), 4.05 (dd, *J* = 14.3, 9.2 Hz, 1H), 3.95 (dd, *J* = 9.1, 4.8 Hz, 1H), 3.63 (s, 3H), 3.51 (dd, *J* = 14.3, 4.8 Hz, 1H), 2.82 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 155.6 (d, *J* = 235.4 Hz), 150.6, 145.4 (d, *J* = 1.7 Hz), 133.8, 127.6, 125.8, 115.6 (d, *J* = 22.1 Hz), 113.6 (d, *J* = 7.3 Hz), 57.5, 52.1, 49.2, 39.5, 34.5, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.07. ESI FTMS exact mass calcd for $(C_{21}H_{26}FNO_2+H)^+$ requires m/z 344.2020, found m/z 344.2018.

methyl 2-(4-(*tert*-butyl)phenyl)-3-((4-chlorophenyl)(methyl)amino)propanoate (3lf):



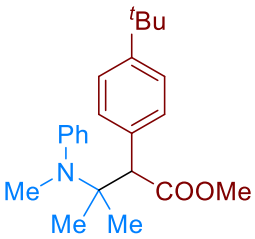
3lf was obtained as a colorless sticky oil (59.3 mg, 82%) from diazo compound **1l** and tertiary amine **2f**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.27 – 7.24 (m, 2H), 7.22 – 7.15 (m, 2H), 6.67 – 6.58 (m, 2H), 4.07 (dd, *J* = 14.6, 9.0 Hz, 1H), 3.96 (dd, *J* = 9.0, 5.1 Hz, 1H), 3.65 (s, 3H), 3.57 (dd, *J* = 14.6, 5.1 Hz, 1H), 2.84 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 150.7, 147.1, 133.6, 129.0, 127.6, 125.8, 121.4, 113.4, 56.7, 52.2, 49.0, 39.3, 34.6, 31.3; ESI FTMS exact mass calcd for $(C_{21}H_{26}ClNO_2+H)^+$ requires m/z 360.1725, found m/z 360.1718.

methyl 2-(4-(*tert*-butyl)phenyl)-3-(methyl(*p*-tolyl)amino)propanoate (3lg):



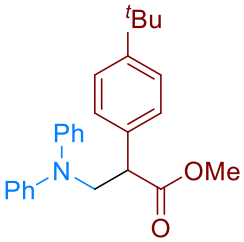
3lg was obtained as a colorless sticky oil (36.6 mg, 54%) from diazo compound **1l** and tertiary amine **2g**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.42 – 7.38 (m, 2H), 7.32 – 7.28 (m, 2H), 7.04 – 6.99 (m, 2H), 6.68 – 6.64 (m, 2H), 4.07 – 3.99 (m, 2H), 3.60 (s, 3H), 3.53 (dd, *J* = 9.8 Hz, 1H), 2.81 (s, 3H), 2.20 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, Acetone) δ 174.1, 151.1, 147.7, 135.2, 130.4, 128.6, 126.5, 126.2, 113.6, 57.8, 52.2, 49.9, 39.4, 35.0, 31.6, 20.3; ESI FTMS exact mass calcd for $(C_{22}H_{29}NO_2+H)^+$ requires m/z 340.2271, found m/z 340.2271.

methyl 2-(4-(tert-butyl)phenyl)-3-methyl-3-(methyl(phenyl)amino)butanoate (3lh):



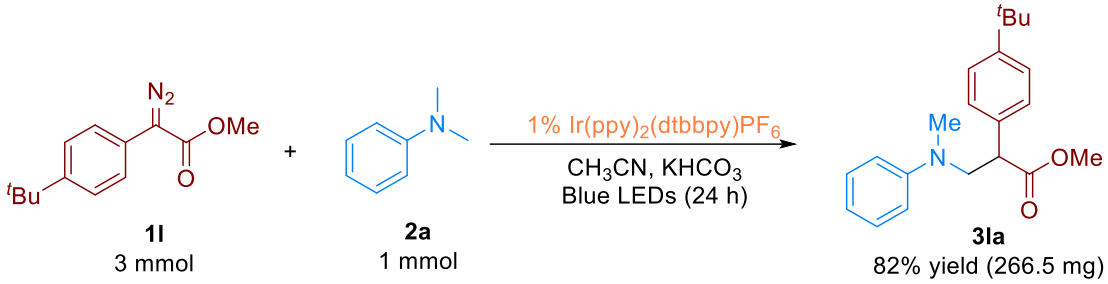
3li was obtained as a colorless sticky oil (38.9 mg, 55%) from diazo compound **1l** and tertiary amine **2h**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.22 – 7.15 (m, 2H), 7.11 – 7.05 (m, 2H), 6.97 – 6.90 (m, 1H), 3.77 (s, 3H), 2.93 (s, 3H), 2.75 – 2.62 (m, 1H), 1.31 (s, 9H), 0.73 (d, *J* = 6.6 Hz, 3H), 0.67 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 150.5, 149.6, 133.4, 129.2, 128.3, 123.9, 123.6, 121.9, 51.3, 40.9, 34.4, 32.4, 31.4, 19.6, 17.8; ESI FTMS exact mass calcd for $(C_{23}H_{31}NO_2+H)^+$ requires m/z 354.2428, found m/z 354.2428.

methyl 2-(4-(*tert*-butyl)phenyl)-3-(diphenylamino)propanoate (3li):



3lh was obtained as a colorless sticky oil (47.2 mg, 61%) from diazo compound **1l** and tertiary amine **2i**; Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.18 (m, 6H), 6.98 – 6.92 (m, 2H), 6.92 – 6.85 (m, 4H), 4.50 (dd, *J* = 14.3, 8.6 Hz, 1H), 4.05 (dd, *J* = 8.5, 5.4 Hz, 1H), 3.95 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.56 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 150.6, 147.8, 133.8, 129.3, 127.8, 125.7, 121.7, 121.4, 55.9, 52.1, 49.5, 34.5, 31.3; ESI FTMS exact mass calcd for $(C_{26}H_{29}NO_2+H)^+$ requires m/z 388.2271, found m/z 388.2271.

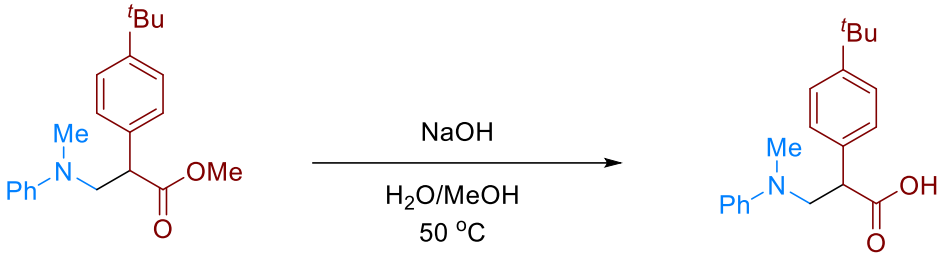
6. Procedure for one-mmol-scale reaction



In a nitrogen-filled glovebox, a 8 mL screw-cap test tube, equipped with a magnetic stir bar, then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (10.0 mg, 0.01 mmol, 1.0 mol%), $KHCO_3$ (150.5 mg, 1.5 mmol, 1.5 equiv), diazo compound **1l** (3.0 mmol, 3.0 equiv), tertiary amine **2a** (1.0 mmol, 1.0 equiv) and anhydrous CH_3CN (5.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LEDs at room temperature for 24 h. Next, the reaction mixture was transferred to a 50 mL round-bottom flask, diluted with 25 mL dichloromethane. The organic phase wasconcentrated under vacuum and purified through flash column chromatography (petroleum ether/ethyl acetate = 100/1) on silica gel to afford pure products **3la** (266.5 mg, 82% yield).

7. Synthetic procedures and characterization data of compounds 4-5

Synthetic procedure and characterization data of compound 4:

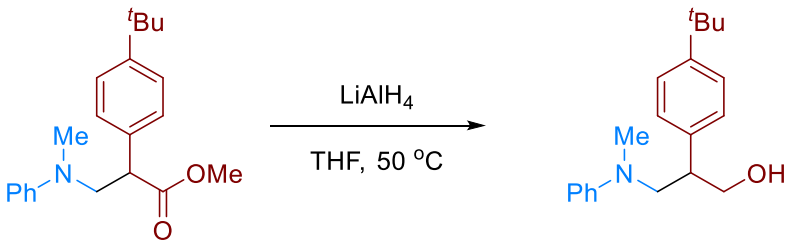


3la **4**, 62% yield

To a mixture of NaOH (20.0 mg, 0.5 mmol) in 0.25 mL H_2O was added the solution of compound **3la** (32.6 mg, 0.1 mmol) in 0.75 mL MeOH, which was stirred at 50 °C for 2 h. After cooling to 0 °C, the mixture was treated with an aqueous solution of 1 N HCl to pH = 1 and extracted with EtOAc (3×5 mL). The combined organic layers were washed with brine (15.0 mL), dried over Na_2SO_4, filtrated and evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane/methanol = 10/1) to afford pure product **4**.

2-(4-(*tert*-butyl)phenyl)-3-(methyl(phenyl)amino)propanoic acid (4): 62% yield (19.3 mg); colorless sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.04 (m, 6H), 6.67 – 6.55 (m, 3H), 3.95 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.72 (t, *J* = 7.1 Hz, 1H), 3.41 (s, 1H), 3.33 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.53 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 150.4, 149.9, 137.6, 129.9, 128.7, 126.1, 117.3, 113.5, 58.2, 52.7, 39.9, 35.1, 32.1; ESI FTMS exact mass calcd for $(C_{20}H_{25}NO_2+H)^+$ requires m/z 312.1958, found m/z 312.1955.

Synthetic procedure and characterization data of compound 5:



3la **5**, 81% yield

To a mixture of $LiAlH_4$ (16.0 mg, 0.5 mmol) in 0.5 mL THF was added the solution of compound **3la** (32.6 mg, 0.1 mmol) in 0.5 mL THF, which was stirred at 50 °C for 10 min. After the completion of the reaction which was indicated by TLC, the reaction mixture was quenched with H_2O and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was

purified through flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) to afford pure product **5**.

2-(4-(*tert*-butyl)phenyl)-3-(methyl(phenyl)amino)propan-1-ol (5): 81% yield (24.2 mg); colorless sticky oil; ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.34 (dd, J = 8.2, 1.7 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.18 – 7.12 (m, 2H), 6.75 – 6.68 (m, 2H), 6.65 – 6.56 (m, 1H), 3.94 (dd, J = 14.7, 6.8 Hz, 1H), 3.89 – 3.76 (m, 3H), 3.42 (dd, J = 14.7, 7.4 Hz, 1H), 3.24 – 3.09 (m, 1H), 2.74 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 150.2, 149.9, 140.2, 129.8, 128.8, 125.9, 116.5, 112.8, 64.9, 56.5, 47.2, 39.6, 34.9, 31.7, 31.7; ESI FTMS exact mass calcd for $(C_{20}H_{27}NO+H)^{+}$ requires m/z 298.2165, found m/z 298.2162.

8. Stern-Volmer fluorescence quenching experiments

A Hitachi F-7000 fluoresence spectrometer was used to record the emission intensities. All $Ir(ppy)_2(dtbbpy)PF_6$ solutions were excited at 400 nm and the emission intensity at 553 nm was observed. CH_3CN was degassed with a stream of Ar for 30 min. In a typical experiment, the emission spectrum of a 2×10^{-5} M solution of $Ir(ppy)_2(dtbbpy)PF_6$ in CH_3CN was collected. Then, appropriate amount of quencher was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 553 nm.

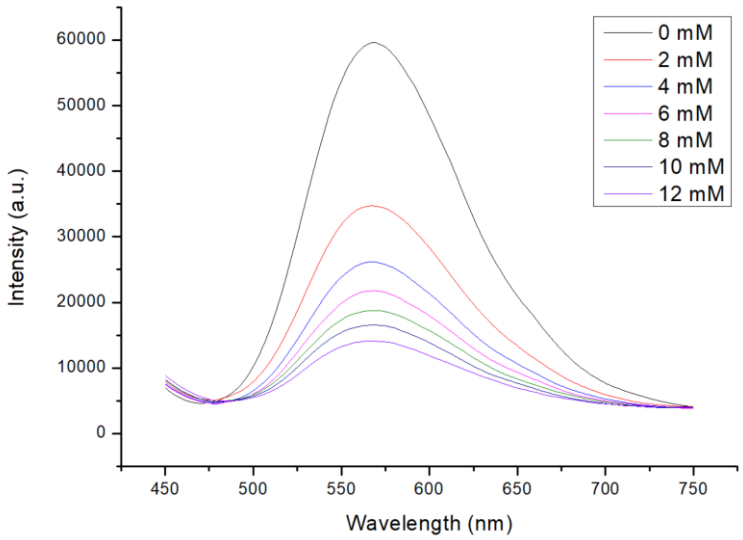


Figure S2. Emission spectra of 2×10^{-5} M Ir(ppy)2(dtbbpy)PF6 at λex = 400nm showing the quenching effect of increasing of aniline **2a**.

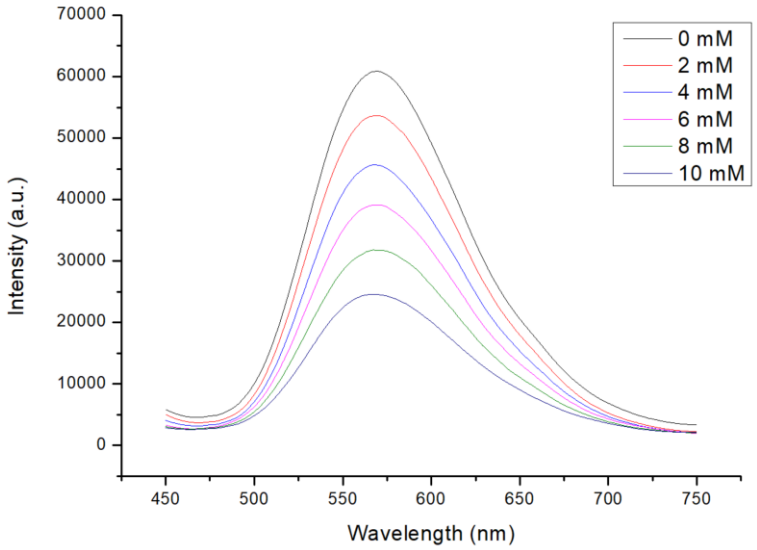


Figure S3. Emission spectra of 2×10^{-5} M Ir(ppy)2(dtbbpy)PF6 at λex = 400nm showing the quenching effect of increasing of diazoacetate **1a**.

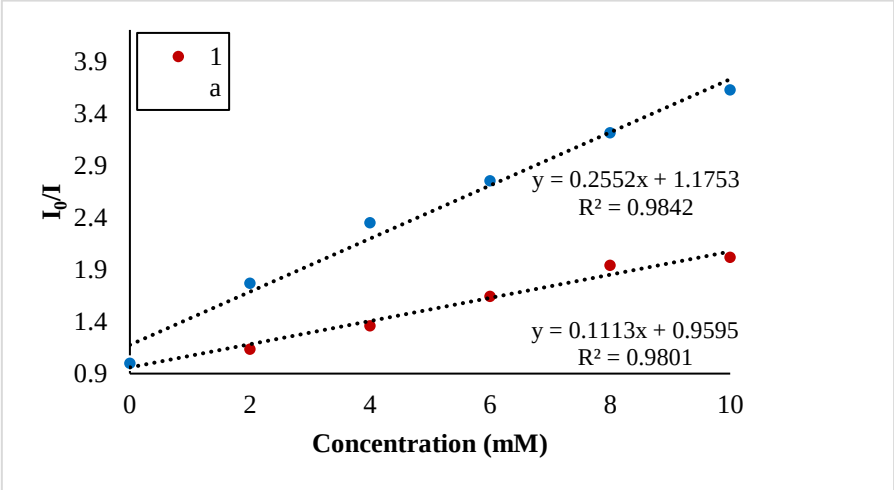


Figure S4. The Stern−Volmer plot.

Stern–Volmer quenching experiments demonstrated that aniline **2a** significantly quenched the fluorescence of $Ir(ppy)_2(dtbbpy)PF_6$, whereas diazoacetate **1a** had a much weaker effect.

9. References

[1] H. Keipour and T. Ollevier, Iron-Catalyzed Carbene Insertion Reactions of α-Diazoesters into Si–H Bonds, *Org. Lett.*, 2017, **19**, 5736-5739.

[2] J. Y. Hwang, A. Y. Ji, S. H. Lee and E. J. Kang, Redox-Selective Iron Catalysis for α-Amino C–H Bond Functionalization via Aerobic Oxidation, *Org. Lett.*, 2020, **22**, 16-21.

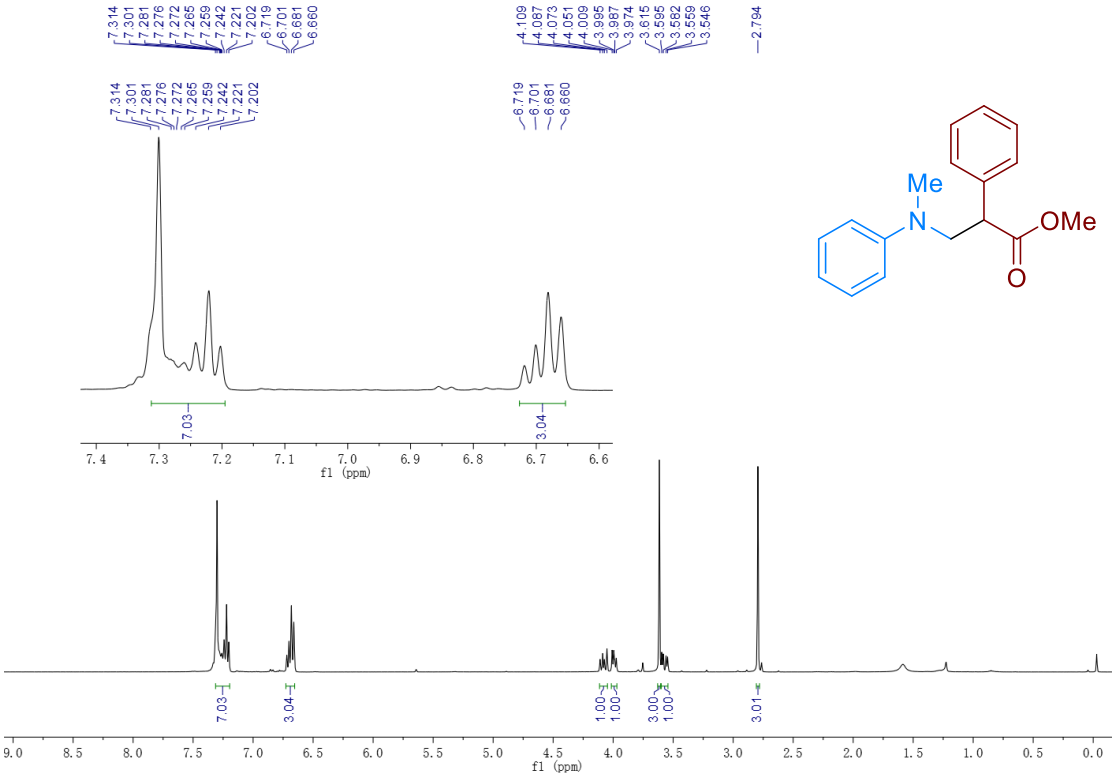
[3] L. Feng, X. Dai, E. Meggers and L. Gong, Three-Component Asymmetric Mannich Reaction Catalyzed by a Lewis Acid with Rhodium-Centered Chirality, *Chem. - Asian J.*, 2017, **12**, 963-967

[4] Davies and Q. Jin, Double C−H Activation Strategy for the Asymmetric Synthesis of C2-Symmetric Anilines, *Org. Lett.*, 2004, **6**, 1769-1772.

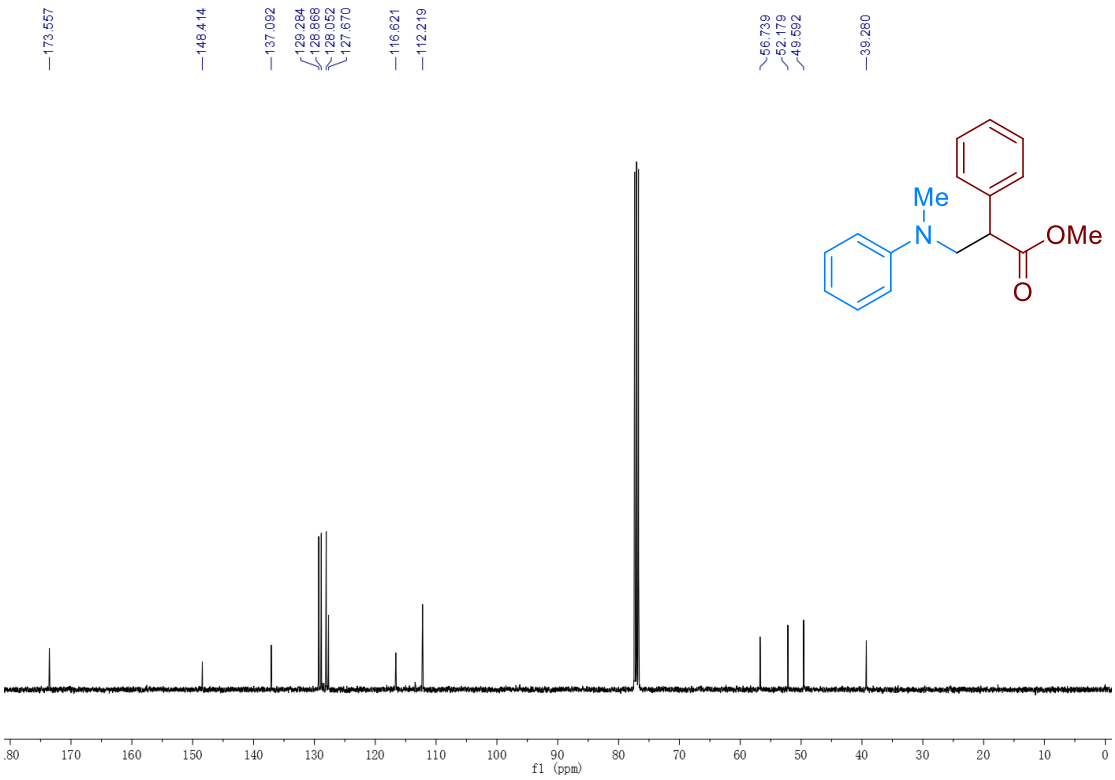
[5] E. M. Kaiser, C.-L. Mao, C. F. Hauser and C. R. Hauser, Conjugate Addition Reactions of Ethyl Atropate with Certain Alkali Nucleophiles, *J. Org. Chem.*, 1970, **35**, 410-414.

10. NMR spectra of all products

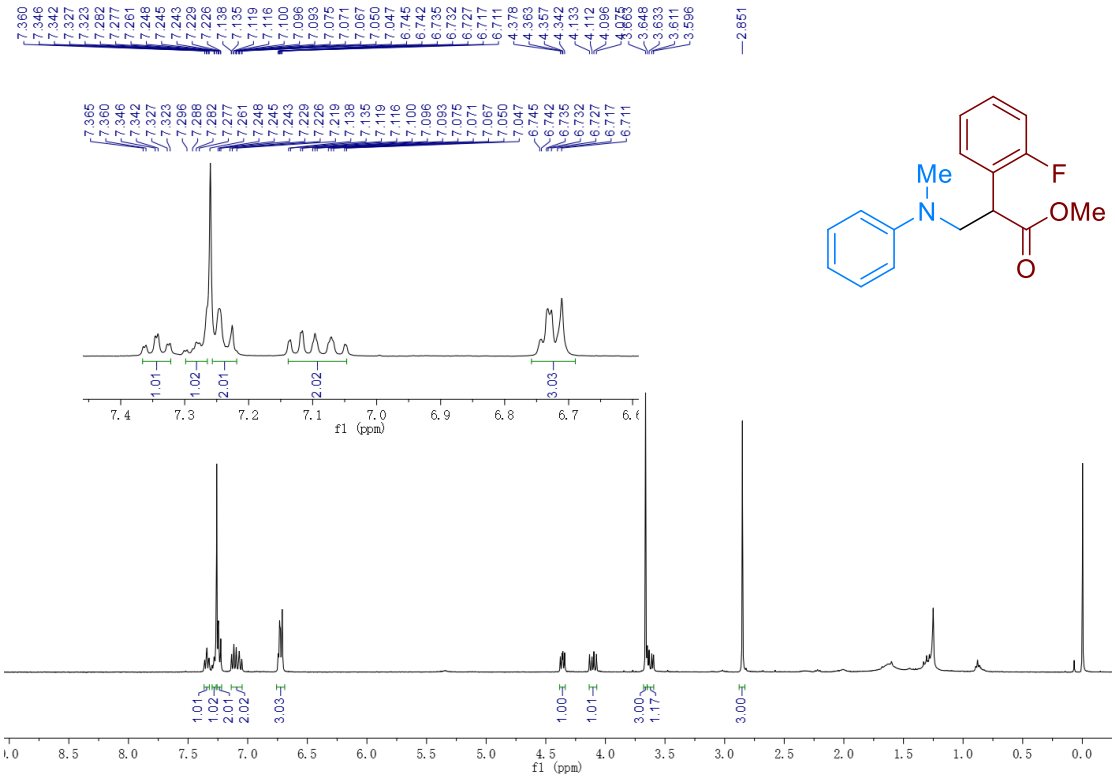
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa:**



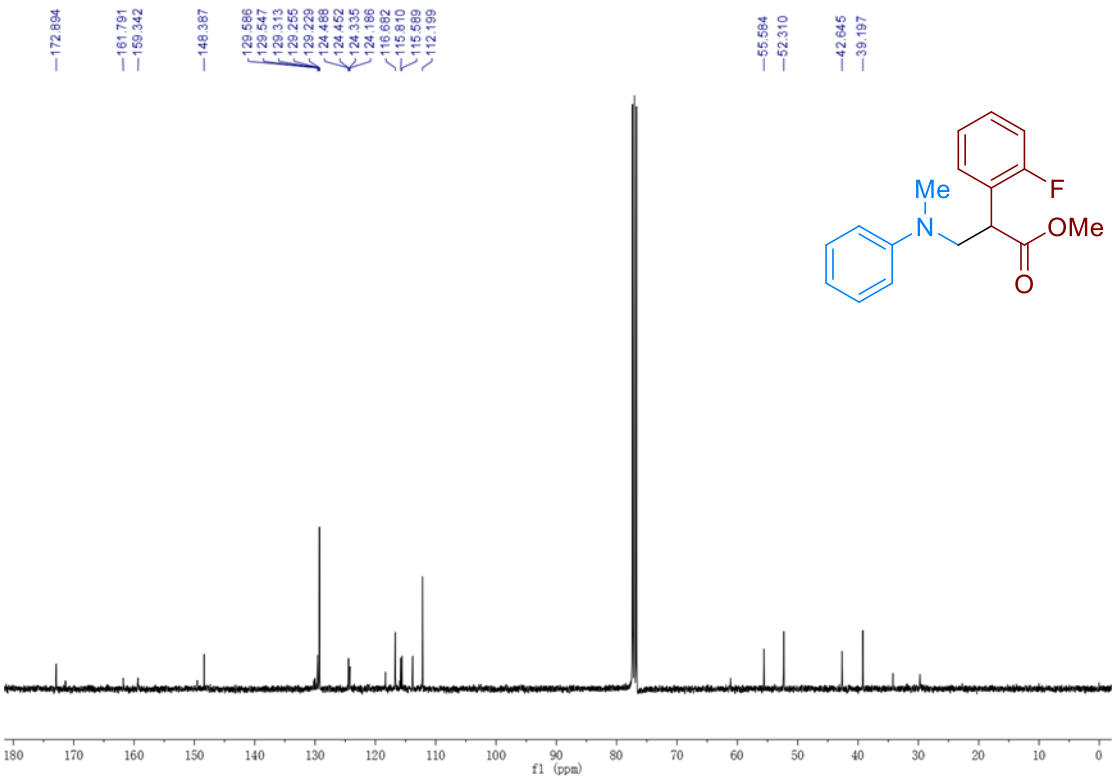
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3aa:**



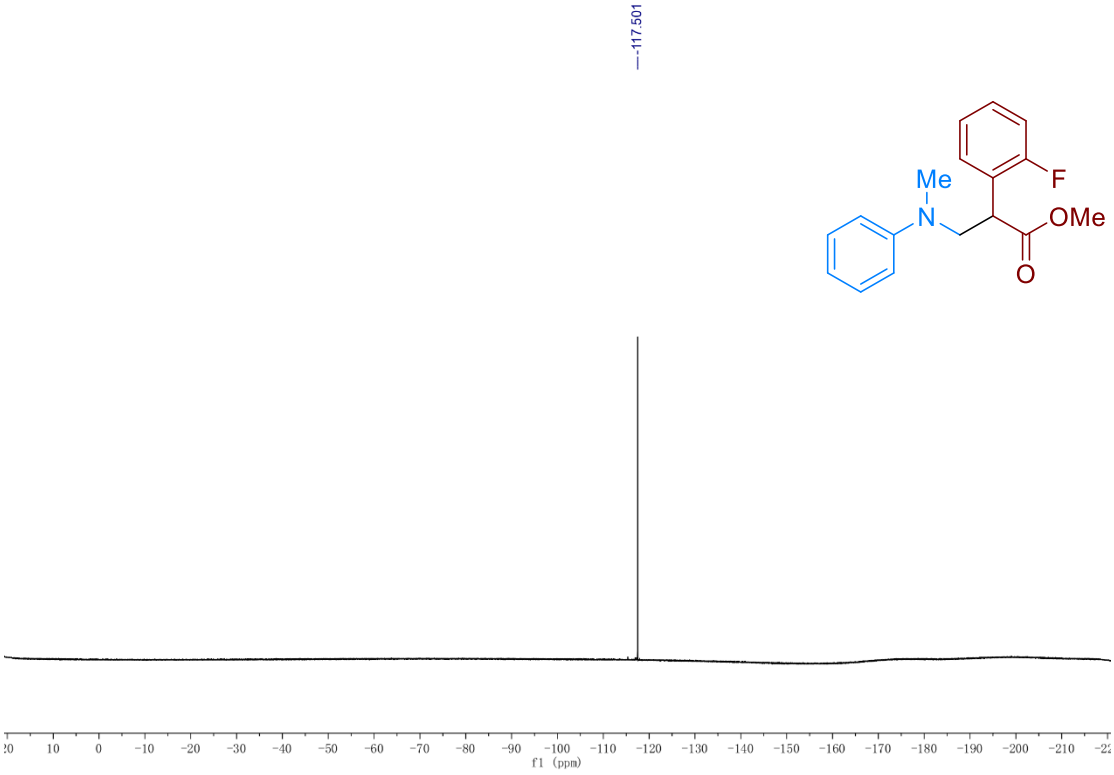
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ba:**



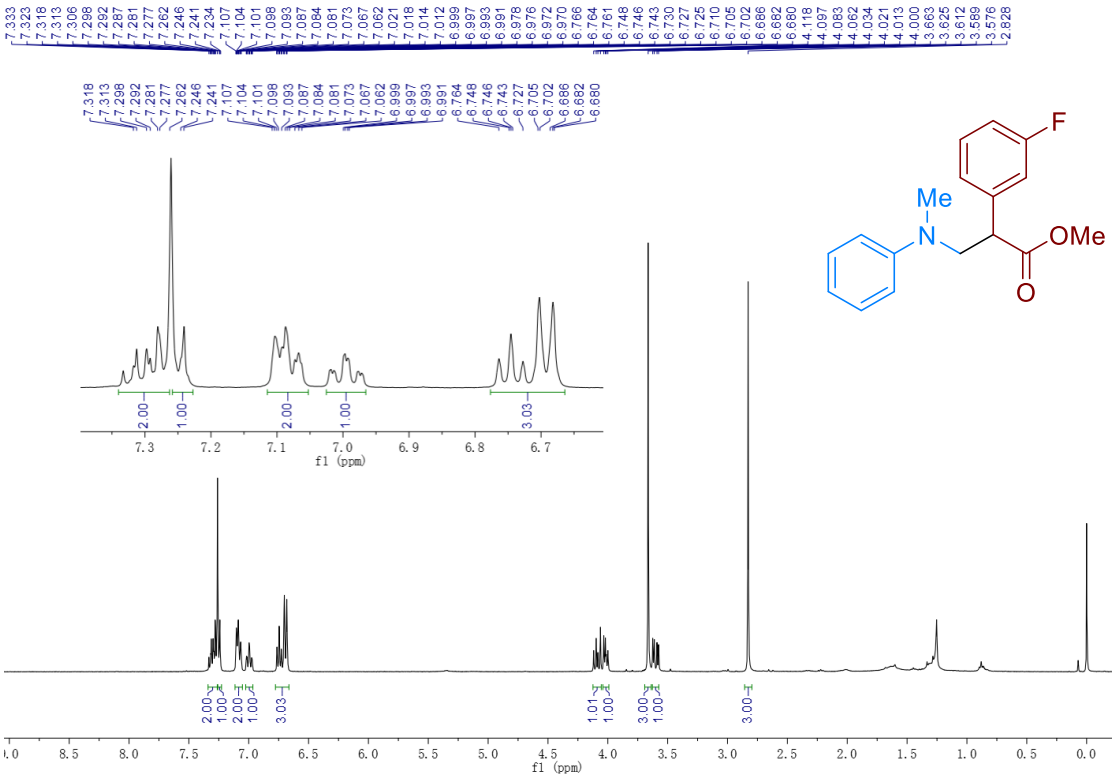
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ba:**



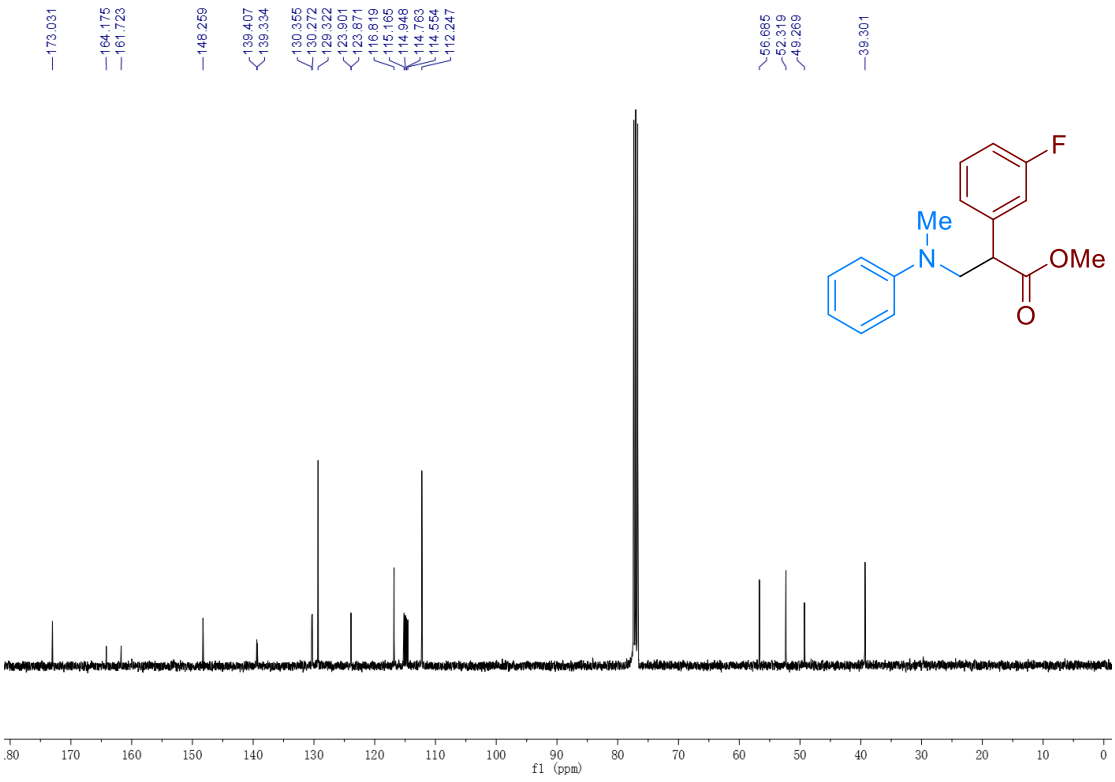
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3ba:**



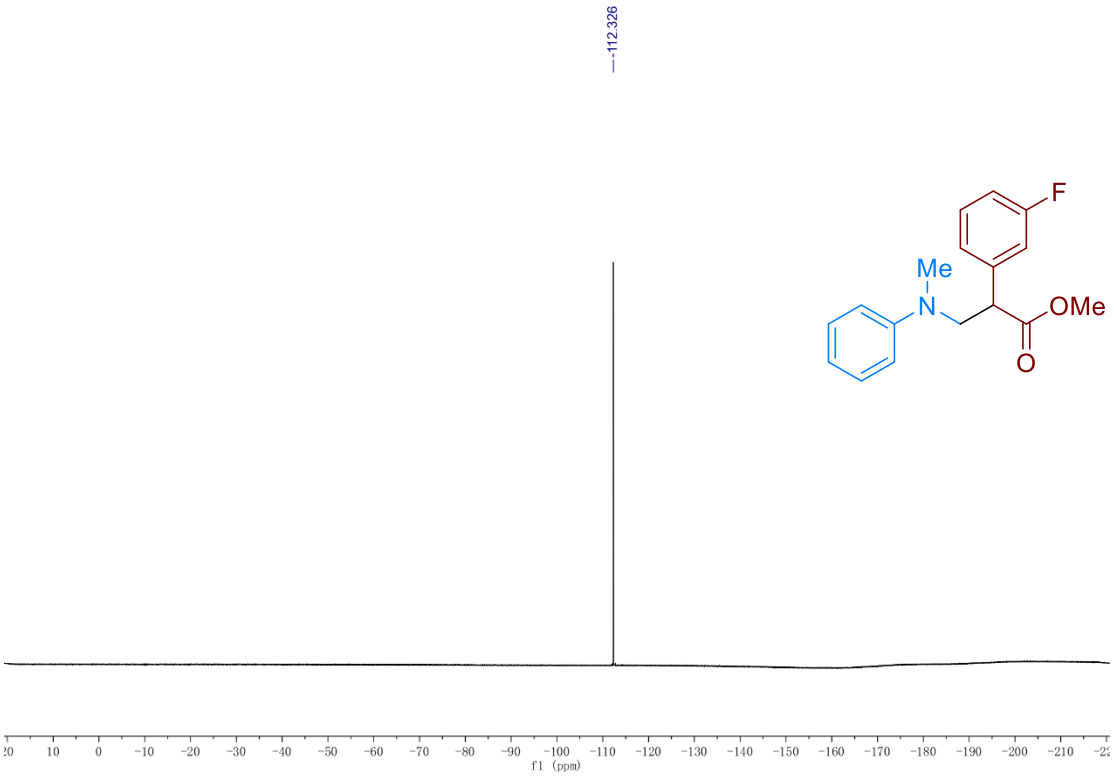
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ca:**



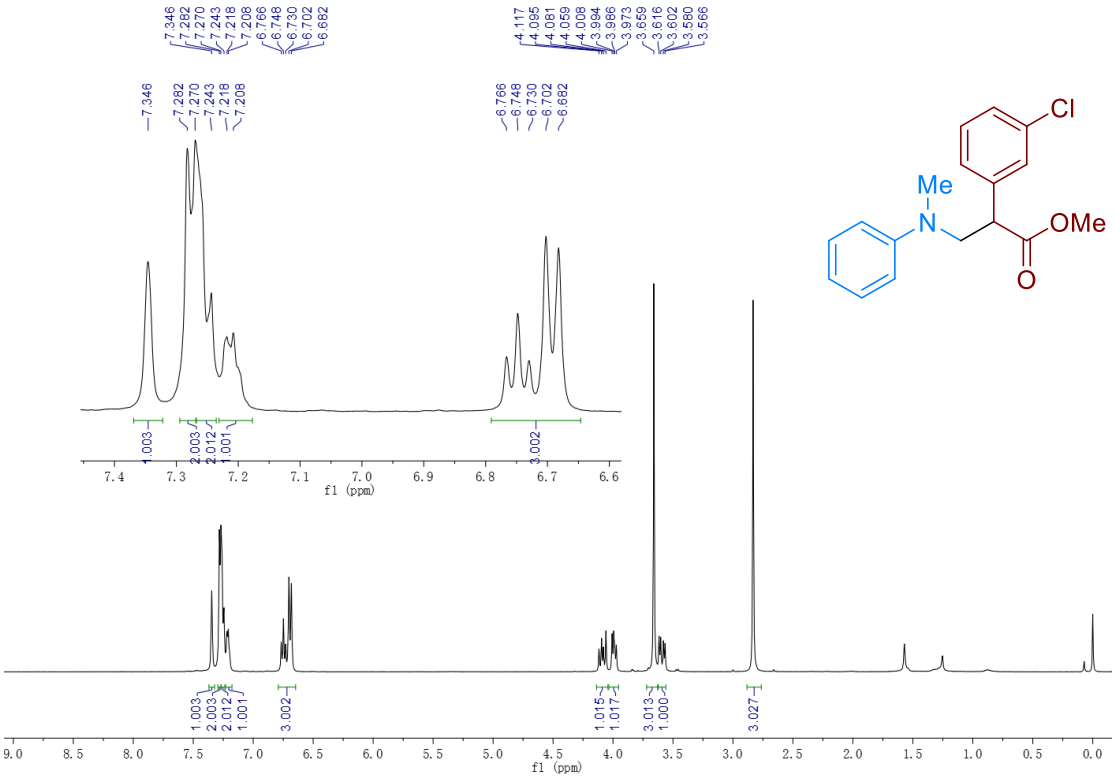
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ca:**



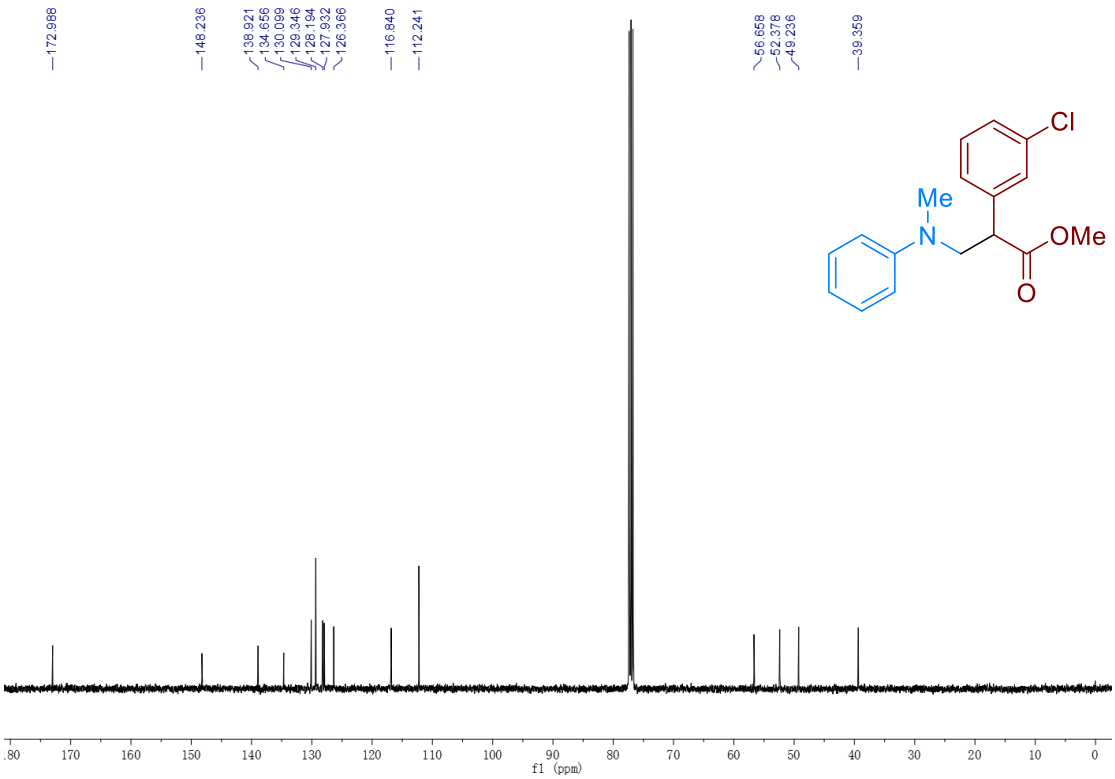
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3ca:**



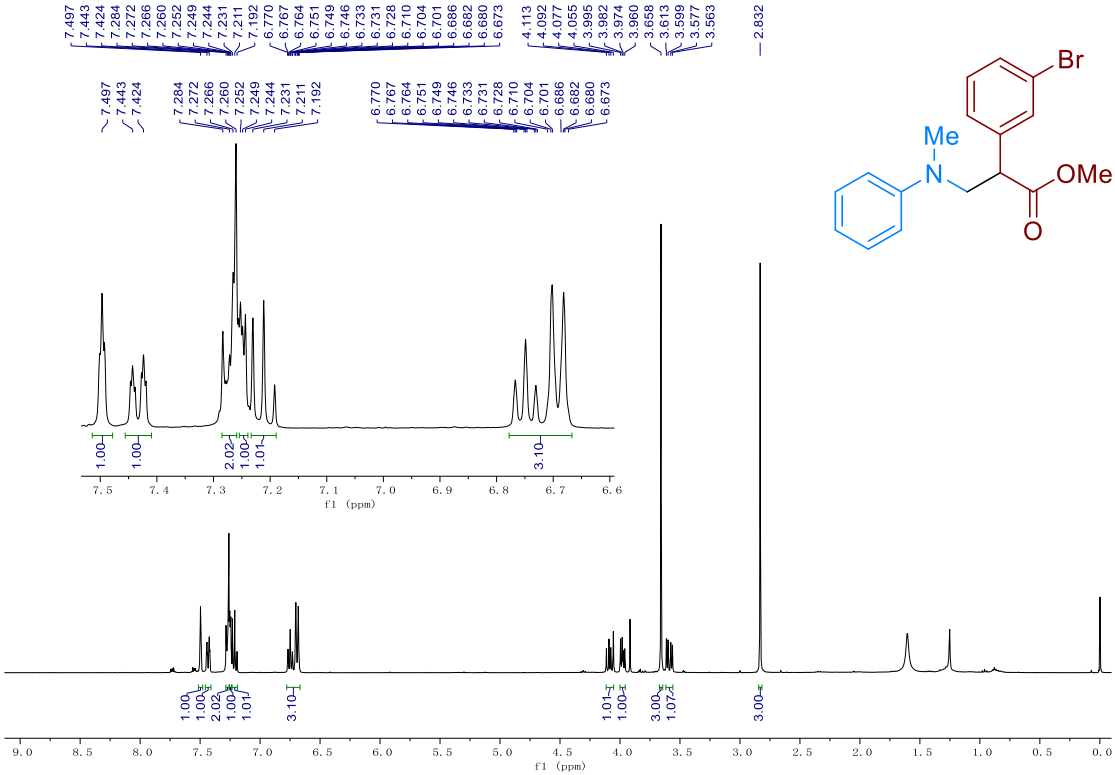
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3da:**



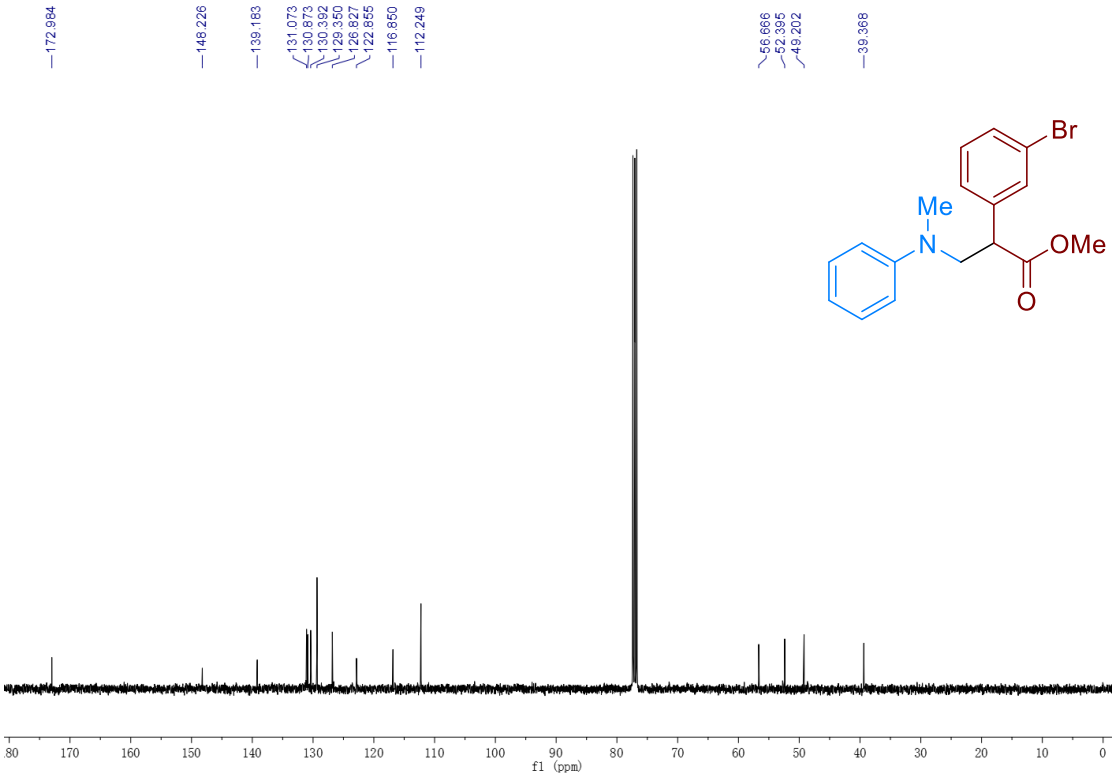
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3da:**



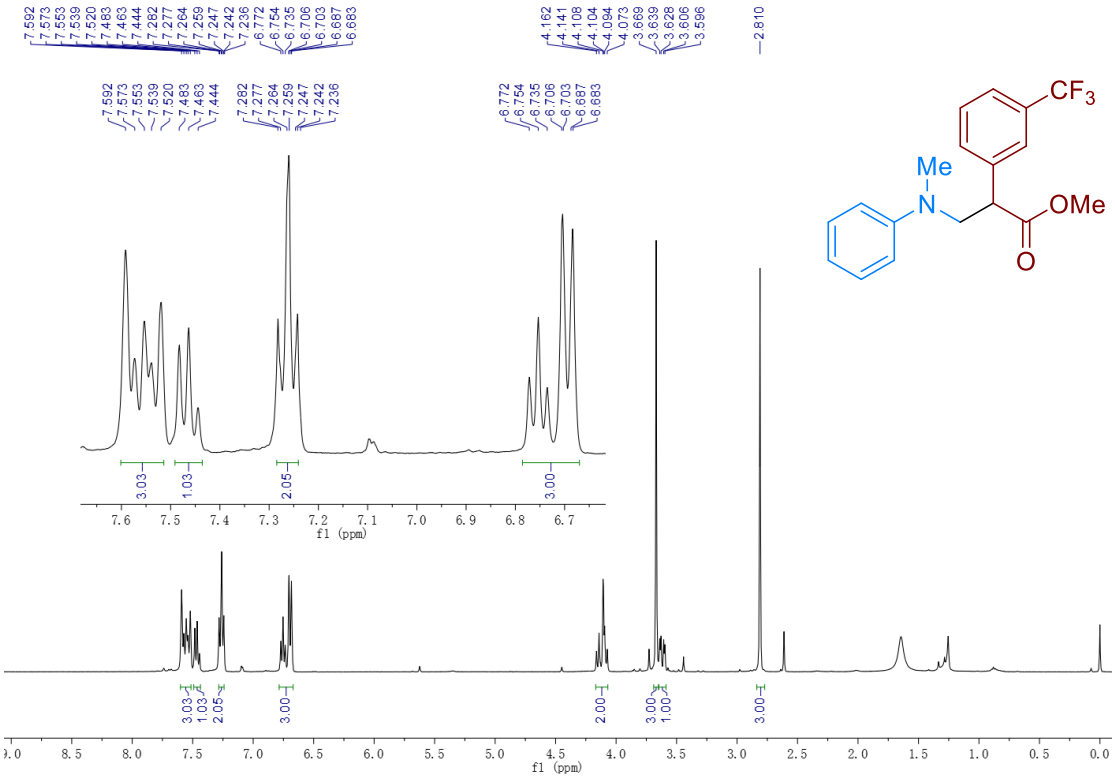
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ea:**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ea:**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3fa:**



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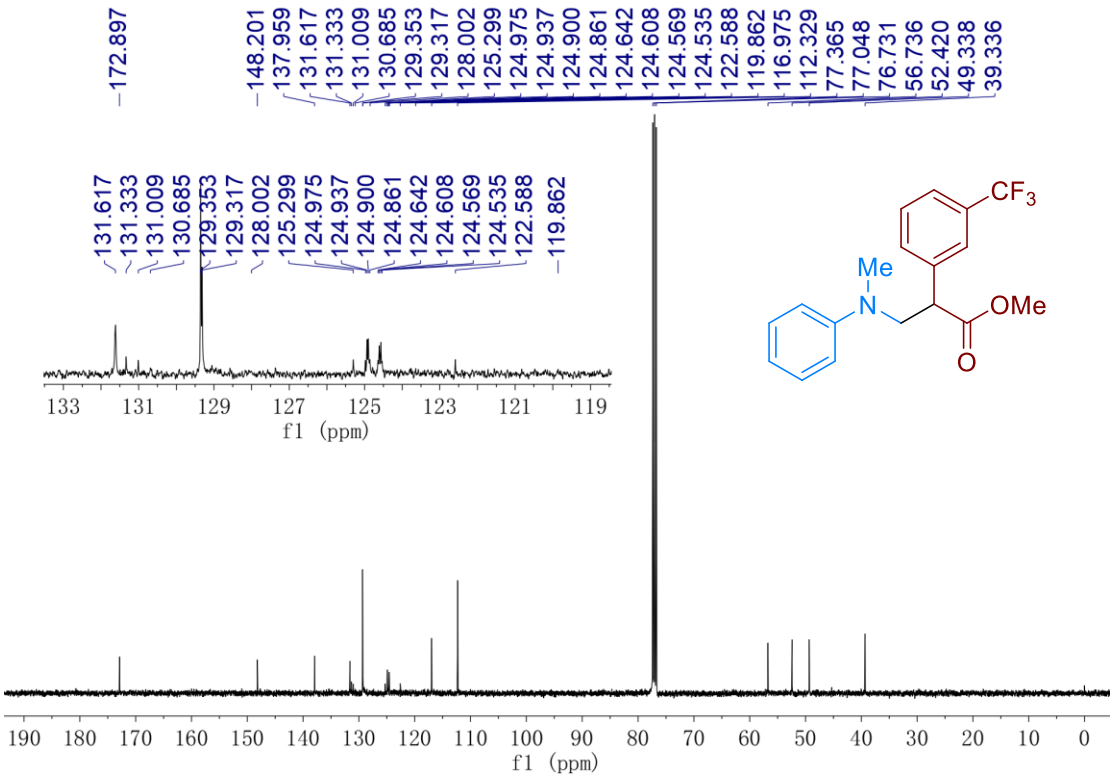
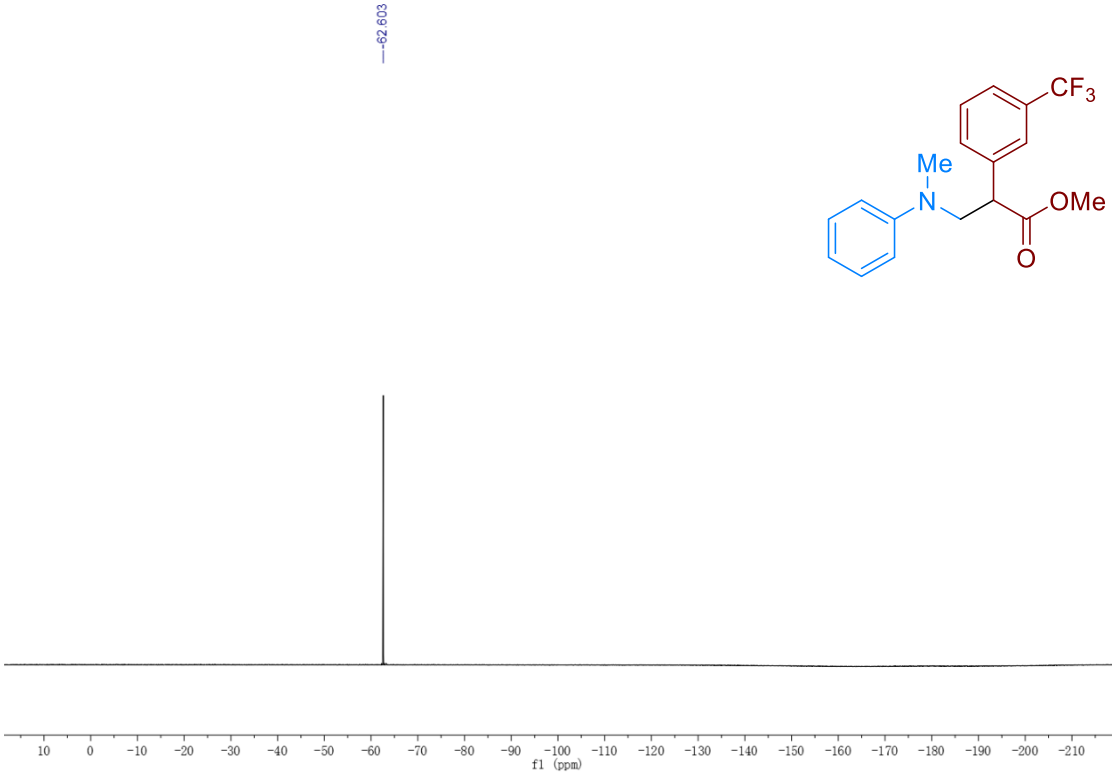
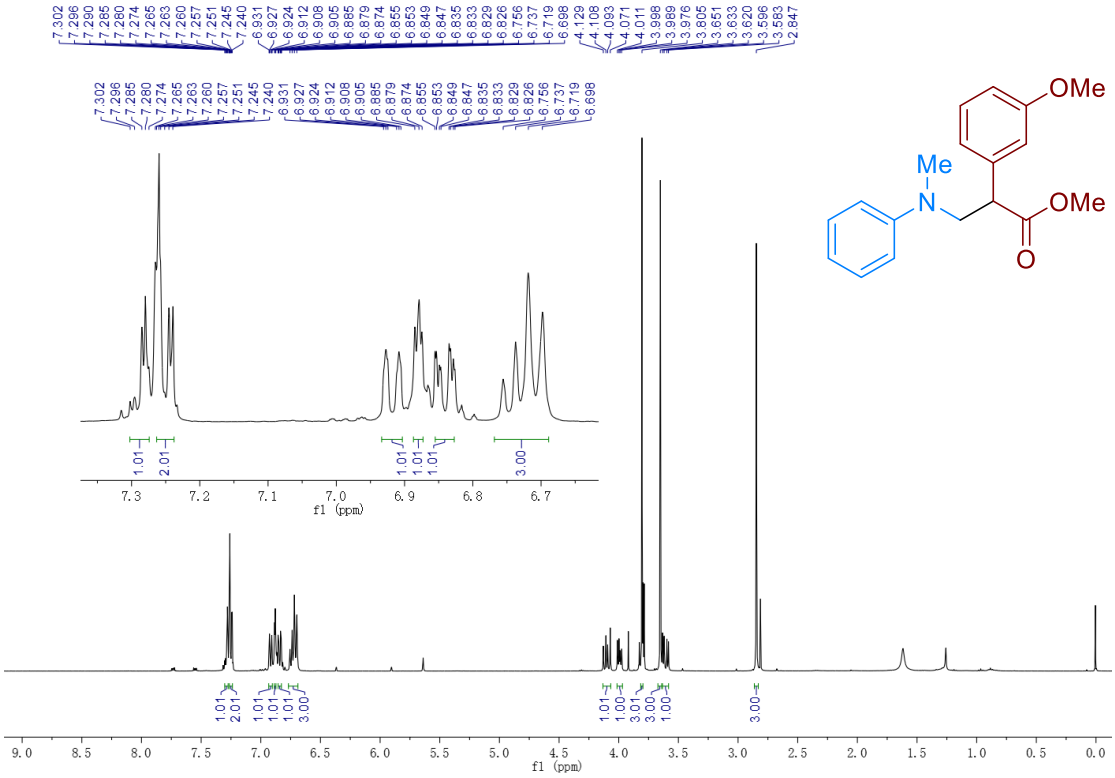


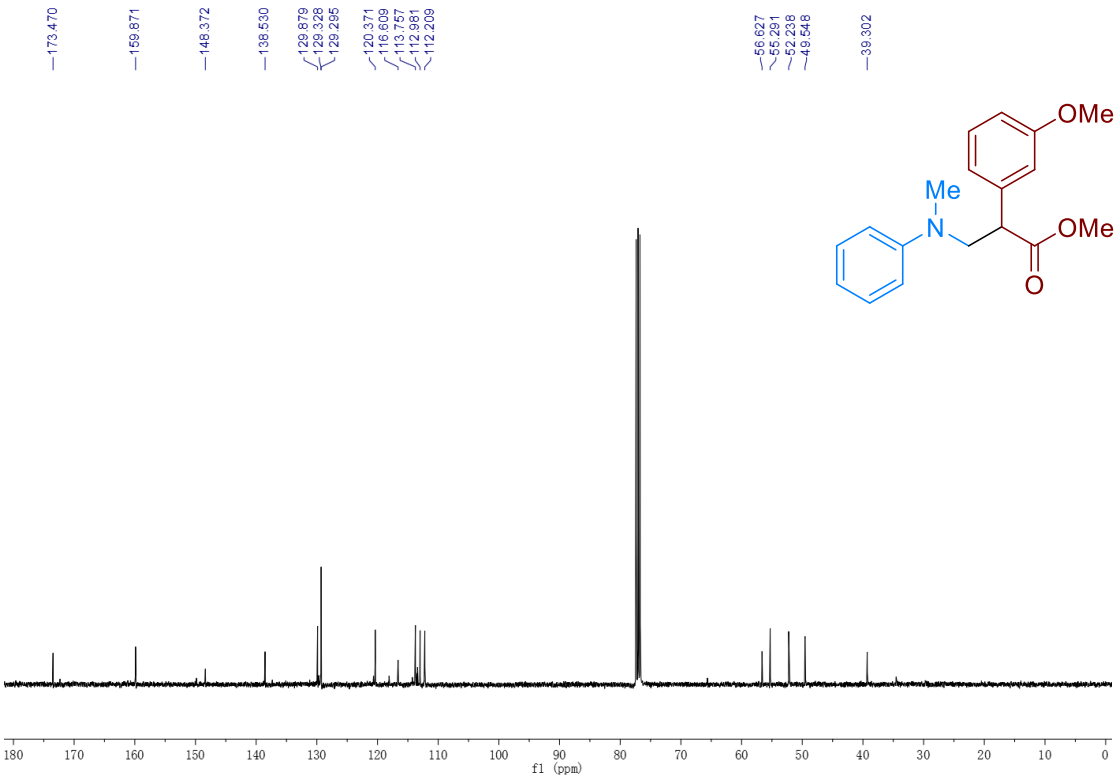
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3ca:**



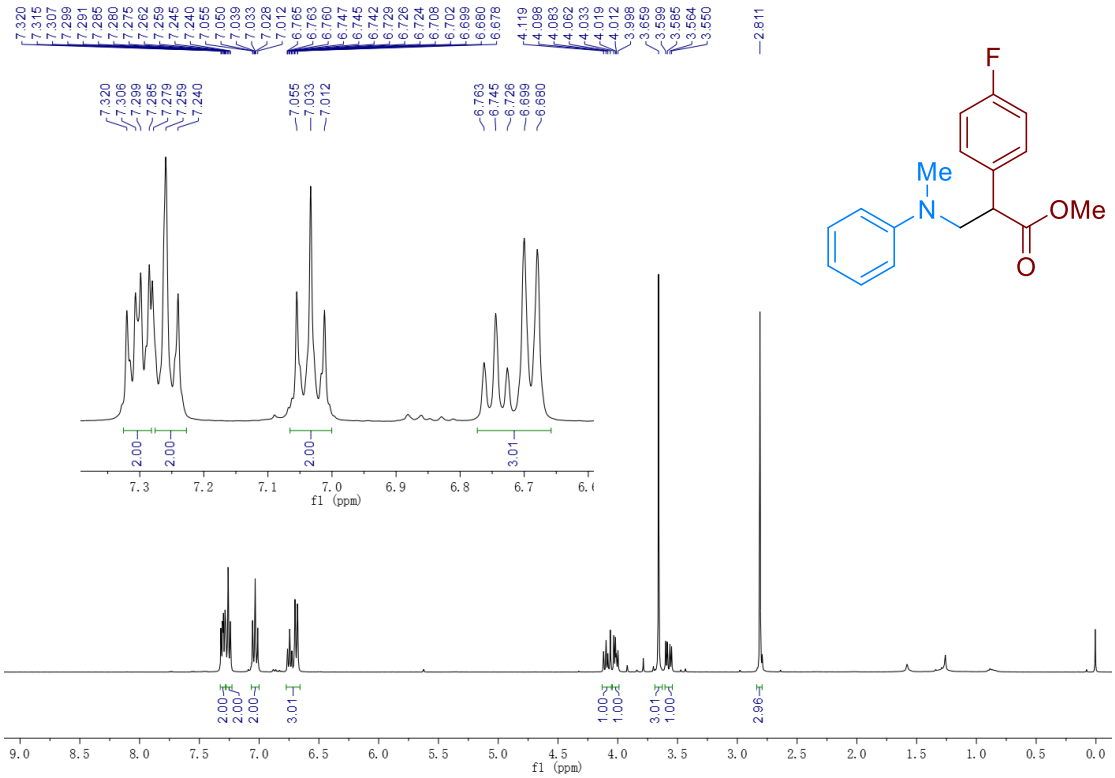
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ga:**



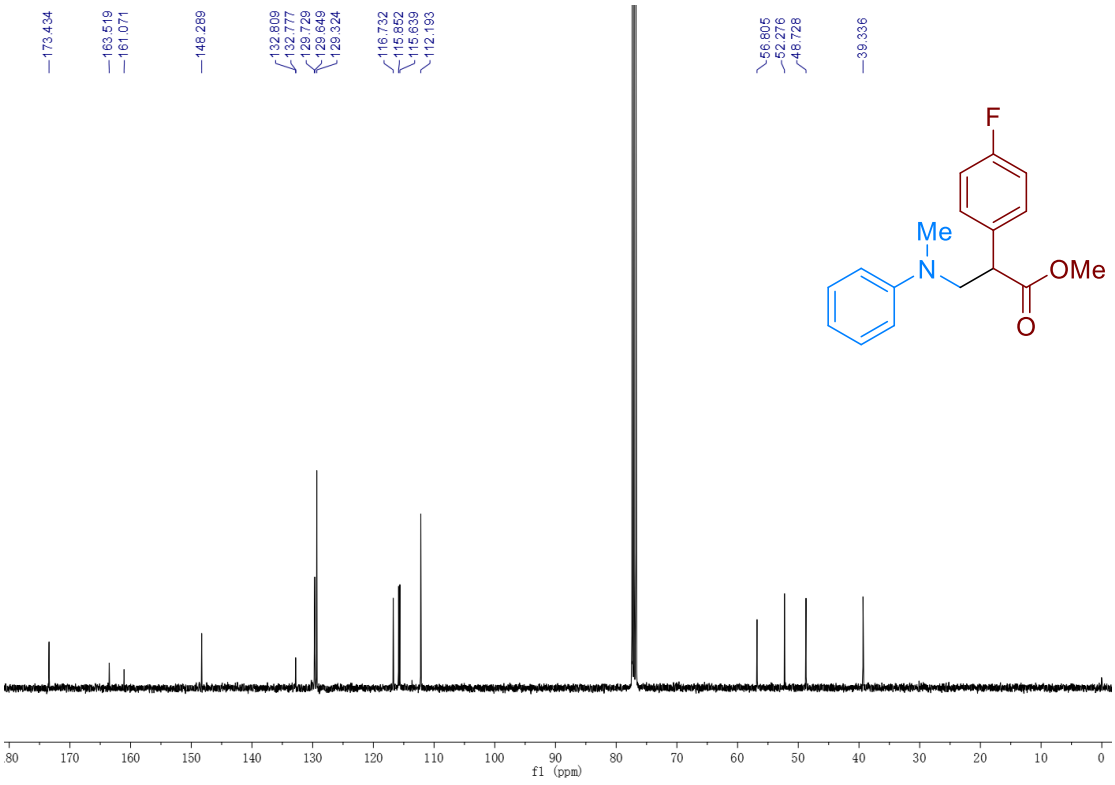
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ga:**



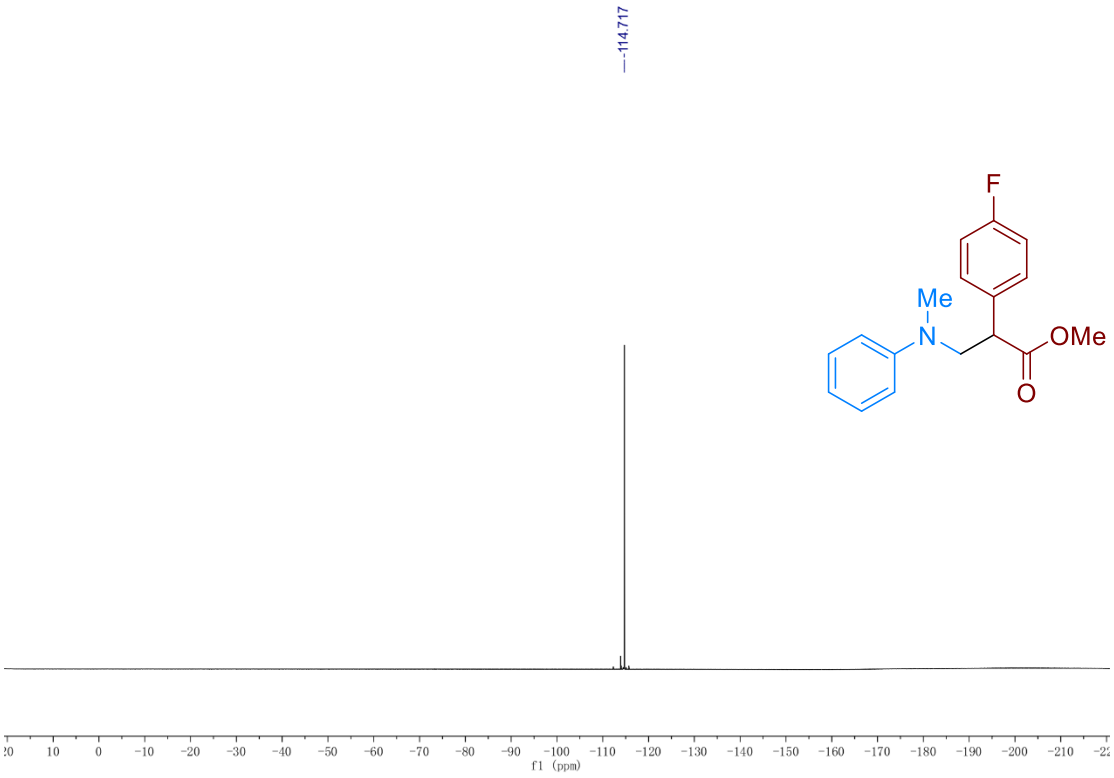
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ha:**



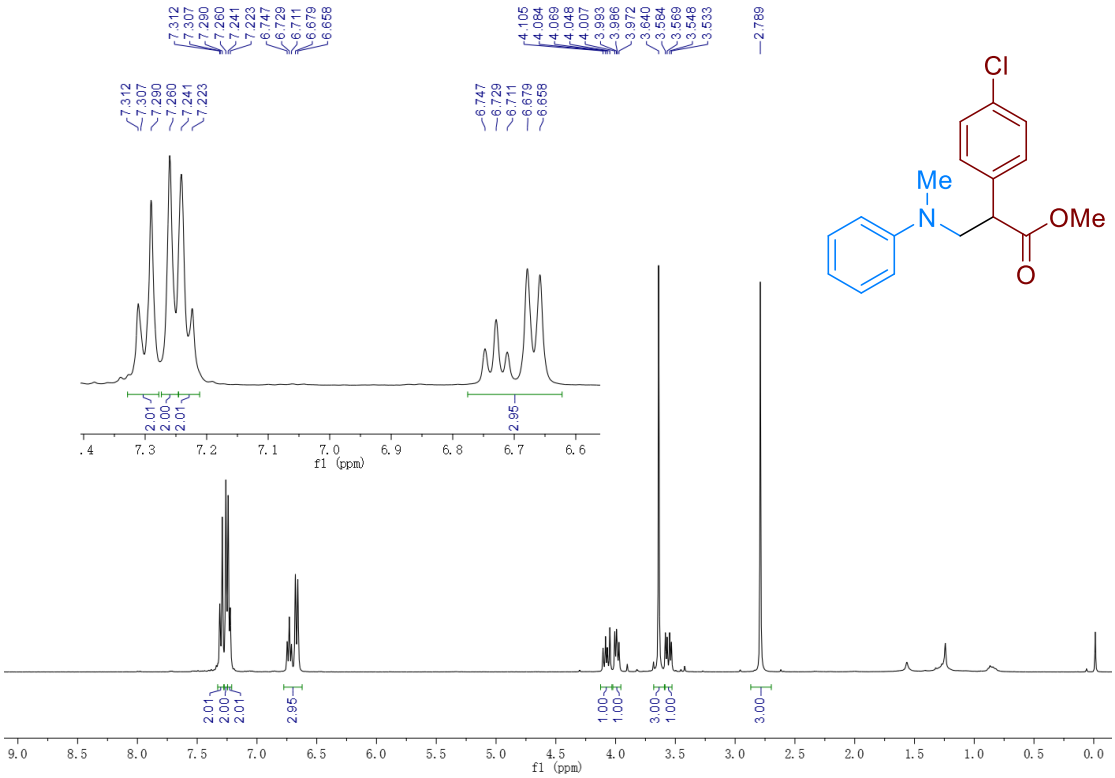
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ha:**



^{19}F NMR (376 MHz, $CDCl_3$) of compound **3ha:**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ia:**



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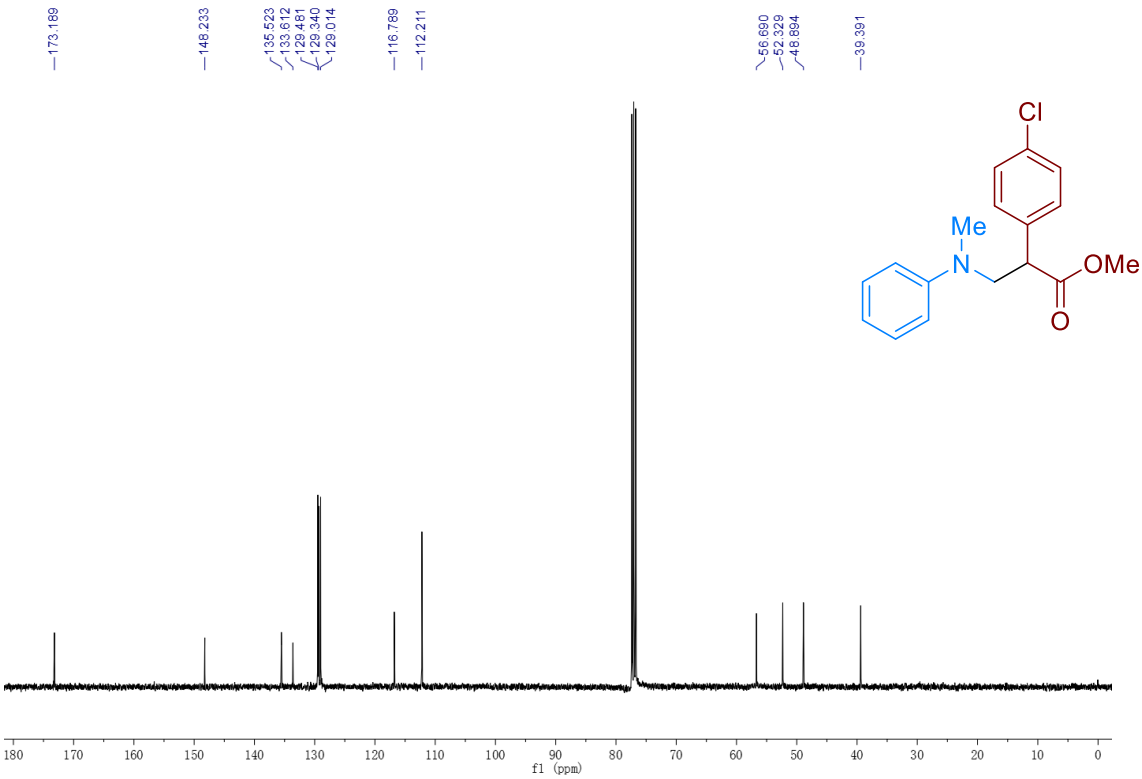

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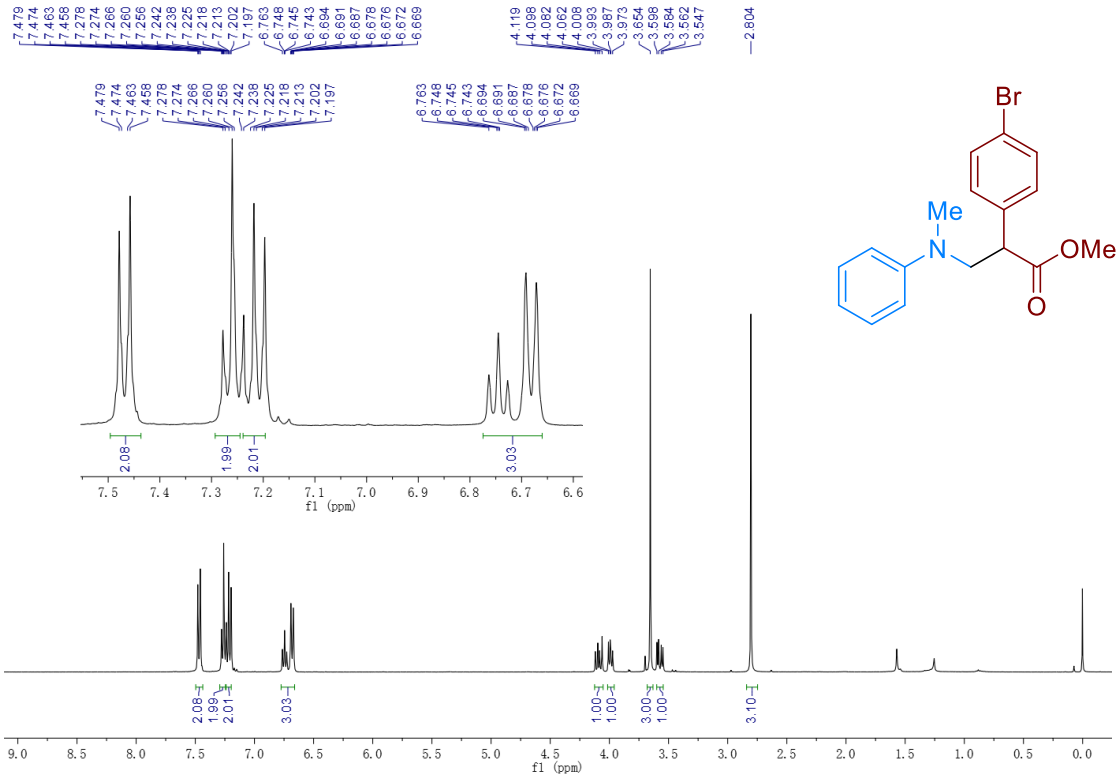

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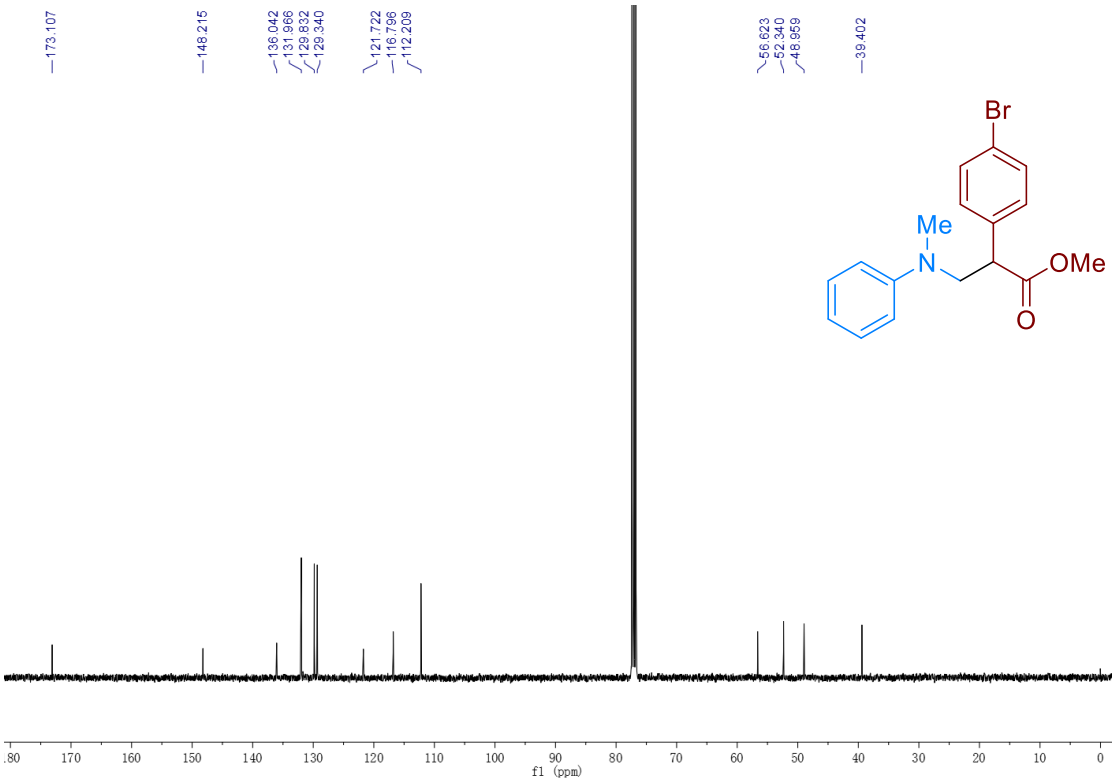

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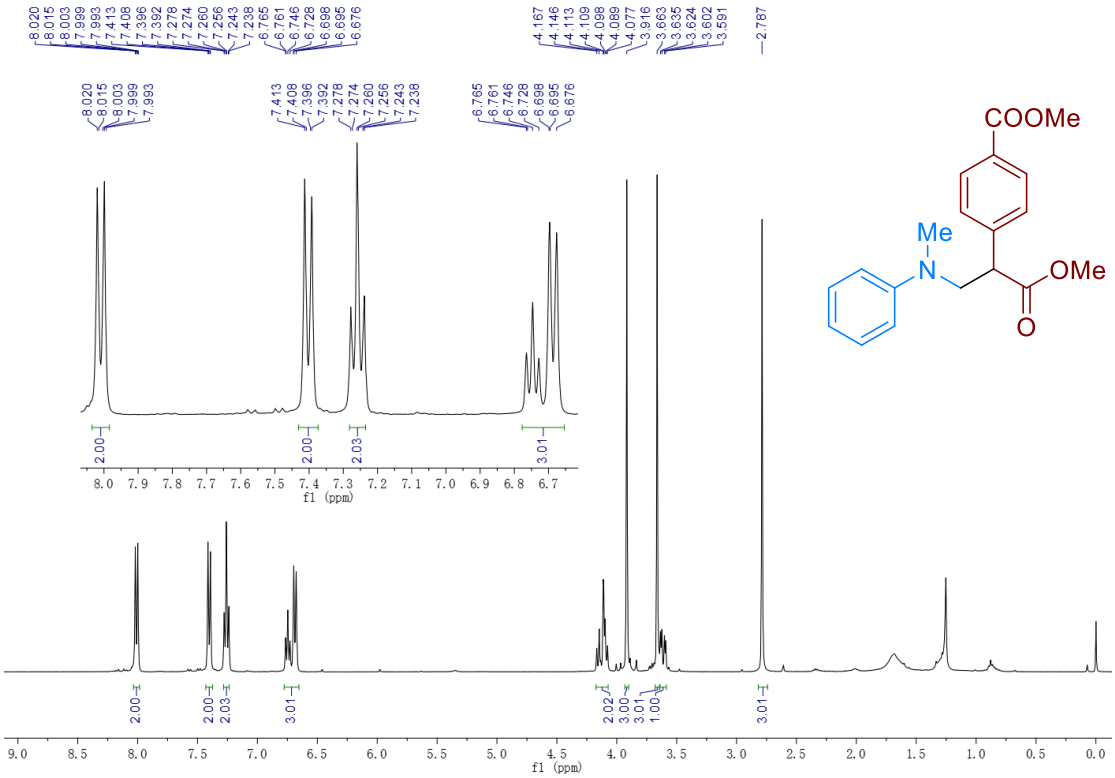

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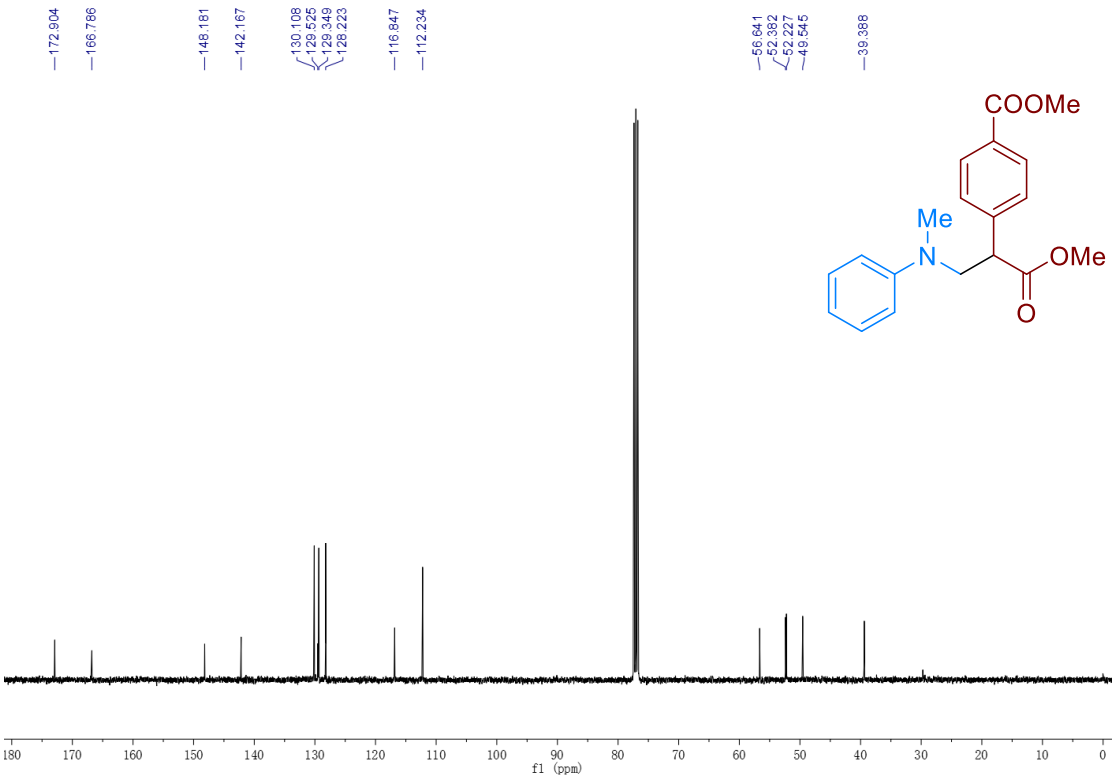
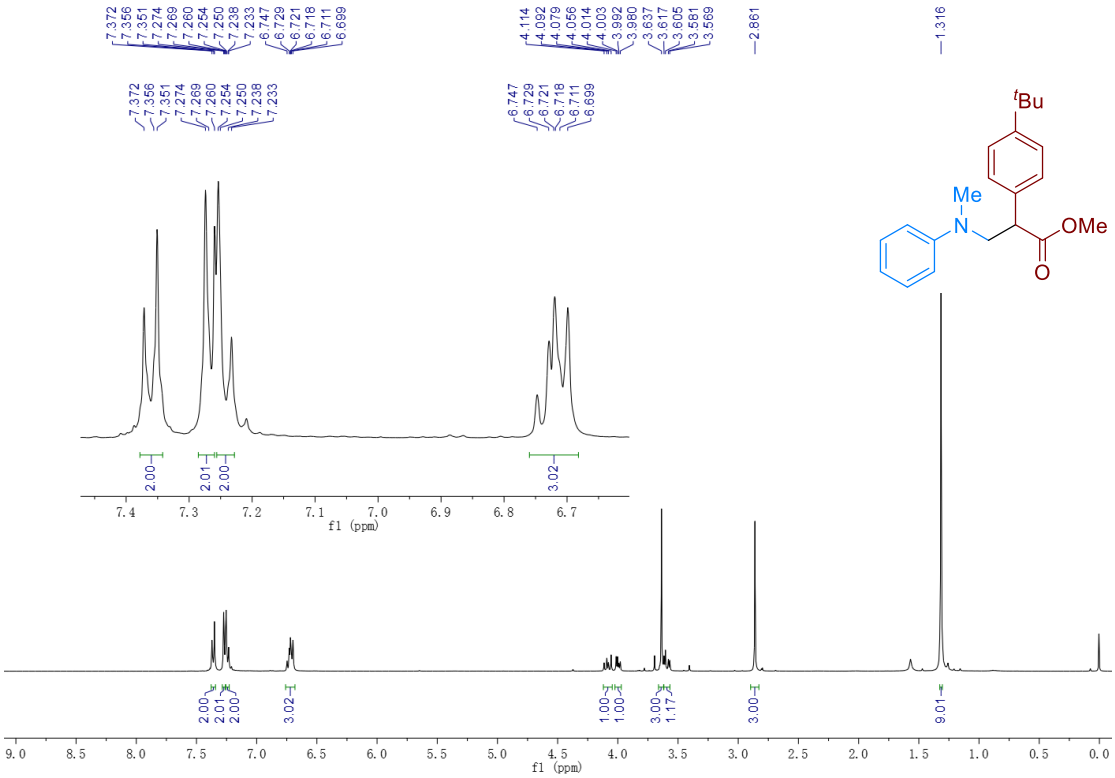


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3la:**



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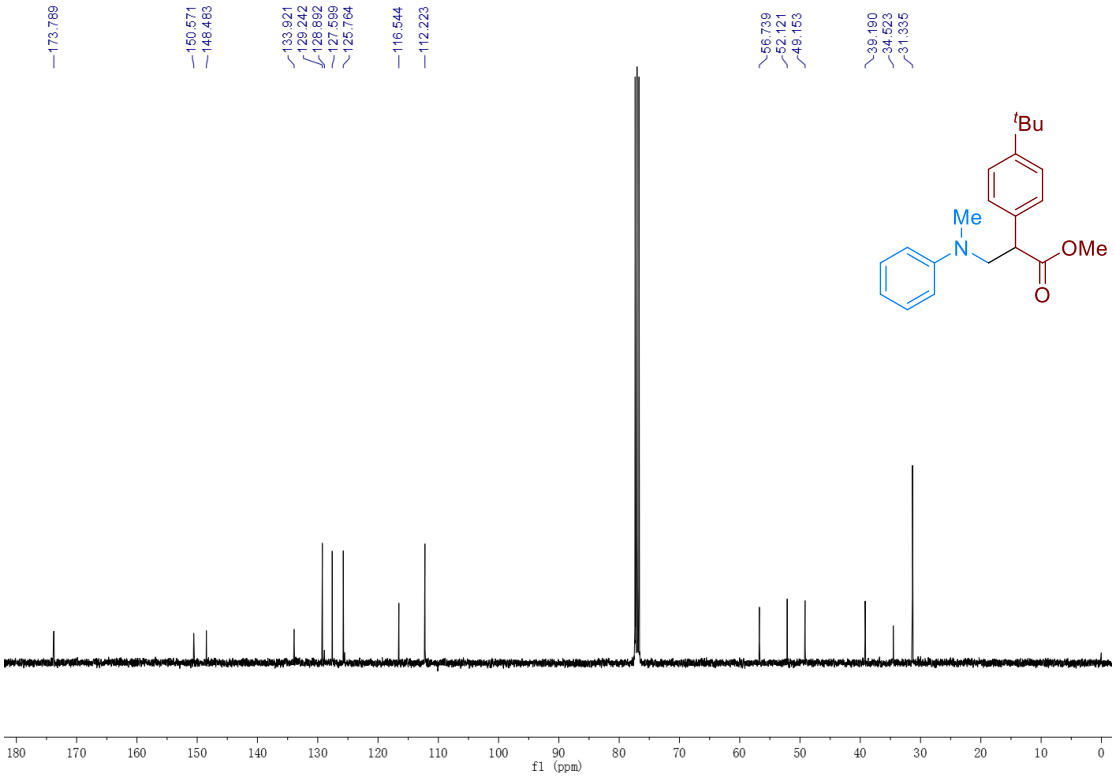

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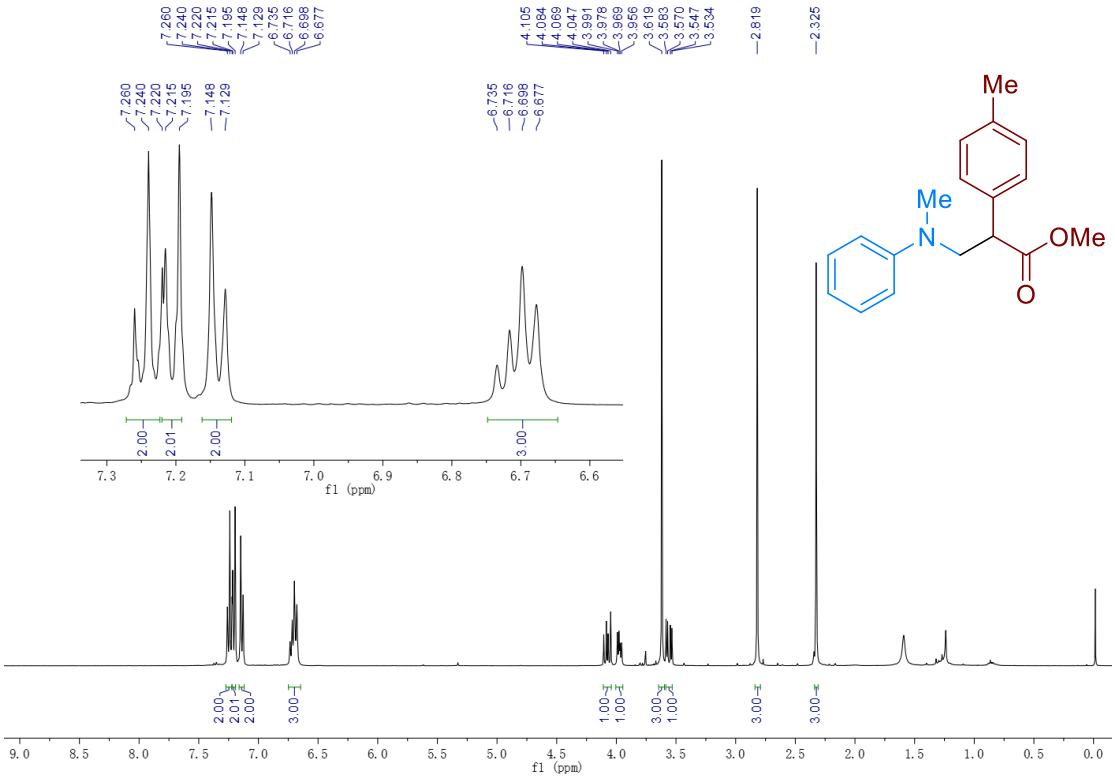

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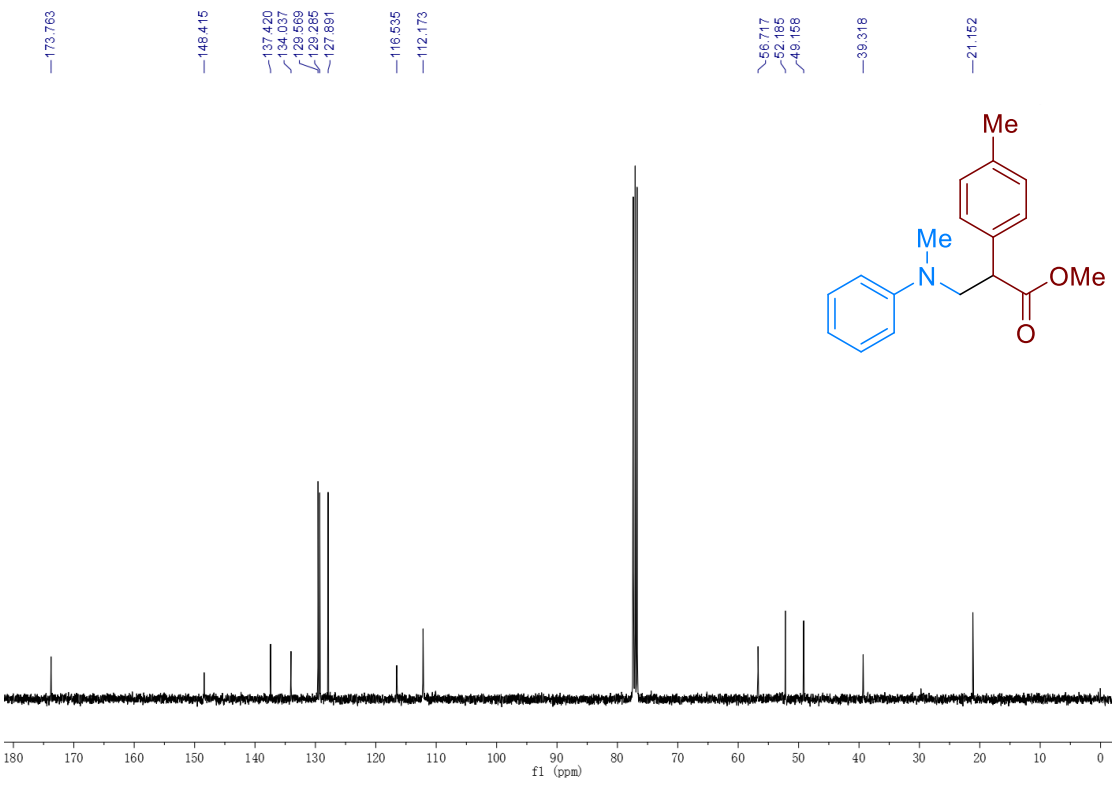
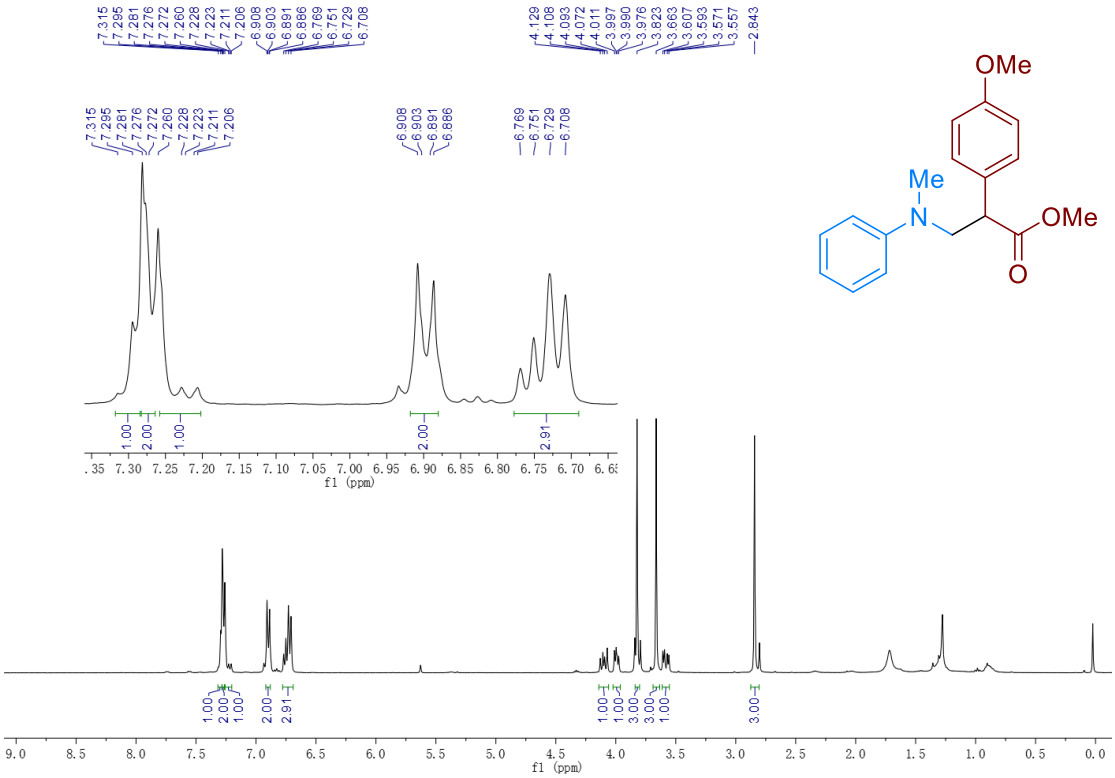


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3na:**



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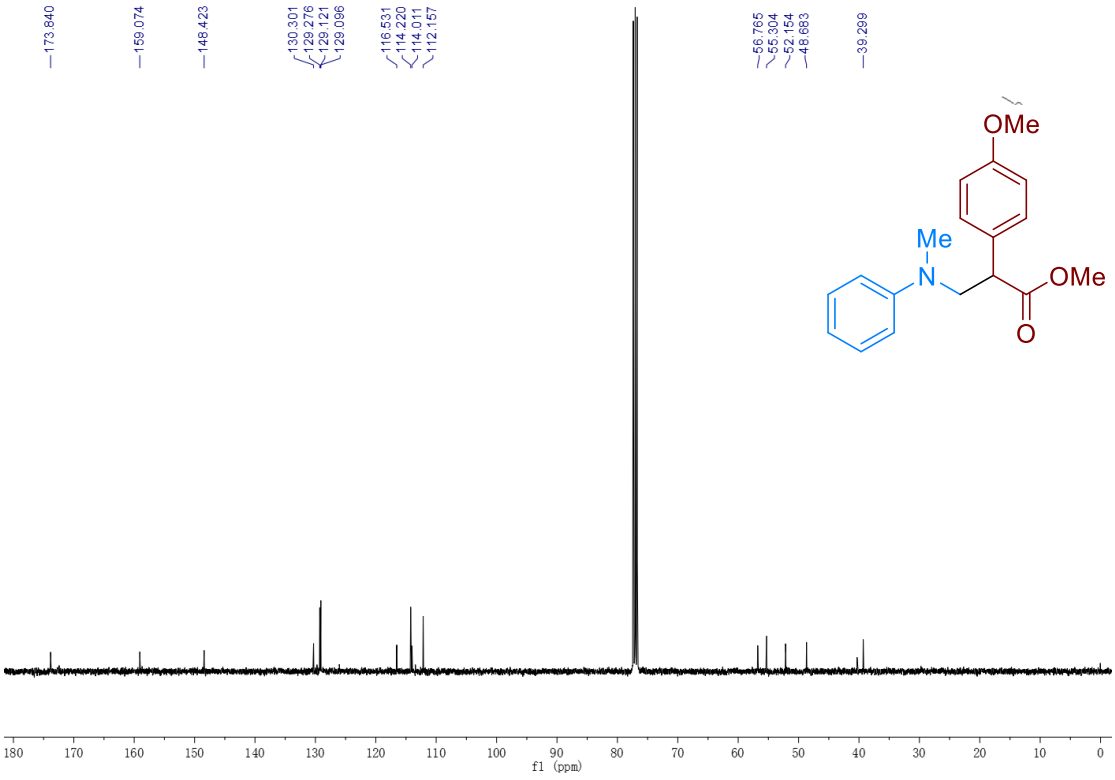

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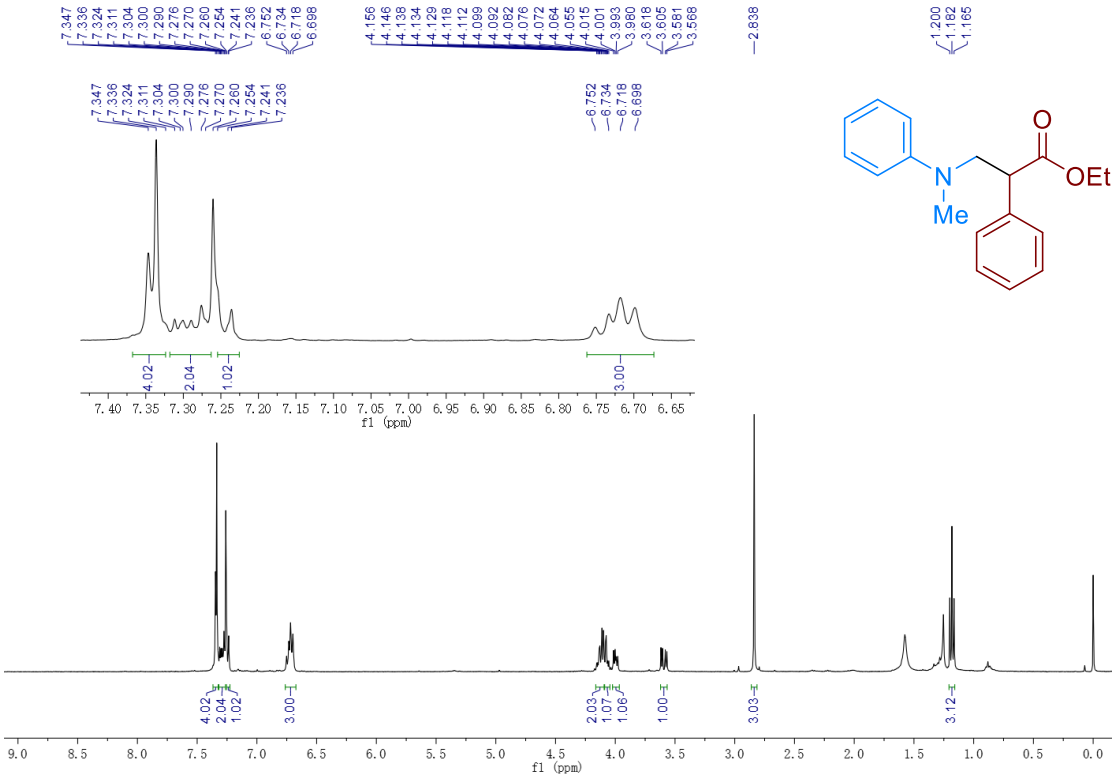
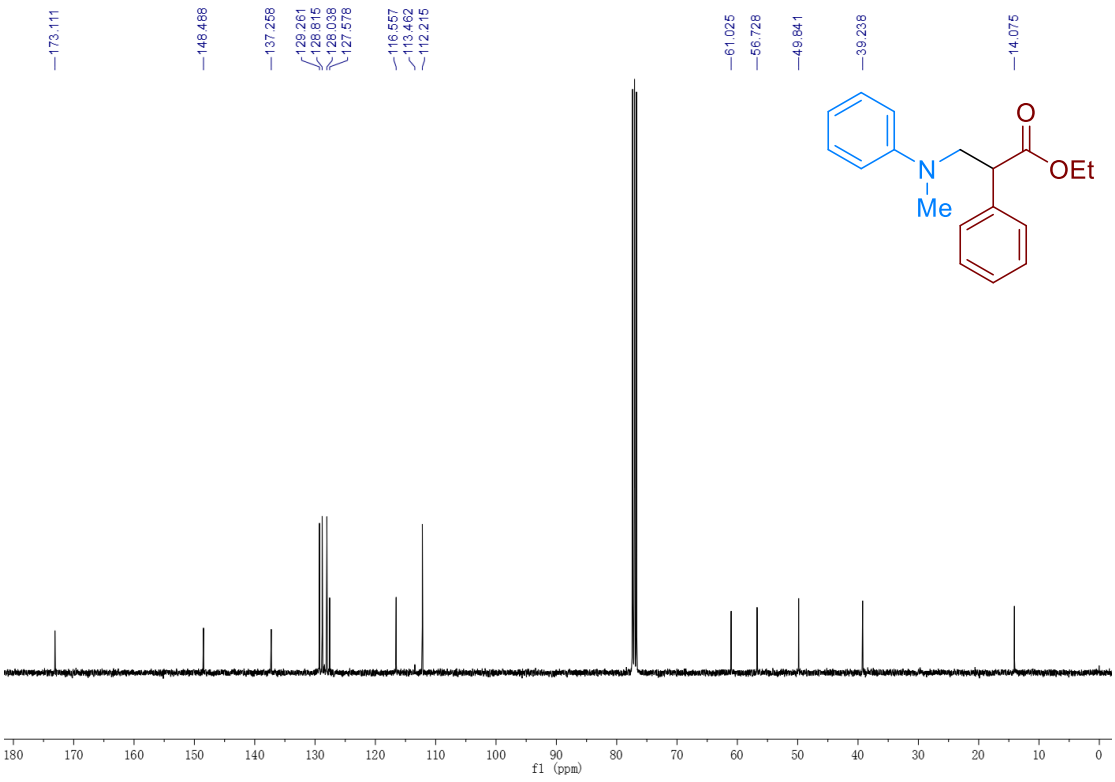
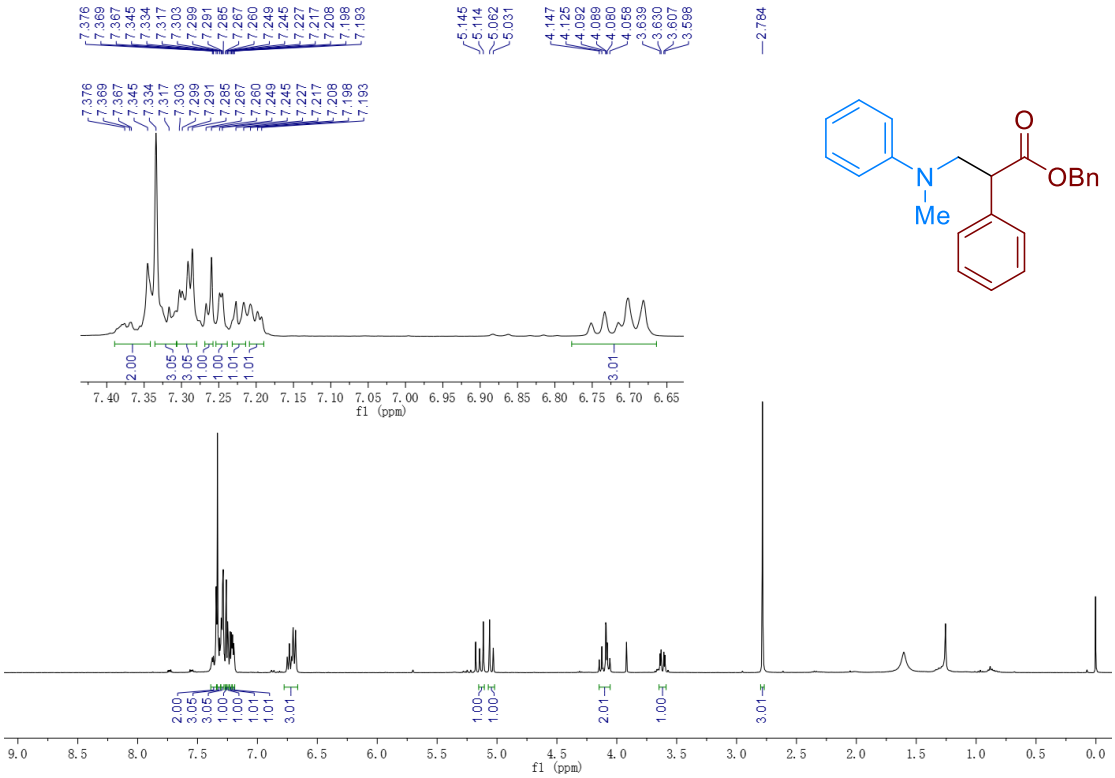


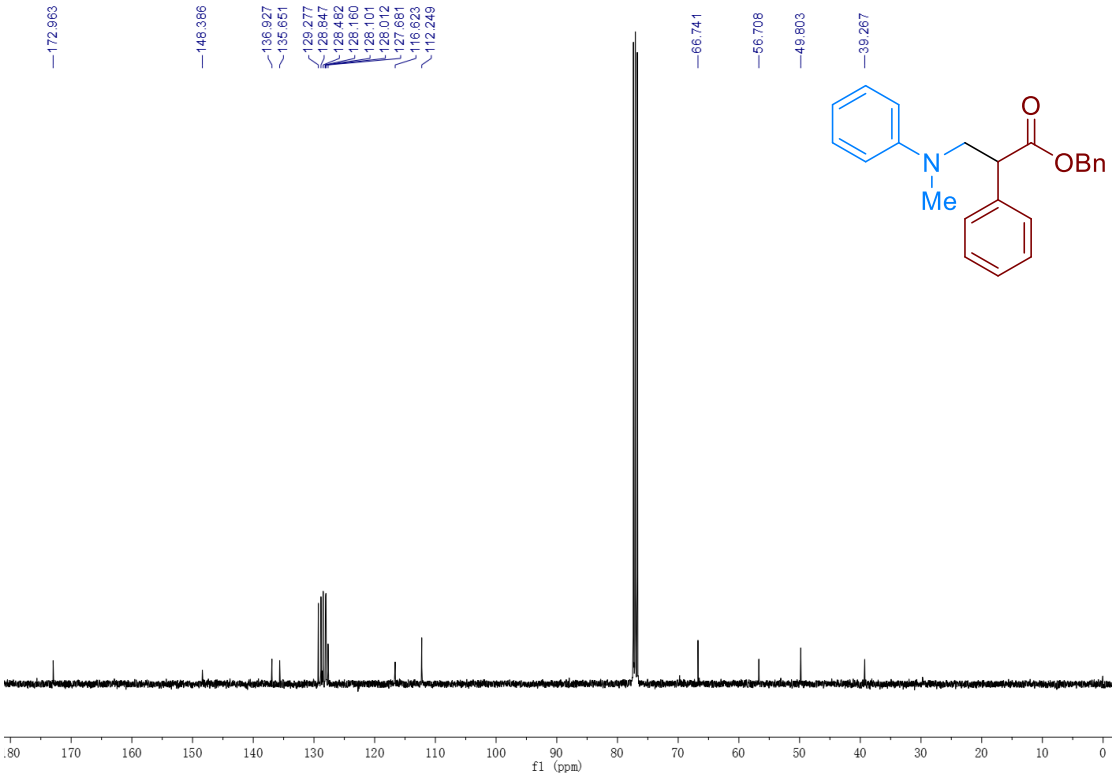
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3oa:**



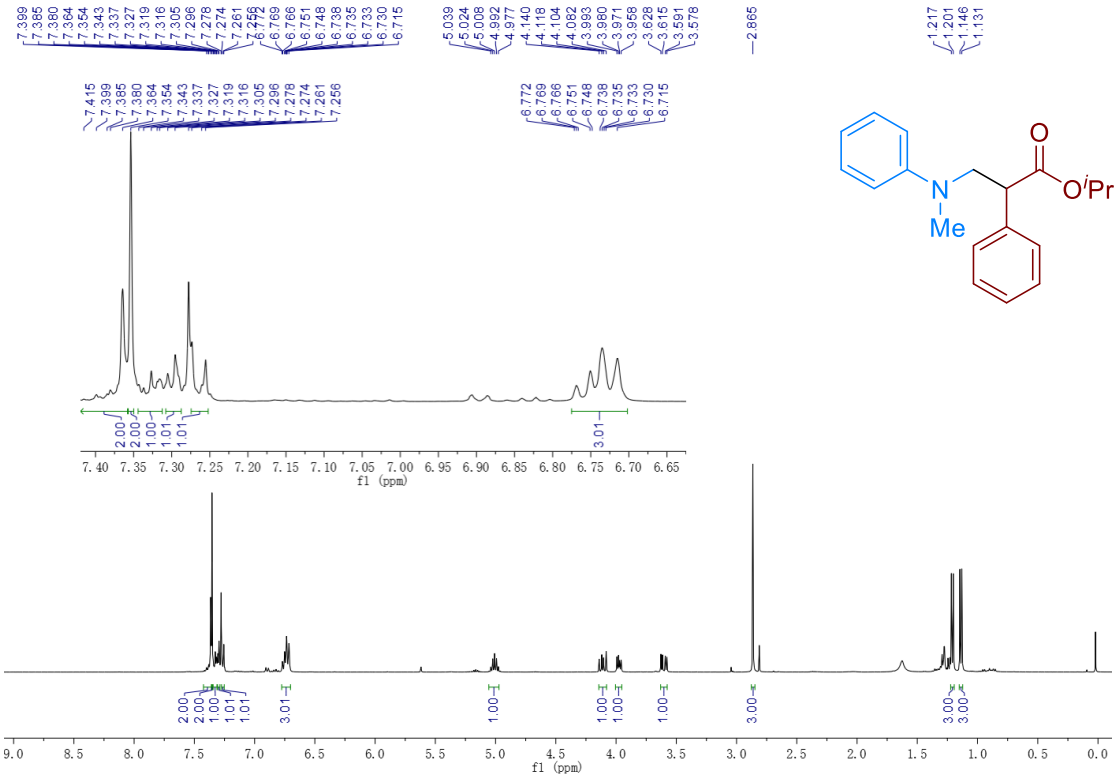
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3pa:**



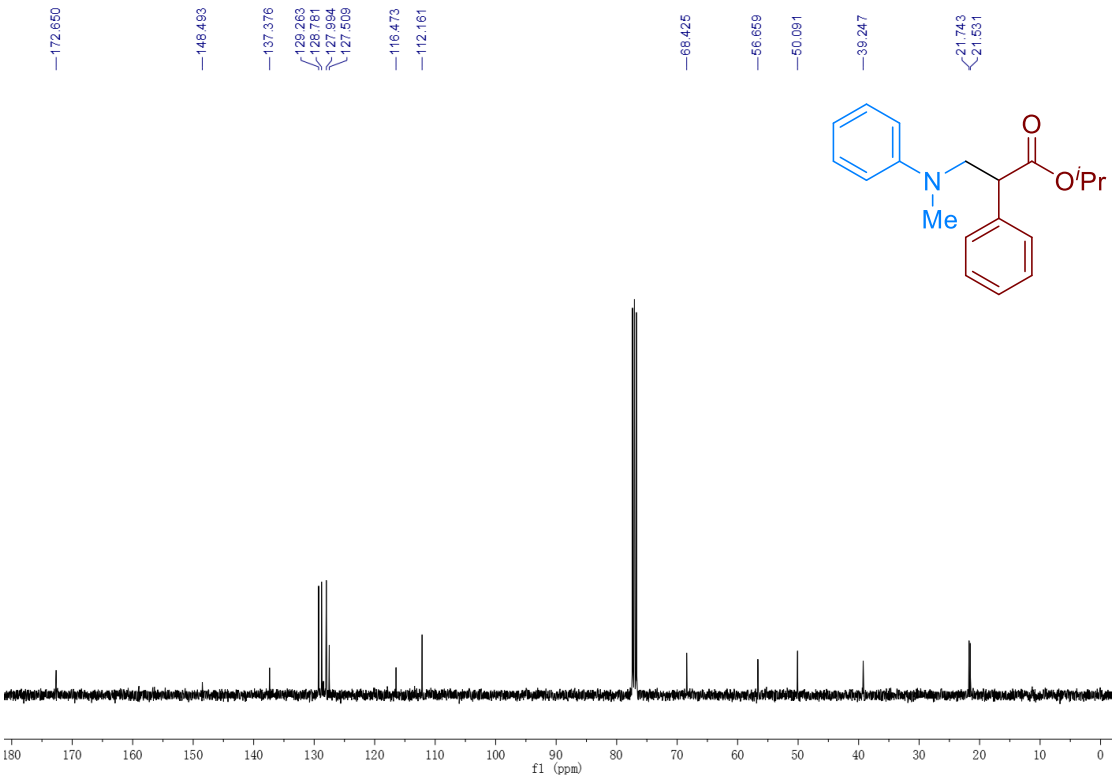
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3pa:**



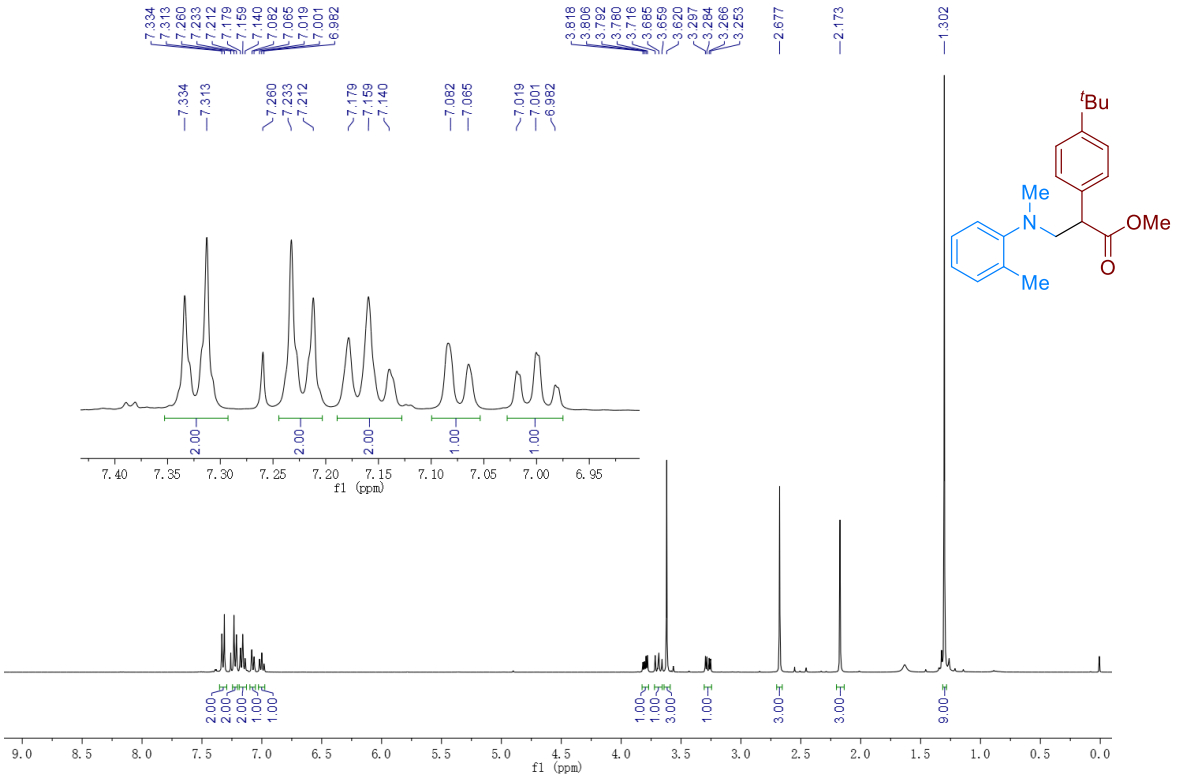
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3qa:**



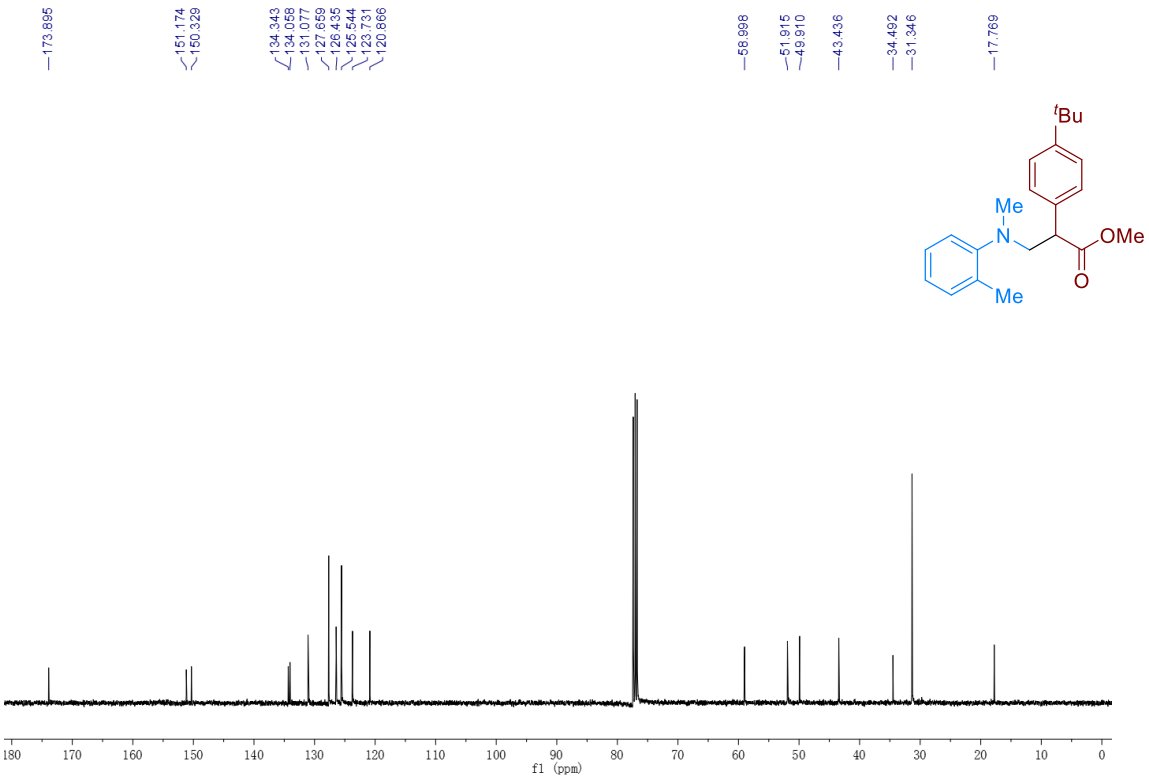
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3qa:**



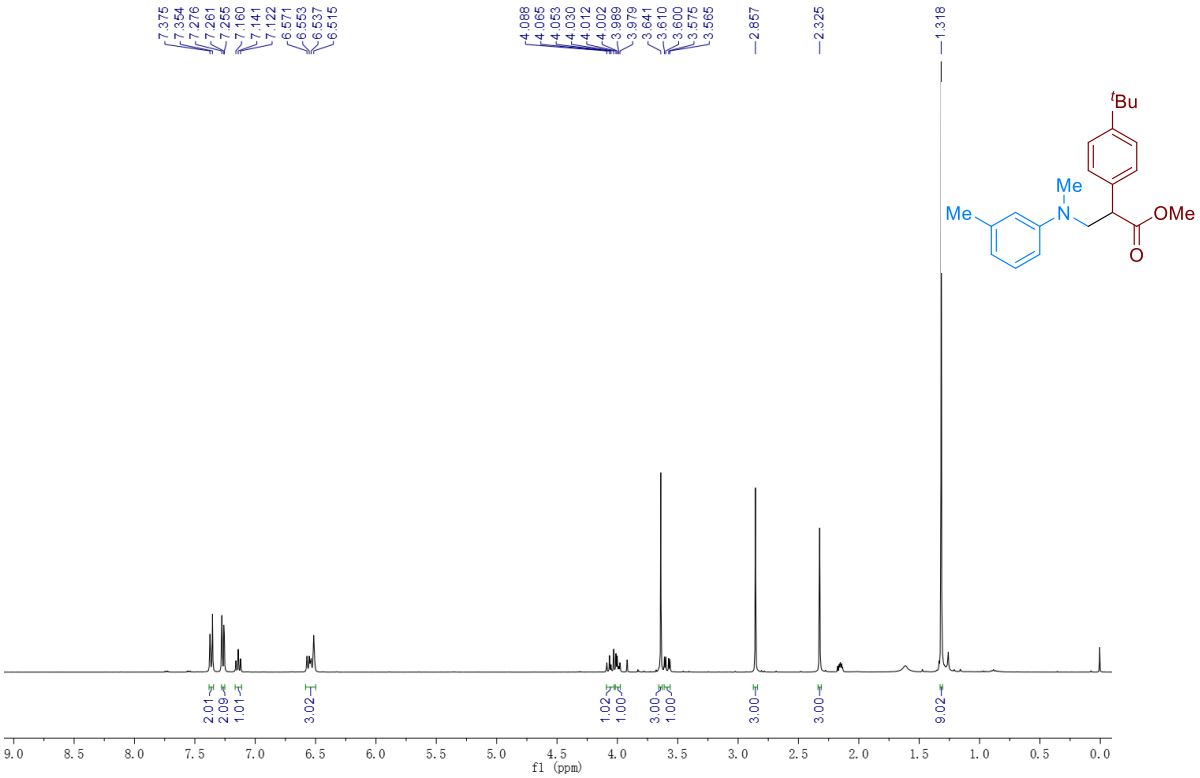
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3lb:**



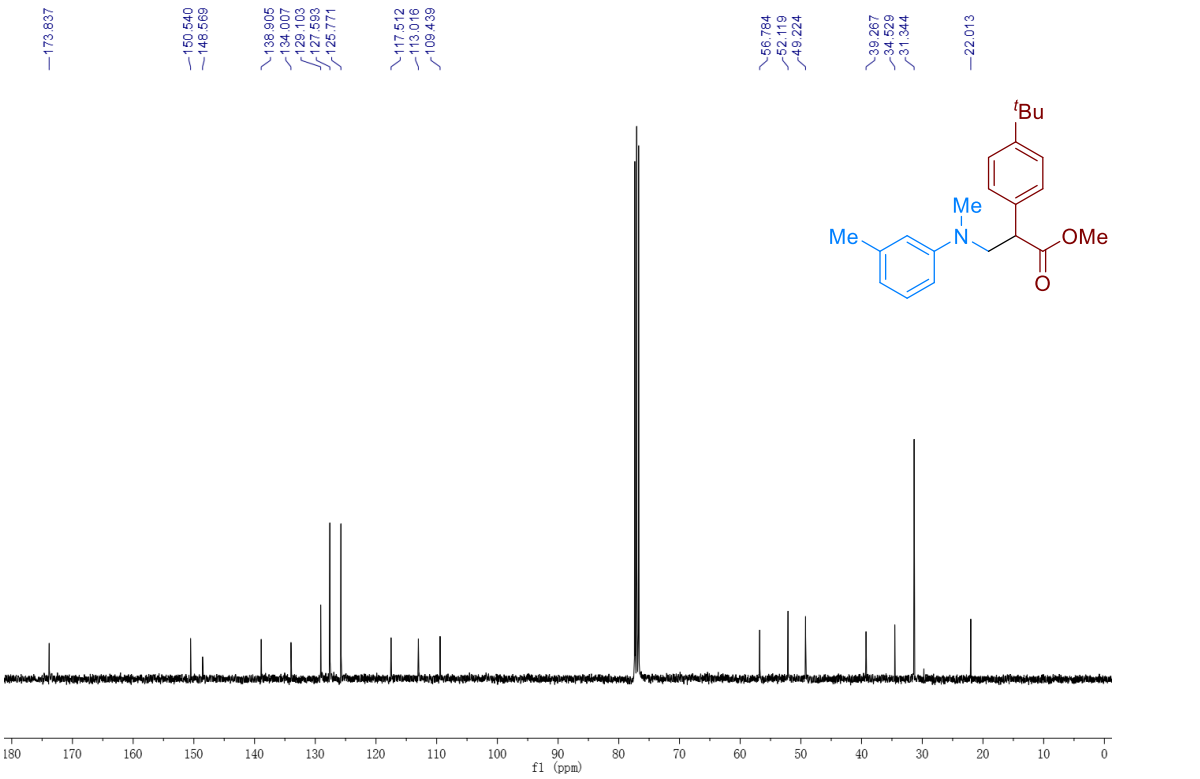
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3lb:**



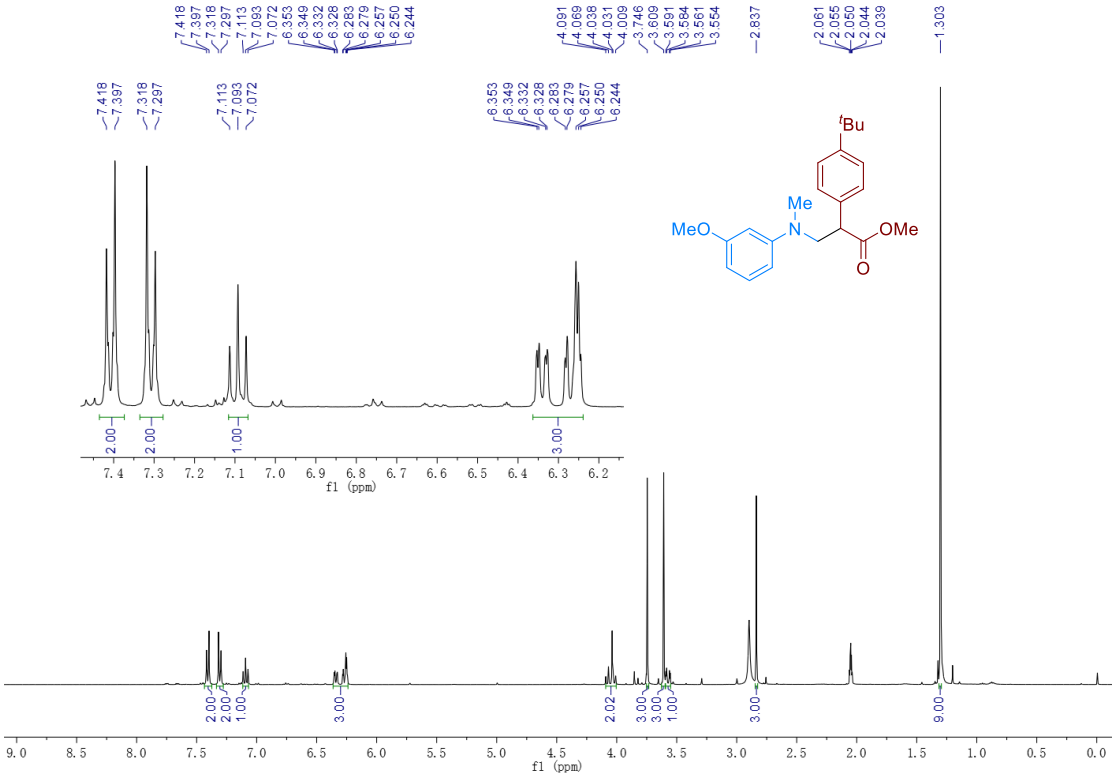
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3lc:**



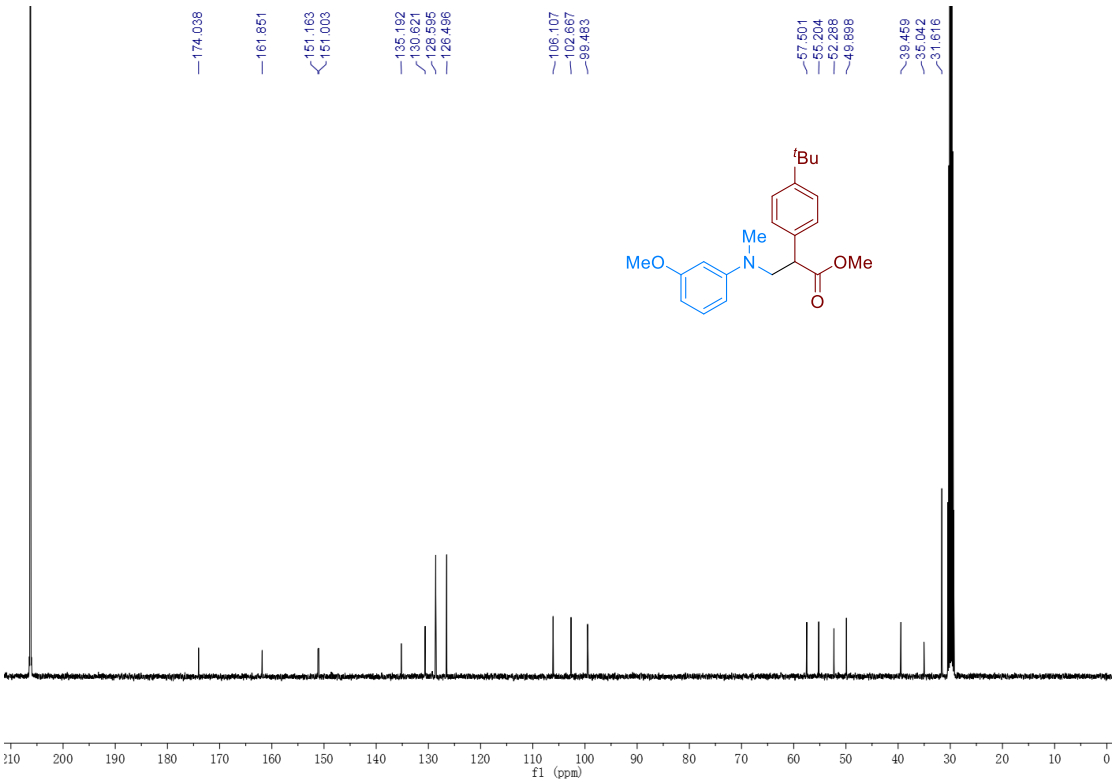
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3lc:**



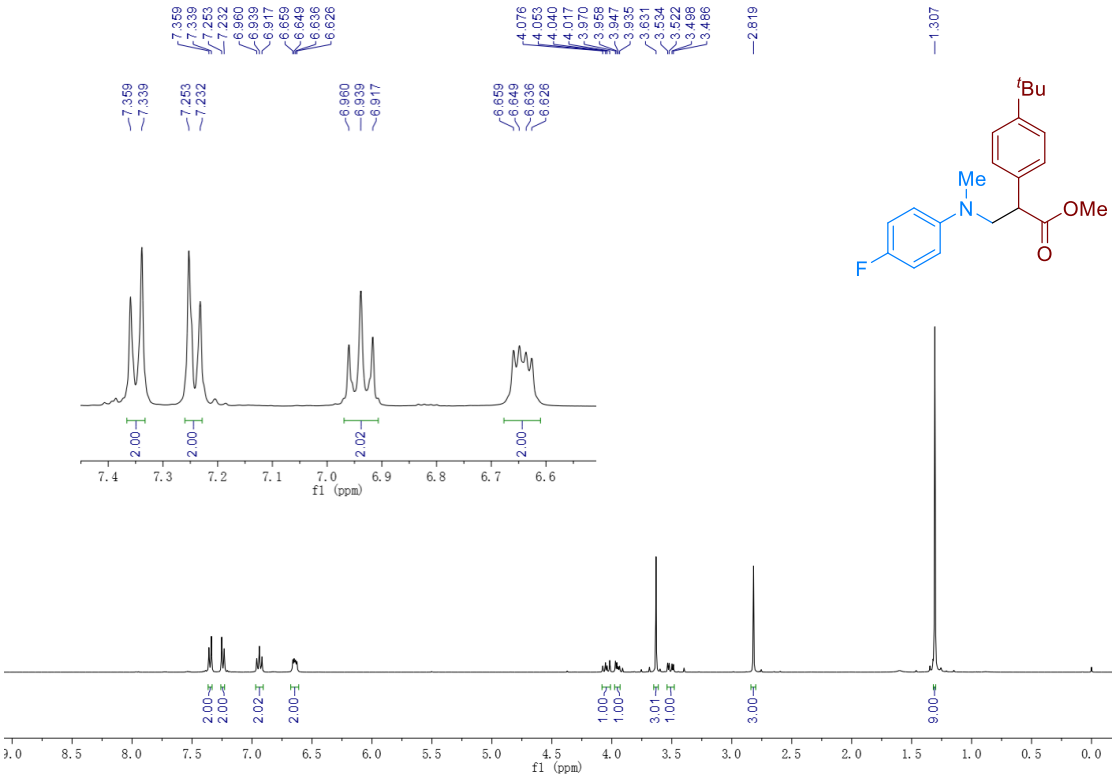
^{1}H NMR (400 MHz, Acetone-d_6) of compound **3ld:**



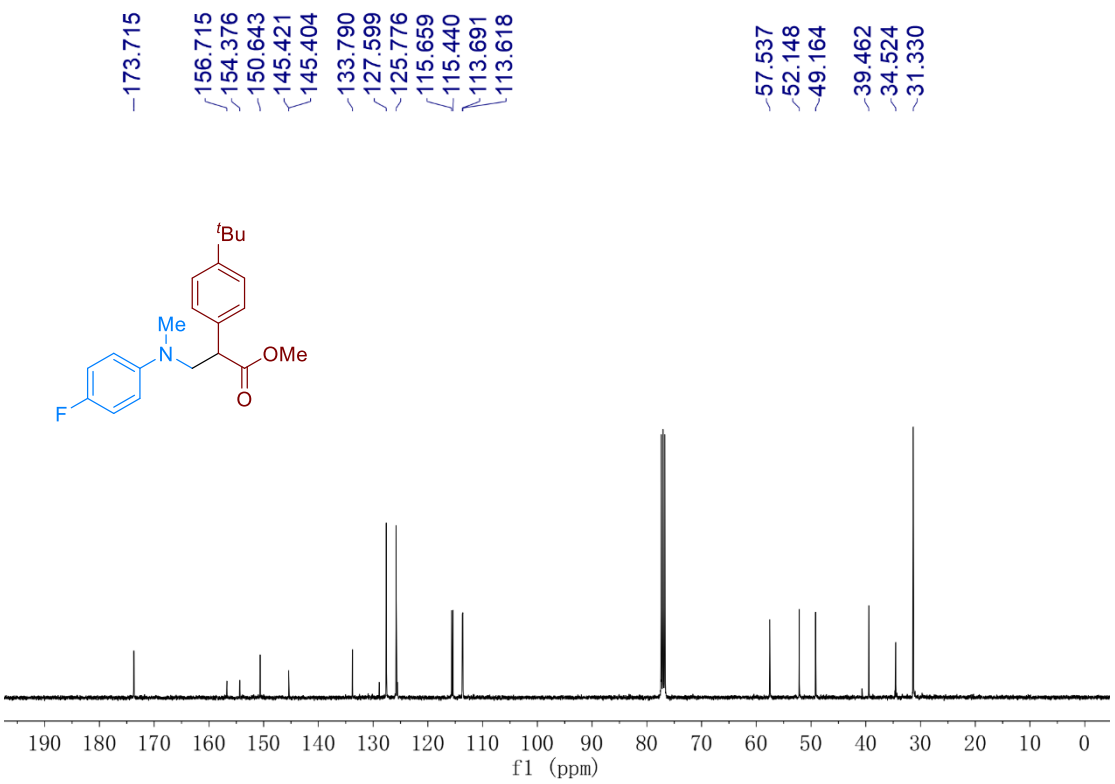
^{13}C NMR (100 MHz, Acetone-d_6) of compound **3ld:**



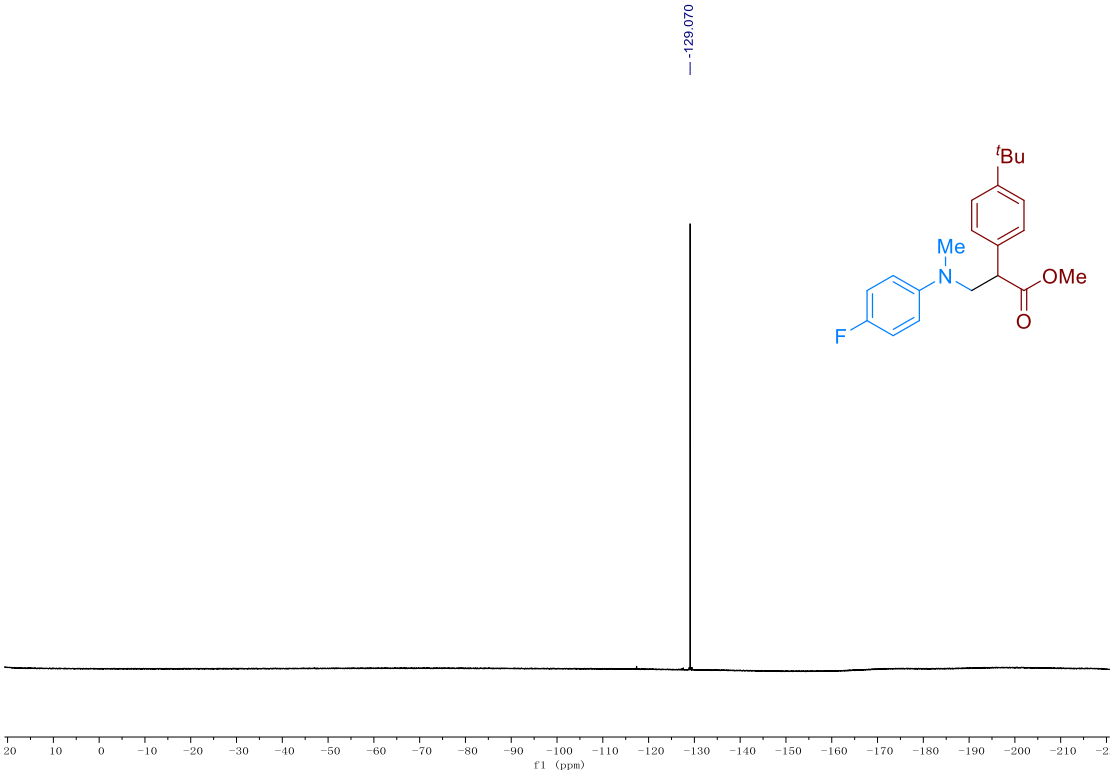
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3le:**



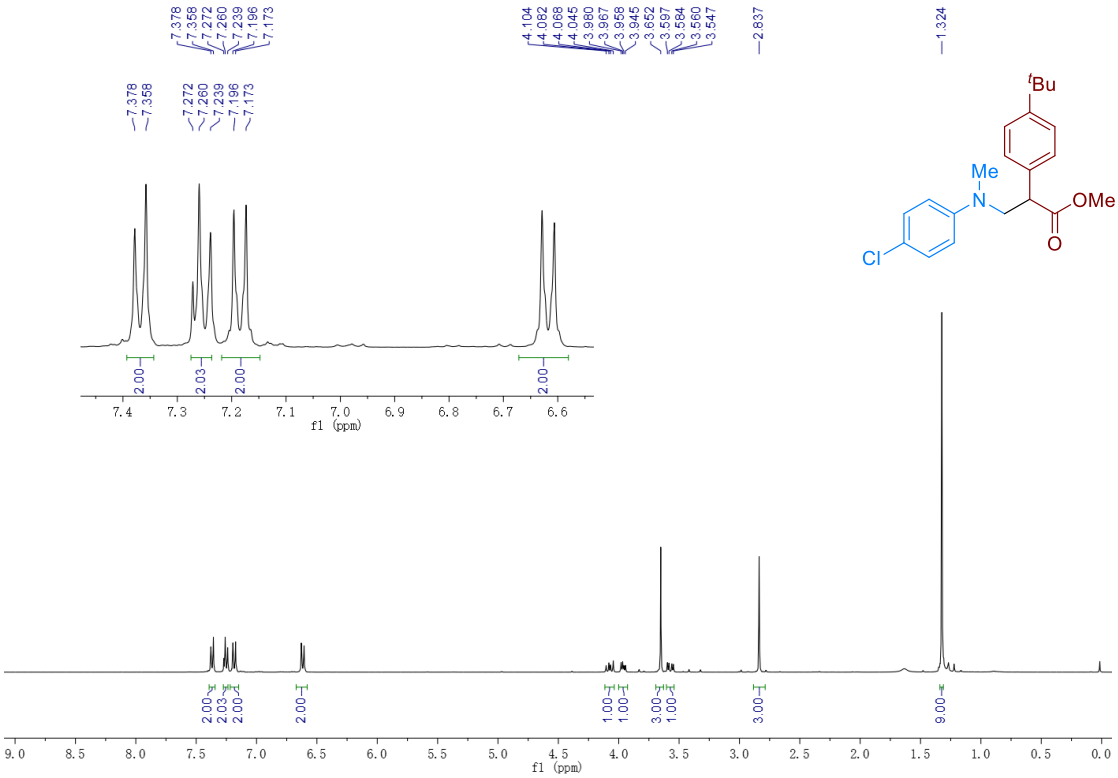
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3le:**



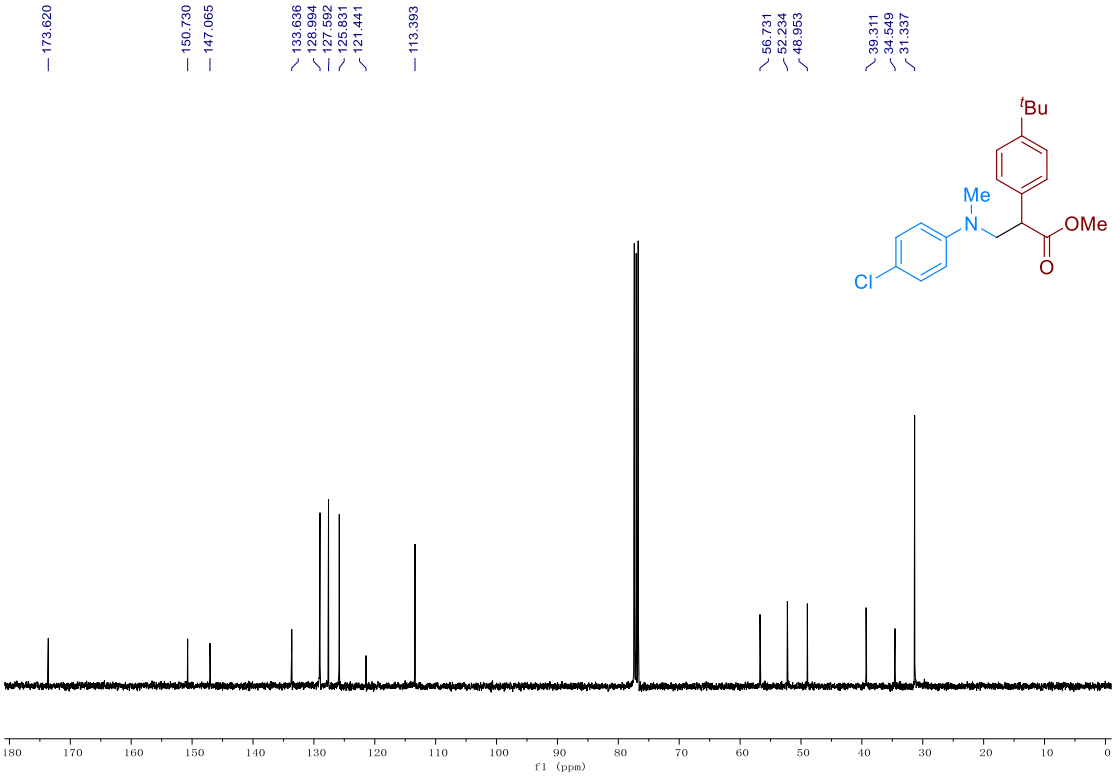
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3le:**



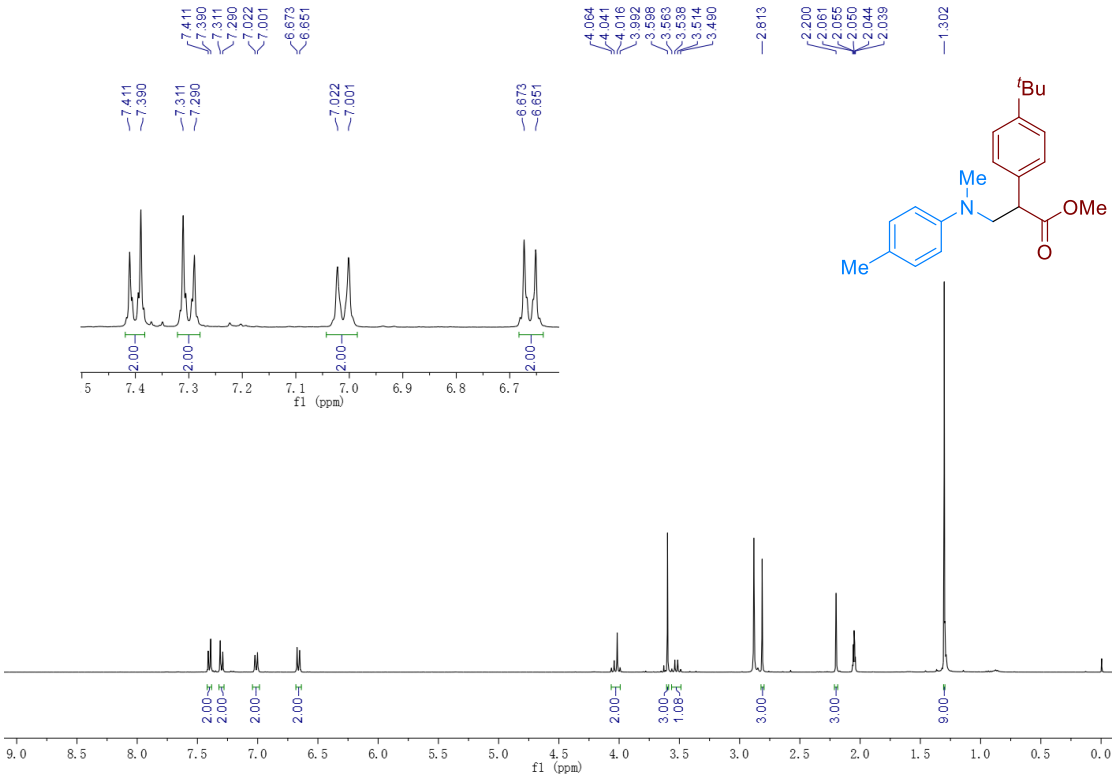
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3lf:**



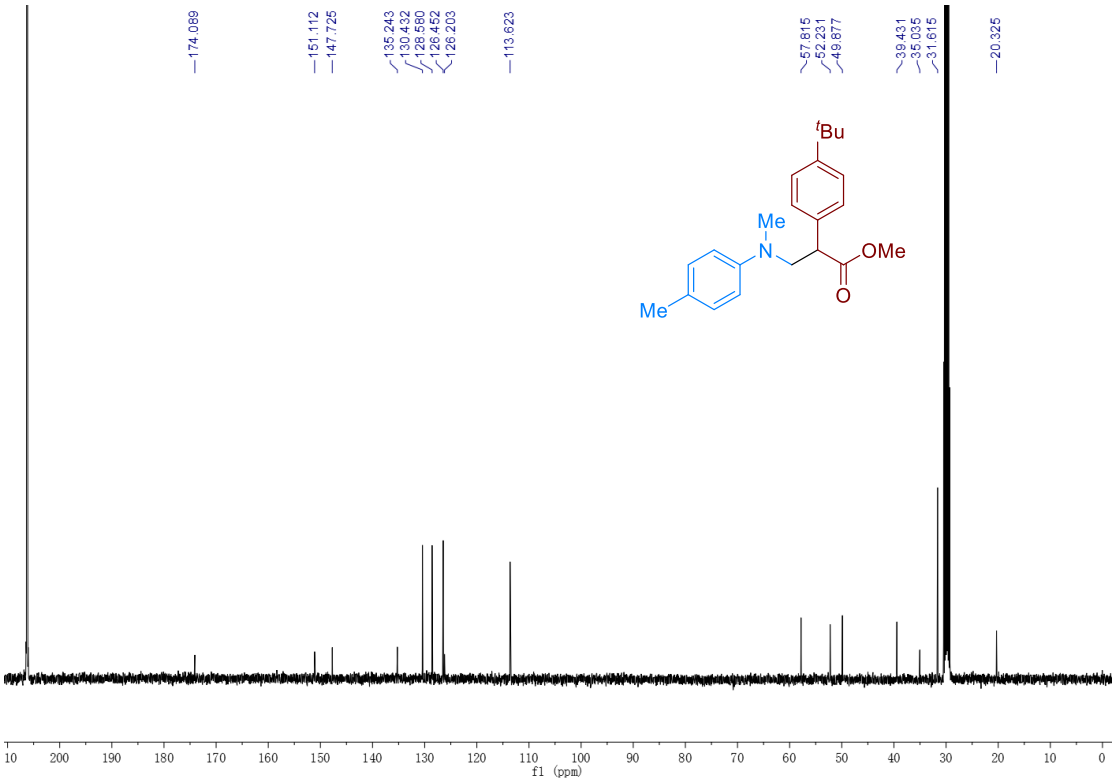
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3lf:**



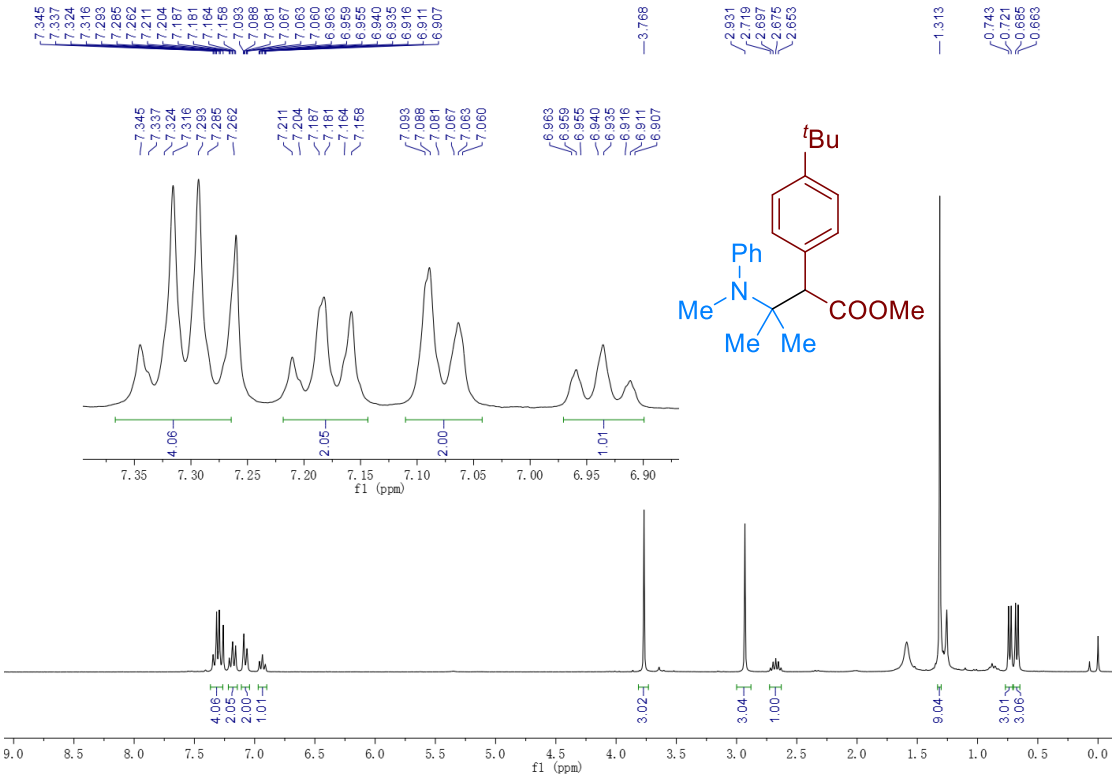
^{1}H NMR (400 MHz, Acetone-d_6) of compound **3lg:**



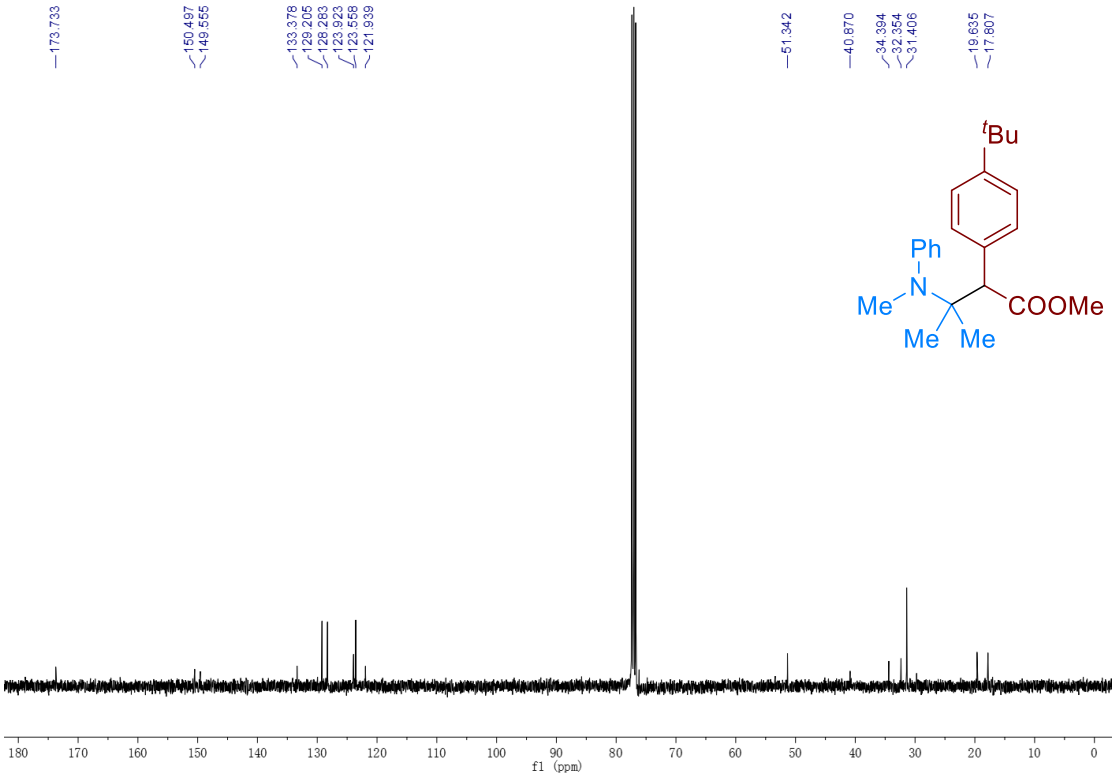
^{13}C NMR (100 MHz, Acetone-d_6) of compound **3lg:**



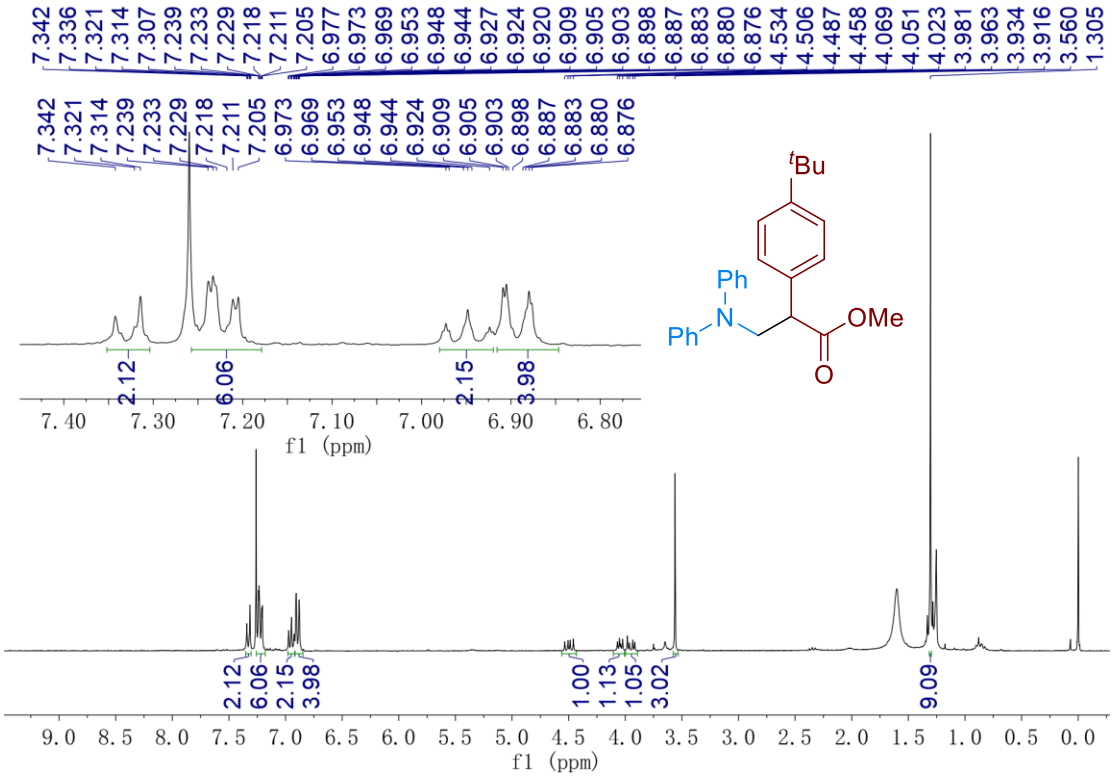
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3lh:**



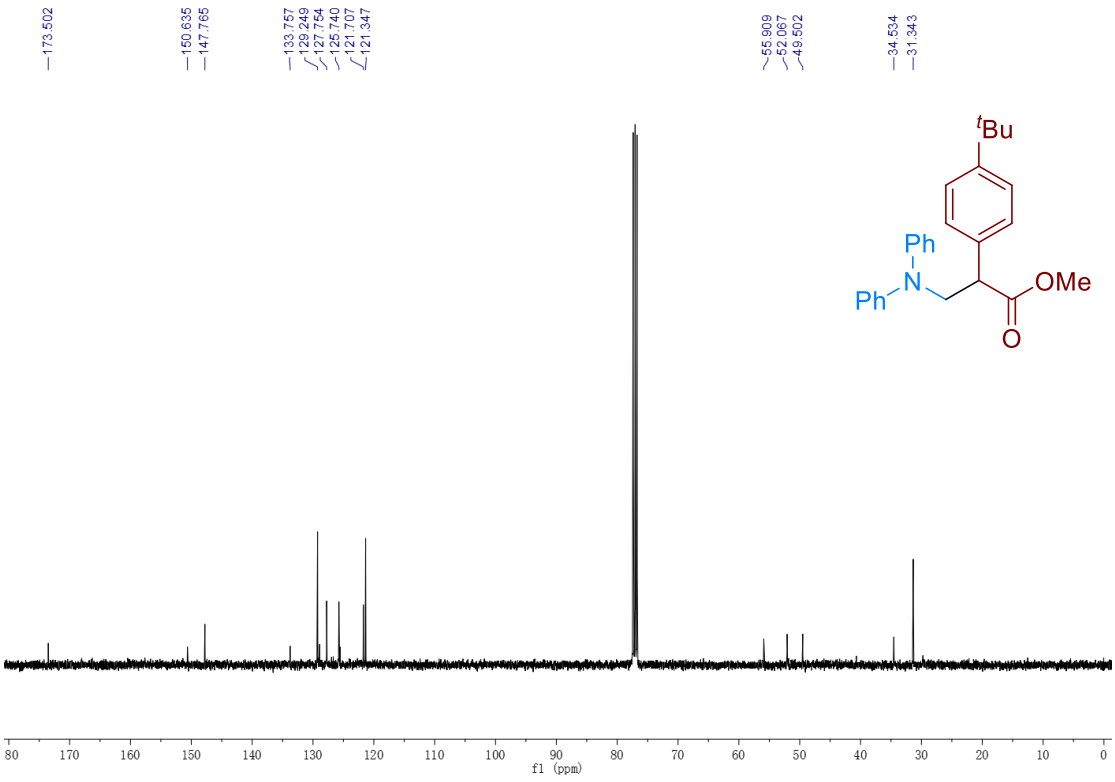
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3lh:**



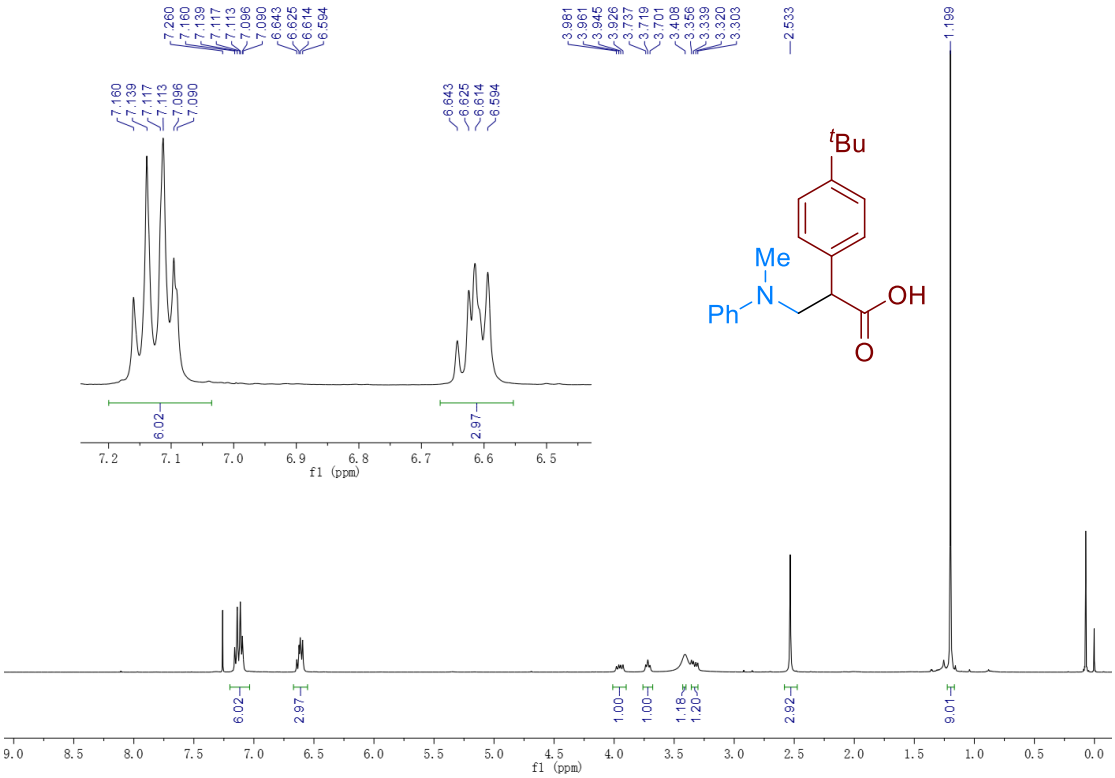
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3li:**



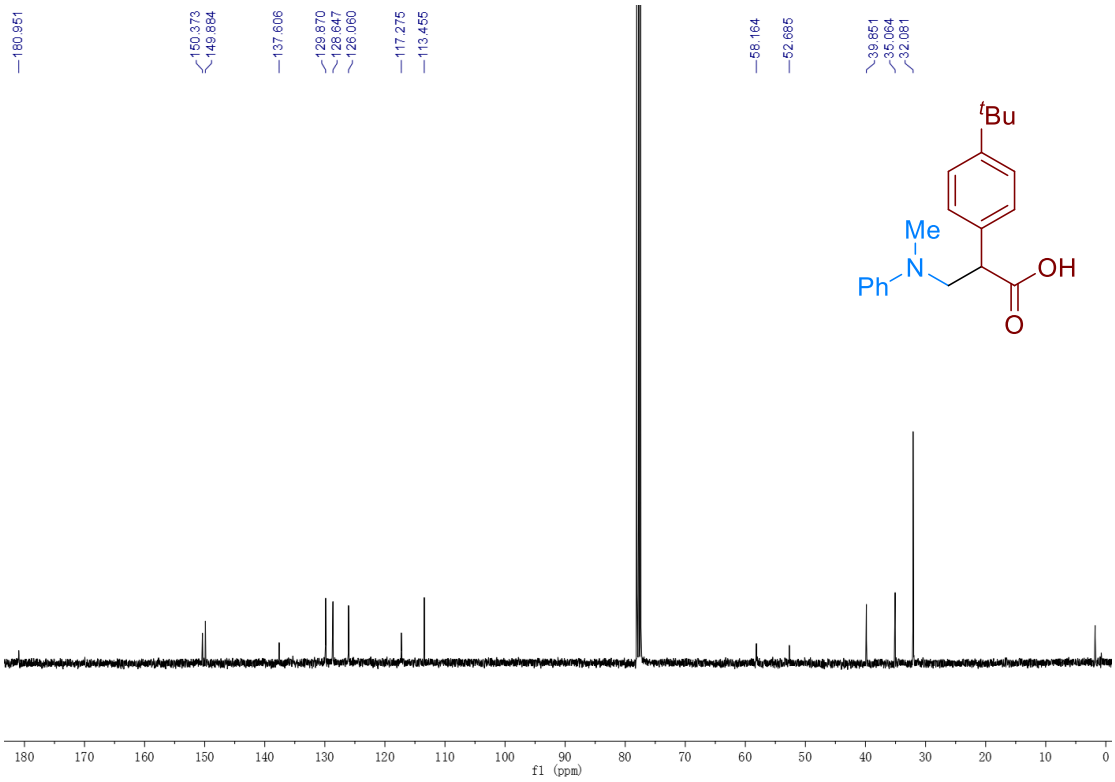
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3li:**



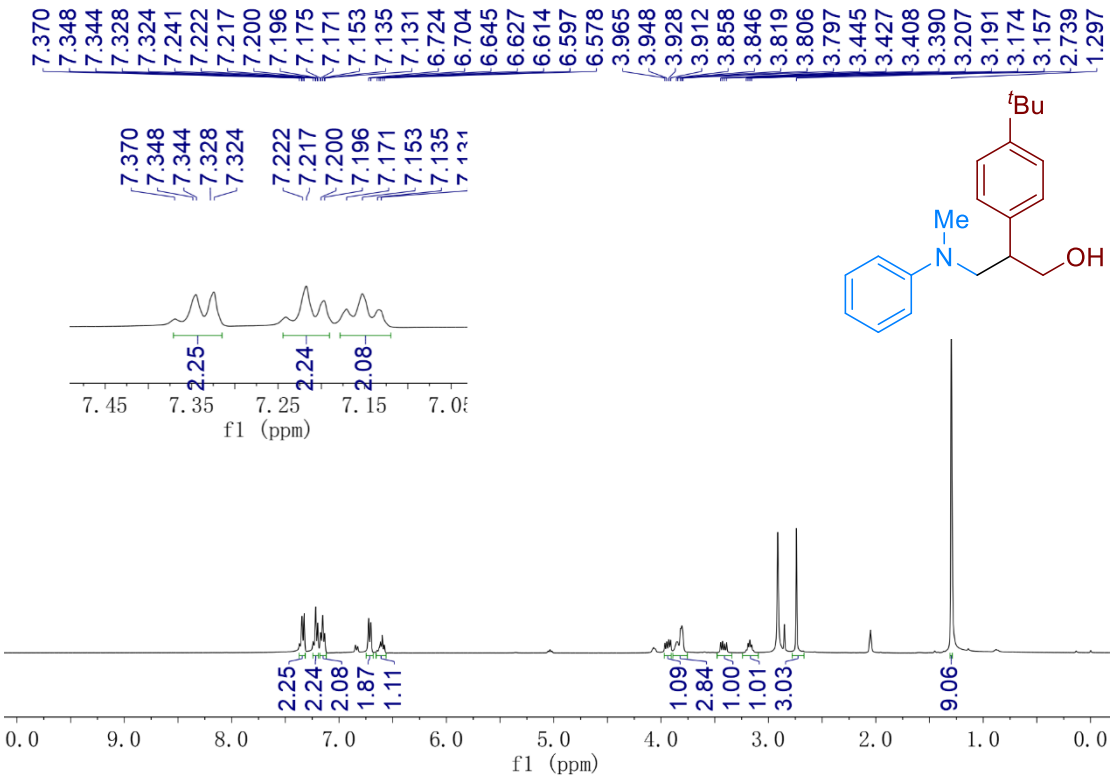
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4:**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **4:**



^{1}H NMR (400 MHz, Acetone-d_6) of compound **5:**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **5:**