

Supporting Information

**Visible light-induced Ni-catalyzed C–heteroatom cross-coupling of aryl
halides via LMCT with DBU to access a Ni(I)/Ni(III) cycle**

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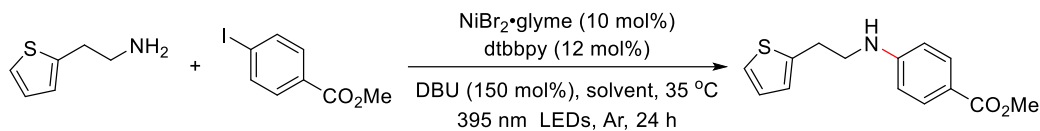
1. General Information

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity $\geq 99.999\%$) unless otherwise mentioned. Commercial reagents were purchased from Adamas, TCI and Aldrich. Tetrahydrofuran (THF) were refluxed over Na/benzophenone and distilled under argon atmosphere. dtbbpy = 4,4'-di-*tert*-butyl-2,2'-dipyridyl. DBU = 1,8-diazabicyclo[5.4.0]-7-undecene. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

^1H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on a Bruker Avance 600 spectrometer at ambient temperature. Data for ^1H NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. All UV-vis measurements were recorded on a Shimadzu UV-vis Spectrophotometer UV-2450. Electron Paramagnetic Resonance (EPR) studies were performed with Magnettech MS-5000.

2. Investigation of the Key Reaction Parameters

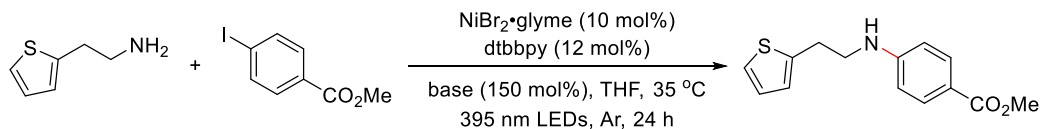
Table S1: Different solvents in the amination of aryl halides



entry	solvent	yield (%)
1	THF	78
2	1,4-dioxane	50
3	DMF	65
4	EtOAc	60
5	DMSO	38
6	MeCN	64
7	Toluene	< 5

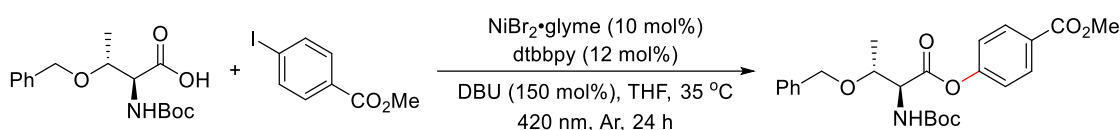
Reaction conditions: methyl 4-iodobenzoate (0.2 mmol), 2-(thiophen-2-yl)ethan-1-amine (0.3 mmol), NiBr₂·glyme (10 mol%), dtbbpy (12 mol%), DBU (150 mol%), solvent (2 mL), 395 nm LEDs, 24 h. The yield was determined by GC using diphenylmethane as an internal standard.

Table S2: Different bases in the amination of aryl halides



entry	base	yield (%)
1	DBU	78
2	TMG	71
3	DABCO	10
4	<i>i</i> Pr ₂ NEt	< 5
5	Et ₃ N	< 5
6	DMAP	< 5
7	Cs ₂ CO ₃	< 5
8	K ₃ PO ₄	< 5
9	K ₂ HPO ₄	< 5

Reaction conditions: methyl 4-iodobenzoate (0.2 mmol), 2-(thiophen-2-yl)ethan-1-amine (0.3 mmol), NiBr₂·glyme (10 mol%), dtbbpy (12 mol%), base (150 mol%), THF (2 mL), 395 nm LEDs, 24 h. The yield was determined by GC using diphenylmethane as an internal standard.

Table S3: Parameters affecting esterification of aryl halides

Entry	variation from the conditions	Yield (%)
1	none	87
2	without light	0
3	395 nm instead of 420 nm	90
4	450 nm instead of 420 nm	94 (91) ^a
5	530 nm instead of 420 nm	< 5

Reaction conditions: methyl 4-iodobenzoate (0.2 mmol), threonine (0.3 mmol), NiBr₂·glyme (10 mol%), dtbbpy (12 mol%), DBU (150 mol%), THF (2 mL), LEDs, 24 h. The yield was determined by GC using diphenylmethane as an internal standard. ^a Isolated yield.

3. Experimental procedures and spectral data

3.1 Experimental procedures

General Procedure for Amination of Aryl Halides

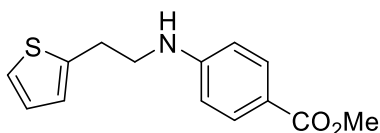
NiBr₂·glyme (10 mol%, 6.2 mg) and dtbbpy (12 mol%, 6.4 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, anhydrous THF (2 mL) was added via a gastight syringe under argon atmosphere, and the mixture was stirred at 50 °C for 0.5 h. Then aryl halide (1.0 equiv, 0.2 mmol), amine (1.5 equiv, 0.3 mmol) and DBU (1.5 equiv, 0.3 mmol) were added. The reaction mixture was stirred under the irradiation of 420 nm LEDs for 24 h. The reaction internal temperature was measured to be 32 °C to 35 °C. After 24 h, the mixture was quenched with saturated brine and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel.

General Procedure for Esterification of Aryl Halides

NiBr₂·glyme (10 mol%, 6.2 mg) and dtbbpy (12 mol%, 6.4 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). To these solids, anhydrous THF (2 mL) was added via a gastight

syringe under argon atmosphere, and the mixture was stirred at 50 °C for 0.5 h. Then aryl halide (1.0 equiv, 0.2 mmol), carboxylic acid (1.5 equiv, 0.3 mmol) and DBU (1.5 equiv, 0.3 mmol) were added. The reaction mixture was stirred under the irradiation of 450 nm LEDs for 24 h. The reaction internal temperature was measured to be 32 °C to 35 °C. After 24 h, the mixture was quenched with saturated brine and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel.

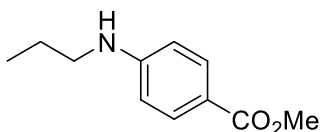
3.2 Spectral Data



methyl 4-((2-(thiophen-2-yl)ethyl)amino)benzoate (3): Following the general procedure, obtained in 92% yield (48.1 mg, eluent: petroleum ether/ethyl acetate = 10/1). ^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, J = 8.8 Hz, 2H), 7.18 (dd, J = 5.1, 1.2 Hz, 1H), 6.95 (dd, J = 5.1, 3.4 Hz, 1H), 6.85 (d, J = 3.3 Hz, 1H), 6.56 (d, J = 8.8 Hz, 2H), 4.26 (br s, 1H), 3.85 (s, 3H), 3.48 (t, J = 6.7 Hz, 2H), 3.14 (t, J = 6.7 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 167.3, 151.5, 141.1, 131.6, 127.1, 125.5, 124.1, 118.6, 111.7, 51.6, 44.5, 29.5.

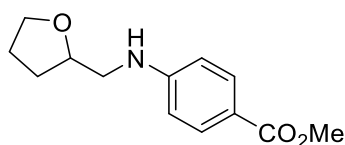
HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{16}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$: 262.0896, found: 262.0891.



Methyl 4-(propylamino)benzoate (4): Following the general procedure, obtained in 80% yield (30.9 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref: *Chem. Commun.* **2007**, 2240).

^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, J = 8.9 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 4.24 (br s, 1H), 3.84 (s, 3H), 3.12 (t, J = 7.1 Hz, 2H), 1.69 – 1.60 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 167.4, 152.1, 131.6, 118.0, 111.4, 51.5, 45.2, 22.5, 11.6.

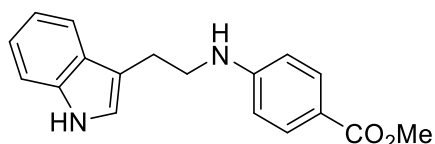


Methyl 4-(((tetrahydrofuran-2-yl)methyl)amino)benzoate (5): Following the general procedure, obtained in 89% yield (41.8 mg, eluent: petroleum ether/ethyl acetate = 5/1).

^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, $J = 8.8$ Hz, 2H), 6.57 (d, $J = 8.8$ Hz, 2H), 4.57 (br s, 1H), 4.15 – 4.07 (m, 1H), 3.91 – 3.86 (m, 1H), 3.84 (s, 3H), 3.80 – 3.76 (m, 1H), 3.31 (dd, $J = 12.6, 3.7$ Hz, 1H), 3.12 (dd, $J = 12.6, 7.6$ Hz, 1H), 2.08 – 1.99 (m, 1H), 1.95 – 1.90 (m, 2H), 1.68 – 1.59 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 167.3, 151.9, 131.5, 118.6, 111.9, 77.2, 68.2, 51.5, 47.6, 29.1, 25.8.

HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 236.1281, found: 236.1284.

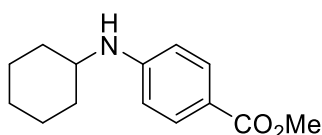


methyl 4-((2-(1H-indol-3-yl)ethyl)amino)benzoate (6): Following the general procedure, obtained in 90% yield (53.0 mg, eluent: petroleum ether/ethyl acetate = 3/1).

^1H NMR (600 MHz, CDCl_3) δ 8.13 (br s, 1H), 7.87 (d, $J = 8.8$ Hz, 2H), 7.61 (d, $J = 7.9$ Hz, 1H), 7.39 (d, $J = 8.1$ Hz, 1H), 7.23 (t, $J = 7.1$ Hz, 1H), 7.15 (t, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 2.2$ Hz, 1H), 6.55 (d, $J = 8.8$ Hz, 2H), 4.23 (br s, 1H), 3.86 (s, 3H), 3.53 (t, $J = 6.8$ Hz, 2H), 3.10 (t, $J = 6.8$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 167.5, 151.9, 136.5, 131.6, 127.3, 122.3, 122.2, 119.6, 118.7, 118.2, 112.9, 111.6, 111.4, 51.6, 43.4, 24.9.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 295.1441, found: 295.1445.

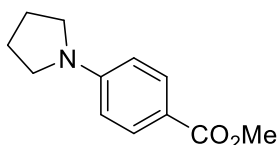


methyl 4-(cyclohexylamino)benzoate (7): Following the general procedure, obtained in 63% yield (29.4 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref: *Synthesis* **2018**, 50, 4637).

^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 8.8$ Hz, 2H), 6.51 (d, $J = 8.8$ Hz, 2H), 4.04 (br

s, 1H), 3.84 (s, 3H), 3.36 – 3.28 (m, 1H), 2.08 – 2.01 (m, 2H), 1.81 – 1.73 (m, 2H), 1.69 – 1.63 (m, 1H), 1.44 – 1.34 (m, 2H), 1.28 – 1.15 (m, 3H).

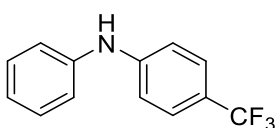
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 167.4, 151.1, 131.6, 117.7, 111.6, 51.5, 51.3, 33.2, 25.8, 24.9.



methyl 4-(pyrrolidin-1-yl)benzoate (8): Following the general procedure, obtained in 70% yield (28.7 mg, eluent: petroleum ether/ethyl acetate = 5/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2019**, *141*, 6392).

^1H NMR (600 MHz, CDCl_3) δ 7.89 (d, J = 8.9 Hz, 2H), 6.50 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 3.34 (t, J = 6.6 Hz, 4H), 2.14 – 1.87 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 167.7, 150.8, 131.4, 116.2, 110.7, 51.6, 47.6, 25.5.

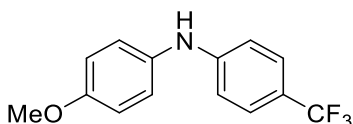


N-phenyl-4-(trifluoromethyl)aniline (9): Following the general procedure, obtained in 60% yield (28.5 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref: *ACS Catal.*, **2016**, *6*, 3515).

^1H NMR (600 MHz, CDCl_3) δ 7.48 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 7.5 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.10 – 7.03 (m, 3H), 5.87 (br s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 146.7, 141.1, 129.6, 126.7 (q, J = 3.7 Hz), 124.7 (q, J = 270.7 Hz), 123.0, 121.6 (q, J = 32.6 Hz), 120.0, 115.3.

$^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3) δ -61.4.



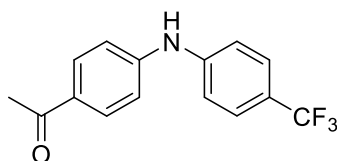
4-methoxy-N-(4-(trifluoromethyl)phenyl)aniline (10): Following the general procedure, obtained in 80% yield (42.7 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.*,

2020, 59, 9527).

^1H NMR (600 MHz, CDCl_3) δ 7.43 (d, $J = 8.6$ Hz, 2H), 7.13 (d, $J = 8.8$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.5$ Hz, 2H), 5.48 (br s, 1H), 3.83 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 155.5, 147.5, 132.6, 125.7 (q, $J = 3.8$ Hz), 123.7 (q, $J = 270.5$ Hz), 123.2, 119.5 (q, $J = 32.7$ Hz), 113.8, 112.8, 54.5.

$^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3) δ -61.2.



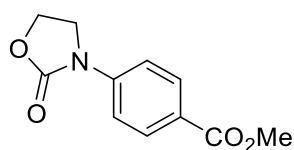
1-(4-((4-(trifluoromethyl)phenyl)amino)phenyl)ethan-1-one (11): Following the general procedure, obtained in 67% yield (37.4 mg, eluent: petroleum ether/ethyl acetate = 3/1).

^1H NMR (600 MHz, CDCl_3) δ 7.92 (d, $J = 8.7$ Hz, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.7$ Hz, 2H), 6.49 (br s, 1H), 2.57 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 196.7, 146.6, 144.4, 130.6, 130.4, 126.8 (q, $J = 3.7$ Hz), 124.3 (q, $J = 271.0$ Hz), 123.9 (q, $J = 32.9$ Hz), 118.2, 116.2, 26.3.

$^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3) δ -61.8.

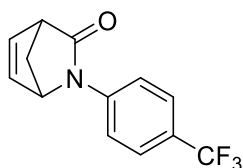
HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{NO}^+ [\text{M}+\text{H}]^+$: 280.0944, found: 280.0940.



methyl 4-(2-oxooxazolidin-3-yl)benzoate (12): Following the general procedure, obtained in 86% yield (38.0 mg, eluent: petroleum ether/ethyl acetate = 3/1). The compound data was in agreement with the literature (Ref: *Org. Lett.*, 2014, 16, 5020).

^1H NMR (600 MHz, CDCl_3) δ 8.03 (d, $J = 8.9$ Hz, 2H), 7.61 (d, $J = 8.9$ Hz, 2H), 4.53 – 4.46 (m, 2H), 4.10 – 4.07 (m, 2H), 3.89 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.5, 154.9, 142.2, 130.7, 125.3, 117.2, 61.4, 52.1, 44.9.



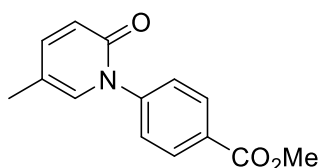
2-(4-(trifluoromethyl)phenyl)-2-azabicyclo[2.2.1]hept-5-en-3-one (13): Following the general procedure, obtained in 70% yield (35.4 mg, eluent: petroleum ether/ethyl acetate = 2/1).

^1H NMR (600 MHz, CDCl_3) δ 7.58 (d, $J = 8.7$ Hz, 2H), 7.53 (d, $J = 8.8$ Hz, 2H), 7.03 (dd, $J = 5.3, 2.0$ Hz, 1H), 6.74 – 6.70 (m, 1H), 4.87 – 4.82 (m, 1H), 3.55 – 3.51 (m, 1H), 2.48 (d, $J = 8.2$ Hz, 1H), 2.32 (d, $J = 8.2$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 177.3, 142.5, 138.8, 138.7, 126.2 (q, $J = 3.8$ Hz), 125.4 (q, $J = 32.9$ Hz), 124.2 (q, $J = 271.7$ Hz), 117.9, 64.2, 56.8, 54.6.

$^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3) δ -62.1.

HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{11}\text{F}_3\text{NO}^+$ $[\text{M}+\text{H}]^+$: 254.0787, found: 254.0782.

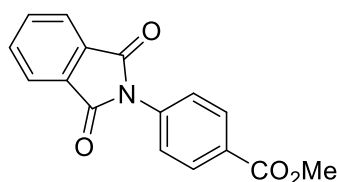


methyl 4-(5-methyl-2-oxopyridin-1(2H)-yl)benzoate (14): Following the general procedure, obtained in 52% yield under irradiation for 48 h (25.3 mg, eluent: petroleum ether/ethyl acetate = 5/1).

^1H NMR (600 MHz, CDCl_3) δ 8.07 – 8.03 (m, 3H), 7.54 (dd, $J = 8.3, 2.4$ Hz, 1H), 7.16 – 7.10 (m, 2H), 6.88 (d, $J = 8.3$ Hz, 1H), 3.90 (s, 3H), 2.30 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.6, 160.8, 158.9, 147.5, 140.6, 131.5, 129.0, 125.7, 119.8, 112.1, 52.1, 17.6.

HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 244.0968, found: 244.0969.

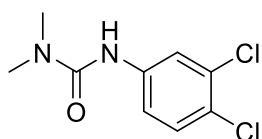


methyl 4-(1,3-dioxoisindolin-2-yl)benzoate (15): Following the general procedure,

obtained in 53% yield (29.8 mg, eluent: CH₂Cl₂). The compound data was in agreement with the literature (Ref: *Angew. Chem., Int. Ed.* **2020**, *59*, 17887).

¹H NMR (600 MHz, CDCl₃) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.97 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 3.94 (s, 3H).

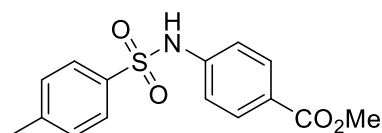
¹³C{¹H} NMR (150 MHz, CDCl₃) δ 166.8, 166.3, 135.9, 134.7, 131.6, 130.4, 129.3, 125.9, 124.0, 52.3.



3-(3,4-dichlorophenyl)-1,1-dimethylurea (16): Following the general procedure, obtained in 50% yield under irradiation for 48 h (23.3 mg, eluent: petroleum ether/ethyl acetate = 3/1). The compound data was in agreement with the literature (Ref: *Synthesis* **2009**, 801).

¹H NMR (600 MHz, CDCl₃) δ 7.60 (d, *J* = 2.5 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.21 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.42 (br s, 1H), 3.02 (s, 6H).

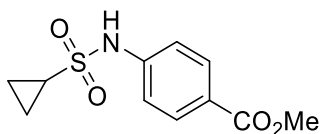
¹³C{¹H} NMR (150 MHz, CDCl₃) δ 155.2, 138.8, 132.5, 130.2, 125.9, 121.4, 119.1, 36.5.



methyl 4-((4-methylphenyl)sulfonamido)benzoate (17): Following the general procedure, obtained in 66% yield (40.3 mg, eluent: petroleum ether/ethyl acetate = 3/1). The compound data was in agreement with the literature (Ref: *Chem. Commun.* **2019**, *55*, 4853).

¹H NMR (600 MHz, CDCl₃) δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.98 (s, 1H), 3.87 (s, 3H), 2.38 (s, 3H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ 166.4, 144.4, 140.9, 135.8, 131.1, 129.9, 127.3, 126.3, 119.1, 52.1, 21.6.

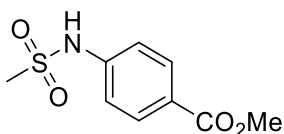


methyl 4-(cyclopropanesulfonamido)benzoate (18): Following the general procedure, obtained in 93% yield (47.5 mg, eluent: petroleum ether/ethyl acetate = 3/1).

^1H NMR (600 MHz, CDCl_3) δ 8.00 (d, $J = 8.7$ Hz, 2H), 7.41 (s, 1H), 7.30 (d, $J = 8.7$ Hz, 2H), 3.90 (s, 3H), 2.56 (tt, $J = 8.0, 4.8$ Hz, 1H), 1.22 (dt, $J = 6.6, 3.3$ Hz, 2H), 1.01 – 0.97 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.6, 141.5, 131.3, 126.2, 119.2, 52.2, 30.5, 5.8.

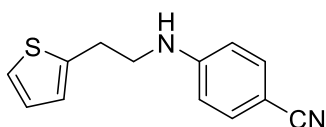
HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_4\text{S}^+$ $[\text{M}+\text{H}]^+$: 256.0638, found: 256.0640.



methyl 4-(methylsulfonamido)benzoate (19): Following the general procedure, obtained in 80% yield (36.7 mg, eluent: petroleum ether/ethyl acetate = 2/1). The compound data was in agreement with the literature (Ref: *Org. Lett.* **2011**, 13, 2564).

^1H NMR (600 MHz, CDCl_3) δ 8.03 (d, $J = 8.6$ Hz, 2H), 7.25 (d, $J = 8.6$ Hz, 2H), 7.19 (s, 1H), 3.91 (s, 3H), 3.09 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.4, 141.2, 131.5, 126.3, 118.2, 52.2, 40.0.

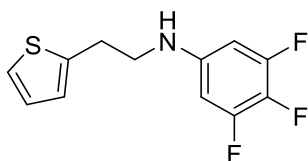


4-((2-(thiophen-2-yl)ethyl)amino)benzonitrile (20): Following the general procedure, obtained in 88% yield (40.2 mg, eluent: petroleum ether/ethyl acetate = 5/1).

^1H NMR (600 MHz, CDCl_3) δ 7.42 (d, $J = 8.8$ Hz, 2H), 7.19 (dd, $J = 5.1, 1.1$ Hz, 1H), 6.96 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.86 (dd, $J = 3.4, 0.9$ Hz, 1H), 6.57 (d, $J = 8.8$ Hz, 2H), 4.39 (br s, 1H), 3.47 (t, $J = 6.7$ Hz, 2H), 3.14 (t, $J = 6.7$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 150.9, 140.8, 133.8, 127.2, 125.6, 124.3, 120.4, 112.4, 99.0, 44.4, 29.4.

HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{13}\text{N}_2\text{S}^+$ $[\text{M}+\text{H}]^+$: 229.0794, found: 229.0788.



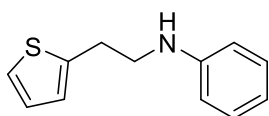
3,4,5-trifluoro-N-(2-(thiophen-2-yl)ethyl)aniline (21): Following the general procedure, obtained in 92% yield (47.3 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 7.19 (dd, $J = 5.1, 1.2$ Hz, 1H), 6.97 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.86 (dd, $J = 3.4, 1.2$ Hz, 1H), 6.21 – 6.13 (m, 2H), 3.59 (br s, 1H), 3.35 (t, $J = 6.7$ Hz, 2H), 3.12 (t, $J = 6.8$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 151.0 (ddd, $J = 245.4, 10.4, 6.1$ Hz), 142.5 (td, $J = 11.1, 2.5$ Hz), 139.9, 131.4 (dt, $J = 239.5, 15.6$ Hz), 126.1, 124.5, 123.2, 95.5 (m), 44.2, 28.3.

$^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3) δ -134.76 (d, $J = 21.7$ Hz), -175.69 (t, $J = 21.5$ Hz).

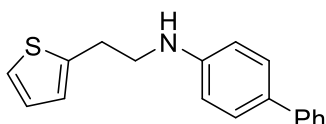
HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{NS}^+$ $[\text{M}+\text{H}]^+$: 258.0559, found: 258.0555.



N-(2-(thiophen-2-yl)ethyl)aniline (22): Following the general procedure, obtained in 90% yield (36.6 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref: *Angew. Chem., Int. Ed.* **2015**, 54, 9042).

^1H NMR (600 MHz, CDCl_3) δ 7.24 – 7.17 (m, 3H), 6.98 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.88 (d, $J = 4.2$ Hz, 1H), 6.76 (t, $J = 7.3$ Hz, 1H), 6.67 (d, $J = 9.2$ Hz, 2H), 3.97 (br s, 1H), 3.46 (t, $J = 6.8$ Hz, 2H), 3.16 (t, $J = 6.8$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 146.4, 140.6, 128.3, 125.9, 124.3, 122.9, 116.9, 112.3, 44.3, 28.6.



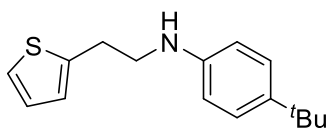
N-(2-(thiophen-2-yl)ethyl)-[1,1'-biphenyl]-4-amine (23): Following the general procedure, obtained in 80% yield (44.7 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 7.58 (dd, $J = 8.3, 1.3$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 2H),

7.43 (t, $J = 7.8$ Hz, 2H), 7.33 – 7.26 (m, 1H), 7.21 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.00 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.91 (dd, $J = 3.5, 1.1$ Hz, 1H), 6.72 (d, $J = 8.6$ Hz, 2H), 3.92 (br s, 1H), 3.51 (t, $J = 6.7$ Hz, 2H), 3.18 (t, $J = 6.7$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 147.1, 141.6, 141.2, 130.5, 128.6, 128.0, 127.0, 126.3, 126.1, 125.3, 123.9, 113.3, 45.2, 29.7.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{18}\text{NS}^+$ $[\text{M}+\text{H}]^+$: 280.1154, found: 280.1160.

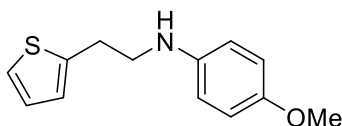


4-(tert-butyl)-N-(2-(thiophen-2-yl)ethyl)aniline (24): Following the general procedure, obtained in 78% yield (40.4 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 7.25 (d, $J = 8.6$ Hz, 2H), 7.18 (d, $J = 5.1$ Hz, 1H), 7.00 – 6.96 (m, 1H), 6.88 (d, $J = 3.3$ Hz, 1H), 6.65 (d, $J = 8.6$ Hz, 2H), 3.99 (br s, 1H), 3.45 (t, $J = 6.8$ Hz, 2H), 3.16 (t, $J = 6.8$ Hz, 2H), 1.31 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 143.9, 140.7, 139.8, 125.9, 125.1, 124.2, 122.8, 112.1, 44.7, 32.9, 30.5, 28.7.

HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{22}\text{NS}^+$ $[\text{M}+\text{H}]^+$: 260.1467, found: 260.1474.

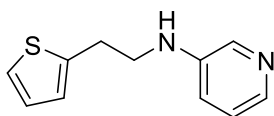


4-methoxy-N-(2-(thiophen-2-yl)ethyl)aniline (25): Following the general procedure, obtained in 91% yield (42.5 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 7.18 (dd, $J = 5.1, 1.1$ Hz, 1H), 6.97 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.87 (d, $J = 2.6$ Hz, 1H), 6.81 (d, $J = 8.9$ Hz, 2H), 6.62 (d, $J = 8.9$ Hz, 2H), 3.77 (s, 3H), 3.55 – 3.35 (m, 3H), 3.13 (t, $J = 6.7$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 152.4, 141.9, 141.9, 127.0, 125.3, 123.9, 115.0, 114.6, 55.8, 46.3, 29.8.

HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{16}\text{NOS}^+$ $[\text{M}+\text{H}]^+$: 234.0947, found: 234.0940.

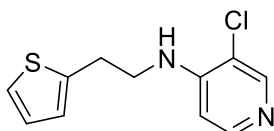


N-(2-(thiophen-2-yl)ethyl)pyridin-3-amine (26): Following the general procedure, obtained in 83% yield (33.9 mg, eluent: petroleum ether/ethyl acetate = 2/1).

^1H NMR (600 MHz, CDCl_3) δ 8.02 (d, $J = 2.8$ Hz, 1H), 7.95 (dd, $J = 4.7, 1.3$ Hz, 1H), 7.17 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.08 (dd, $J = 8.5, 4.9$ Hz, 1H), 6.95 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.88 (ddd, $J = 8.3, 2.9, 1.4$ Hz, 1H), 6.86 – 6.84 (m, 1H), 3.97 (br s, 1H), 3.43 (t, $J = 6.7$ Hz, 2H), 3.13 (t, $J = 6.7$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 143.8, 141.2, 138.7, 136.1, 127.1, 125.5, 124.1, 123.8, 118.9, 44.8, 29.5.

HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{S}^+$ $[\text{M}+\text{H}]^+$: 205.0794, found: 205.0782.

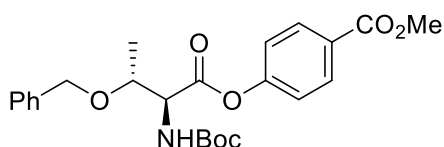


3-chloro-N-(2-(thiophen-2-yl)ethyl)pyridin-4-amine (27): Following the general procedure, obtained in 72% yield (34.4mg, eluent: petroleum ether/ethyl acetate = 2/1).

^1H NMR (600 MHz, CDCl_3) δ 8.23 (s, 1H), 8.14 (d, $J = 5.7$ Hz, 1H), 7.19 (d, $J = 6.1$ Hz, 1H), 6.96 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.87 (d, $J = 2.7$ Hz, 1H), 6.52 (d, $J = 5.7$ Hz, 1H), 4.99 (br s, 1H), 3.54 – 3.48 (m, 2H), 3.17 (t, $J = 6.8$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 148.9, 148.3, 147.8, 140.3, 127.2, 125.7, 124.4, 116.9, 105.5, 44.0, 29.3.

HRMS (ESI) Calcd for $\text{C}_{11}\text{H}_{12}\text{ClN}_2\text{S}^+$ $[\text{M}+\text{H}]^+$: 239.0404, found: 239.0409; for $\text{C}_{11}\text{H}_{12}^{37}\text{ClN}_2\text{S}^+$ $[\text{M}+\text{H}]^+$: 241.0375, found: 241.0378.



methyl 4-((O-benzyl-N-(tert-butoxycarbonyl)-L-threonyl)oxy)benzoate (28):

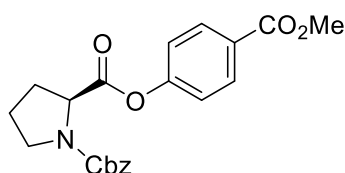
Following the general procedure, obtained in 91% yield (80.7 mg, eluent: petroleum ether/ethyl acetate = 4/1).

^1H NMR (600 MHz, CDCl_3) δ 8.03 (d, $J = 8.7$ Hz, 2H), 7.35 – 7.26 (m, 5H), 7.04 (d, $J =$

8.7 Hz, 2H), 5.38 (d, $J = 9.7$ Hz, 1H), 4.65 (d, $J = 11.6$ Hz, 1H), 4.56 (dd, $J = 9.7, 2.3$ Hz, 1H), 4.44 (d, $J = 11.6$ Hz, 1H), 4.34 (qd, $J = 6.4, 2.5$ Hz, 1H), 3.91 (s, 3H), 1.47 (s, 9H), 1.36 (d, $J = 6.2$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 169.4, 166.3, 156.2, 154.2, 137.6, 131.2, 128.5, 127.9, 127.9, 127.8, 80.2, 74.5, 70.9, 58.7, 52.2, 28.3, 16.1.

HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{30}\text{NO}_7^+$ $[\text{M}+\text{H}]^+$: 444.2017, found: 444.2022.



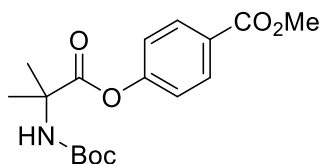
1-benzyl 2-(4-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate (29):

Following the general procedure, obtained in 88% yield (67.5 mg, eluent: petroleum ether/ethyl acetate = 3/1).

^1H NMR (600 MHz, CDCl_3) δ 8.06 (d, $J = 8.7$ Hz, 1H), 7.97 (d, $J = 8.7$ Hz, 1H), 7.40 – 7.29 (m, 5H), 7.19 (d, $J = 8.7$ Hz, 1H), 6.83 (d, $J = 8.7$ Hz, 1H), 5.27 (d, $J = 12.2$ Hz, 0.5H), 5.23 – 5.14 (m, 1H), 5.06 (d, $J = 12.2$ Hz, 0.5H), 4.64 – 4.53 (m, 1H), 3.91 (s, 3H), 3.74 – 3.54 (m, 2H), 2.46 – 2.33 (m, 1H), 2.26 – 2.16 (m, 1H), 2.11 – 1.95 (m, 2H). (mixture of rotamers)

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 170.86, 170.79, 166.31, 166.22, 154.96, 154.28, 154.18, 153.95, 136.57, 136.28, 131.13, 131.09, 128.58, 128.49, 128.23, 128.05, 127.90, 127.84, 127.80, 121.50, 121.26, 67.37, 67.21, 59.47, 58.93, 52.23, 52.20, 47.09, 46.55, 31.08, 30.00, 24.53, 23.69. (mixture of rotamers)

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_6^+$ $[\text{M}+\text{H}]^+$: 384.1442, found: 384.1451.



methyl 4-((2-((tert-butoxycarbonyl)amino)-2-methylpropanoyl)oxy)benzoate (30):

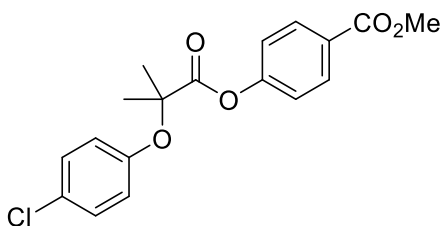
Following the general procedure, obtained in 90% yield (60.7 mg, eluent: petroleum ether/ethyl acetate = 5/1).

^1H NMR (600 MHz, CDCl_3) δ 8.06 (d, $J = 8.7$ Hz, 2H), 7.18 (d, $J = 8.7$ Hz, 2H), 5.08 (s,

1H), 3.90 (s, 3H), 1.61 (s, 6H), 1.44 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 173.0, 166.4, 154.9, 154.7, 131.2, 127.7, 121.5, 80.2, 56.2, 52.2, 28.3, 25.4.

HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_6^+$ $[\text{M}+\text{H}]^+$: 338.1598, found: 338.1590.

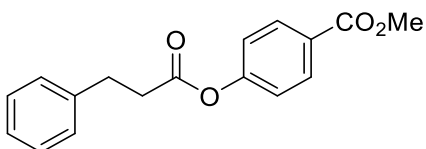


methyl 4-((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)benzoate (31): Following the general procedure, obtained in 94% yield (65.6 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 8.07 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 8.9 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 3.91 (s, 3H), 1.74 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 172.3, 166.3, 154.0, 153.8, 131.3, 129.4, 128.1, 127.7, 121.4, 120.4, 79.5, 52.4, 25.3.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{18}\text{ClO}_5^+$ $[\text{M}+\text{H}]^+$: 349.0837, found: 349.0841; for $\text{C}_{18}\text{H}_{18}^{37}\text{ClO}_5^+$ $[\text{M}+\text{H}]^+$: 351.0808, found: 351.0810.

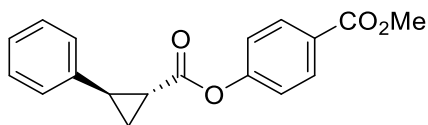


methyl 4-((3-phenylpropanoyl)oxy)benzoate (32): Following the general procedure, obtained in 80% yield (45.5 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 8.05 (d, J = 8.8 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.27 – 7.22 (m, 3H), 7.08 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 3.07 (t, J = 7.7 Hz, 2H), 2.90 (t, J = 7.7 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 170.9, 166.3, 154.3, 139.9, 131.2, 128.7, 128.4, 127.7, 126.6, 121.6, 52.2, 36.0, 30.9.

HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{17}\text{O}_4^+$ $[\text{M}+\text{H}]^+$: 285.1121, found: 285.1128.

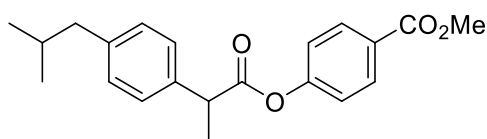


methyl 4-((2-phenylcyclopropane-1-carbonyl)oxy)benzoate (33): Following the general procedure, obtained in 81% yield (48.0 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 8.07 (d, $J = 8.7$ Hz, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.21 (m, 1H), 7.20 (d, $J = 8.7$ Hz, 2H), 7.18 – 7.14 (m, 2H), 3.90 (s, 3H), 2.70 (ddd, $J = 9.3, 6.7, 4.1$ Hz, 1H), 2.14 (ddd, $J = 8.4, 5.3, 4.1$ Hz, 1H), 1.76 (ddd, $J = 9.3, 5.3, 4.7$ Hz, 1H), 1.50 (ddd, $J = 8.4, 6.7, 4.7$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 171.5, 166.3, 154.4, 139.4, 131.2, 128.7, 127.7, 126.9, 126.3, 121.6, 52.2, 27.4, 24.1, 17.9.

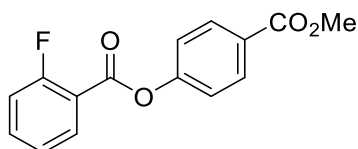
HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{17}\text{O}_4^+$ $[\text{M}+\text{H}]^+$: 297.1121, found: 297.1126.



methyl 4-((2-(4-isobutylphenyl)propanoyl)oxy)benzoate (34): Following the general procedure, obtained in 80% yield (54.5 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2019**, 58, 9575).

^1H NMR (600 MHz, CDCl_3) δ 8.02 (d, $J = 8.8$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.07 (d, $J = 8.8$ Hz, 2H), 3.94 (q, $J = 6.9$ Hz, 1H), 3.89 (s, 3H), 2.47 (d, $J = 7.2$ Hz, 2H), 1.90 – 1.83 (m, 1H), 1.61 (d, $J = 7.2$ Hz, 3H), 0.91 (d, $J = 6.6$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 172.7, 166.3, 154.6, 141.0, 136.9, 131.1, 129.6, 127.6, 127.2, 121.5, 52.2, 45.3, 45.1, 30.2, 22.4, 18.5.



4-(methoxycarbonyl)phenyl 2-fluorobenzoate (35): Following the general procedure, obtained in 91% yield (49.9 mg, eluent: petroleum ether/ethyl acetate = 5/1).

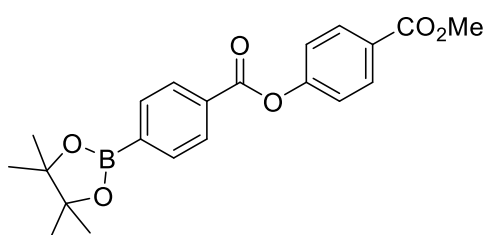
^1H NMR (600 MHz, CDCl_3) δ 8.15 – 8.08 (m, 3H), 7.62 (dddd, $J = 8.3, 7.3, 4.8, 1.8$ Hz,

1H), 7.33 (d, $J = 8.8$ Hz, 2H), 7.29 (td, $J = 7.6, 1.1$ Hz, 1H), 7.22 (ddd, $J = 10.9, 8.3, 1.1$ Hz, 1H), 3.93 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.33, 162.39 (d, $J = 261.9$ Hz), 162.20 (d, $J = 4.0$ Hz), 154.25, 135.57 (d, $J = 9.2$ Hz), 132.58, 131.25, 127.95, 124.25 (d, $J = 3.9$ Hz), 121.75, 117.67 (d, $J = 9.3$ Hz), 117.33 (d, $J = 22.2$ Hz), 52.25.

$^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3) δ -107.86.

HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{12}\text{FO}_4^+$ $[\text{M}+\text{H}]^+$: 275.0714, found: 275.0720.



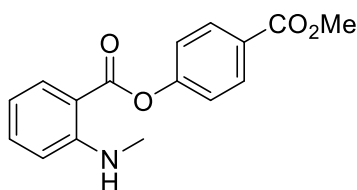
4-(methoxycarbonyl)phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)

benzoate (36): Following the general procedure, obtained in 93% yield (71.1 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 8.17 (d, $J = 8.1$ Hz, 2H), 8.13 (d, $J = 8.7$ Hz, 2H), 7.94 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.7$ Hz, 2H), 3.93 (s, 3H), 1.37 (s, 12H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.4, 164.7, 154.6, 134.9, 131.3, 131.2, 129.2, 127.8, 121.8, 84.4, 52.2, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{24}\text{BO}_6^+$ $[\text{M}+\text{H}]^+$: 383.1661, found: 383.1653; for $\text{C}_{21}\text{H}_{24}^{10}\text{BO}_6^+$ $[\text{M}+\text{H}]^+$: 382.1697, found: 382.1693.



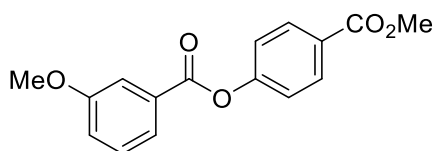
4-(methoxycarbonyl)phenyl 2-(methylamino)benzoate (37): Following the general procedure, obtained in 86% yield (49.1 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, Acetone) δ 8.11 (d, $J = 8.7$ Hz, 2H), 8.08 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.56 (br s, 1H), 7.50 (ddd, $J = 8.6, 7.0, 1.7$ Hz, 1H), 7.40 (d, $J = 8.7$ Hz, 2H), 6.81 (dd, $J = 8.5, 1.1$ Hz, 1H), 6.67 (ddd, $J = 8.1, 7.0, 1.1$ Hz, 1H), 3.90 (s, 3H), 2.95 (d, $J = 5.1$ Hz,

3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, Acetone) δ 167.9, 167.5, 156.7, 154.6, 137.5, 133.6, 132.6, 129.4, 124.2, 116.2, 112.9, 109.9, 53.3, 30.6.

HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_4^+$ $[\text{M}+\text{H}]^+$: 286.1074, found: 286.1077.

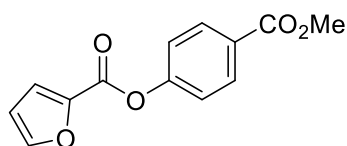


4-(methoxycarbonyl)phenyl 3-methoxybenzoate (38): Following the general procedure, obtained in 78% yield (44.7 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 8.13 (d, $J = 8.8$ Hz, 2H), 7.80 (ddd, $J = 7.7, 1.6, 1.0$ Hz, 1H), 7.69 (dd, $J = 2.7, 1.5$ Hz, 1H), 7.43 (t, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 8.8$ Hz, 2H), 7.19 (ddd, $J = 8.3, 2.7, 1.0$ Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.4, 164.5, 159.8, 154.6, 131.3, 130.4, 129.7, 127.8, 122.7, 121.8, 120.5, 114.6, 55.6, 52.2.

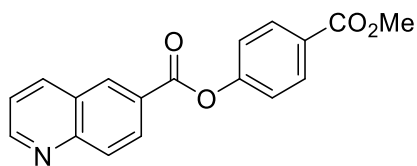
HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_5^+$ $[\text{M}+\text{H}]^+$: 287.0914, found: 287.0917.



4-(methoxycarbonyl)phenyl furan-2-carboxylate (39): Following the general procedure, obtained in 65% yield under 420 nm LEDs irradiation for 48 h (32.0 mg, eluent: petroleum ether/ethyl acetate = 5/1). The compound data was in agreement with the literature (*J. Chem. Soc., Perkin Trans. 1*, **1978**, 876).

^1H NMR (600 MHz, CDCl_3) δ 8.11 (d, $J = 8.9$ Hz, 2H), 7.69 (dd, $J = 1.7, 0.8$ Hz, 1H), 7.40 (dd, $J = 3.5, 0.9$ Hz, 1H), 7.30 (d, $J = 8.9$ Hz, 2H), 6.60 (dd, $J = 3.5, 1.7$ Hz, 1H), 3.92 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.3, 156.3, 153.8, 147.5, 143.6, 131.3, 128.0, 121.6, 120.0, 112.4, 52.3.

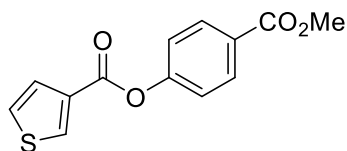


4-(methoxycarbonyl)phenyl quinoline-6-carboxylate (40): Following the general procedure, obtained in 74% yield (45.5 mg, eluent: petroleum ether/ethyl acetate = 5/1).

^1H NMR (600 MHz, CDCl_3) δ 9.07 (dd, $J = 4.2, 1.6$ Hz, 1H), 8.78 (d, $J = 1.8$ Hz, 1H), 8.44 (dd, $J = 8.8, 1.9$ Hz, 1H), 8.34 (d, $J = 7.8$ Hz, 1H), 8.25 (d, $J = 8.8$ Hz, 1H), 8.16 (d, $J = 8.7$ Hz, 2H), 7.54 (dd, $J = 8.3, 4.2$ Hz, 1H), 7.37 (d, $J = 8.7$ Hz, 2H), 3.94 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.3, 164.1, 154.5, 152.8, 150.1, 137.8, 132.1, 131.3, 130.0, 129.3, 128.0, 127.5, 127.2, 122.2, 121.8, 52.3.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{14}\text{NO}_4^+$ $[\text{M}+\text{H}]^+$: 308.0917, found: 308.0919.

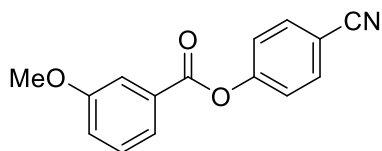


4-(methoxycarbonyl)phenyl thiophene-3-carboxylate (41): Following the general procedure, obtained in 79% yield (41.4 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 8.33 (dd, $J = 3.0, 1.2$ Hz, 1H), 8.12 (d, $J = 8.8$ Hz, 2H), 7.66 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.40 (dd, $J = 5.1, 3.1$ Hz, 1H), 7.29 (d, $J = 8.8$ Hz, 2H), 3.93 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.4, 160.5, 154.4, 134.5, 132.4, 131.2, 128.2, 127.8, 126.6, 121.8, 52.2.

HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{11}\text{O}_4\text{S}^+$ $[\text{M}+\text{H}]^+$: 263.0373, found: 263.0373.

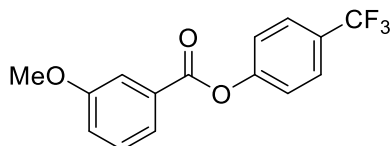


4-cyanophenyl 3-methoxybenzoate (42): Following the general procedure, obtained in 88% yield (44.6 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref: *Chem. Commun.* **2020**, 56, 8273).

^1H NMR (600 MHz, CDCl_3) δ 7.79 (dt, $J = 7.7, 1.3$ Hz, 1H), 7.74 (d, $J = 8.7$ Hz, 2H), 7.68 (dd, $J = 2.7, 1.5$ Hz, 1H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 8.7$ Hz, 2H), 7.21 (dd,

$J = 8.6, 3.0$ Hz, 1H), 3.89 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 164.2, 159.8, 154.3, 133.8, 129.9, 129.8, 123.0, 122.7, 120.7, 118.3, 114.7, 109.9, 55.6.



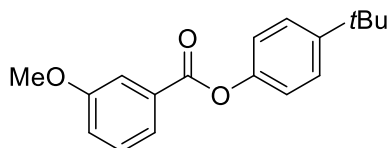
4-(trifluoromethyl)phenyl 3-methoxybenzoate (43): Following the general procedure, obtained in 85% yield (50.4 mg, eluent: petroleum ether/ethyl acetate = 20/1).

^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, $J = 7.7$ Hz, 1H), 7.73 – 7.69 (m, 3H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.21 (dd, $J = 8.0, 2.3$ Hz, 1H), 3.89 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 163.5, 158.8, 152.5, 129.2, 128.7, 127.2 (q, $J = 32.8$ Hz), 125.8 (q, $J = 3.7$ Hz), 122.9 (q, $J = 272.0$ Hz), 121.6, 121.2, 119.5, 113.6, 54.5.

$^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3) δ -62.19.

HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{12}\text{F}_3\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 297.0733, found: 297.0743.

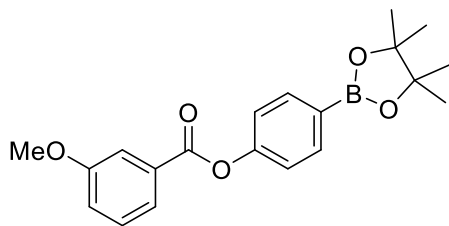


4-(tert-butyl)phenyl 3-methoxybenzoate (44): Following the general procedure, obtained in 63% yield under 395 nm LEDs irradiation for 40 h (35.8 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 7.82 (d, $J = 7.7$ Hz, 1H), 7.72 (dd, $J = 2.7, 1.5$ Hz, 1H), 7.45 (d, $J = 8.7$ Hz, 2H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.18 (dd, $J = 8.3, 2.6$ Hz, 1H), 7.15 (d, $J = 8.7$ Hz, 2H), 3.89 (s, 3H), 1.35 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 165.2, 159.7, 148.8, 148.6, 131.0, 129.6, 126.4, 122.6, 121.0, 120.1, 114.5, 55.5, 34.5, 31.5.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 285.1485, found: 285.1488.



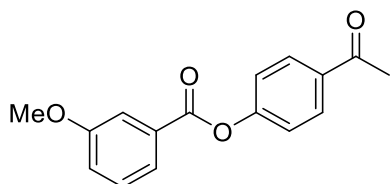
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl 3-methoxybenzoate (45):

Following the general procedure, obtained in 88% yield under 395 nm LEDs irradiation for 40 h (62.3 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 7.90 (d, $J = 8.5$ Hz, 2H), 7.81 (dt, $J = 7.7, 1.3$ Hz, 1H), 7.71 (dd, $J = 2.7, 1.5$ Hz, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.24 (d, $J = 8.5$ Hz, 2H), 7.18 (dd, $J = 8.7, 3.1$ Hz, 1H), 3.88 (s, 3H), 1.36 (s, 12H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 164.9, 159.7, 153.5, 136.3, 130.8, 129.6, 122.6, 121.1, 120.3, 114.5, 84.0, 55.5, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{24}\text{BO}_5^+$ $[\text{M}+\text{H}]^+$: 355.1711, found: 355.1703; for $\text{C}_{20}\text{H}_{24}^{10}\text{BO}_5^+$ $[\text{M}+\text{H}]^+$: 354.1748, found: 354.1743.

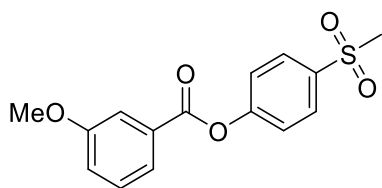


4-acetylphenyl 3-methoxybenzoate (46): Following the general procedure, obtained in 76% yield under 395 nm LEDs irradiation for 40 h (41.1 mg, eluent: petroleum ether/ethyl acetate = 5/1).

^1H NMR (600 MHz, CDCl_3) δ 8.06 (d, $J = 8.6$ Hz, 2H), 7.81 (d, $J = 7.7$ Hz, 1H), 7.69 (dd, $J = 2.7, 1.5$ Hz, 1H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 8.6$ Hz, 2H), 7.20 (dd, $J = 8.2, 2.5$ Hz, 1H), 3.89 (s, 3H), 2.63 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 196.9, 164.6, 159.8, 154.7, 134.8, 130.3, 130.0, 129.7, 122.7, 122.0, 120.5, 114.6, 55.6, 26.7.

HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_4^+$ $[\text{M}+\text{H}]^+$: 271.0965, found: 271.0967.

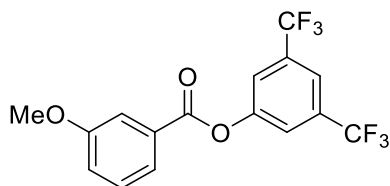


4-(methylsulfonyl)phenyl 3-methoxybenzoate (47): Following the general procedure, obtained in 74% yield under 395 nm LEDs irradiation for 40 h (45.3 mg, eluent: petroleum ether/ethyl acetate = 3/1).

^1H NMR (600 MHz, CDCl_3) δ 8.03 (d, J = 8.6 Hz, 2H), 7.80 (d, J = 7.6 Hz, 1H), 7.68 (s, 1H), 7.47 – 7.42 (m, 3H), 7.21 (dd, J = 8.2, 2.1 Hz, 1H), 3.89 (s, 3H), 3.09 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 164.4, 159.8, 155.0, 137.8, 129.9, 129.8, 129.4, 123.0, 122.7, 120.7, 114.6, 55.6, 44.7.

HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_5\text{S}^+$ $[\text{M}+\text{H}]^+$: 307.0635, found: 307.0630.



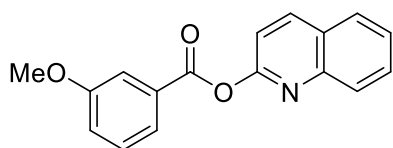
2,6-bis(trifluoromethyl)pyridin-4-yl 3-methoxybenzoate (48): Following the general procedure, obtained in 70% yield under 395 nm LEDs irradiation for 40 h (51.0 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 7.83 – 7.78 (m, 2H), 7.74 (s, 2H), 7.69 (dd, J = 2.7, 1.6 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.23 (dd, J = 8.0, 2.9 Hz, 1H), 3.89 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 163.2, 158.8, 150.4, 132.0 (q, J = 34.0 Hz), 128.8, 128.5, 121.8 (q, J = 272.9 Hz), 121.7, 119.9, 118.7 (p, J = 3.8 Hz), 113.7, 54.5. (one carbon signal is overlapped)

$^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3) δ -62.89.

HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{11}\text{F}_6\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 365.0607, found: 365.0616.



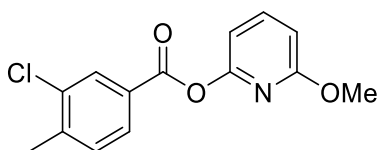
quinolin-2-yl 3-methoxybenzoate (49): Following the general procedure, obtained in 67% yield under 395 nm LEDs irradiation for 40 h (37.4 mg, eluent: petroleum ether/ethyl

acetate = 5/1).

^1H NMR (600 MHz, CDCl_3) δ 8.30 (d, $J = 8.7$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.91 – 7.86 (m, 2H), 7.79 – 7.73 (m, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 8.6$ Hz, 1H), 7.21 (dd, $J = 8.2, 2.3$ Hz, 1H), 3.89 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 164.9, 159.7, 156.7, 146.7, 140.0, 130.3, 130.3, 129.7, 128.7, 127.6, 127.3, 126.7, 123.0, 120.8, 115.9, 114.5, 55.6.

HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 280.0968, found: 280.0962.

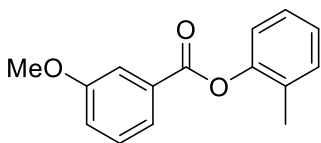


6-methoxypyridin-2-yl 3-chloro-4-methylbenzoate (50): Following the general procedure, obtained in 50% yield under 395 nm LEDs irradiation for 40 h (27.8 mg, eluent: petroleum ether/ethyl acetate = 10/1).

^1H NMR (600 MHz, CDCl_3) δ 8.19 (d, $J = 1.7$ Hz, 1H), 7.99 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.70 (t, $J = 7.9$ Hz, 1H), 7.37 (d, $J = 7.9$ Hz, 1H), 6.74 – 6.69 (m, 2H), 3.91 (s, 3H), 2.47 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 163.8, 163.8, 156.1, 142.6, 141.3, 134.8, 131.1, 130.9, 128.5, 108.7, 107.7, 53.9, 20.5. (one carbon signal is overlapped)

HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{13}\text{ClNO}_3^+$ $[\text{M}+\text{H}]^+$: 278.0578, found: 278.0585; for $\text{C}_{14}\text{H}_{13}^{37}\text{ClNO}_3^+$ $[\text{M}+\text{H}]^+$: 280.0549, found: 280.0553.

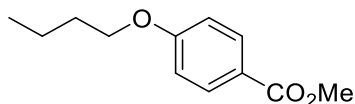


o-tolyl 3-methoxybenzoate (51): Following the general procedure, obtained in 26% yield under 395 nm LEDs irradiation for 40 h (12.6 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref: Tetrahedron Lett., **2011**, 52, 1112).

^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, $J = 7.6$ Hz, 1H), 7.65 (s, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.20 (d, $J = 7.5$ Hz, 1H), 7.17 (d, $J = 6.3$ Hz, 1H), 7.13 – 7.09 (m, 2H), 7.05 (d, $J = 7.9$ Hz, 1H), 3.80 (s, 3H), 2.16 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 163.7, 158.6, 148.5, 130.1, 129.7, 129.27, 128.6,

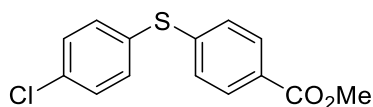
126.0, 125.1, 121.5, 120.9, 119.1, 113.4, 54.5, 15.2.



methyl 4-(4-butoxyphenyl)benzoate (52): Following the general procedure using 1-butanol as the nucleophile, obtained in 65% yield under 420 nm LEDs irradiation in DMF (27.1 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.*, **2020**, *59*, 12714).

^1H NMR (600 MHz, CDCl_3) δ 7.98 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 4.01 (t, $J = 6.5$ Hz, 2H), 3.88 (s, 3H), 1.82 – 1.75 (m, 2H), 1.54 – 1.46 (m, 2H), 0.98 (t, $J = 7.4$ Hz, 3H).

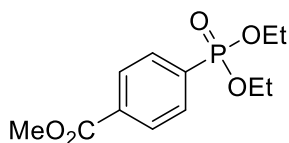
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.9, 163.0, 131.6, 122.3, 114.1, 67.9, 51.8, 31.2, 19.2, 13.8.



methyl 4-((4-chlorophenyl)thio)benzoate (53): Following the general procedure using 4-chlorothiophenol as the nucleophile, obtained in 60% yield under 420 nm LEDs irradiation in DMF (33.5 mg, eluent: petroleum ether/ethyl acetate = 15/1). The compound data was in agreement with the literature (Ref: *Chem. Commun.*, **2015**, *51*, 16613).

^1H NMR (600 MHz, CDCl_3) δ 7.91 (d, $J = 8.5$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.6$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 3.89 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.6, 143.5, 134.9, 134.7, 131.2, 130.2, 129.9, 127.9, 52.2. (one carbon signal is overlapped)



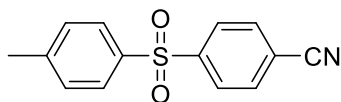
methyl 4-(diethoxyphosphoryl)benzoate (54): Following the general procedure using diethyl phosphite as the nucleophile, obtained in 88% yield under 420 nm LEDs

irradiation in THF (47.9 mg, eluent: petroleum ether/ethyl acetate = 5/1). The compound data was in agreement with the literature (Ref: *Chem. Commun.*, **2019**, 55, 14035).

^1H NMR (600 MHz, CDCl_3) δ 8.13 (dd, $J = 8.2, 3.9$ Hz, 2H), 7.90 (dd, $J = 13.0, 8.2$ Hz, 2H), 4.23 – 4.13 (m, 2H), 4.14 – 4.07 (m, 2H), 3.95 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 166.2, 133.5 (d, $J = 3.2$ Hz), 133.2 (d, $J = 186.5$ Hz), 131.8 (d, $J = 10.0$ Hz), 129.4 (d, $J = 14.9$ Hz), 62.4 (d, $J = 5.5$ Hz), 52.5, 16.3 (d, $J = 6.3$ Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3) δ 17.05.



4-tosylbenzonitrile (55): Following the general procedure using sodium 4-methylbenzenesulfinate as the nucleophile, obtained in 68% yield under 420 nm LEDs irradiation in DMA using 50 mol% DBU (35.0 mg, eluent: petroleum ether/ethyl acetate = 3/1). The compound data was in agreement with the literature (Ref: *Org. Lett.* **2021**, 23, 3663).

^1H NMR (600 MHz, CDCl_3) δ 8.03 (d, $J = 8.5$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 2.41 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ 146.3, 145.3, 137.1, 133.1, 130.3, 128.2, 128.1, 117.3, 116.7, 21.7.

4. UV-vis. Data

UV-vis measurements were recorded on a Shimadzu UV-vis Spectrophotometer UV-2450. It was observed that the reaction mixture exhibits a clear absorption in the visible region (up to 480 nm, blue line, Figure S1). This absorption onset explains the different performance of the purple, blue and green LEDs. Removing 4-iodobenzoate **2** and propylamine from the reaction mixture did not change the absorption wavelength or intensity (purple line), whereas removing Ni(dtbbpy)Br₂ caused a significant reduction in the absorption intensity (grey line). Upon adding 15 equiv of DBU (relative to Ni) to the Ni(dtbbpy)Br₂ solution, the absorption of the Ni solution blue-shifted significantly (purple line vs. red line).

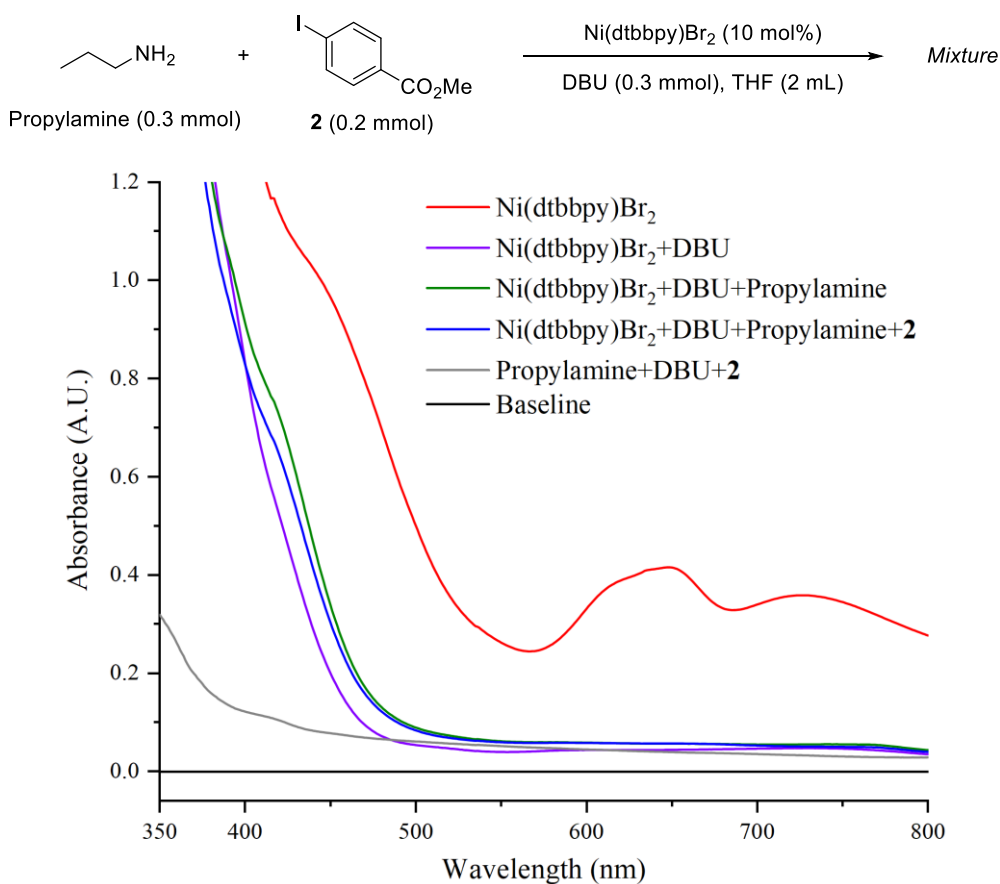


Figure S1. UV-vis absorption spectrum of the reaction mixture

5. EPR and HRMS studies

Electron Paramagnetic Resonance (EPR) studies were performed with Magnettech MS-5000. A DMF solution containing Ni(dtbbpy)Br₂, 5 equiv of propylamine and 5 equiv of DBU was injected into a glass tube. The tube was frozen with liquid nitrogen and evacuated for 10 min, and then sintered to seal through a flame gun to remove oxygen. Upon irradiating the tube with 395 nm LEDs for 6 h, the color of the solution changed from yellow to dark brown. Finally, the EPR spectrum was collected on a frozen solution at 100 K with a microwave power of 10 mW. Similar EPR signals can also be obtained through the above process using THF or MeCN as solvent, but they are weaker. Control experiments showed that only irradiating the Ni(dtbbpy)Br₂ solution added with DBU will generate the EPR signal.

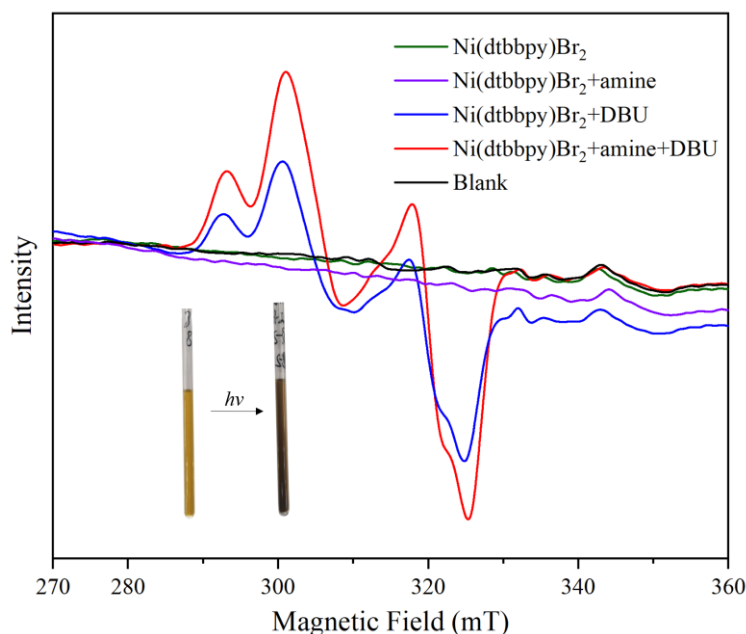


Figure S2. EPR spectrum measured by irradiating the Ni(dtbbpy)Br₂ solution

In a nitrogen-filled glove box, Ni(cod)₂ (0.1 mmol) and dtbbpy (0.1 mmol) were placed in a transparent Schlenk tube equipped with a stirring bar. To these solids, anhydrous DMF (2 mL) was added via a gastight syringe, and the mixture was stirred at room temperature for 0.5 h. Then Ni(dtbbpy)Br₂ (0.1 mmol) was added. After stirring for 4 hours in glove box, the reaction mixture was transferred to an EPR tube. EPR spectrum of the in situ-made Ni(I) species was collected on a frozen solution at 100 K and revealed a signal with $g_{\parallel} = 2.26$ and $g_{\perp} = 2.07$, which are consistent with literature reports (*Angew. Chem. Int. Ed.*, **2020**, *59*, 12714; *Angew. Chem. Int. Ed.*, **2015**, *54*, 9876). When DBU

(0.4 mmol) was added to the in situ-made Ni(I) species before the test, the EPR spectrum obtained would generate new signal peak (bottom of Figure S3).

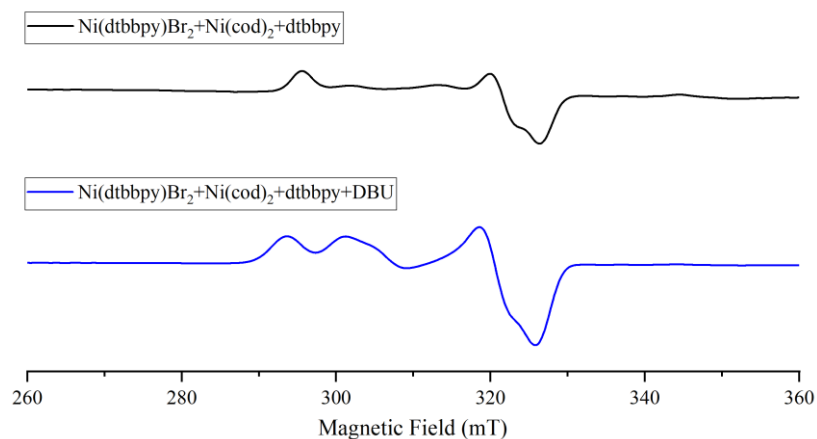


Figure S3. EPR spectrum of the in situ-made Ni(I) species with or without DBU

Ni(dtbbpy)(*o*-Tol)Br can be excited to a ³MLCT state and undergoes homolysis of the nickel–carbon bond to generate aryl radicals and Ni(I) species. We also collected the EPR spectrum of the irradiated Ni(dtbbpy)(*o*-Tol)Br and DBU. By comparison, we found that the signal generated by irradiating Ni(dtbbpy)Br₂ and DBU solution is similar to that obtained by irradiating Ni(dtbbpy)(*o*-Tol)Br and DBU solution, and the signal obtained by mixing in situ-made Ni(I) and DBU, indicating that irradiating Ni(dtbbpy)Br₂ and DBU generated Ni(I) species.

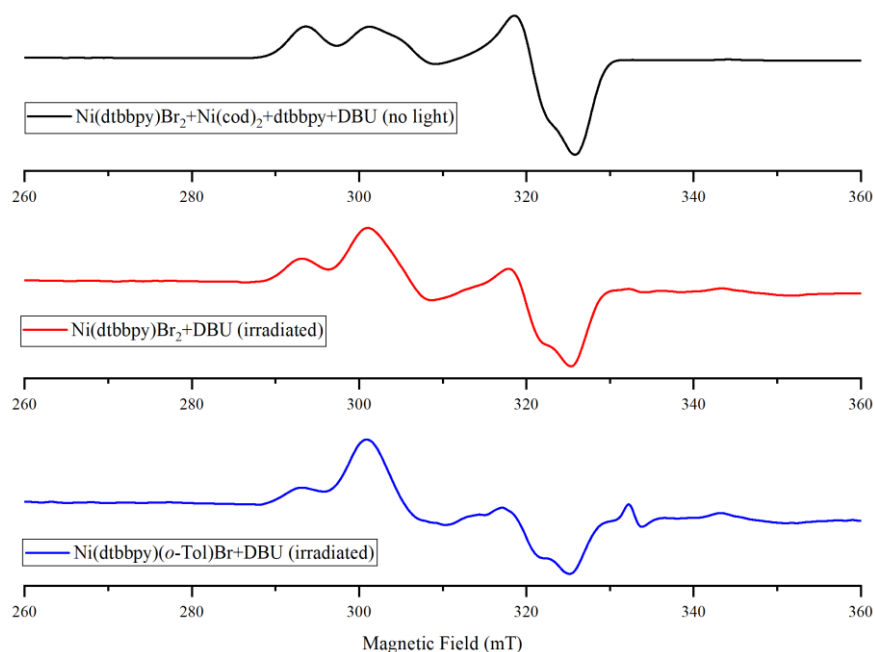


Figure S4. Comparison of three EPR spectra

2,2,6,6-tetramethylpiperidinoxy (TEMPO) was used as the radical scavenger to detect the DBU radical cation, which would be formed by photoinduced LMCT of Ni(dtbbpy)Br₂ and DBU as we envisioned. HRMS analysis of the irradiated the mixture of Ni(dtbbpy)Br₂, DBU and TEMPO revealed the formation of a coupling product of the DBU cation radical and TEMPO.

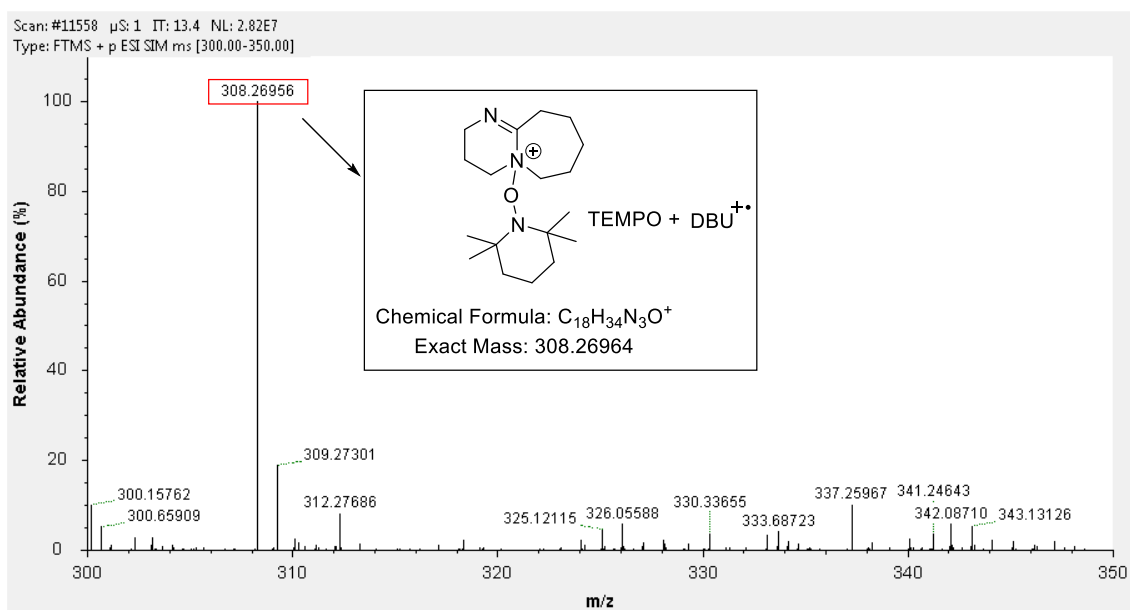
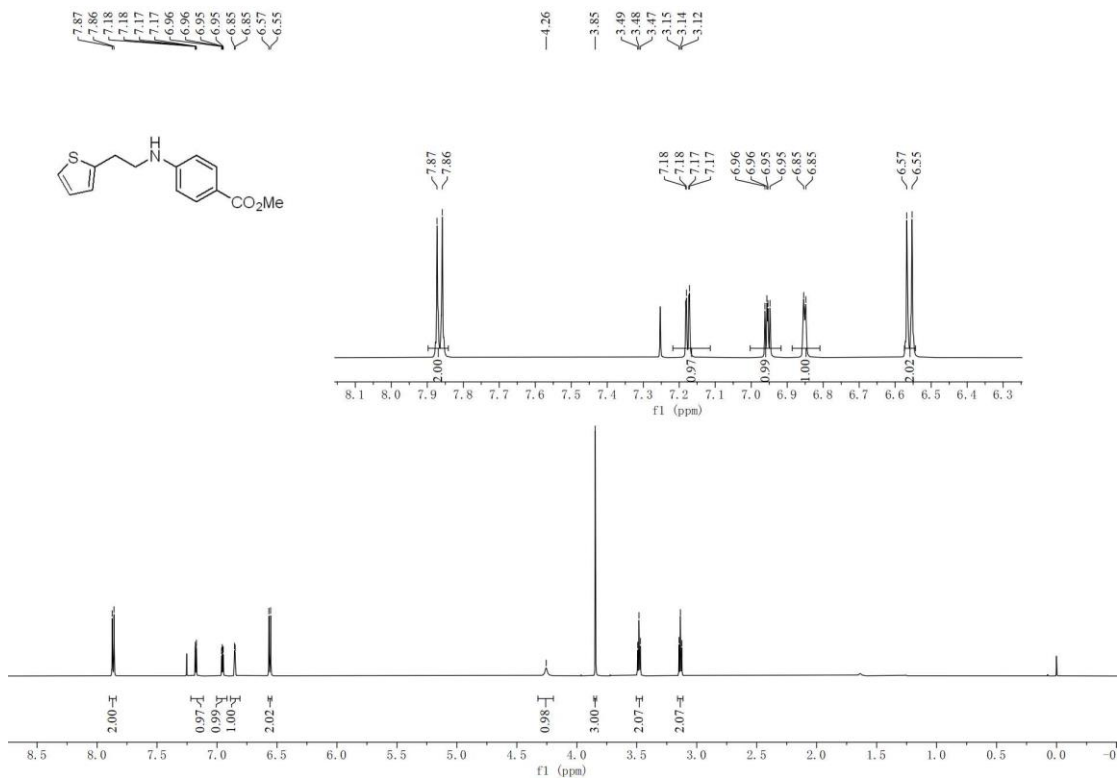


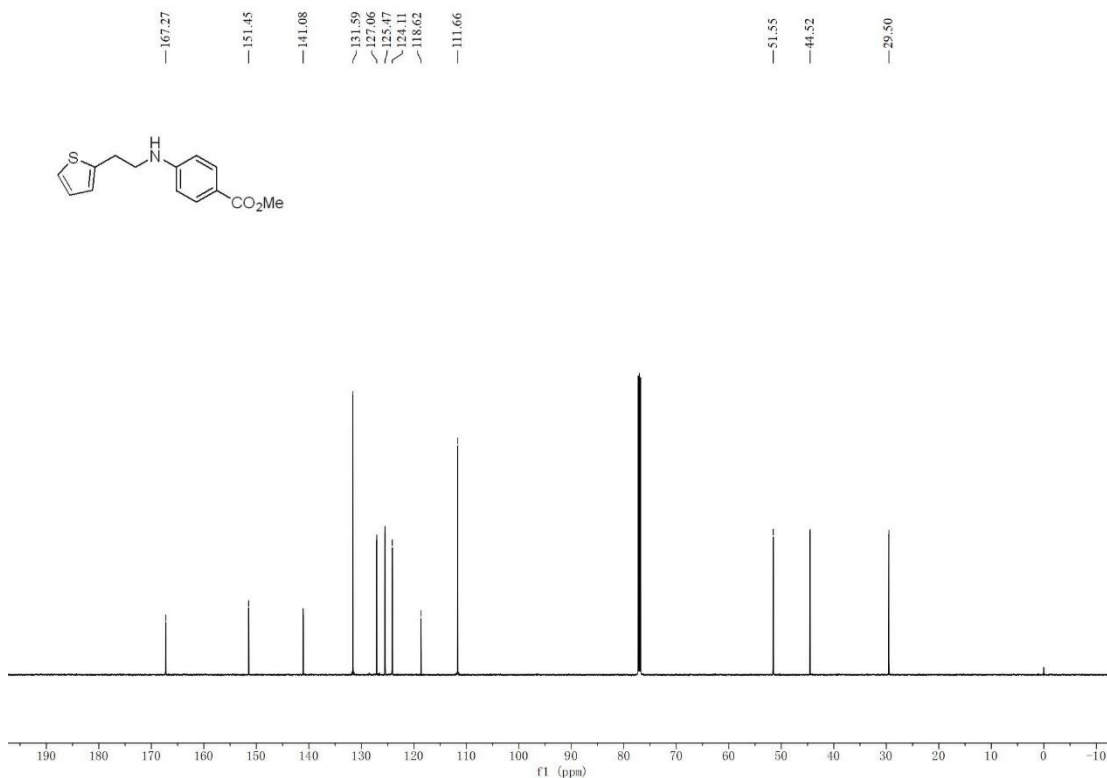
Figure S5. Mass spectrometry of the coupling product of the DBU cation radical and TEMPO.

6. NMR Spectra

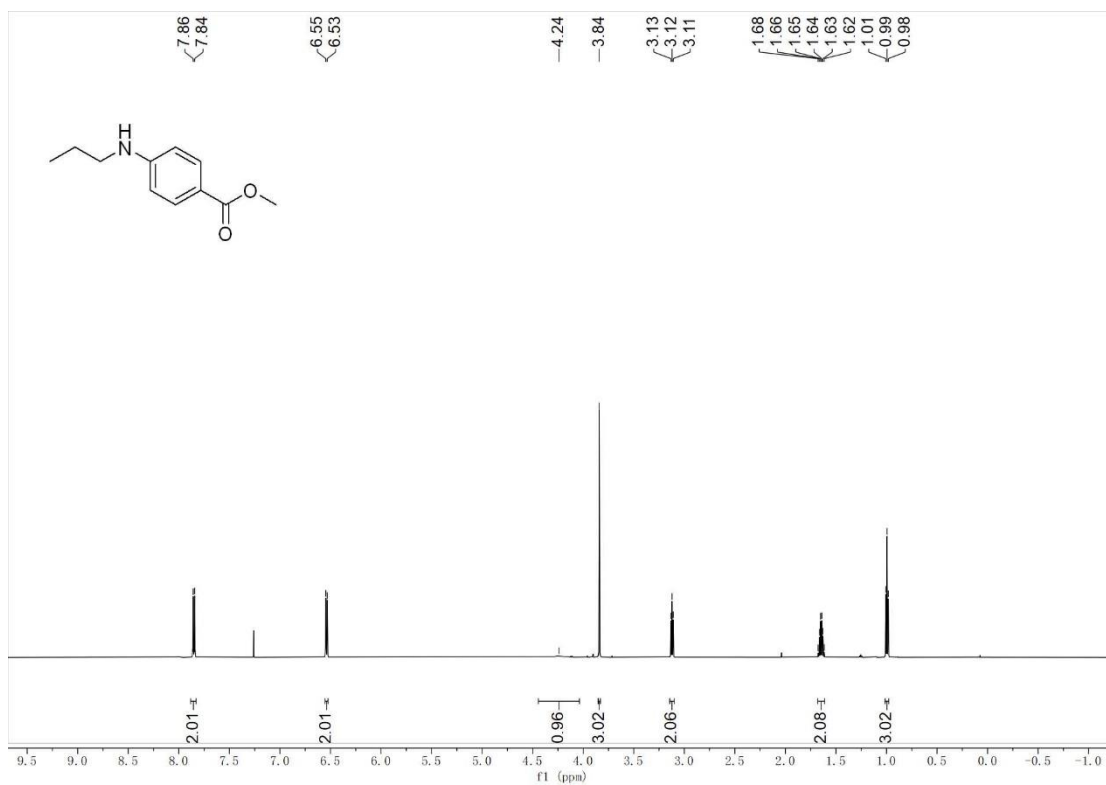
^1H NMR of compound (3)



$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (3)



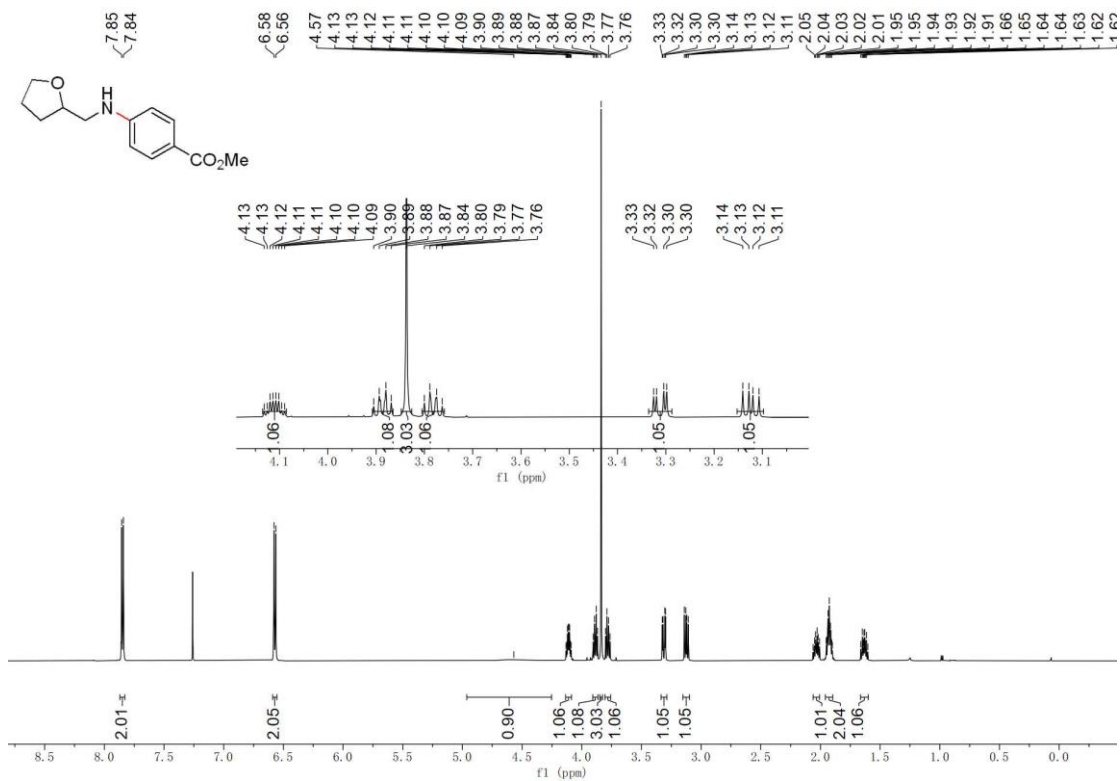
^1H NMR of compound (4)



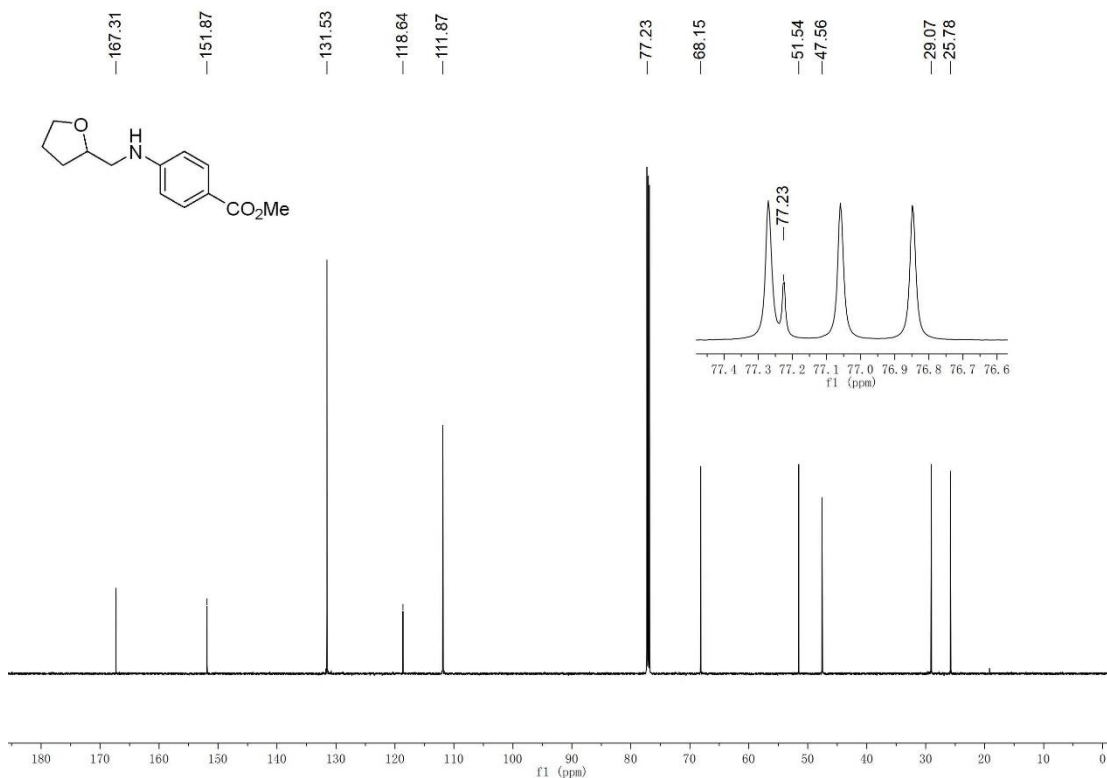
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (4)



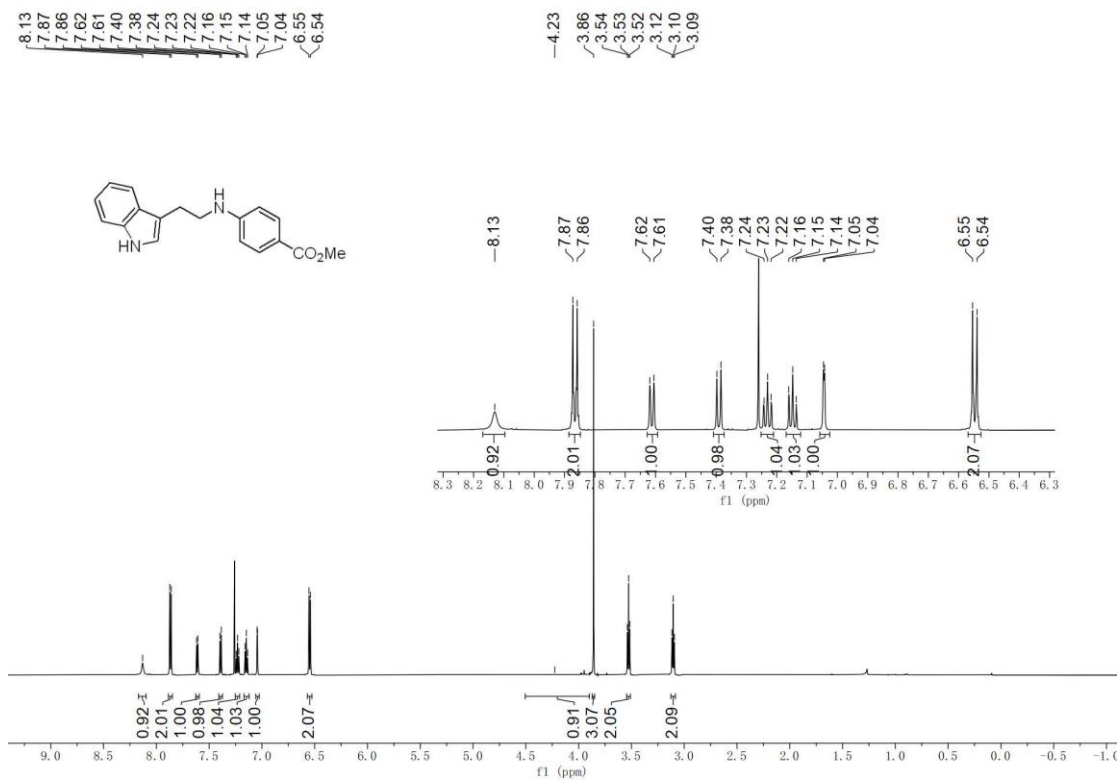
¹H NMR of compound (5)



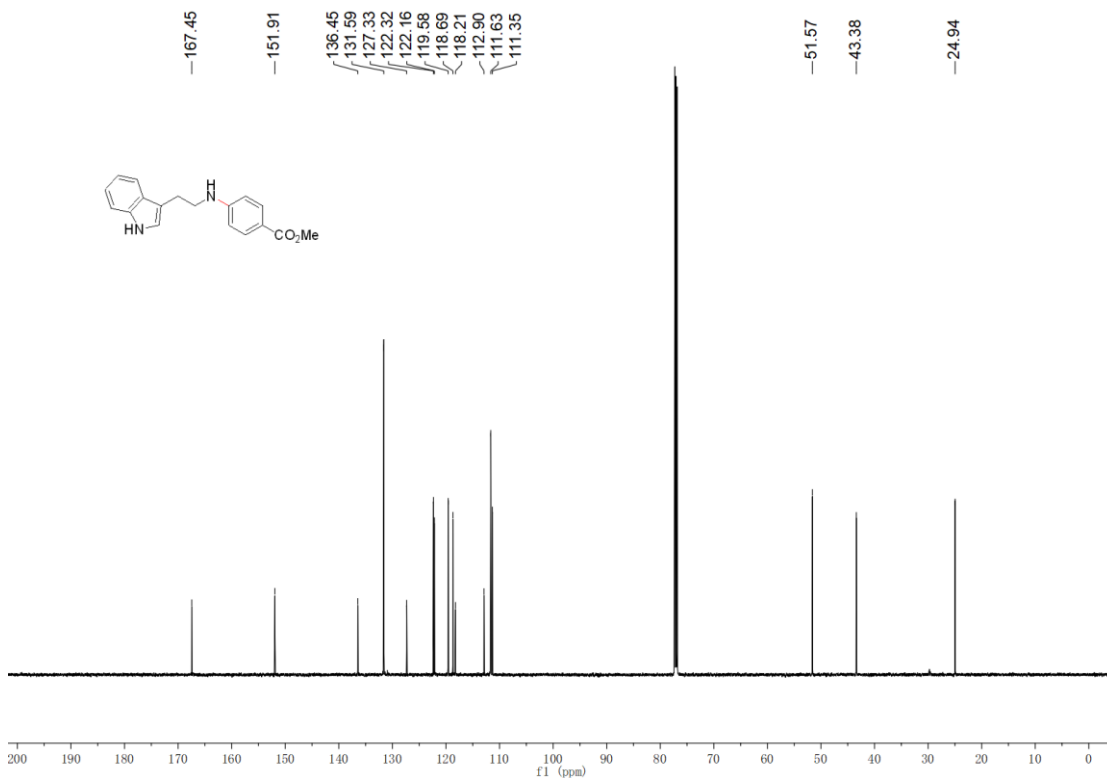
¹³C {¹H} NMR of compound (5)



^1H NMR of compound (6)



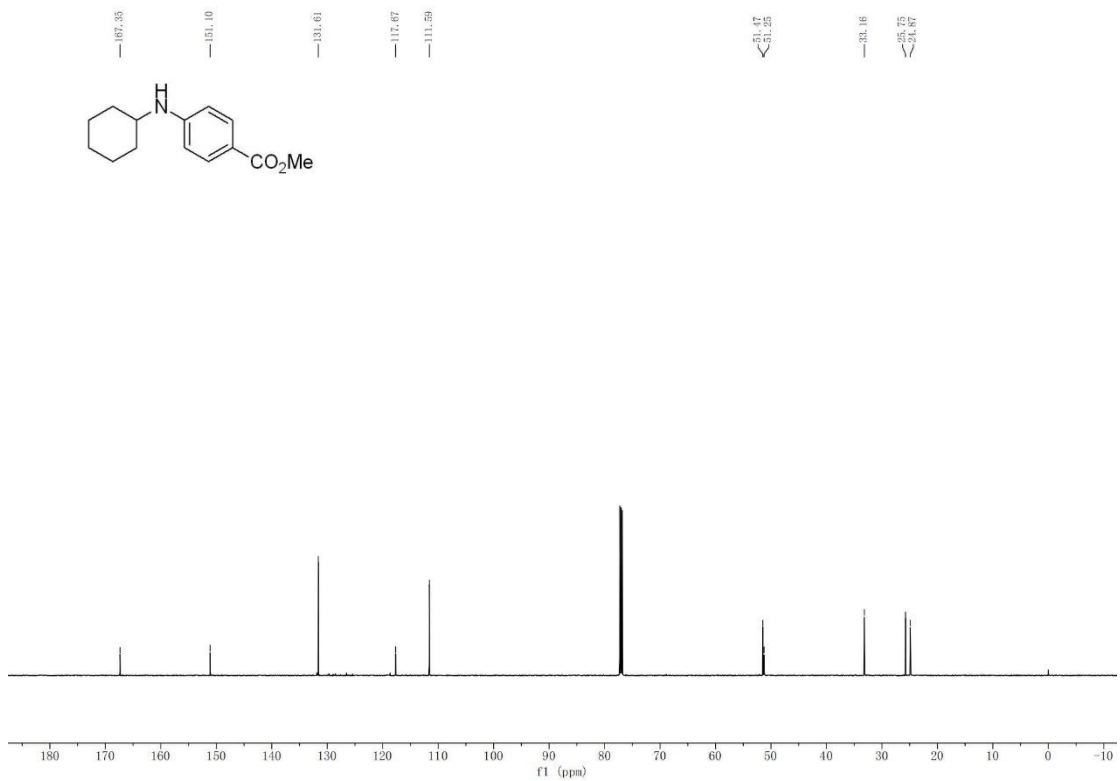
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (6)



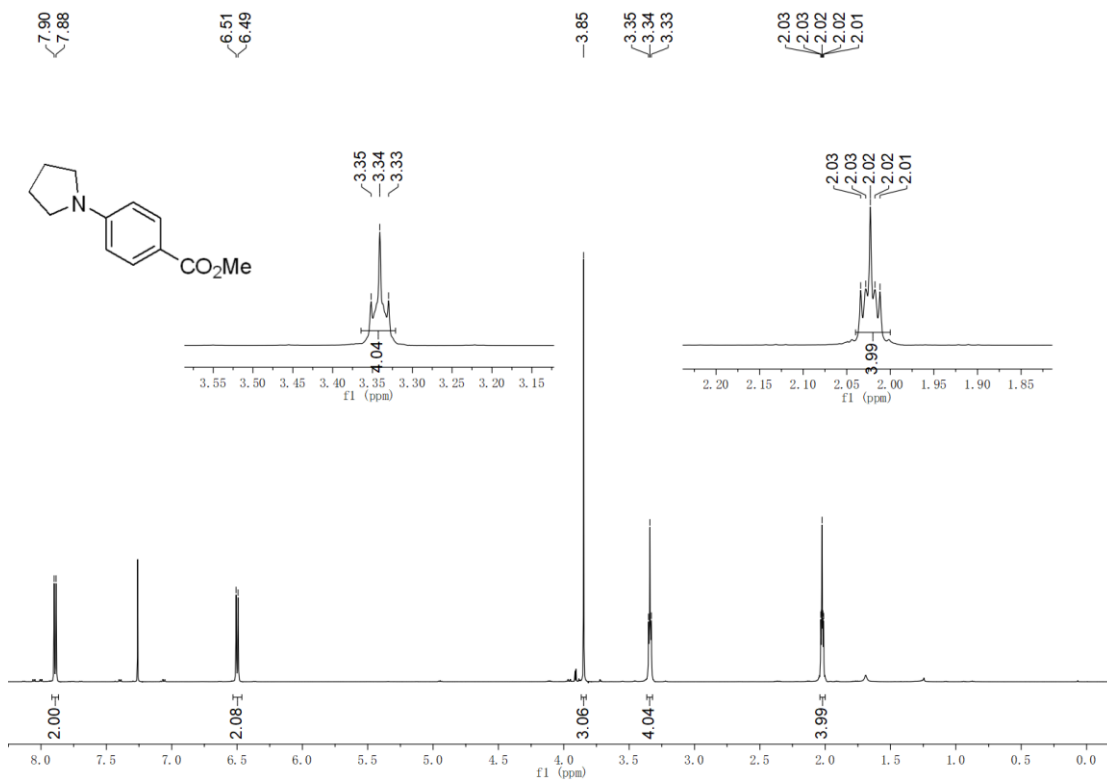
^1H NMR of compound (7)



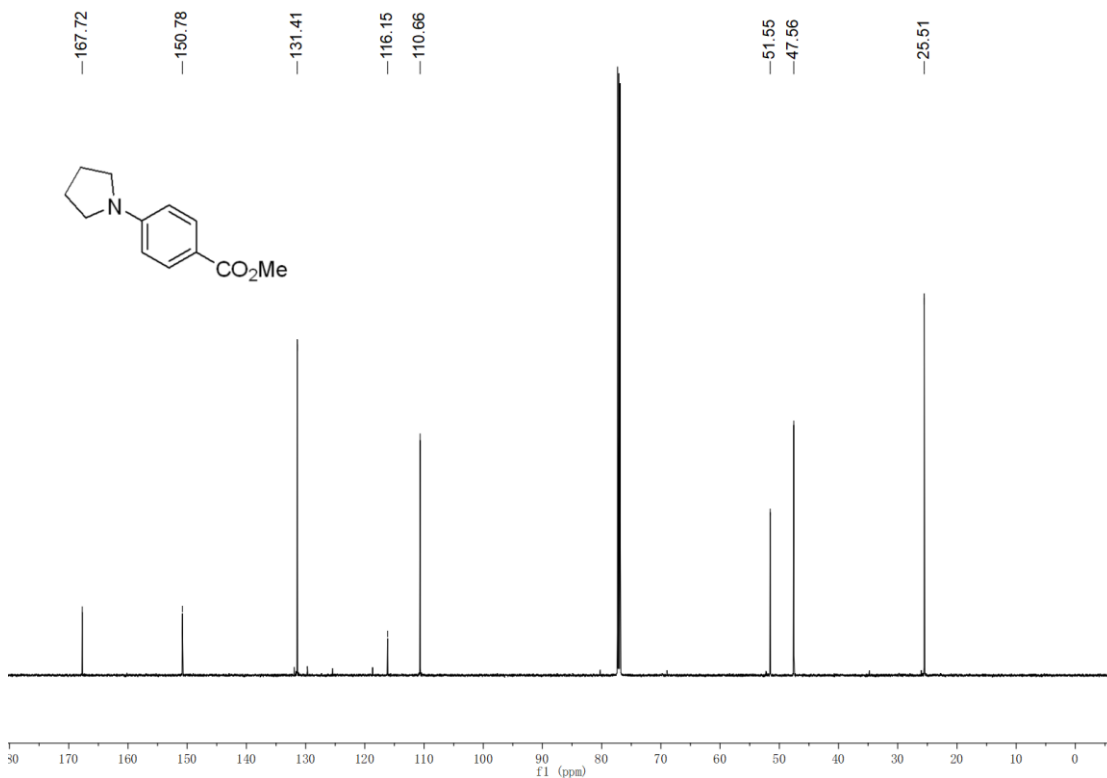
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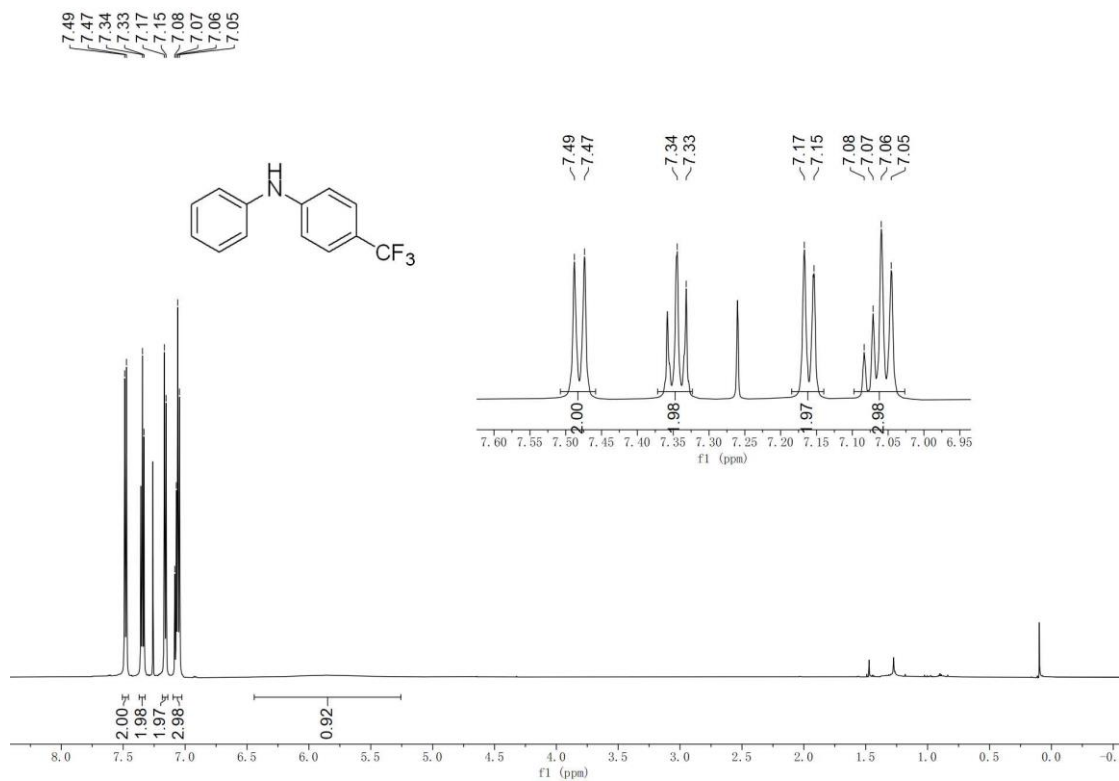
^1H NMR of compound (8)



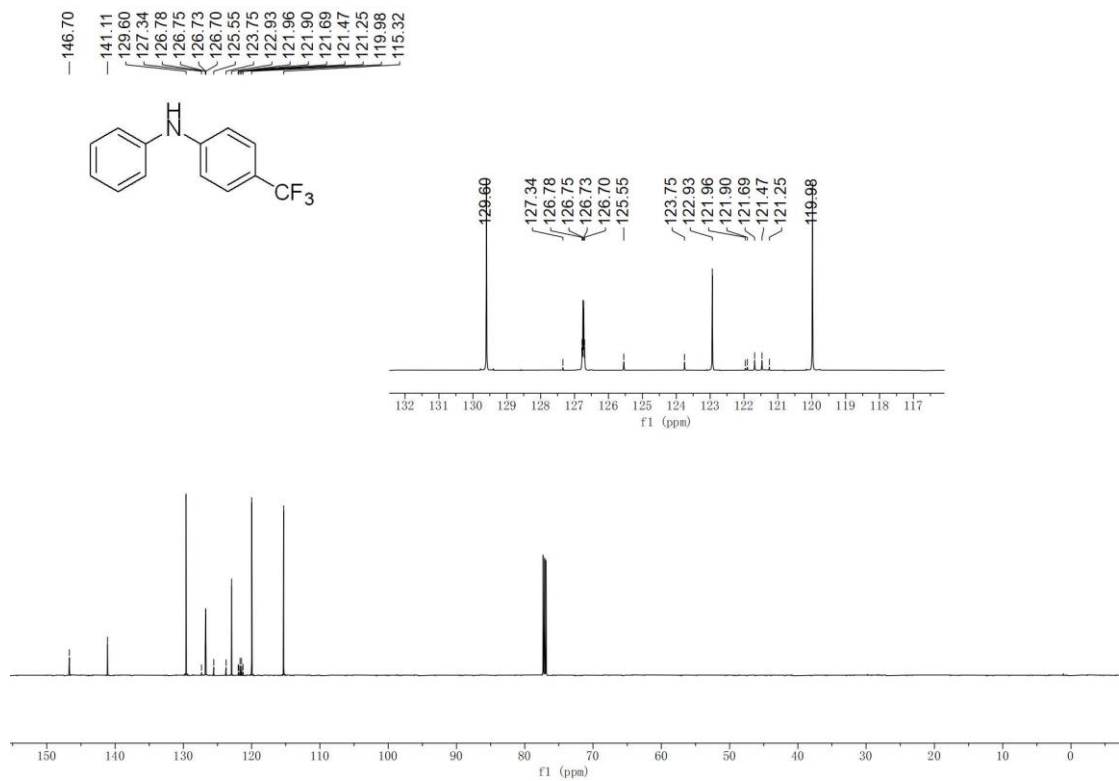
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (8)



^1H NMR of compound (9)



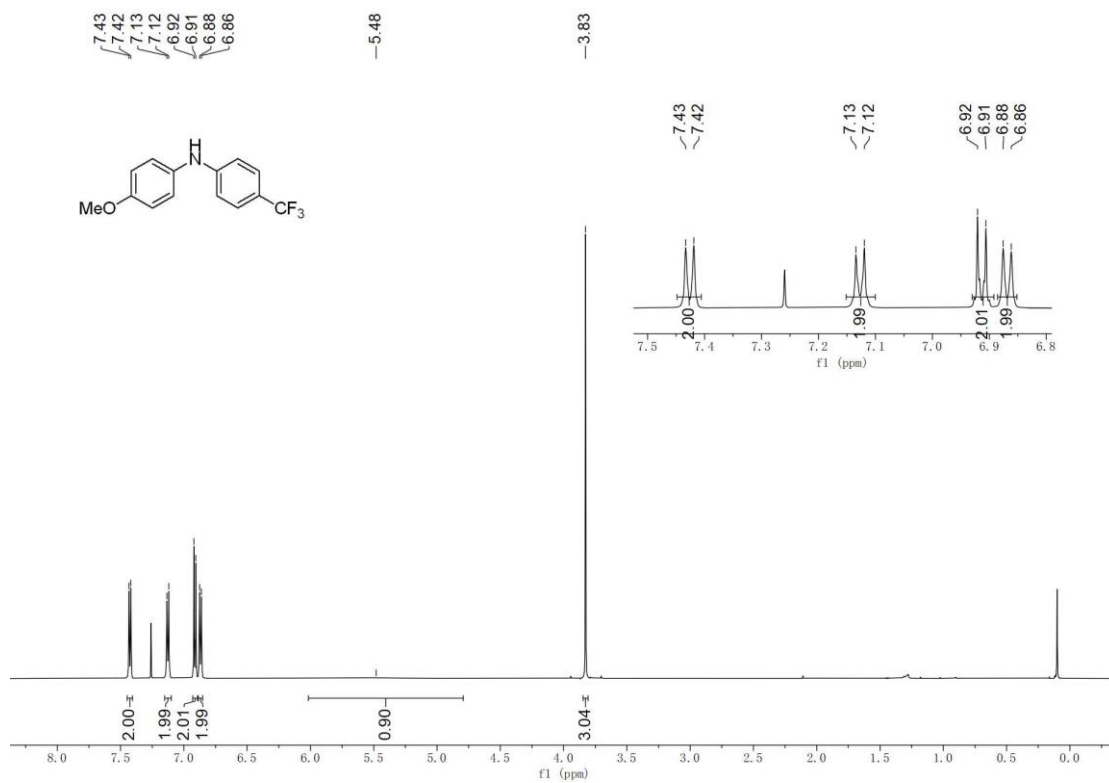
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (9)



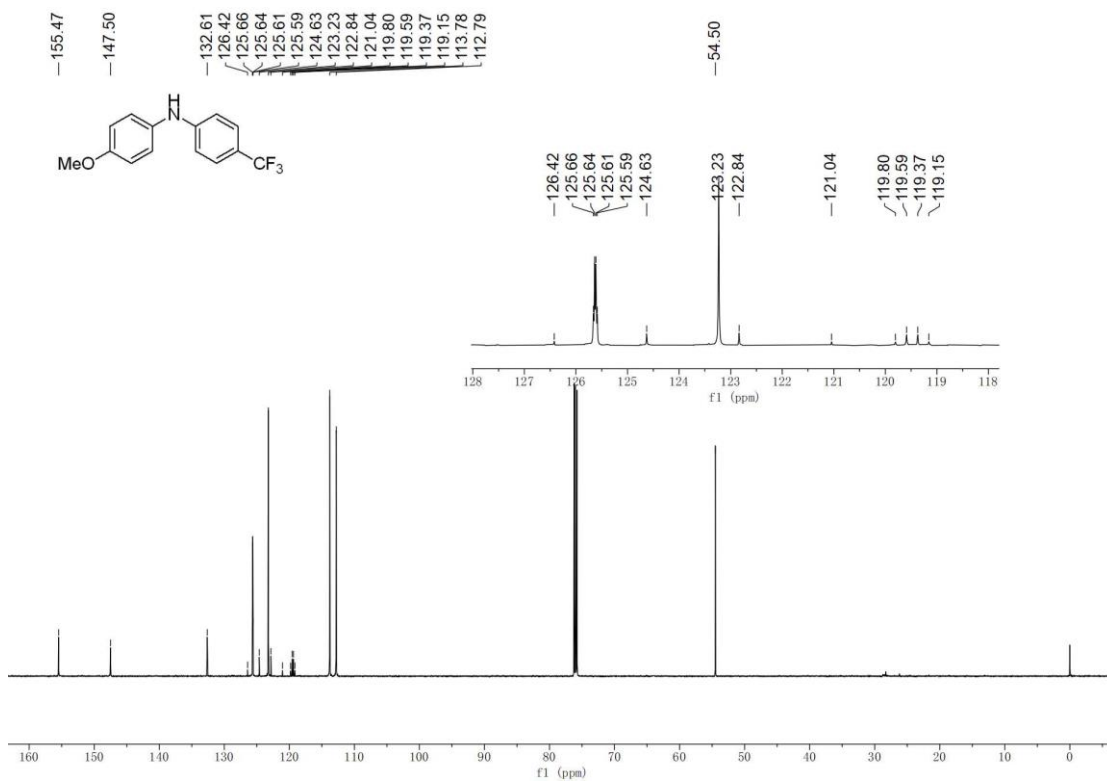
$^{19}\text{F}\{^1\text{H}\}$ NMR of compound (9)



^1H NMR of compound (10)



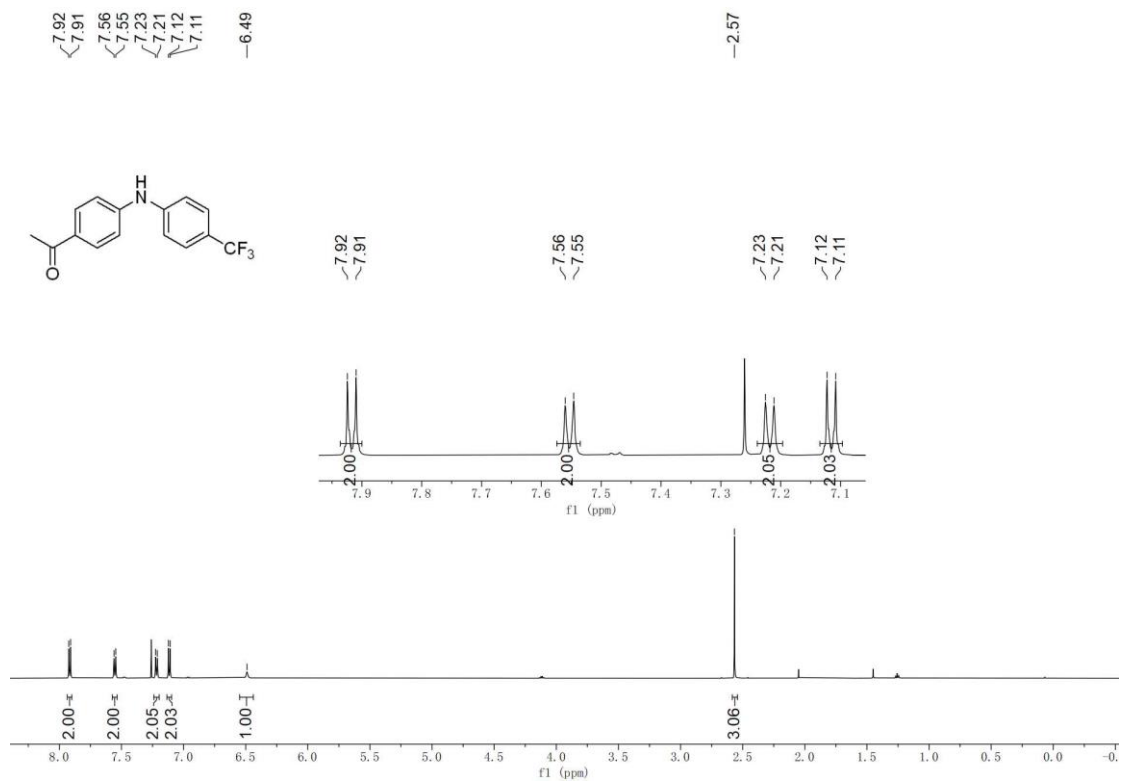
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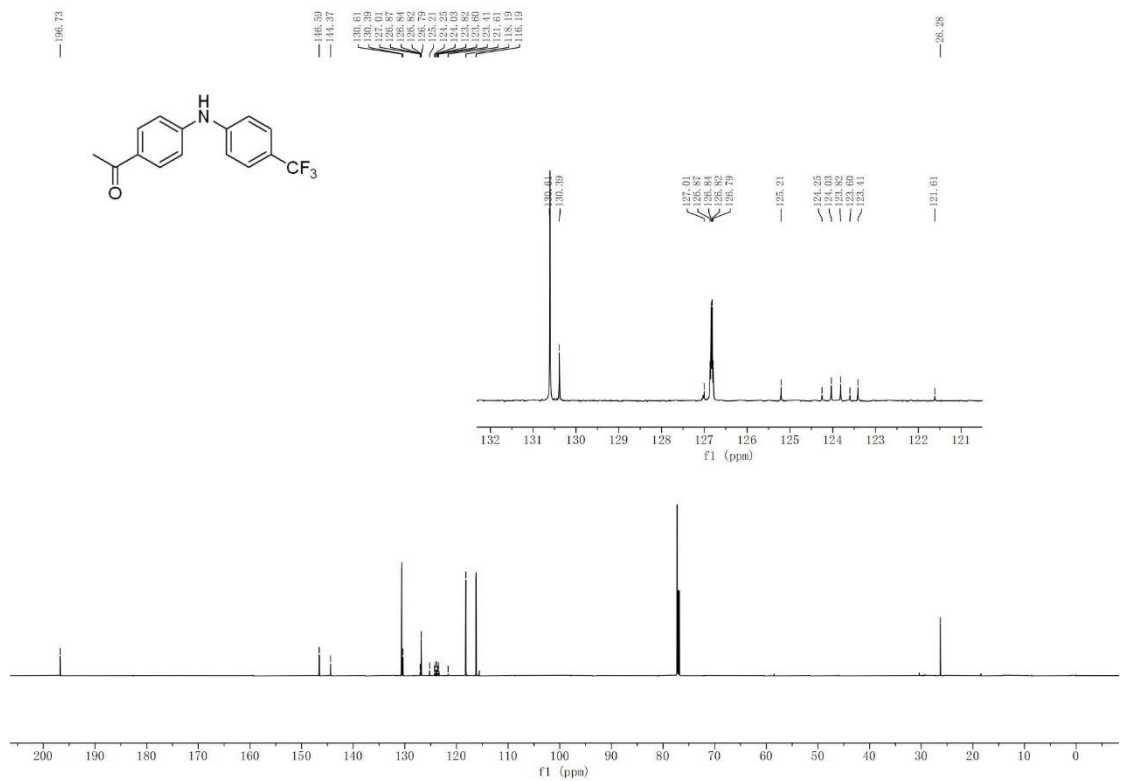
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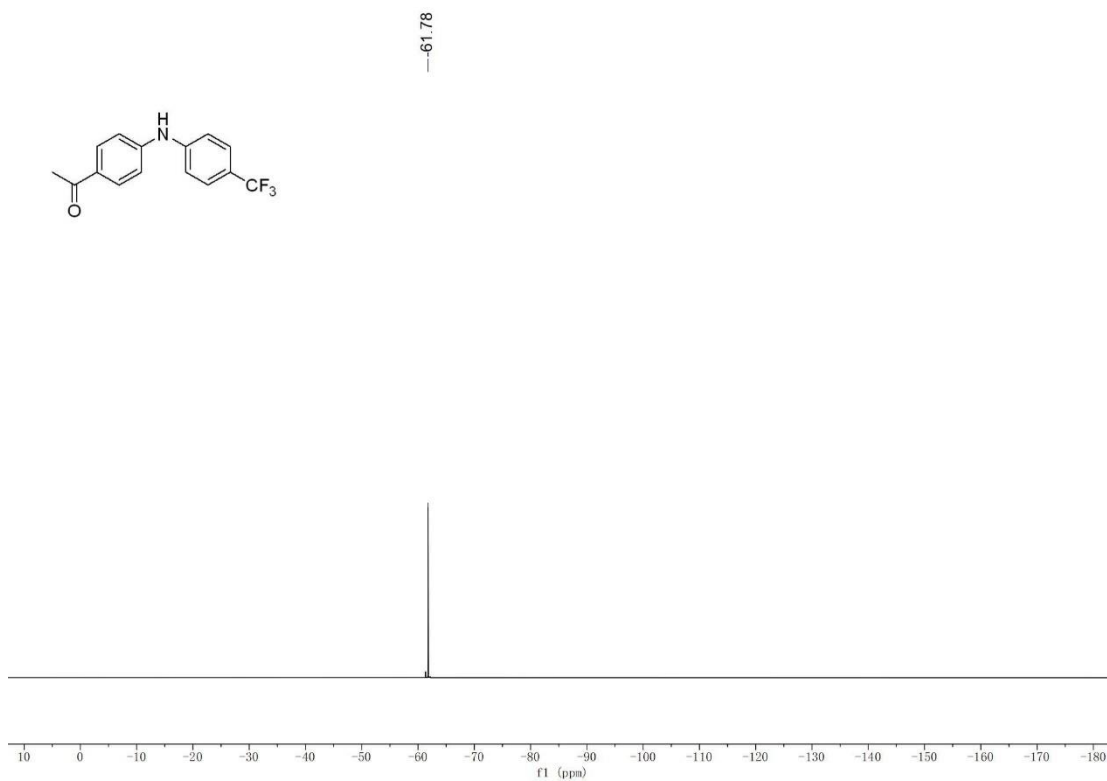
¹H NMR of compound (11)



¹³C{¹H} NMR of compound (11)



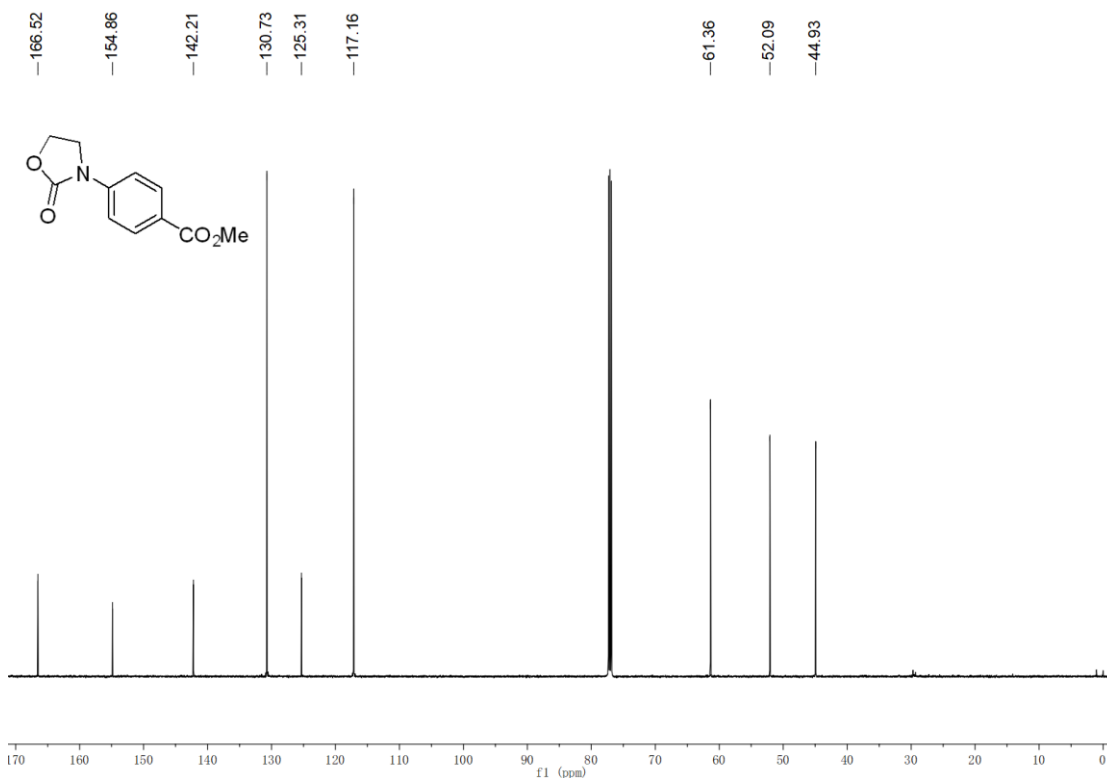
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^1H NMR of compound (12)



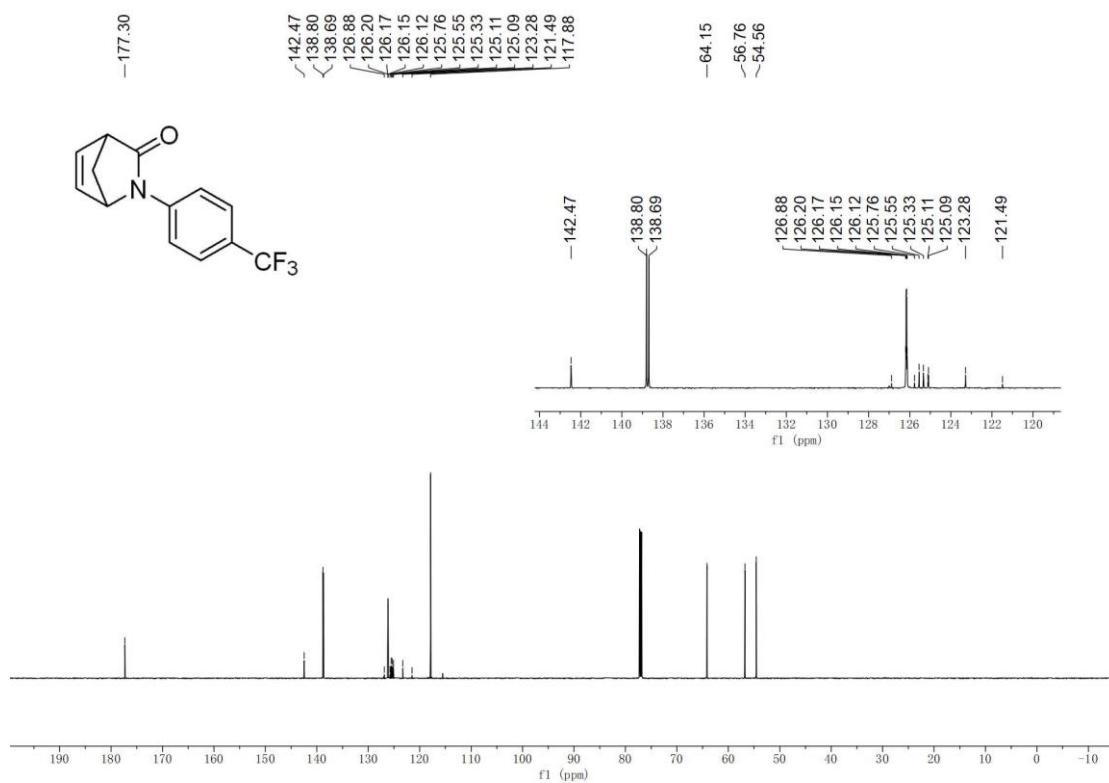
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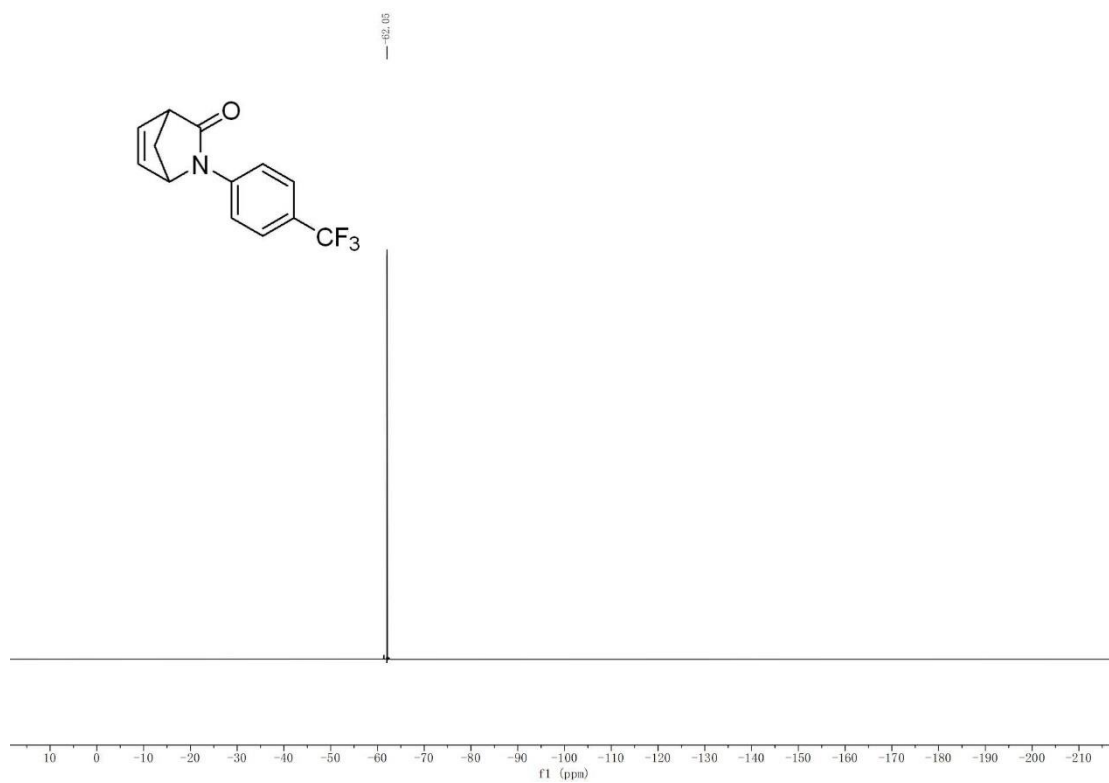
^1H NMR of compound (13)



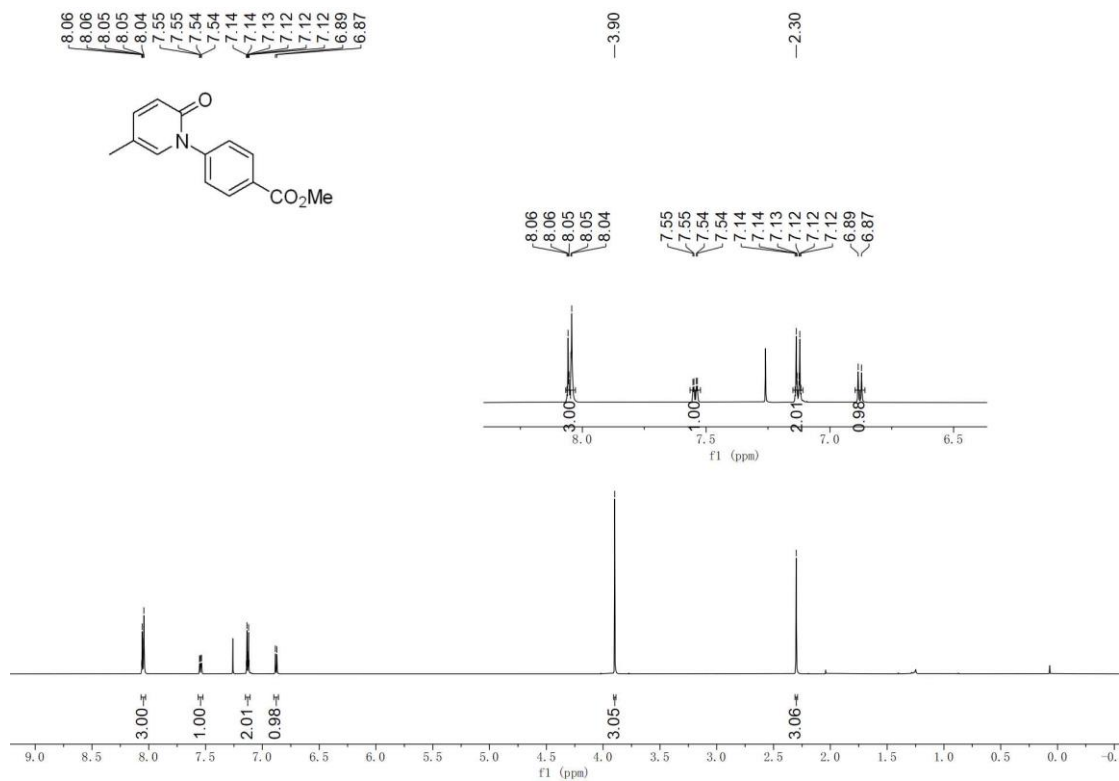
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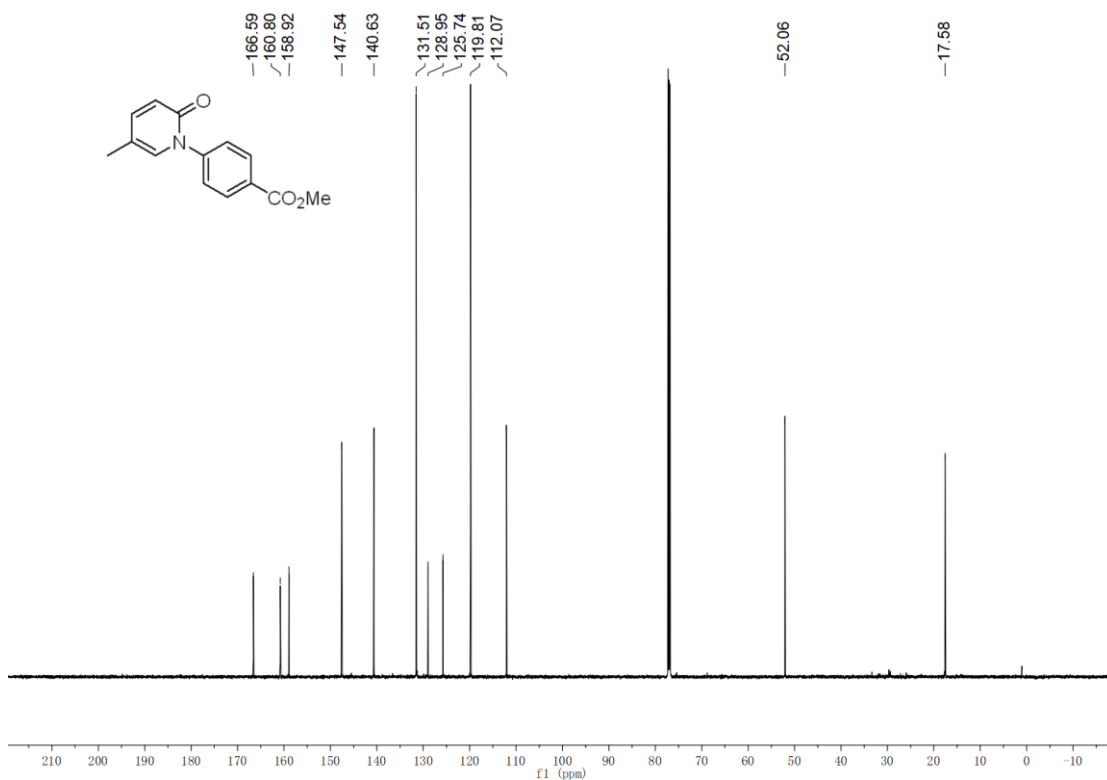
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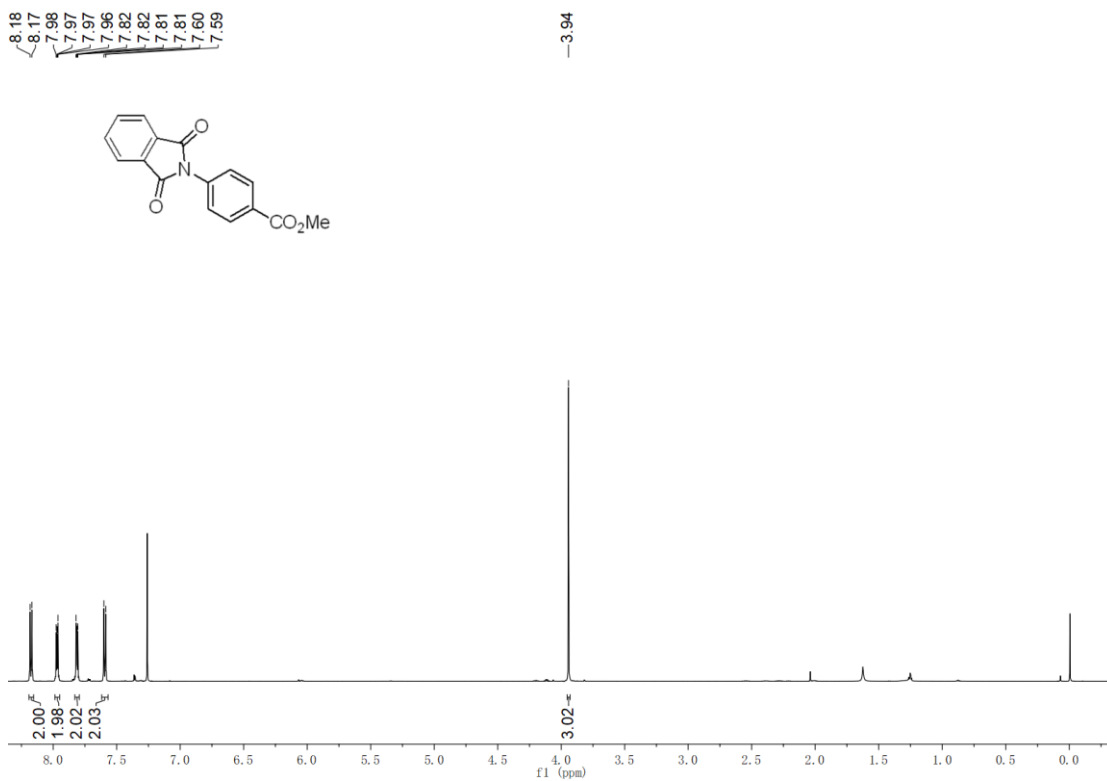
^1H NMR of compound (14)



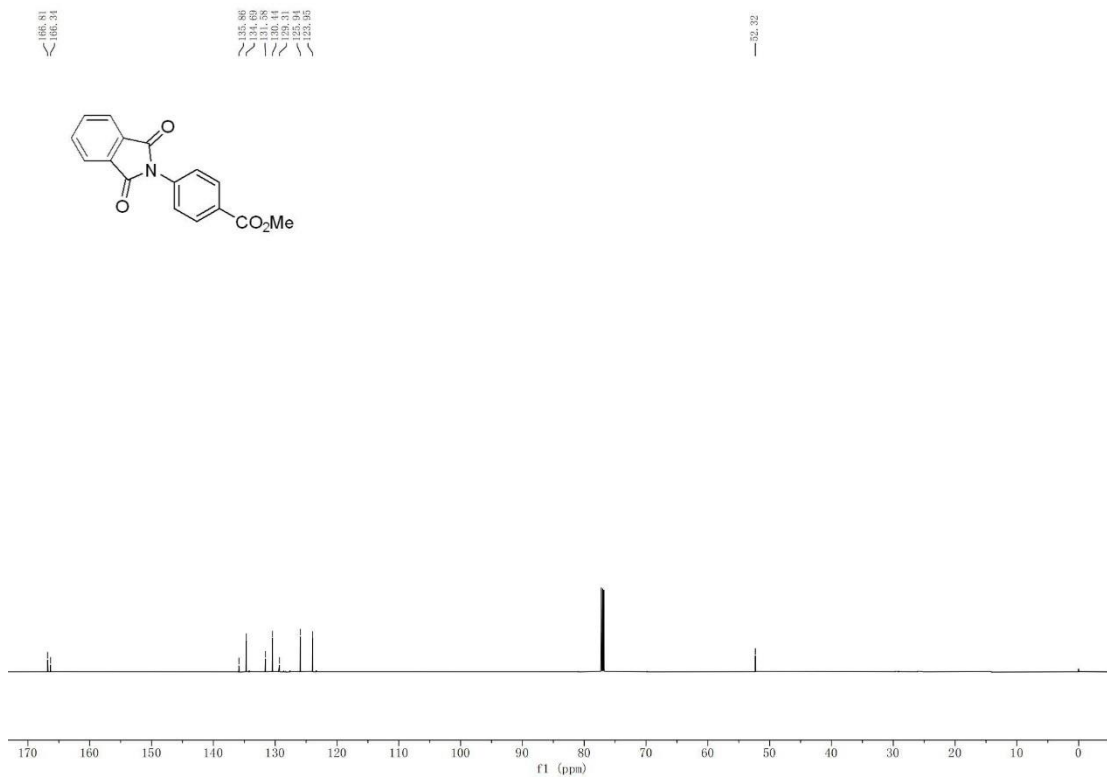
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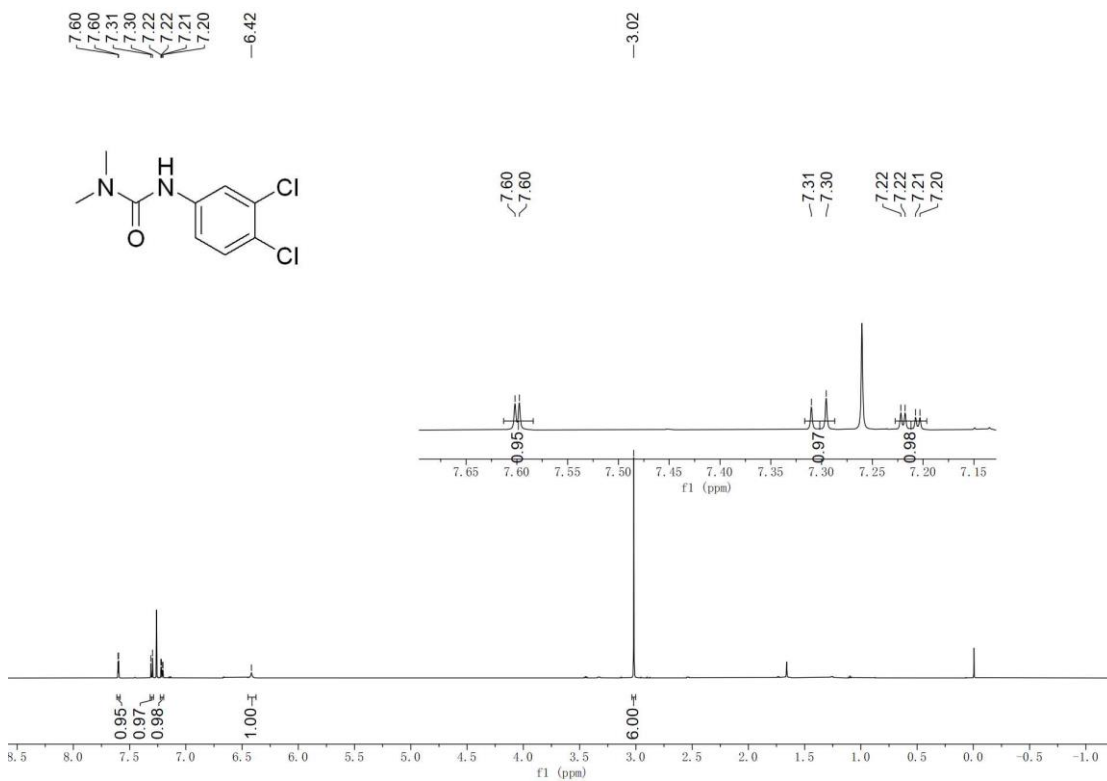
^1H NMR of compound (15)



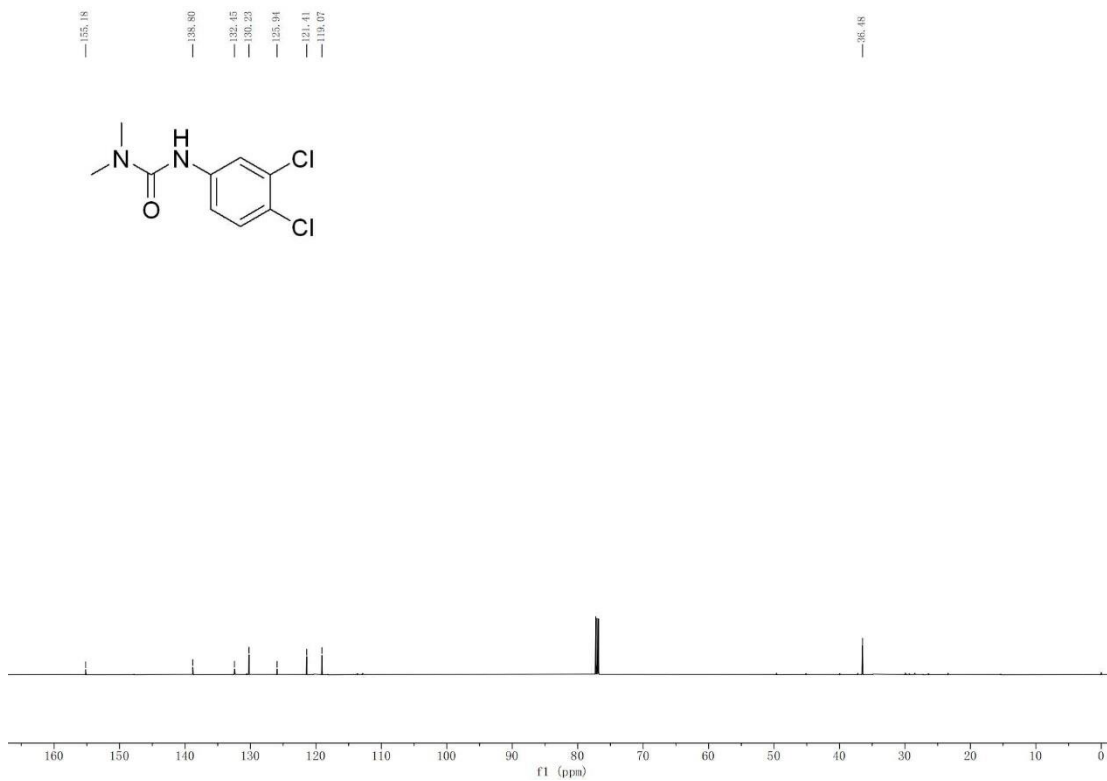
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (15)



^1H NMR of compound (16)



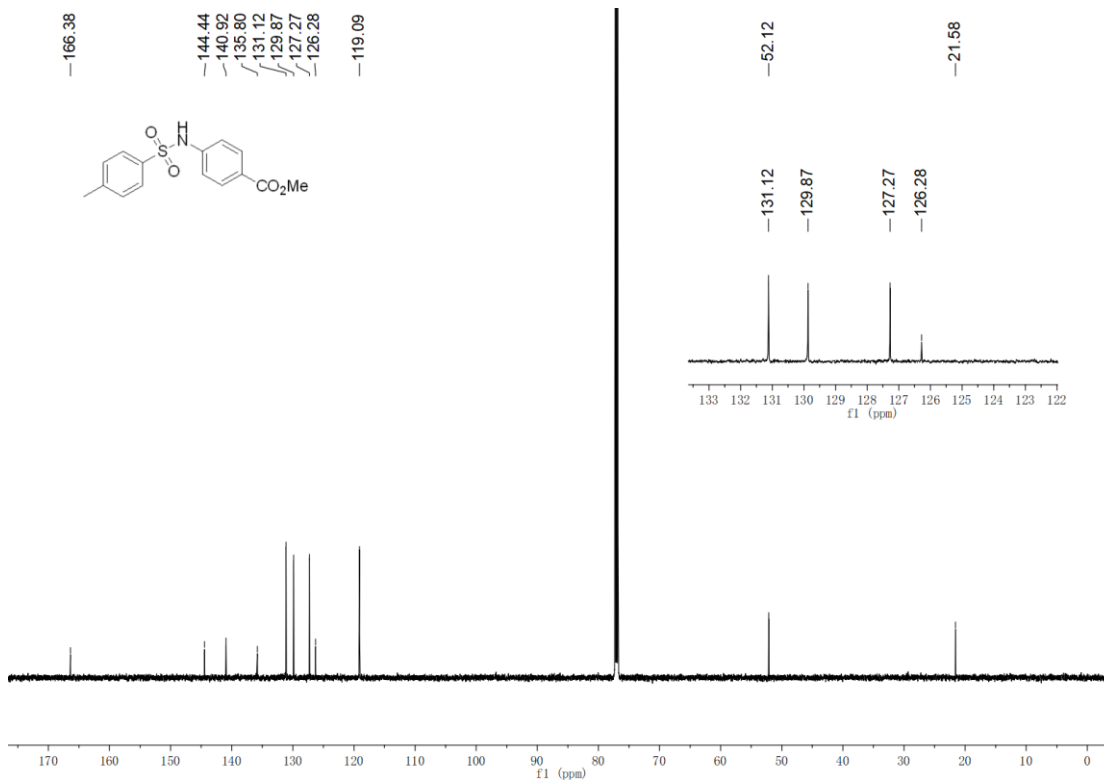
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (16)



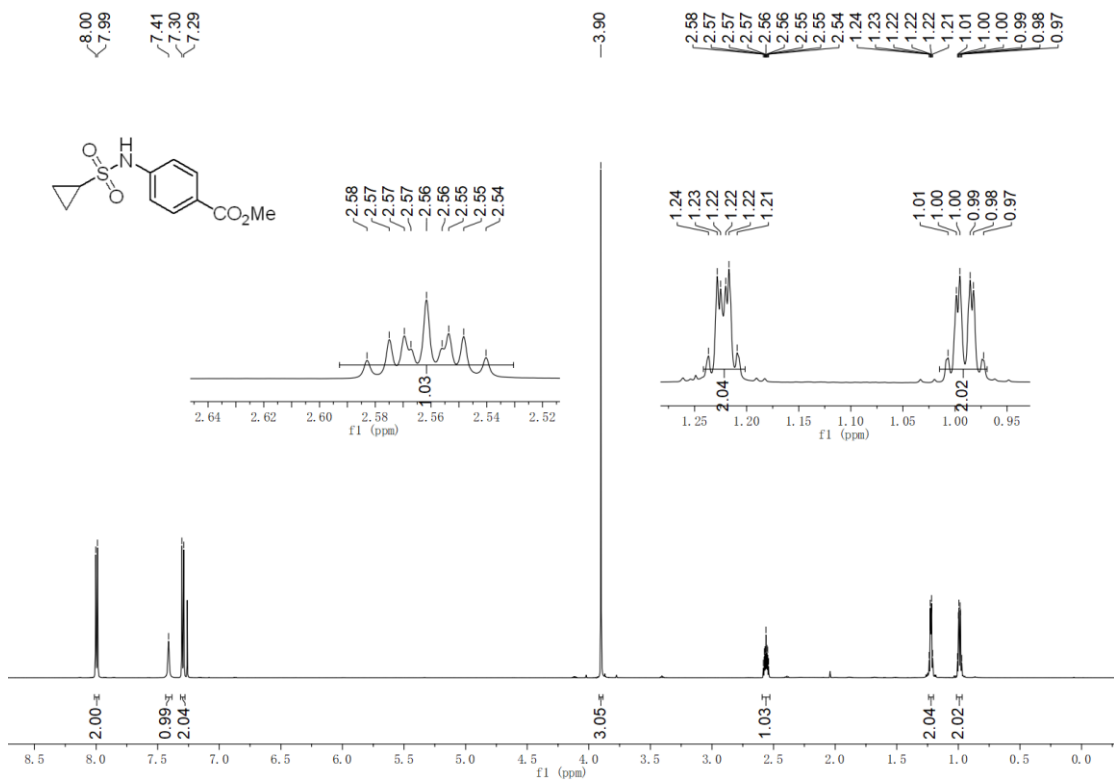
^1H NMR of compound (17)



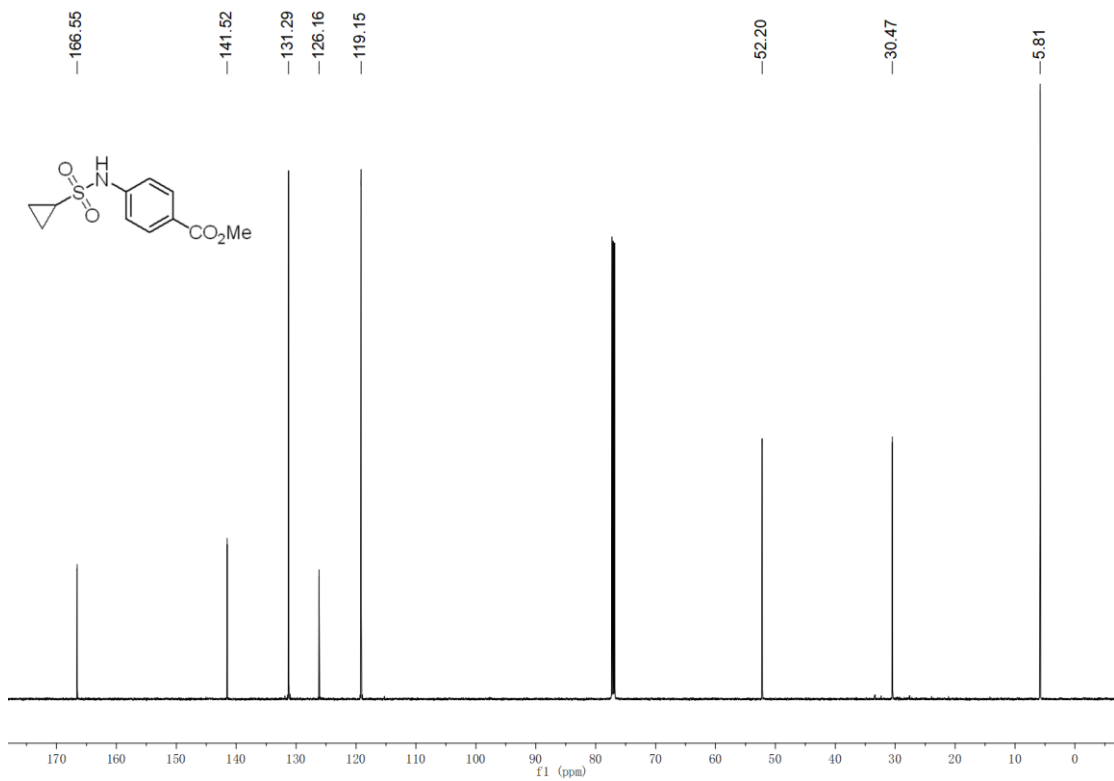
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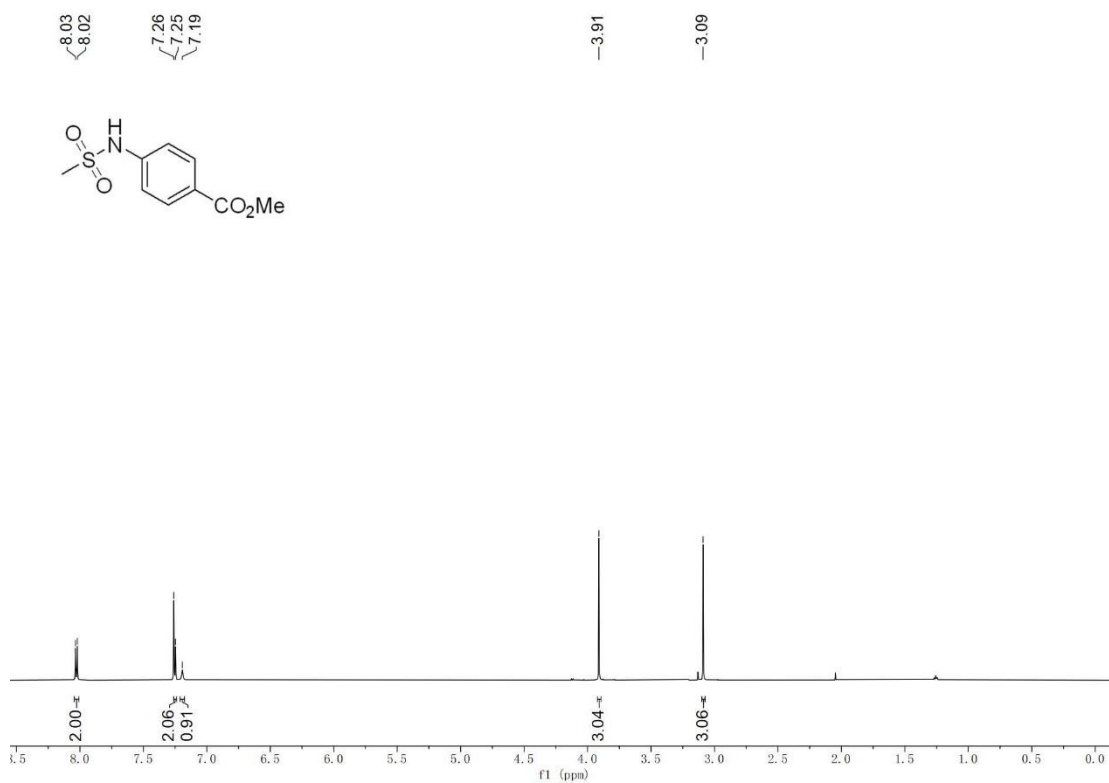
^1H NMR of compound (18)



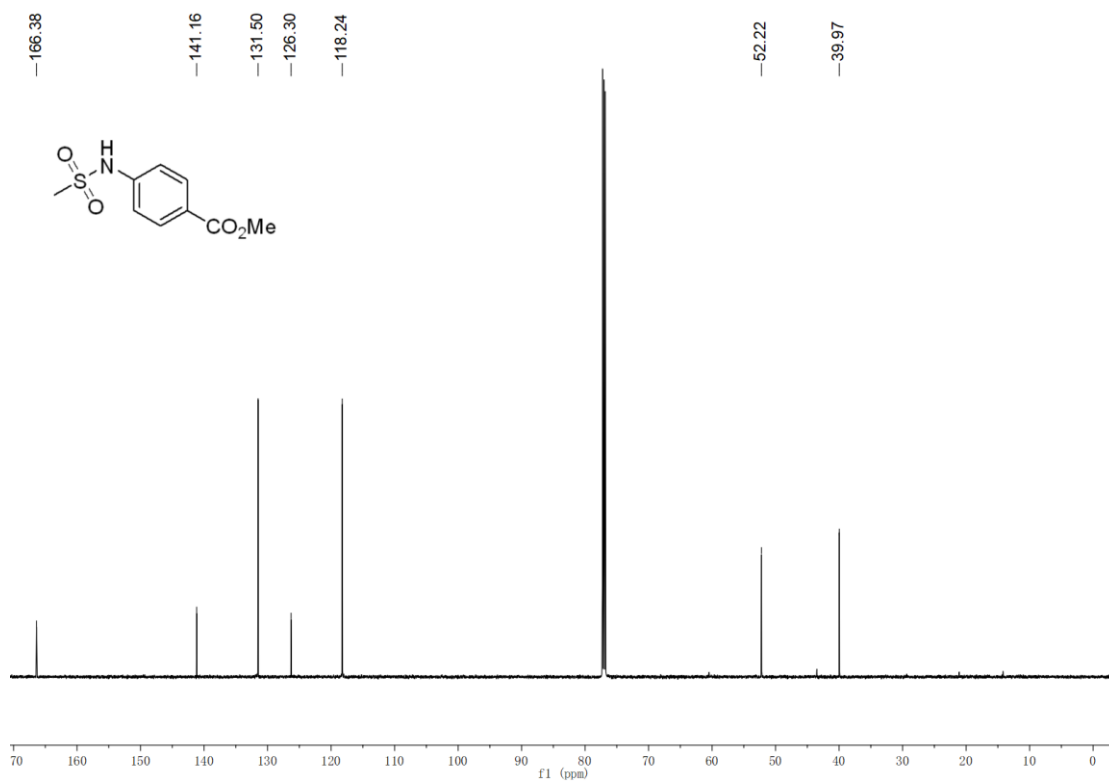
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (18)



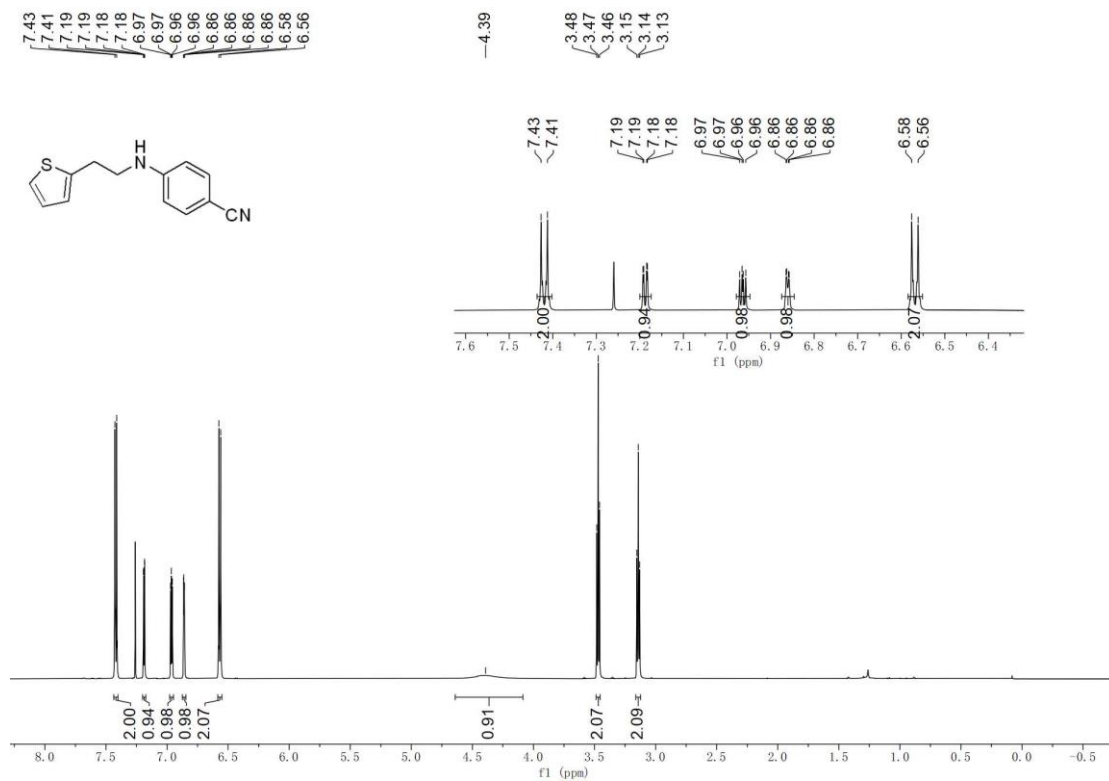
^1H NMR of compound (19)



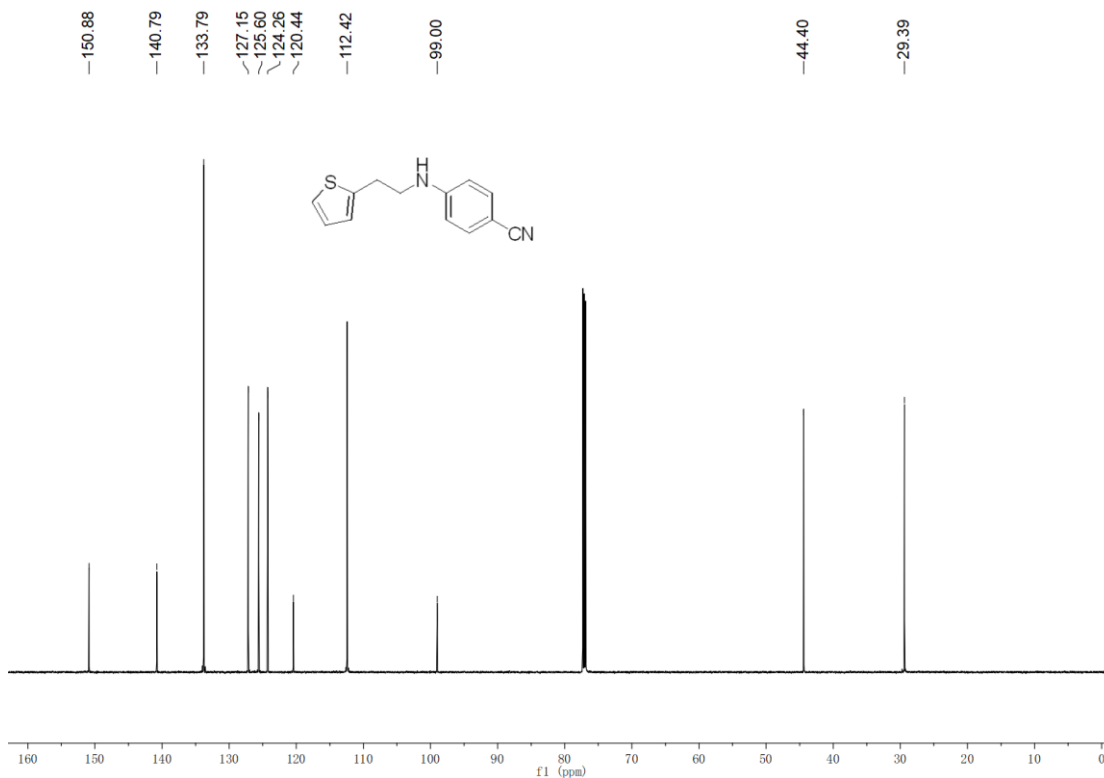
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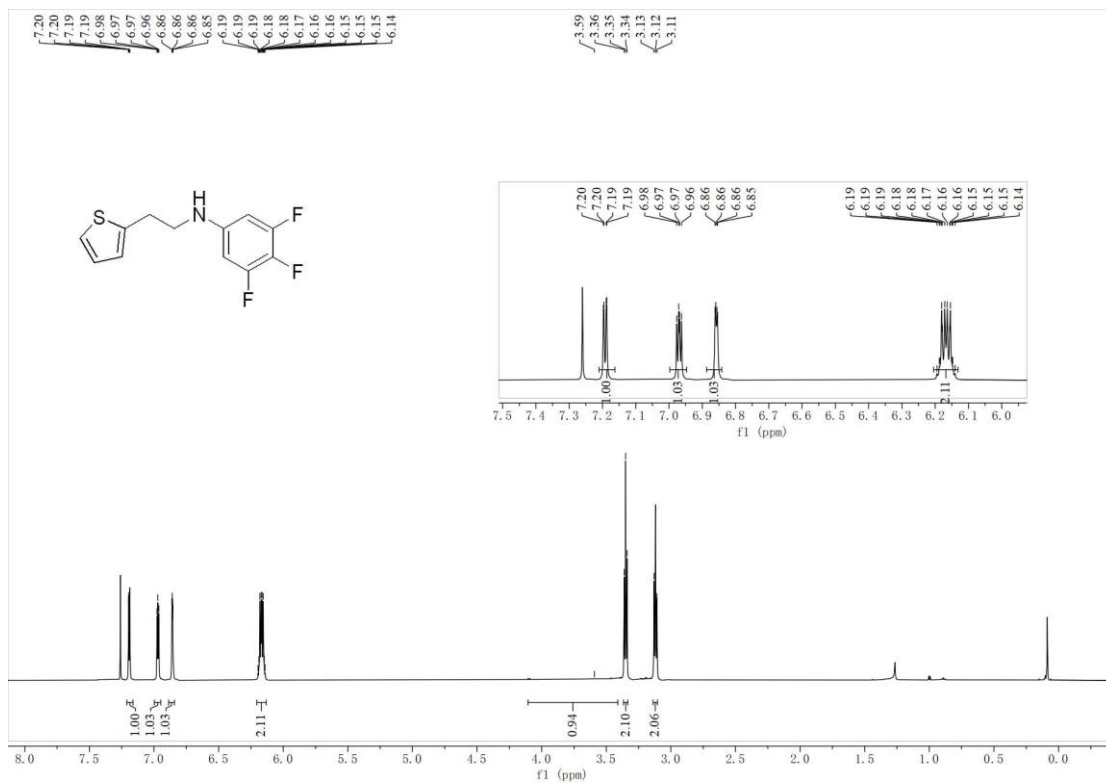
^1H NMR of compound (20)



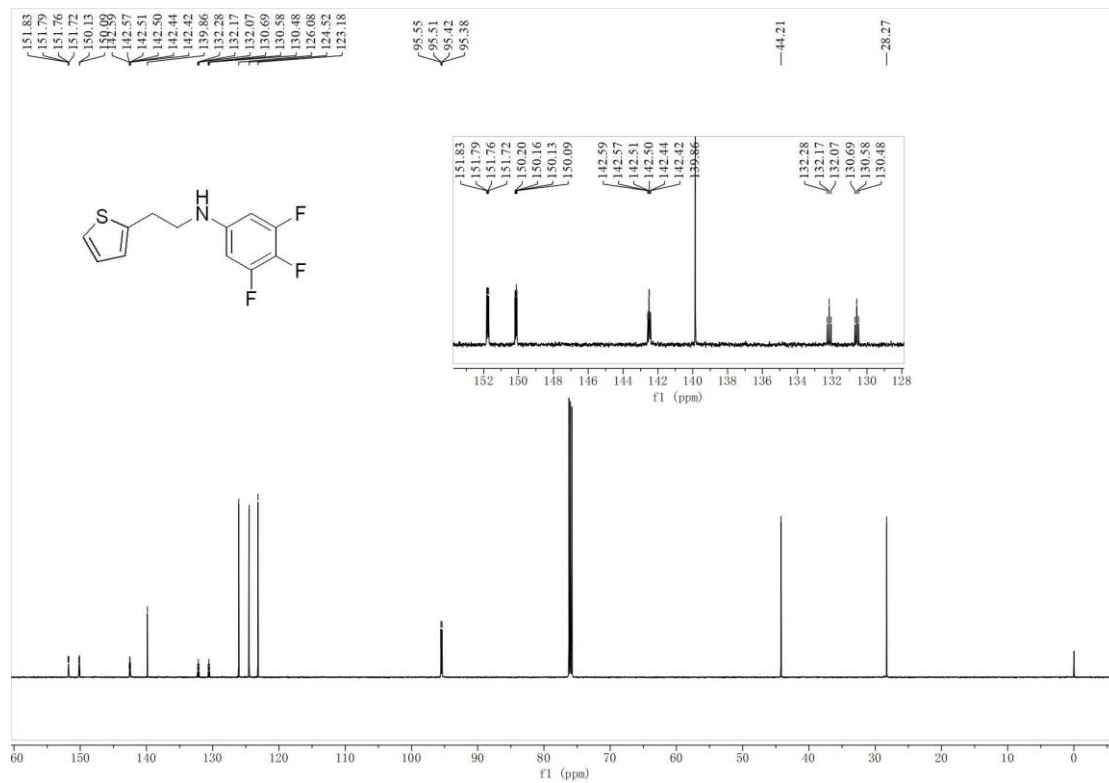
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (20)



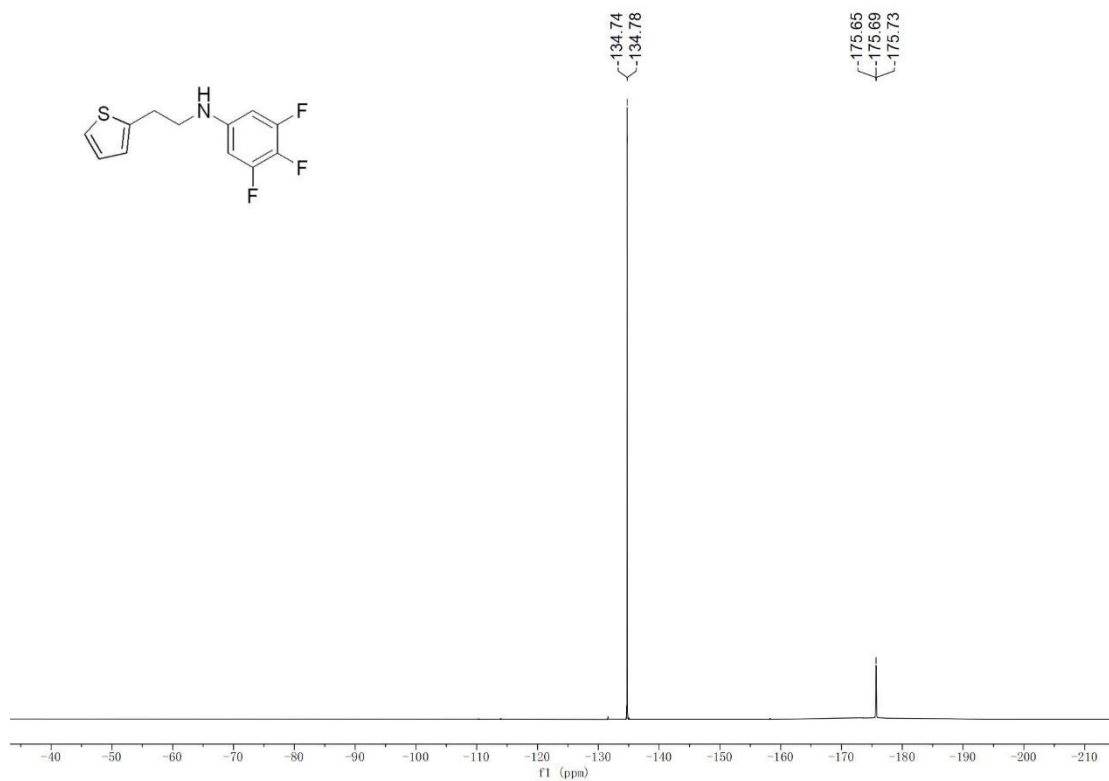
¹H NMR of compound (21)



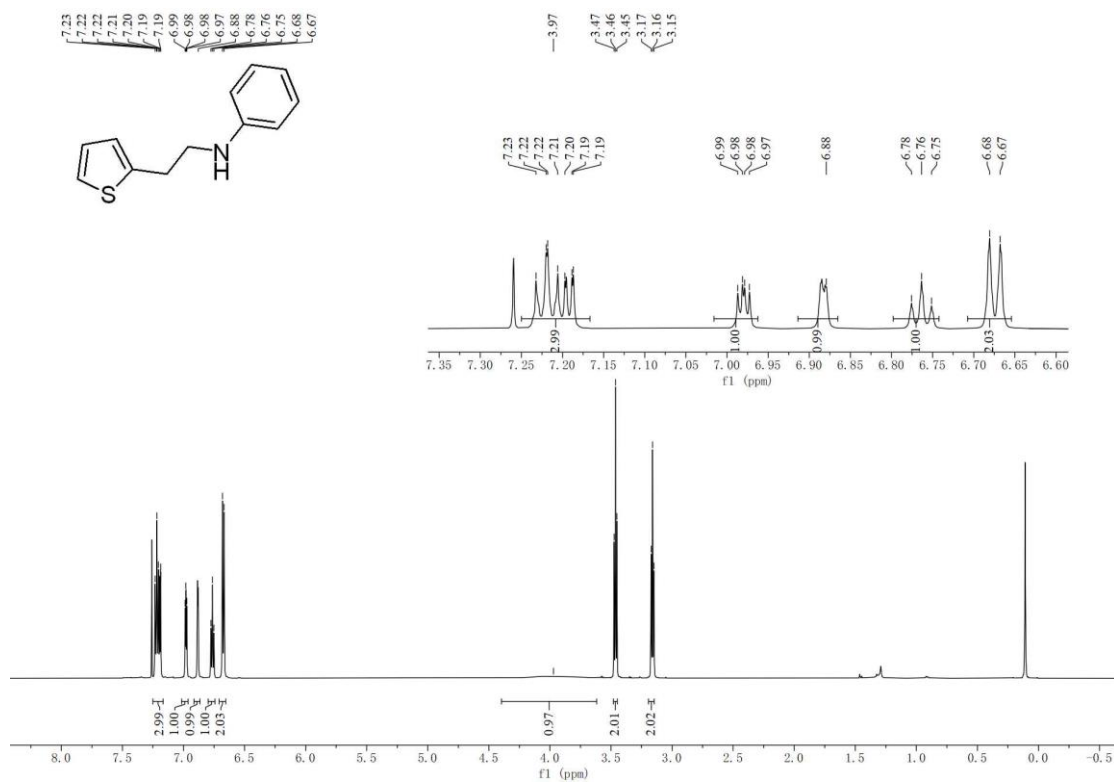
¹³C{¹H} NMR of compound (21)



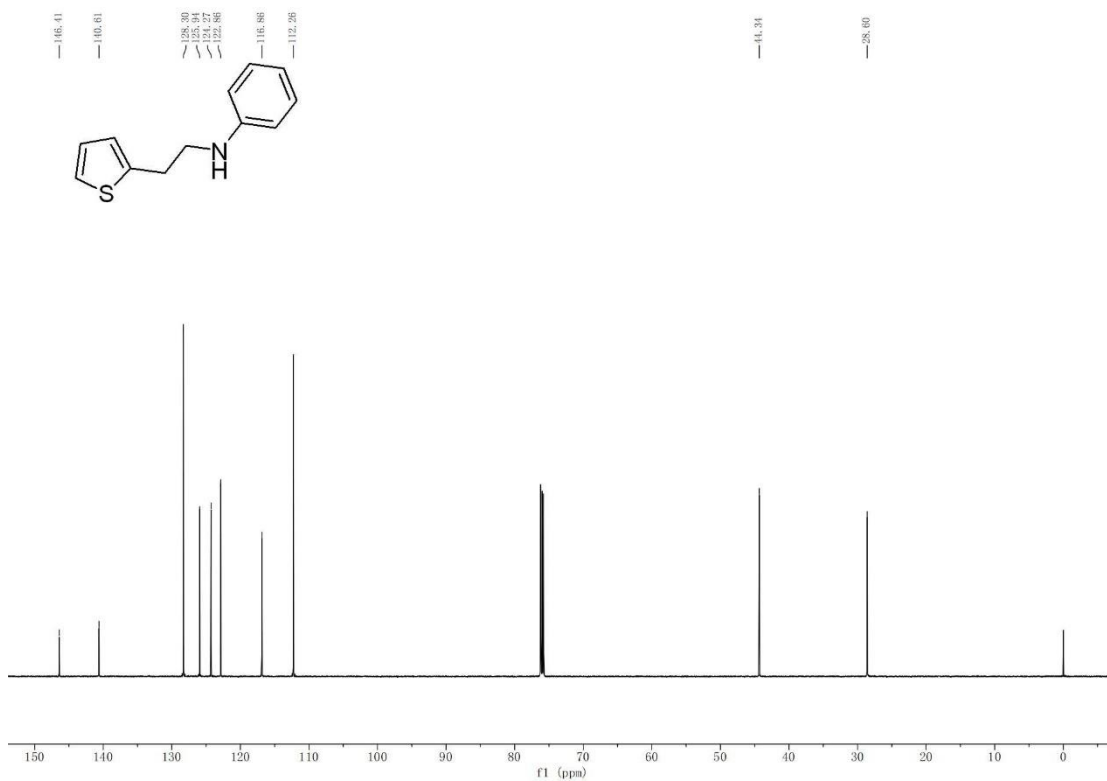
$^{19}\text{F}\{^1\text{H}\}$ NMR of compound (21)



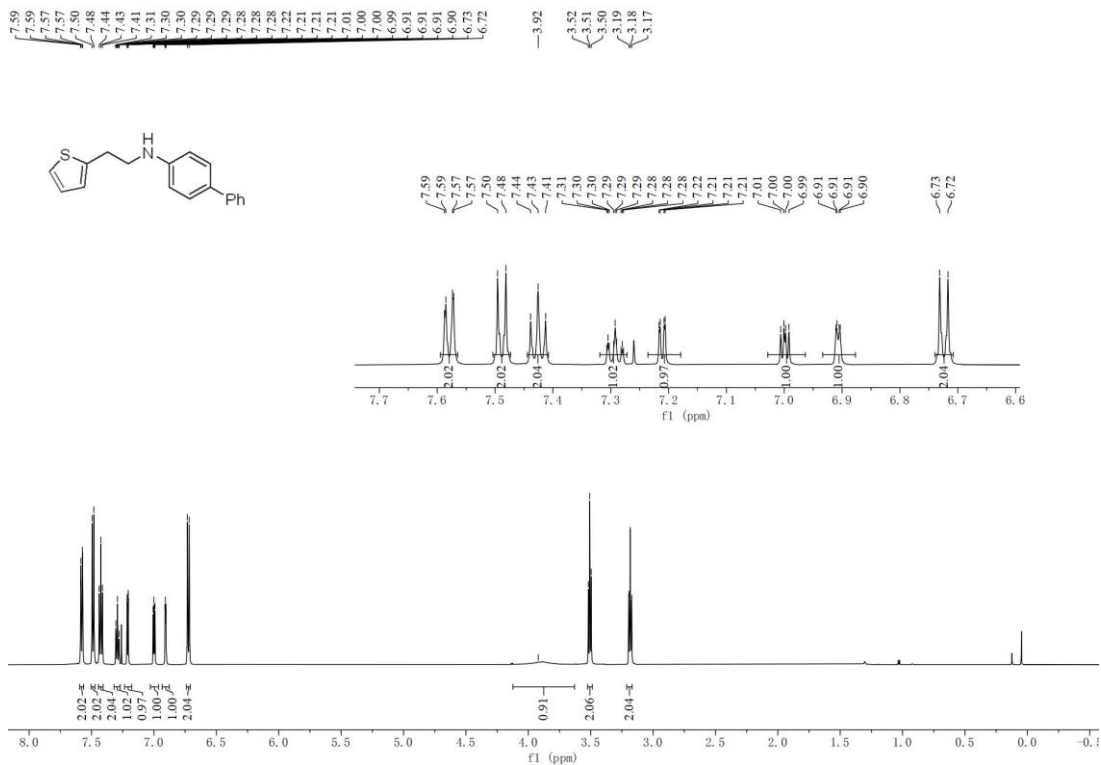
^1H NMR of compound (22)



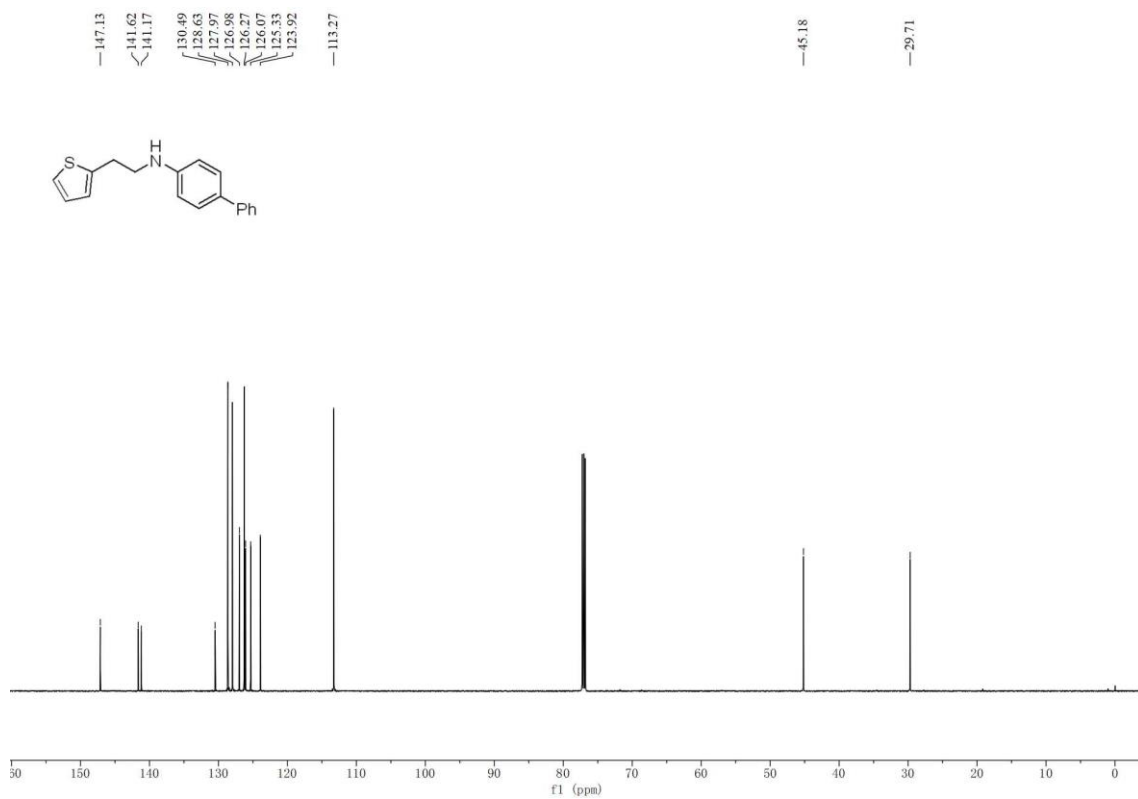
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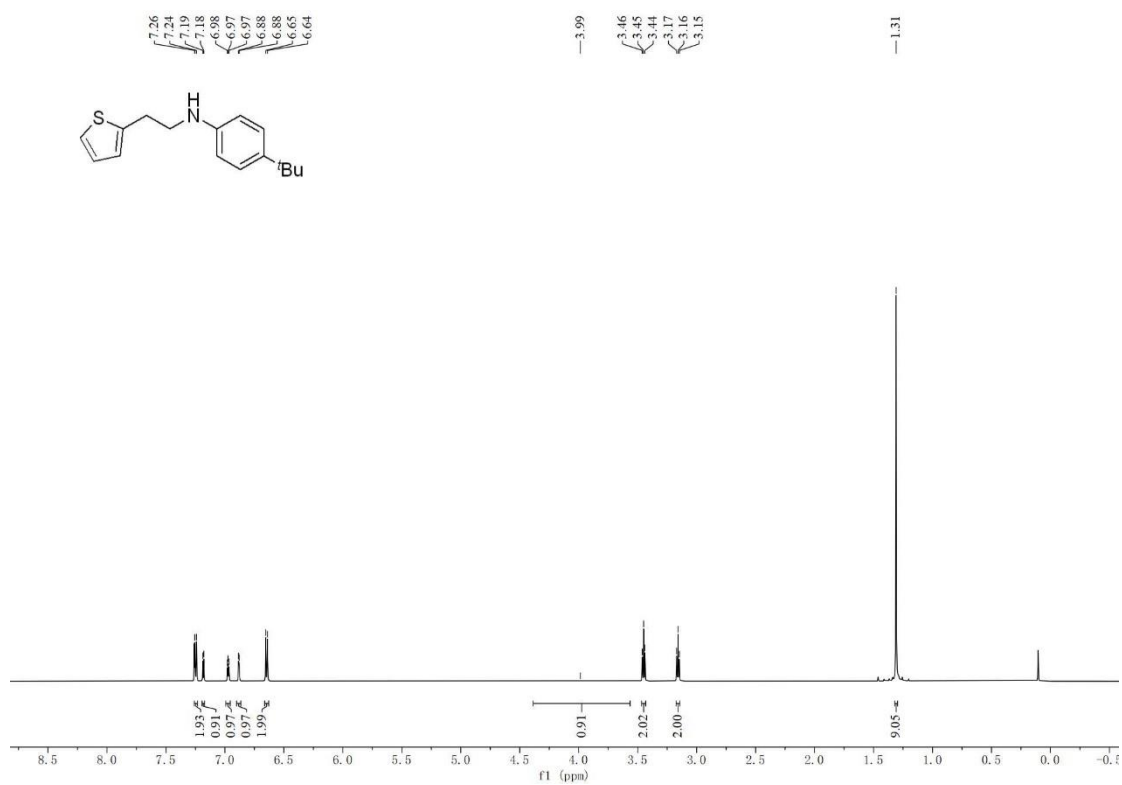
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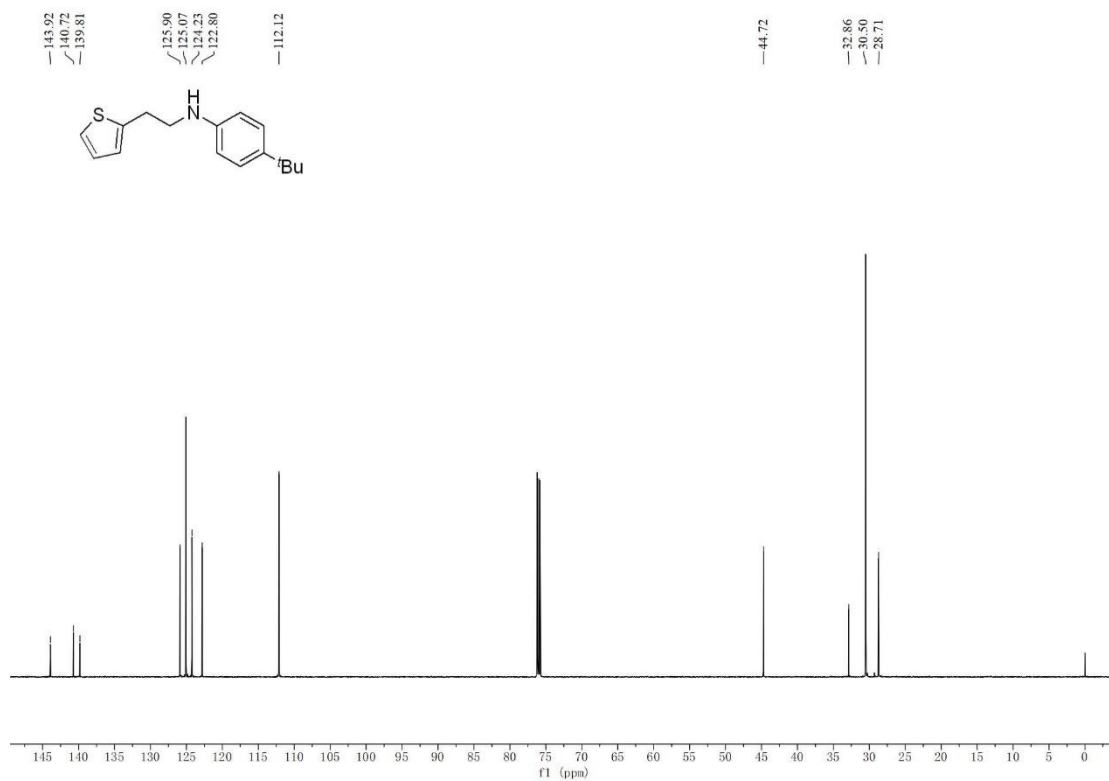
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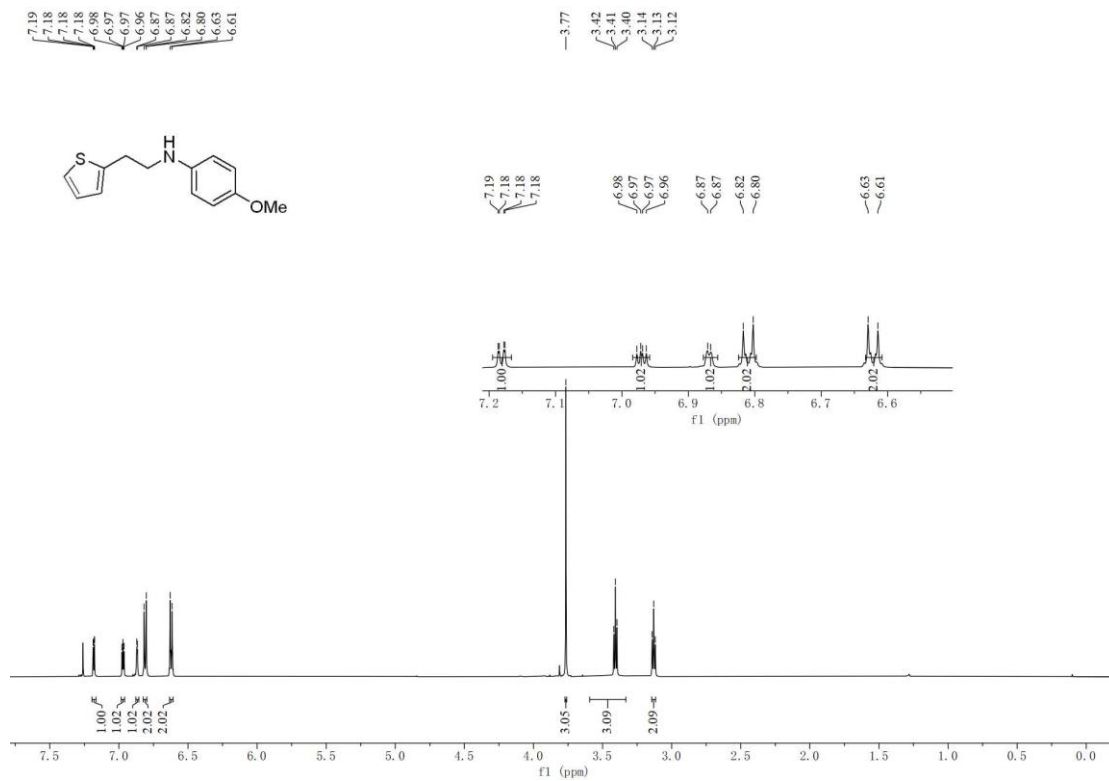
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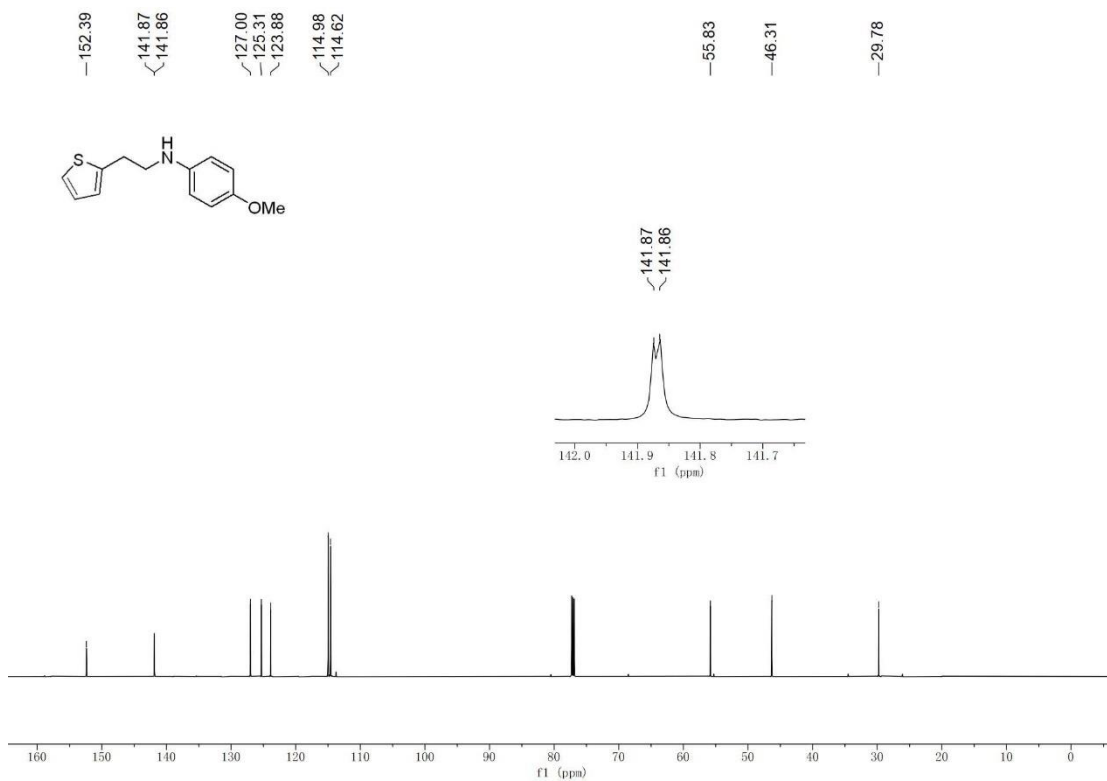
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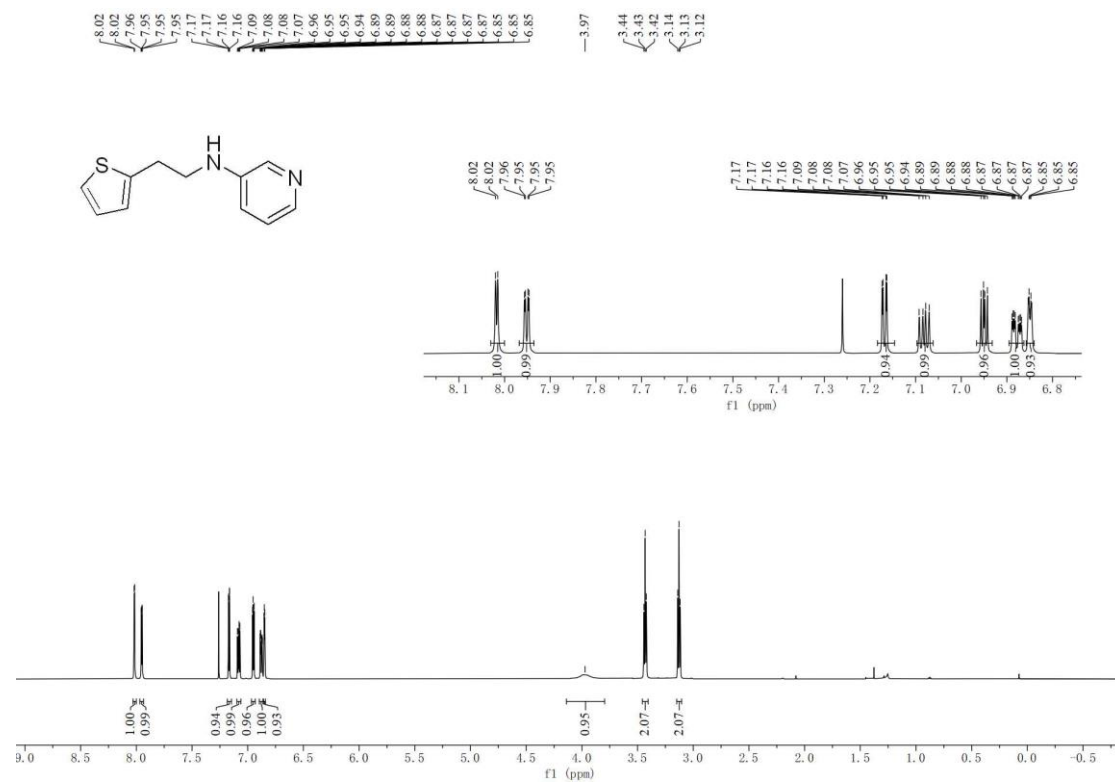
^1H NMR of compound (25)



$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (25)



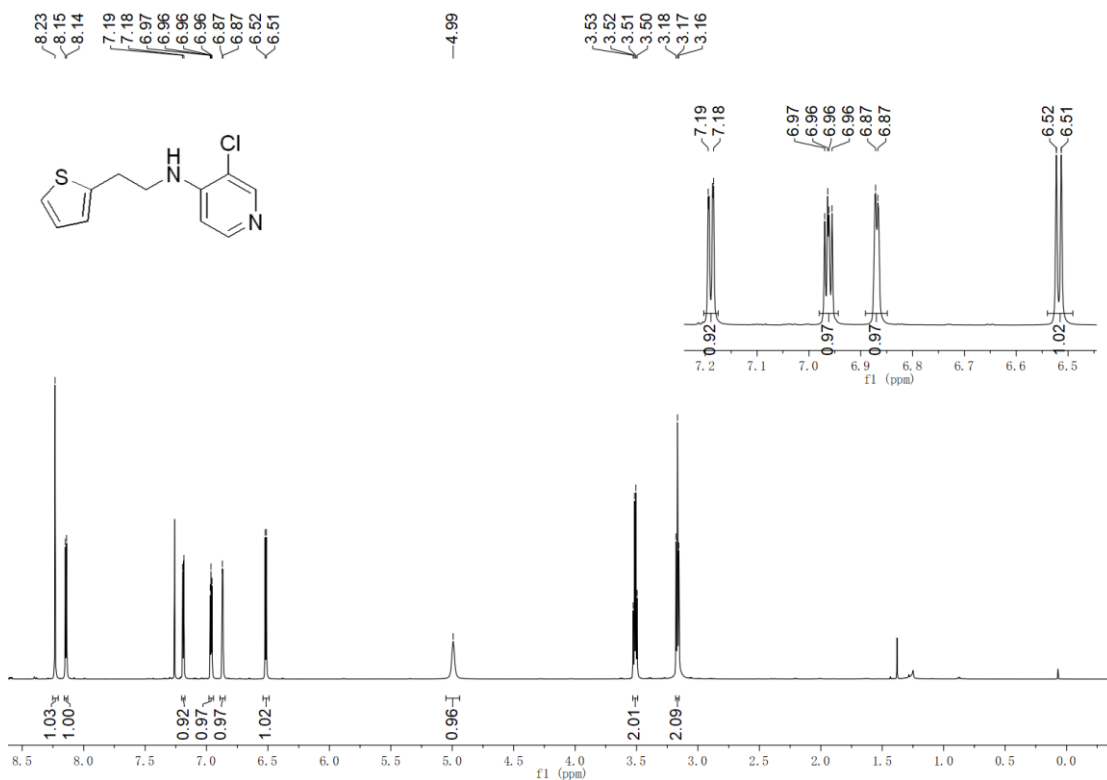
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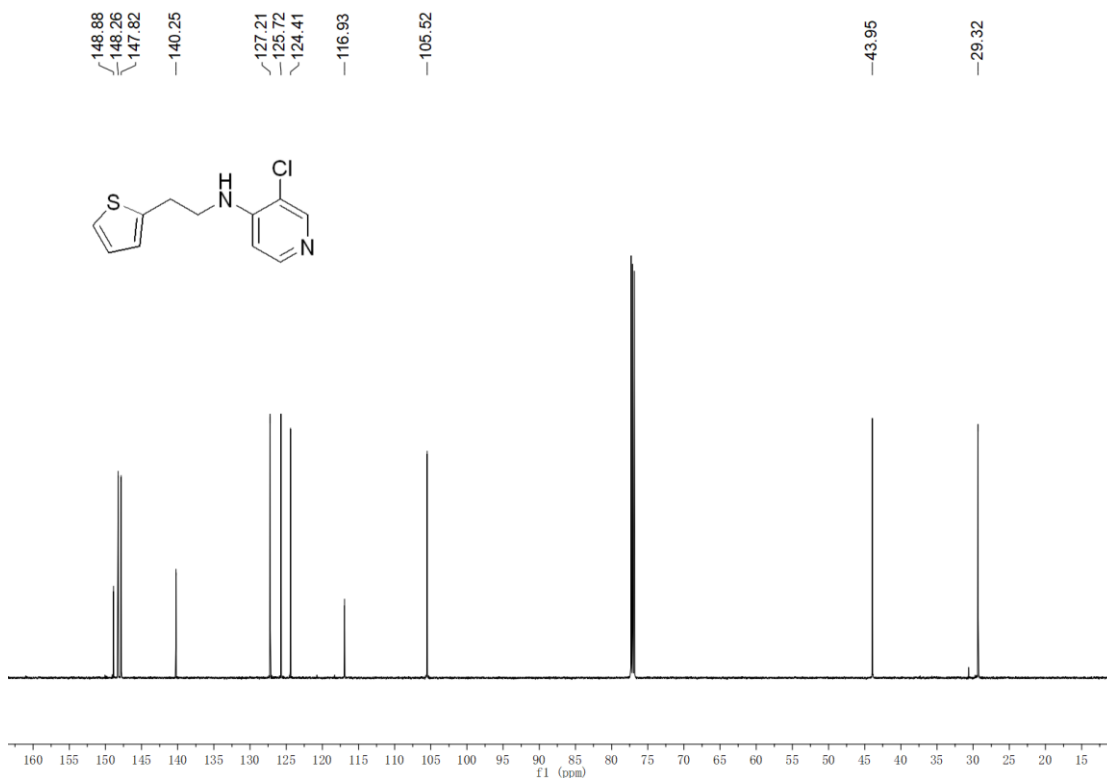
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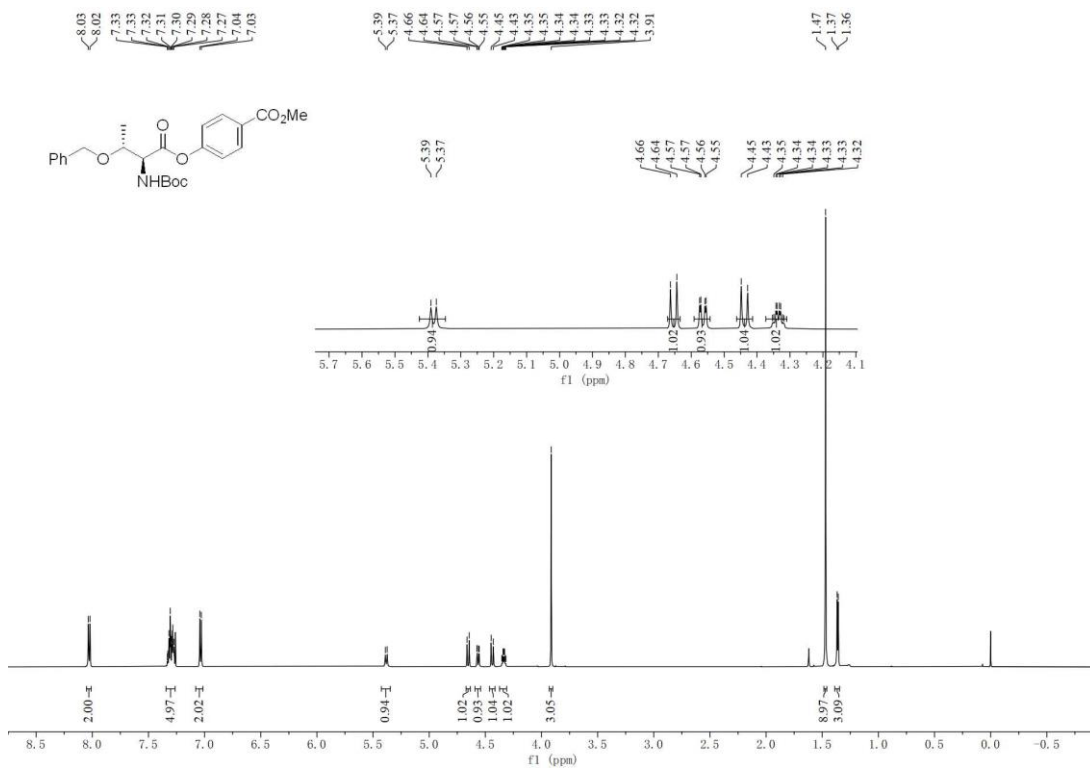
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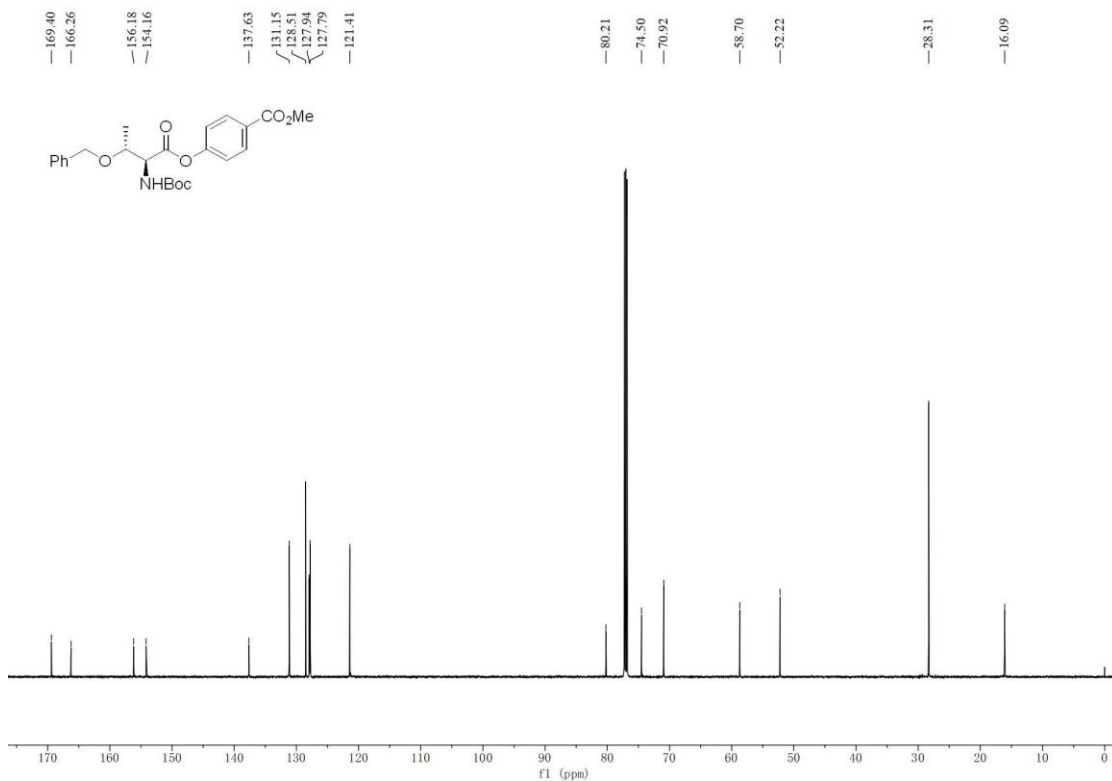
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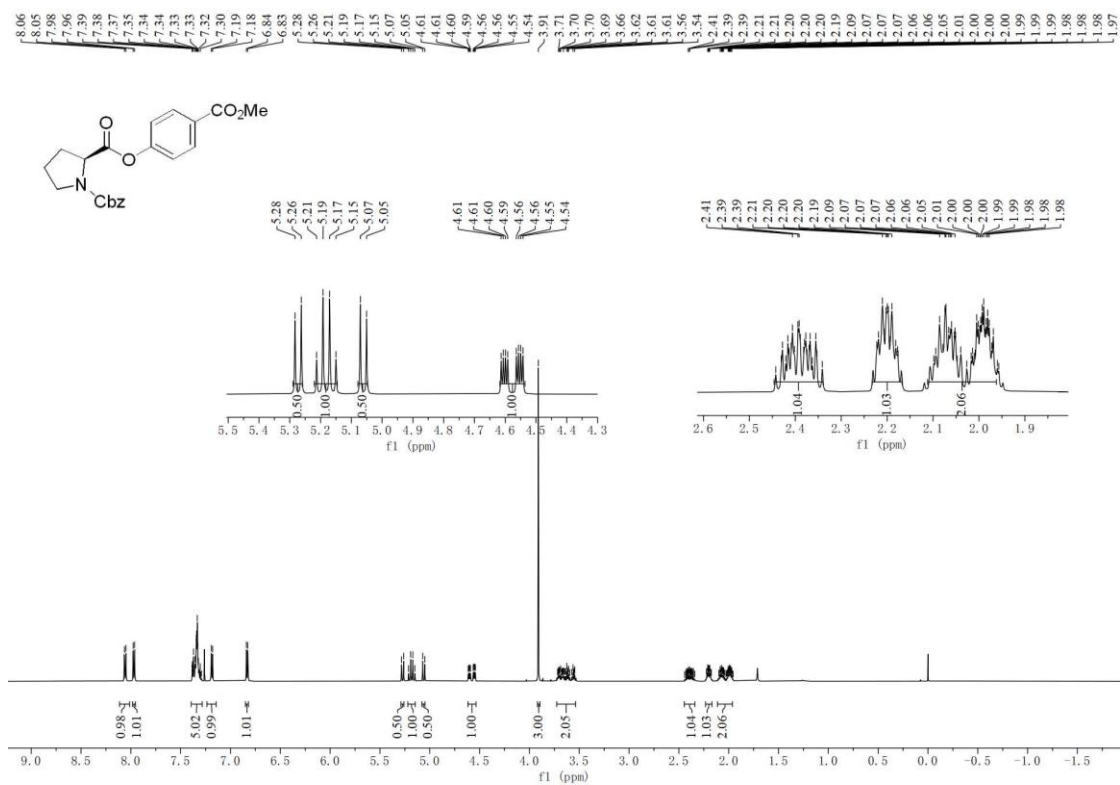
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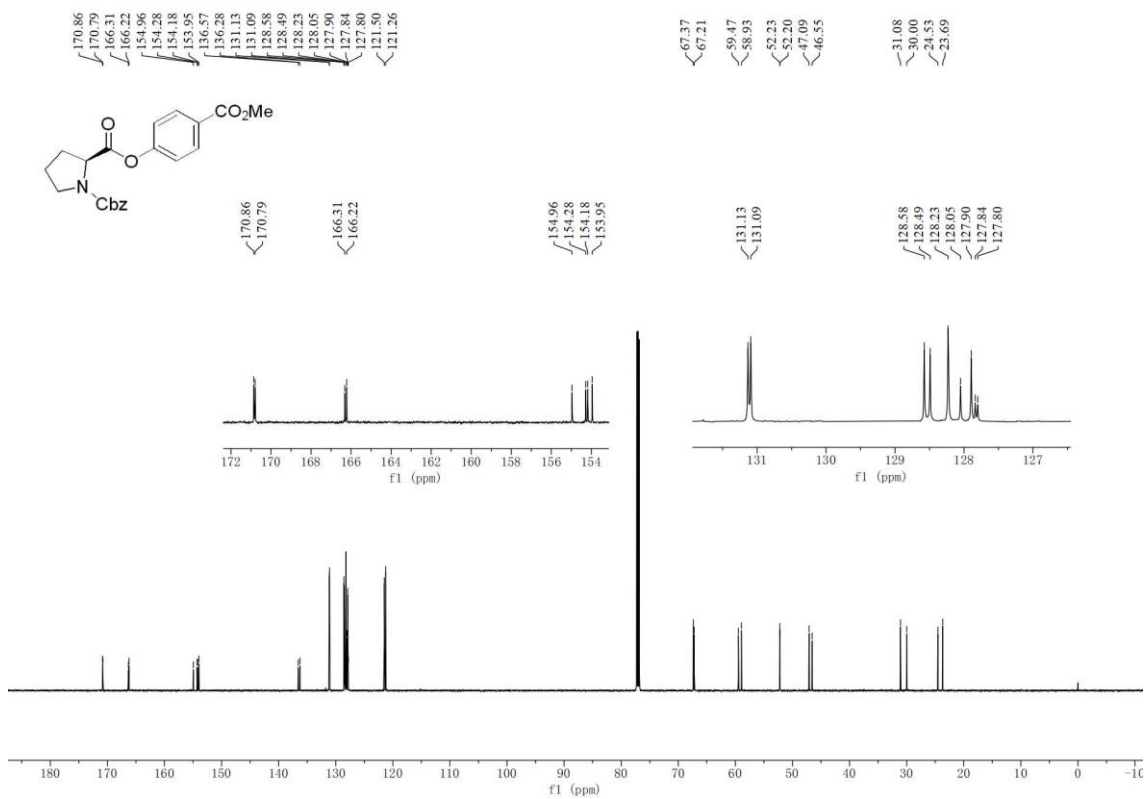
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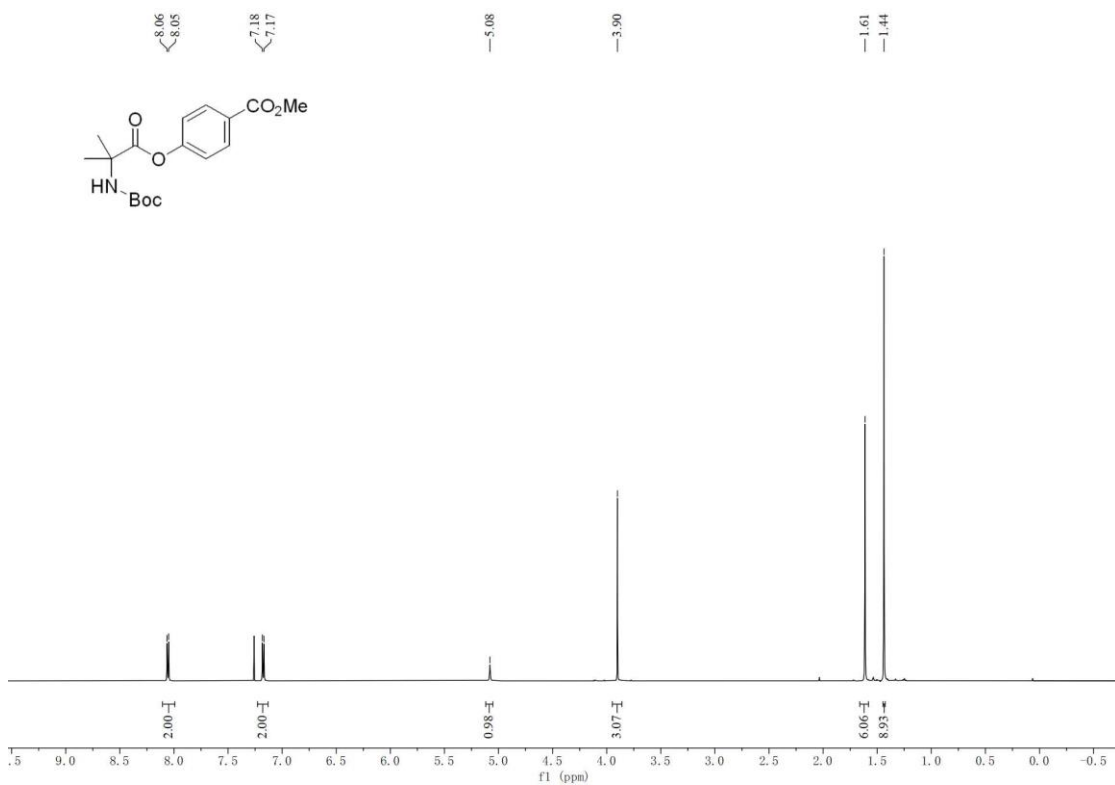
^1H NMR of compound (29)



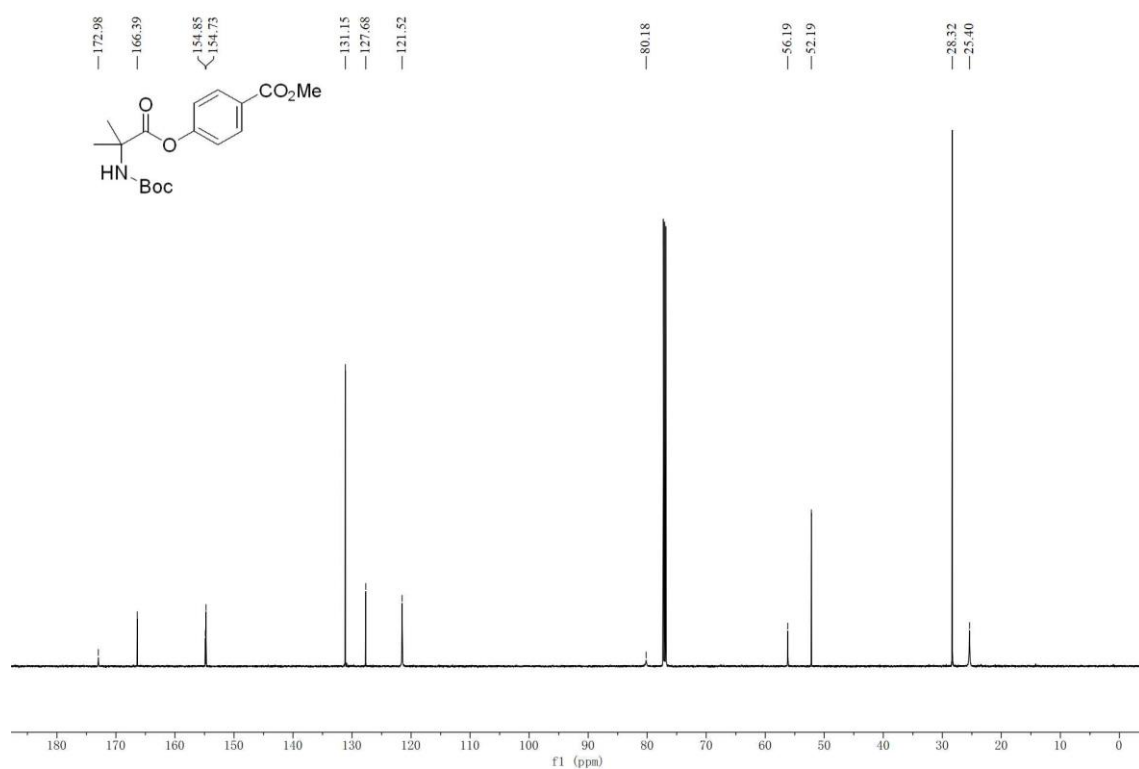
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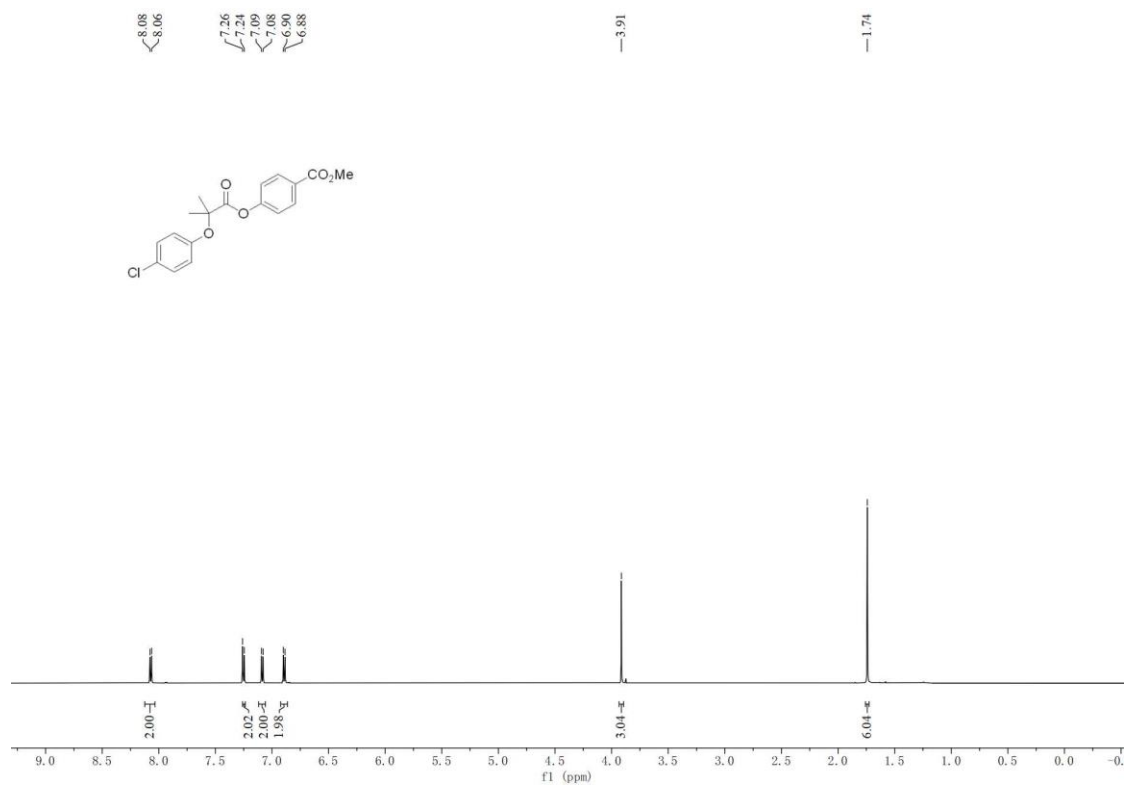
^1H NMR of compound (30)



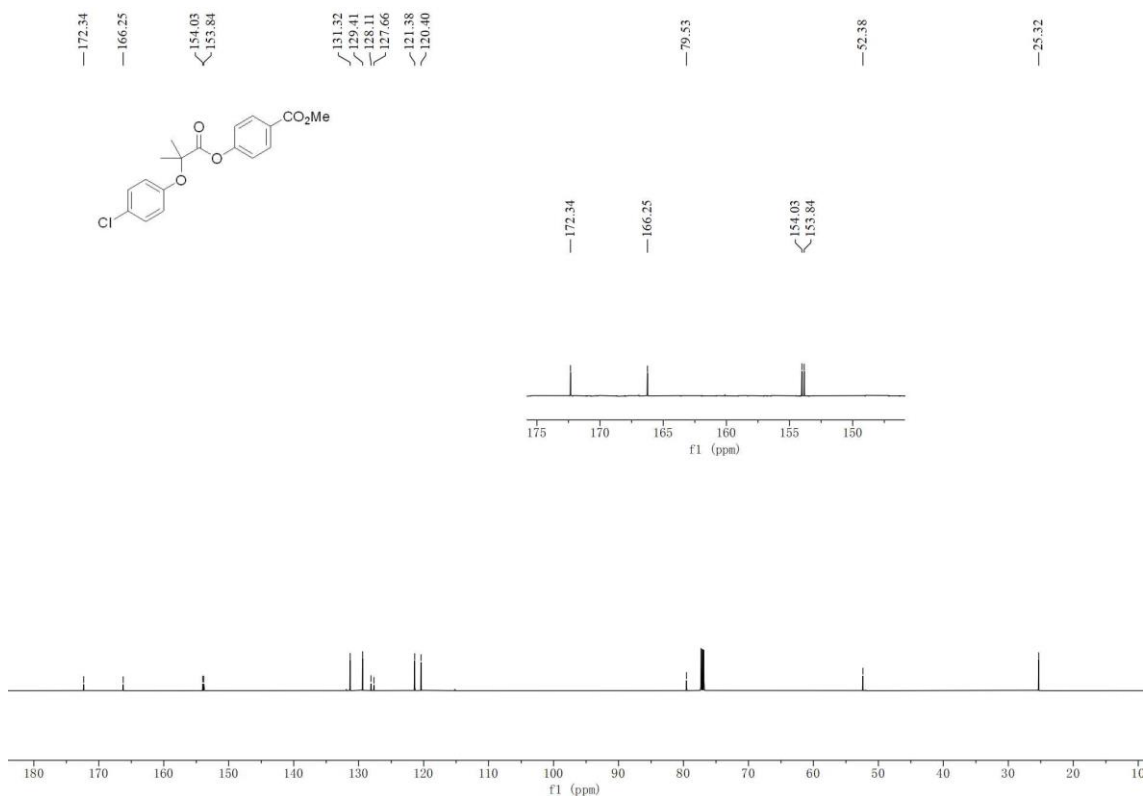
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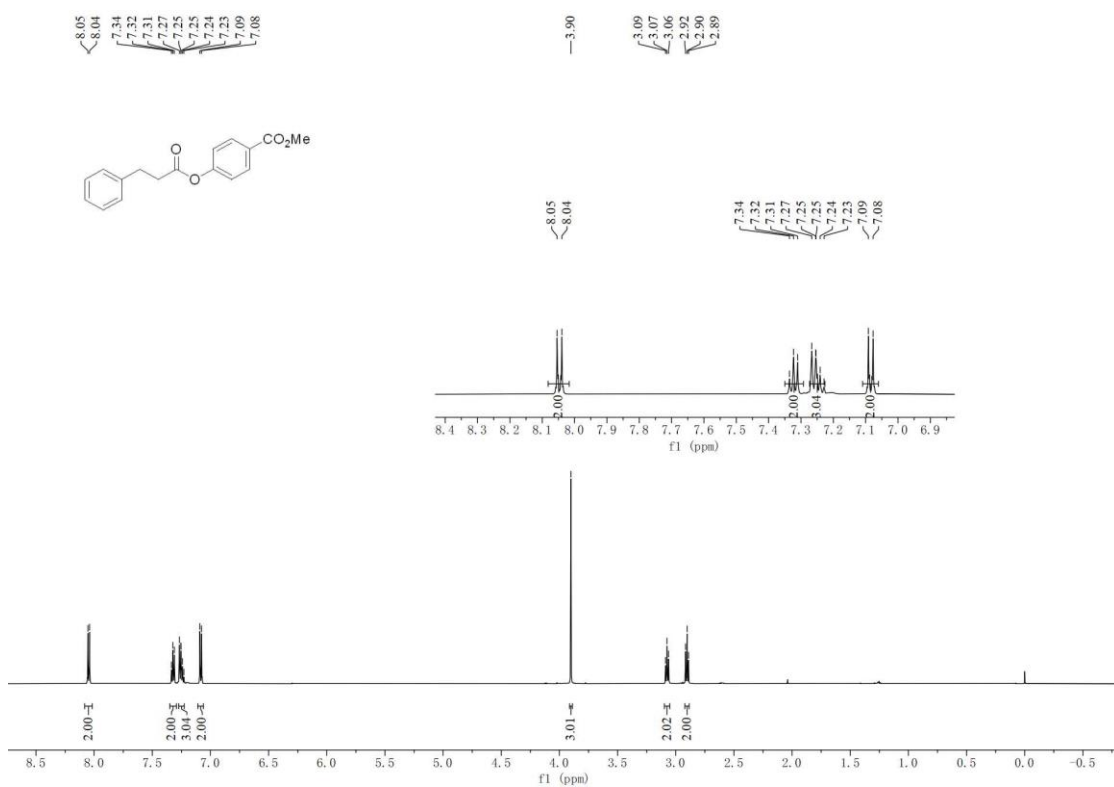
^1H NMR of compound (31)



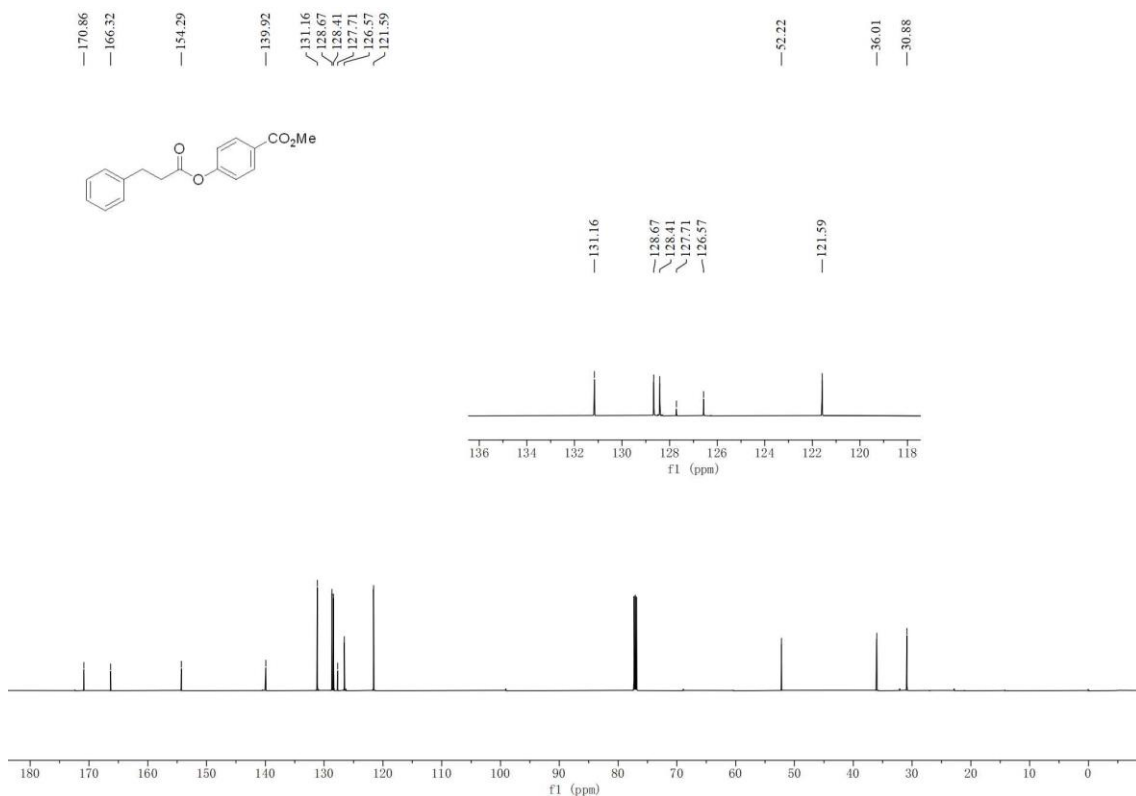
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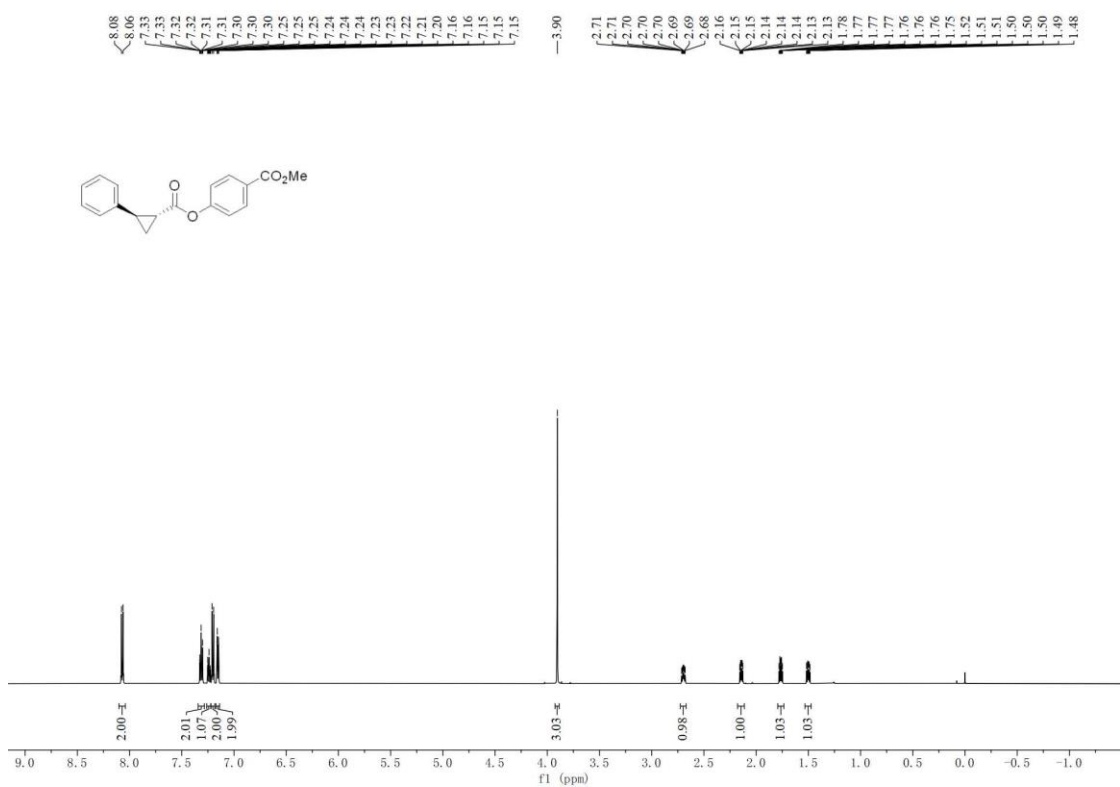
^1H NMR of compound (32)



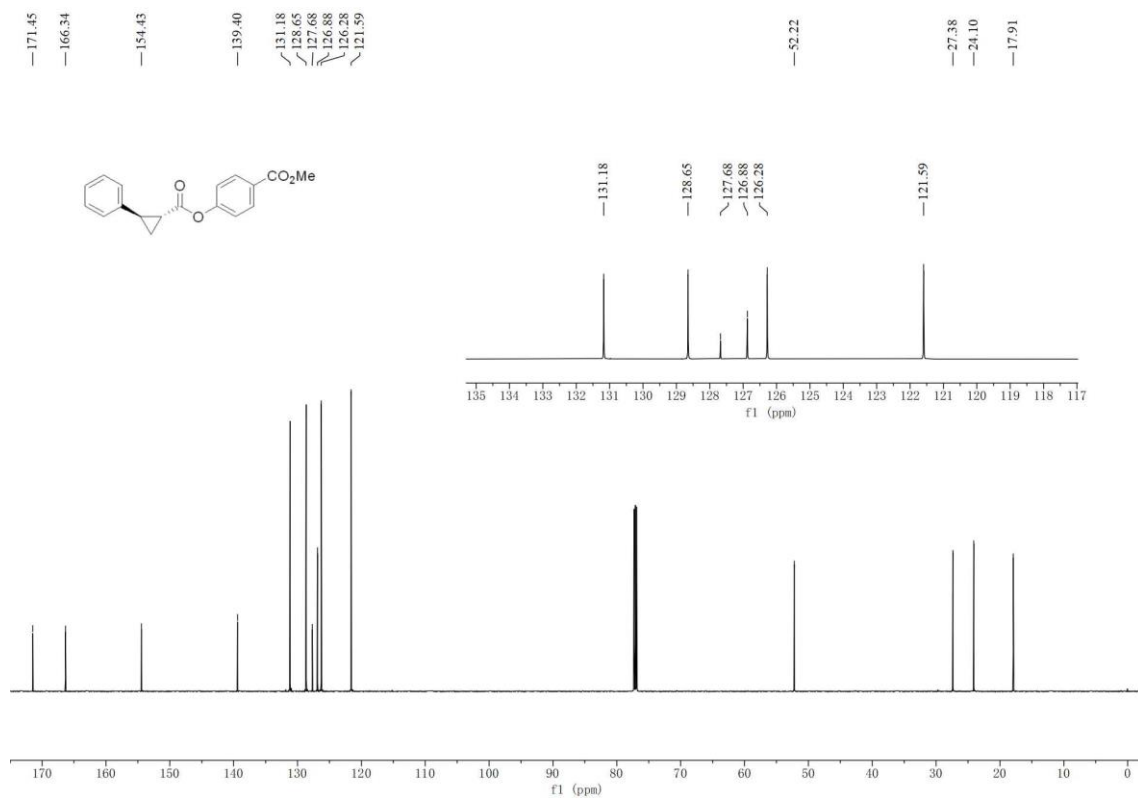
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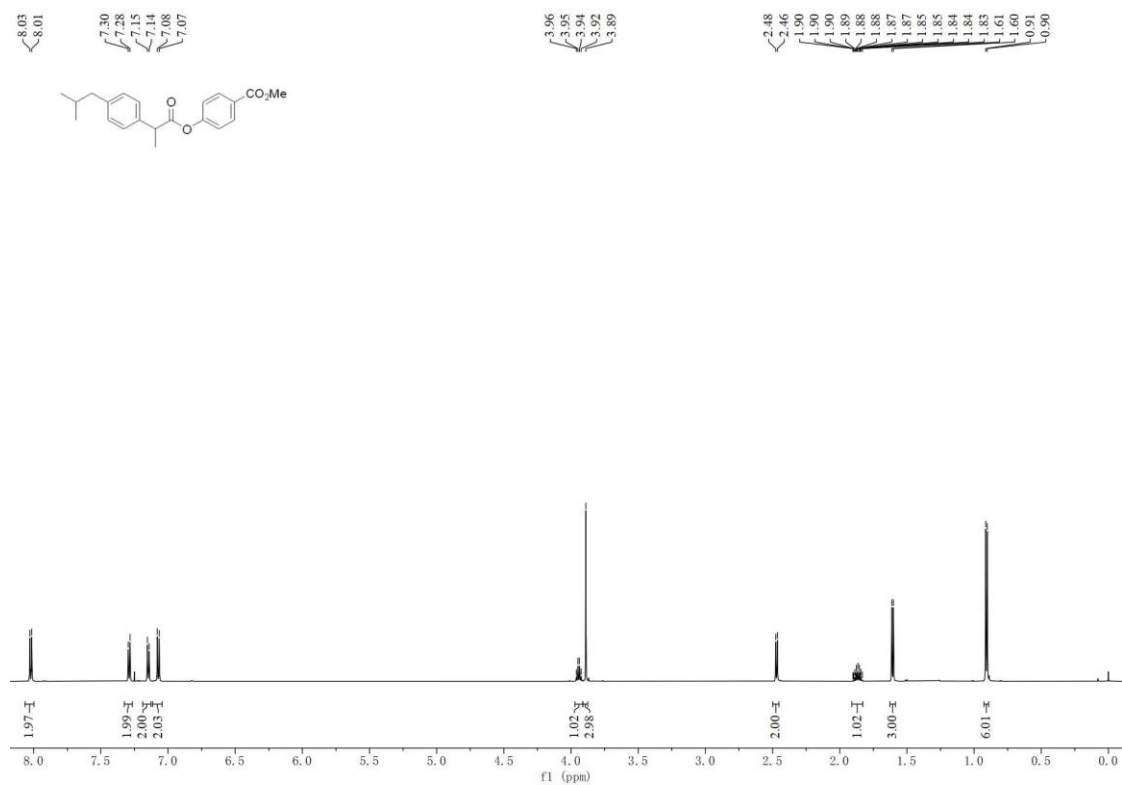
^1H NMR of compound (33)



$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (33)



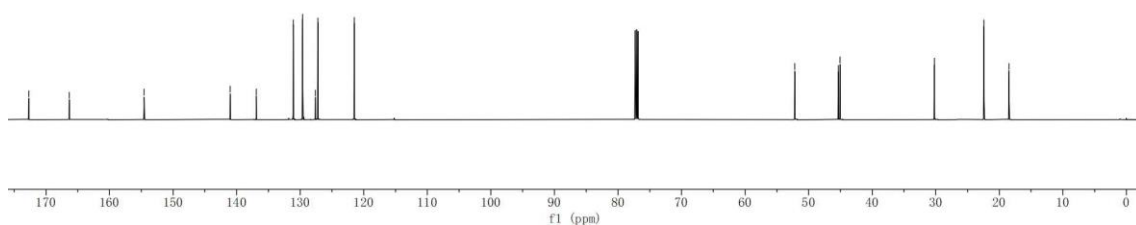
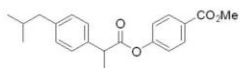
^1H NMR of compound (34)



$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (34)

— 172.72
— 166.34
— 154.55
— 141.02
— 136.91
— 131.09
— 129.61
— 127.62
— 127.22
— 121.49

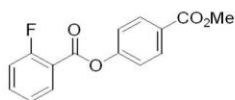
— 52.19
— 45.32
— 45.06
— 30.21
— 22.41
— 18.47



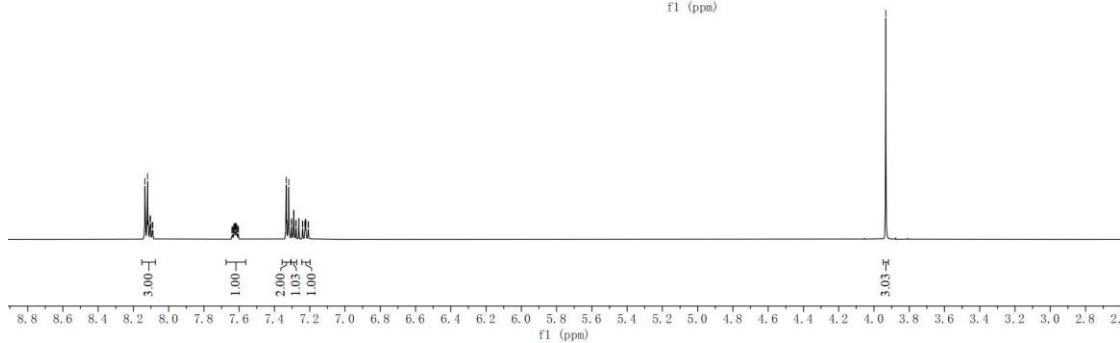
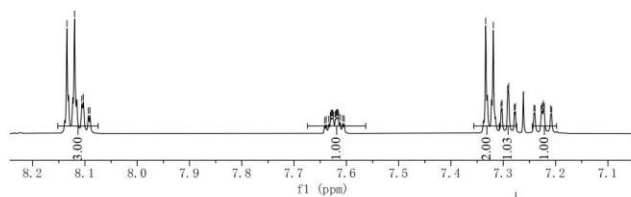
^1H NMR of compound (35)

8.13
8.12
8.11
8.10
8.09
7.64
7.63
7.63
7.63
7.62
7.62
7.62
7.62
7.61
7.61
7.60
7.33
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7.22
7.22
7.21
7.21

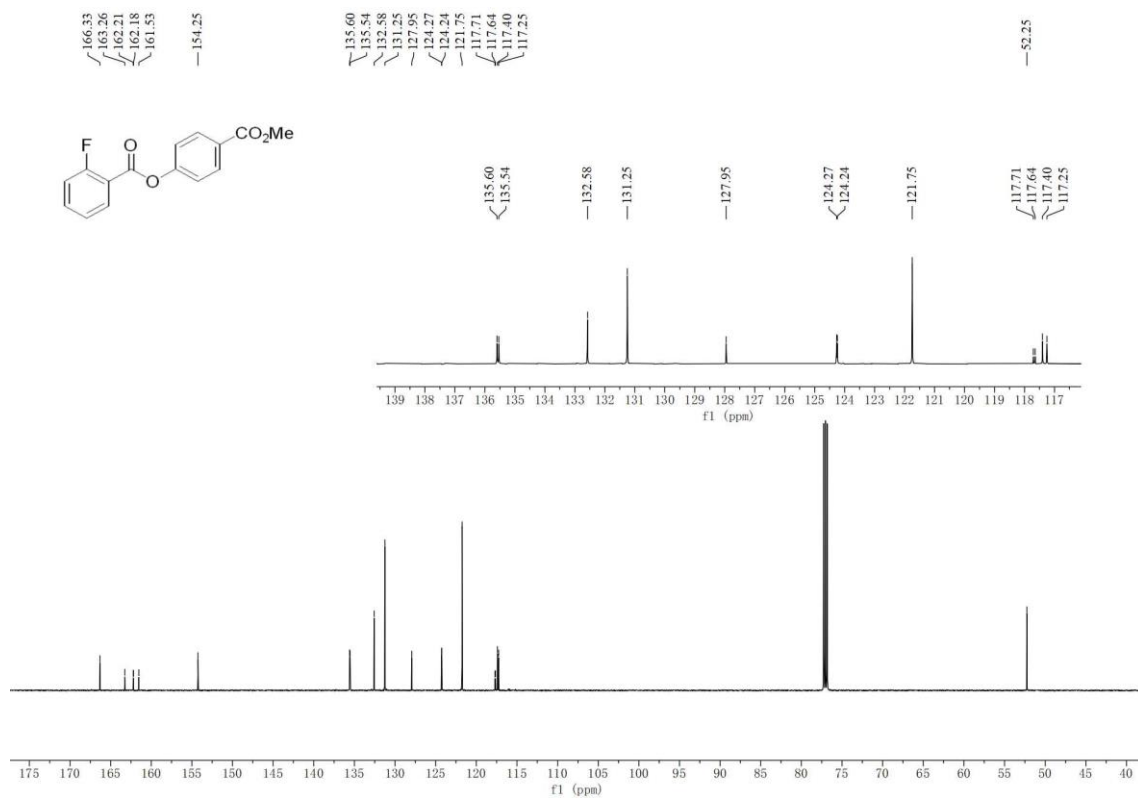
3.93



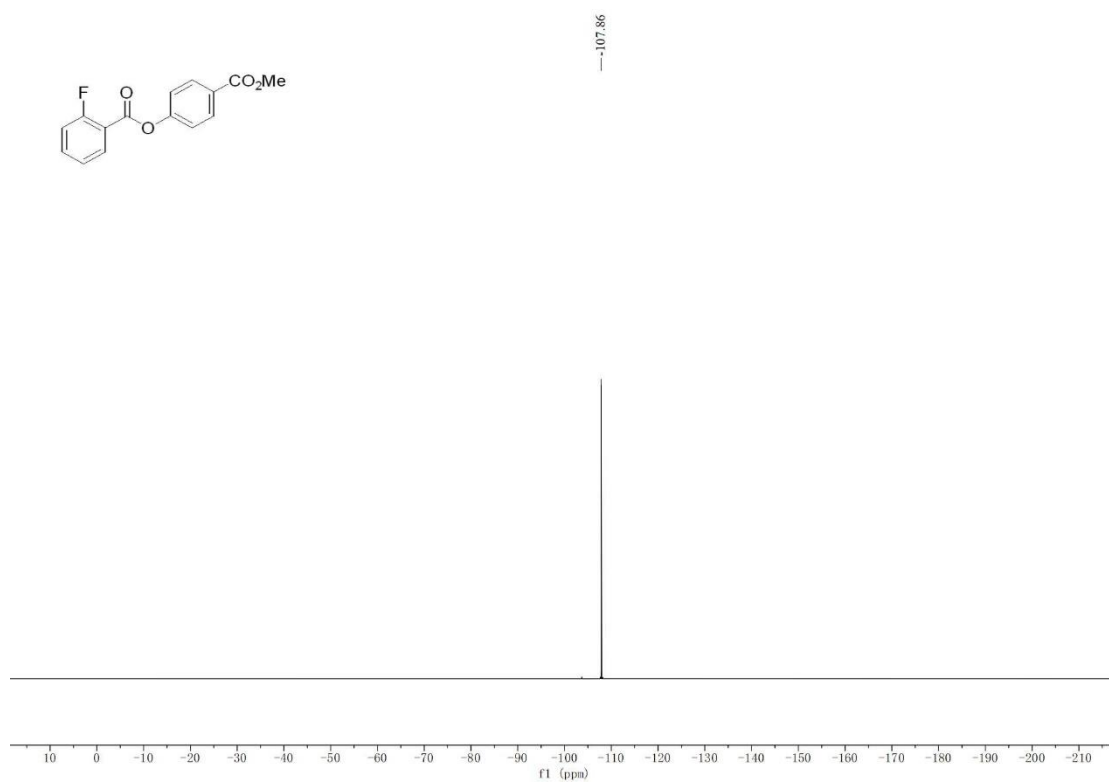
8.13
8.12
8.11
8.10
8.09
7.64
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7.62
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7.23
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7.22
7.22
7.21
7.21



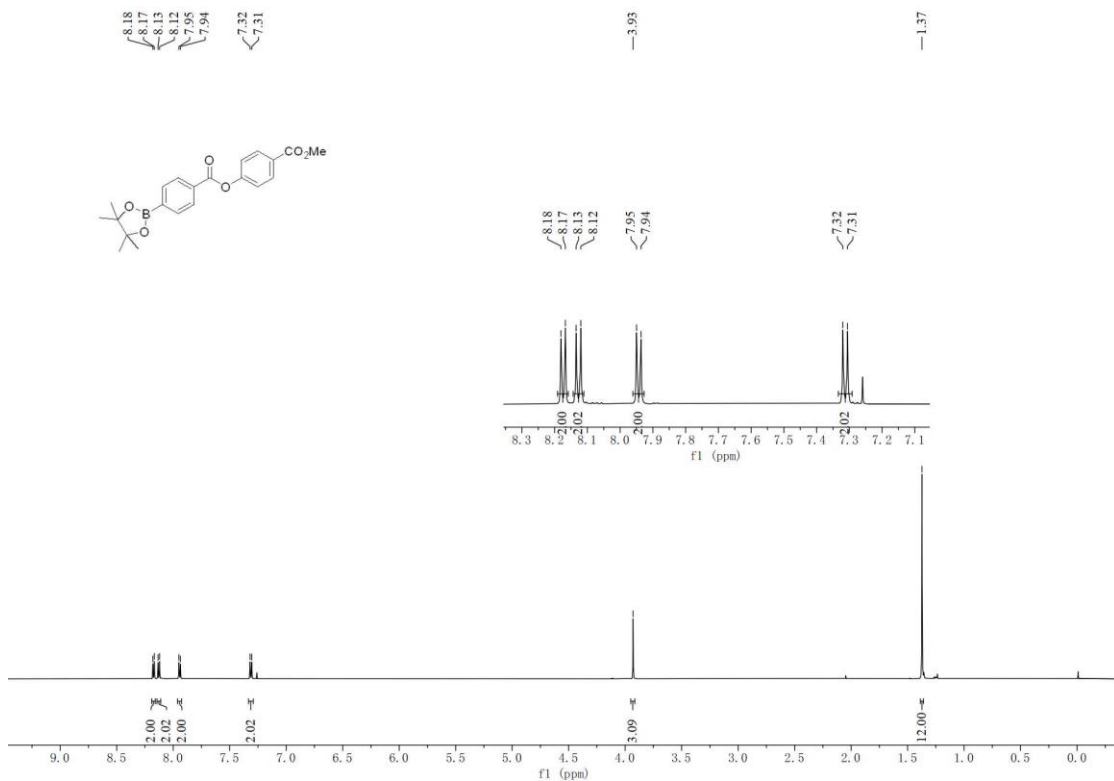
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (35)



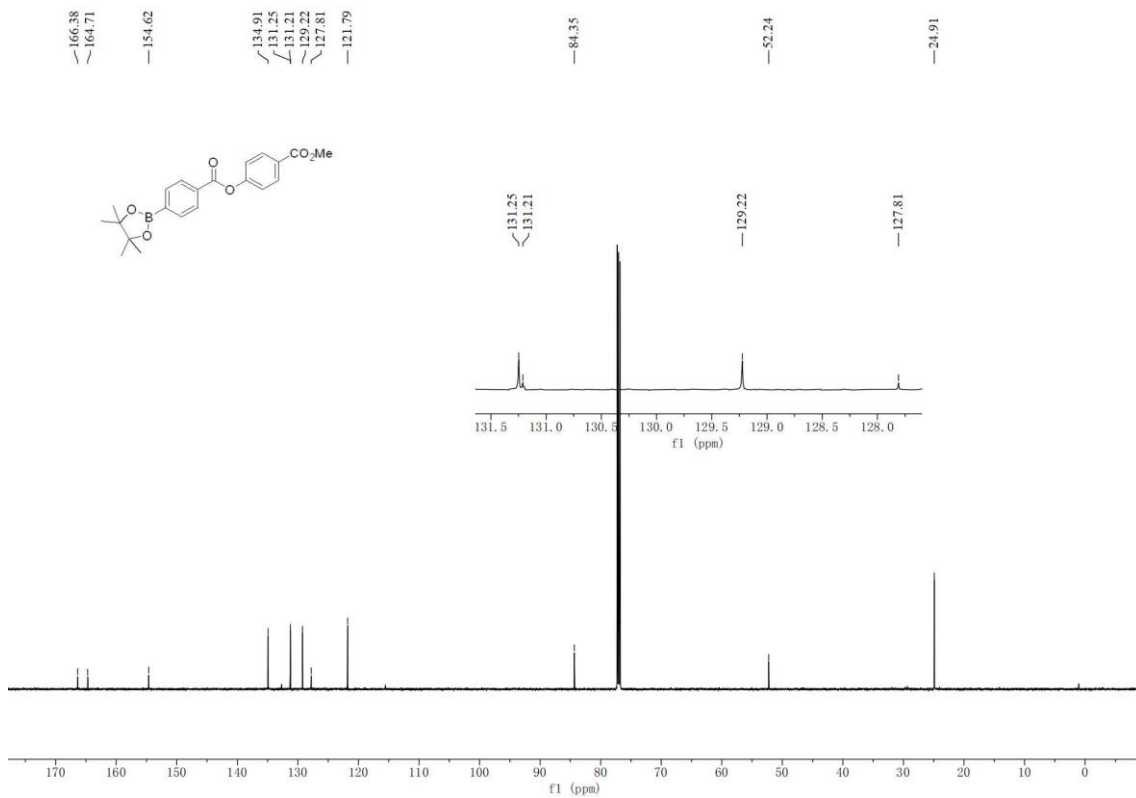
$^{19}\text{F}\{^1\text{H}\}$ NMR of compound (35)



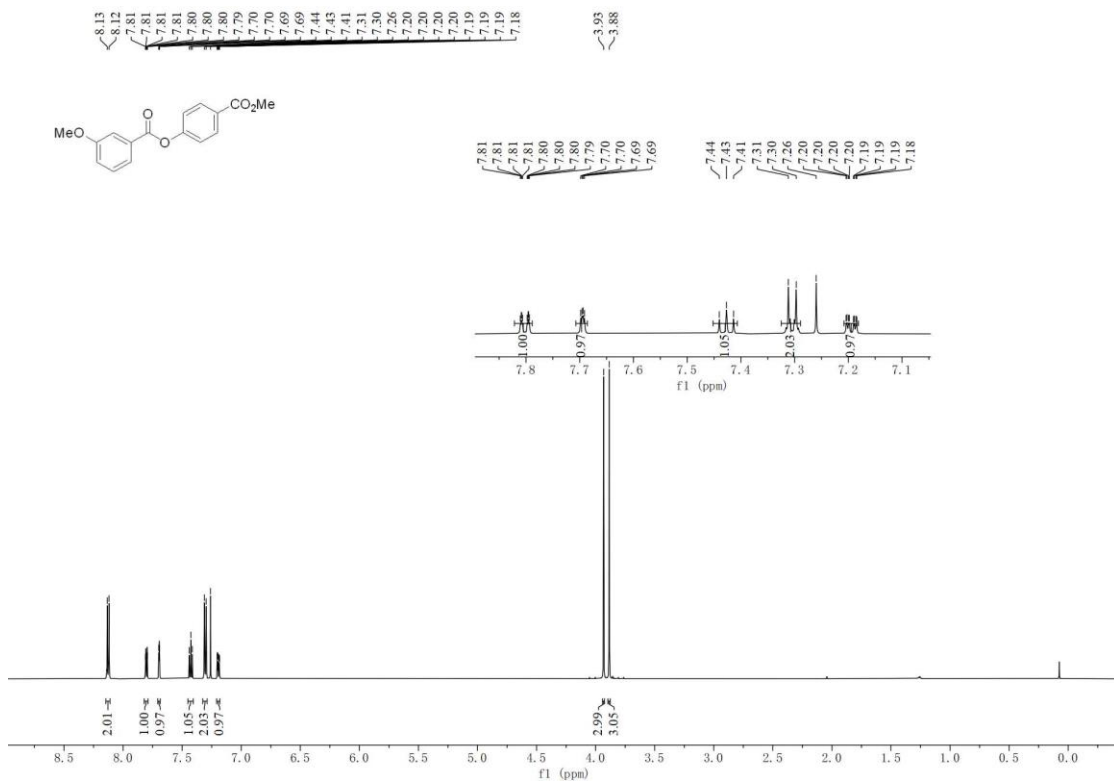
^1H NMR of compound (36)



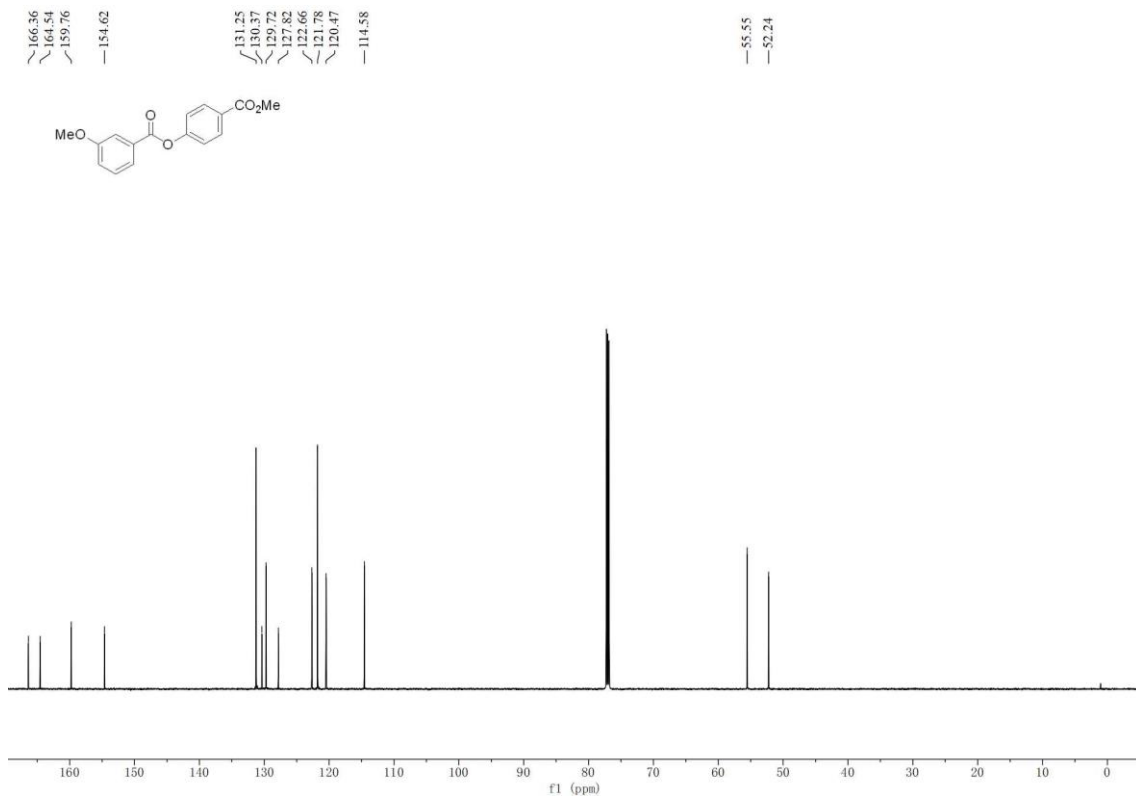
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (36)



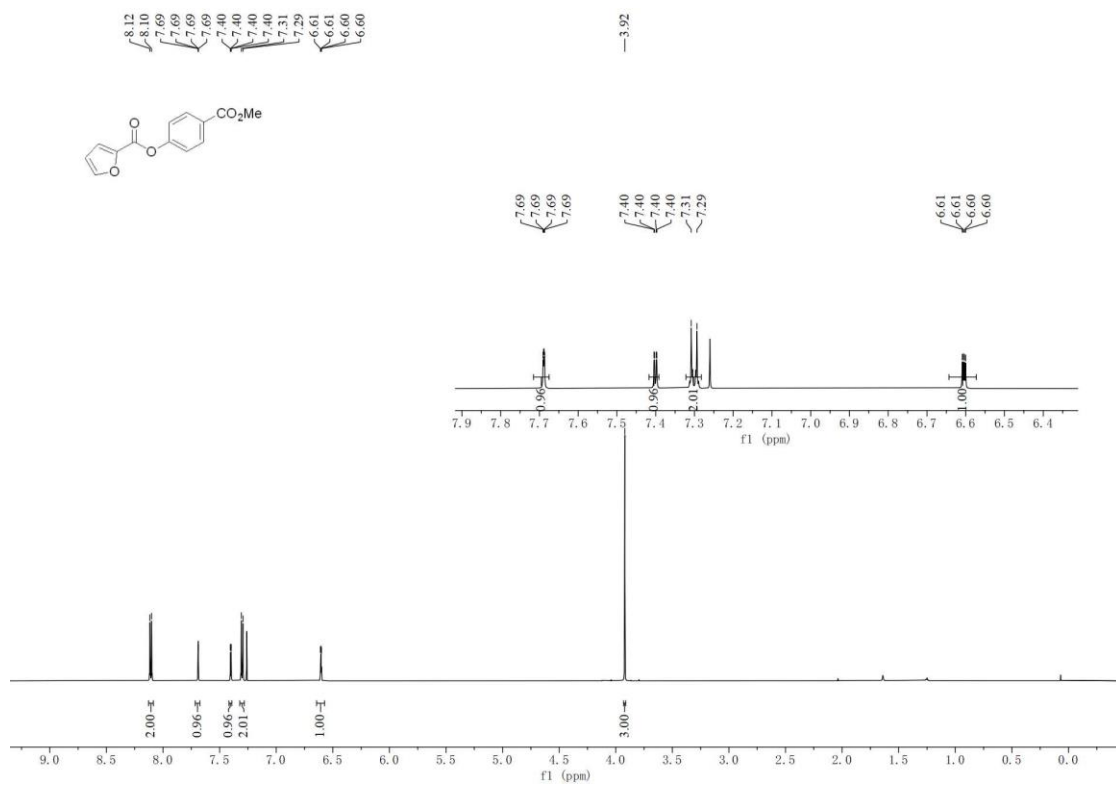
¹H NMR of compound (38)



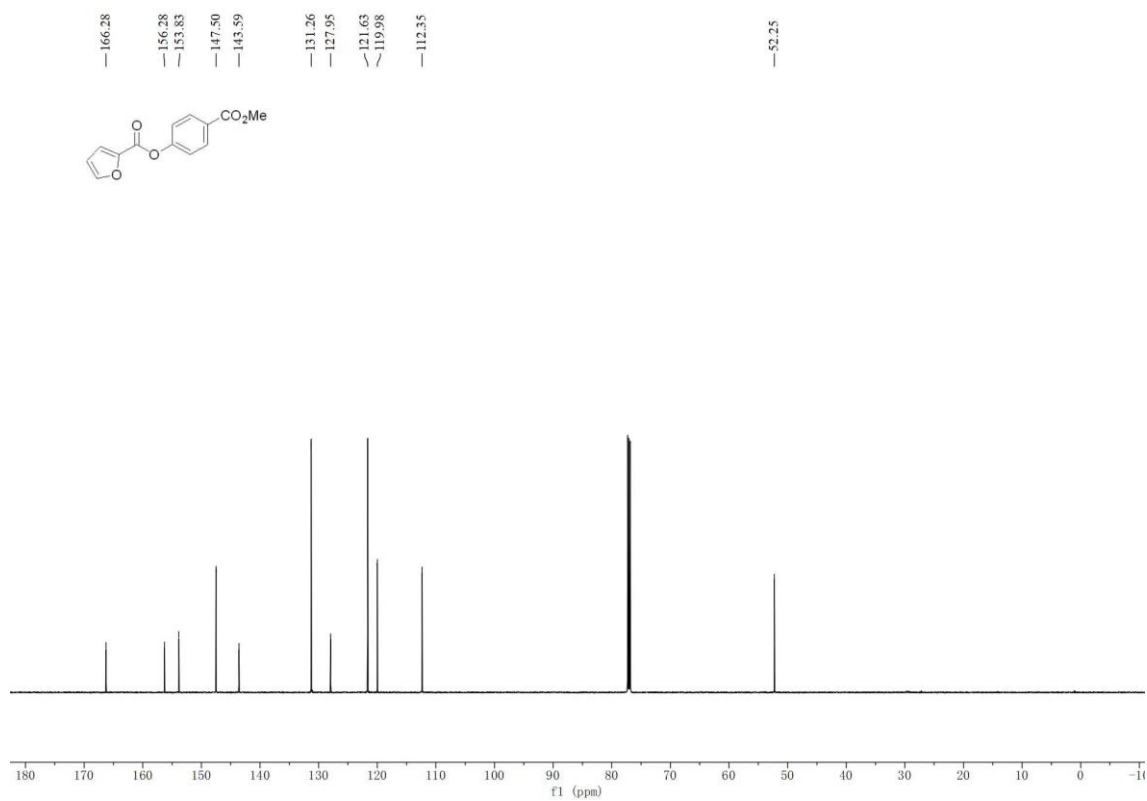
¹³C {¹H} NMR of compound (38)



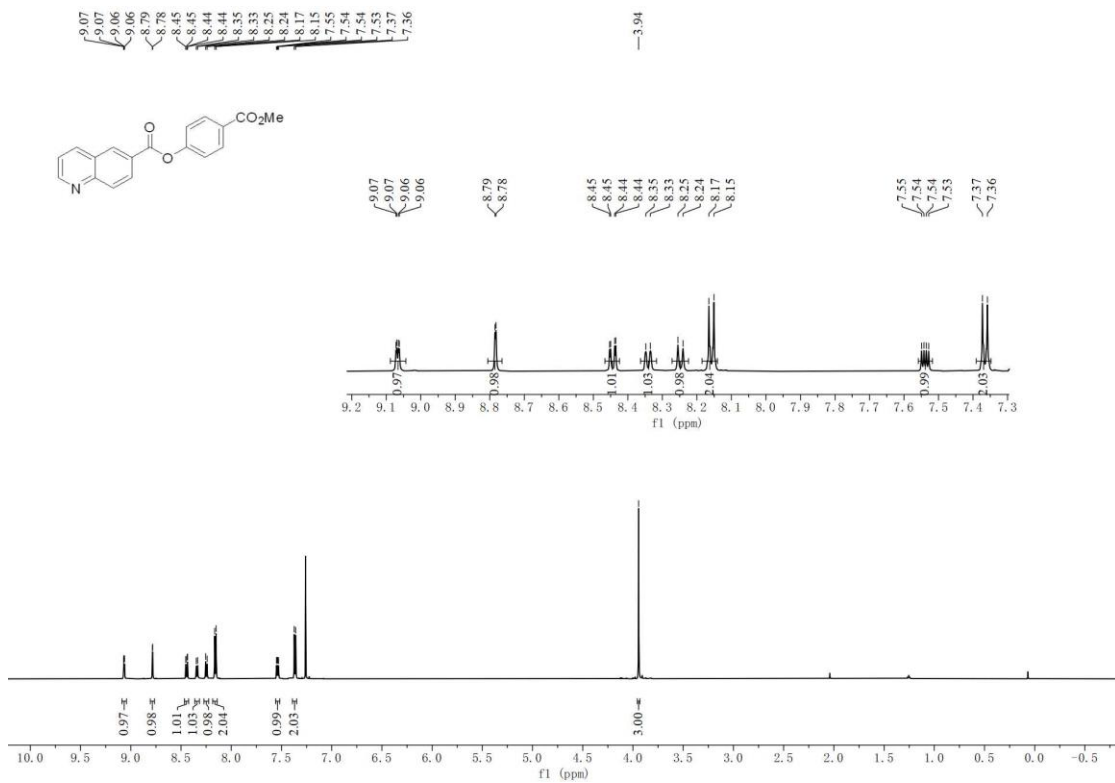
^1H NMR of compound (39)



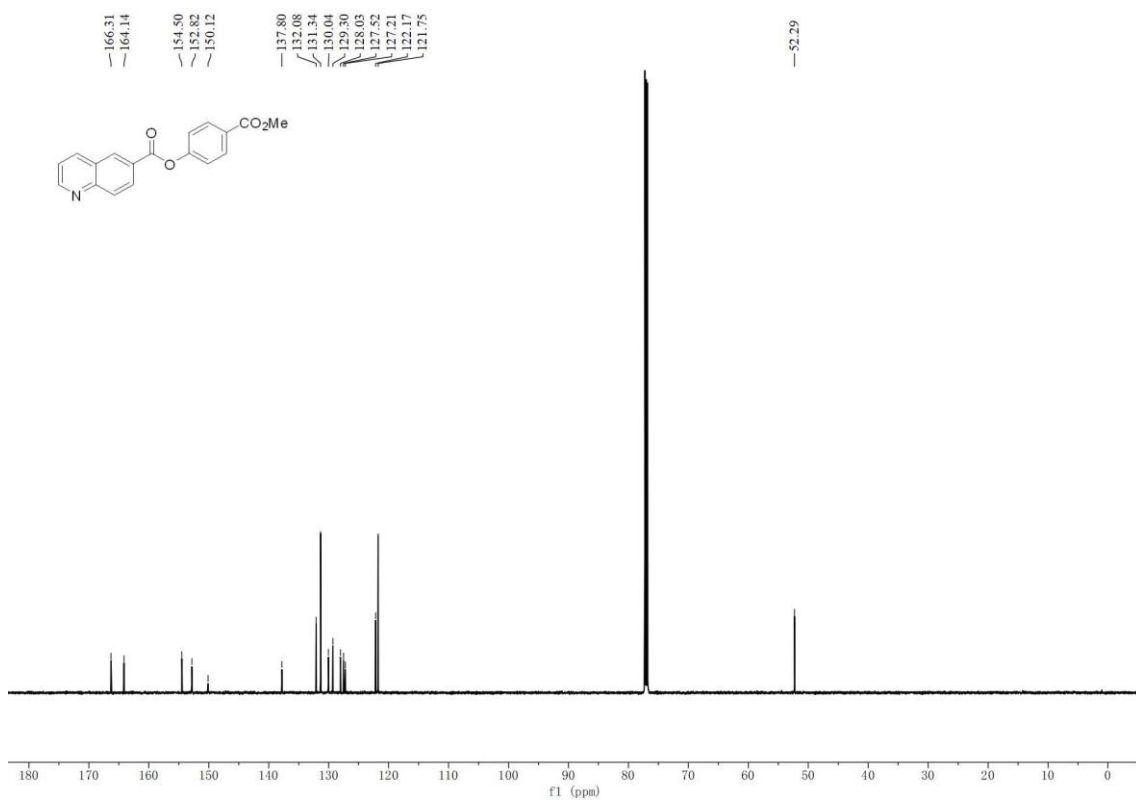
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (39)



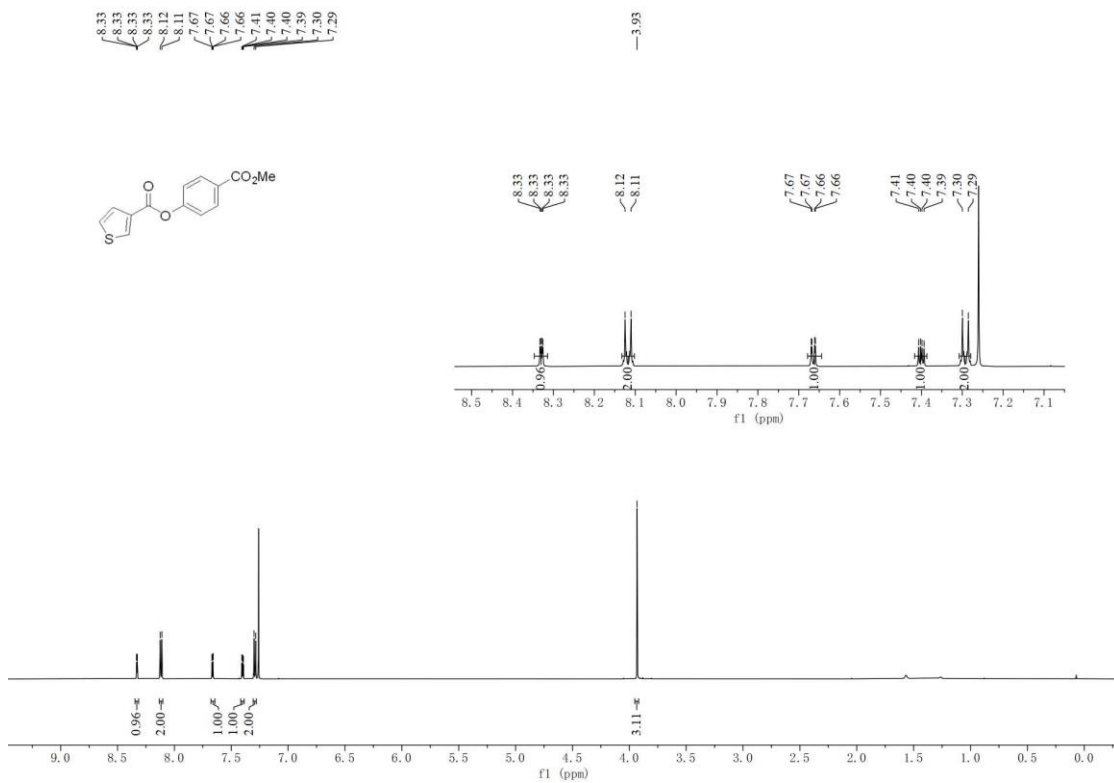
¹H NMR of compound (40)



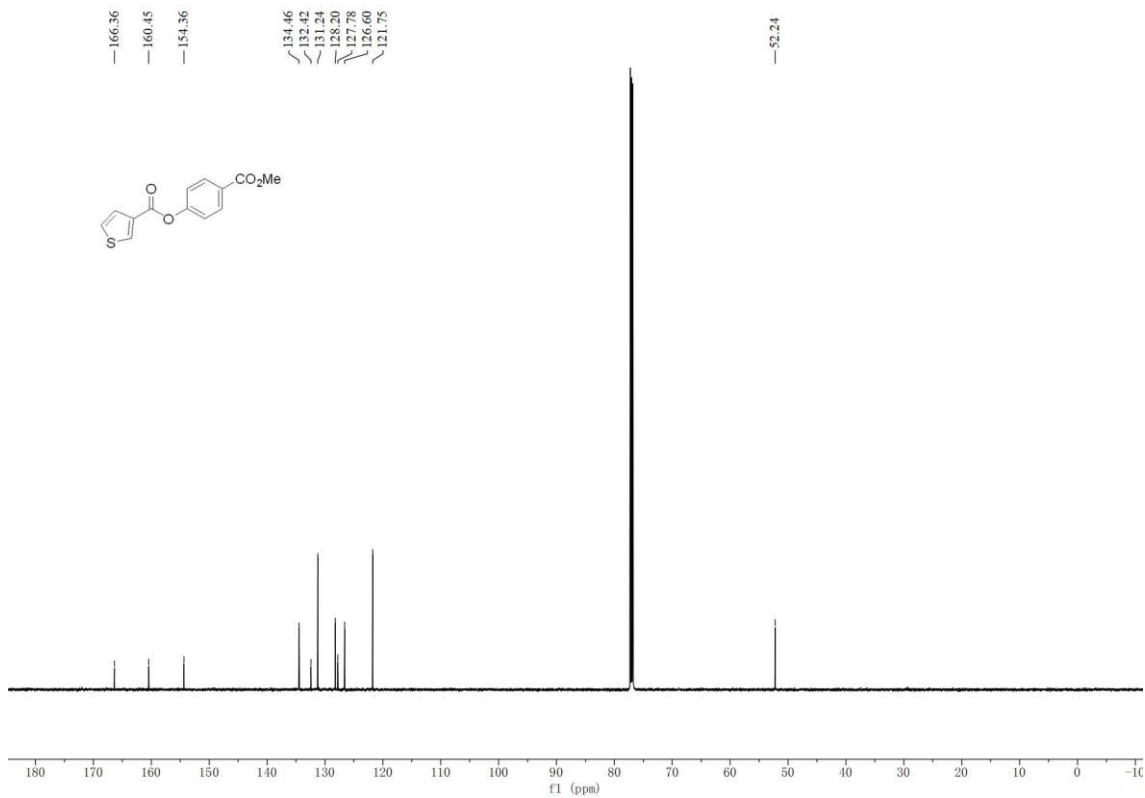
¹³C{¹H} NMR of compound (40)



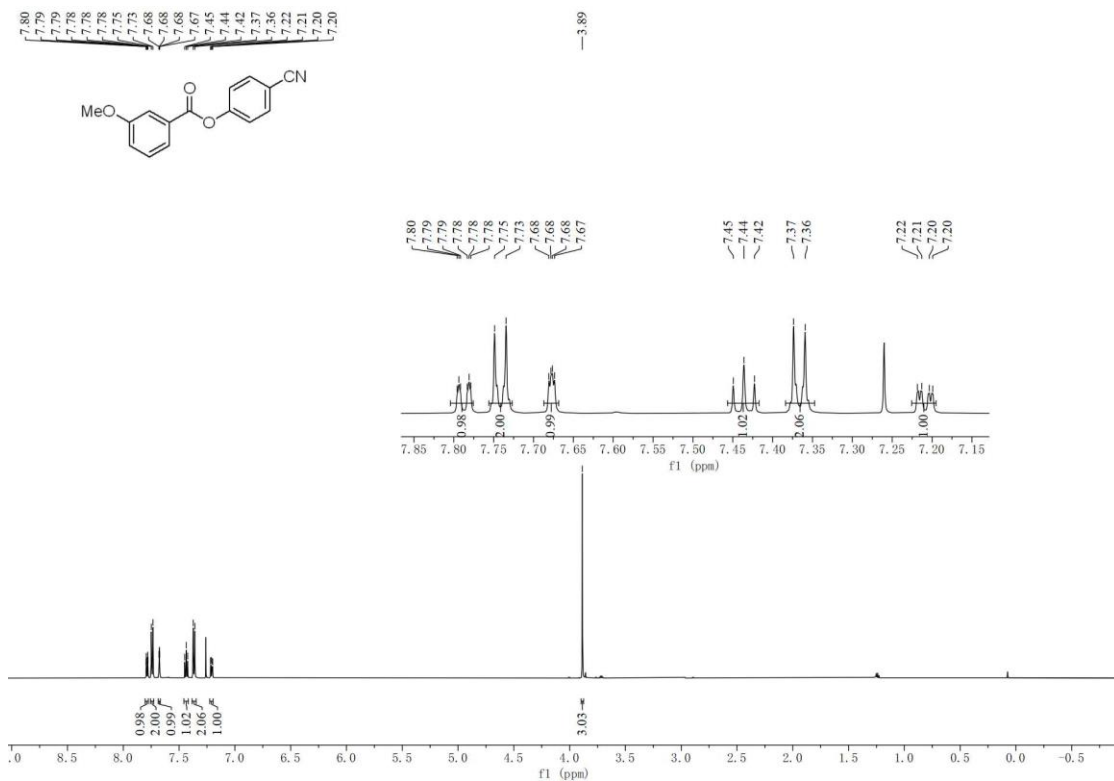
^1H NMR of compound (41)



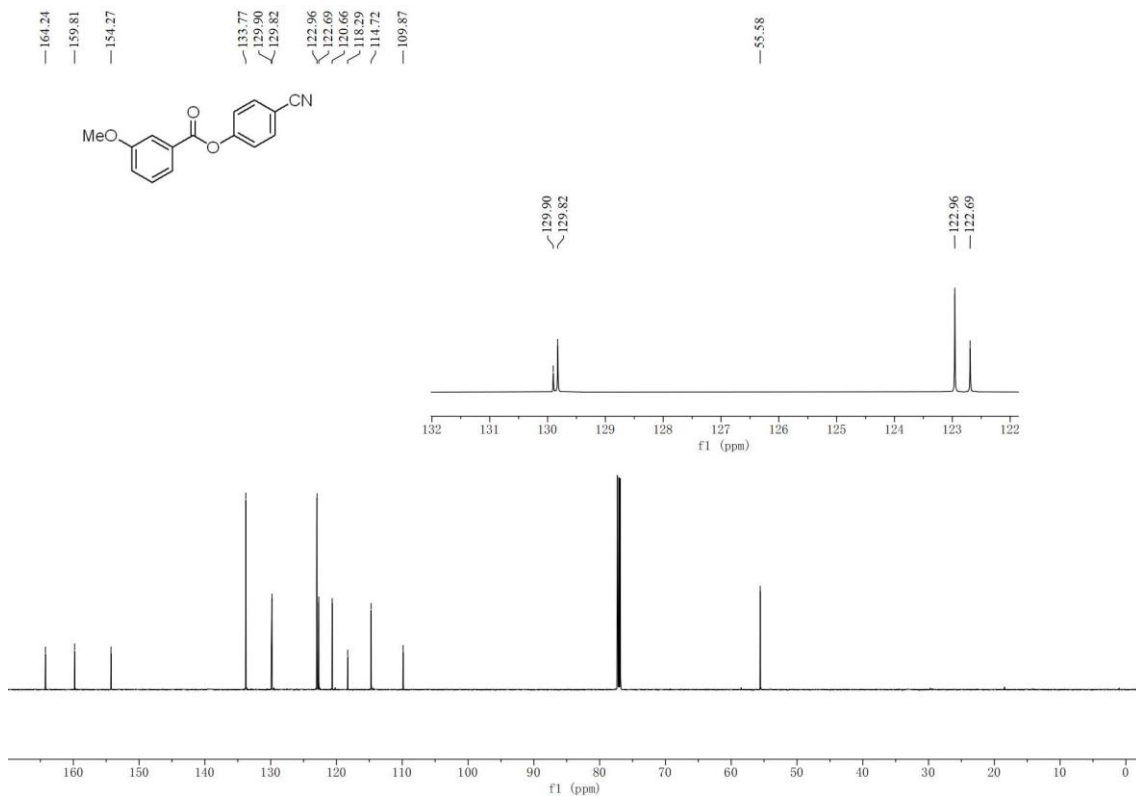
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (41)



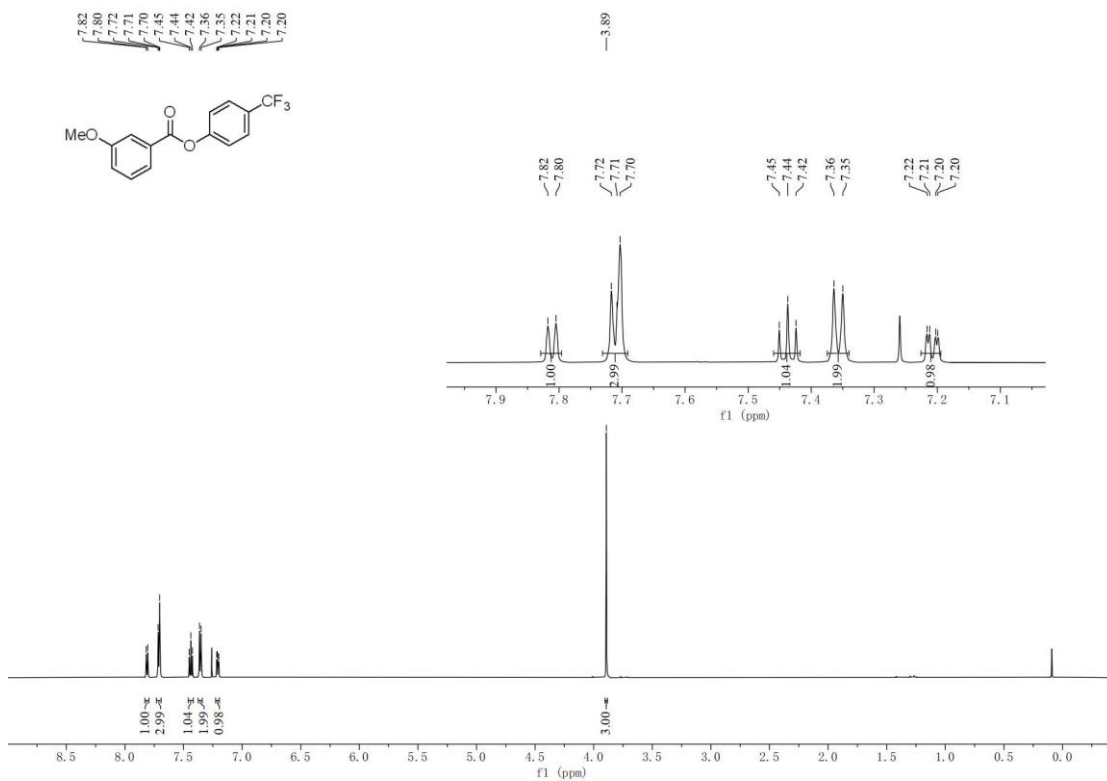
¹H NMR of compound (42)



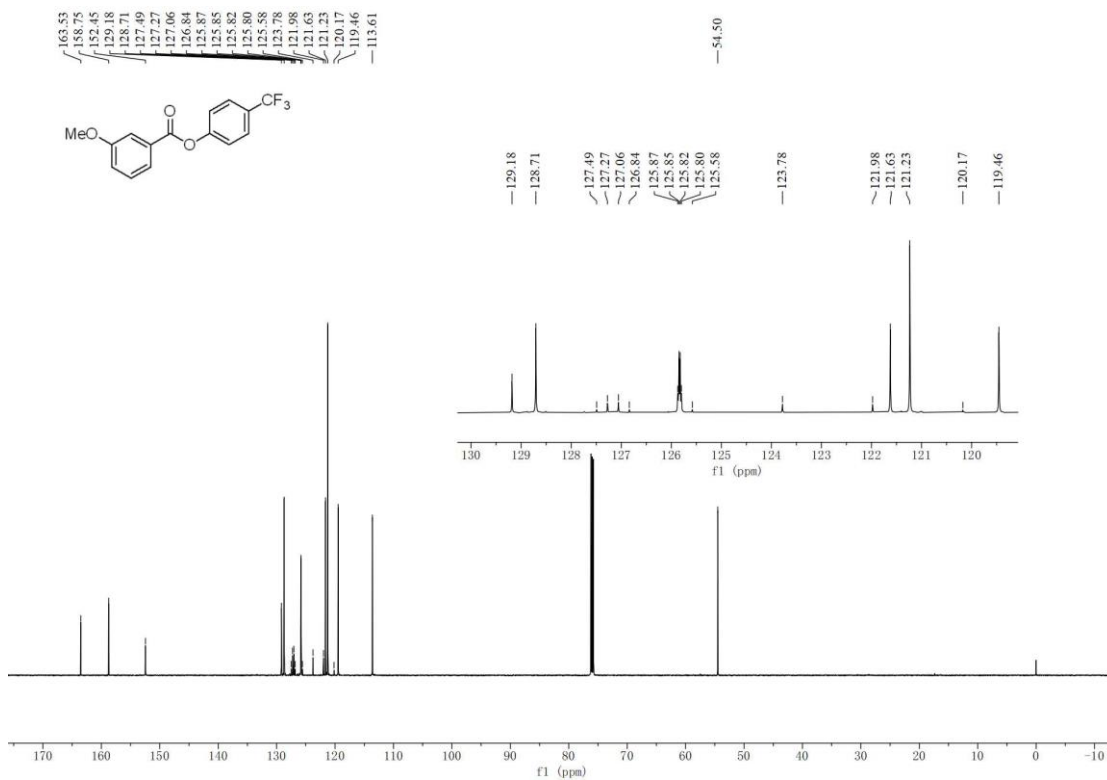
¹³C {¹H} NMR of compound (42)



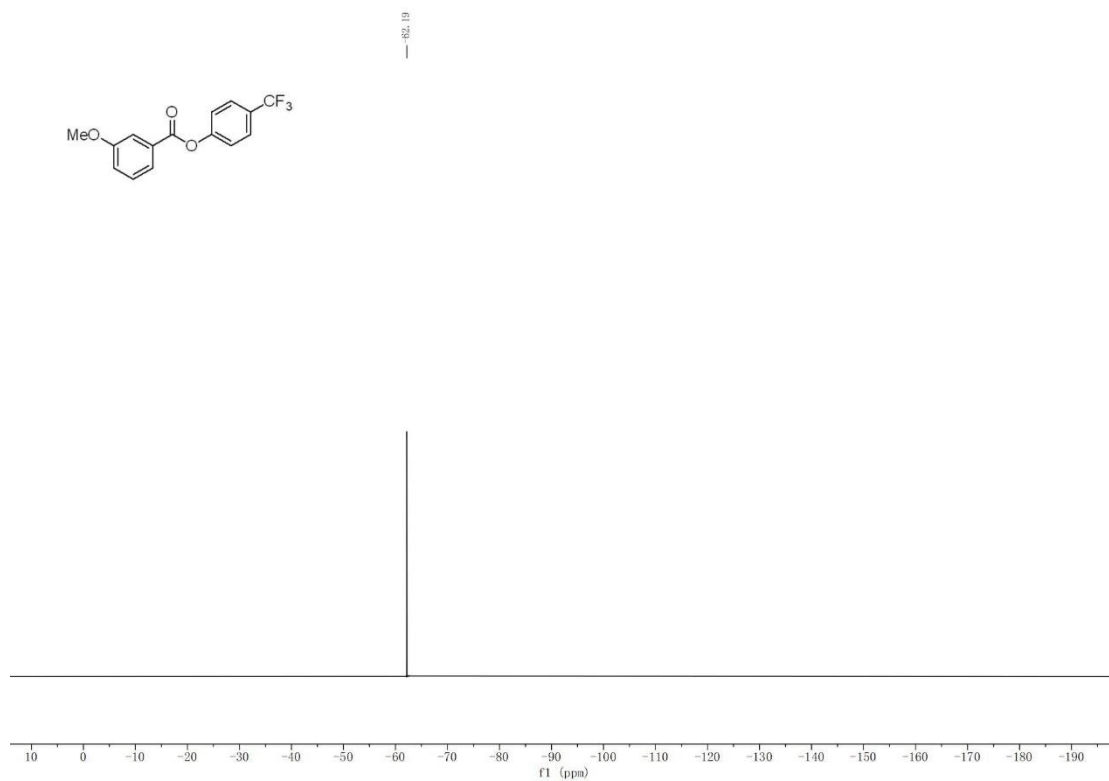
¹H NMR of compound (43)



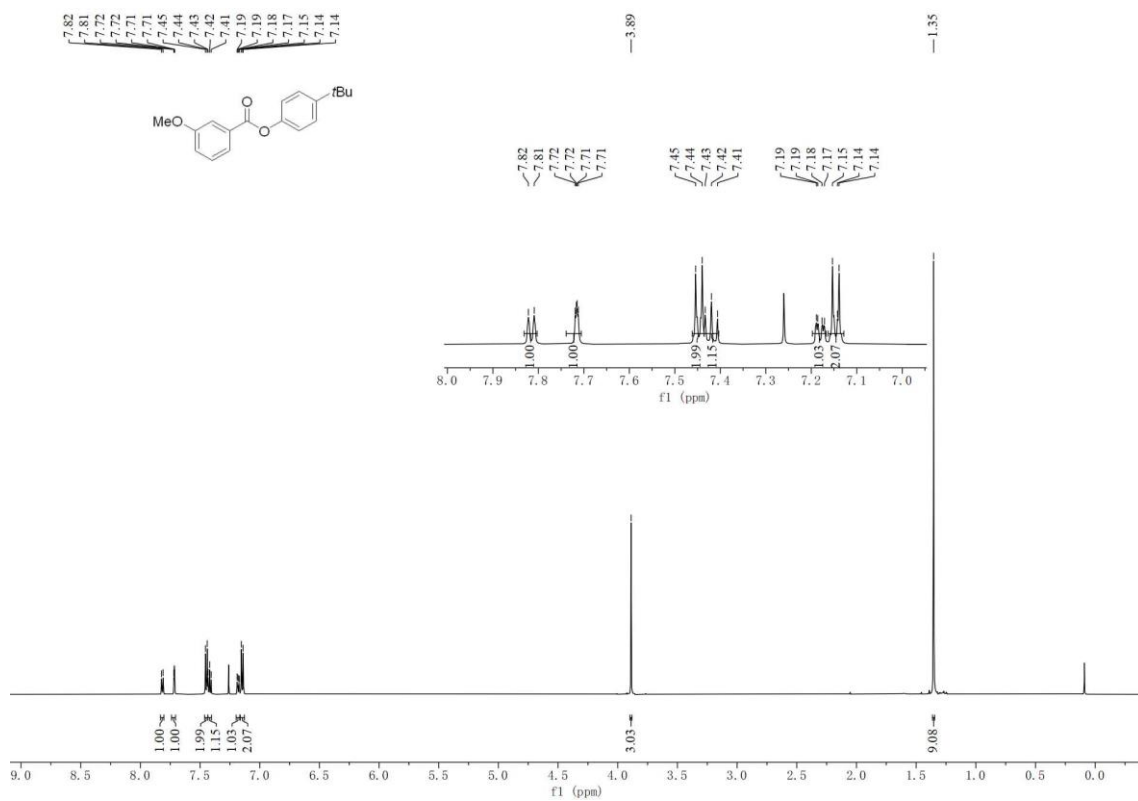
¹³C{¹H} NMR of compound (43)



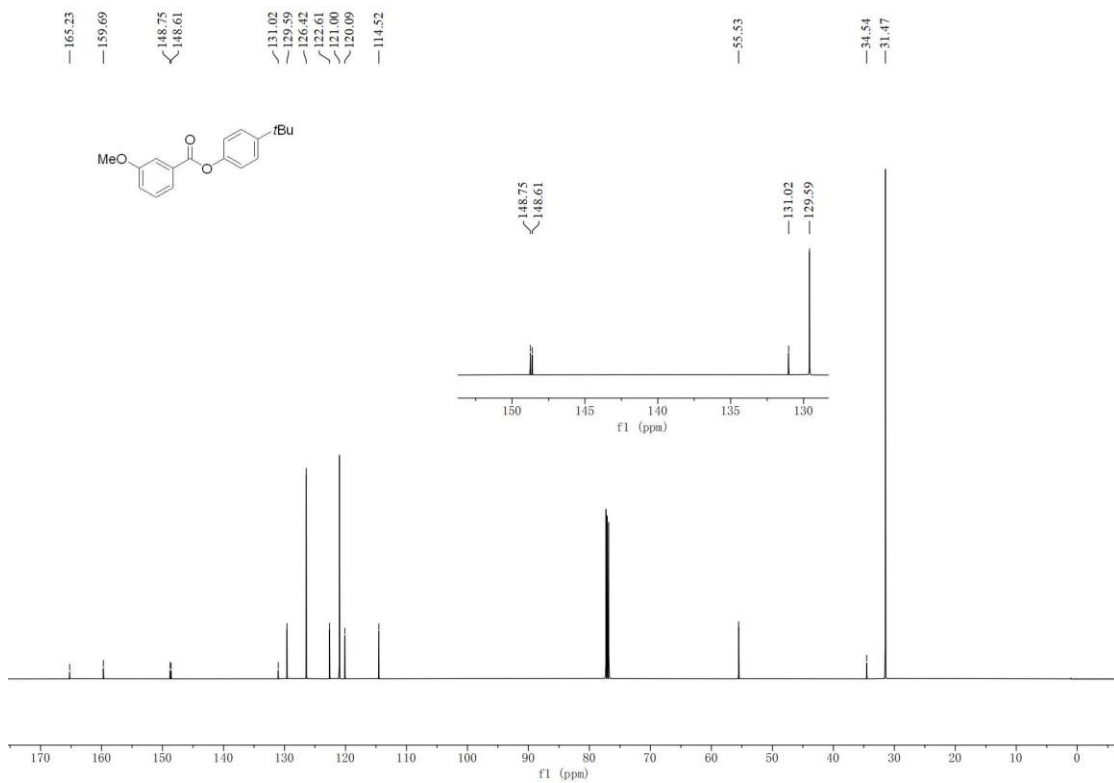
$^{19}\text{F}\{^1\text{H}\}$ NMR of compound (43)



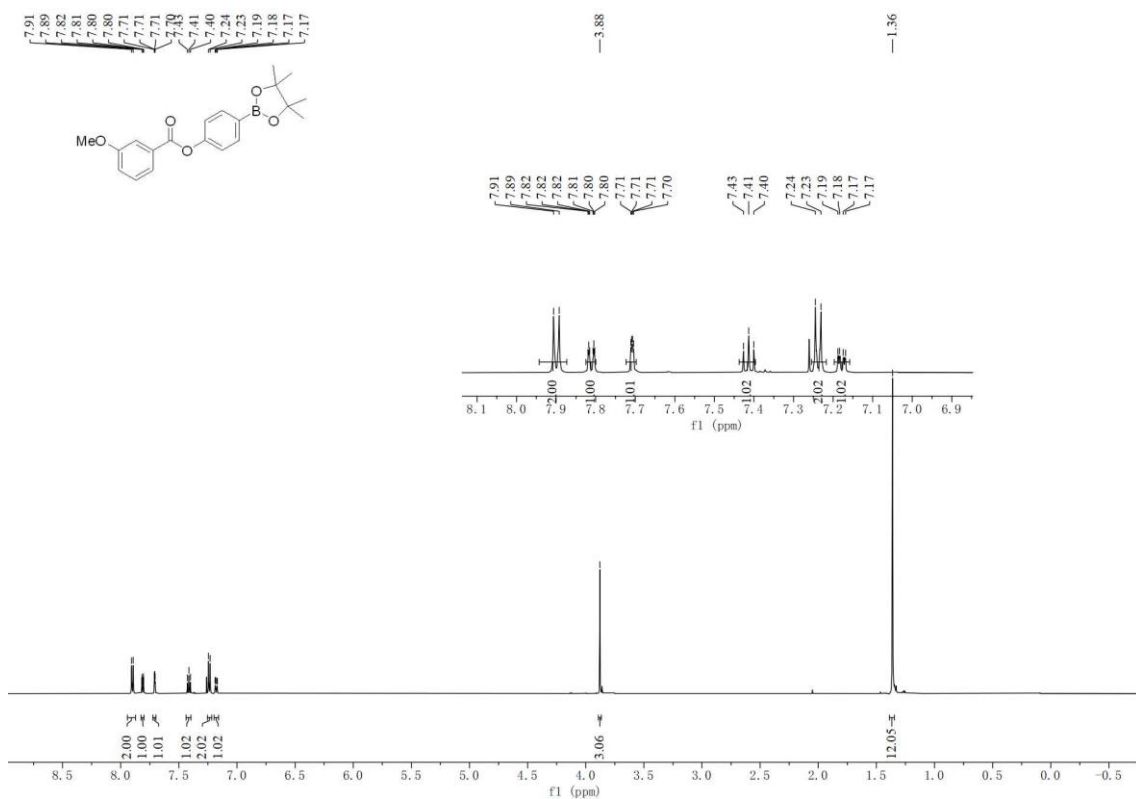
^1H NMR of compound (44)



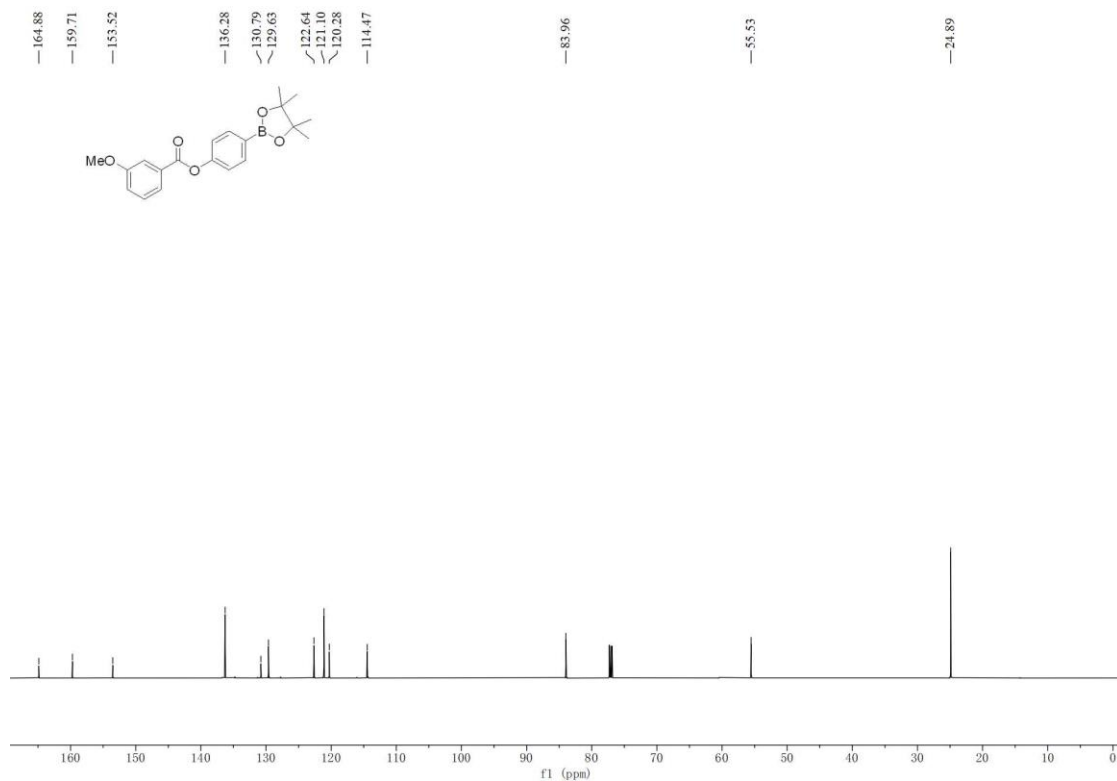
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (44)



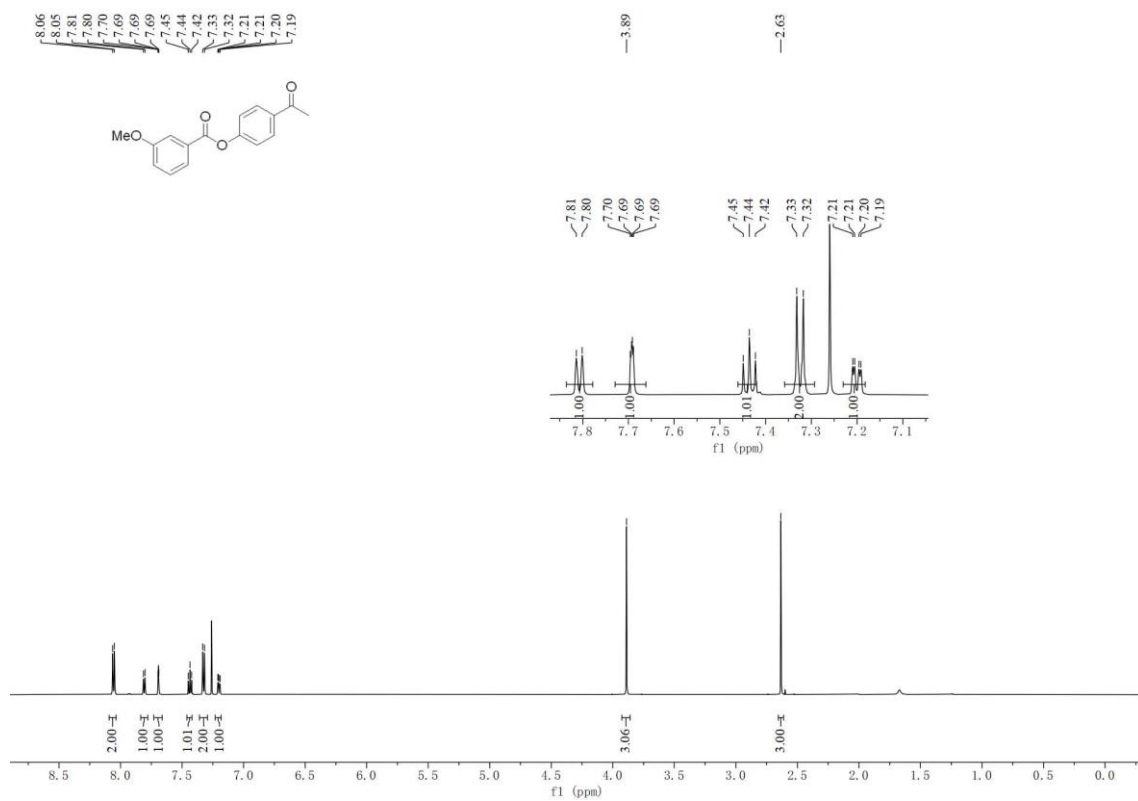
^1H NMR of compound (45)



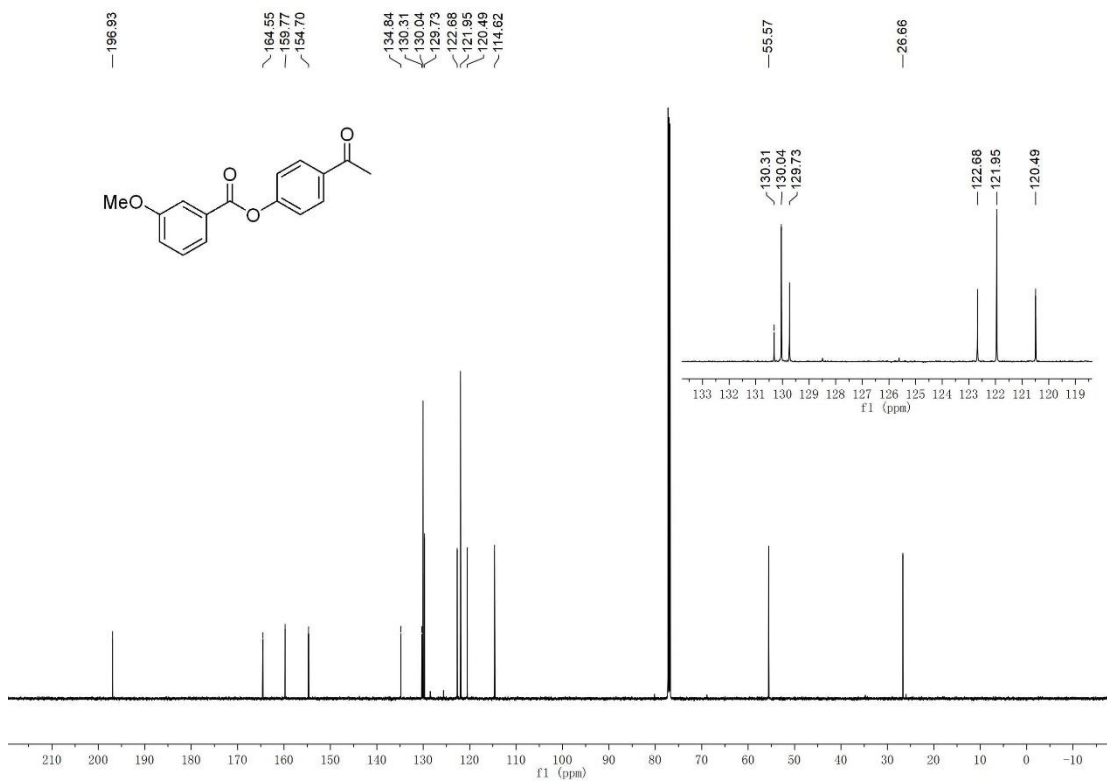
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (45)



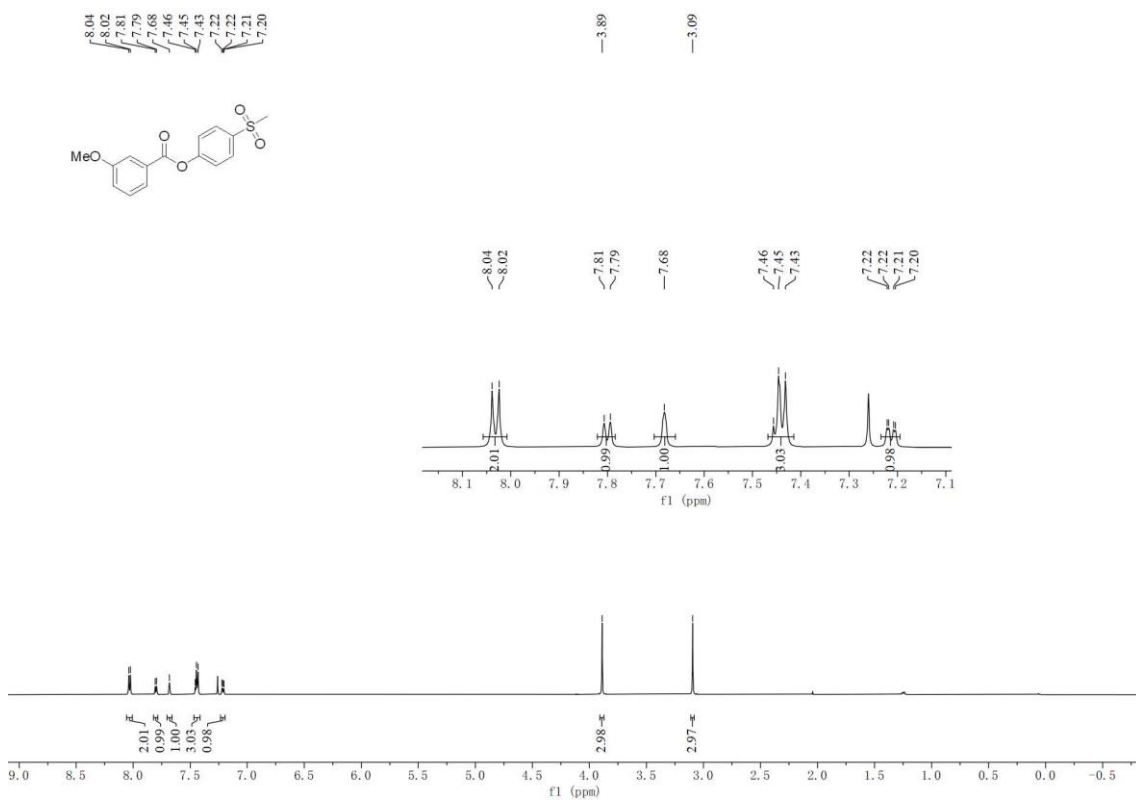
^1H NMR of compound (46)



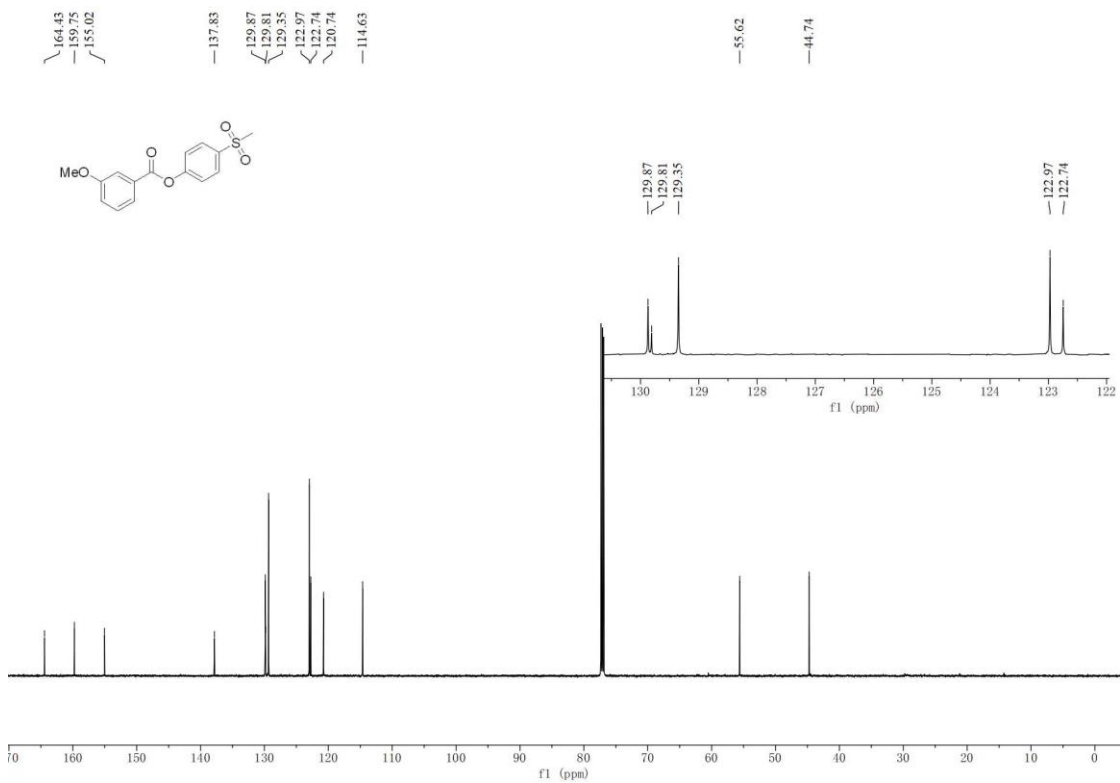
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (46)



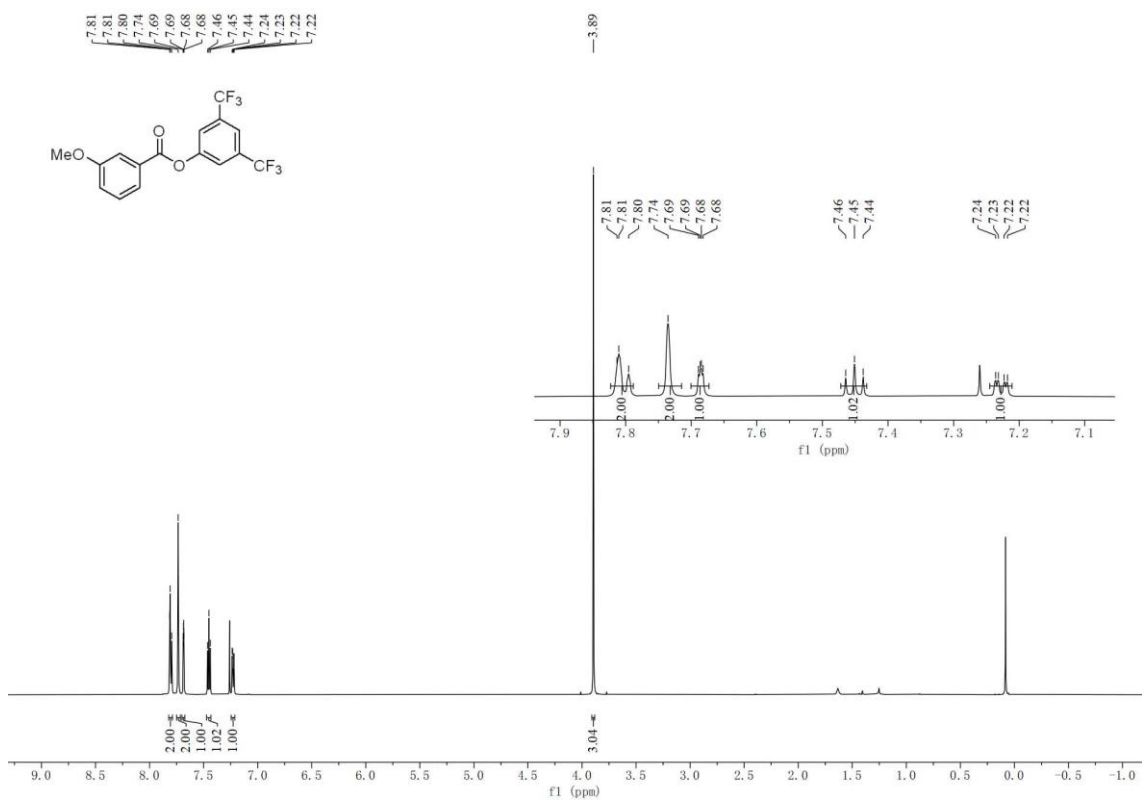
^1H NMR of compound (47)



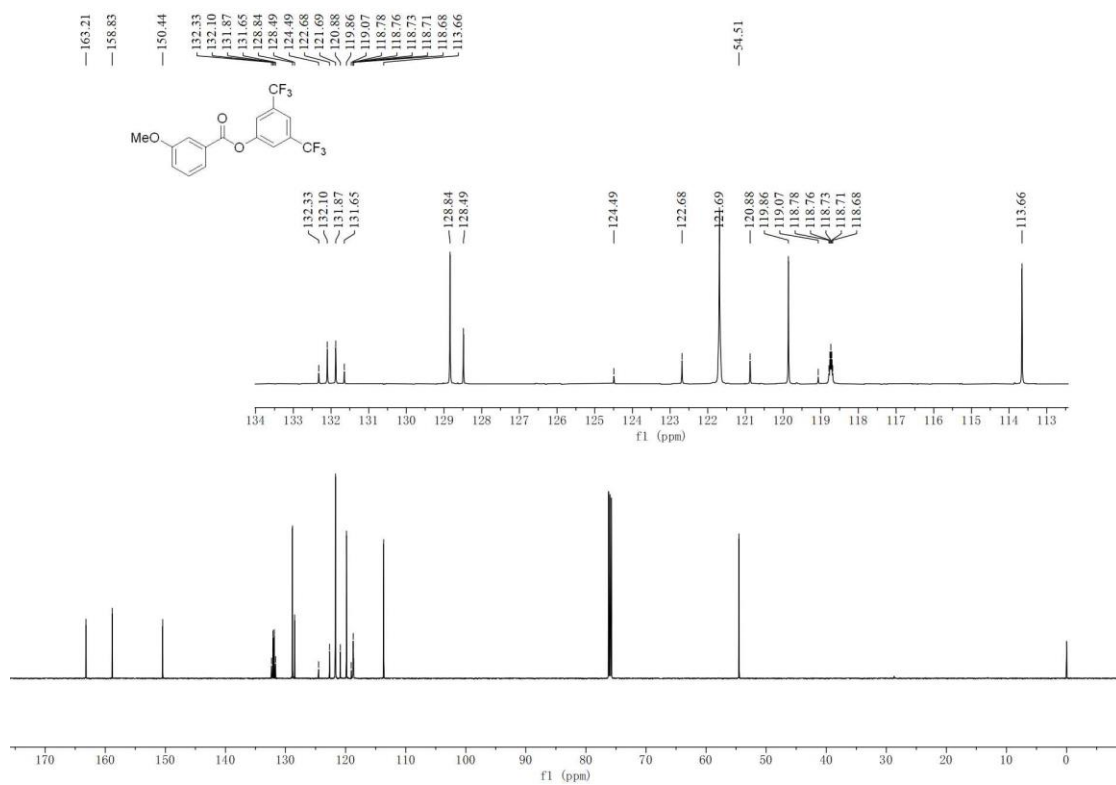
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (47)



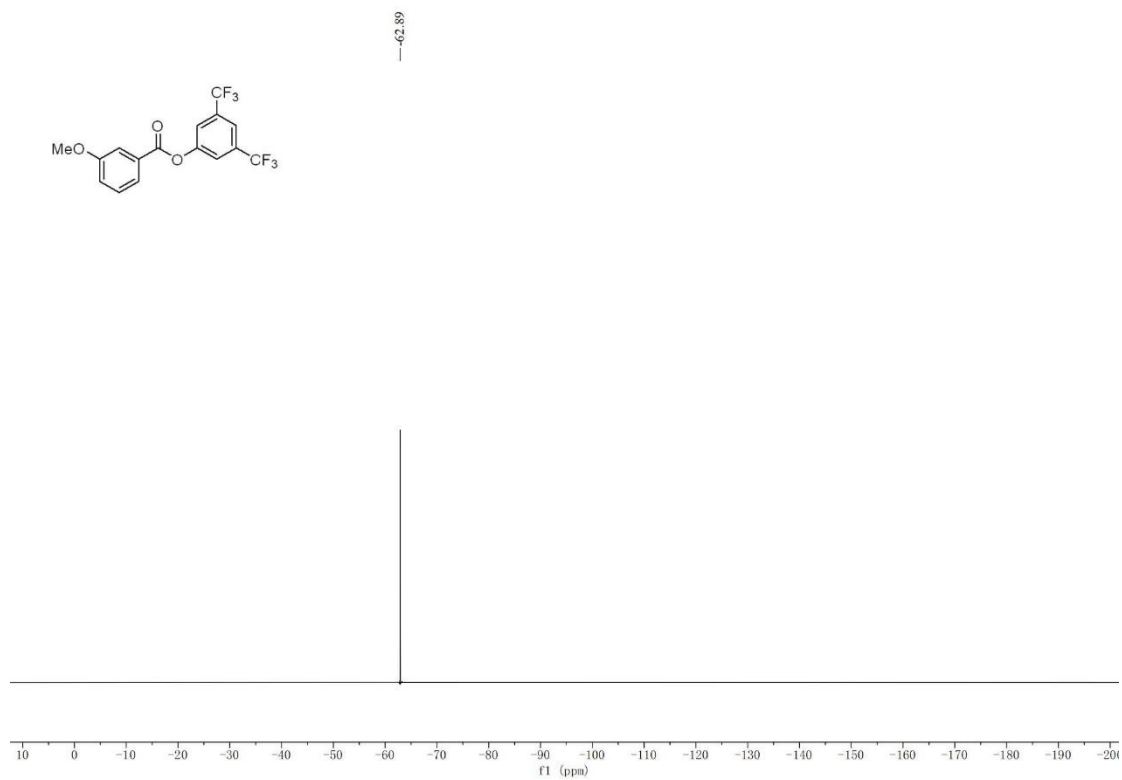
^1H NMR of compound (48)



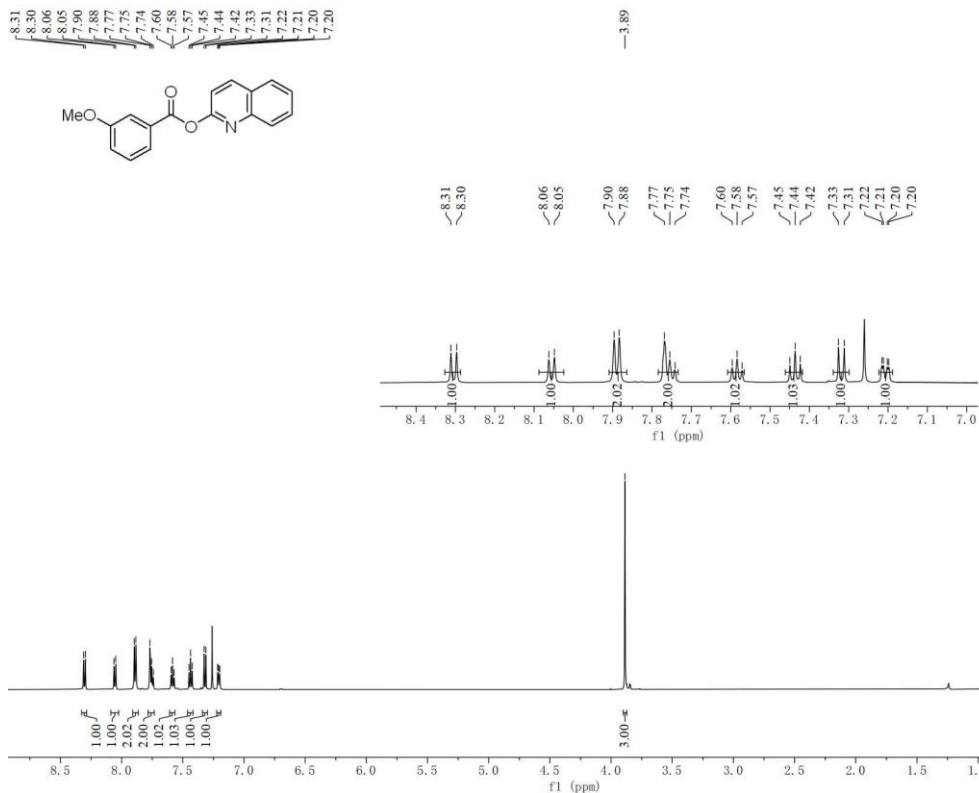
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (48)



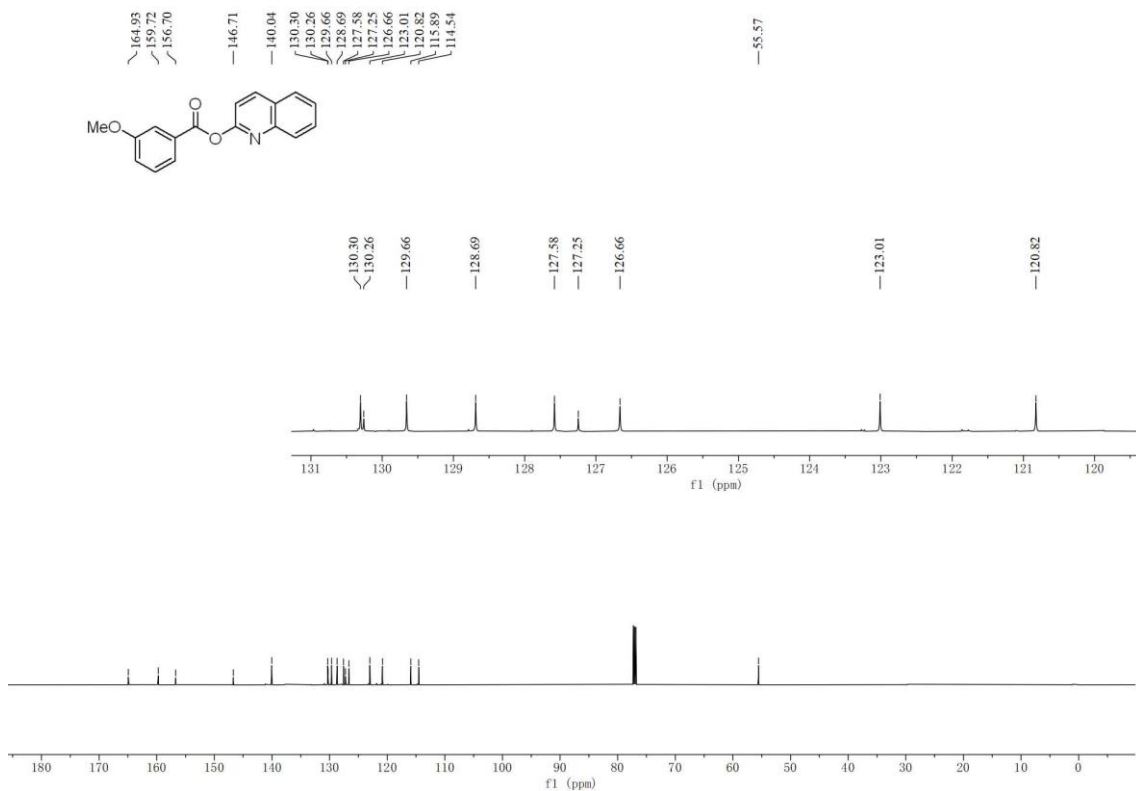
$^{19}\text{F}\{^1\text{H}\}$ NMR of compound (48)



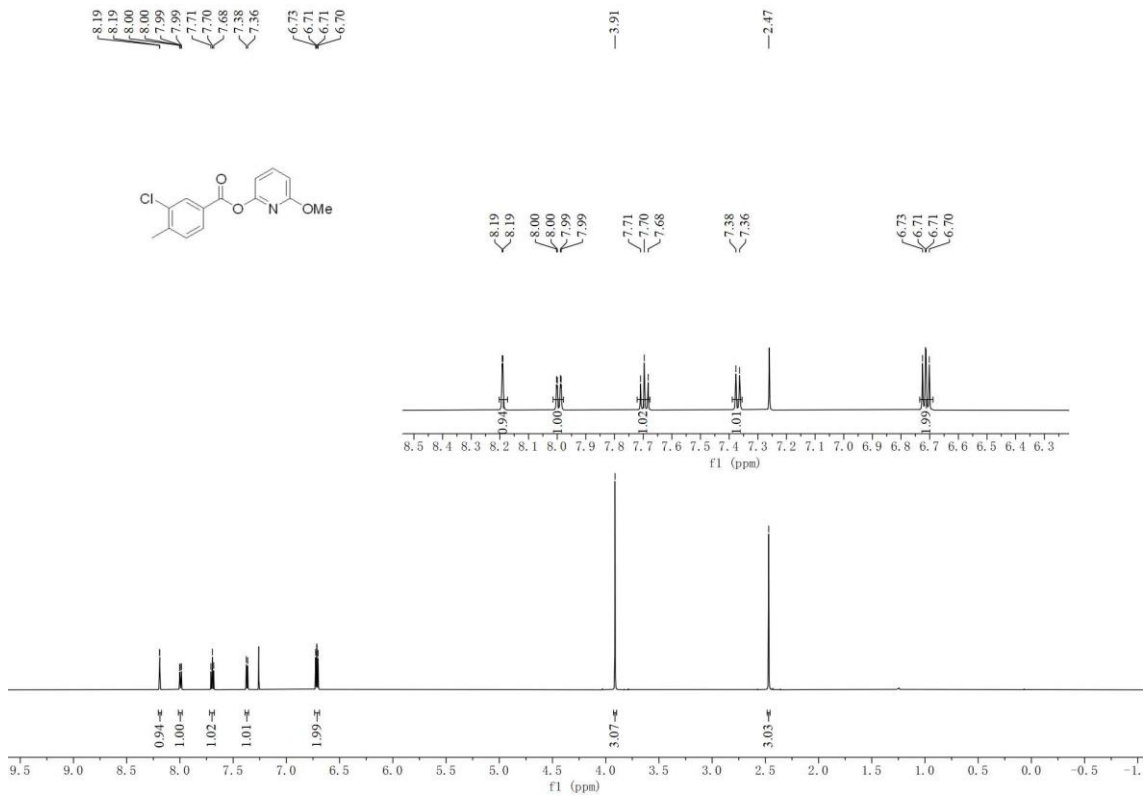
^1H NMR of compound (49)



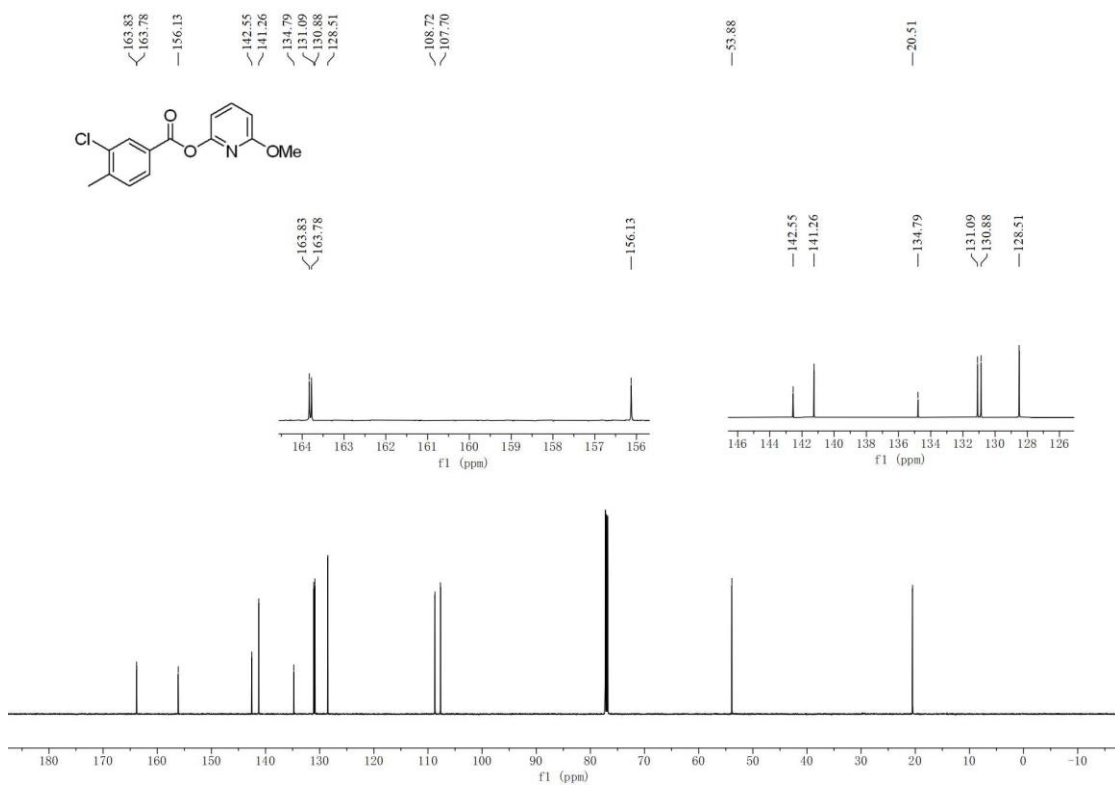
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (49)



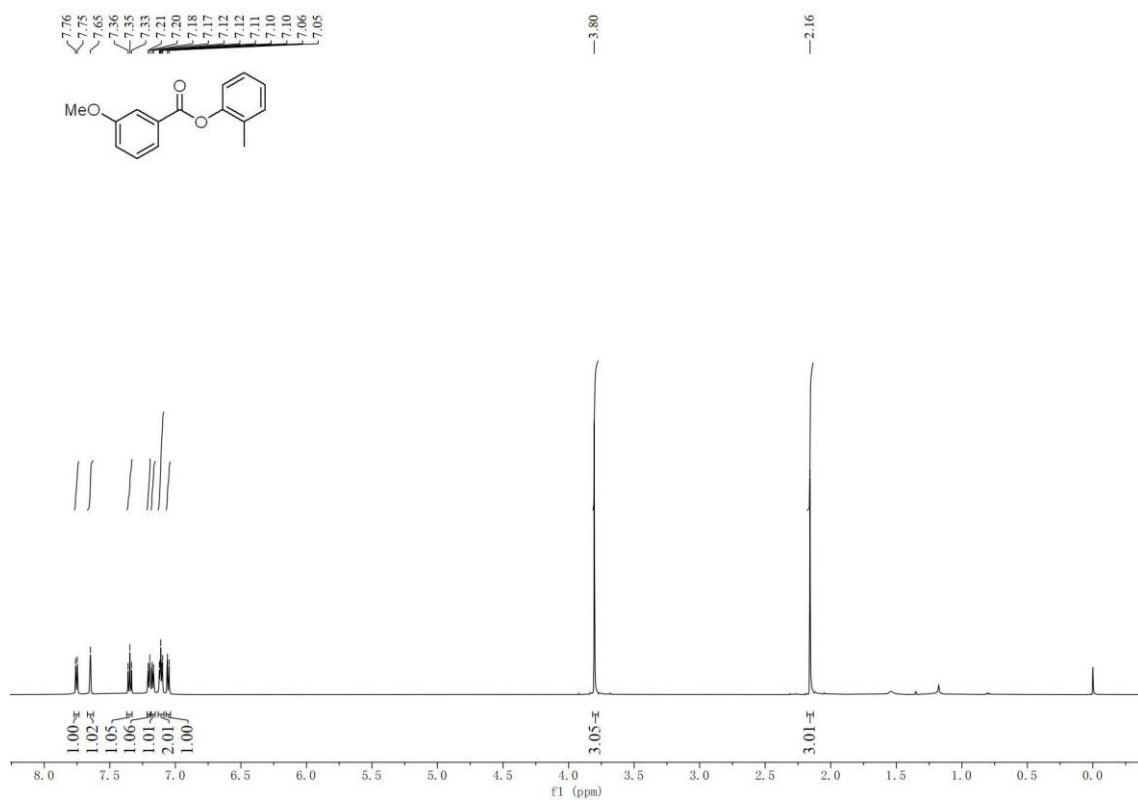
^1H NMR of compound (50)



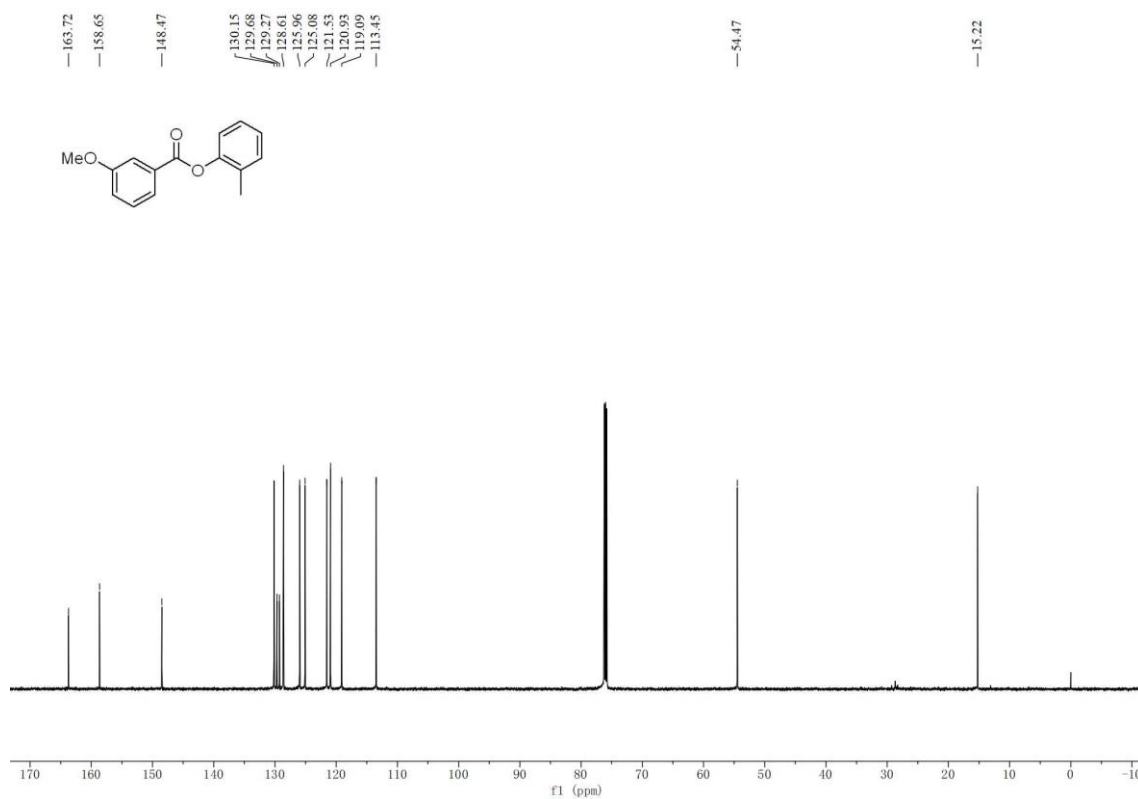
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (50)



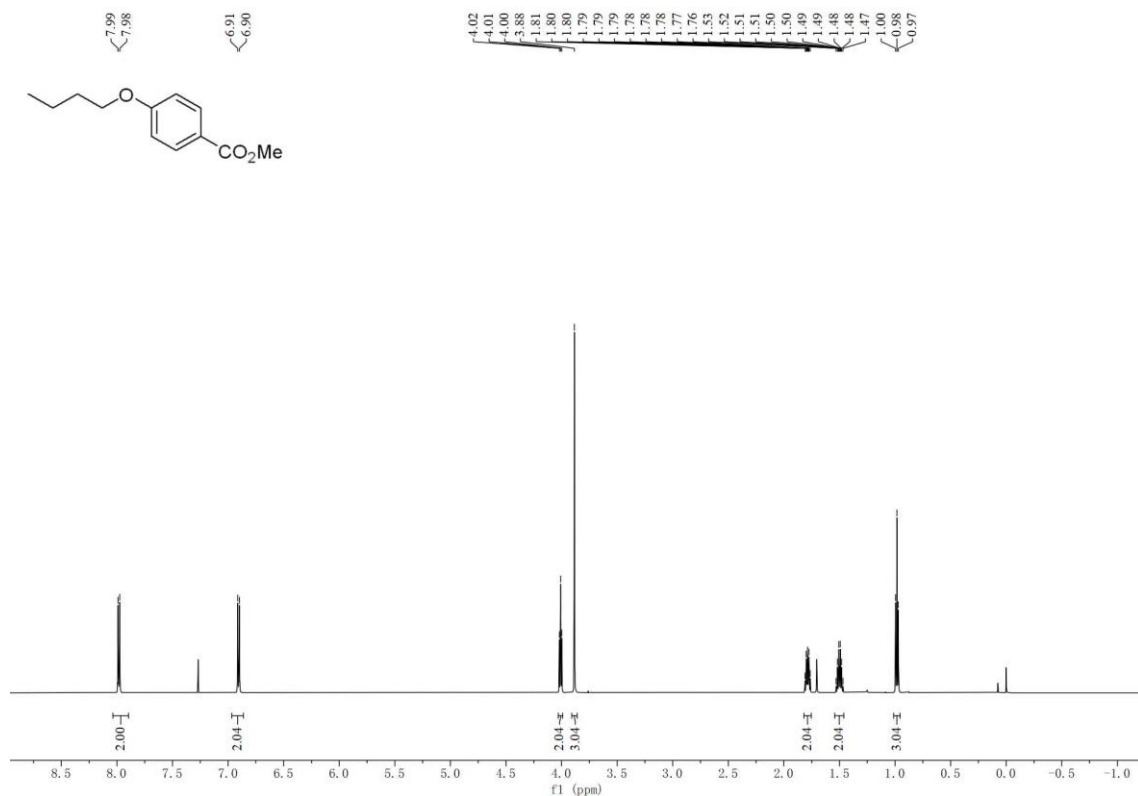
^1H NMR of compound (51)



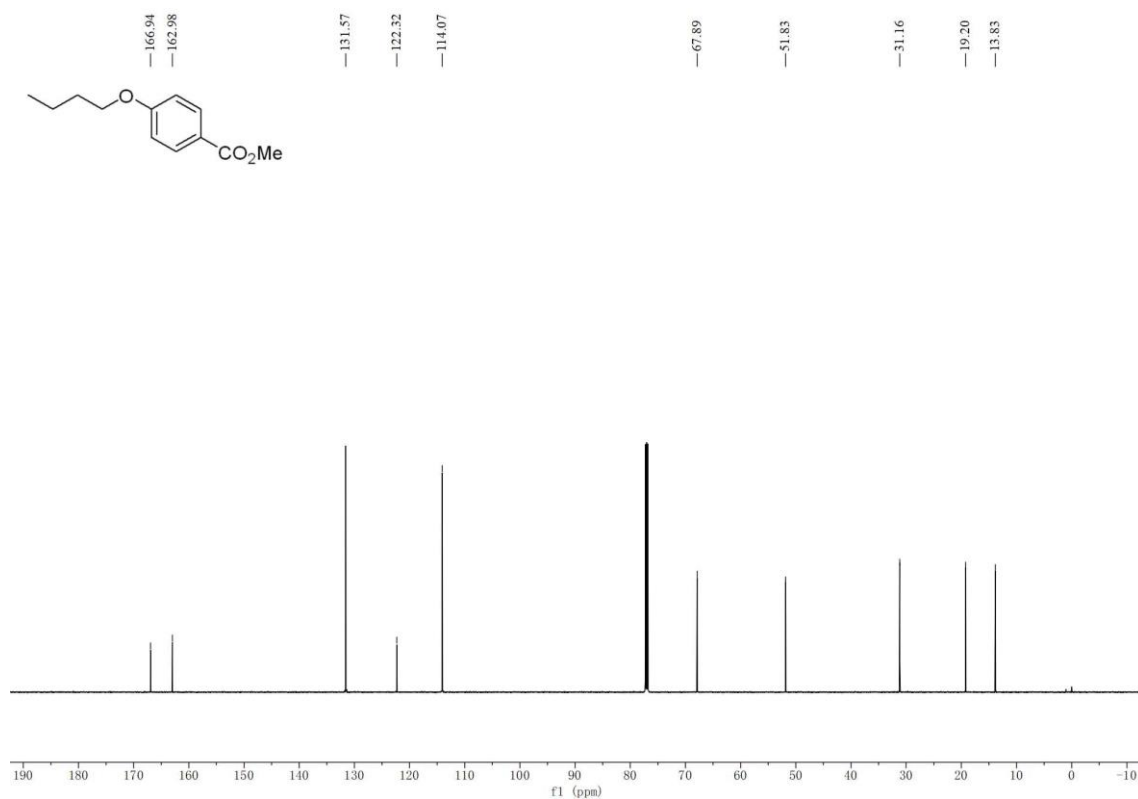
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (51)



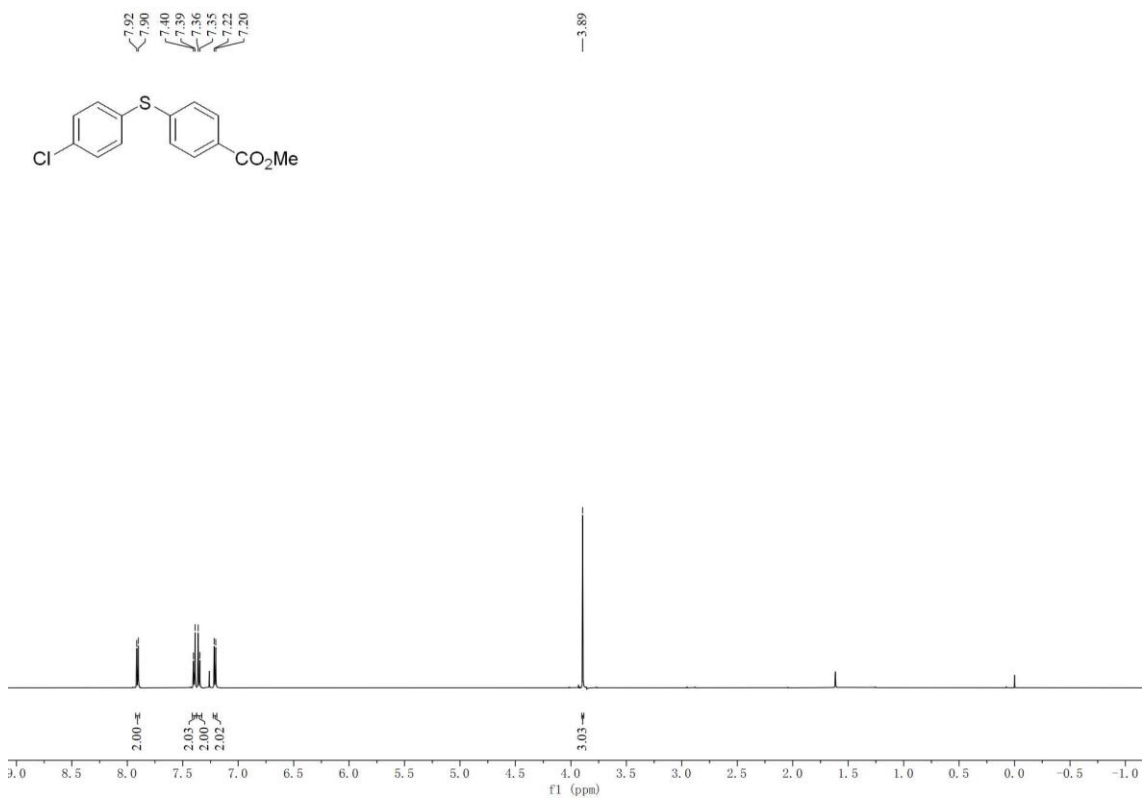
^1H NMR of compound (52)



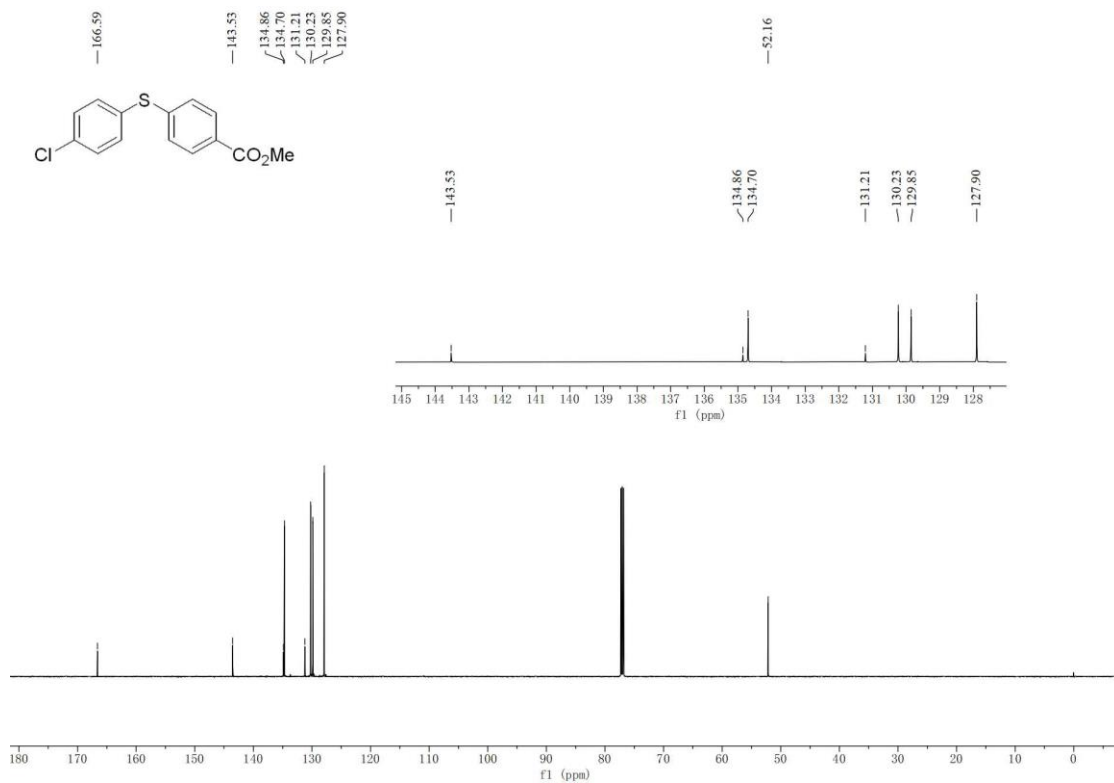
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (52)



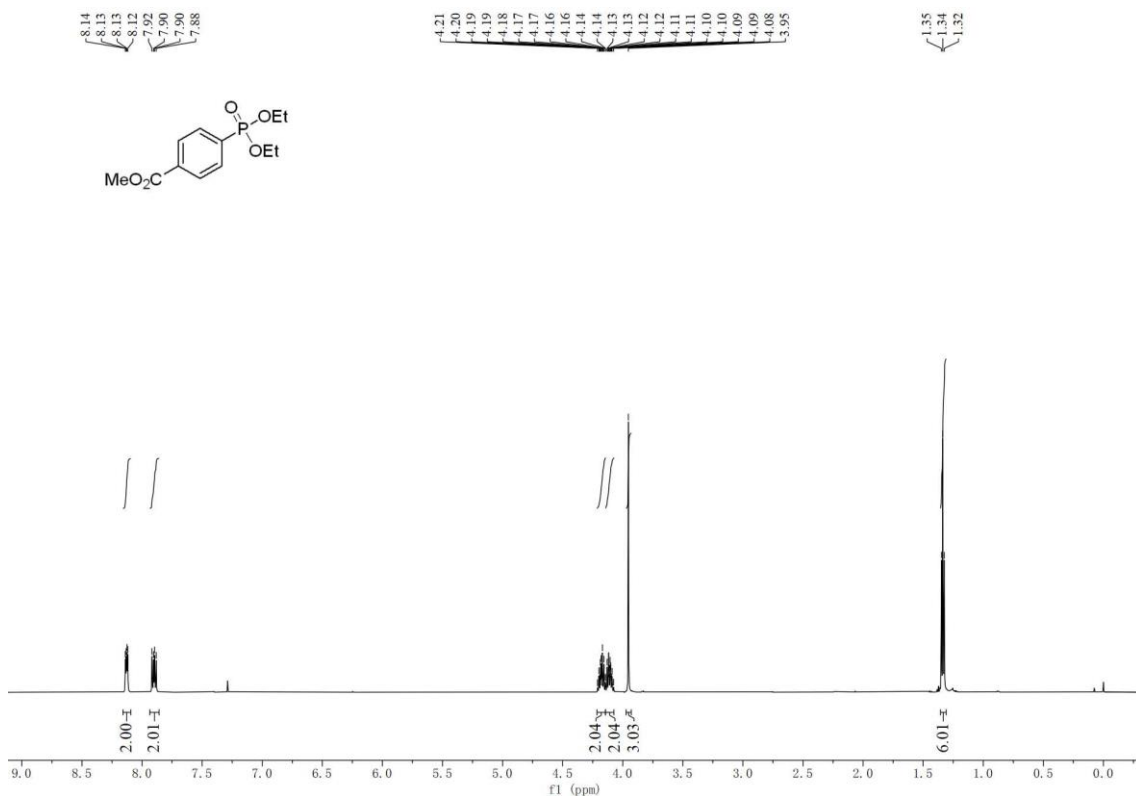
^1H NMR of compound (53)



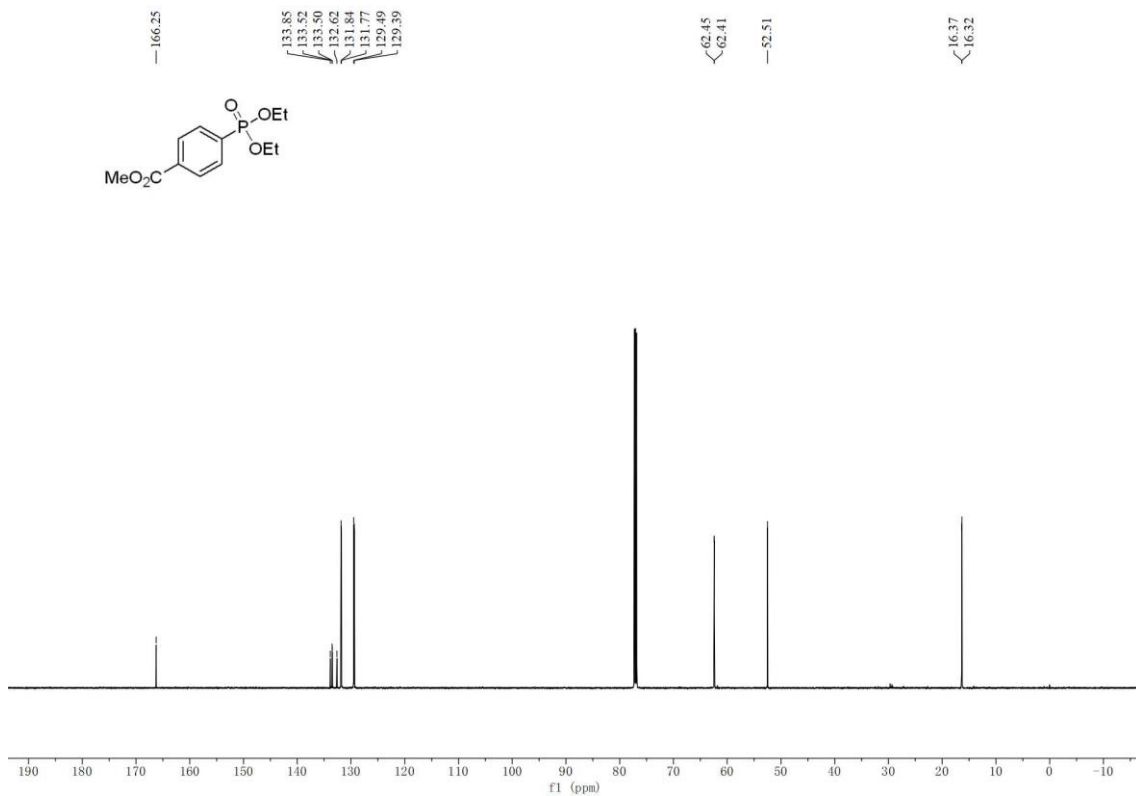
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (53)



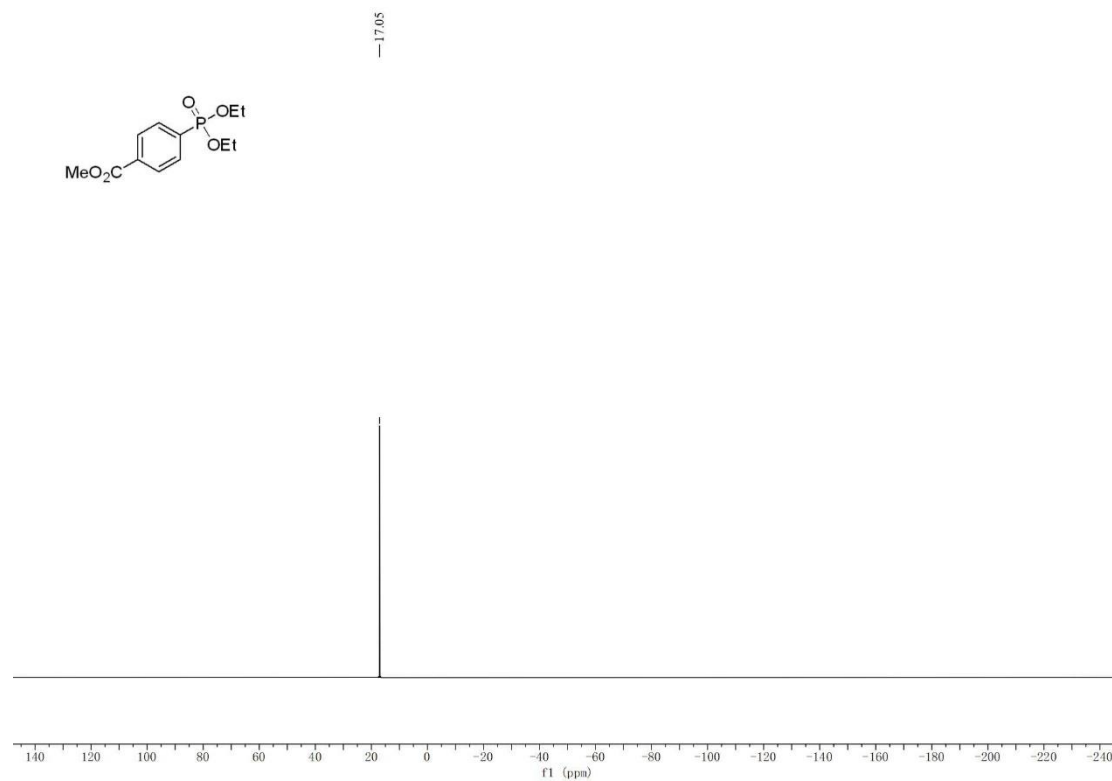
^1H NMR of compound (54)



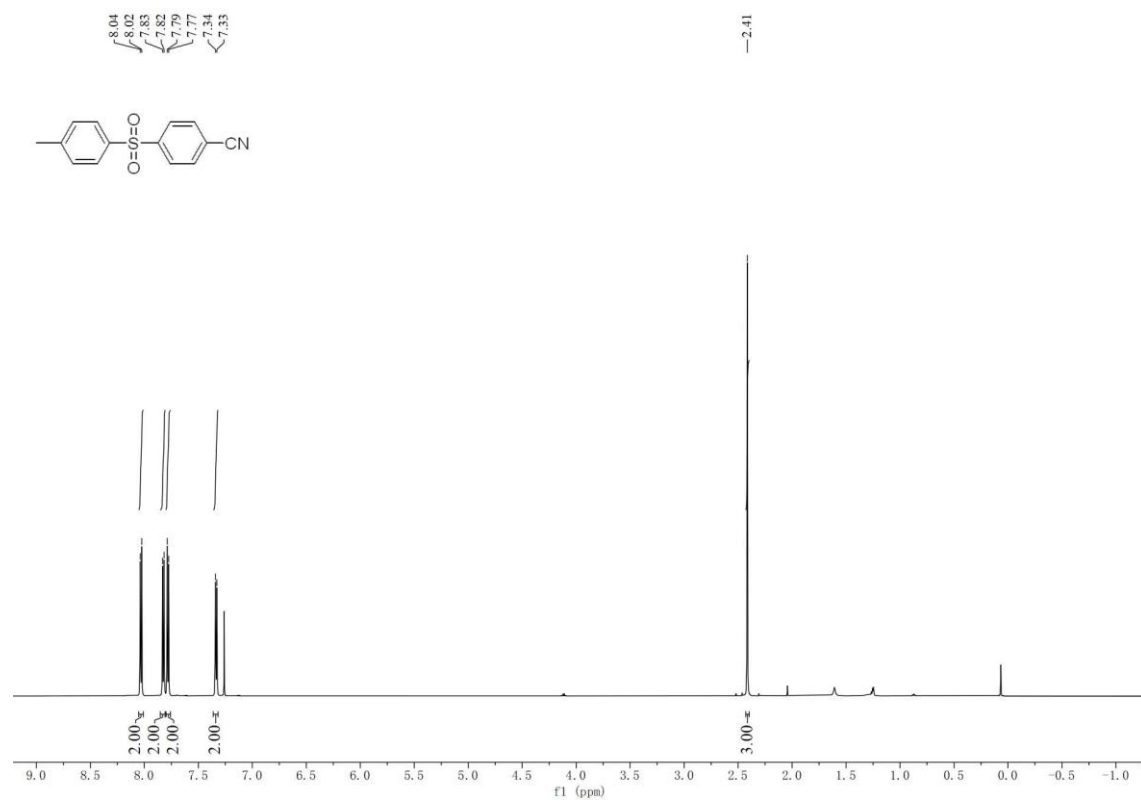
$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (54)



$^{31}\text{P}\{^1\text{H}\}$ NMR of compound (54)



^1H NMR of compound (55)



$^{13}\text{C}\{^1\text{H}\}$ NMR of compound (55)

