Supporting Information

Photoredox-Catalyzed Multicomponent Petasis Reaction with Alkyltrifluoroborates

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1. General considerations:

1.1 General

All chemical transformations were conducted under an inert atmosphere of argon utilizing Schlenk line techniques with a 4- or 5-port dual-bank manifold. NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K using a 500 MHz. ^{1}H NMR spectra were referenced to residual non-deuterated chloroform (δ 7.26) in $CDCl_3$. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.16). Coupling constants, *J*, are reported in hertz (Hz). HRMS data was obtained by either ESI or CI with a TOF spectrometer in CH_3CN or CH_2Cl_2. Accurate mass measurements were acquired on Waters instruments. Waters software calibrates and reports using neutral atomic masses. The mass of the electron in not included. Reactions were monitored by ^{1}H NMR, and/or by TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using *p*-anisaldehyde stain, and/or UV light. Flash chromatography was accomplished using an automated system (visualizing at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). Solvents were purified by use of drying cartridges through a solvent delivery system. Melting points are uncorrected. Irradiation of reaction vessels was accomplished using blue LEDs (Light-emitting diode) at a distance of ~3-5 cm. A fan was employed to ensure reactions remained at or near rt when using LEDs.

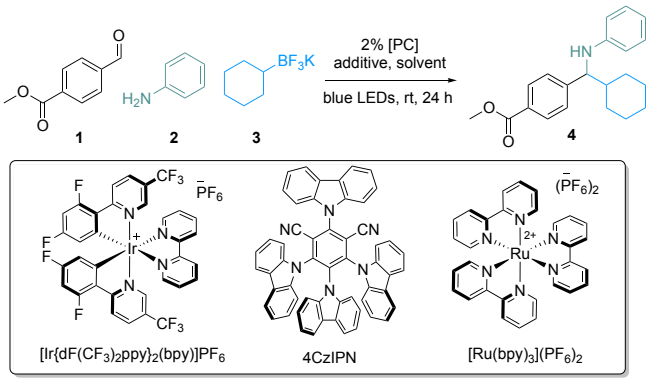
1.2 Chemicals

Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. Na_2SO_4, $MgSO_4$, acetone, pentane, hexanes, and EtOAc were used as purchased. CH_2Cl_2 was purchased and dried *via* a solvent delivery system. $NaHSO_4$ was purchased and used after grinding with a pestle and mortar. Anhydrous 1,4-dioxane was purchased and stored over 4Å molecular sieves. Aldehydes, alkyltrifluoroborates, and amines were purchased

from commercial suppliers and used without further purification. The photocatalyst [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ was prepared in-house as reported in the literature.[1]

2. Optimization of the Reaction Conditions

Table 1. Optimization of the reaction conditions[a]

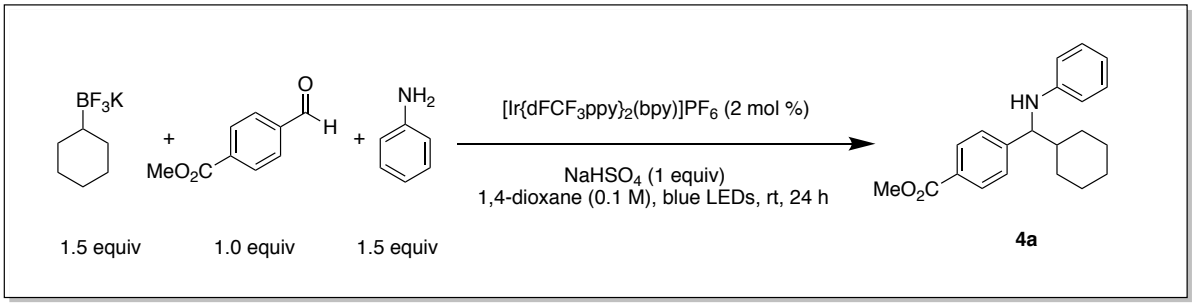


Entry	[PC]	Additive	Solvent	Yield[b]
1	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	-	acetonitrile	70
2	4CzIPN	-	acetonitrile	22
3	[Ru(bpy)$_3$](PF$_6$)$_2$	-	acetonitrile	10
4	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	-	acetone	19
5	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	-	DMF	23
6	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	-	1,4-dioxane	64
7	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	NaHSO$_4$	acetonitrile	65
8	***[Ir(dtbbpy)(ppy)$_2$]PF$_6$***	***NaHSO$_4$***	***1,4-dioxane***	***89(84)***
9	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	NaHSO$_4$	DMSO	84
10	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	benzoic acid	1,4-dioxane	14
11	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	CSA	1,4-dioxane	67
12[c]	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	NaHSO$_4$/H$_2$O	1,4-dioxane	86
13	No photocatalyst	NaHSO$_4$	1,4-dioxane	0
14[d]	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	NaHSO$_4$	1,4-dioxane	0

[a] **1** (0.1 mmol), **2** (0.15 mmol), **3** (0.15 mmol), [PC] (2 mol %), additive (0.1 mmol) in dry, degassed solvent (1.0 mL, 0.1 M) under blue LED irradiation for 24 h. [b] NMR yield using 1,3,5-trimethoxybenzene as internal standard. Isolated yield in parenthesis. [c] 10 equiv H$_2$O added [d] No light.

[1] Kelly, C. B.; Patel, N. R.; Primer, D. N.; Jouffroy, M.; Tellis, J. C.; Molander, G. A. *Nature Protocols* **2017**, *12*, 472.

3. General Procedure for Alkylation:



Methyl 4-(Cyclohexyl(phenylamino)methyl)benzoate (4)

To an 8 mL reaction vial equipped with a stir bar was added [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ (10.0 mg, 0.01 mmol, 2 mol %), alkyltrifluoroborate (140.0 mg, 0.75 mmol, 1.5 equiv), aldehyde (82.0 mg, 0.5 mmol, 1.0 equiv), amine (68.0 μL, 0.75 mmol, 1.5 equiv), and $NaHSO_4$ (60.0 mg, 0.5 mmol, 1.0 equiv). The vial was sealed with a cap containing a TFE lined silicone septa and placed under an argon *via* an inlet needle. The vial was evacuated three times *via* an inlet needle then purged with argon. Dry and degassed 1,4-dioxane was then added (5.0 mL, 0.1 M). If the amine or aldehyde were in the liquid state, they were added at this point directly *via* microsyringe. The reaction was placed under blue LED irradiation and vigorously stirred for 24 h. The reaction was maintained at approximately 24 °C *via* a fan. After completion, the reaction mixture was taken to dryness and then purified on an automated liquid chromatographic system (24 g column, 100:0→85:15 hexanes/EtOAc) to obtain the pure product, **4**, (136 mg, 84% yield) as a solid (mp = 59-61 °C). [*Note: In some cases, the reaction forms a slurry. Consistent stirring is imperative for the full conversion of imines to the desired alkylated products].*

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 2H), 4.23 – 4.12 (m, 2H), 3.90 (s, 3H), 1.87 (d, *J* = 12.6 Hz, 1H), 1.80 – 1.61 (m, 4H), 1.59 – 1.48 (m, 1H), 1.31 – 1.00 (m, 5H).

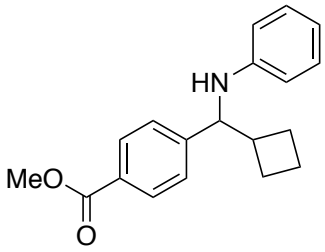
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 148.5, 147.6, 129.8, 129.2, 129.0, 127.4, 117.4, 113.3, 63.5, 52.1, 44.9, 30.3, 29.5, 26.5, 26.5, 26.4.

FT-IR (cm^{-1}, neat, ATR) 3404, 2924, 2851, 1706, 1600, 1502, 1277, 1103, 747, 691.

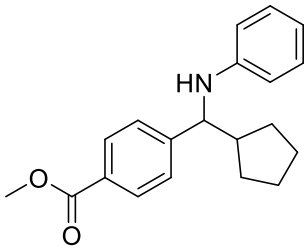
HRMS (EI) calcd for $C_{21}H_{25}NO_2$ $[M]^+$: 323.1885, found: 323.1871.

4. Compound Characterization Data:

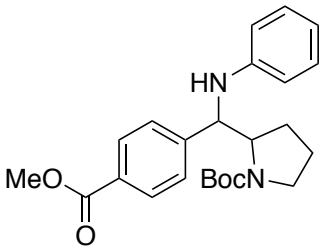
4.1 Alkyltrifluoroborate Scope:



Methyl 4-(Cyclobutyl(phenylamino)methyl)benzoate, 5 (140 mg, 95% yield) was prepared according to the general procedure. The desired amine **5** was isolated as a solid (mp = 100-102 °C) (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 2H), 4.22 (d, *J* = 8.6 Hz, 1H), 4.02 (s, 1H), 3.89 (s, 3H), 2.59 – 2.47 (m, 1H), 2.19 – 2.07 (m, 1H), 1.96 – 1.74 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 148.3, 147.5, 130.0, 129.2, 129.14 126.7, 117.7, 113.5, 63.8, 52.1, 42.4, 26.2, 25.5, 17.7. **FT-IR** (cm^{-1}, neat, ATR) 3361, 1702, 1602, 1313, 1282, 1114, 745, 691. **HRMS** (EI) calcd for $C_{19}H_{21}NO_2$ $[M]^+$: 295.1572, found: 295.1565.

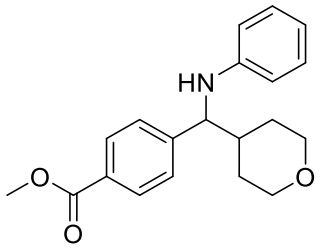


Methyl 4-(Cyclopentyl(phenylamino)methyl)benzoate, 6 (81 mg, 52% yield) was prepared according to the general procedure. The desired amine **6** was isolated as a solid (mp = 103-104 °C) (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 8.4 Hz, 2H), 4.21 (s, 1H), 4.14 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H), 2.22 – 2.10 (m, 1H), 1.94 – 1.84 (m, 1H), 1.71 – 1.55 (m, 3H), 1.53 – 1.38 (m, 3H), 1.33 – 1.24 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 149.7, 147.4, 129.9, 129.2, 129.0, 127.1, 117.5, 113.4, 63.1, 52.1, 47.7, 30.2, 30.0, 25.3, 25.3. **FT-IR** (cm^{-1}, neat, ATR) 3350, 2953, 2870, 1702, 1601, 1283, 1114, 745, 691. **HRMS** (EI) calcd for $C_{20}H_{23}NO_2$ $[M]^+$: 309.1729, found: 309.1725.

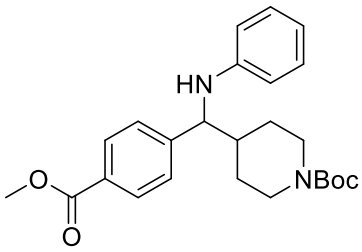


***tert*-Butyl 2-((4-(Methoxycarbonyl)phenyl)(phenylamino)methyl)pyrrolidine-1-carboxylate, 7** (72 mg, 35% yield) was prepared according to the general procedure. The desired amine **7** was isolated as an oil (24 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 2H), 4.27 – 4.15 (m, 2H), 3.90 (s, 3H), 3.51 – 3.03 (m, 2H), 1.86 (d, *J* = 18.0 Hz, 2H), 1.75 – 1.60 (m, 3H), 1.52 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 157.5, 148.3, 148.0, 130.1, 129.6, 129.1, 127.9, 116.7, 112.7, 80.5, 63.7, 62.0, 52.2, 47.1, 28.6, 27.7,

23.7. **FT-IR** (cm^{-1}, neat, ATR) 3380, 2940, 2850, 1721, 1674, 1602, 1392, 1367, 1277, 1160. **HRMS** (ES+) calcd for $C_{24}H_{30}N_2O_4Na$ $[M+Na]^+$: 433.2103, found: 433.2111.

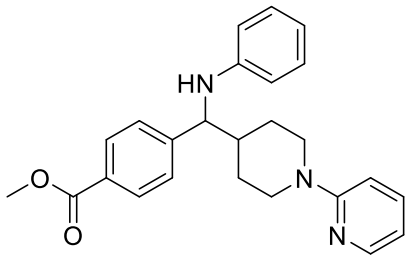


Methyl 4-((Phenylamino)(tetrahydro-2H-pyran-4-yl)methyl)benzoate, 8 (96 mg,59% yield) was prepared according to the general procedure. The desired amine **8** was isolated as an oil (24 g column, 90:10→60:40 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.07 (t, *J* = 7.9 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 2H), 4.23 – 4.06 (m, 2H), 4.02 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.95 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.89 (s, 3H), 3.40 – 3.26 (m, 2H), 1.94 – 1.84 (m, 1H), 1.78 (d, *J* = 13.4 Hz, 1H), 1.54 – 1.42 (m, 2H), 1.32 (d, *J* = 13.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 147.6, 147.2, 130.0, 129.3, 129.3, 127.3, 117.9, 113.5, 68.1, 63.0, 52.2, 42.3, 29.7. **FT-IR** (cm^{-1}, neat, ATR): 3398, 2950, 2844, 1716, 1600, 1277, 1113, 750, 693. **HRMS** (EI) calcd for $C_{20}H_{23}NO_3$ $[M]^+$: 325.1678, found: 325.1674.

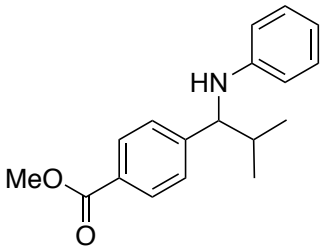


***tert*-Butyl 4-((4-(Methoxycarbonyl)phenyl)(phenylamino)methyl)piperidine-1-carboxylate, 9** (176 mg, 83% yield) was prepared according to the general procedure. The desired amine **9** was isolated as an oil (24 g column, 100:0→80:20 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz,

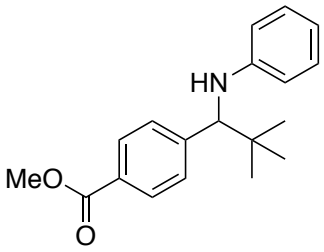
2H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 2H), 4.35 – 3.99 (m, 4H), 3.89 (s, 3H), 2.62 (d, *J* = 12.8 Hz, 2H), 1.95 – 1.71 (m, 2H), 1.52 – 1.37 (m, 10H), 1.35 – 1.19 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 154.81, 147.7, 147.2, 130.0, 129.3, 129.3, 127.3, 117.8, 113.5, 79.7, 62.8, 52.2, 43.9, 43.3, 29.5, 28.9, 28.6. **FT-IR** (cm^{-1}, neat, ATR) 3385, 2949, 2851, 1673, 1427, 1278, 729. **HRMS** (ES+) calcd for $C_{25}H_{33}N_2O_4$ $[M+H]^+$: 425.2440, found: 425.2456.



Methyl 4-((Phenylamino)(1-(pyridin-2-yl)piperidin-4-yl)methyl)benzoate, 10 (139 mg, 69% yield) was prepared according to the general procedure. The desired amine **10** was isolated as a solid (mp = 163-165 °C) (24 g column, 80:20→50:50 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 3.8 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.46 (dd, *J* = 11.3, 4.3 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.65 (t, *J* = 8.7 Hz, 2H), 6.62 – 6.57 (m, 1H), 6.50 (d, *J* = 7.9 Hz, 2H), 4.45 – 4.14 (m, 4H), 3.91 (s, 3H), 2.82 – 2.69 (m, 2H), 2.01 – 1.86 (m, 2H), 1.58 – 1.40 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.8, 159.2, 147.9, 147.6, 147.0, 137.4, 129.8, 129.1, 127.1, 117.5, 113.3, 112.9, 107.1, 62.6, 52.0, 45.5, 45.4, 43.3, 29.1, 28.4. **FT-IR** (cm^{-1}, neat, ATR) 3450, 2950, 2850, 1702, 1593, 1477, 1432, 1283, 773. **HRMS** (EI) calcd for $C_{25}H_{27}N_3O_2$ $[M]^+$: 401.2103, found: 401.2088.

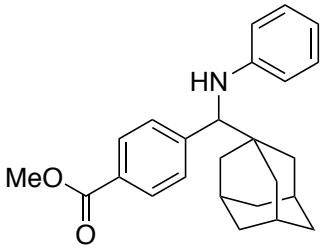


Methyl 4-(2-Methyl-1-(phenylamino)propyl)benzoate, 11 (68 mg, 48% yield) was prepared according to the general procedure. The desired amine **11** was isolated as a solid (mp = 84-86 °C) (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 8.3 Hz, 2H), 4.20 (d, *J* = 5.7 Hz, 1H), 4.15 (s, 1H), 3.91 (s, 3H), 2.14 – 2.02 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 148.2, 147.3, 129.5, 129.0, 128.8, 127.2, 117.3, 113.2, 63.6, 51.9, 34.7, 19.6, 18.4. **FT-IR** (cm^{-1}, neat, ATR) 3367, 2951, 1705, 1602, 1283, 1107, 746, 691. **HRMS** (EI) calcd for $C_{18}H_{21}NO_2$ $[M]^+$: 283.1572, found: 283.1570.

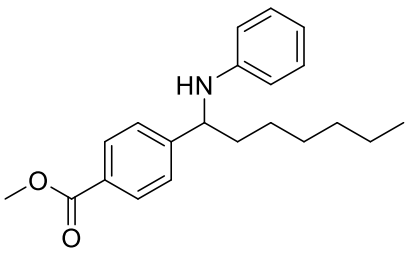


Methyl 4-(2,2-Dimethyl-1-(phenylamino)propyl)benzoate, 12 (122 mg, 82% yield) was prepared according to the general procedure. The desired amine **12** was isolated as an oil (24 g column, 100:0 → 90:10 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.08 – 7.01 (m, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.49 – 6.42 (m, 2H), 4.28 (s, 1H), 4.11 (s, 1H), 3.90 (s, 3H), 1.01 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 147.5, 147.1, 129.2, 129.2, 129.0, 128.7, 117.4, 113.3, 67.3, 52.2, 35.1, 27.2.

FT-IR (cm^{-1}, neat, ATR) 3423, 2955, 1707,1600, 1506, 1315, 1285, 1098, 743. **HRMS** (EI) calcd for $C_{19}H_{23}NO_2$ $[M]^+$: 297.1741, found: 297.1729.

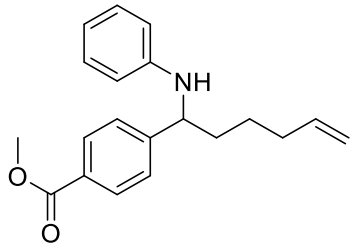


Methyl 4-((Adamantan-1-yl)(phenylamino)methyl)benzoate, 13 (173 mg, 92% yield) was prepared according to the general procedure. The desired amine **13** was isolated as a solid (mp = 92-94 °C) (24 g column, 100:0→90:10 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.05 (t, *J* = 7.9 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 2H), 4.38 (s, 1H), 3.95 (s, 1H), 3.90 (s, 3H), 2.01 (s, 3H), 1.71 (dd, *J* = 11.3, 3.8 Hz, 6H), 1.60 (d, *J* = 11.8 Hz, 3H), 1.52 (d, *J* = 11.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 147.7, 146.3, 129.2, 129.1, 129.0, 128.9, 117.3, 113.3, 68.1, 52.2, 39.4, 37.0, 36.7, 28.6. **FT-IR** (cm^{-1}, neat, ATR) 3361, 2899, 2847, 1703, 1600, 1517, 1430, 1290, 730. **HRMS** (EI) calcd for $C_{25}H_{29}NO_2$ $[M]^+$: 375.2198, found, 375.2207.

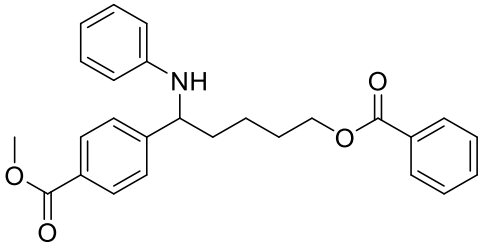


Methyl 4-(1-(Phenylamino)heptyl)benzoate, 14 (104 mg, 64% yield) was prepared according to the general procedure except for using 34W blue Kessil lamp as light source. The desired amine **14** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 2H), 4.34 (t, *J* = 6.6 Hz,

1H), 4.08 (s, 1H), 3.90 (s, 3H), 1.88 – 1.69 (m, 2H), 1.46 – 1.19 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.17, 150.13, 147.31, 130.12, 129.29, 129.04, 126.57, 117.61, 113.39, 58.34, 52.17, 39.01, 31.83, 29.30, 26.37, 22.73, 14.20. **FT-IR** (cm^{-1}, neat, ATR) 3399, 2927, 2855, 1712, 1601, 1503, 14345, 1275, 1112, 747. **HRMS** (ES+) calcd for $C_{21}H_{28}NO_2$ $[M+H]^+$: 326.2120, found: 326.2140.

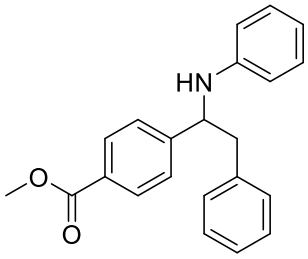


Methyl 4-(1-(Phenylamino)hex-5-en-1-yl)benzoate, 15 (84 mg, 54% yield) was prepared according to the general procedure except for using 34W blue Kessil lamp as light source. The desired amine **15** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.1 Hz, 2H), 6.66 (t, *J* = 6.8 Hz, 1H), 6.49 (d, *J* = 7.5 Hz, 2H), 5.78 (td, *J* = 16.3, 6.7 Hz, 1H), 5.08 – 4.94 (m, 2H), 4.38 (s, 1H), 4.11 (s, 1H), 3.91 (s, 3H), 2.10 (d, *J* = 6.5 Hz, 2H), 1.91 – 1.74 (m, 2H), 1.61 – 1.40 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 149.9, 147.2, 138.2, 130.1, 129.3, 129.1, 126.6, 117.7, 115.3, 113.4, 58.2, 52.2, 38.3, 33.6, 25.6. **FT-IR** (cm^{-1}, neat, ATR) 3400, 2936, 2851, 1600, 1503, 1434, 1275, 1111, 911, 748, 692. **HRMS** (ES+) calcd for $C_{20}H_{24}NO_2$ $[M+H]^+$: 310.1807, found: 310.1797.

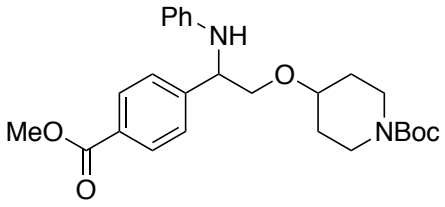


Methyl 4-(5-(Benzoyloxy)-1-(phenylamino)pentyl)benzoate, 16 (125 mg, 60% yield) was prepared according to the general procedure except for using 34W blue Kessil lamp as light source. The desired amine **16** was

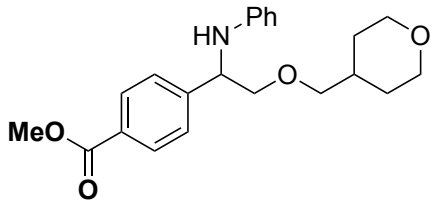
isolated as an oil (24 g column, 100:0→80:20 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 4H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.38 (dd, *J* = 7.6, 5.9 Hz, 4H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 4.40 (t, *J* = 6.5 Hz, 1H), 4.37 – 4.27 (m, 2H), 4.18 (s, 1H), 3.90 (s, 3H), 1.96 – 1.76 (m, 4H), 1.66 – 1.45 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 166.8, 149.7, 147.2, 133.1, 130.4, 130.2, 129.7, 129.3, 129.2, 128.5, 126.6, 117.7, 113.4, 64.6, 58.1, 52.2, 38.3, 28.7, 22.9. **FT-IR** (cm^{-1}, neat, ATR) 3400, 2949, 1713, 1600, 1504, 1313, 1272, 1111, 710. **HRMS** (ES+) Calcd for $C_{26}H_{28}NO_4$ $[M+H]^+$: 418.2018, found: 418.2030.



Methyl 4-(2-Phenyl-1-(phenylamino)ethyl)benzoate, 17 (109 mg, 66% yield) was prepared according to the general procedure. The desired amine **17** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.37– 7.27 (m, 3H), 7.19 – 7.07 (m, 4H), 6.72 (d, *J* = 7.1 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 4.71 (t, *J* = 6.6 Hz, 1H), 4.26 (s, 1H), 3.94 (s, 3H), 3.22 – 3.04 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 149.1, 147.1, 137.3, 130.2, 129.4, 129.3, 128.8, 127.1, 126.8, 118.1, 113.9, 59.4, 52.2, 45.0. **FT-IR** (cm^{-1}, neat, ATR) 3380, 2940, 2863, 1717, 1602, 1504, 1313, 1276, 1098, 1018. **HRMS** (ES+) Calcd for $C_{22}H_{21}NO_2$ $[M+H]^+$: 332.1651, found: 332.1668.

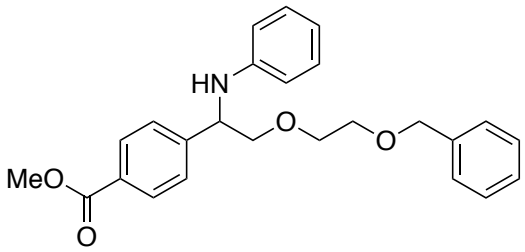


***tert*-Butyl 4-(2-(4-(Methoxycarbonyl)phenyl)-2-(phenylamino)ethoxy)piperidine-1-carboxylate, 18** (165 mg, 73% yield) was prepared according to the general procedure. The desired amine **18** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.14 – 6.96 (m, 2H), 6.83 – 6.59 (m, 1H), 6.55 – 6.36 (m, 2H), 4.71 (s, 1H), 4.53 (dd, *J* = 7.8, 4.1 Hz, 1H), 3.89 (s, 3H), 3.75 (dd, *J* = 9.7, 4.0 Hz, 1H), 3.66 (m, 2H), 3.56 (dd, *J* = 9.7, 7.8 Hz, 1H), 3.48 (tt, *J* = 7.7, 3.6 Hz, 1H), 3.10 (ddq, *J* = 13.4, 5.6, 3.5 Hz, 2H), 1.93 – 1.61 (m, 2H), 1.45 (s, 11H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 154.9, 147.3, 146.4, 130.1, 129.5, 129.2, 127.0, 118.2, 114.1, 79.6, 75.1, 72.1, 67.2, 60.5, 58.5, 52.2, 28.5. **FT-IR** (cm^{-1}, neat, ATR) 3380, 2928, 1686, 1419, 1275, 1101. **HRMS** Calcd for $C_{26}H_{35}N_2O_5$ $[M+1]^+$: 455.2546, found: 455.2563.

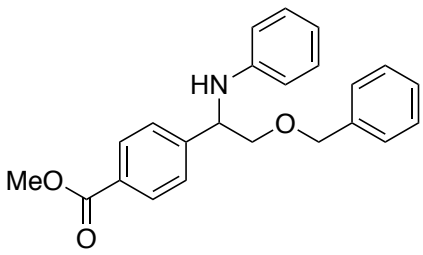


Methyl 4-(1-(Phenylamino)-2-((tetrahydro-2*H*-pyran-4-yl)methoxy)ethyl)benzoate, 19 (135 mg, 73% yield) was prepared according to the general procedure. The desired amine **19** was isolated as an oil (24 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 2H), 4.01 – 3.93 (m, 2H), 3.90 (s, 3H), 3.68 (dd, *J* = 10.0, 4.1 Hz, 1H), 3.54 (dd, *J* = 10.0, 8.1 Hz, 1H), 3.46 – 3.30 (m, 3H), 2.00 – 1.75 (m, 2H), 1.76 – 1.51 (m, 4H), 1.44 – 1.17 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.8, 147.2, 146.2, 129.9, 129.3, 129.0,

126.8, 117.9, 113.8, 76.0, 74.8, 67.5, 57.9, 52.0, 35.3, 29.8, 29.7. **FT-IR** (cm^{-1}, neat, ATR) 2851, 1718, 1279, 1111, 906, 725. **HRMS** Calcd for $C_{22}H_{28}NO_4$ $[M+1]^+$: 370.2018, found: 370.2002.



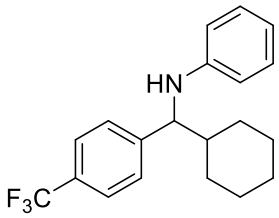
Methyl 4-(2-(2-(Benzyloxy)ethoxy)-1-(phenylamino)ethyl)benzoate, 20 (152 mg, 75% yield) was prepared according to the general procedure. The desired amine **20** was isolated as an oil (24 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 – 7.91 (m, 2H), 7.55 – 7.42 (m, 2H), 7.42 – 7.28 (m, 5H), 7.18 – 6.94 (m, 2H), 6.75 – 6.60 (m, 1H), 6.55 – 6.35 (m, 2H), 4.77 (s, 1H), 4.56 (s, 3H), 3.90 (s, 3H), 3.78 (dd, *J* = 10.1, 4.0 Hz, 1H), 3.74 – 3.68 (m, 1H), 3.67 – 3.57 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 147.5, 146.4, 138.2, 130.1, 129.5, 129.2, 128.6, 127.9, 127.9, 127.0, 118.0, 114.0, 75.3, 73.5, 70.6, 69.5, 58.2, 52.2. **FT-IR** (cm^{-1}, neat, ATR) 3027, 2950, 1717, 1601, 1503, 1277, 1112. **HRMS** (ES+) calcd for $C_{25}H_{28}NO_4$ $[M+H]^+$: 406.2018, found: 406.2038.



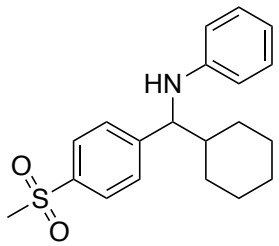
Methyl 4-(2-(Benzyloxy)-1-(phenylamino)ethyl)benzoate, 21 (121 mg, 67% yield) was prepared according to the general procedure. The desired amine **21** was isolated as an oil (24 g column, 100:0 → 85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 – 7.93 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.18 (m, 5H), 7.14 – 6.96 (m, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.56 – 6.40 (m, 2H), 4.67 (s, 1H), 4.63 – 4.48 (m, 3H), 3.91

(s, 3H), 3.77 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.61 (dd, *J* = 9.9, 7.9 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 147.3, 146.4, 137.7, 130.1, 129.5, 129.2, 128.7, 128.1, 127.9, 127.0, 118.1, 114.0, 74.1, 73.2, 58.2, 52.2. **FT-IR** (cm^{-1}, neat, ATR) 3380, 2940, 2850, 1716, 1601, 1503, 1312, 1275, 1099. **HRMS** Calcd for $C_{23}H_{23}NO_3$ $[M]^+$: 361.1678, found: 361.1665.

4.2 Aldehyde Scope:

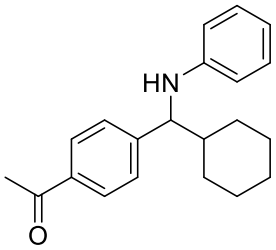


***N*-(Cyclohexyl(4-(trifluoromethyl)phenyl)methyl)aniline, 22** (133 mg, 80% yield) was prepared according to the general procedure. The desired amine **22** was isolated as an oil (24 g column, 100:0 → 85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 4.04 – 4.32 (m, 2H), 1.89 (d, *J* = 12.6 Hz, 1H), 1.85 – 1.67 (m, 4H), 1.58 (d, *J* = 12.8 Hz, 1H), 1.30 – 1.05 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.2, 147.0, 129.1, 129.0 (q, *J* = 32.3 Hz), 127.5, 125.2 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.2 Hz), 117.3, 113.1, 63.1, 44.7, 30.1, 29.2, 26.2, 26.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.23. **FT-IR** (cm^{-1}, neat, ATR) 3425, 2926, 2853, 1502, 1322, 1118, 747. **HRMS** (EI) calcd for $C_{20}H_{22}F_3N$ $[M]^+$: 333.1704, found: 333.1716.

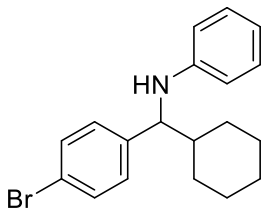


***N*-(Cyclohexyl(4-(methylsulfonyl)phenyl)methyl)aniline, 23** (119 mg, 69% yield) was prepared according to the general procedure. The desired amine **23** was isolated as a solid (mp = 177-179 °C) (24 g column, 80:20→

40:60 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 2H), 4.30 – 4.13 (m, 2H), 3.05 (s, 3H), 1. 62 – 1.90 (m, 5H), 1.53 (d, *J* = 12.3 Hz, 1H), 1.27 – 1.01 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.8, 147.2, 139.2, 129.3, 128.3, 127.6, 117.7, 113.3, 63.3, 44.9, 44.7, 30.3, 29.3, 26.4, 26.4. **FT-IR** (cm^{-1}, neat, ATR) 3368, 2925, 2851, 1600, 1503, 1600, 1147, 748. **HRMS** (EI) calcd for $C_{20}H_{25}NO_2S$ $[M]^+$: 343.1606, found: 343.1619.

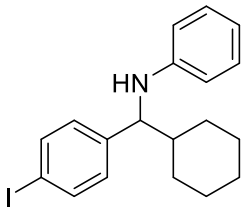


1-(4-(Cyclohexyl(phenylamino)methyl)phenyl)ethan-1-one, 24 (77 mg, 50% yield) was prepared according to the general procedure. The desired amine **24** was isolated as a solid (mp = 93-95 °C) (24 g column, 100:0→ 85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 2H), 6.63 (t, *J* = 7.1 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 2H), 4.14 – 4.24 (m, 2H), 2.59 (s, 3H), 1.88 (d, *J* = 12.3 Hz, 1H), 1.83 – 1.64 (m, 4H), 1.56 (d, *J* = 12.2 Hz, 1H), 1.29 – 1.02 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.7, 148.5, 147.3, 135.9, 129.0, 128.3, 127.4, 117.2, 113.1, 63.2, 44.7, 30.1, 29.2, 26.5, 26.2, 26.2. **FT-IR** (cm^{-1}, neat, ATR) 3388, 2922, 2850, 1667, 1601, 1267, 745. **HRMS** (EI) calcd for $C_{21}H_{25}NO$ $[M]^+$: 307.1936, found: 307.1931.

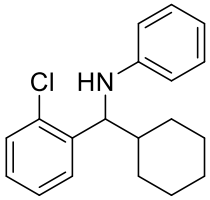


***N*-((4-Bromophenyl)(cyclohexyl)methyl)aniline, 25** (129 mg, 75% yield) was prepared according to the general procedure. The desired amine **25** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 2H), 4.13 (s, 1H), 4.10 (d, *J* = 6.1 Hz, 1H), 1.87 (d, *J* = 12.5 Hz, 1H), 1.83 – 1.71 (m, 2H), 1.71 – 1.60 (m, 2H), 1.56 (d, *J* = 12.9 Hz, 1H), 1.30 – 1.00 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.3, 141.7, 131.2, 129.0, 128.9, 120.4, 117.2, 113.1, 62.8, 44.7, 30.0, 29.3, 26.3, 26.2, 26.2. **FT-IR** (cm^{-1}, neat, ATR) 3425, 2922, 2850, 1599, 1501, 1484, 1317, 1071, 746, 690. **HRMS** (EI) calcd for $C_{19}H_{22}BrN$ $[M]^+$: 343.0936, found: 343.0908.

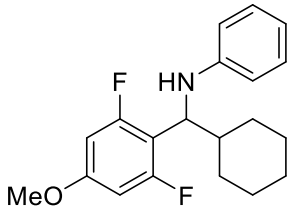


***N*-(Cyclohexyl(4-iodophenyl)methyl)aniline, 26** (125 mg, 64% yield) was prepared according to the general procedure. The desired amine **26** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.12 – 7.03 (m, 4H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 8.4 Hz, 2H), 4.17 – 4.04 (m, 2H), 1.87 (d, *J* = 12.7 Hz, 1H), 1.82 – 1.71 (m, 2H), 1.71 – 1.60 (m, 2H), 1.58 – 1.53 (m, 1H), 1.27 – 1.00 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.3, 142.4, 137.2, 129.2, 129.0, 117.2, 113.1, 91.9, 62.9, 44.7, 30.0, 29.2, 26.3, 26.2, 26.2. **FT-IR** (cm^{-1}, neat, ATR) 3425, 2922, 2850, 1599, 1501, 1480, 1004, 746, 690. **HRMS** (EI) calcd for $C_{19}H_{22}NI$ $[M]^+$: 391.0797, found: 391.0792.

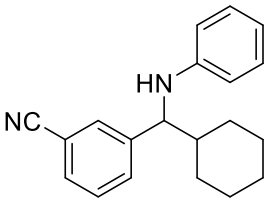


***N*-((2-Chlorophenyl)(cyclohexyl)methyl)aniline, 27** (101 mg, 67% yield) was prepared according to the general procedure. The desired amine **27** was isolated as a solid (mp = 94-96 °C) (24 g column, 100:0→90:10

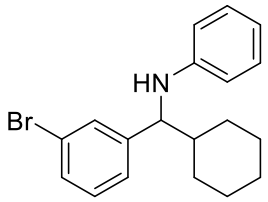
hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 2H), 7.24 – 7.07 (m, 4H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 2H), 4.70 (d, *J* = 6.2 Hz, 1H), 4.23 (s, 1H), 1.95 (d, *J* = 12.2 Hz, 1H), 1. 67 – 1.97 (m, 4H), 1.58 (d, *J* = 12.0 Hz, 1H), 1.37 – 1.11 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.5, 140.4, 133.7, 129.7, 129.3, 128.5, 128.0, 127.0, 117.4, 113.2, 59.5, 43.9, 30.4, 29.0, 26.7, 26.6, 26.6. **FT-IR** (cm^{-1}, neat, ATR) 3399, 2923, 2852, 1598, 1505, 1320, 1032, 746, 690. **HRMS** (ES+) calcd for $C_{19}H_{23}ClN$ $[M+H]^+$: 300.1519, found: 300.1542.



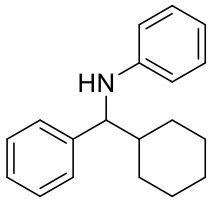
***N*-(Cyclohexyl(2,6-difluoro-4-methoxyphenyl)methyl)aniline, 28** (108 mg, 65% yield) was prepared according to the general procedure. The desired amine **28** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.8 Hz, 2H), 6.67 – 6. 58 (m, 3H), 6.38 (d, *J* = 10.5 Hz, 2H), 4.50 (d, *J* = 9.4 Hz, 1H), 4.15 (s, 1H), 3.72 (s, 3H), 2.24 (d, *J* = 13.1 Hz, 1H), 1.88 – 1.77 (m, 2H), 1.74 – 1.65 (m, 2H), 1.44 (d, *J* = 12.7 Hz, 1H), 1.32 – 1.17 (m, 3H), 1.12 – 0.97 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0 (dd, *J* = 243.9, 12.7 Hz), 159.7 (t, *J* = 14.6 Hz), 147.8, 129.4, 117.4, 113.1, 110.5 (t, *J* = 18.4 Hz), 98.2 (d, *J* = 30.4 Hz), 55.8, 54.0, 42.7, 31.2, 30.3, 26.6, 26.2, 26.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.96. **FT-IR** (cm^{-1}, neat, ATR) 3412, 2924, 2850, 1635, 1496, 1137, 747. **HRMS** (EI) calcd for $C_{20}H_{23}F_2NO$ $[M]^+$: 331.1748, found: 331.1736.



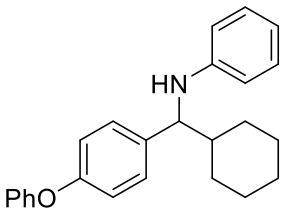
3-(Cyclohexyl(phenylamino)methyl)benzonitrile, 29 (64 mg, 44% yield) was prepared according to the general procedure. The desired amine **29** was isolated as a solid (mp = 135-137 °C) (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.54 (dd, *J* = 17.2, 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 2H), 4.16 (d, *J* = 6.1 Hz, 2H), 1.88 – 1.74 (m, 3H), 1.72 – 1.62 (m, 2H), 1.54 (d, *J* = 12.6 Hz, 1H), 1.30 – 1.01 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.9, 144.4, 131.7, 130.8, 130.6, 129.1, 129.0, 119.0, 117.5, 113.1, 112.3, 62.9, 44.7, 30.0, 29.1, 26.2, 26.1, 26.1. **FT-IR** (cm^{-1}, neat, ATR) 2925, 2852, 2228, 1601, 1503, 1317, 907, 730, 692. **HRMS** (EI) calcd for $C_{20}H_{22}N_2$ $[M]^+$: 290.1783, found: 290.1788.



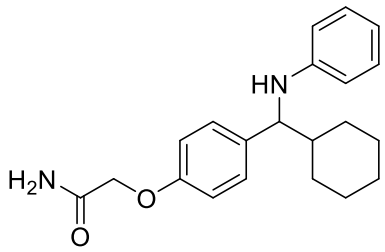
***N*-((3-Bromophenyl)(cyclohexyl)methyl)aniline, 30** (93 mg, 54% yield) was prepared according to the general procedure. The desired amine **30** was isolated as an oil (24 g column, 100:0→90:10 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.29 – 7.21 (m, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 7.7 Hz, 2H), 4.27 – 3.94 (m, 2H), 1.88 (d, *J* = 11.8 Hz, 1H), 1.83 – 1.71 (m, 2H), 1.71 – 1.59 (m, 2H), 1.55 (d, *J* = 12.3 Hz, 1H), 1.28 – 1.01 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.3, 145.4, 130.1, 129.9, 129.7, 129.0, 125.9, 122.5, 117.2, 113.1, 63.0, 44.8, 30.1, 29.2, 26.3, 26.2, 26.2. FT-**IR** (cm^{-1}, neat, ATR) 3420, 2922, 2850, 1600, 1501, 1616, 1252, 747, 690. **HRMS** (ES+) calcd for $C_{19}H_{23}NBr$ $[M+H]^+$: 344.1014, found: 344.0996.



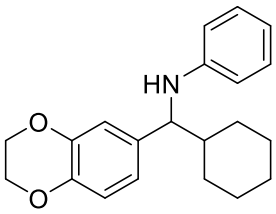
***N*-(Cyclohexyl(phenyl)methyl)aniline, 31** (122 mg, 92% yield) was prepared according to the general procedure. The desired amine **31** was isolated as an oil (24 g column, 100:0→90:10 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.28 – 7.23 (m, 1H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 2H), 4.26 – 4.04 (m, 2H), 1.93 (d, *J* = 12.2 Hz, 1H), 1.84 – 1.64 (m, 4H), 1.58 (d, *J* = 12.5 Hz, 1H), 1.30 – 1.05 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.7, 142.6, 129.0, 128.1, 127.2, 126.7, 116.8, 113.1, 63.3, 44.8, 30.2, 29.4, 26.4, 26.3, 26.3. **FT-IR** (cm^{-1}, neat, ATR) 3425, 2922, 2850, 1599, 1501, 1317, 745, 700, 690. **HRMS** (ES+) calcd for $C_{19}H_{24}N$ $[M+H]^+$: 266.1909, found, 266.1913.



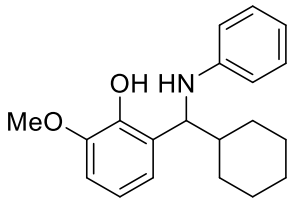
***N*-(Cyclohexyl(4-phenoxyphenyl)methyl)aniline, 32** (93 mg, 52% yield) was prepared according to the general procedure. The desired amine **32** was isolated as an oil (24 g column, 100:0→90:10 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 3H), 7.04 (d, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 2H), 4.29 – 4.08 (m, 2H), 1.94 (d, *J* = 12.4 Hz, 1H), 1.85 – 1.75 (m, 2H), 1.71 (d, *J* = 12.1 Hz, 2H), 1.59 (d, *J* = 12.6 Hz, 1H), 1.33 – 1.04 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.2, 155.9, 147.7, 137.4, 129.6, 129.0, 128.4, 123.1, 118.8, 118.5, 116.9, 113.1, 62.8, 44.9, 30.1, 29.5, 26.4, 26.3, 26.3. **FT-IR** (cm^{-1}, neat, ATR) 3423, 2922, 2850, 1600, 1501, 1487, 745, 689. **HRMS** (EI) calcd for $C_{25}H_{27}NO$ $[M]^+$: 357.2093, found: 357.2093.



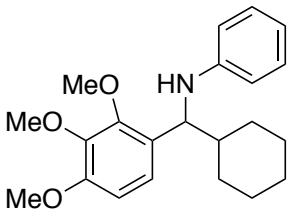
2-(4-(Cyclohexyl(phenylamino)methyl)phenoxy)acetamide, 33 (105 mg, 62% yield) was prepared according to the general procedure. The desired amine **33** was isolated as a solid (mp = 104-106 °C) (24 g column, 80:20 →30:70 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.56 (s, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 4.48 (s, 2H), 4.16 (s, 1H), 4.09 (d, *J* = 6.2 Hz, 1H), 1.89 (d, *J* = 12.6 Hz, 1H), 1.82 – 1.71 (m, 2H), 1.70 – 1.59 (m, 2H), 1.54 (d, *J* = 12.7 Hz, 1H), 1.28 – 1.00 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.1, 155.9, 147.6, 136.3, 129.0, 128.4, 116.9, 114.3, 113.1, 67.1, 62.6, 44.9, 30.0, 29.4, 26.3, 26.3, 26.2. **FT-IR** (cm^{-1}, neat, ATR) 3440, 3180, 2932, 2852, 1683, 1598, 1506, 1238, 752. **HRMS** (EI) calcd for $C_{21}H_{26}N_2O_2$ $[M]^+$: 338.1994, found: 338.2002.



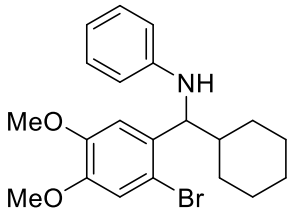
***N*-(Cyclohexyl(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)methyl)aniline, 34** (113 mg, 70% yield) was prepared according to the general procedure. The desired amine **34** was isolated as a solid (mp = 127-128 °C) (24 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.7 Hz, 2H), 6.74 – 6.82 (m, 3H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 2H), 4.23 (s, 4H), 4.09 – 4.17 (br s, 1H), 4.01 (d, *J* = 6.3 Hz, 1H), 1.91 (d, *J* = 12.6 Hz, 1H), 1.81 – 1.69 (m, 2H), 1.69 – 1.52 (m, 3H), 1.28 – 0.98 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.9, 143.4, 142.4, 136.2, 129.2, 120.4, 117.0, 117.0, 116.0, 113.4, 64.5, 64.4, 63.0, 45.0, 30.3, 29.8, 26.6, 26.5, 26.5. **FT-IR** (cm^{-1}, neat, ATR) 3435, 2931, 2848, 1603, 1504, 1286, 1065, 749. **HRMS** (EI) calcd for $C_{21}H_{25}NO_2$ $[M]^+$: 323.1885, found: 323.1895.



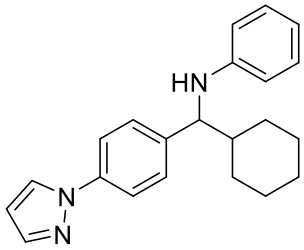
2-(Cyclohexyl(phenylamino)methyl)-6-methoxyphenol, 35 (120 mg, 77% yield) was prepared according to the general procedure. The desired amine **35** was isolated as an oil (24 g column, 100:0 → 60:40 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.7 Hz, 2H), 6.88 – 6.80 (m, 2H), 6.80 – 6.74 (m, 1H), 6.74 – 6.64 (m, 3H), 4.95 – 4.05 (m, 2H), 3.88 (s, 3H), 2.09 (d, *J* = 17.0 Hz, 1H), 1.92 – 1.80 (m, 2H), 1.66 – 1.80 (m, 2H), 1.60 (d, *J* = 12.1 Hz, 1H), 1.35 – 1.10 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.8, 146.7, 144.1, 129.0, 127.6, 120.7, 119.1, 117.7, 113.9, 109.1, 60.2, 55.78, 43.4, 30.1, 29.9, 26.4, 26.3. **FT-IR** (cm^{-1}, neat, ATR) 3625, 3412, 2922, 2849, 1601, 1476, 1248, 1074, 746, 691. **HRMS** (ES+) calcd for $C_{20}H_{26}NO_2$ $[M+H]^+$: 312.1964, found: 312.1986.



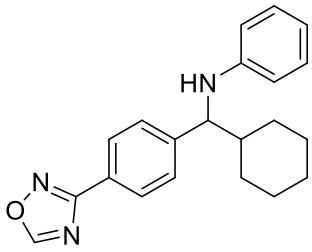
***N*-(Cyclohexyl(2,3,4-trimethoxyphenyl)methyl)aniline, 36** (93 mg, 52% yield) was prepared according to the general procedure. The desired amine **36** was isolated as an oil (24 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.63 – 6.55 (m, 4H), 4.39 (d, *J* = 7.5 Hz, 1H), 4.17 (s, 1H), 4.00 (s, 3H), 3.88 (s, 3H), 3.83 (s, 3H), 2.04 (d, *J* = 12.8 Hz, 1H), 1.80 (d, *J* = 11.3 Hz, 1H), 1.76 – 1.65 (m, 3H), 1.49 (d, *J* = 12.7 Hz, 1H), 1.32 – 1.01 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.3, 151.7, 148.0, 141.9, 129.0, 128.2, 122.2, 116.6, 113.0, 106.8, 60.7, 60.5, 58.2, 55.8, 44.0, 30.7, 29.8, 26.5, 26.4, 26.3. **FT-IR** (cm^{-1}, neat, ATR) 3400, 2924, 2849, 1600, 1492, 1278, 1092, 746, 691. **HRMS** (EI) calcd for $C_{22}H_{29}NO_3$ $[M]^+$: 355.2147, found: 355.2143.



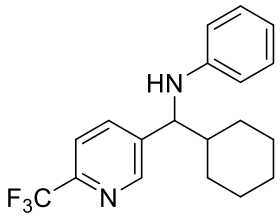
***N*-((2-Bromo-4,5-dimethoxyphenyl)(cyclohexyl)methyl)aniline, 37** (176 mg, 87% yield) was prepared according to the general procedure. The desired amine **37** was isolated as an oil (24 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.8 Hz, 2H), 7.00 (s, 1H), 6.81 (s, 1H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 4.48 (d, *J* = 6.2 Hz, 1H), 4.15 (s, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 1.91 (d, *J* = 12.4 Hz, 1H), 1.82 – 1.62 (m, 4H), 1.53 (d, *J* = 15.5 Hz, 1H), 1.31 – 1.09 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.8, 148.4, 147.6, 133.9, 129.3, 117.4, 115.5, 113.9, 113.4, 111.1, 61.8, 56.2, 56.1, 44.3, 30.3, 29.0, 26.7, 26.5. **FT-IR** (cm^{-1}, neat, ATR) 3404, 2925, 2850, 1600, 1499, 1436, 1317, 1249, 1154, 730. **HRMS** (ES+) calcd for $C_{21}H_{27}BrNO_2$ $[M+H]^+$: 404.1225, found: 404.1244.



***N*-((4-(1H-Pyrazol-1-yl)phenyl)(cyclohexyl)methyl)aniline, 38** (146 mg, 88% yield) was prepared according to the general procedure. The desired amine **38** was isolated as an oil (24 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.4 Hz, 1H), 7.72 (d, *J* = 1.4 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.09 (t, *J* = 7.9 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 2H), 6.47 – 6.42 (m, 1H), 4.18 (d, *J* = 6.1 Hz, 2H), 1.91 (d, *J* = 12.6 Hz, 1H), 1.83 – 1.64 (m, 4H), 1.60 (d, *J* = 12.8 Hz, 1H), 1.29 – 1.03 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.7, 141.2, 141.1, 139.2, 129.2, 128.4, 126.8, 119.4, 117.4, 113.5, 107.6, 63.2, 45.1, 30.3, 29.6, 26.6, 26.5, 26.5. **FT-IR** (cm^{-1}, neat, ATR) 3406, 2923, 2850, 1600, 1522, 1501, 1393, 746, 691. **HRMS** (EI) calcd for $C_{22}H_{25}N_3$ $[M]^+$: 331.2048, found: 331.2046.

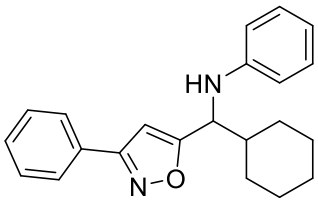


***N*-((4-(1,2,4-Oxadiazol-3-yl)phenyl)(cyclohexyl)methyl)aniline, 39** (123 mg, 74% yield) was prepared according to the general procedure. The desired amine **39** was isolated as a solid (mp = 119-121 °C) (24 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 7.7 Hz, 2H), 4.35 – 4.05 (m, 2H), 1.90 (d, *J* = 12.4 Hz, 1H), 1.83 – 1.63 (m, 4H), 1.58 (d, *J* = 12.4 Hz, 1H), 1.28 – 1.04 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.8, 164.7, 147.6, 146.8, 129.3, 128.0, 127.7, 125.0, 117.5, 113.4, 63.5, 45.0, 30.3, 29.5, 26.5, 26.5, 26.4. **FT-IR** (cm^{-1}, neat, ATR) 3340, 2929, 2850, 1599, 1497, 1333, 1273, 1119, 751, 695. **HRMS** (EI) calcd for $C_{21}H_{23}N_3O$ $[M]^+$: 333.1841, found: 333.1844.

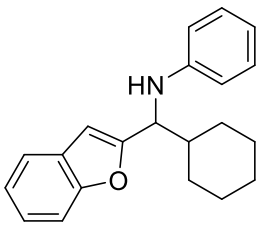


***N*-(Cyclohexyl(6-(trifluoromethyl)pyridin-3-yl)methyl)aniline, 40** (126 mg, 75% yield) was prepared according to the general procedure. The desired amine **40** was isolated as a solid (mp = 131-133 °C) (24 g column, 100:0→80:20 hexanes/EtOAc). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 7.80 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.68 (s, 1H), 6.46 (s, 2H), 4.26 (d, *J* = 5.9 Hz, 1H), 4.13 (s, 1H), 1.89 – 1.65 (m, 5H), 1.58 (d, *J* = 12.3 Hz, 1H), 1.27 – 1.03 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.7, 147.0 (q, *J* = 34.6 Hz), 146.8, 141.9, 136.1, 129.4, 121.8 (q, *J* = 273.9 Hz), 120.3 (d, *J* = 2.4 Hz), 118.1, 113.4, 61.2, 44.8, 30.1, 29.3, 26.3, 26.3, 26.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -67.63. **FT-IR** (cm^{-1}, neat, ATR) 3320,

2938, 2849, 1601, 1496, 1334, 1180, 1081, 747. **HRMS** (ES+) calcd for $C_{19}H_{22}F_3N_2$ $[M+H]^+$: 335.1735, found: 335.1745.

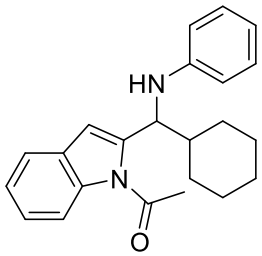


***N*-(Cyclohexyl(3-phenylisoxazol-5-yl)methyl)aniline, 41** (133 mg, 80% yield) was prepared according to the general procedure. The desired amine **41** was isolated as a solid (mp = 127-128 °C) (24 g column, 100:0→80:20 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.17 (dd, *J* = 8.2, 7.6 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 2H), 6.42 (s, 1H), 4.50 (d, *J* = 6.0 Hz, 1H), 3.90 – 4.24 (brs, 1H), 2.02 – 1.88 (m, 2H), 1.75 – 1.85 (m, 2H), 1.70 (t, *J* = 10.0 Hz, 2H), 1.36 – 1.12 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.4, 162.3, 147.0, 130.07, 129.5, 129.3, 129.0, 127.0, 118.4, 113.5, 100.2, 56.8, 42.8, 29.7, 29.4, 26.4, 26.3, 26.2. **FT-IR** (cm^{-1}, neat, ATR) 3329, 2925, 2853, 1598, 1497, 1324, 765, 688. **HRMS** (EI) calcd for $C_{22}H_{24}N_2O$ $[M]^+$: 332.1889, found: 332.1885.

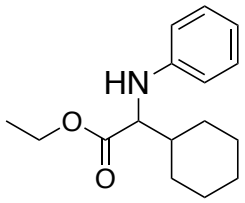


***N*-(Benzofuran-2-yl(cyclohexyl)methyl)aniline, 42** (86 mg, 56% yield) was prepared according to the general procedure. The desired amine **42** was isolated as a solid (mp = 109-111 °C) (24 g column, 100:0→90:10 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 11.9, 7.9 Hz, 2H), 7.29 – 7.11 (m, 4H), 6.73 – 6.63 (m, 3H), 6.55 (s, 1H), 4.41 (d, *J* = 6.2 Hz, 1H), 4.09 (s, 1H), 2.02 – 1.93 (m, 2H), 1.85 – 1.62 (m, 4H), 1.35 – 1.14 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.3, 154.6, 147.3, 129.1, 128.3, 123.4, 122.5, 120.6, 117.6,

113.3, 111.0, 103.7, 57.5, 42.4, 29.8, 29.4, 26.3, 26.1, 26.1. **FT-IR** (cm^{-1}, neat, ATR) 3395, 2928, 2852, 1598, 1501, 1454, 1248, 750, 692. **HRMS** (EI) calcd for $C_{21}H_{23}NO$ $[M]^+$: 305.1780, found: 305.1769.



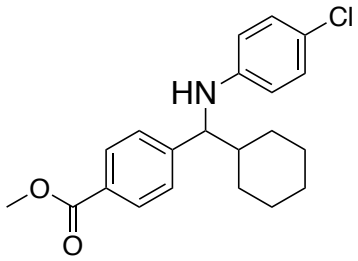
1-(2-(Cyclohexyl(phenylamino)methyl)-1H-indol-1-yl)ethan-1-one, 43 (49 mg, 28% yield) was prepared according to the general procedure. The desired amine **43** was isolated as an oil (24 g column, 100:0→80:20 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.23 (m, 3H), 7.10 (t, *J* = 7.7 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 2H), 4.48 (d, *J* = 5.3 Hz, 1H), 4.09 (s, 1H), 2.58 (s, 3H), 1.95 (d, *J* = 12.0 Hz, 2H), 1.85 – 1.66 (m, 4H), 1.31 – 1.11 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.4, 147.7, 136.3, 129.5, 129.07, 125.1, 123.8, 123.4, 122.8, 119.3, 117.4, 116.8, 113.1, 56.2, 43.5, 30.4, 29.2, 26.3, 24.0. **FT-IR** (cm^{-1}, neat, ATR) 3398, 2924, 2851, 1694, 1600, 1448, 1328, 1218, 746, 730. **HRMS** (EI) calcd for $C_{23}H_{26}N_2O$ $[M]^+$: 346.2045, found: 346.2048.



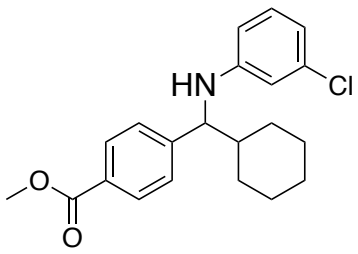
Ethyl 2-Cyclohexyl-2-(phenylamino)acetate, 44 (101 mg, 77 % yield) was prepared according to the general procedure. The desired amine **44** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.06 (m, 2H), 6.72 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.66 – 6.56 (m, 2H), 4.24 – 4.05 (m, 3H), 3.86 (d, *J* = 6.1 Hz, 1H), 1.98 – 1.81 (m, 1H), 1.83 – 1.72 (m, 3H), 1.72 – 1.60 (m, 2H), 1.37 – 1.00 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.8, 147.6, 129.4, 118.2, 113.6, 62.2, 60.9, 41.5, 29.8, 29.3, 26.3, 26.3,

26.2, 14.5. **FT-IR** (cm^{-1}, neat, ATR) 2980, 2926, 2853, 1728, 1602, 1505, 1256, 1178, 1146. **HRMS** (ES+) calcd for $C_{16}H_{24}NO_2$ $[M+H]^+$: 262.1807, found: 262.1804.

4.3 Amine Scope:

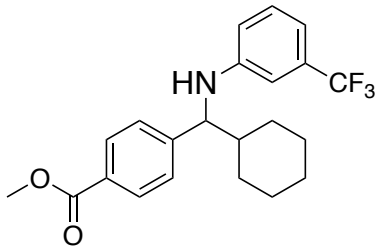


Methyl 4-(((4-Chlorophenyl)amino)(cyclohexyl)methyl)benzoate, 45 (77 mg, 43% yield) was prepared according to the general procedure. The desired amine **45** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.37 (d, *J* = 8.9 Hz, 2H), 4.22 (s, 1H), 4.12 (d, *J* = 6.1 Hz, 1H), 3.89 (s, 3H), 1.84 (d, *J* = 12.4 Hz, 1H), 1.81 – 1.56 (m, 4H), 1.58 – 1.38 (m, 1H), 1.28 – 0.87 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 147.9, 146.0, 129.8, 129.1, 129.0, 127.4, 122.0, 114.4, 63.6, 52.2, 44.8, 30.2, 29.5, 26.4, 26.4, 26.4. **FT-IR** (cm^{-1}, neat, ATR) 3406, 2927, 2853, 1710, 1599, 1498, 1312,1281. **HRMS** (ES+) calcd for $C_{21}H_{25}ClNO_2$ $[M+H]^+$: 358.1574, found: 358.1583.

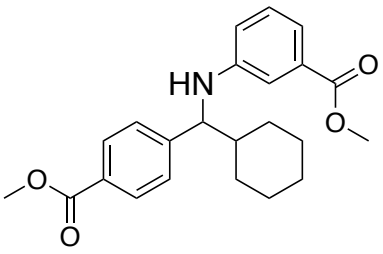


Methyl 4-(((3-Chlorophenyl)amino)(cyclohexyl)methyl)benzoate, 46 (118 mg, 66% yield) was prepared according to the general procedure. The desired amine **46** was isolated as an oil (24 g column, 100:0→85:15

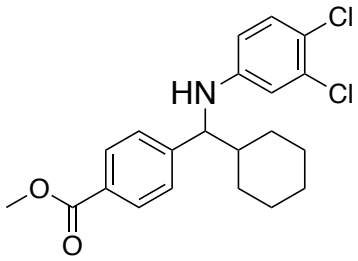
hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 – 7.83 (m, 2H), 7.49 – 7.29 (m, 2H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.57 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 6.45 (t, *J* = 2.1 Hz, 1H), 6.32 (ddd, *J* = 8.3, 2.3, 1.0 Hz, 1H), 4.27 (s, 1H), 4.14 (d, *J* = 6.1 Hz, 1H), 3.90 (s, 3H), 1.84 (d, *J* = 13.0 Hz, 1H), 1.80 – 1.57 (m, 4H), 1.51 (dd, *J* = 12.8, 3.4 Hz, 1H), 1.34 – 0.81 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 148.6, 147.7, 134.9, 130.2, 129.8, 129.2, 127.3, 117.3, 113.1, 111.5, 67.2, 63.3, 52.2, 44.8, 30.3, 29.4, 26.4, 26.37. **FT-IR** (cm^{-1}, neat, ATR) 2927, 1710, 1596, 1576, 1499, 1484, 1278, 1114, 907, 730. **HRMS** (ES+) calcd for $C_{21}H_{24}ClNO_2$ $[M+H]^+$: 358.1574, found: 358.1574.



Methyl 4-(Cyclohexyl((3-(trifluoromethyl)phenyl)amino)methyl)benzoate, 47 (125 mg, 64% yield) was prepared according to the general procedure. The desired amine **47** was isolated as an oil (24 g column, 100:0→ 85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 – 7.76 (m, 2H), 7.56 – 7.29 (m, 2H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.72 (t, *J* = 2.0 Hz, 1H), 6.55 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.38 (s, 1H), 4.18 (d, *J* = 6.2 Hz, 1H), 3.90 (s, 3H), 2.06 – 1.79 (m, 1H), 1.81 – 1.61 (m, 4H), 1.53 – 1.42 (m, 1H), 1.36 – 0.71 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 147.6, 147.5, 131.5 (q, *J* = 31.8 Hz), 129.9, 129.7, 129.2, 127.3, 124.3 (q, *J* = 272.4 Hz), 115.9, 113.8 (q, *J* = 3.7 Hz), 109.9 (q, *J* = 4.0 Hz), 63.4, 52.2, 44.8, 30.3, 29.6, 26.4, 26.4, 26.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.96. **FT-IR** (cm^{-1}, neat, ATR) 2929, 2854, 1709, 1612, 1436, 1341, 1313, 1280, 1162, 1116. **HRMS** (ES+) calcd for $C_{22}H_{25}F_3NO_2$ $[M+H]^+$: 392.1837, found: 392.1847.

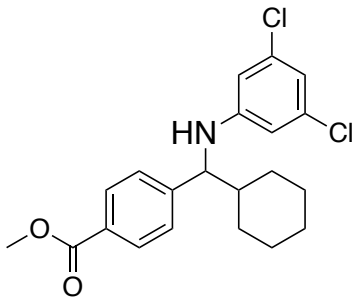


Methyl 3-((Cyclohexyl(4-(methoxycarbonyl)phenyl)methyl)amino)benzoate, 48 (123 mg, 68% yield) was prepared according to the general procedure. The desired amine **48** was isolated as an oil (24 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.21 (t, *J* = 2.0 Hz, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.59 (dd, *J* = 8.1, 2.5 Hz, 1H), 4.34 (s, 1H), 4.21 (d, *J* = 6.1 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 1.87 (d, *J* = 12.3 Hz, 1H), 1.79 – 1.58 (m, 4H), 1.51 (d, *J* = 12.9 Hz, 1H), 1.35 – 0.96 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.5, 167.1, 147.9, 147.5, 131.0, 129.8, 129.2, 129.1, 127.3, 118.5, 117.3, 114.4, 63.3, 52.1, 52.1, 44.8, 30.3, 29.5, 26.4, 26.4, 26.3. **FT-IR** (cm^{-1}, neat, ATR) 2928, 2853, 1717, 1605, 1436, 1330, 1278, 1108. **HRMS** (ES+) calcd for $C_{23}H_{28}NO_4$ $[M+H]^+$: 382.2018, found: 382.2037.

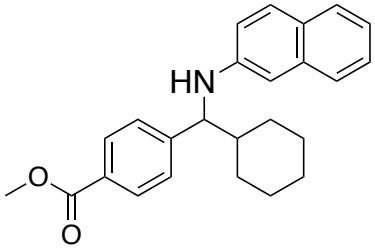


Methyl 4-(Cyclohexyl((3,4-dichlorophenyl)amino)methyl)benzoate, 49 (133 mg, 68% yield) was prepared according to the general procedure. The desired amine **49** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 – 7.83 (m, 2H), 7.38 – 7.29 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.53 (d, *J* = 2.7 Hz, 1H), 6.28 (dd, *J* = 8.7, 2.8 Hz, 1H), 4.30 (s, 1H), 4.10 (d, *J* = 6.2 Hz, 1H), 3.90 (s, 3H), 1.83 (d, *J* = 12.9 Hz, 1H), 1.79 – 1.58 (m, 4H), 1.50 (d, *J* = 13.0 Hz, 1H), 1.31 – 0.88 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 147.2, 146.9, 132.7, 130.6, 129.9, 129.3, 127.2, 119.9, 114.5, 112.8, 63.4, 52.2, 44.7,

30.2, 29.5, 26.4, 26.3, 26.3. **FT-IR** (cm^{-1}, neat, ATR) 2929, 2853, 1708, 1597, 1490, 1282. **HRMS** (ES+) calcd for $C_{21}H_{24}Cl_2NO_2$ $[M+H]^+$: 392.1184, found: 392.1194.

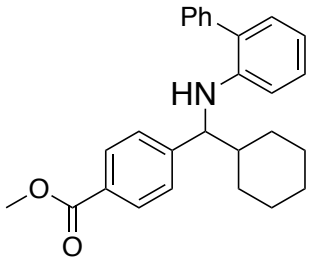


Methyl 4-(Cyclohexyl((3,5-dichlorophenyl)amino)methyl)benzoate, 50 (110 mg, 56% yield) was prepared according to the general procedure. The desired amine **50** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.58 (t, *J* = 1.7 Hz, 1H), 6.32 (d, *J* = 1.9 Hz, 2H), 4.32 (s, 1H), 4.11 (d, *J* = 6.3 Hz, 1H), 3.90 (d, *J* = 1.3 Hz, 3H), 1.91 – 1.59 (m, 5H), 1.48 (d, *J* = 13.1 Hz, 1H), 1.32 – 0.75 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 149.1, 147.0, 135.4, 129.9, 129.3, 127.2, 117.2, 111.5, 63.2, 52.2, 44.7, 30.2, 29.4, 26.3, 26.3, 26.3. **FT-IR** (cm^{-1}, neat, ATR) 2927, 2853, 1706, 1589, 1572, 1451, 1436, 1280, 1112. **HRMS** (ES+) calcd for $C_{21}H_{24}Cl_2NO_2$ $[M+H]^+$: 392.1184, found: 392.1176.

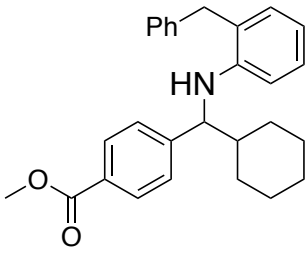


Methyl 4-(Cyclohexyl(naphthalen-2-ylamino)methyl)benzoate, 51 (77 mg, 41% yield) was prepared according to the general procedure. The desired amine **51** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.53 (m, 2H), 7.51 – 7.34 (m,

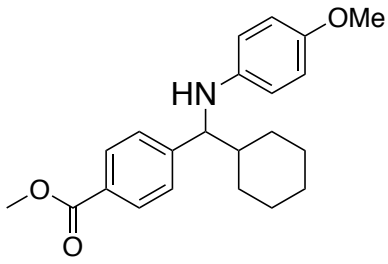
3H), 7.34 – 7.18 (m, 1H), 7.13 (ddd, *J* = 7.9, 6.7, 1.2 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 4.34 (s, 1H), 4.32 (d, *J* = 6.2 Hz, 1H), 3.88 (s, 3H), 1.89 (d, *J* = 12.8 Hz, 1H), 1.85 – 1.62 (m, 4H), 1.63 – 1.55 (m, 1H), 1.33 – 0.96 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 148.2, 145.0, 135.1, 129.8, 129.0, 129.0, 127.6, 127.5, 127.4, 126.3, 126.0, 122.1, 118.0, 105.6, 63.5, 52.1, 44.9, 30.3, 29.5, 26.5, 26.5, 26.4. **FT-IR** (cm^{-1}, neat, ATR) 2925, 2852, 1710, 1629, 1520, 1278, 1113, 827, 732. **HRMS** (ES+) calcd for $C_{25}H_{28}NO_2$ $[M+H]^+$: 374.2120, found: 374.2119.



Methyl 4-(([1,1'-Biphenyl]-2-ylamino)(cyclohexyl)methyl)benzoate, 52 (80 mg, 40% yield) was prepared according to the general procedure. The desired amine **52** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 – 7.81 (m, 2H), 7.58 – 7.48 (m, 4H), 7.41 (tt, *J* = 6.5, 1.8 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.08 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.02 (td, *J* = 7.8, 1.7 Hz, 1H), 6.69 (td, *J* = 7.4, 1.1 Hz, 1H), 6.33 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.46 (s, 1H), 4.19 (d, *J* = 5.8 Hz, 1H), 3.90 (s, 3H), 1.71 – 1.50 (m, 5H), 1.50 – 1.38 (m, 1H), 1.20 – 0.65 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 148.5, 144.2, 139.6, 130.1, 129.7, 129.6, 129.1, 129.0, 128.6, 127.9, 127.5, 127.3, 117.0, 111.4, 63.5, 52.1, 44.9, 30.5, 29.0, 26.5, 26.4, 26.4. **FT-IR** (cm^{-1}, neat, ATR) 2925, 2852, 1720, 1508, 1489, 1435, 1277, 1105. **HRMS** (ES+) calcd for $C_{27}H_{30}NO_2$ $[M+H]^+$: 400.2277, found: 400.2277.



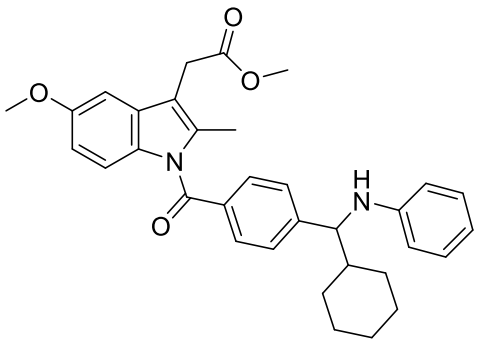
Methyl 4-(((2-Benzylphenyl)amino)(cyclohexyl)methyl)benzoate, 53 (114 mg, 55% yield) was prepared according to the general procedure. The desired amine **53** was isolated as an oil (24 g column, 100:0→85:15 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 – 7.77 (m, 2H), 7.35 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.32 – 7.21 (m, 3H), 7.13 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.96 (td, *J* = 7.8, 1.6 Hz, 1H), 6.64 (td, *J* = 7.3, 1.1 Hz, 1H), 6.21 (d, *J* = 8.1 Hz, 1H), 4.08 (d, *J* = 5.1 Hz, 1H), 4.00 (s, 3H), 3.88 (s, 3H), 1.60 (dd, *J* = 20.7, 9.4 Hz, 3H), 1.41 (dddd, *J* = 15.3, 12.5, 6.5, 3.3 Hz, 2H), 1.29 (d, *J* = 13.6 Hz, 1H), 1.16 – 0.91 (m, 3H), 0.82 – 0.61 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 148.4, 145.2, 139.8, 131.1, 129.6, 129.0, 128.7, 128.7, 127.9, 127.2, 126.9, 124.5, 116.8, 111.4, 62.6, 52.1, 44.9, 39.4, 30.2, 28.5, 26.5, 26.4, 26.3. **FT-IR** (cm^{-1}, neat, ATR) 2925, 2852, 1718, 1605, 1510, 1450, 1435, 1277, 1113, 1103. **HRMS** (ES+) calcd for $C_{28}H_{32}NO_2$ $[M+H]^+$: 414.2433, found: 414.2450.



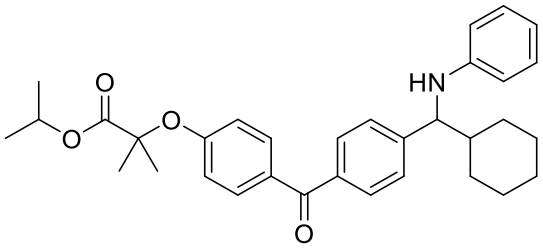
Methyl 4-(Cyclohexyl((4-methoxyphenyl)amino)methyl)benzoate, 54 (88 mg, 50% yield) was prepared according to the general procedure with 2 equivalents of $NaHSO_4$. The desired amine **54** was isolated as an oil (24 g column, 100:0→80:20 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.41 (d, *J* = 8.5 Hz, 2H), 4.10 (d, *J* = 6.0 Hz, 1H), 3.91 (s, 1H), 3.89

(s, 3H), 3.67 (s, 3H), 1.86 (d, *J* = 12.8 Hz, 1H), 1.78 – 1.61 (m, 4H), 1.53 (d, *J* = 13.1 Hz, 1H), 1.25 – 0.99 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 152.0, 148.8, 141.8, 129.7, 128.9, 127.5, 114.9, 114.5, 64.3, 55.9, 52.1, 45.0, 30.3, 29.5, 26.5, 26.5, 26.4. **FT-IR** (cm^{-1}, neat, ATR) 2925, 2852, 1713, 1509, 1277, 1234, 1178, 1106, 818. **HRMS** (ES+) calcd for $C_{22}H_{28}NO_3$ $[M+H]^+$: 354.2069, found: 354.2055.

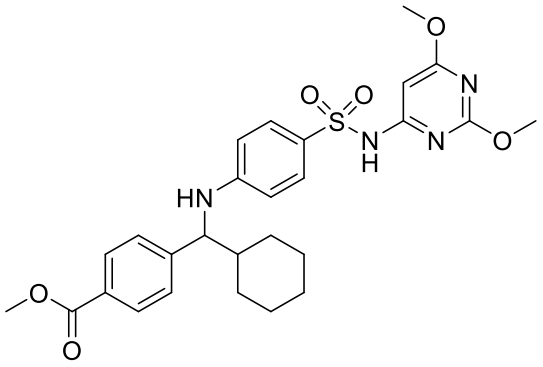
4.4 Bioactive molecule modification:



Methyl 2-(1-(4-(Cyclohexyl(phenylamino)methyl)benzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate, 55 (127.5 mg, 81 % yield) was prepared according to the general procedure in 0.3 mmol scale. The desired amine was isolated as a solid (mp = 68-70 °C) (12 g column, 100:0→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.97 (s, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.67 (t, *J* = 7.0 Hz, 1H), 6.61 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 2H), 4.52 – 4.18 (m, 2H), 3.85 (s, 3H), 3.71 (s, 3H), 3.68 (s, 2H), 2.37 (s, 3H), 1.92 (d, *J* = 12.2 Hz, 1H), 1.85 – 1.66 (m, 4H), 1.59 (d, *J* = 12.3 Hz, 1H), 1.30 – 1.07 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.4, 169.4, 155.8, 148.2, 147.2, 136.0, 134.1, 131.0, 130.5, 129.6, 129.0, 127.7, 117.3, 115.0, 113.2, 112.0, 111.4, 101.0, 63.4, 55.6, 52.0, 44.6, 30.1, 30.1, 29.4, 26.3, 26.2, 26.2, 13.2. **FT-IR** (cm^{-1}, neat, ATR) 3400, 2927, 1600, 1477, 1312, 1223, 734. **HRMS** (ES+) calcd for $C_{33}H_{37}N_2O_4$ $[M+H]^+$: 525.2753, found: 525.2758.

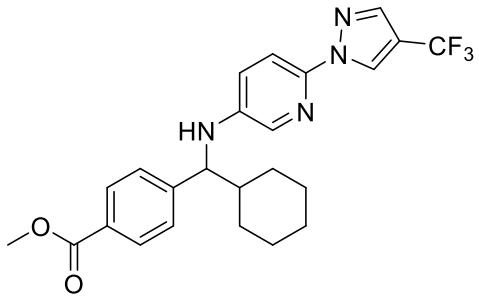


Isopropyl 2-(4-(4-(Cyclohexyl(phenylamino)methyl)benzoyl)phenoxy)-2-methylpropanoate, 56 (114 mg, 74 % yield) was prepared according to the general procedure in 0.3 mmol scale. The desired amine was isolated as a solid (mp = 58-60 °C) (12 g column, 100:0→80:20 hexanes/EtOAc). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 5.16 – 5.00 (m, 1H), 4.36 – 4.15 (m, 2H), 1.88 (d, *J* = 12.8 Hz, 1H), 1.82 – 1.61 (m, 10H), 1.57 (d, *J* = 12.9 Hz, 1H), 1.25 – 1.06 (m, 11H). **^{13}C NMR** (126 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 173.3, 159.6, 147.6, 136.9, 132.2, 130.9, 130.1, 129.3, 127.3, 117.4, 117.3, 113.3, 79.5, 69.4, 63.4, 45.0, 30.4, 29.5, 26.5, 26.4, 25.6, 25.5, 21.7. **FT-IR** (cm^{-1}, neat, ATR) 3395, 2926, 1728, 1598, 1248, 1145, 735. **HRMS** (ES+) calcd for $C_{33}H_{40}NO_4$ $[M+H]^+$: 514.2957, found: 514.2950.



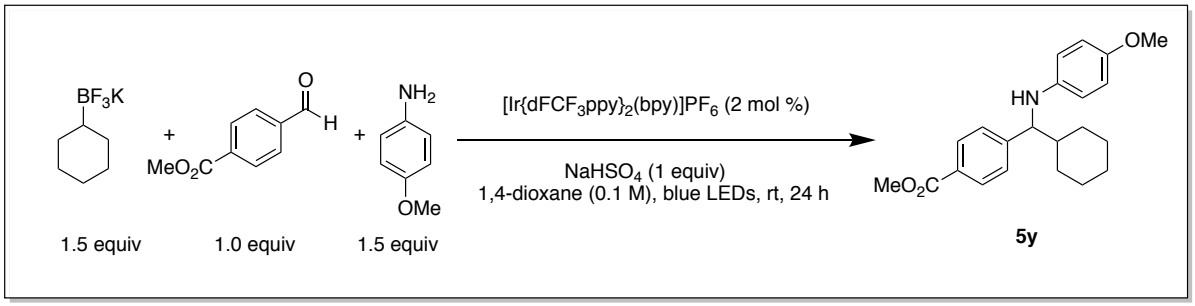
Methyl 4-(Cyclohexyl((4-(*N*-(2,6-dimethoxypyrimidin-4-yl)sulfamoyl)phenyl)amino)methyl)benzoate, 57 (97 mg, 36 % yield) was prepared according to the general procedure. The desired amine was isolated as a solid (mp = 212-214 °C) (24 g column, 60:40→20:80 hexanes/EtOAc). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.46 (d, *J* = 8.9 Hz, 2H), 6.19 (s, 1H), 4.85

(d, *J* = 6.0 Hz, 1H), 4.18 (t, *J* = 5.8 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 1.84 (d, *J* = 12.8 Hz, 1H), 1.80 – 1.60 (m, 4H), 1.48 (d, *J* = 13.0 Hz, 1H), 1.24 – 0.98 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.6, 166.7, 164.7, 158.8, 151.4, 146.4, 129.8, 129.4, 129.2, 127.0, 125.4, 112.2, 85.3, 62.8, 54.6, 55.0, 52.0, 44.3, 30.0, 29.3, 26.1, 26.0, 26.0. **FT-IR** (cm^{-1}, neat, ATR) 3260, 2928, 1718, 1592, 1347, 1280, 1148, 1088, 574. **HRMS** (ES+) calcd for $C_{27}H_{33}N_4O_6S$ $[M+H]^+$: 541.2121, found: 541.2131.

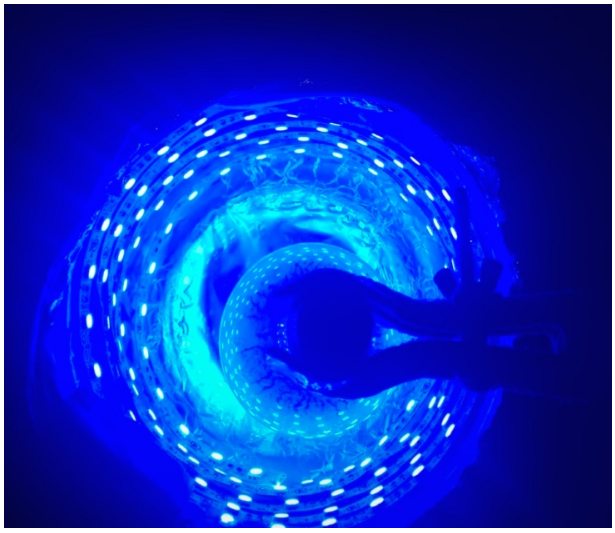


Methyl 4-(Cyclohexyl((6-(4-(trifluoromethyl)-1H-pyrazol-1-yl)pyridin-3-yl)amino)methyl)benzoate, 60 (133 mg, 58 % yield) was prepared according to the general procedure. The desired amine was isolated as a viscous oil (24 g column, 90:10→70:30 hexanes/EtOAc). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.79 (s, 1H), 7.69 (d, *J* = 2.8 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.88 (dd, *J* = 8.9, 2.9 Hz, 1H), 4.42 (s, 1H), 4.20 (d, *J* = 4.1 Hz, 1H), 3.90 (s, 3H), 1.90 (d, *J* = 12.6 Hz, 1H), 1.83 – 1.64 (m, 4H), 1.54 (d, *J* = 13.0 Hz, 1H), 1.28 – 1.03 (m, 5H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.7, 146.5, 142.7, 142.0, 137.6 (d, *J* = 2.8 Hz), 132.8, 129.7, 129.2, 127.1, 125.3 (q, *J* = 3.7 Hz), 122.5 (q, *J* = 266.0 Hz), 122.1, 114.5 (q, *J* = 38.5 Hz), 113.1, 63.3, 51.9, 44.5, 29.8, 29.4, 26.1, 26.1, 26.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -56.75. **FT-IR** (cm^{-1}, neat, ATR) 3380, 2929, 2850, 1708, 1495, 1402, 1263, 1114, 967, 733. **HRMS** (ES+) calcd for $C_{24}H_{26}F_3N_4O_2$ $[M+H]^+$: 459.2008, found: 459.2001 .

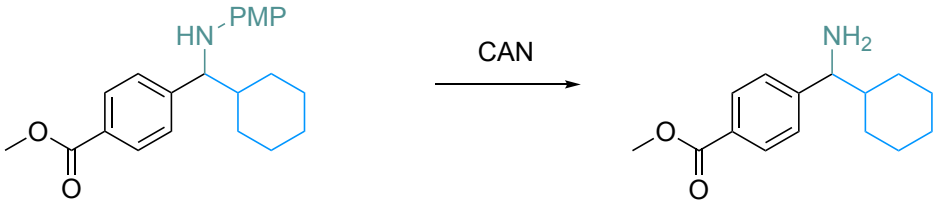
5. Large Scale Reaction and Removal of *p*-Methoxyphenylamines:



To an oven dried, 50 mL round bottom flask equipped with a stir bar were added [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ (60.6 mg, 0.06 mmol, 2 mol %), aldehyde (0.4925 g, 3.0 mmol, 1.0 equiv), alkyltrifluoroborate (0.8553 g, 4.5 mmol, 1.5 equiv), $NaHSO_4$ (0.7203 g, 6.0 mmol, 2.0 equiv), and amine (0.5542 g, 4.5 mmol, 1.5 equiv). The flask was sealed with a rubber septum, evacuated, and purged with argon three times *via* an inlet needle. The flask was then charged with dry and degassed 1,4-dioxane (30 mL, 0.1 M). The reaction mixture was then stirred vigorously under light irradiation (blue LEDs) as shown below. The reaction temperature was maintained at approximately 24 °C *via* a fan. Once judged complete by crude ^{1}H NMR (~24 h), the reaction was taken to dryness and then purified on an automated liquid chromatographic system to obtain the pure product, 541 mg, (51%) as an oil.



6. Representative Procedure for Deprotection of *p*-Methoxyphenylamines



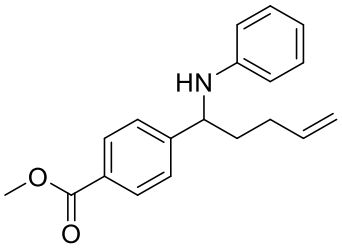
54, 177 mg, 0.5 mmol

61, 75 mg, 61 %

Methyl 4-(Amino(cyclohexyl)methyl)benzoate, 61 (75 mg, 61% yield) was prepared according to the following procedure: To a solution of amine (0.50 mmol) in MeOH:H_2O (28 mL) was added CAN (3.0 equiv) at 0 °C. The reaction was stirred at this temperature for 1 hour, then allowed to warm up to room temperature overnight. Upon completion, the mixture was washed with DCM (5 mL) then the aqueous later was made alkaline by adding 2N NaOH. The solution was extracted with ethyl acetate (4 x 20 mL) and then washed with brine, dried over $MgSO_4$, and isolated by flash chromatography (silica gel, hexane: ethyl acetate (1:1, 2% Et_3N). The desired amine was isolated as a viscous yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.53 – 6.91 (m, 2H), 3.90 (s, 3H), 3.67 (d, *J* = 7.3 Hz, 1H), 2.03 – 0.46 (m, 14H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.2, 150.8, 129.7, 128.9, 127.5, 127.3, 61.6, 52.1, 45.3, 30.1, 29.4, 26.5, 26.3. **FT-IR** (cm^{-1}, neat, ATR) 3375, 2923, 2850, 1717, 1275, 1111, 770. **HRMS** calcd for $C_{15}H_{22}NO_2$ $[M+H]^+$: 248.1651, found: 248.1647.

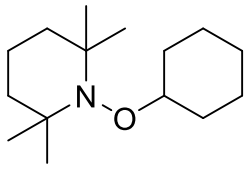
7. Mechanistic Studies:

6.1 Ring-opening Radical Clock: To an 8 mL reaction vial equipped with a stir bar were added $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ (10.0 mg, 0.01 mmol, 2 mol %), potassium (cyclopropylmethyl)trifluoroborate (121.5 mg, 0.75 mmol, 1.5 equiv), methyl 4-formylbenzoate (82.0 mg, 0.5 mmol, 1.0 equiv), and $NaHSO_4$ (60.0 mg, 0.5 mmol, 1.0 equiv). The vial was sealed with a cap containing a TFE lined silicone septa and placed under an argon *via* an inlet needle. The vial was evacuated three times *via* an inlet needle then purged with argon. Dry and degassed 1,4-dioxane was then added (5.0 mL, 0.1 M). Aniline (68.0 μL, 0.75 mmol, 1.5 equiv) was added *via* microsyringe. The reaction was placed under 34 W blue Kessil lamp irradation and vigorously stirred for 24 h. The reaction was maintained at approximately 24 °C *via* a fan. After completion, the reaction mixture was taken to dryness and then purified on an automated liquid chromatographic system (12 g column, 100:0→90:10 hexanes/EtOAc) to obtain the pure product **62**, (49.0 mg, 33% yield) as an oil.

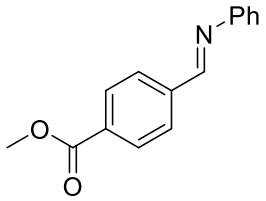


Methyl 4-(1-(Phenylamino)pent-4-en-1-yl)benzoate. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 2H), 6.67 (t, *J* = 7.0 Hz, 1H), 6.51 (d, *J* = 7.7 Hz, 2H), 5.85 (td, *J* = 16.6, 6.6 Hz, 1H), 5.15 – 4.98 (m, 2H), 4.42 (t, *J* = 6.3 Hz, 1H), 4.14 (s, 1H), 3.92 (s, 3H), 2.24 – 2.11 (m, 2H), 1.98 – 1.84 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 149.5, 146.9, 137.4, 129.9, 129.1, 128.9, 126.4, 117.5, 115.6, 113.2, 57.5, 51.9, 37.6, 30.3. **FT-IR** (cm^{-1}, neat, ATR) 3398, 2950, 2848, 1600, 1503, 1275, 1112, 748, 692. **HRMS** (EI) calcd for $C_{19}H_{21}NO_2$ $[M]^+$: 295.1572, found: 295.1567.

6.2 TEMPO Quenching Reaction: To an 8 mL reaction vial equipped with a stir bar were added $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ (10.0 mg, 0.01 mmol, 2 mol %), potassium cyclohexyltrifluoroborate (140.0 mg, 0.75 mmol, 1.5 equiv), methyl 4-formylbenzoate (82.0 mg, 0.5 mmol, 1.0 equiv), TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] (156.0 mg, 1.0 mmol, 2.0 equiv) and $NaHSO_4$ (60.0 mg, 0.5 mmol, 1.0 equiv). The vial was sealed with a cap containing a TFE lined silicone septa and placed under an argon *via* an inlet needle. The vial was evacuated three times *via* an inlet needle then purged with argon. Dry and degassed 1,4-dioxane was then added (5.0 mL, 0.1 M). Aniline (68.0 μL, 0.75 mmol, 1.5 equiv) was added *via* microsyringe. The reaction was placed under blue LED irradiation and vigorously stirred for 24 h. The reaction was maintained at approximately 24 °C *via* a fan. After completion, the reaction mixture was taken to dryness and then purified on an automated liquid chromatographic system (12 g column, 100:0→80:20 hexanes/EtOAc) to obtain the **63**, (57.5 mg, 48% yield) as an oil and **64** (110 mg, 92% yield).



1-(Cyclohexyloxy)-2,2,6,6-tetramethylpiperidine, **63.** It was isolated as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.65 – 3.50 (m, 1H), 2.10 – 1.97 (m, 2H), 1.78 – 1.68 (m, 2H), 1.60 – 1.42 (m, 6H), 1.29 – 1.07 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 81.9, 59.7, 40.4, 34.6, 33.0, 26.1, 25.2, 20.4, 17.5.



Methyl 4-((Phenylimino)methyl)benzoate, 64, was isolated as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.19 – 8.13 (m, 2H), 8.03 – 7.95 (m, 2H), 7.47 – 7.39 (m, 2H), 7.33 – 7.21 (m, 3H), 3.97 (s, 3H).

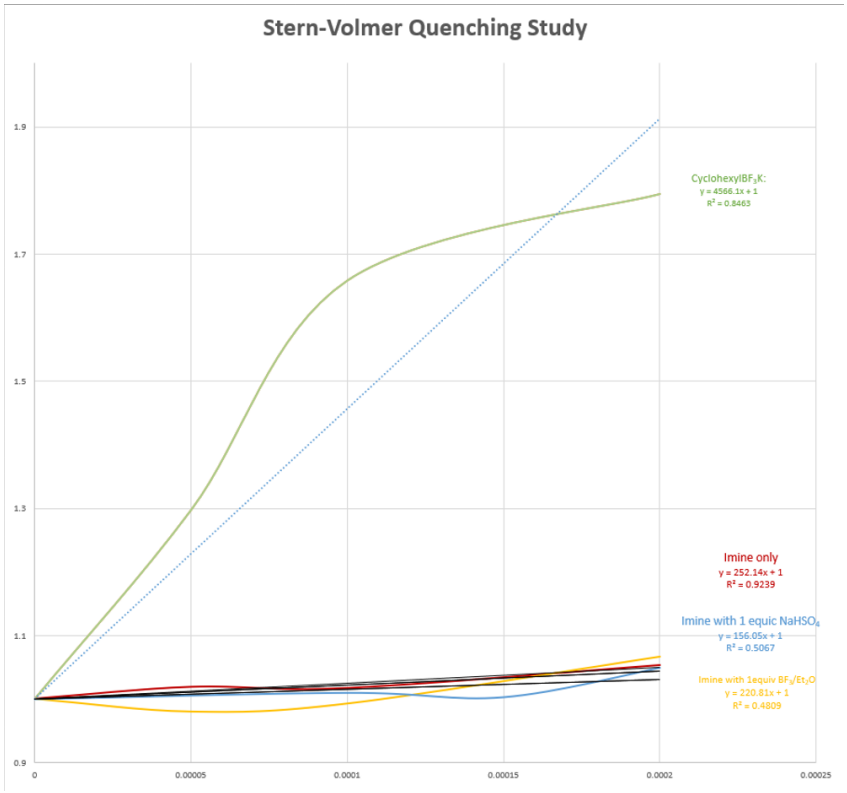
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.49, 158.98, 151.44, 139.92, 132.26, 129.89, 129.14, 128.55, 126.41, 120.81, 52.23.

6.3 Imine as starting material: To an 8 mL reaction vial equipped with a stir bar were added $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ (10.0 mg, 0.01 mmol, 2 mol %), alkyltrifluoroborate (140.0 mg, 0.75 mmol, 1.5 equiv), **64** (120 mg, 0.5 mmol, 1.0 equiv), and $NaHSO_4$ (60.0 mg, 0.5 mmol, 1.0 equiv). The vial was sealed with a cap containing a TFE lined silicone septa and placed under an argon *via* an inlet needle. The vial was evacuated three times *via* an inlet needle then purged with argon. Dry and degassed 1,4-dioxane was then added (5.0 mL, 0.1 M). Aniline (68.0 μL, 0.75 mmol, 1.5 equiv) was added at this point directly *via* microsyringe. The reaction was placed under blue LED irradiation and vigorously stirred for 24 h. The reaction was maintained at approximately 24 °C *via* a fan. After completion, the reaction mixture was taken to dryness and then purified on an automated liquid chromatographic system (24 g column, 100:0→85:15 hexanes/EtOAc) to obtain **4** (142 mg, 88% yield) as a white solid.

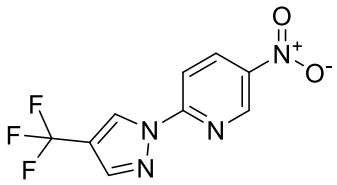
Stern-Volmer Quenching Studies:

Stern-Volmer experiments were conducted on a Horiba Fluorolog® Spectrofluorometer. Stock solutions of substrates, photocatalyst, and base were prepared with dry dioxane. For cyclohexyl BF_3K, the solution was prepared using MeCN as an alternative solvent due to solubility issues of the reagent. The solutions were mixed and purged with argon for 30 sec right before measurement. The samples were excited at 420 nm, and emission data were recorded at 473 nm. I_0/I values of each sample were calculated from the average of three scans per data point. Linear regression of I_0/I against concentration was carried out to yield Ksv.

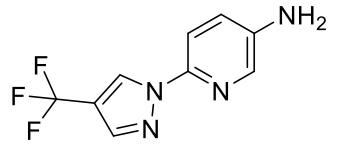
As shown below, strong quenching of the photocatalyst by alkyltrifluoroborate is observed. In comparison, no significant quenching of the photocatalyst is observed by the imine, with or without additives.



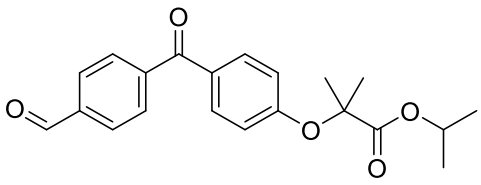
8. Preparation of Starting Material:



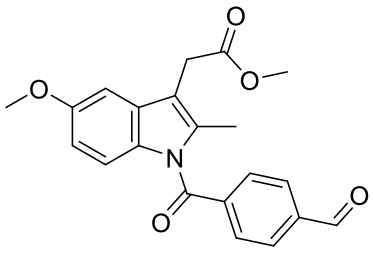
5-Nitro-2-(4-(trifluoromethyl)-1H-pyrazol-1-yl)pyridine, **58** (95% yield) A mixture of 4-(trifluoromethyl)-1H-imidazole (1048 mg, 7.7 mmol), 2-chloro-5-nitropyridine (1.110 g. 14.7 mmol), and K_2CO_3 (2070 mg, 15.0 mmol) in MeCN (8 mL) was heated at 85 °C. overnight. The reaction was diluted with H_2O and extracted with EtOAc (3×25 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered with Celite, and concentrated to generate a white solid (1.717 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.31 (d, *J* = 2.6 Hz, 1H), 8.98 – 8.90 (m, 1H), 8.67 (dd, *J* = 9.0, 2.7 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 8.00 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.5, 1448, 142.8, 140.4 (q, *J* = 2.6 Hz), 134.5, 127.6 (q, *J* = 3.9 Hz), 121.9 (q, *J* = 266.9 Hz), 117.0 (q, *J* = 38.9 Hz), 112.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -57.47.



6-(4-(Trifluoromethyl)-1H-pyrazol-1-yl)pyridin-3-amine, **59** (98% yield) 10 wt % Palladium on carbon (250 mg) was added to the solution of 5-nitro-2-(4-(trifluoromethyl)-1H-pyrazol-1-yl)pyridine (1.717 g) in 20 mL of EtOAc. The mixture was heated to 50 ºC. The reaction was filtered through Celite, rinsing with MeOH. The filtrate was concentrated to give 6-(4-(trifluoromethyl)-1H-imidazol-1-yl)pyridin-3-amine as an oil (1.487 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.85 (d, *J* = 10.3 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 9.1 Hz, 1H), 3.82 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.0, 142.0, 137.8 (d, *J* = 2.9 Hz), 134.3, 125.6 (q, *J* = 3.5 Hz), 124.3, 122.6 (q, *J* = 266.1 Hz), 114.7 (q, *J* = 37.8 Hz), 113.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -56.75.



Isopropyl 2-(4-(4-Formylbenzoyl)phenoxy)-2-methylpropanoate, To an oven-dried 20 mL-Schlenk tube equipped with a stir bar was added $NiCl_2$•$6H_2O$ (9.6 mg, 0.02 mmol), Cs_2CO_3 (97.7 mg, 0.3 mmol), 4CzIPN (7.9 mg, 0.01 mmol), dtbbpy (12.8 mg, 0.024 mmol), and Fenofibrate (72 mg, 0.2 mmol). Then, DMF (10 mL) was added, and 2,2-diethoxyacetic acid (45 μL, 0.3mmol) was injected into the tube by syringe under a N_2 atmosphere. The mixture was degassed for 30 min by bubbling an N_2 stream, then sealed with Parafilm. The solution was then stirred at rt under the irradiation of a blue LED strip for 24 h. After completion of the reaction, the mixture was quenched by addition of 0.5 mL of 3.0 M HCl, stirred for 2 h, and extracted with Et_2O (three times). The combined organic layers were washed with brine and then dried(anhyd Na_2SO_4) and evaporated in vacuum. The desired products were obtained after purification by flash chromatography on silica gel (12 g column, 100:0→80:20 hexanes/EtOAc). The desired aldehyde was isolated as a white solid (80 mg, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.97 – 5.13 (m, 1H), 1.65 (s, 6H), 1.19 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.6, 191.8, 173.1, 160.3, 143.4, 138.3, 132.3, 130.1, 129.9, 129.6, 117.4, 79.6, 69.5, 25.5, 21.7.

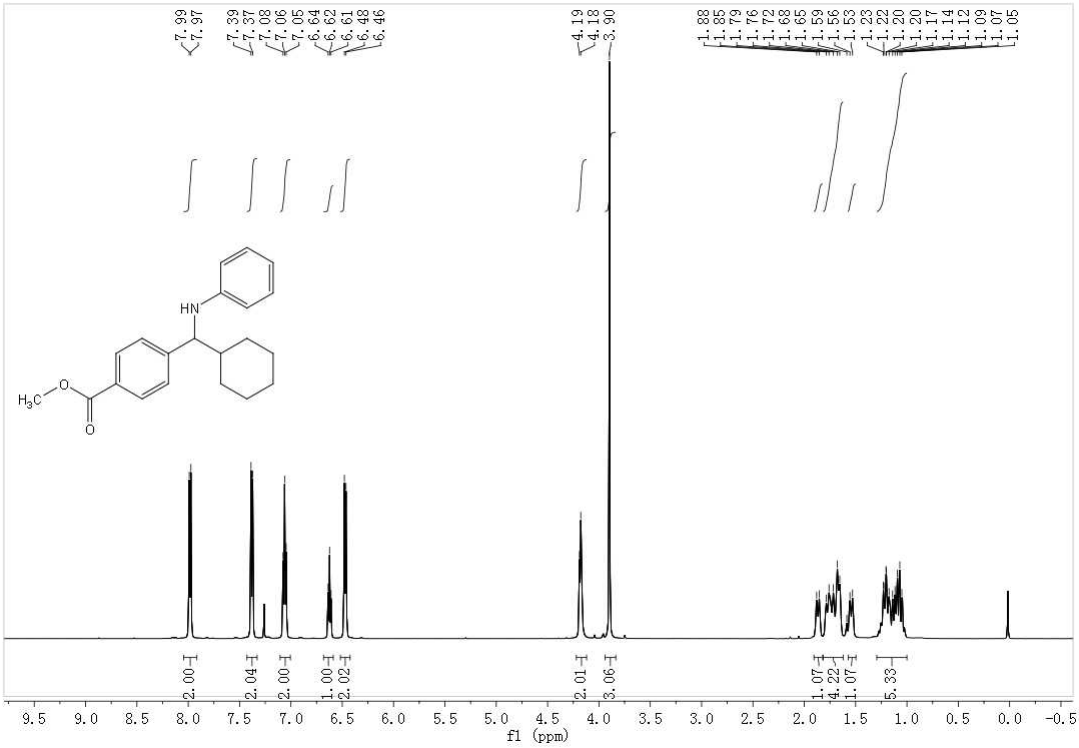


Methyl 2-(1-(4-Formylbenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate, To an oven-dried 20 mL-Schlenk tube equipped with a stir bar was added $NiCl_2$•$6H_2O$ (9.6 mg, 0.02 mmol), Cs_2CO_3 (97.7 mg, 0.3

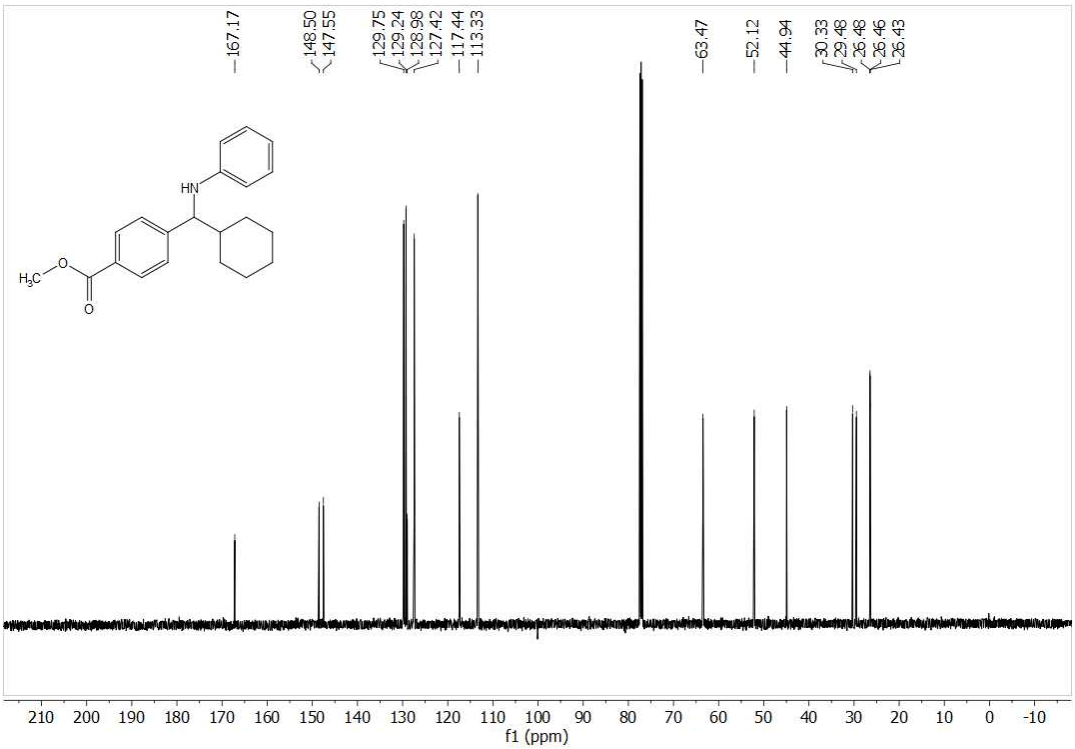
mmol), 4CzIPN (7.9 mg, 0.01 mmol), dtbbpy (12.8 mg, 0.024 mmol), and Indomethacin methyl ester (74 mg, 0.2 mmol). Then, DMF (10 mL) was added, and 2,2-diethoxyacetic acid (45 μL, 0.3mmol) was injected into the tube by syringe under a N_2 atmosphere. The mixture was degassed for 30 min by bubbling N_2 stream, then sealed with Parafilm. The solution was then stirred at rt under the irradiation of a blue LED strip for 24 h. After completion of the reaction, the mixture was quenched by addition of 0.5 mL of 3.0 M HCl, stirred for 2 h, and extracted with Et_2O (three times). The combined organic layers were washed with brine and then dried (anhyd Na_2SO_4) and evaporated in vacuum. The desired products were obtained after purification by flash chromatography on silica gel (12 g column, 100:0→70:30 hexanes/EtOAc). The desired aldehyde was isolated as an oil (79 mg, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.00 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 2.6 Hz, 1H), 6.85 (d, *J* = 8.9 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.67 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 191.5, 171.4, 168.4, 156.4, 141.0, 138.9, 136.0, 131.0, 130.8, 130.1, 130.0, 115.3, 113.3, 111.9, 101.6, 55.9, 52.3, 30.3, 13.7.

9. **NMR Spectrum**

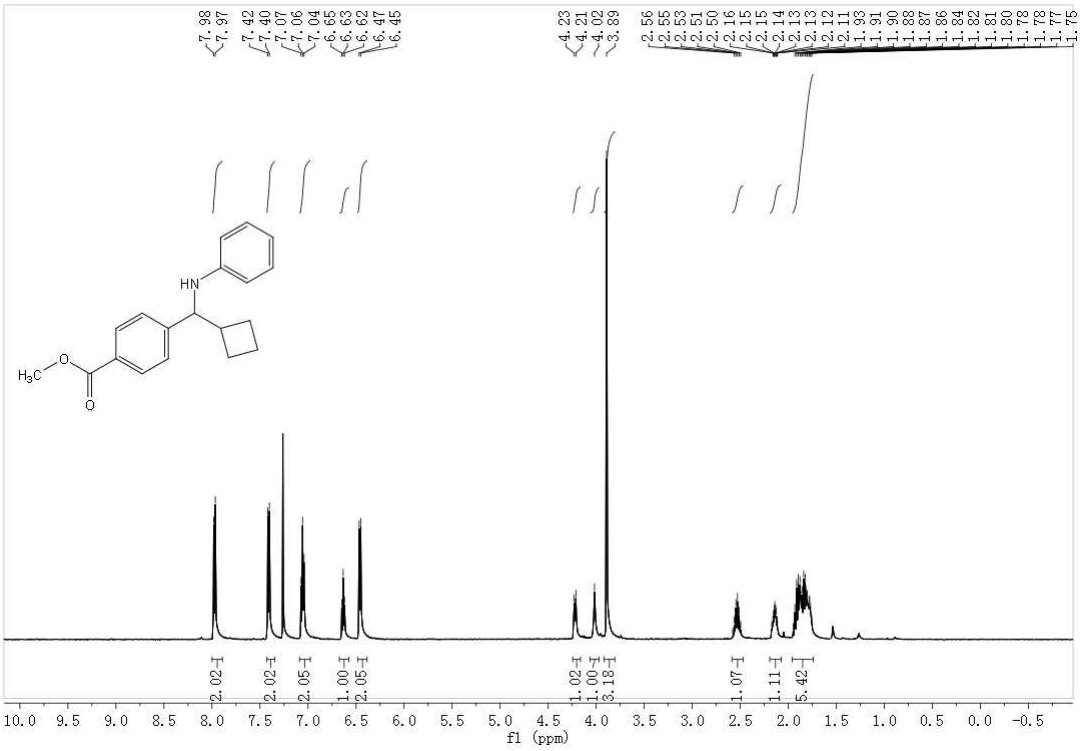
^{1}H NMR spectrum of compound **4** ($CDCl_3$, 500 MHz).



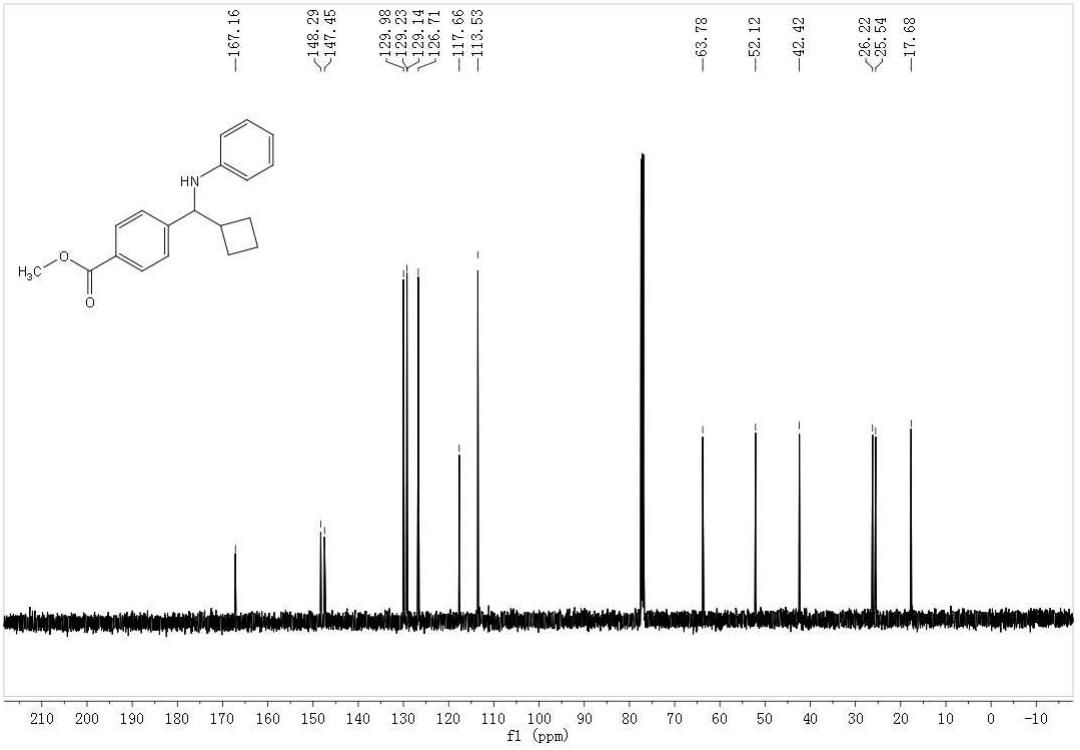
^{13}C NMR spectrum of compound **4** ($CDCl_3$, 126 MHz).



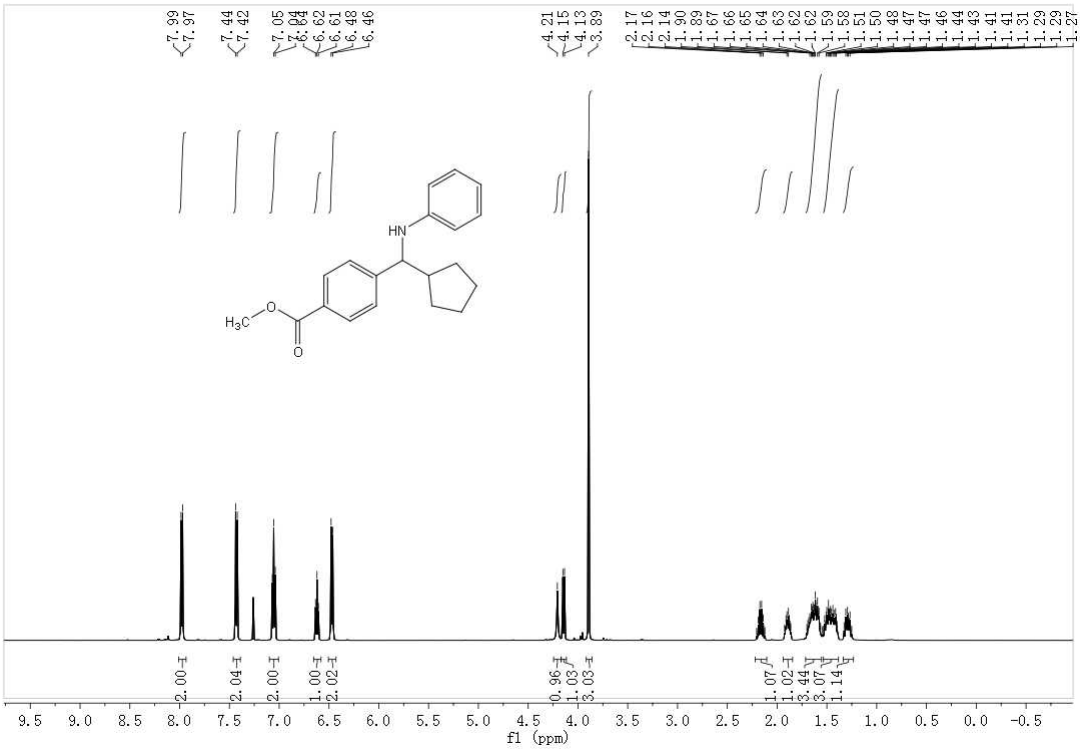
^{1}H NMR spectrum of compound **5** ($CDCl_3$, 500 MHz).



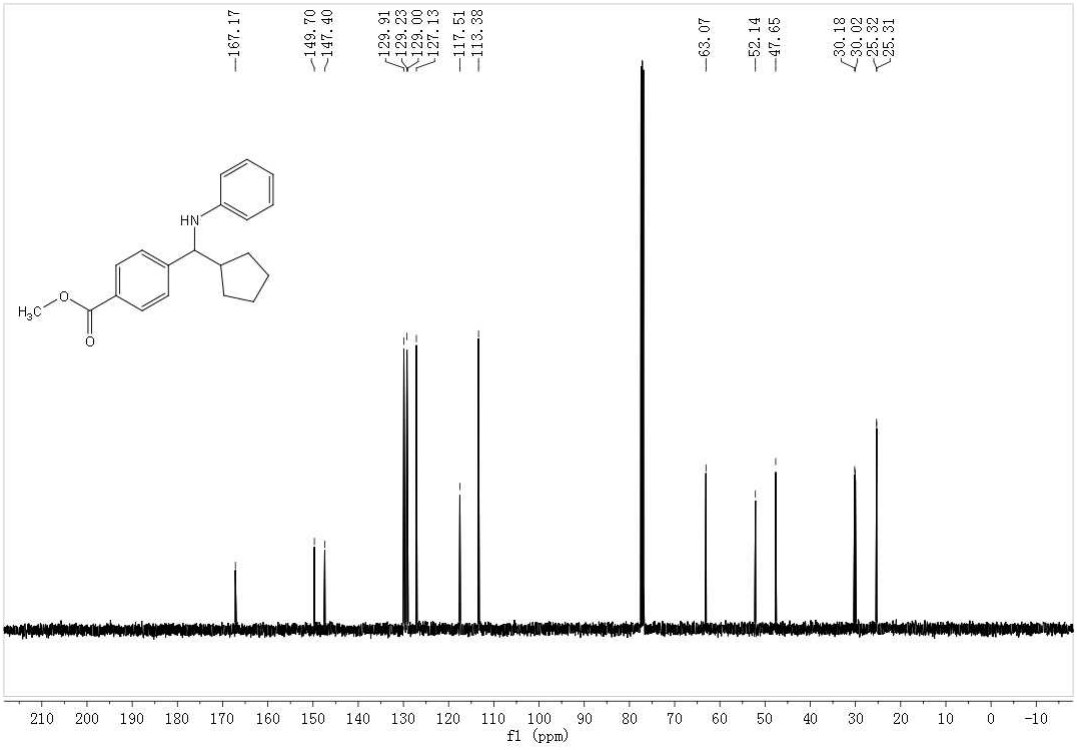
^{13}C NMR spectrum of compound **5** ($CDCl_3$, 126 MHz).



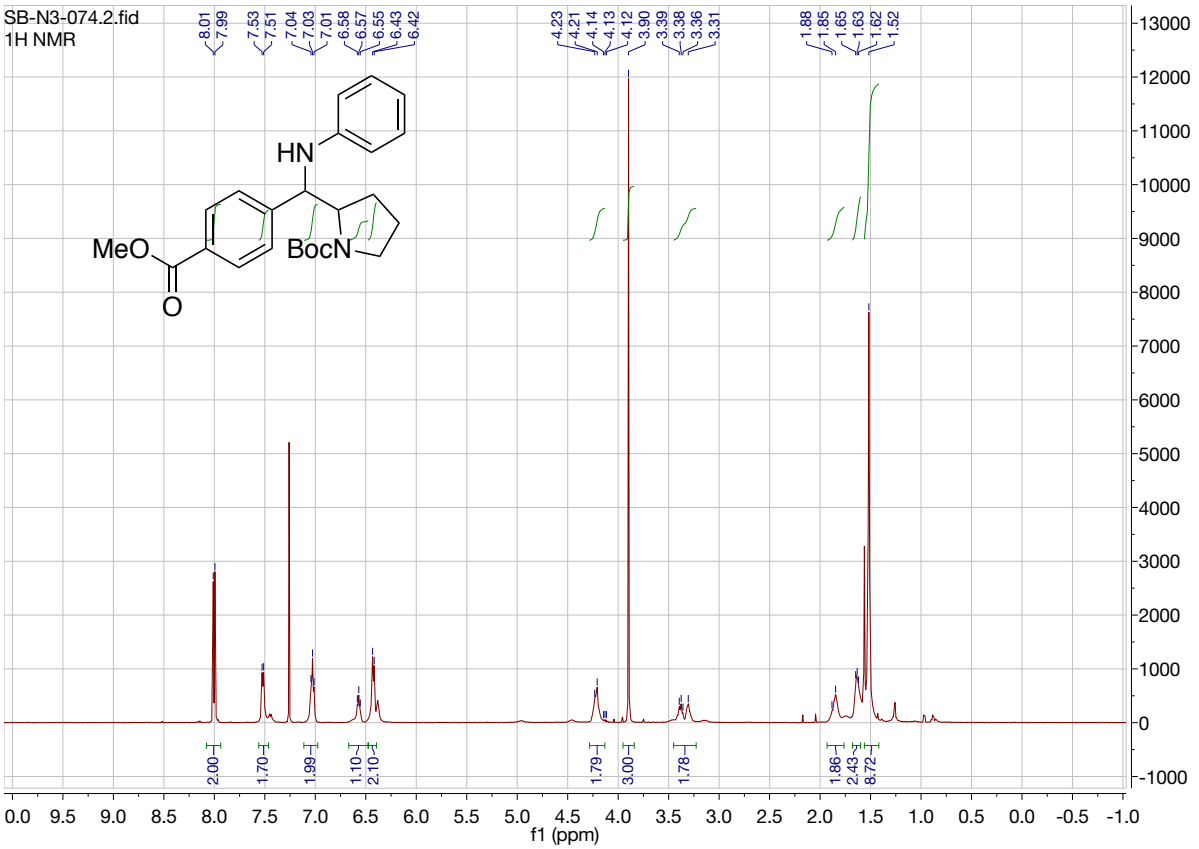
^{1}H NMR spectrum of compound **6** ($CDCl_3$, 500 MHz).



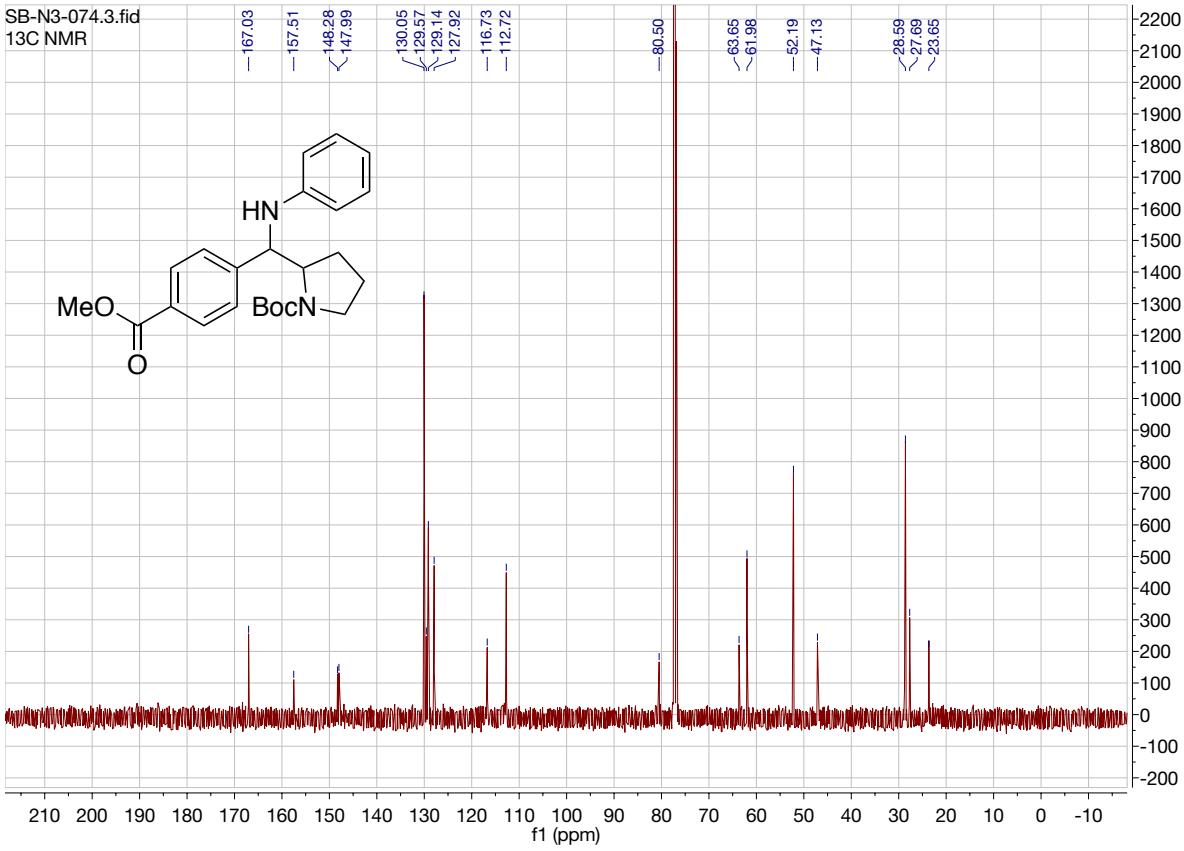
^{13}C NMR spectrum of compound **6** ($CDCl_3$, 126 MHz).



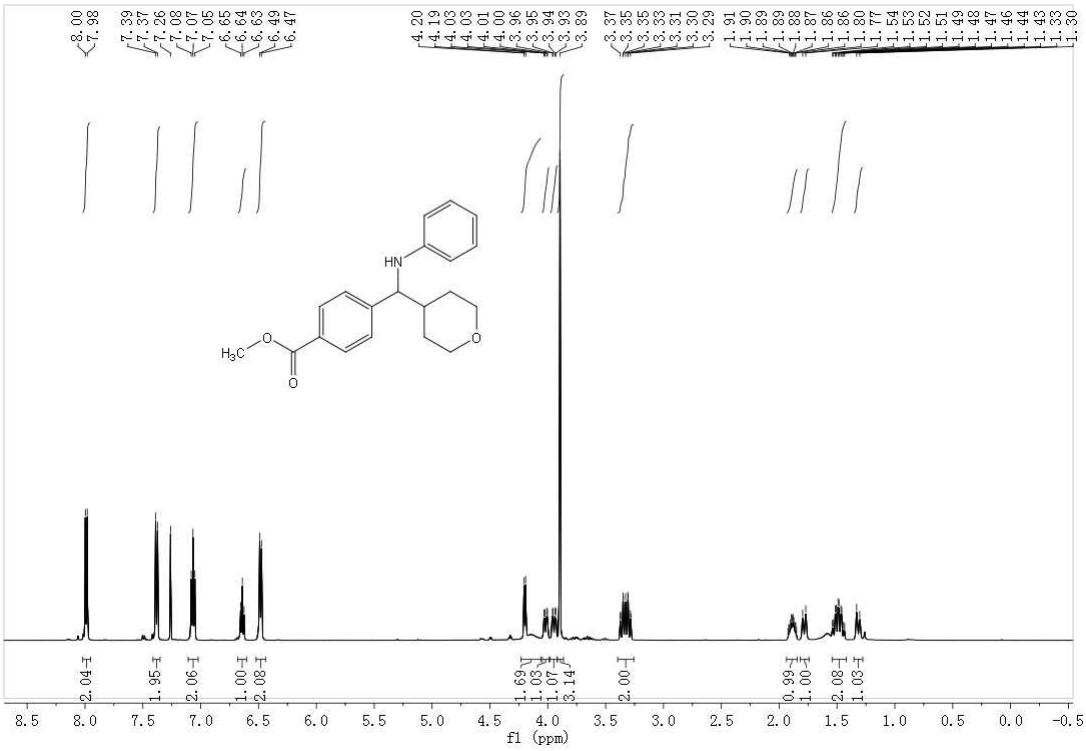
[1] H NMR spectrum of compound **7** ($CDCl_3$, 500 MHz).



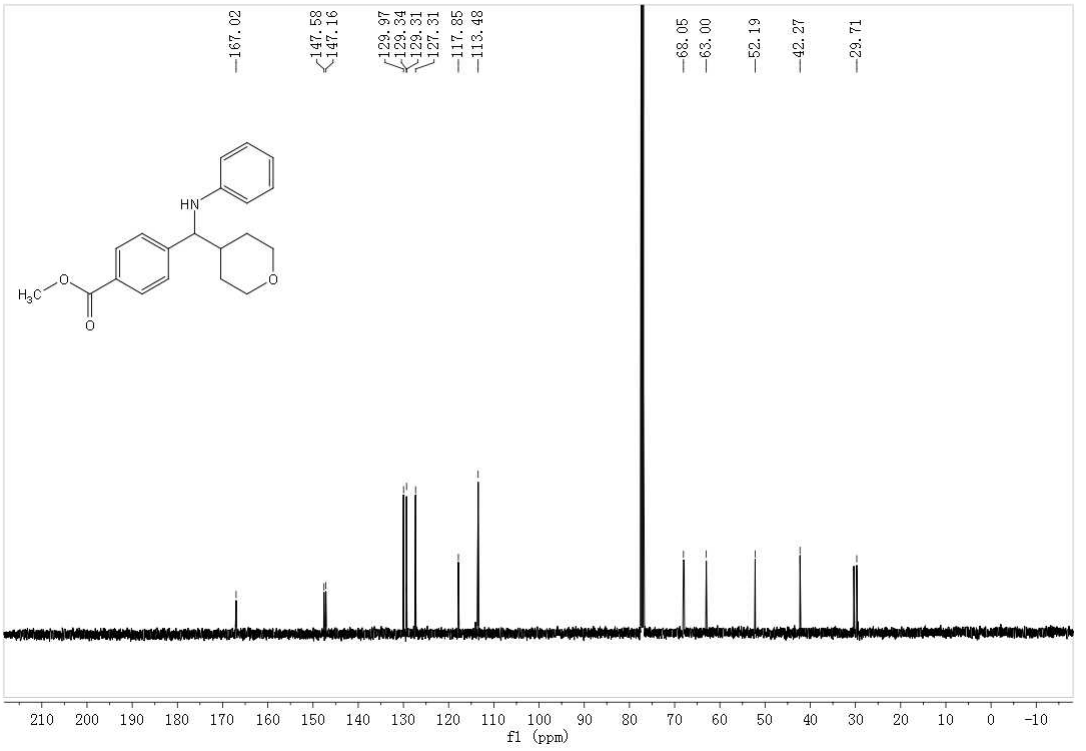
[13] C NMR spectrum of compound **7** ($CDCl_3$, 126 MHz).



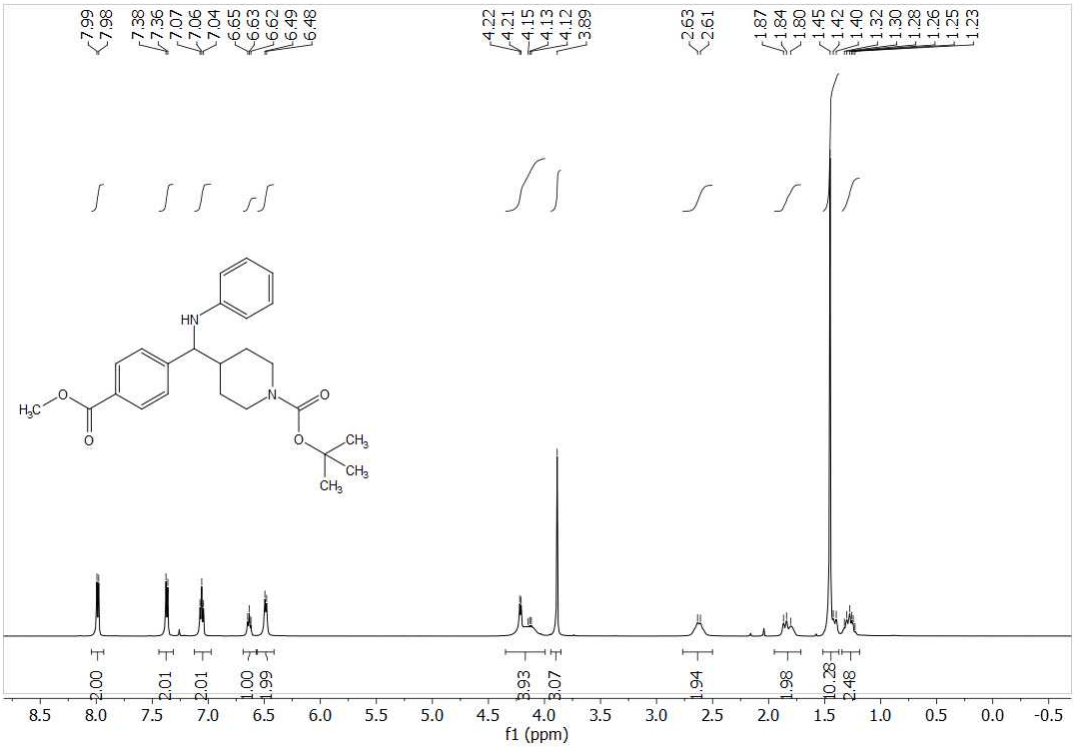
^{1}H NMR spectrum of compound **8** ($CDCl_3$, 500 MHz).



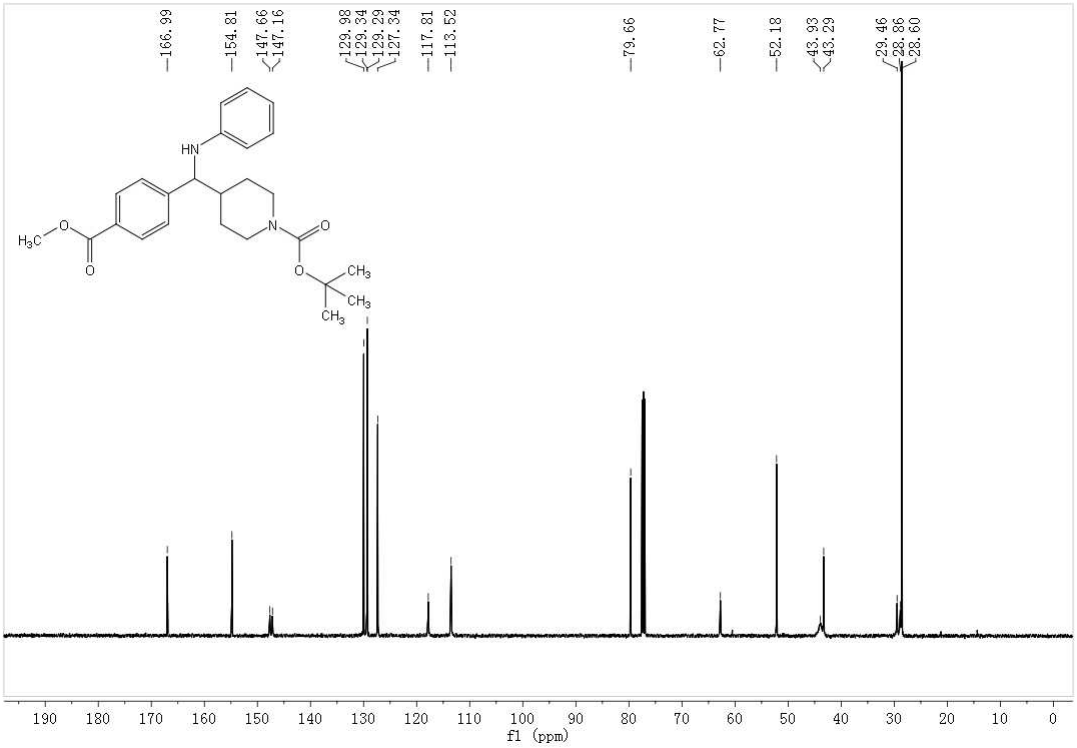
^{13}C NMR spectrum of compound **8** ($CDCl_3$, 126 MHz).



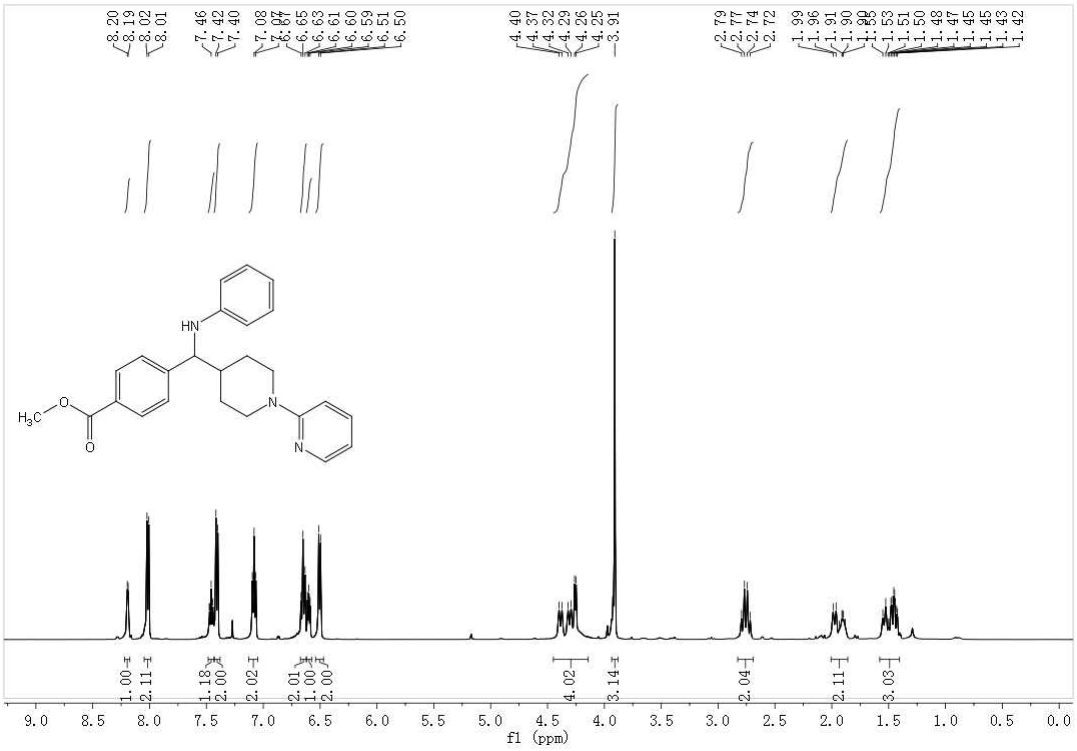
^{1}H NMR spectrum of compound **9** ($CDCl_3$, 500 MHz).



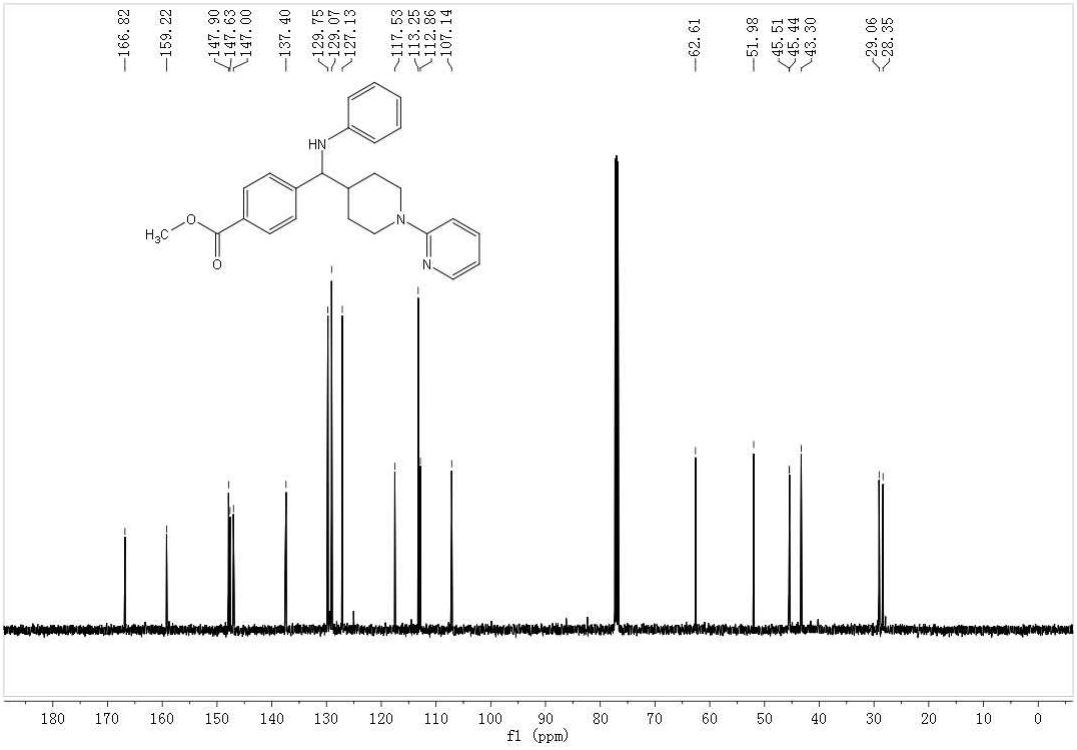
^{13}C NMR spectrum of compound **9** ($CDCl_3$, 126 MHz).



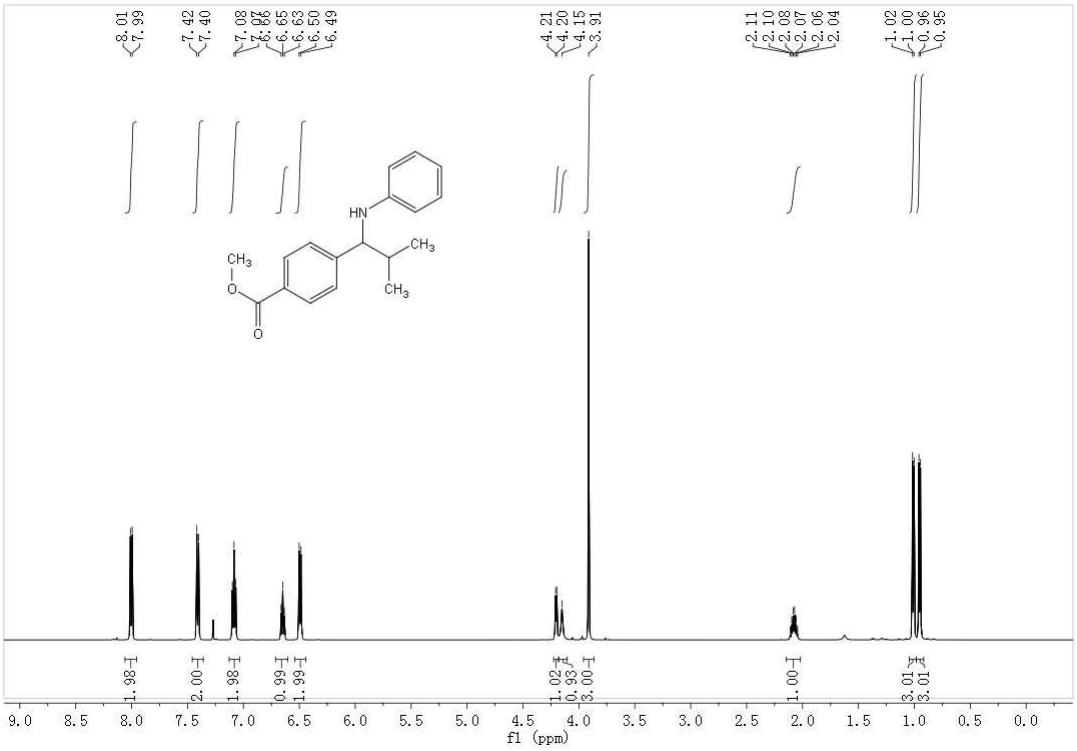
^{1}H NMR spectrum of compound **10** ($CDCl_3$, 500 MHz).



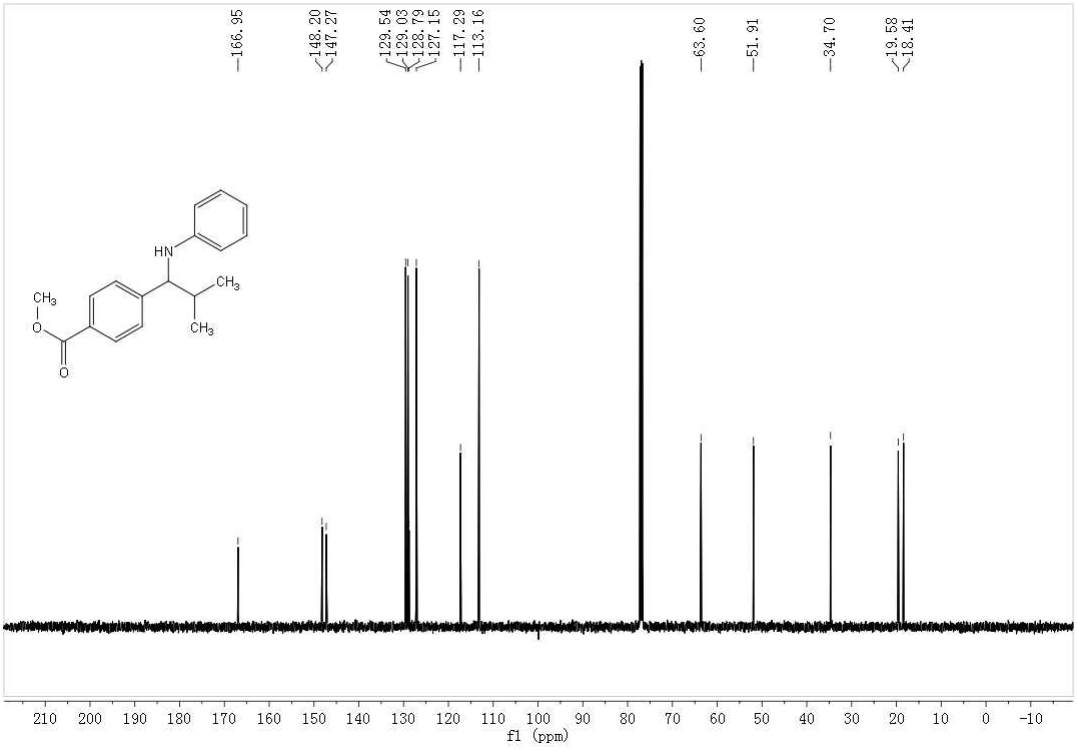
^{13}C NMR spectrum of compound **10** ($CDCl_3$, 126 MHz).



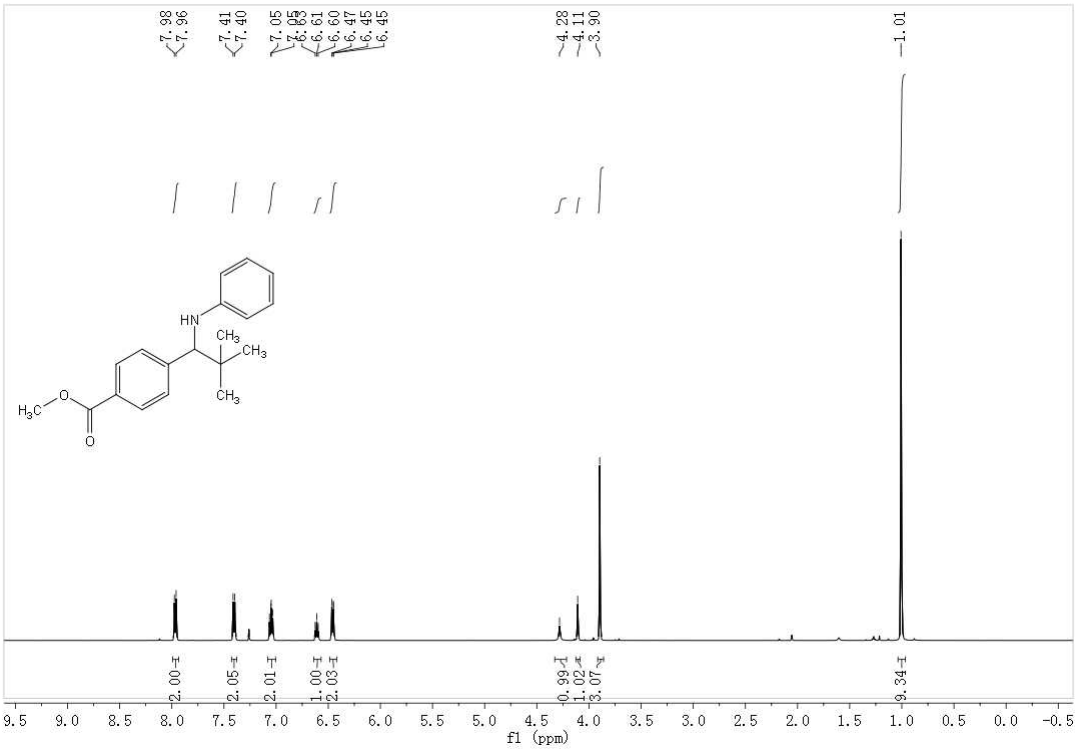
^{1}H NMR spectrum of compound **11** ($CDCl_3$, 500 MHz).



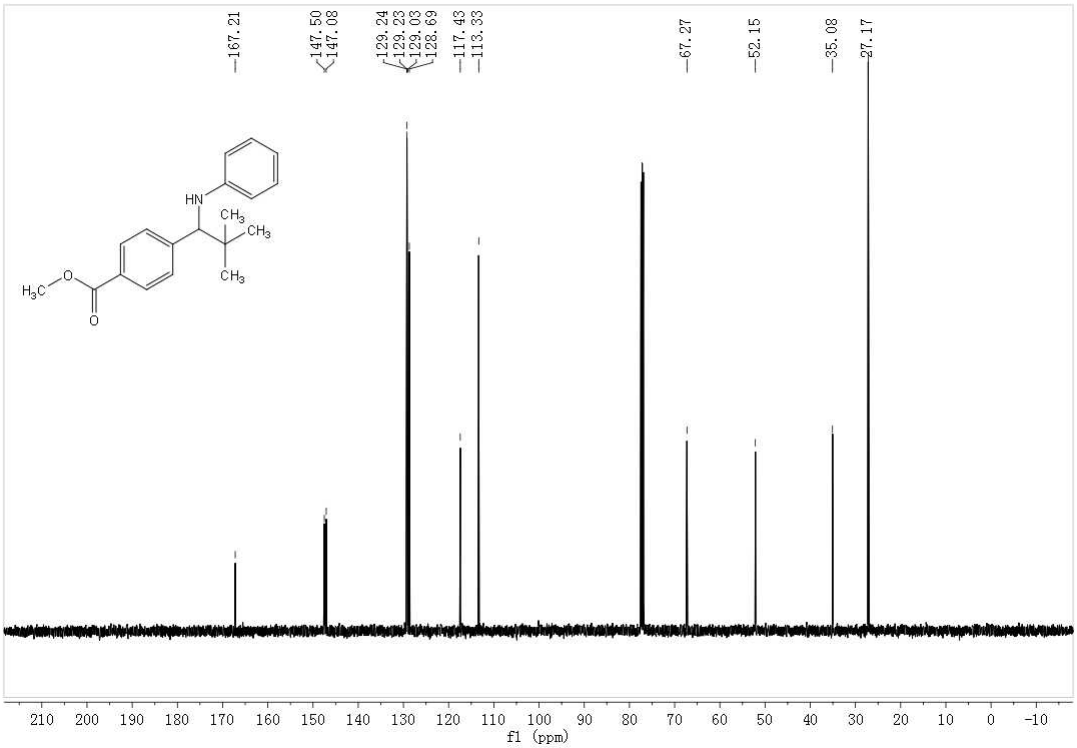
^{13}C NMR spectrum of compound **11** ($CDCl_3$, 126 MHz).



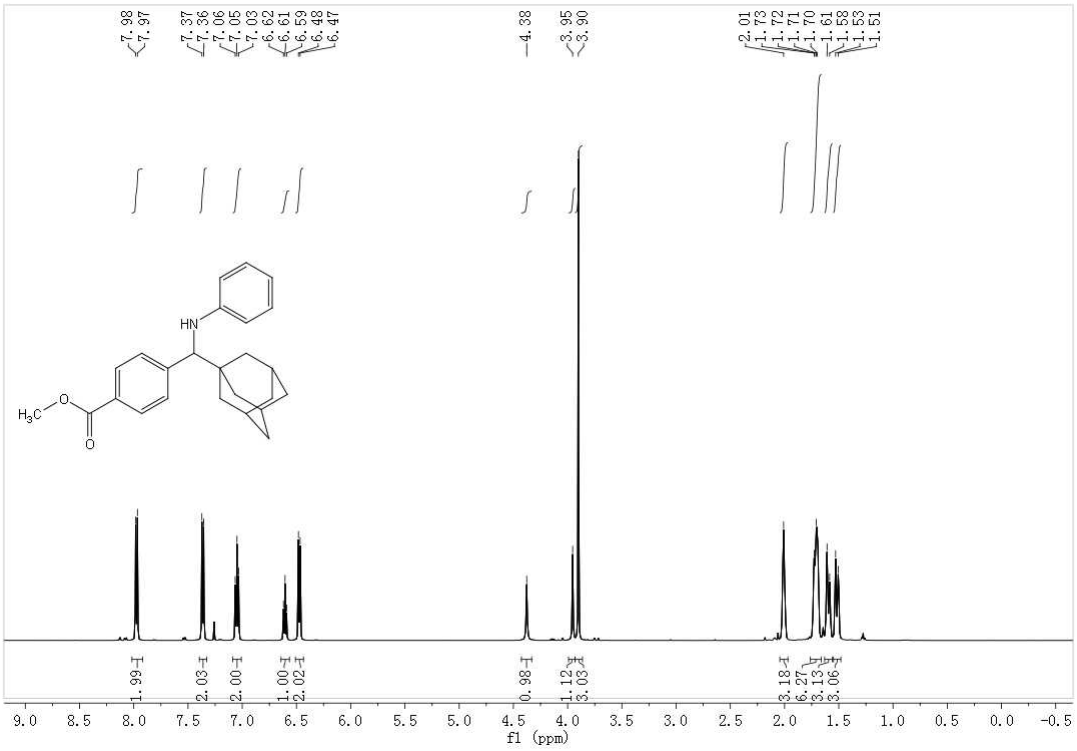
^{1}H NMR spectrum of compound **12** ($CDCl_3$, 500 MHz).



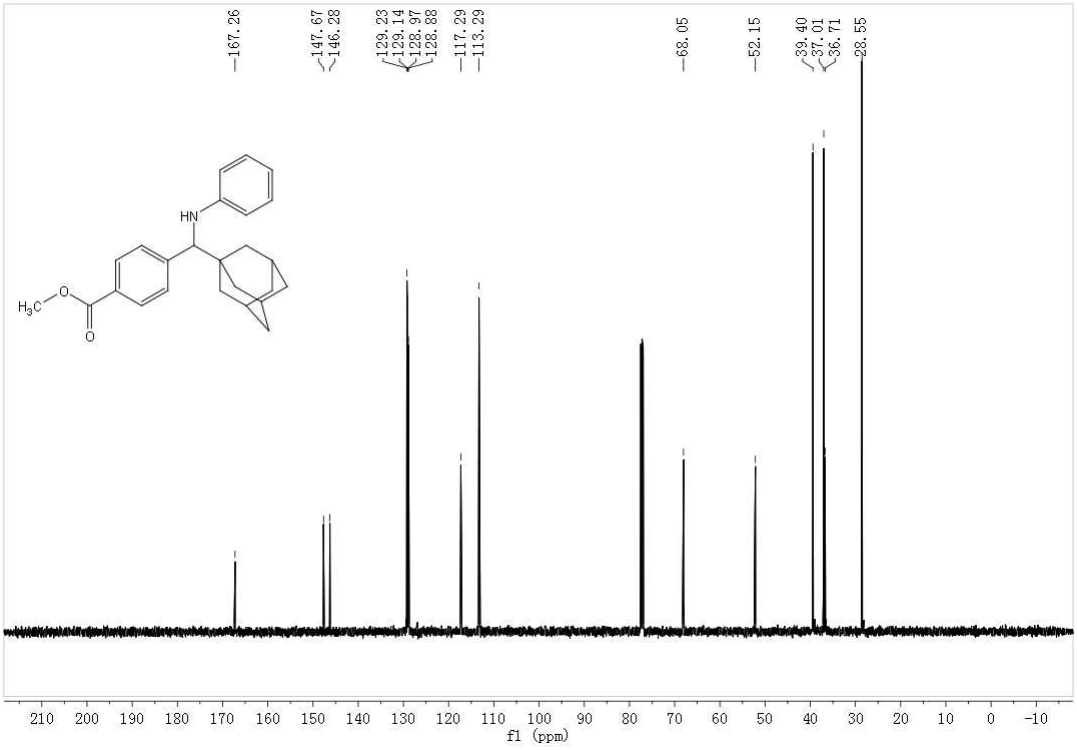
^{13}C NMR spectrum of compound **12** ($CDCl_3$, 126 MHz).



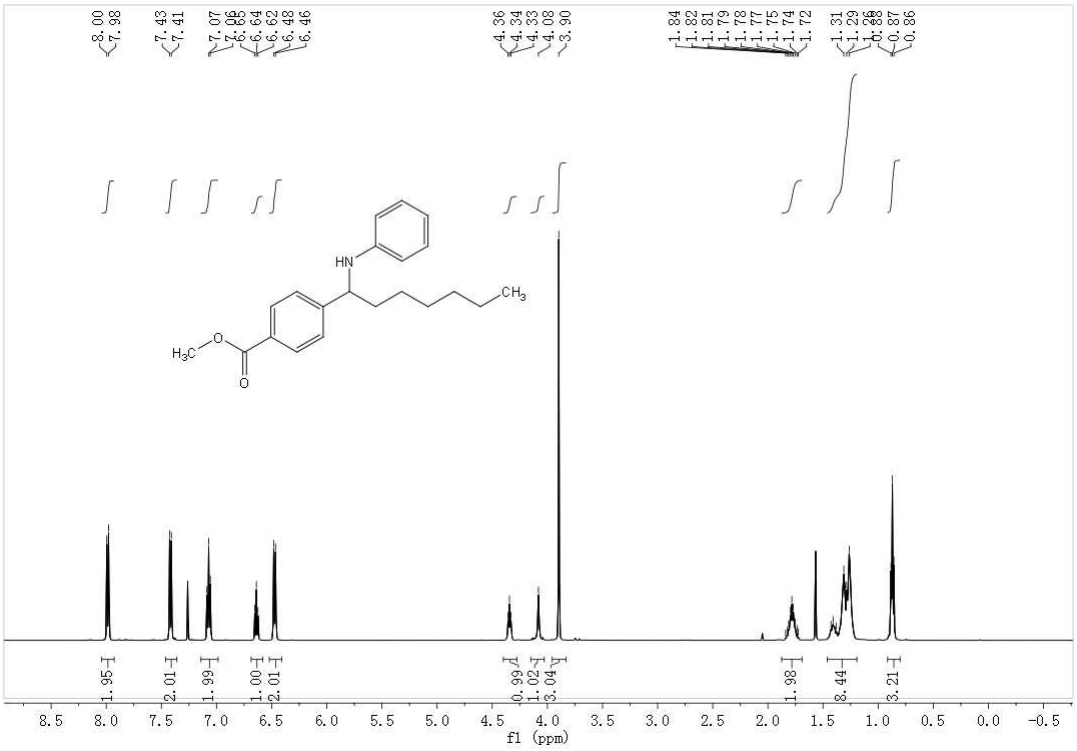
[1] H NMR spectrum of compound **13** ($CDCl_3$, 500 MHz).



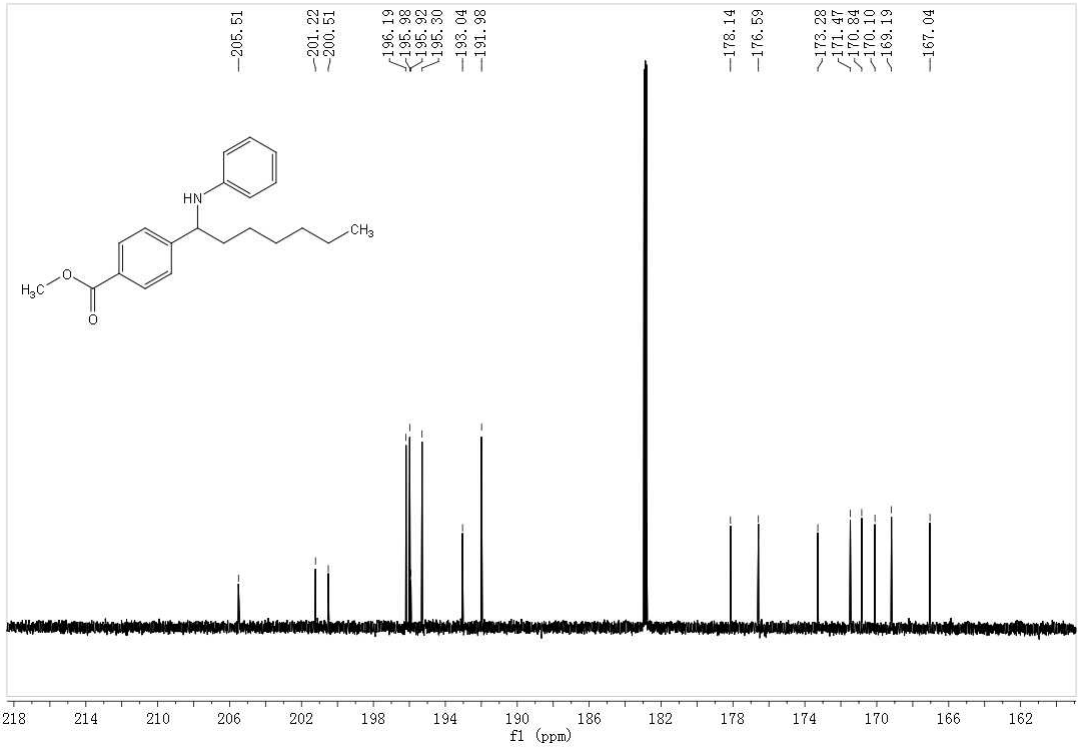
[13] C NMR spectrum of compound **13** ($CDCl_3$, 126 MHz).



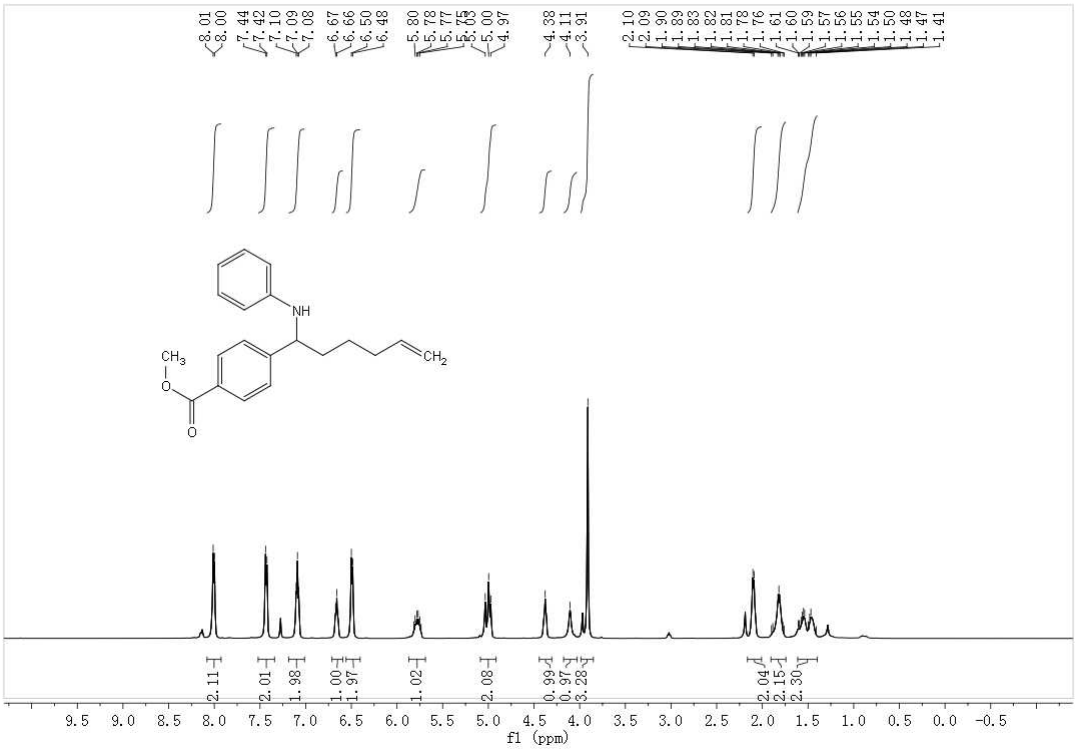
^{1}H NMR spectrum of compound **14** ($CDCl_3$, 500 MHz).



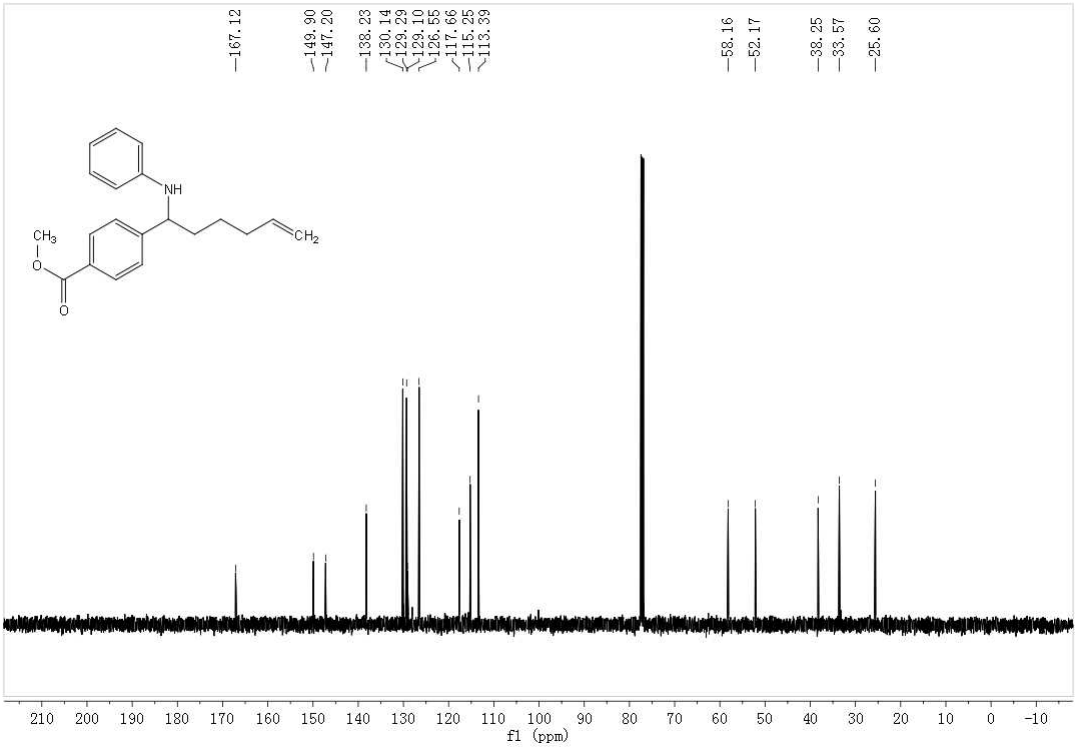
^{13}C NMR spectrum of compound **14** ($CDCl_3$, 126 MHz).



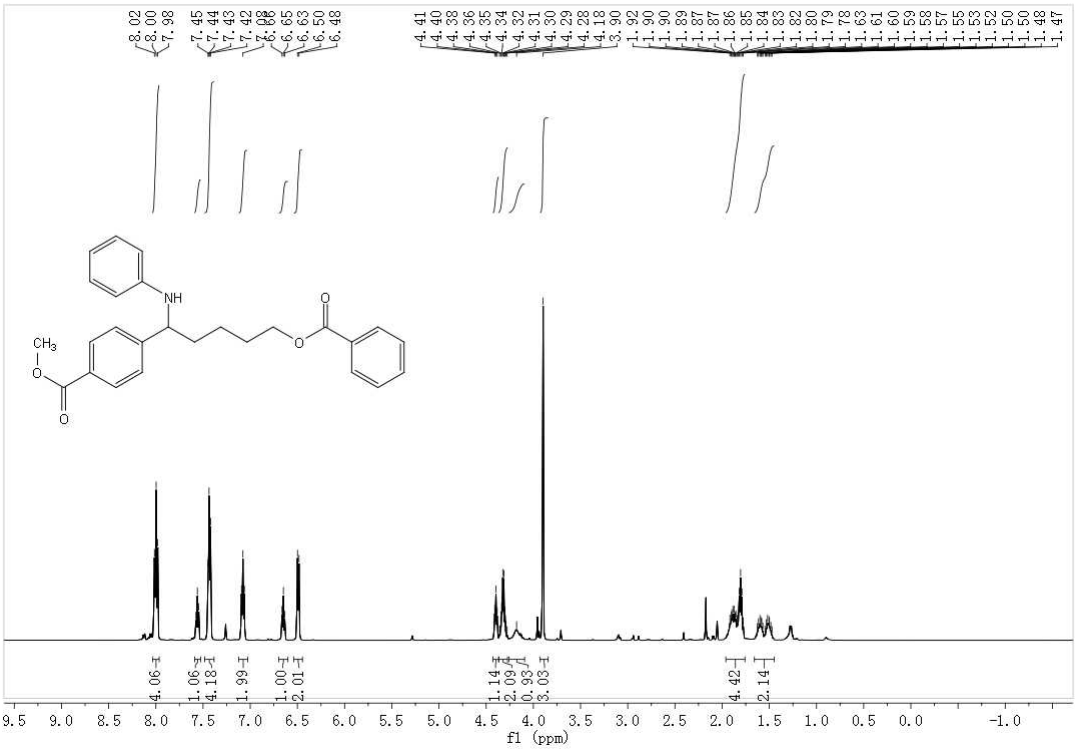
^{1}H NMR spectrum of compound **15** ($CDCl_3$, 500 MHz).



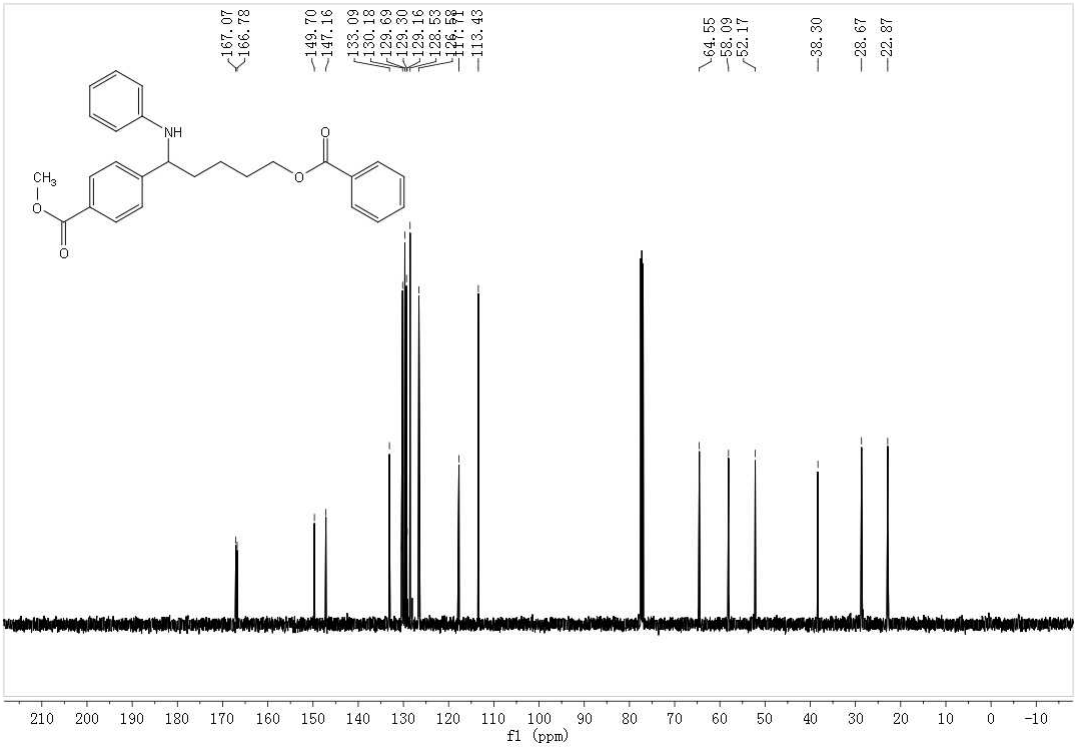
^{13}C NMR spectrum of compound **15** ($CDCl_3$, 126 MHz).



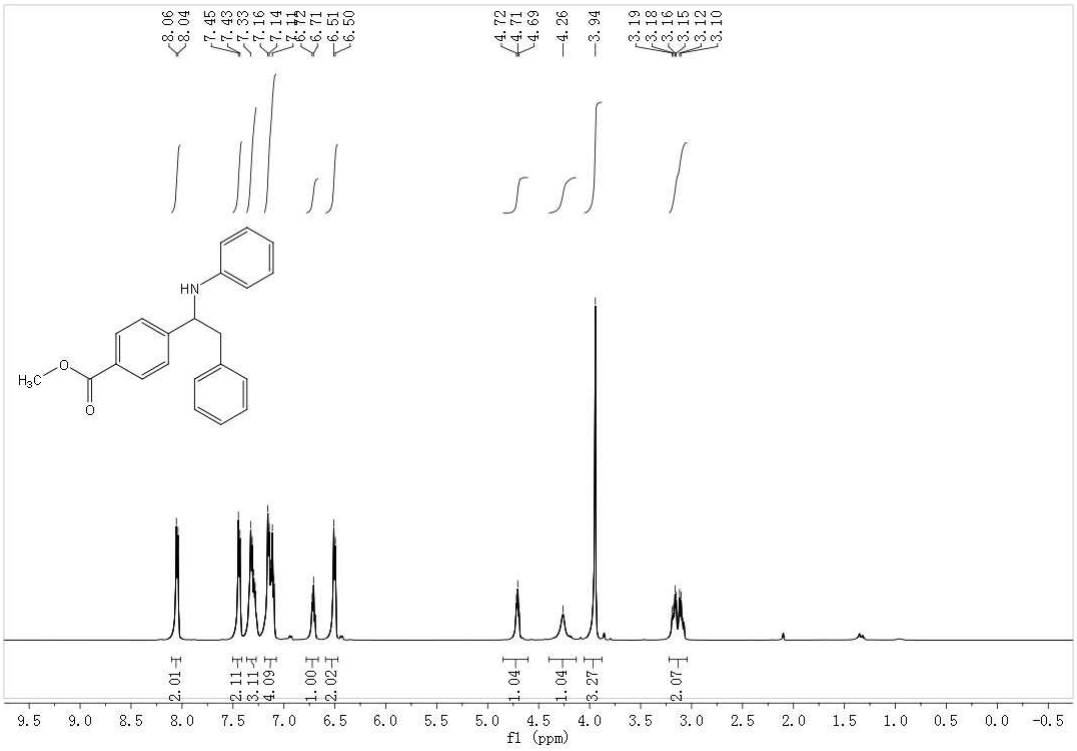
^{1}H NMR spectrum of compound **16** ($CDCl_3$, 500 MHz).



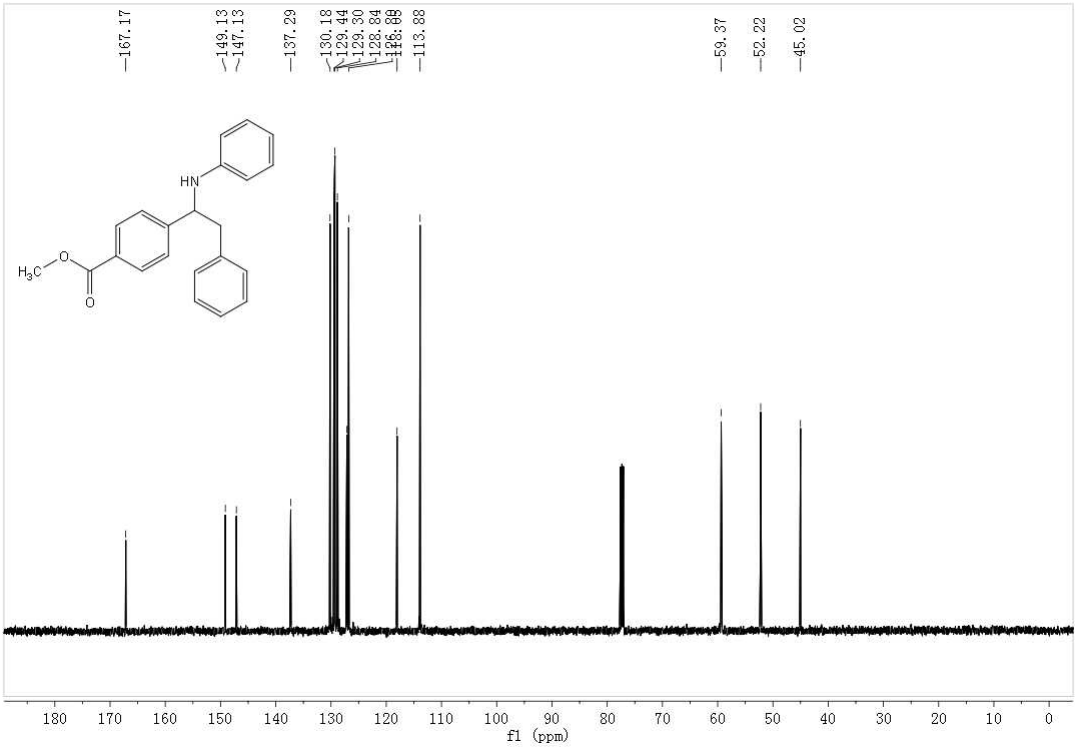
^{13}C NMR spectrum of compound **16** ($CDCl_3$, 126 MHz).



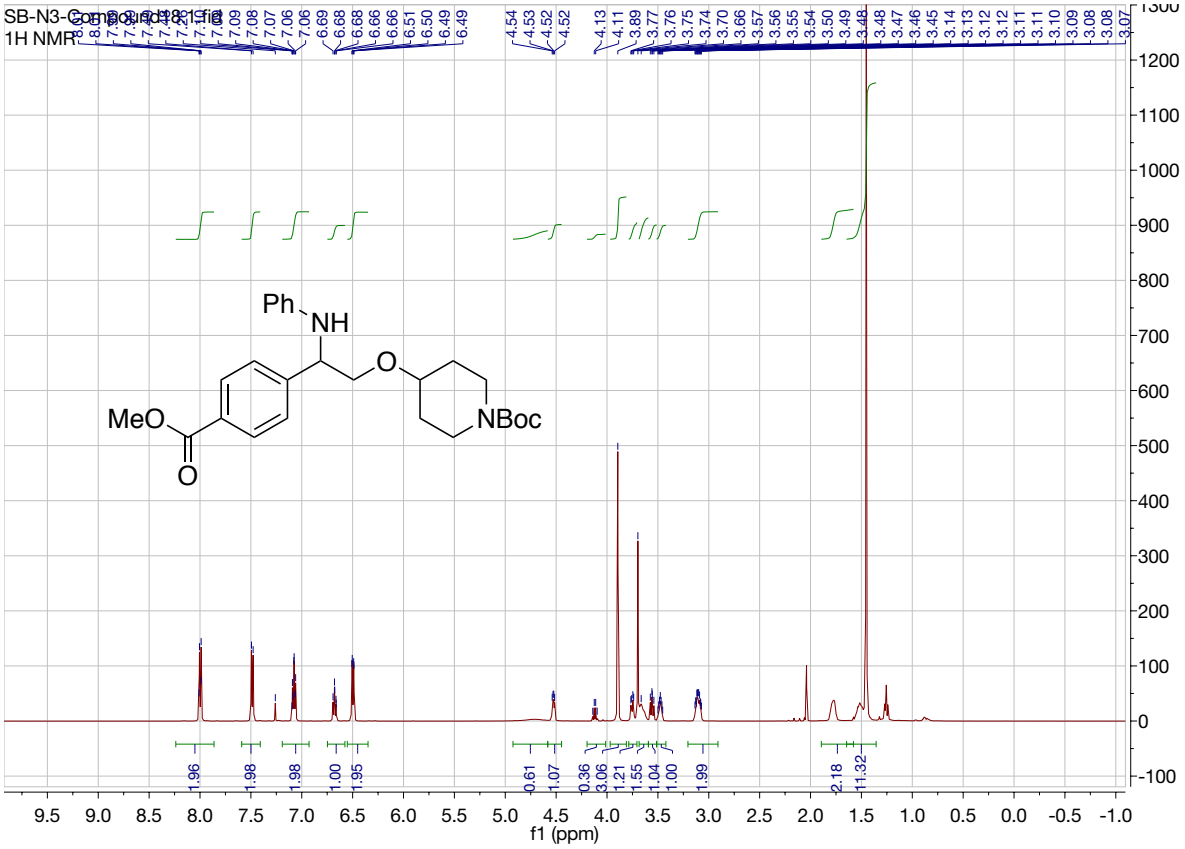
^{1}H NMR spectrum of compound **17** ($CDCl_3$, 500 MHz).



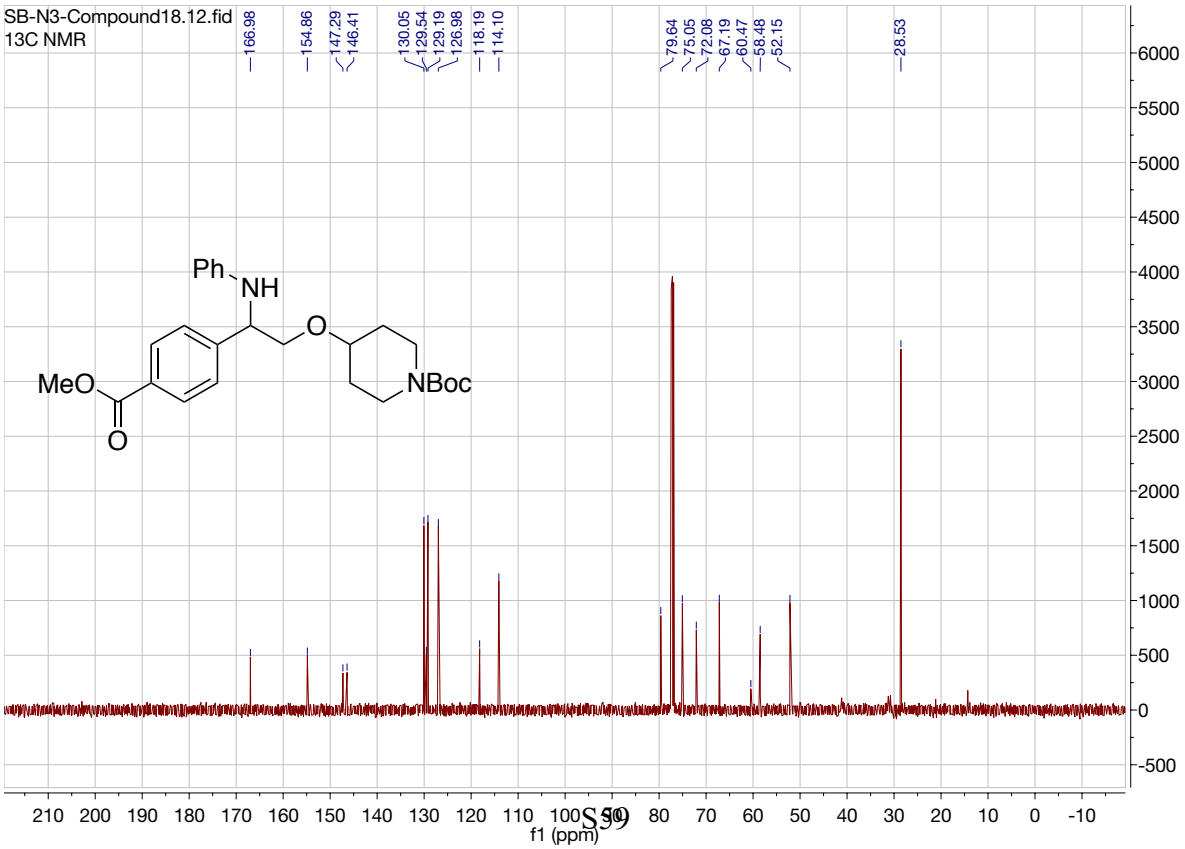
^{13}C NMR spectrum of compound **17** ($CDCl_3$, 126 MHz).



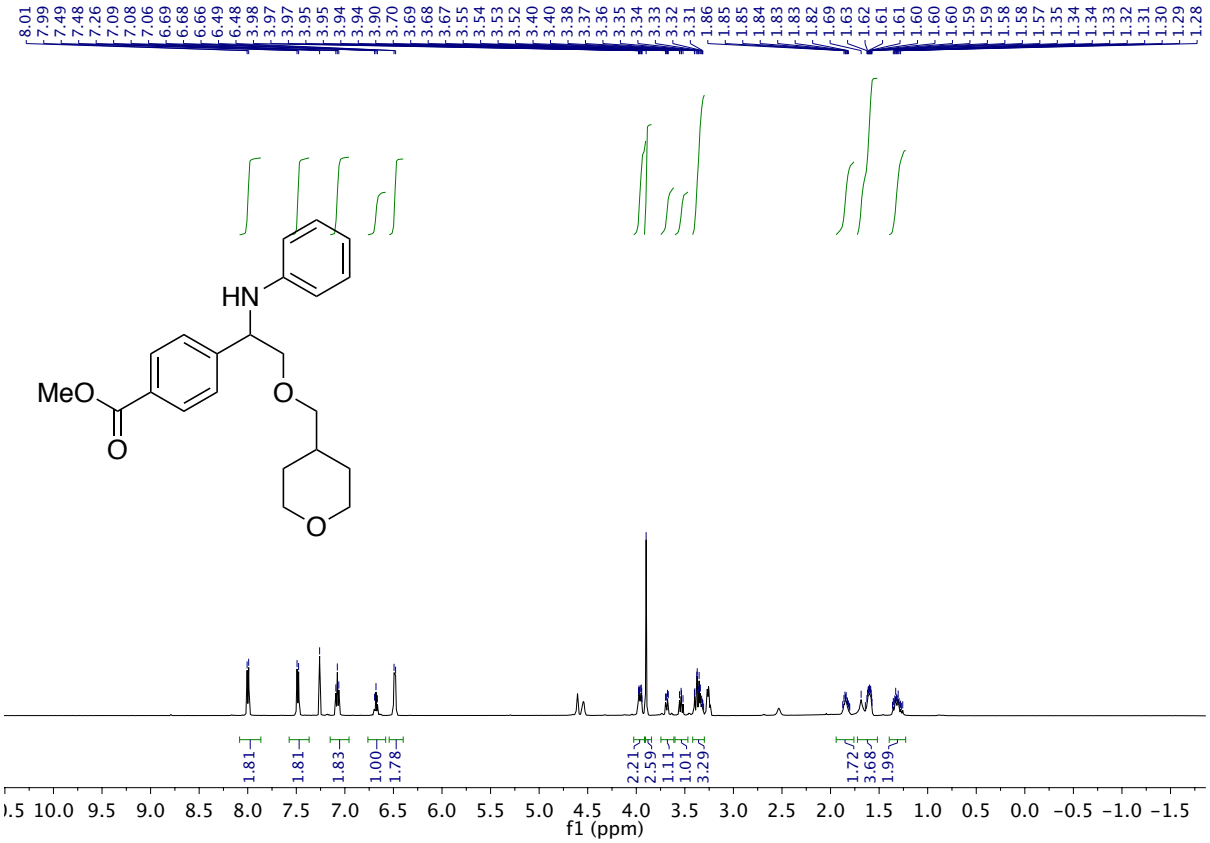
^{1}H NMR spectrum of compound **18** ($CDCl_3$, 500 MHz).



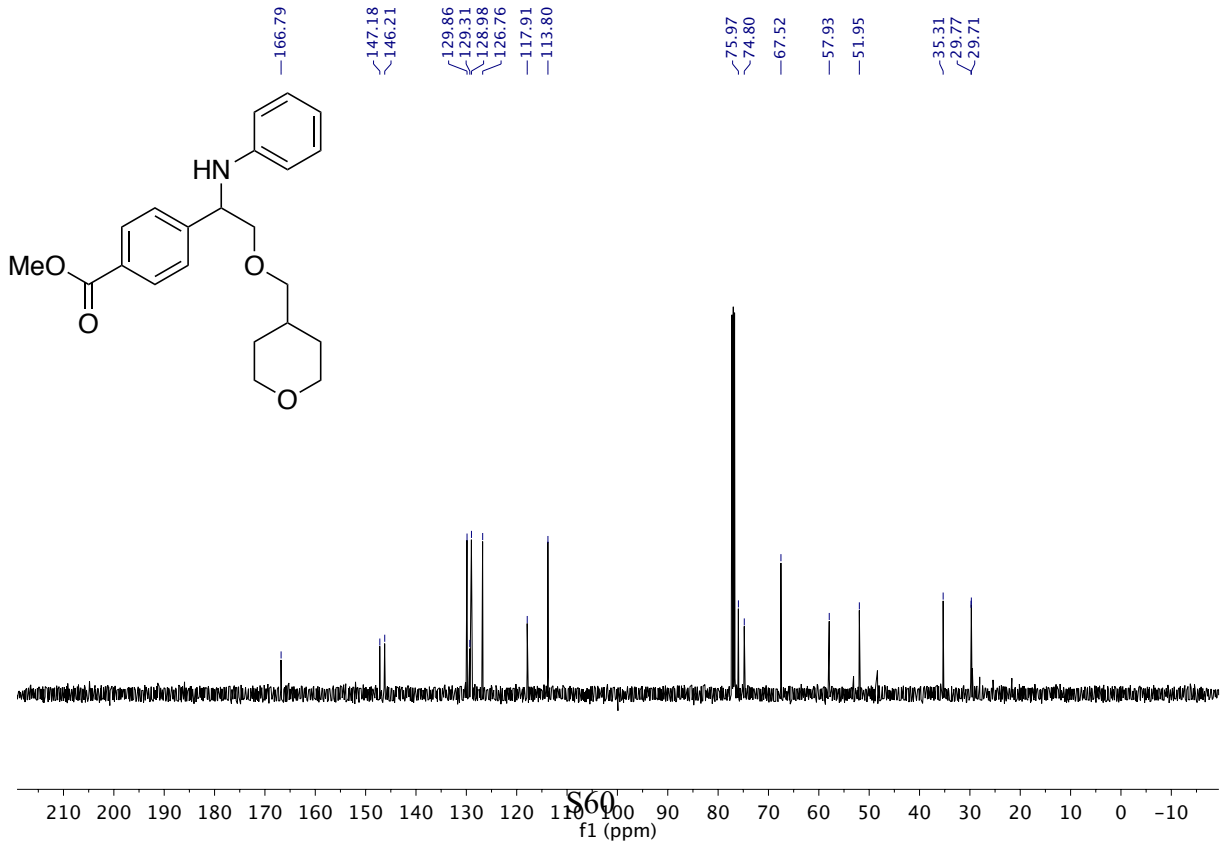
^{13}C NMR spectrum of compound **18** ($CDCl_3$, 126 MHz).



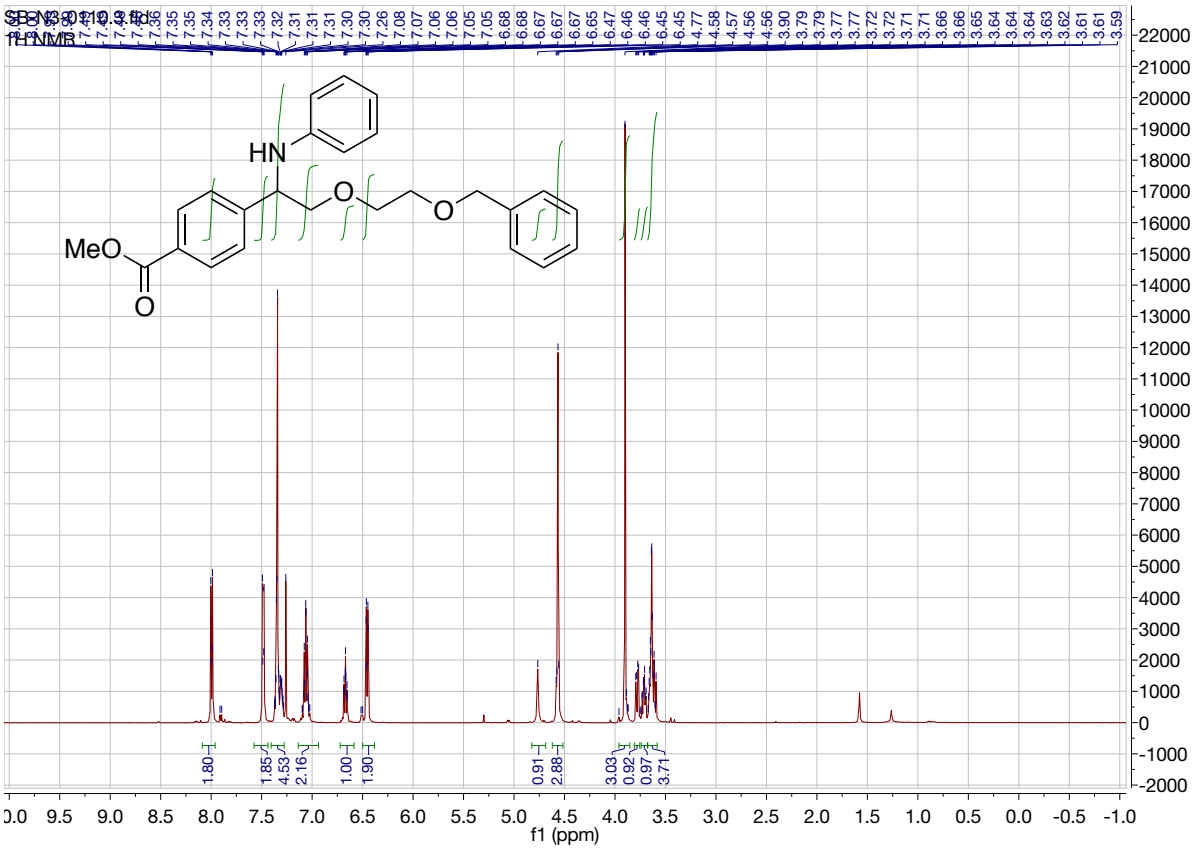
^{1}H NMR spectrum of compound **19** ($CDCl_3$, 500 MHz).



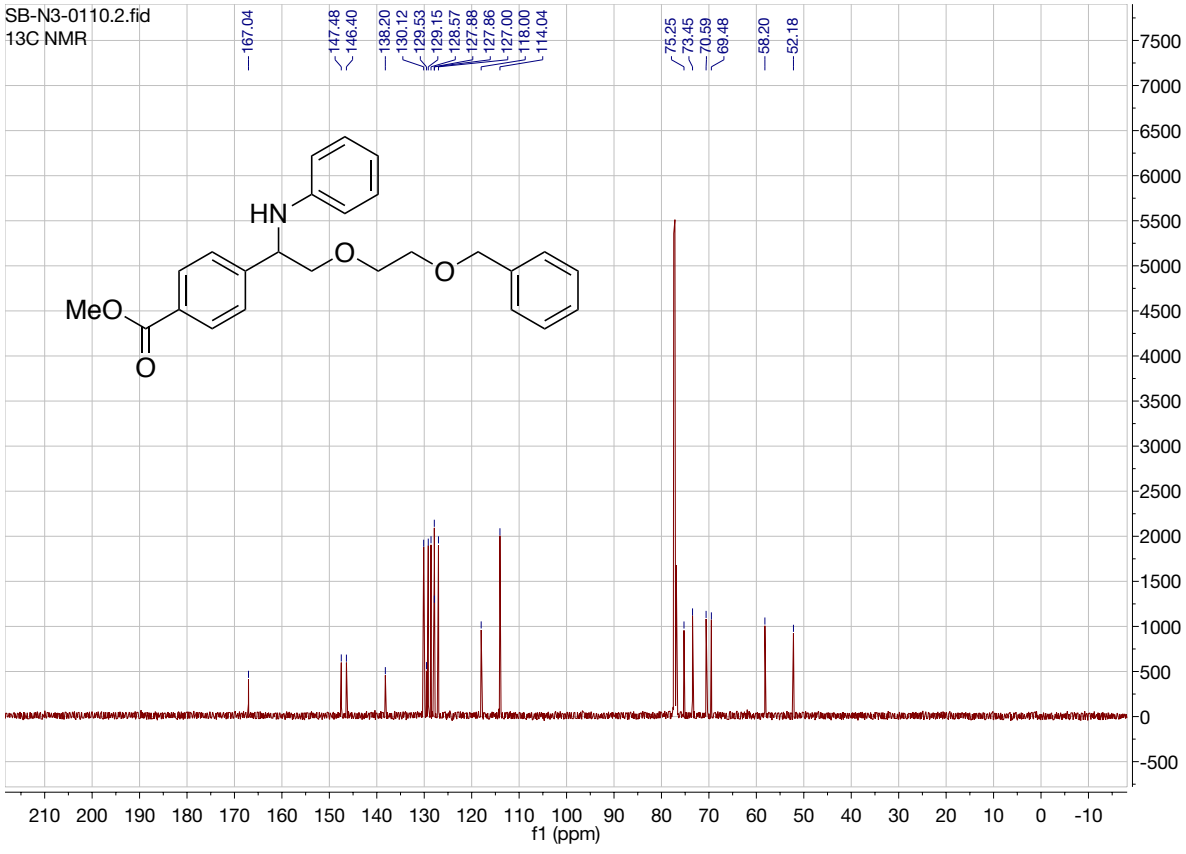
^{13}C NMR spectrum of compound **19** ($CDCl_3$, 126 MHz).



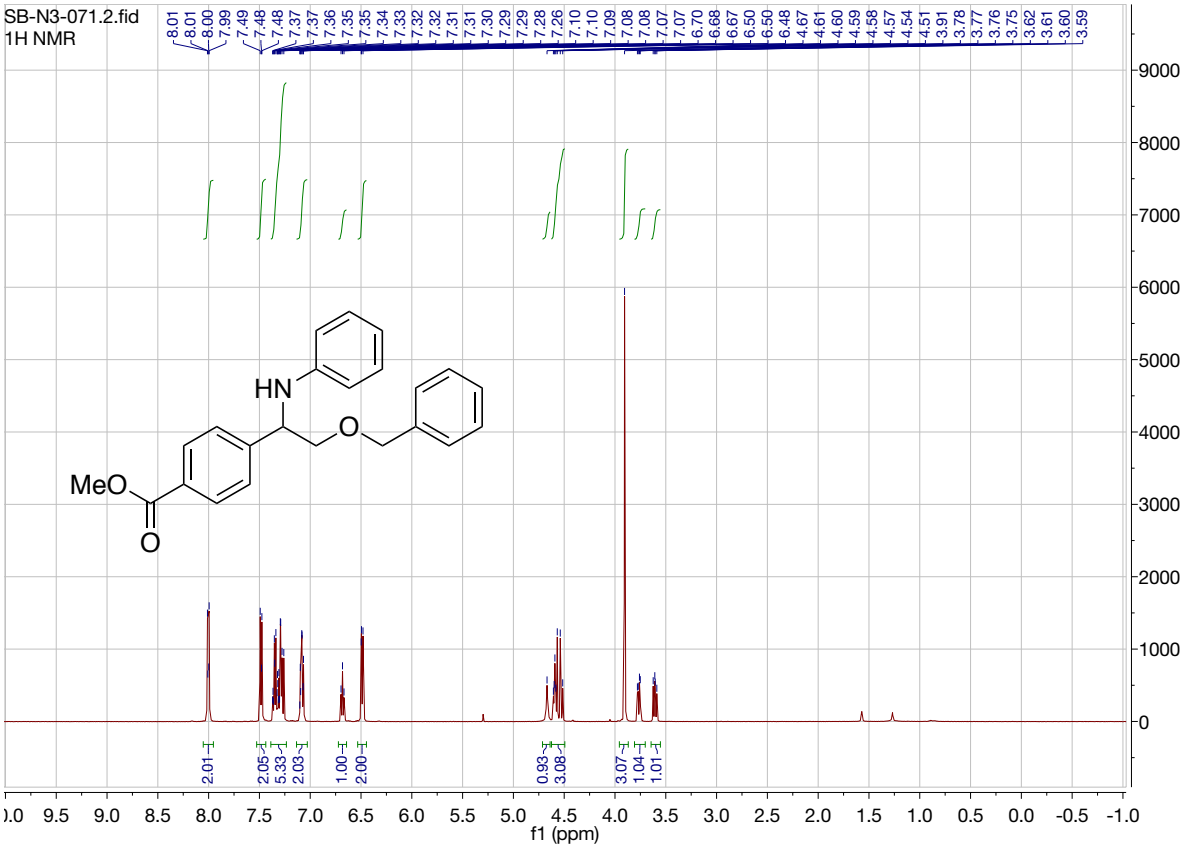
[1] H NMR spectrum of compound **20** ($CDCl_3$, 500 MHz).



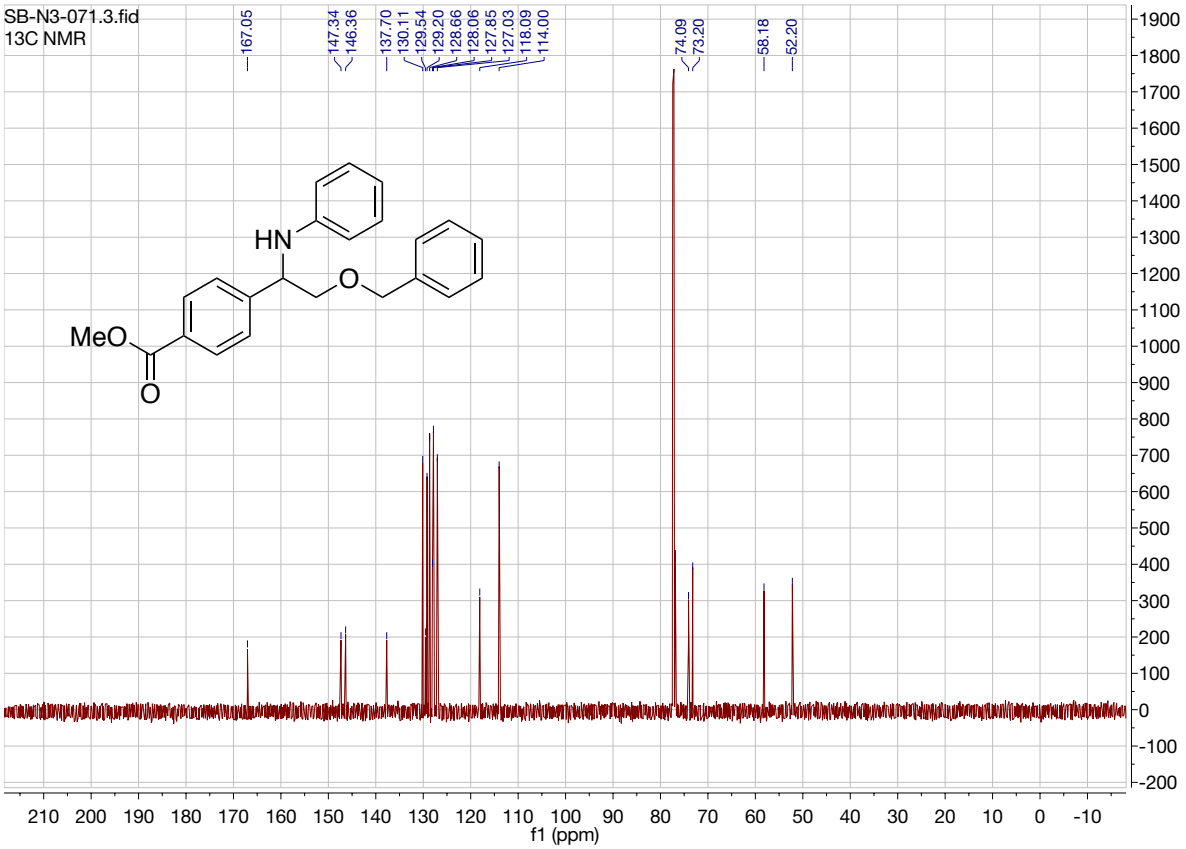
[13] C NMR spectrum of compound **20** ($CDCl_3$, 126 MHz).



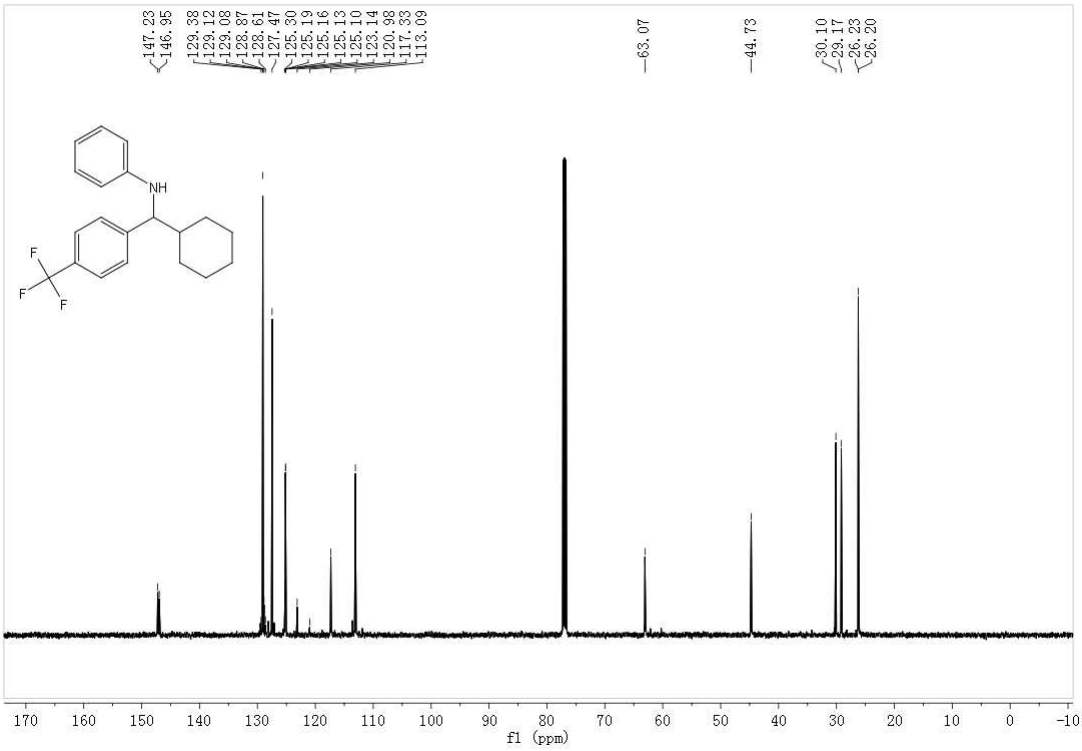
^{1}H NMR spectrum of compound **21** ($CDCl_3$, 500 MHz).



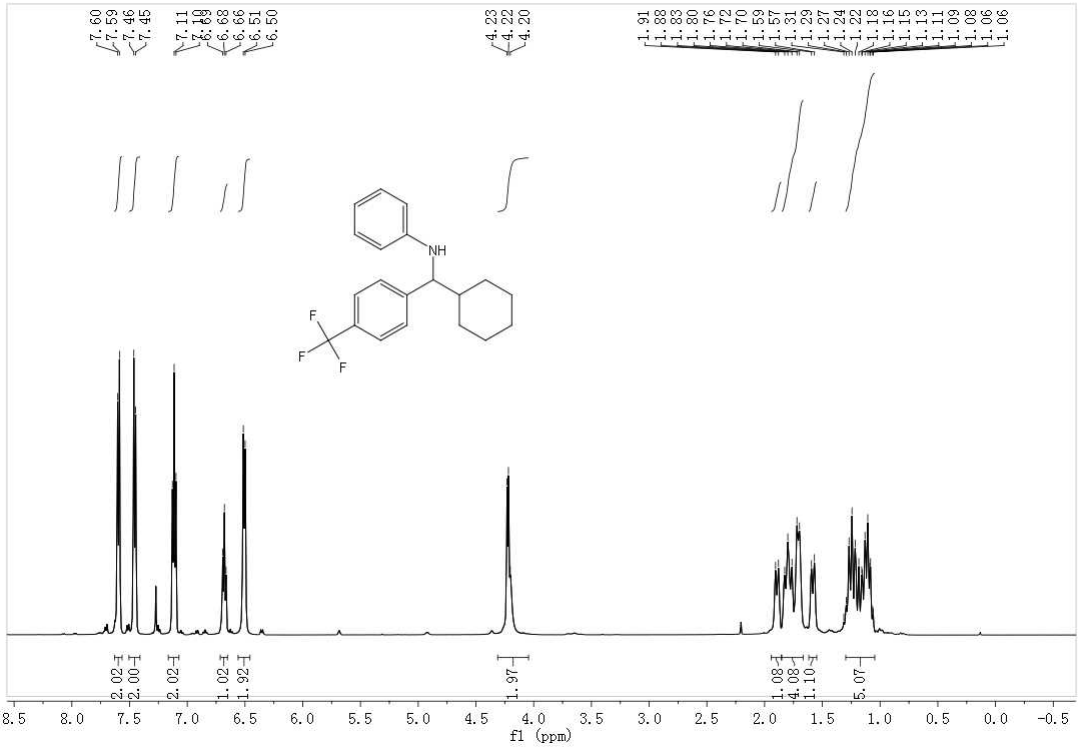
^{13}C NMR spectrum of compound **21** ($CDCl_3$, 126 MHz).



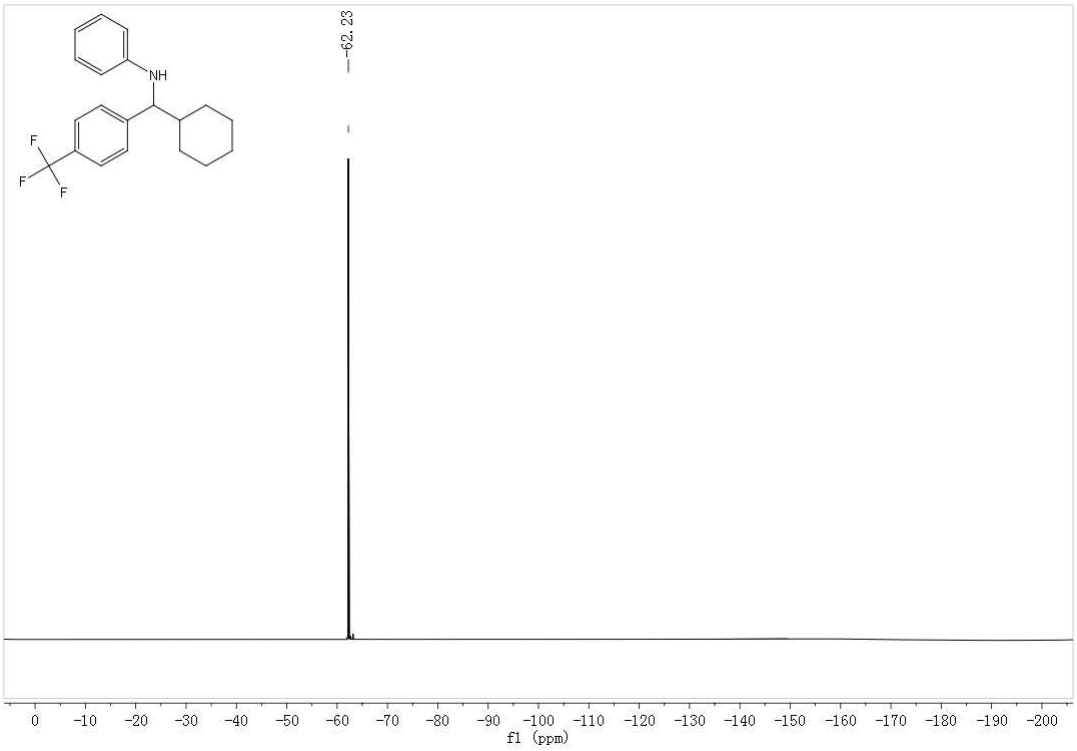
^{1}H NMR spectrum of compound **22** ($CDCl_3$, 500 MHz).



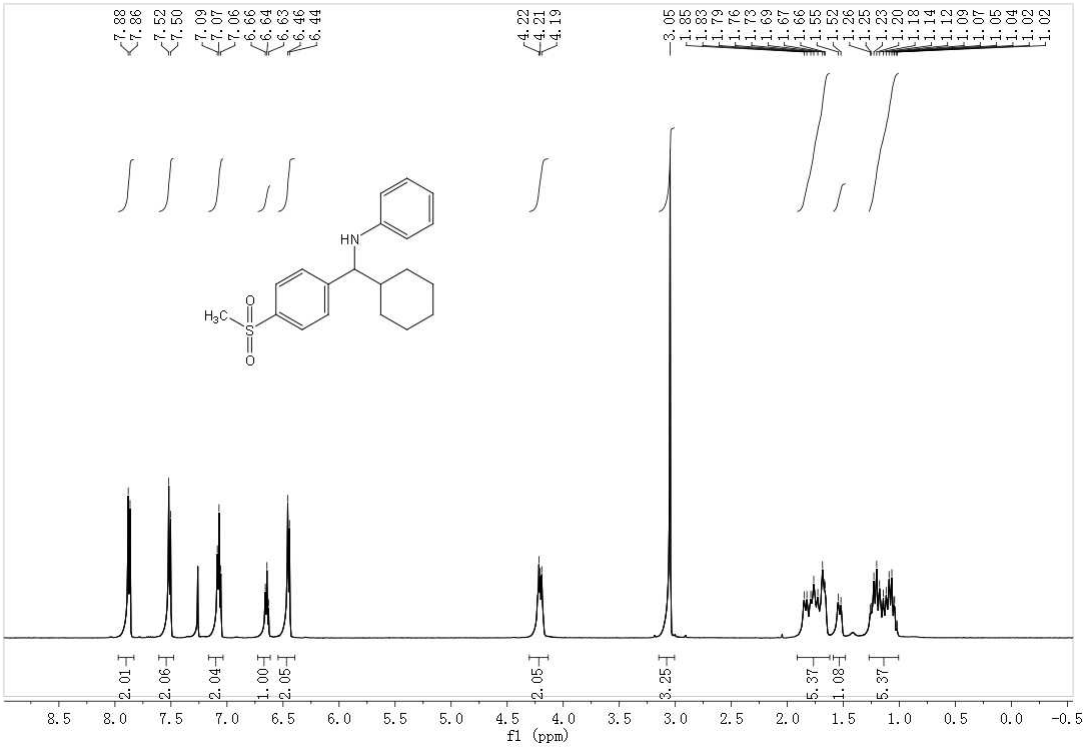
^{13}C NMR spectrum of compound **22** ($CDCl_3$, 126 MHz).



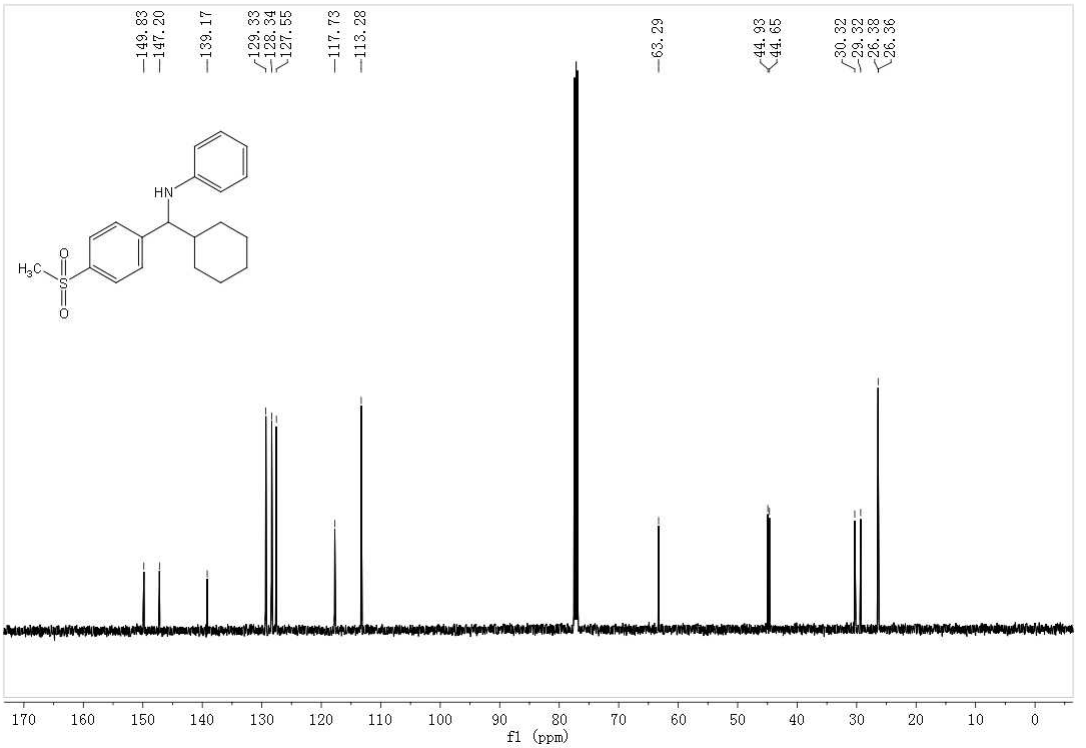
^{19}F NMR spectrum of compound **22** ($CDCl_3$, 471 MHz).



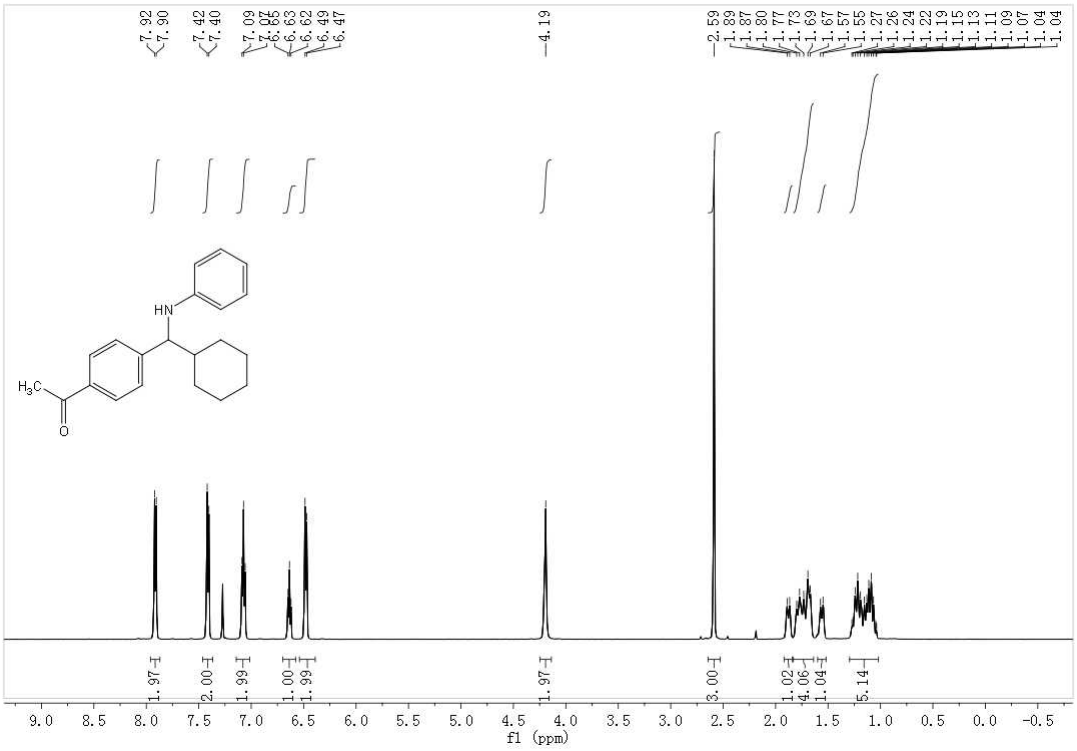
^{1}H NMR spectrum of compound **23** ($CDCl_3$, 500 MHz).



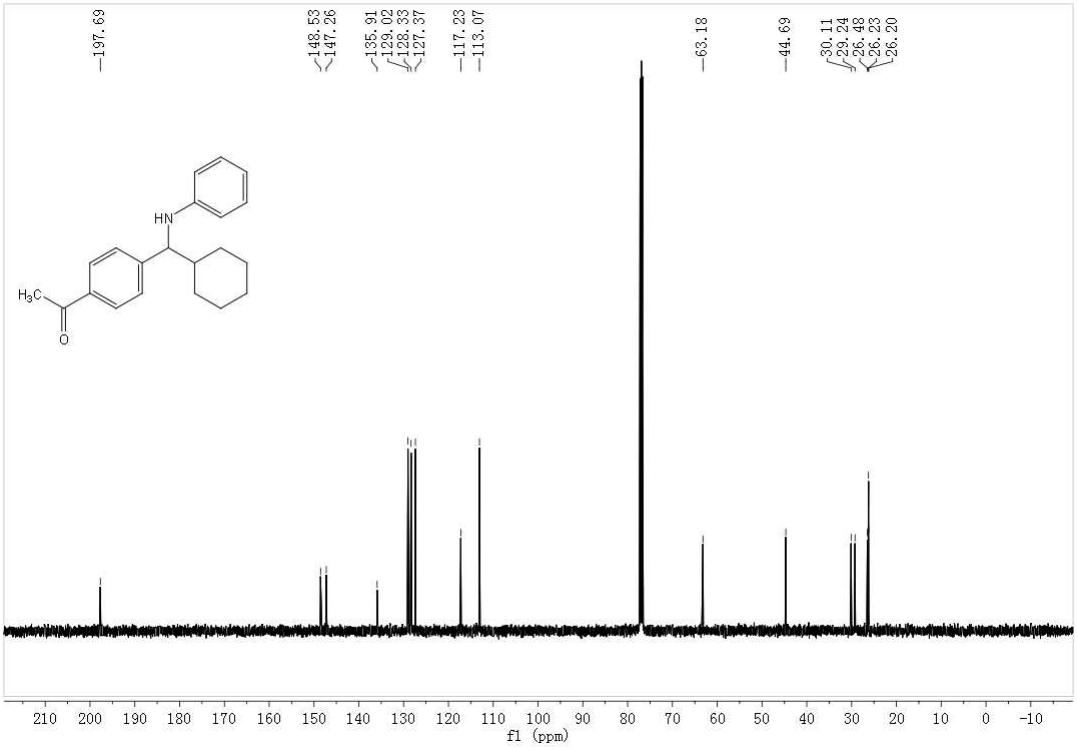
^{13}C NMR spectrum of compound **23** ($CDCl_3$, 126 MHz).



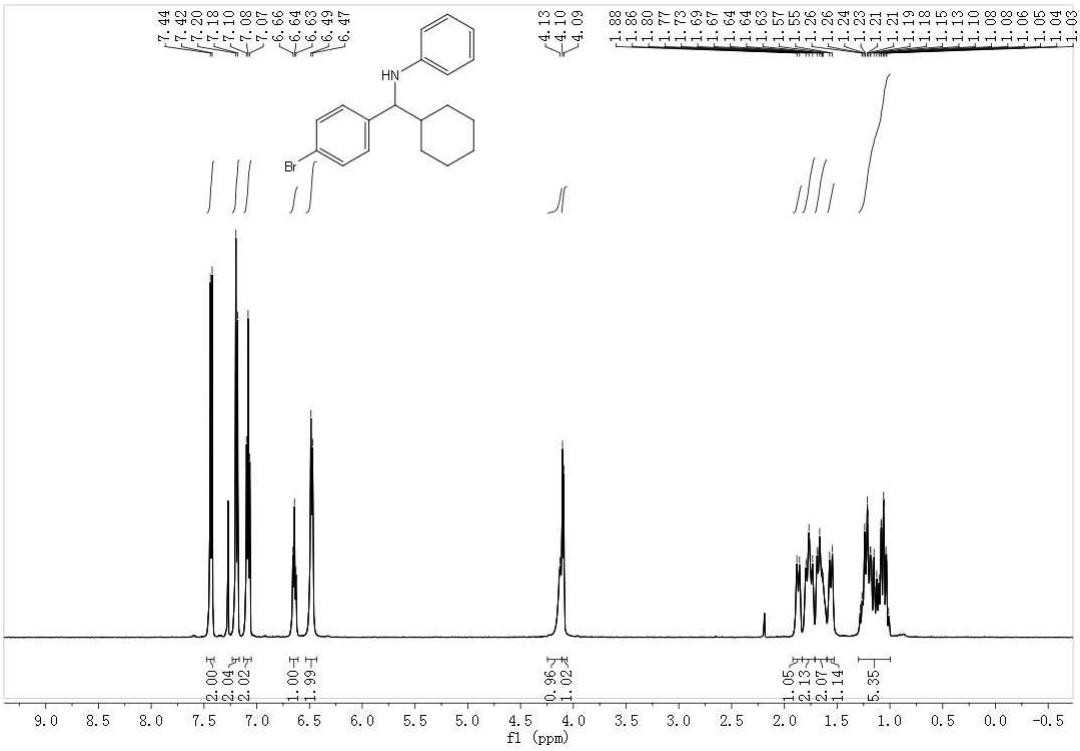
^{1}H NMR spectrum of compound **24** ($CDCl_3$, 500 MHz).



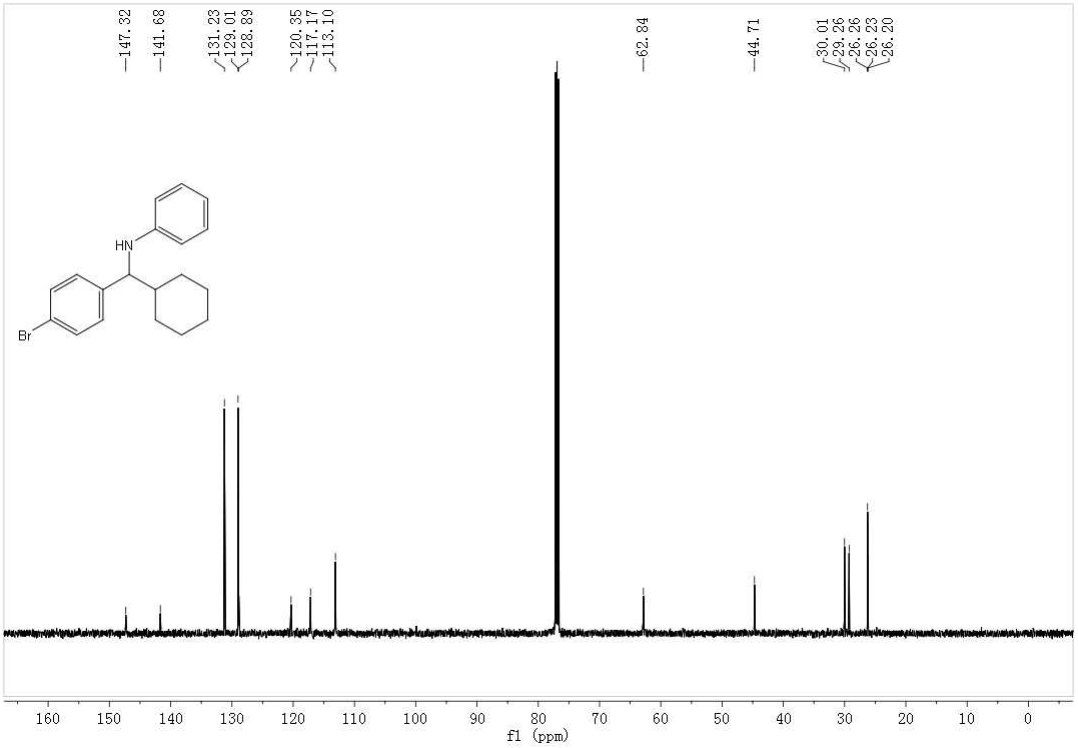
^{13}C NMR spectrum of compound **24** ($CDCl_3$, 126 MHz).



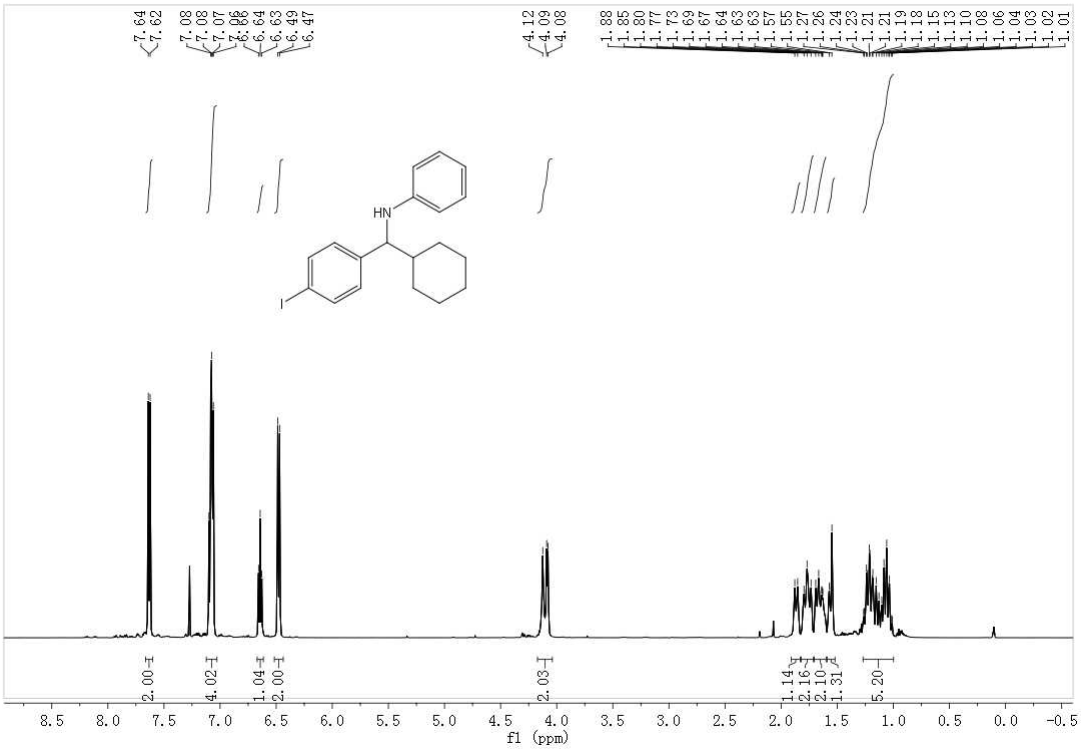
^{1}H NMR spectrum of compound **25** ($CDCl_3$, 500 MHz).



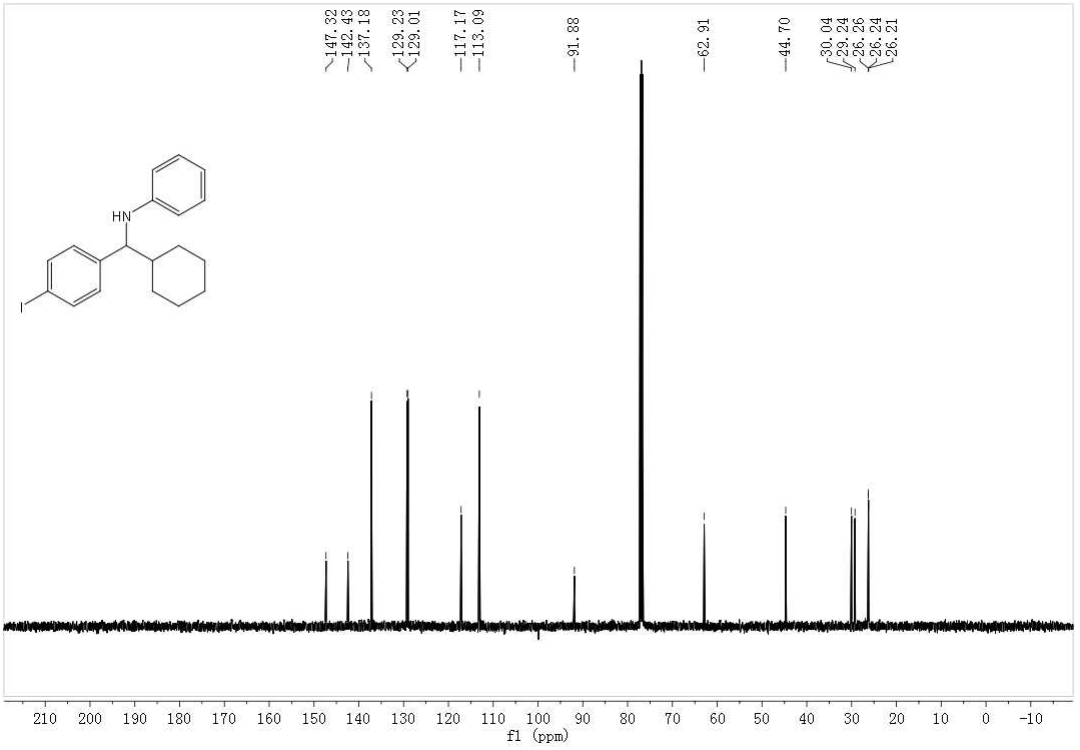
^{13}C NMR spectrum of compound **25** ($CDCl_3$, 126 MHz).



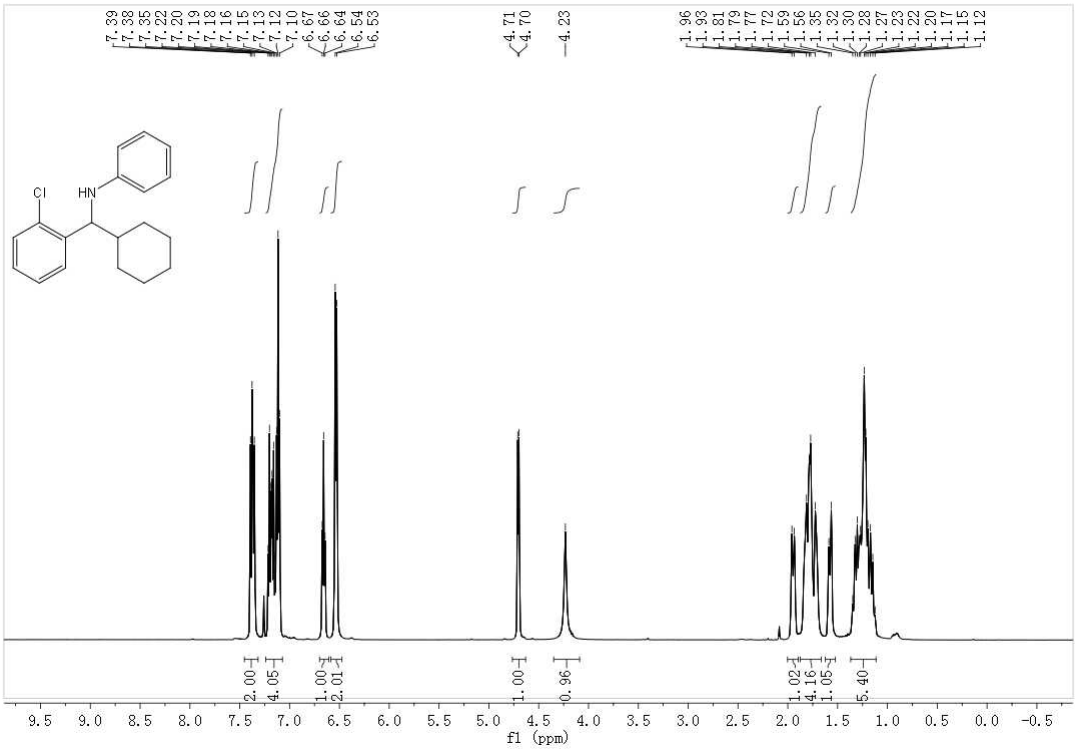
[1] H NMR spectrum of compound **26** ($CDCl_3$, 500 MHz).



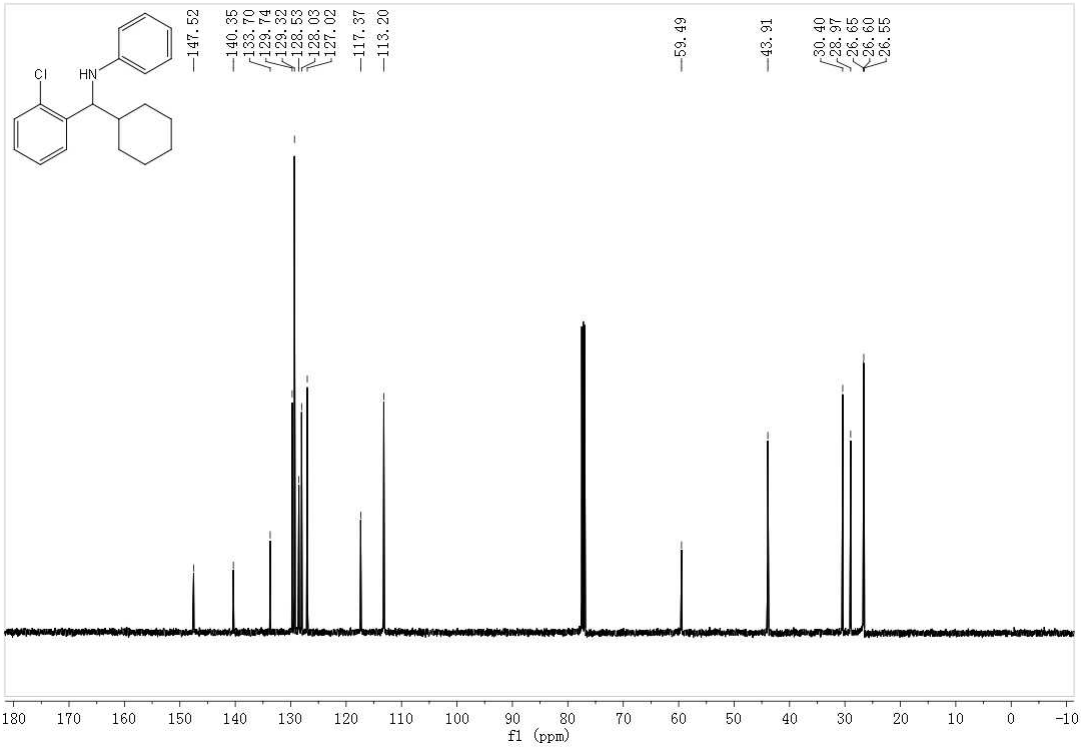
[13] C NMR spectrum of compound **26** ($CDCl_3$, 126 MHz).



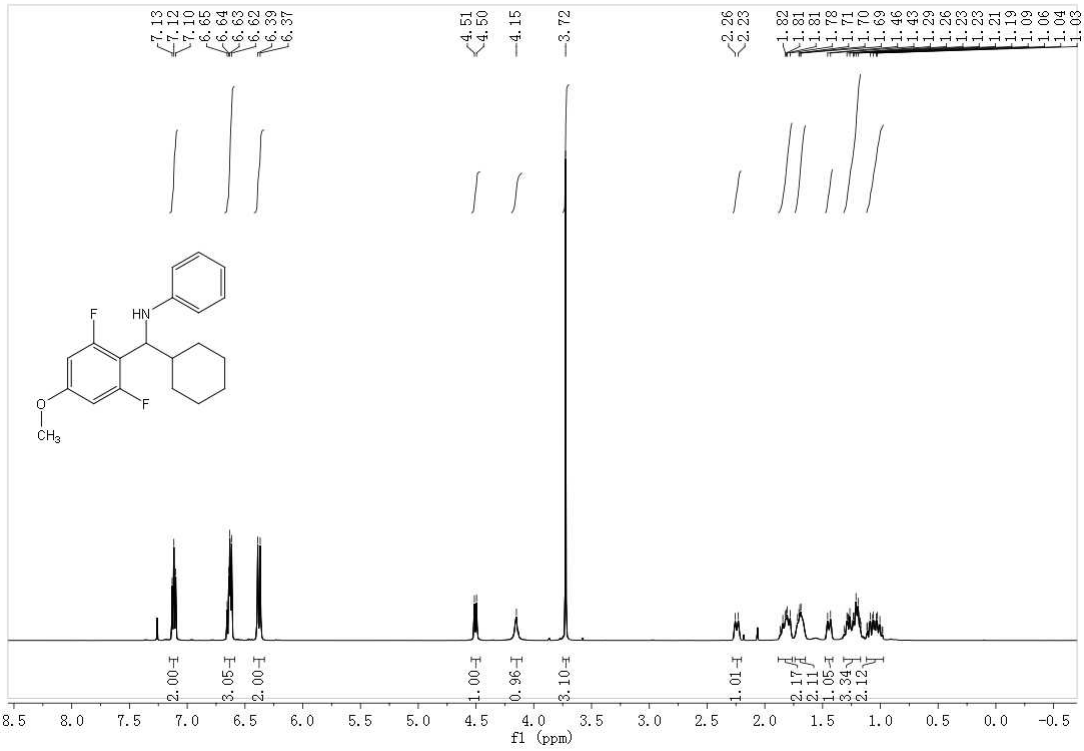
^{1}H NMR spectrum of compound **27** ($CDCl_3$, 500 MHz).



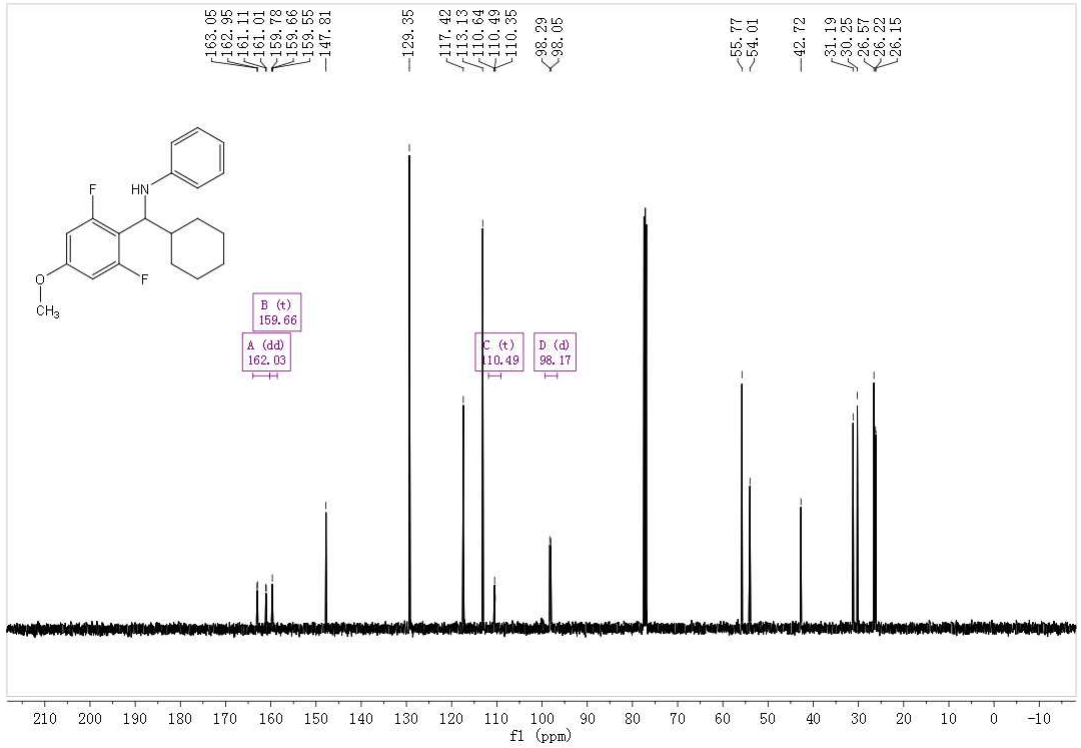
^{13}C NMR spectrum of compound **27** ($CDCl_3$, 126 MHz).



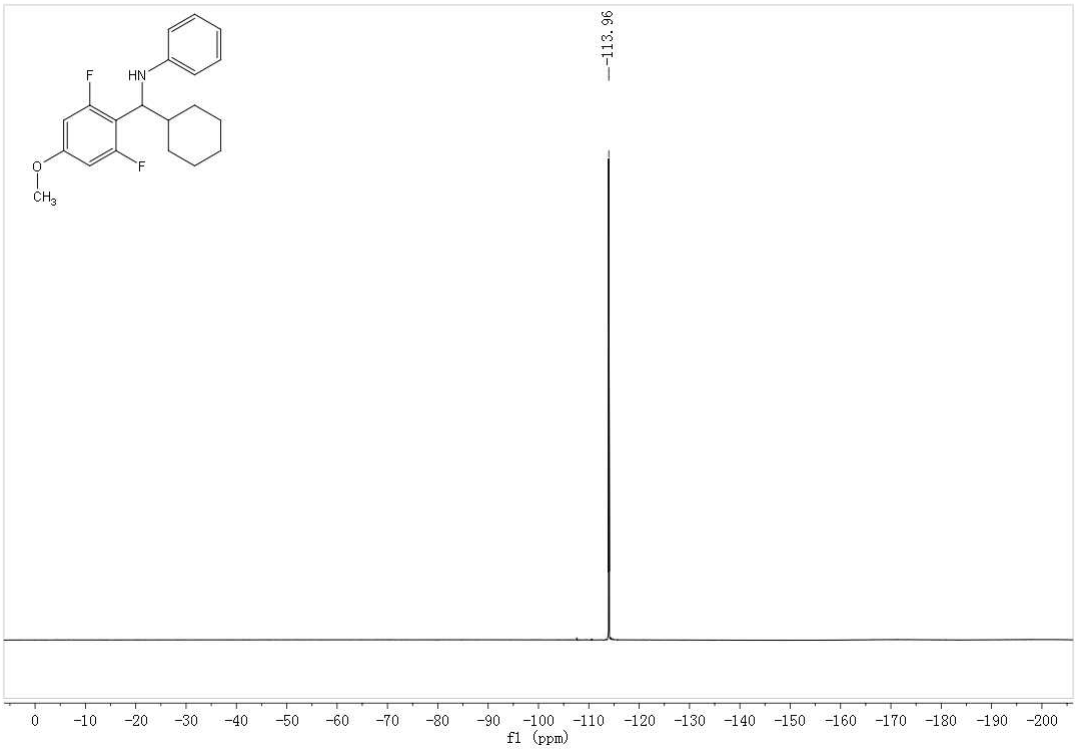
^{1}H NMR spectrum of compound **28** ($CDCl_3$, 500 MHz).



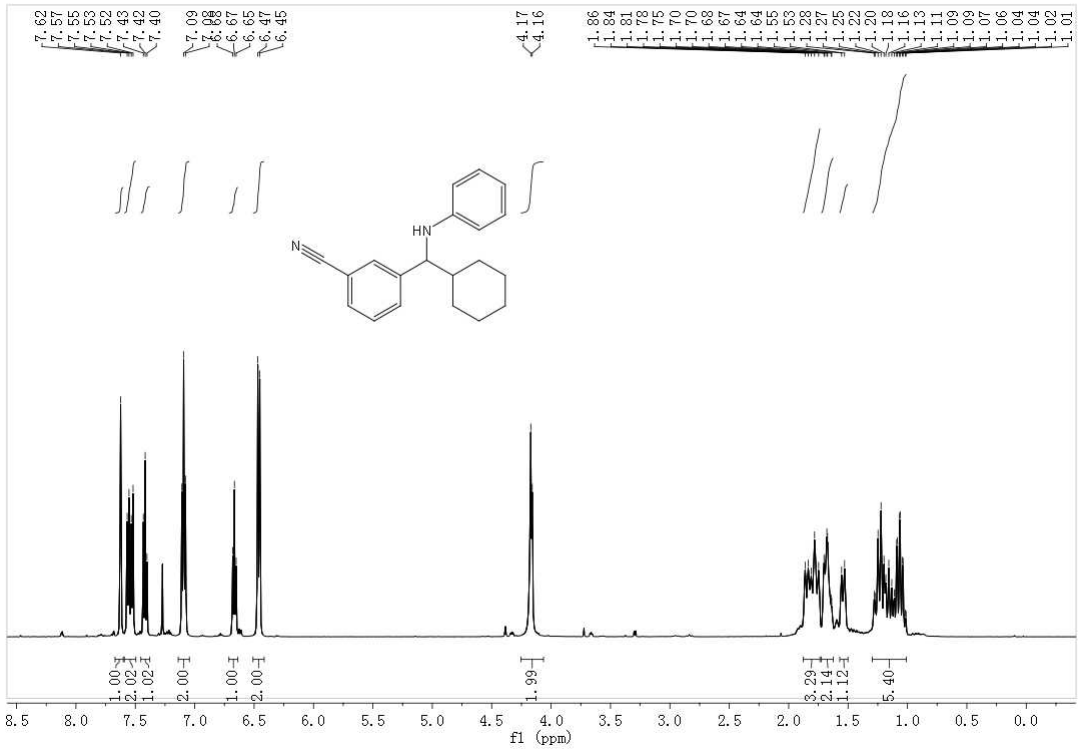
^{13}C NMR spectrum of compound **28** ($CDCl_3$, 126 MHz).



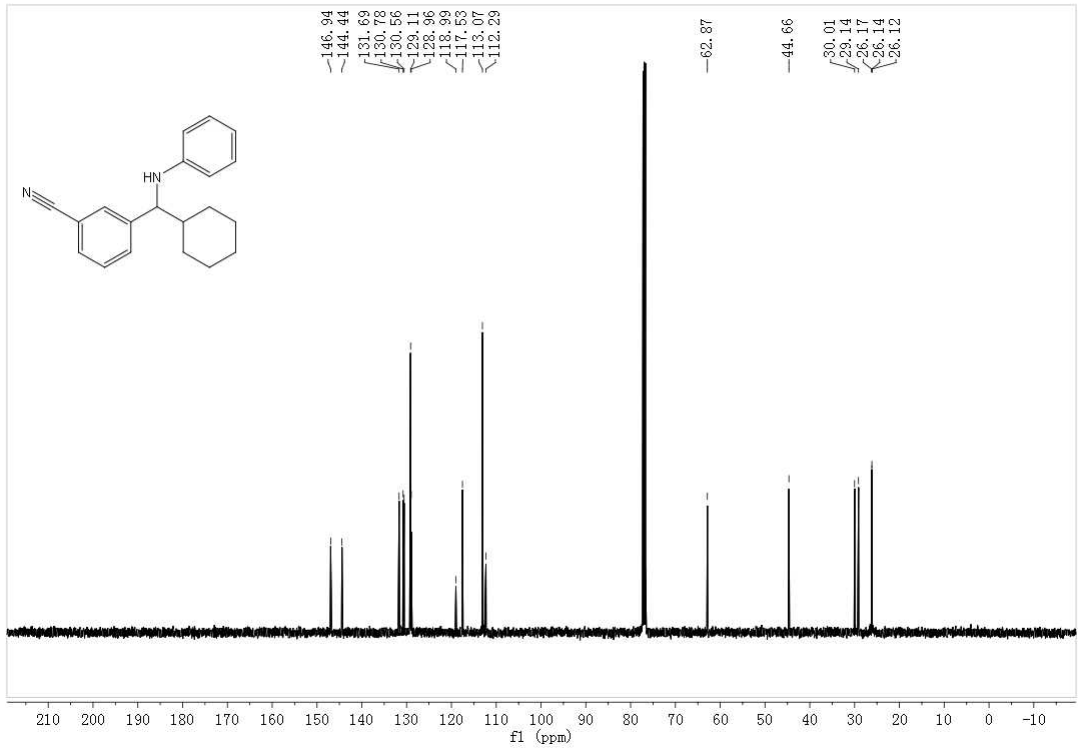
^{19}F NMR spectrum of compound **28** ($CDCl_3$, 471 MHz).



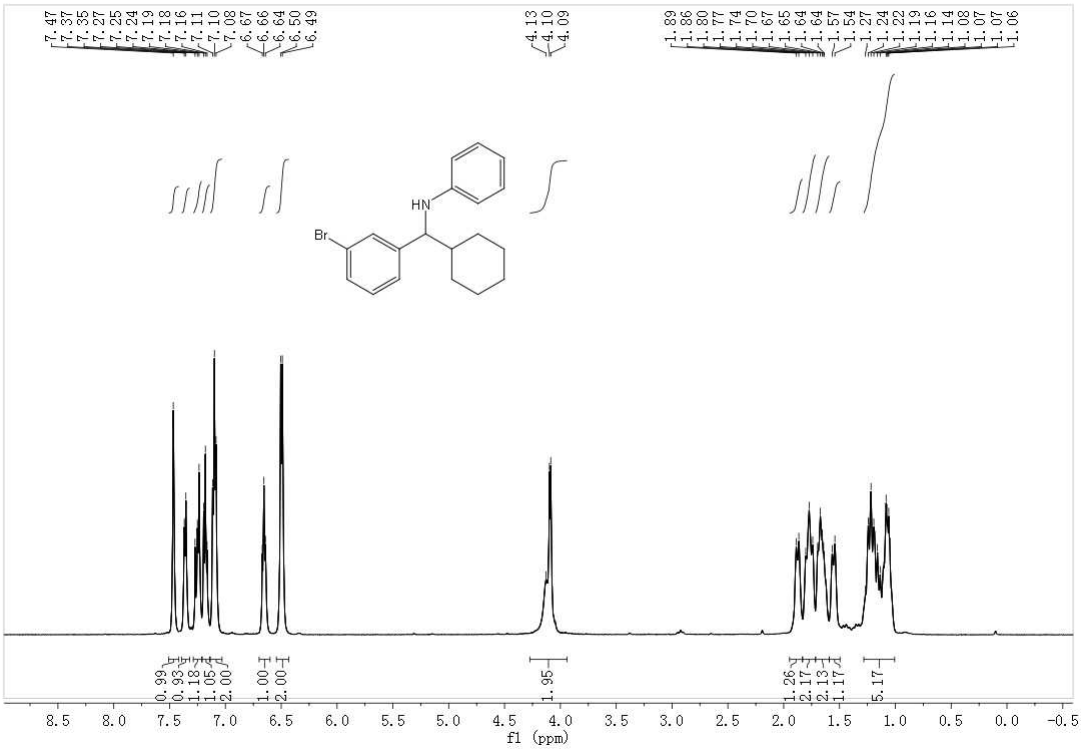
^{1}H NMR spectrum of compound **29** ($CDCl_3$, 500 MHz).



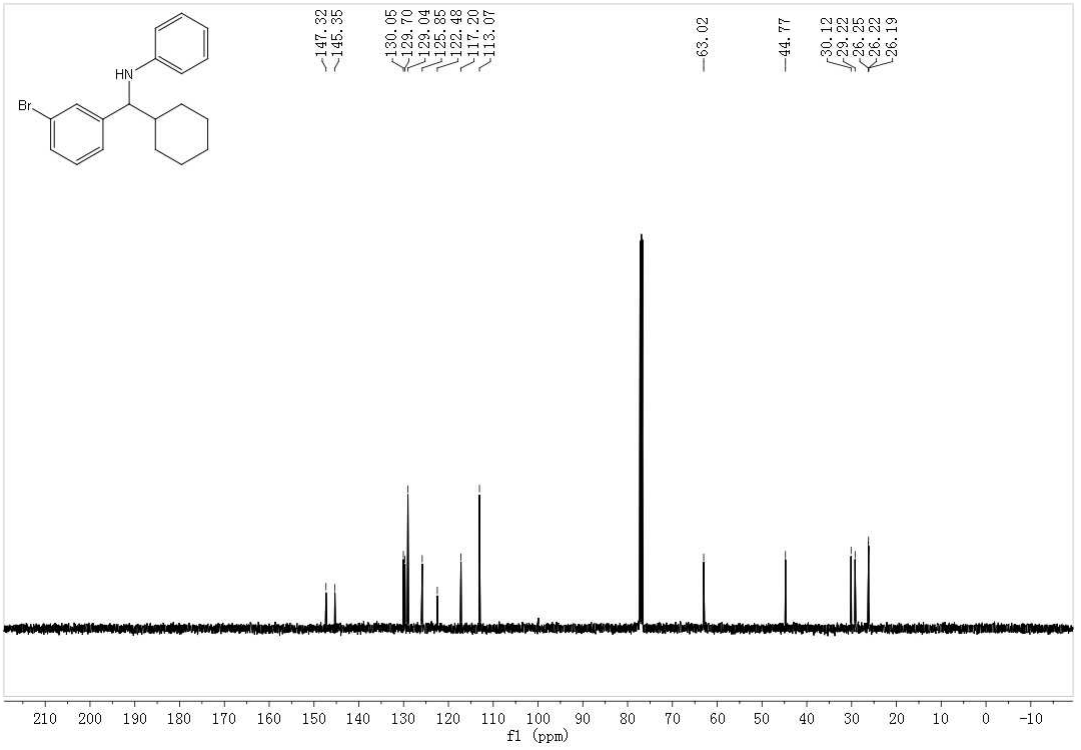
^{13}C NMR spectrum of compound **29** ($CDCl_3$, 126 MHz).



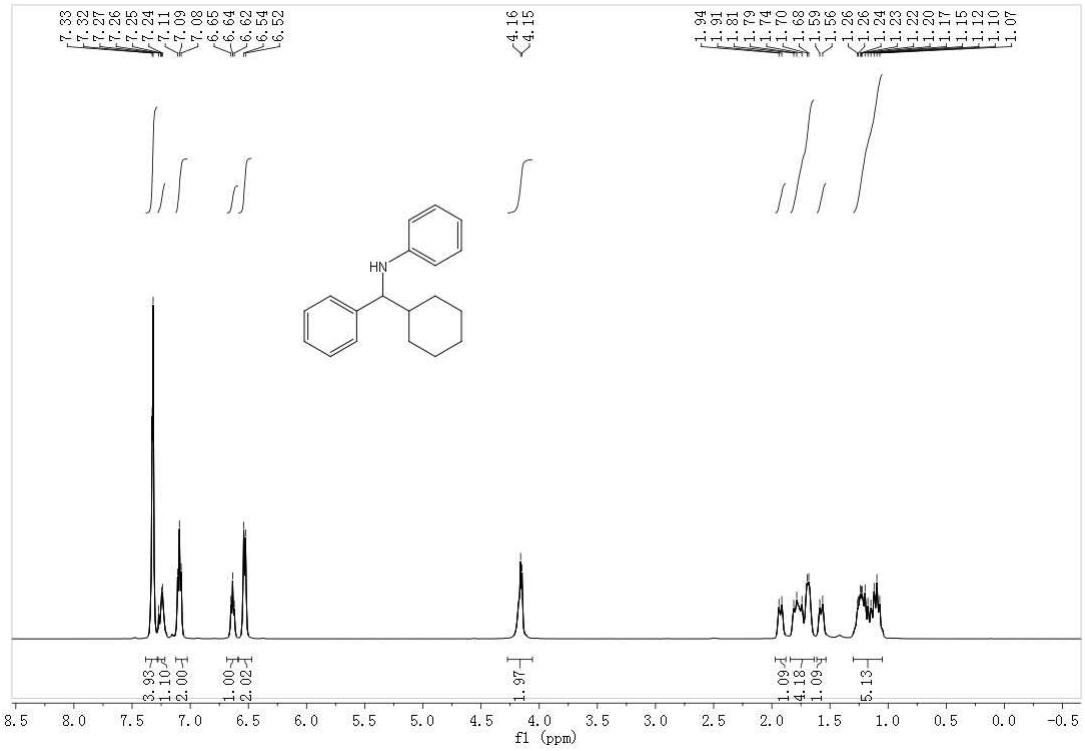
^{1}H NMR spectrum of compound **30** ($CDCl_3$, 500 MHz).



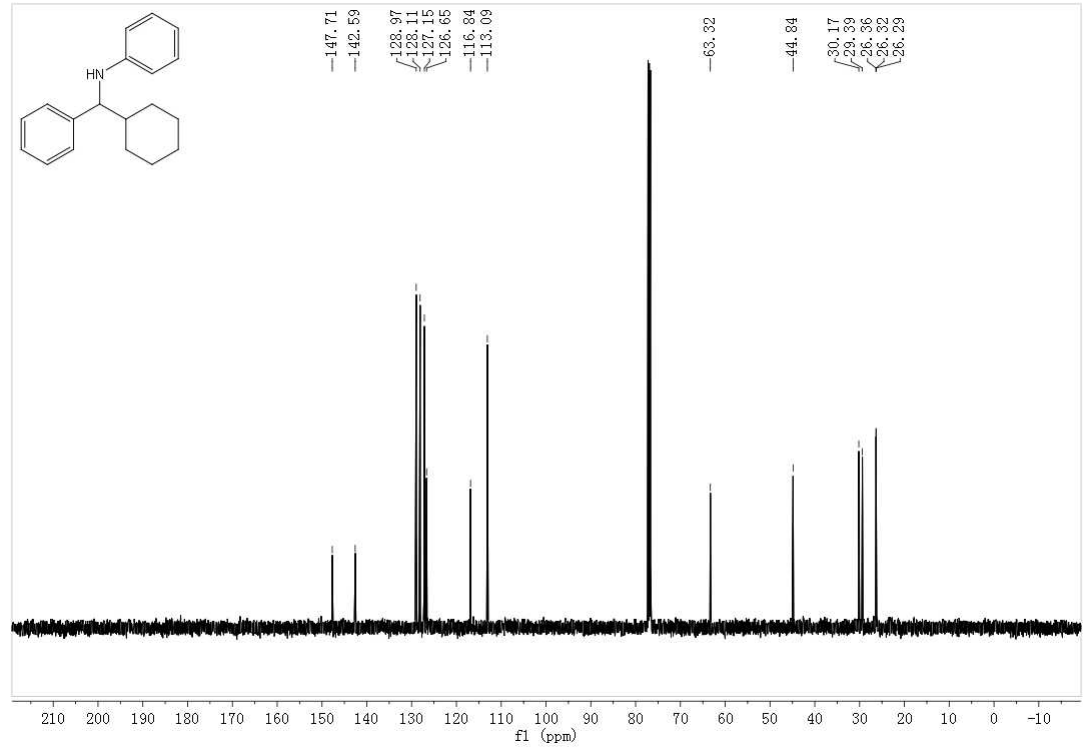
^{13}C NMR spectrum of compound **30** ($CDCl_3$, 126 MHz).



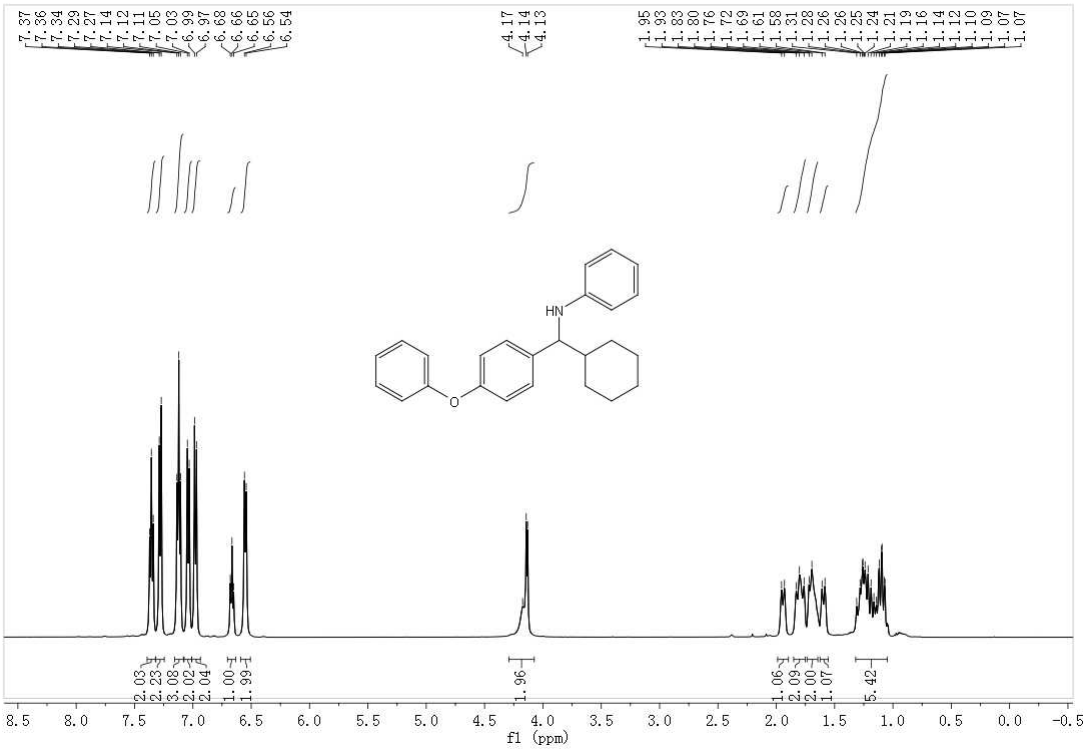
^{1}H NMR spectrum of compound **31** ($CDCl_3$, 500 MHz).



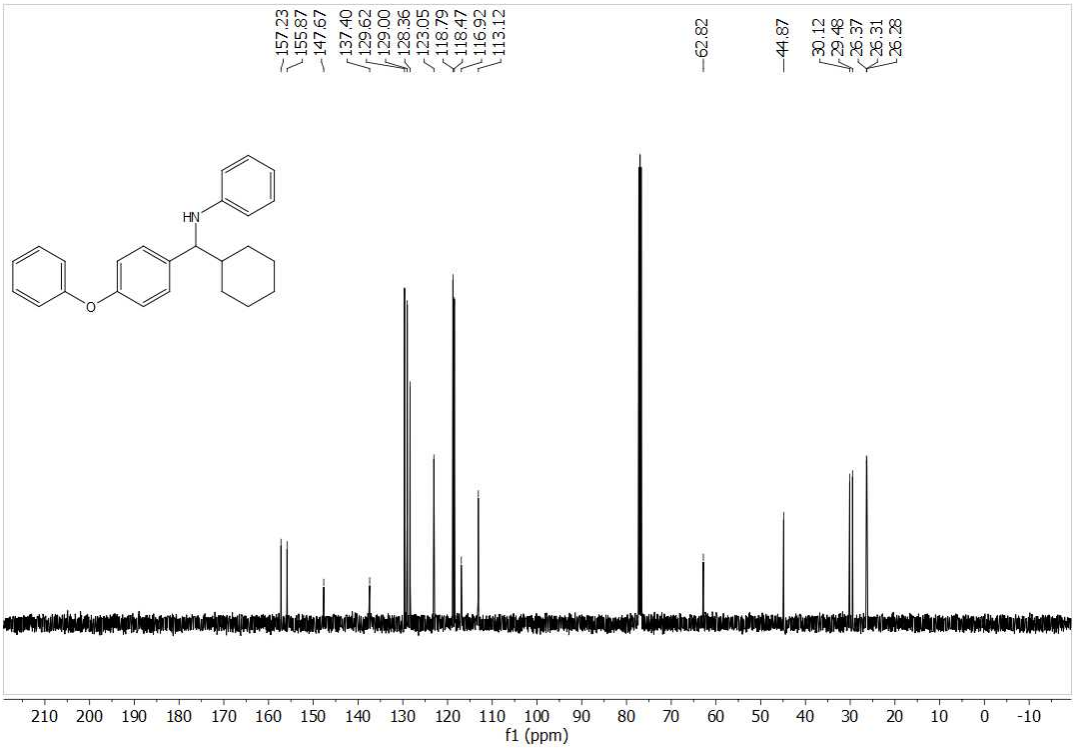
^{13}C NMR spectrum of compound **31** ($CDCl_3$, 126 MHz).



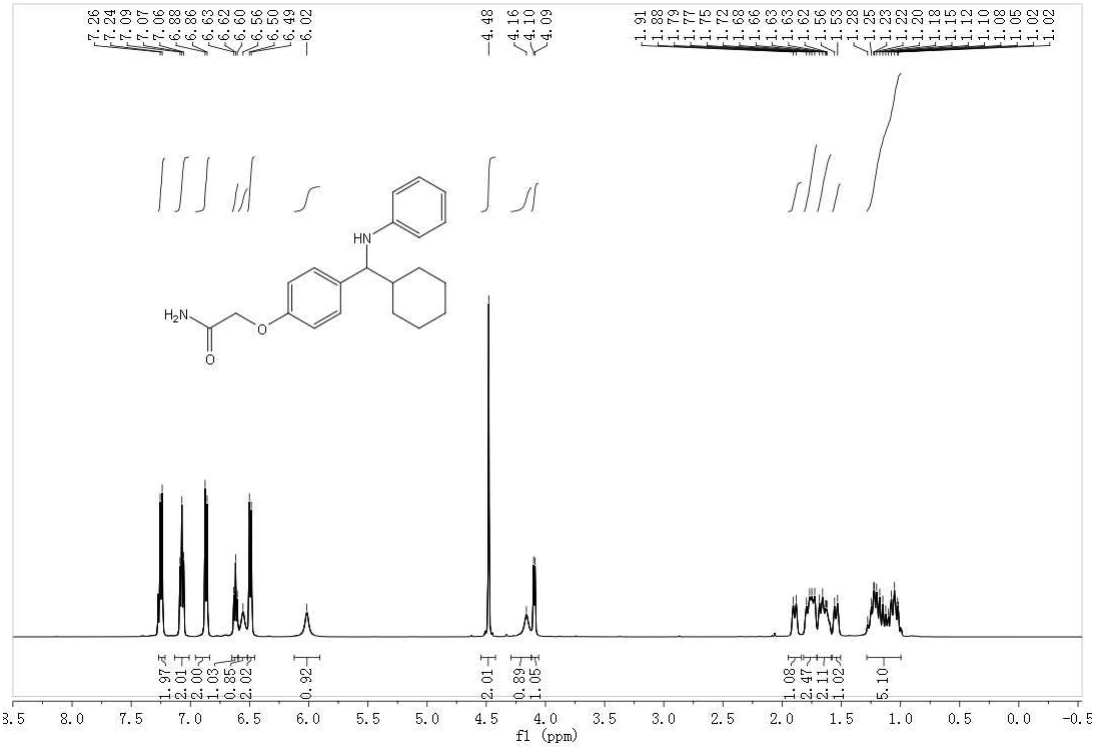
^{1}H NMR spectrum of compound **32** ($CDCl_3$, 500 MHz).



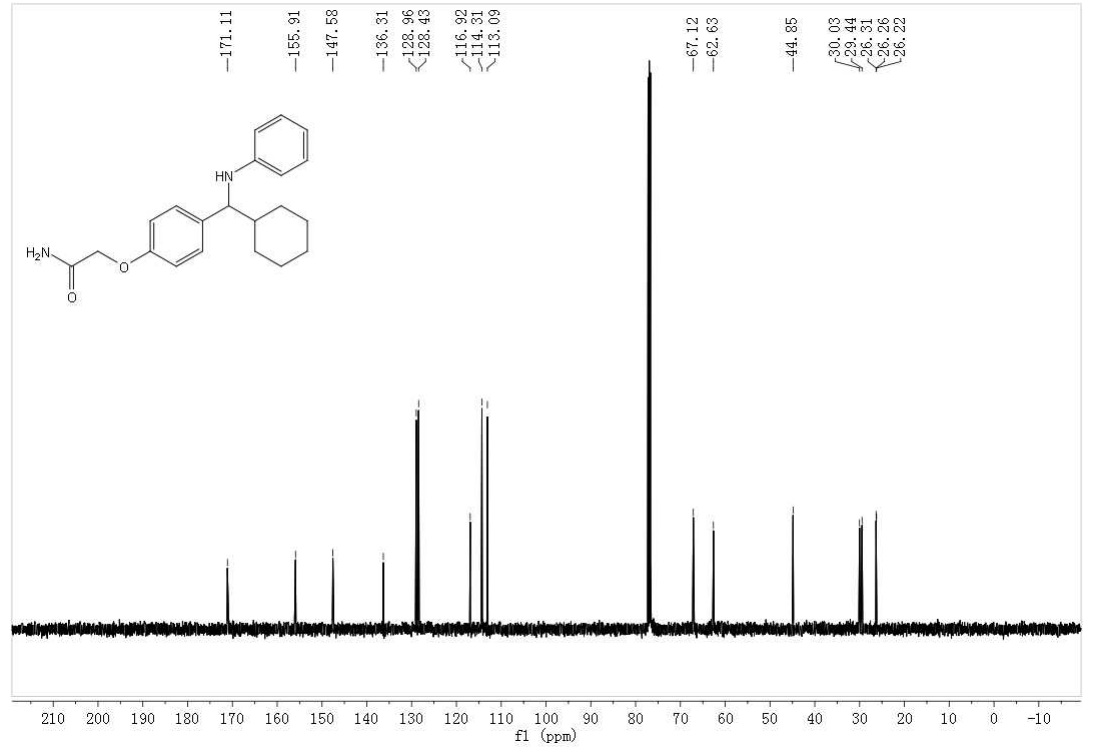
^{13}C NMR spectrum of compound **32** ($CDCl_3$, 126 MHz).



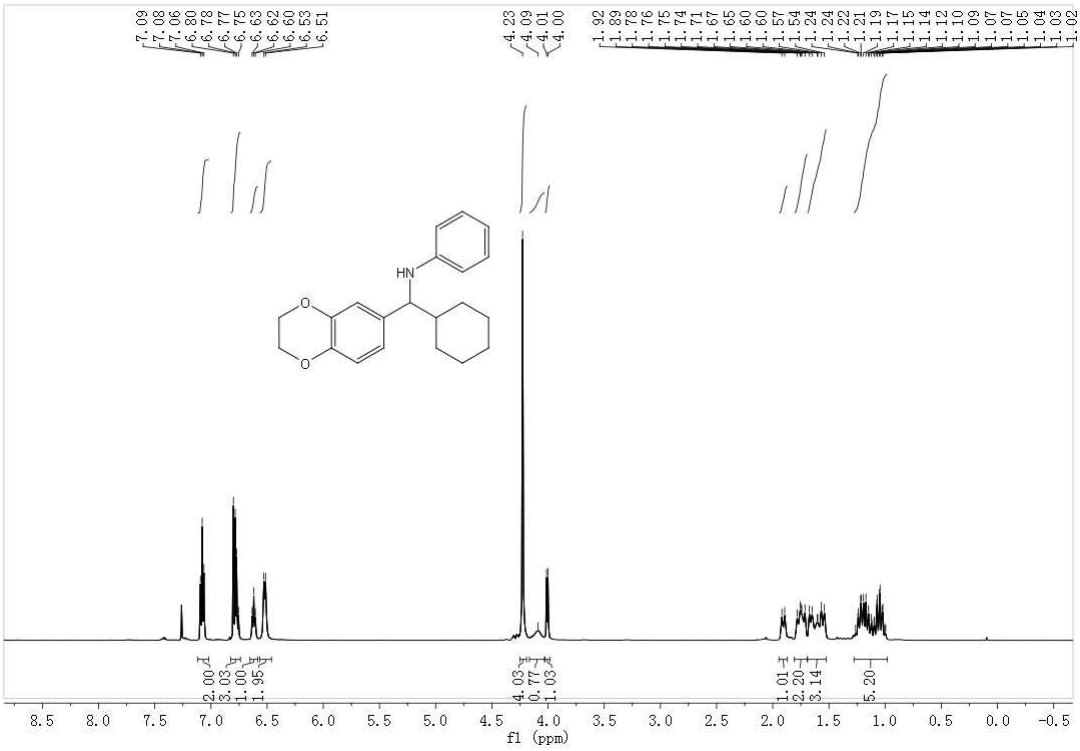
^{1}H NMR spectrum of compound **33** ($CDCl_3$, 500 MHz).



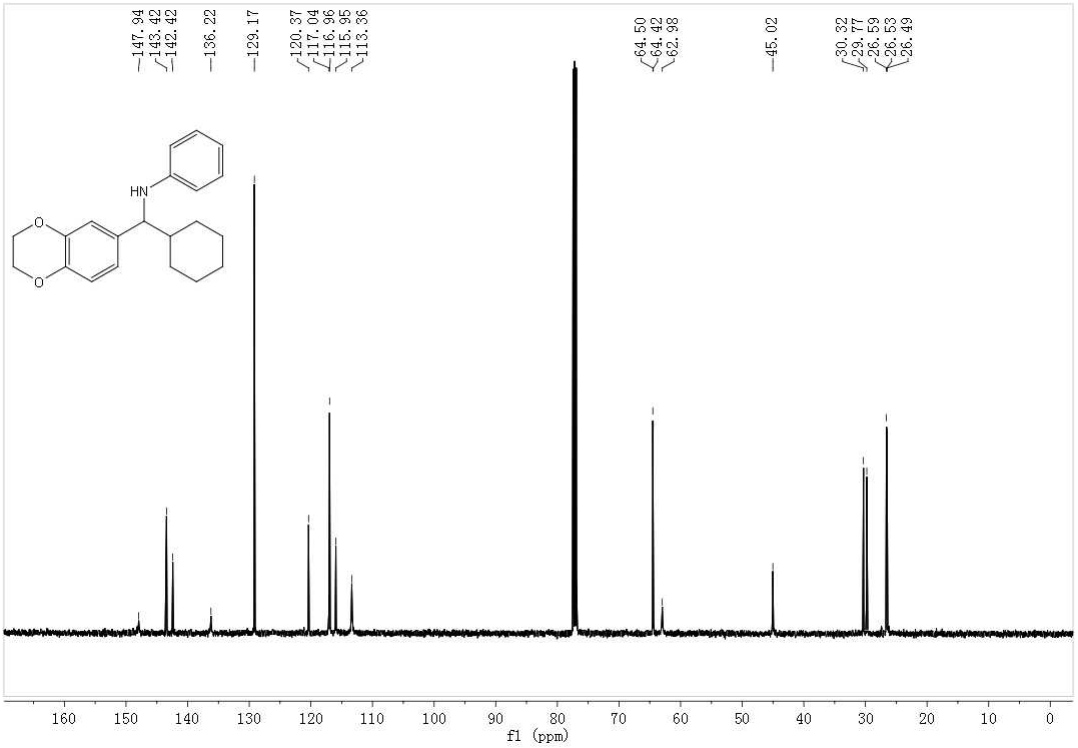
^{13}C NMR spectrum of compound **33** ($CDCl_3$, 126 MHz).



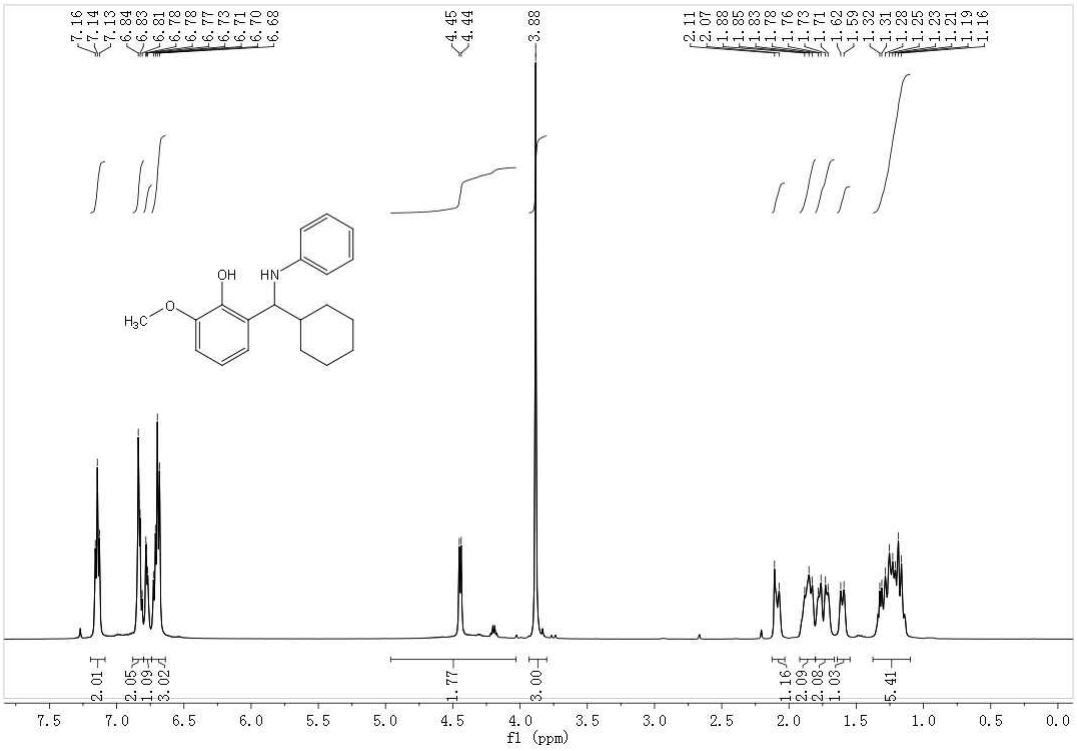
^{1}H NMR spectrum of compound **34** ($CDCl_3$, 500 MHz).



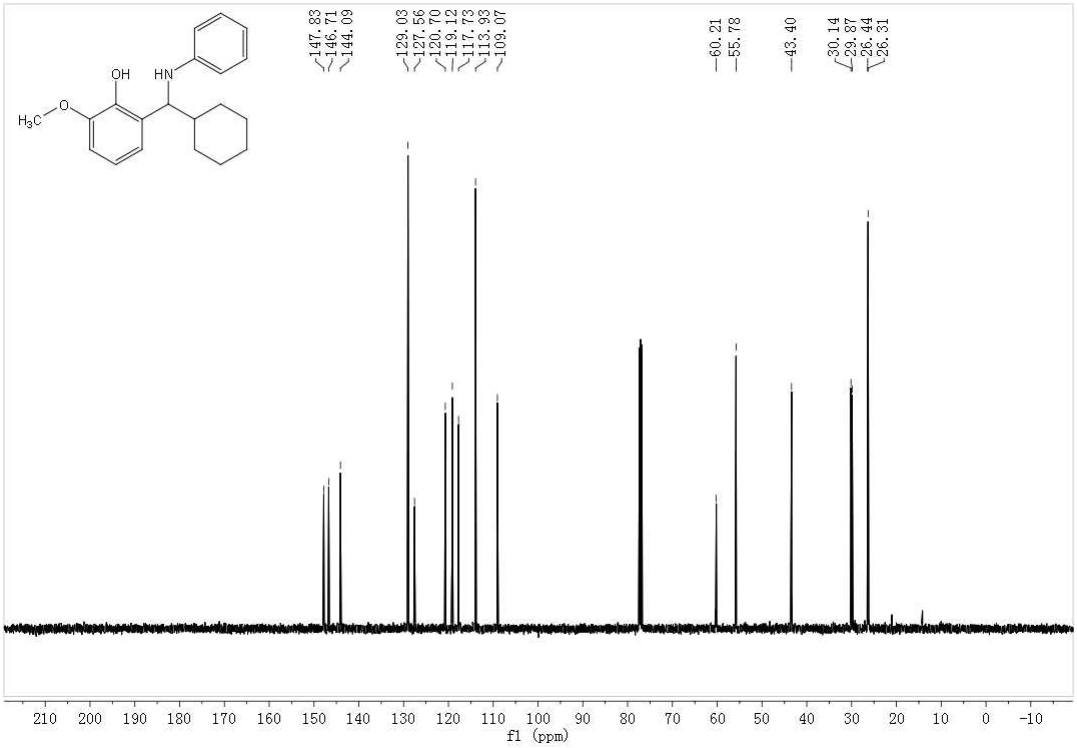
^{13}C NMR spectrum of compound **34** ($CDCl_3$, 126 MHz).



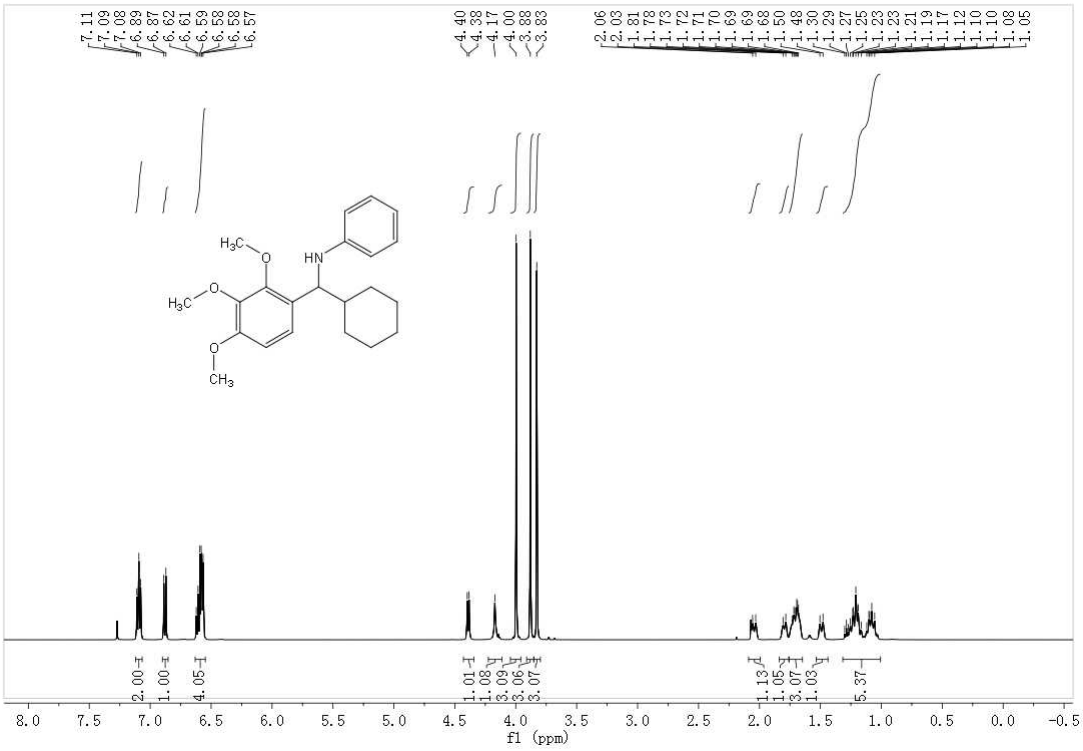
^{1}H NMR spectrum of compound **35** ($CDCl_3$, 500 MHz).



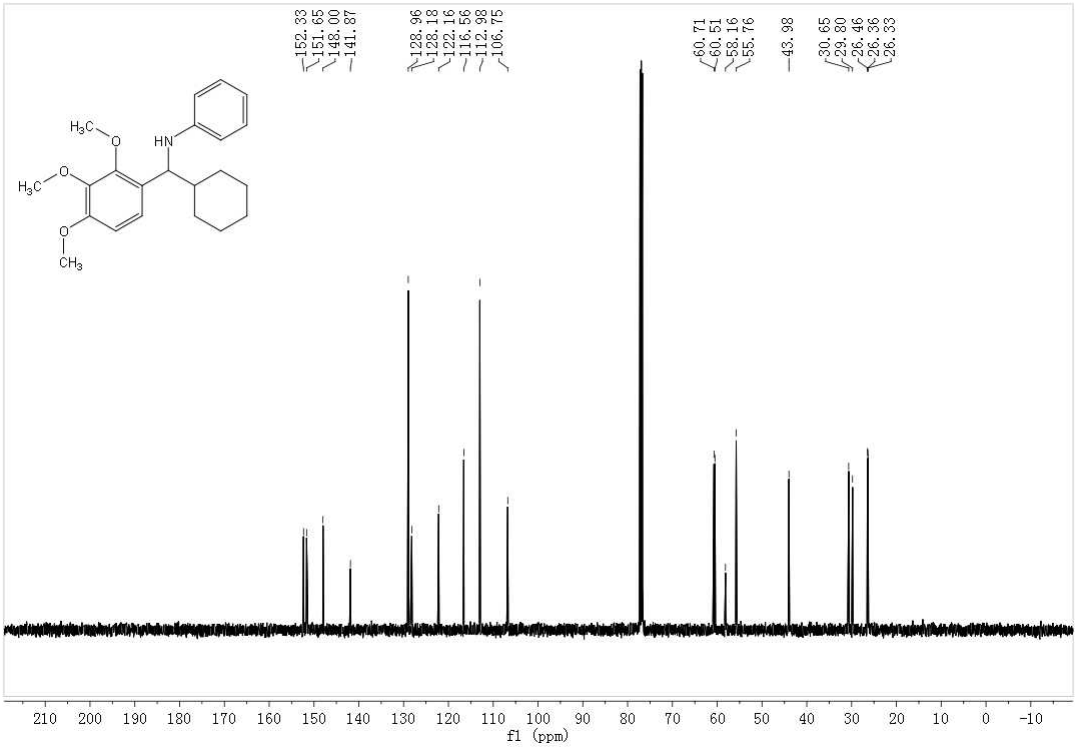
^{13}C NMR spectrum of compound **35** ($CDCl_3$, 126 MHz).



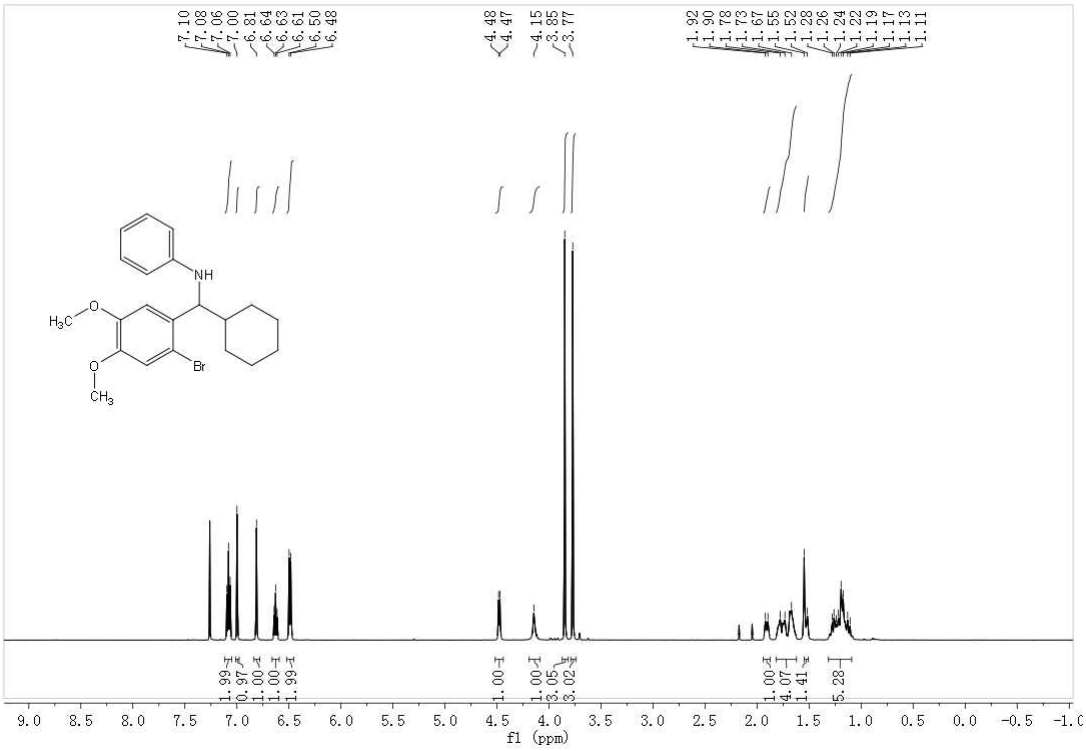
^{1}H NMR spectrum of compound **36** ($CDCl_3$, 500 MHz).



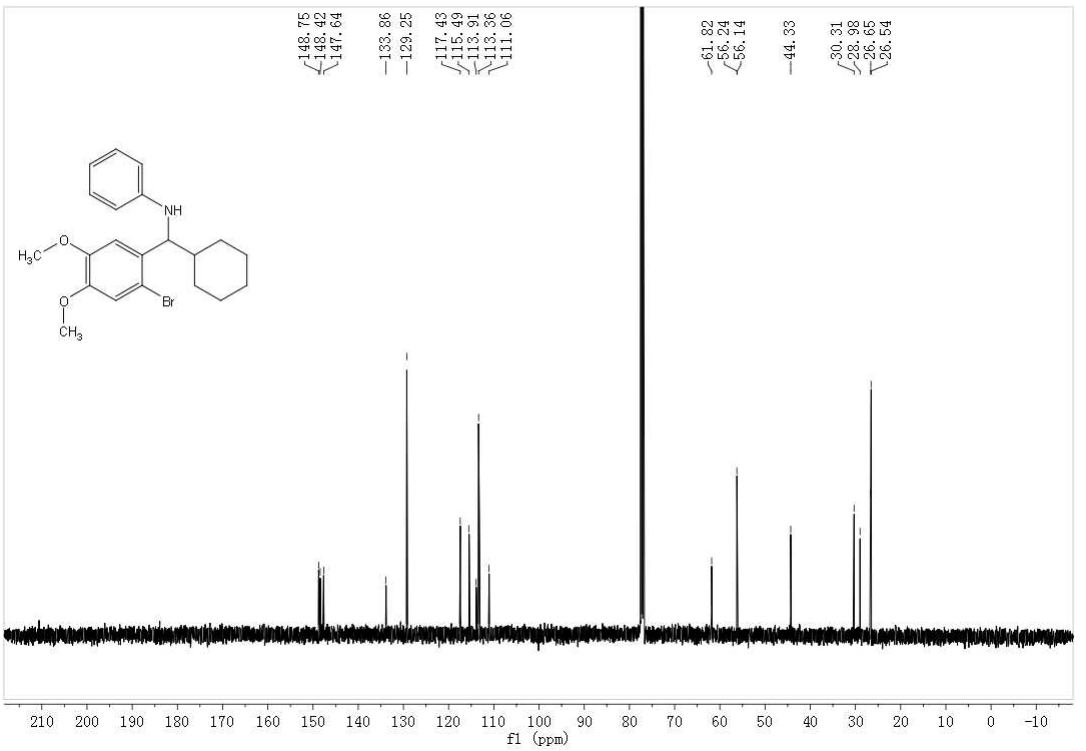
^{13}C NMR spectrum of compound **36** ($CDCl_3$, 126 MHz).



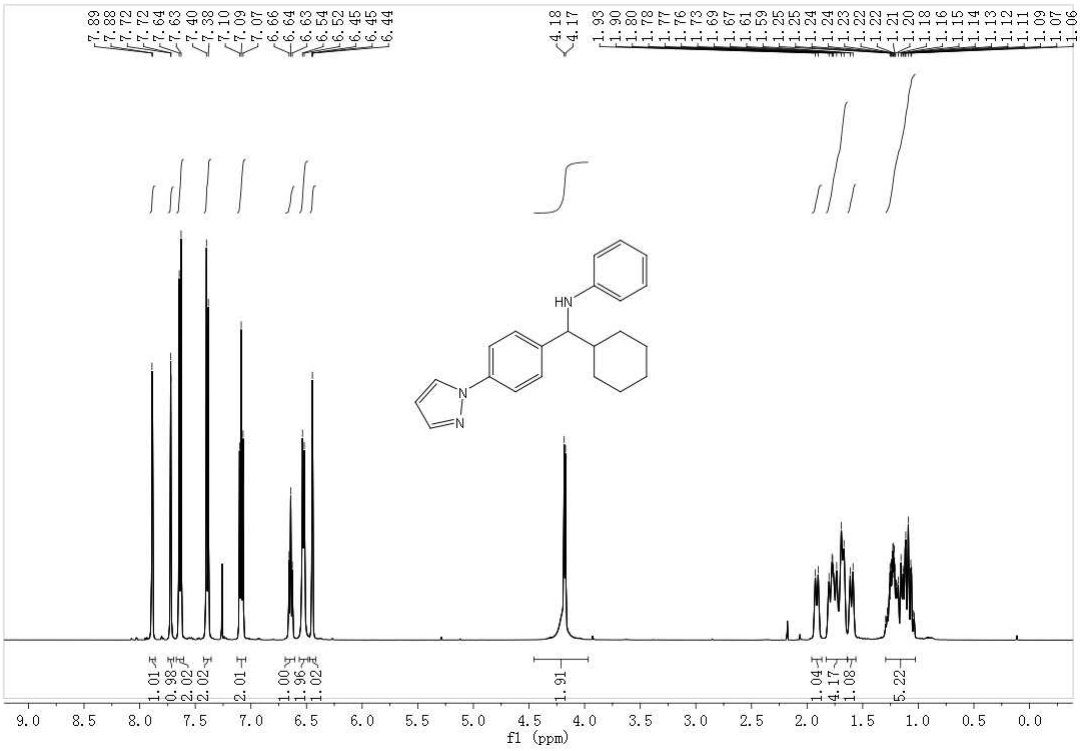
^{1}H NMR spectrum of compound **37** ($CDCl_3$, 500 MHz).



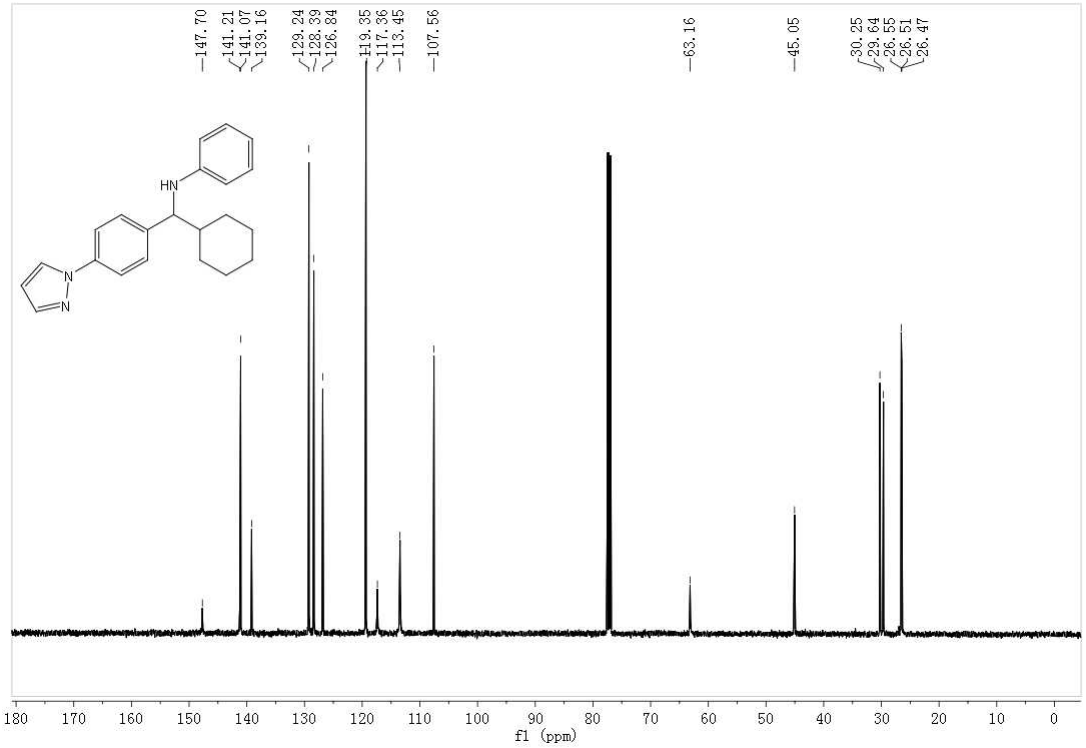
^{13}C NMR spectrum of compound **37** ($CDCl_3$, 126 MHz).



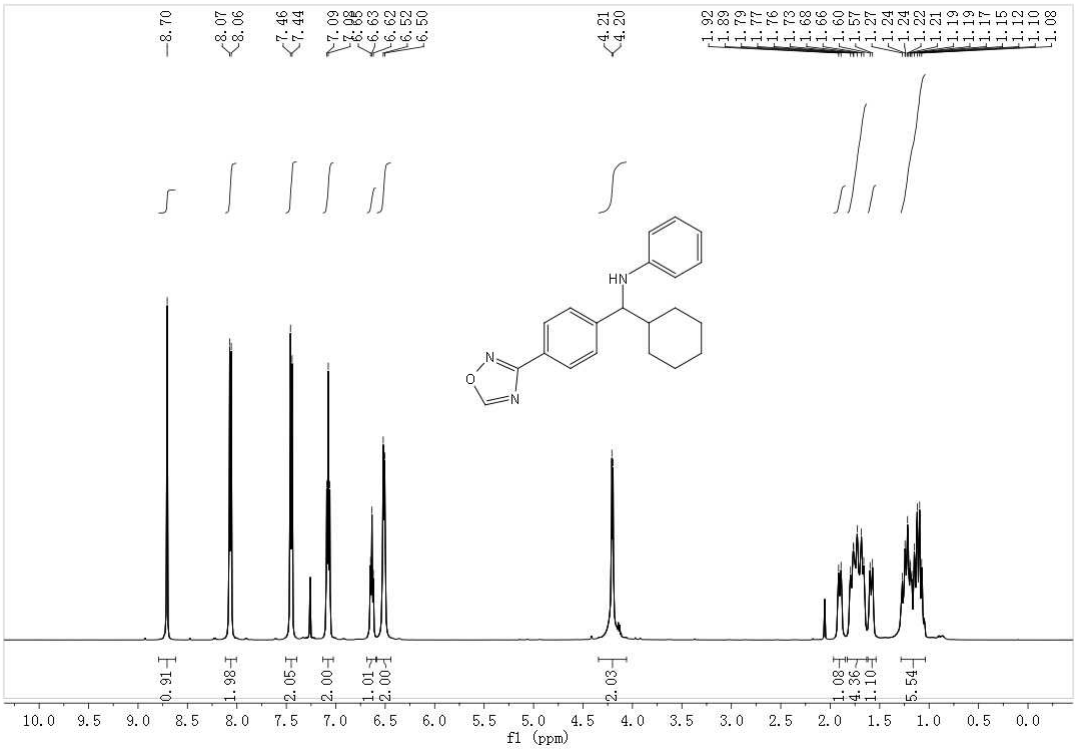
^{1}H NMR spectrum of compound **38** ($CDCl_3$, 500 MHz).



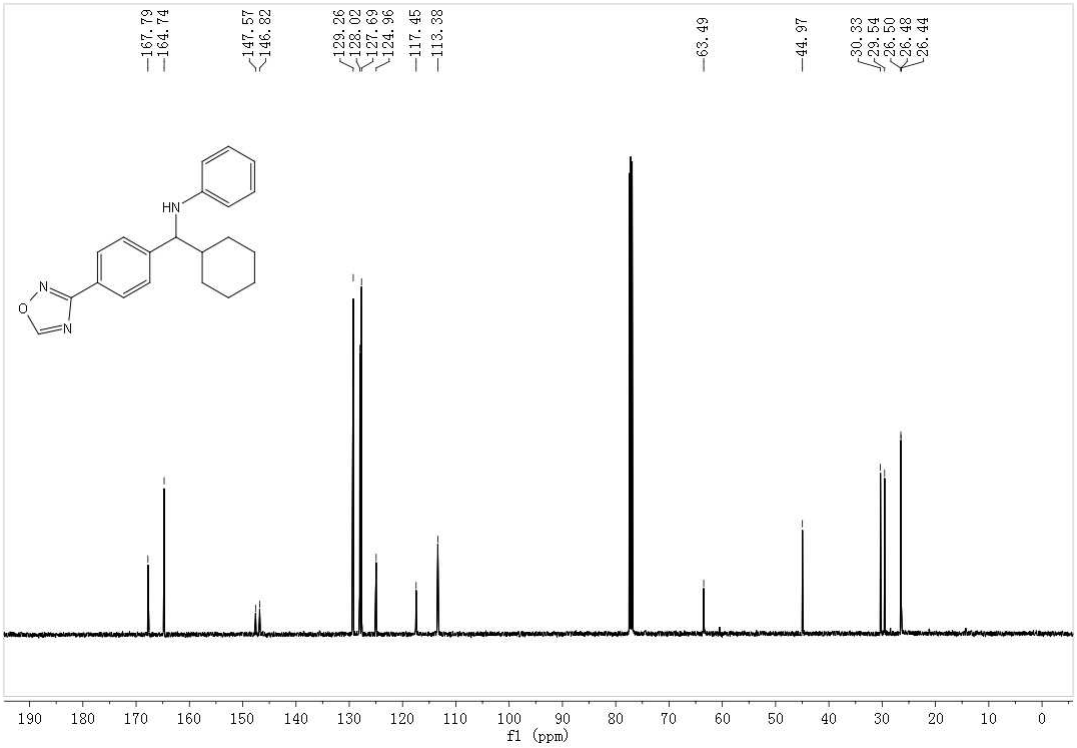
^{13}C NMR spectrum of compound **38** ($CDCl_3$, 126 MHz).



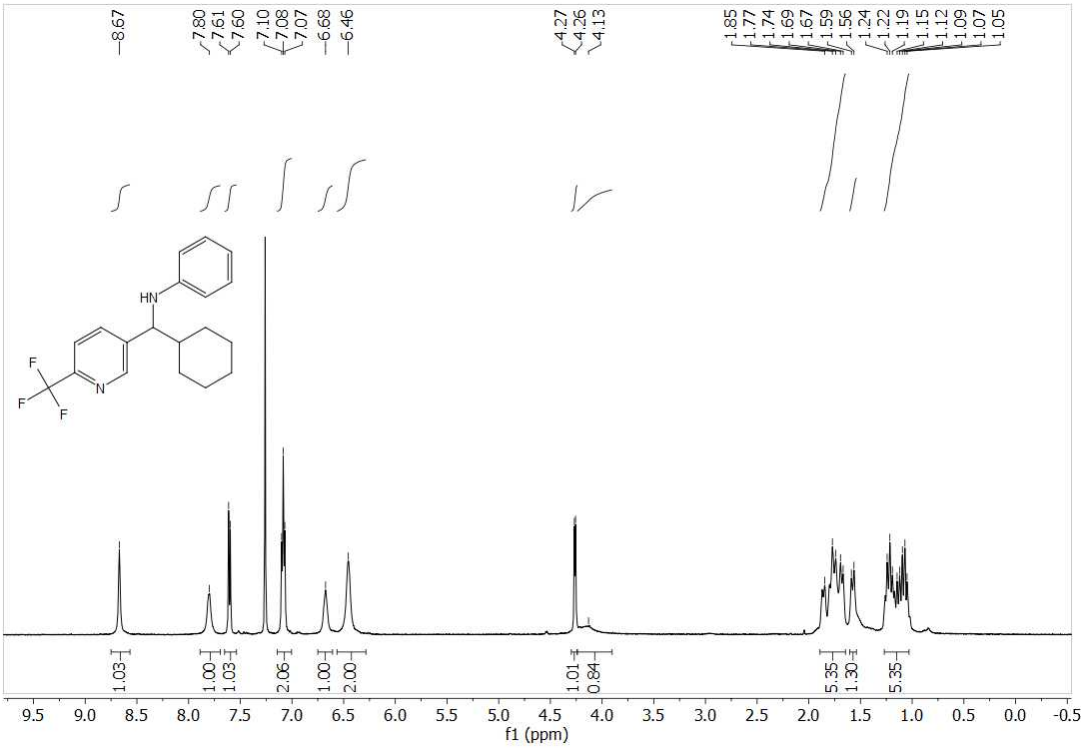
^{1}H NMR spectrum of compound **39** ($CDCl_3$, 500 MHz).



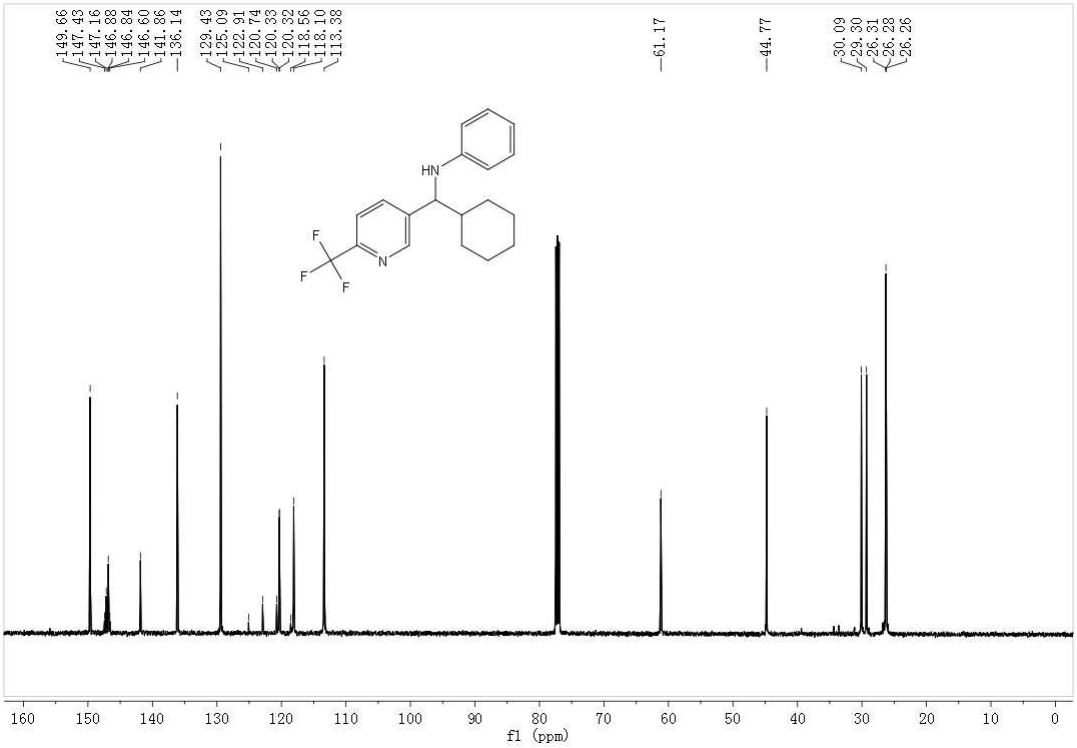
^{13}C NMR spectrum of compound **39** ($CDCl_3$, 126 MHz).



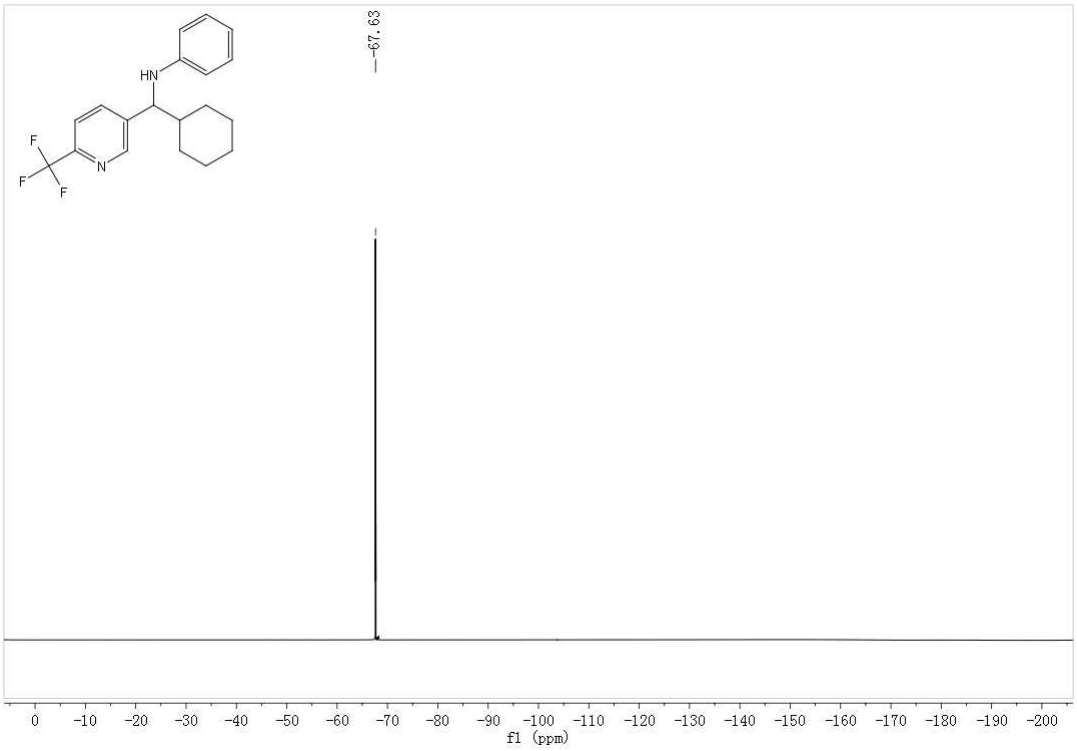
^{1}H NMR spectrum of compound **40** ($CDCl_3$, 500 MHz).



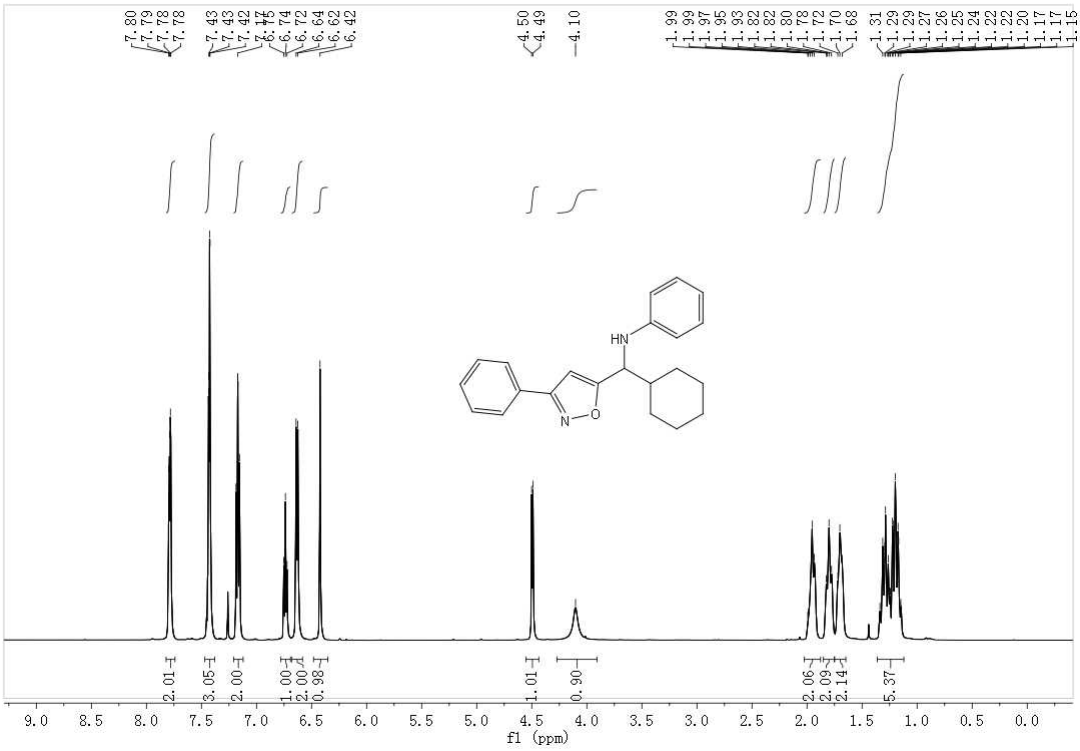
^{13}C NMR spectrum of compound **40** ($CDCl_3$, 126 MHz).



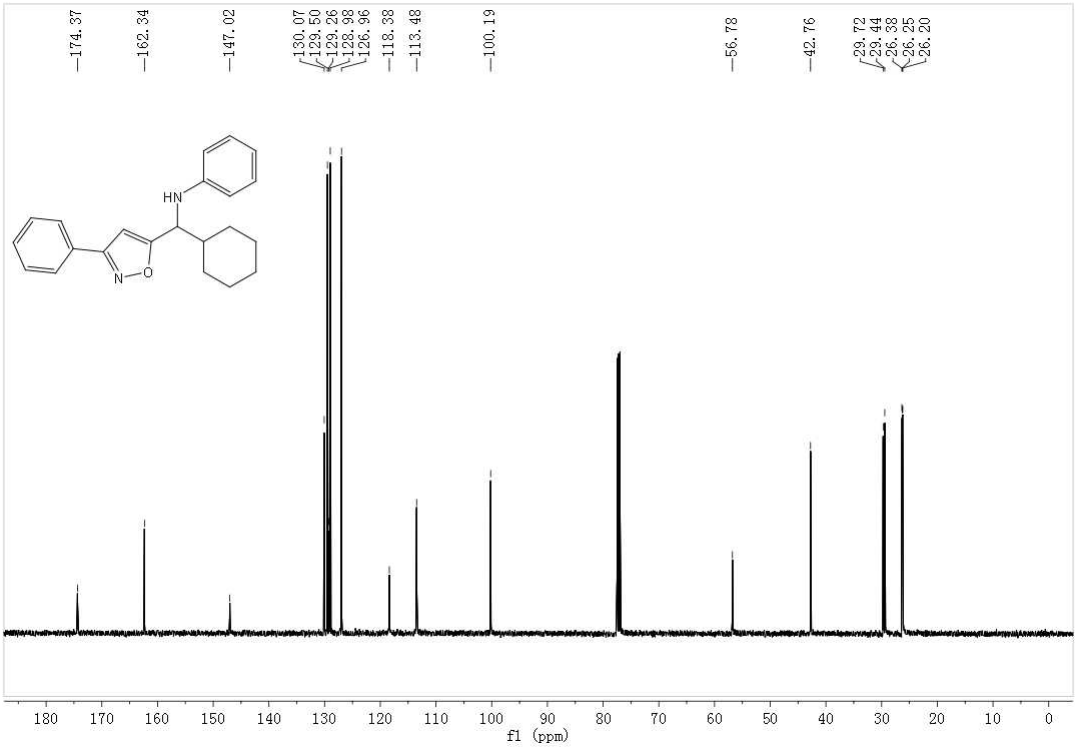
^{19}F NMR spectrum of compound **40** ($CDCl_3$, 471 MHz).



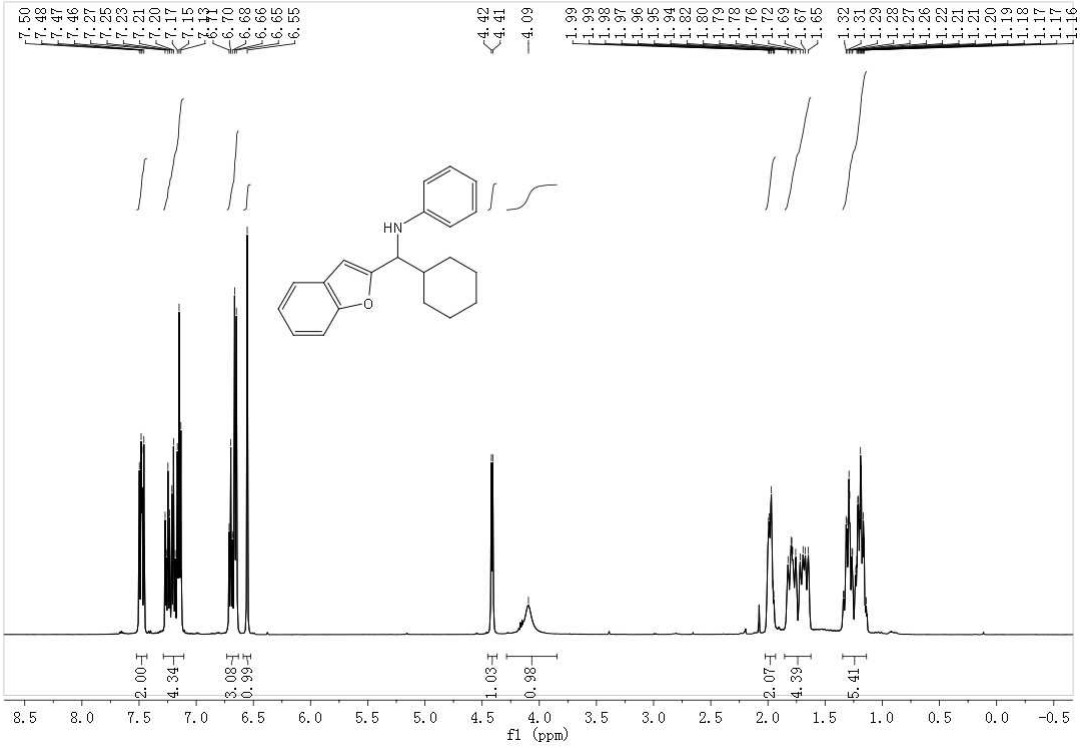
^{1}H NMR spectrum of compound **41** ($CDCl_3$, 500 MHz).



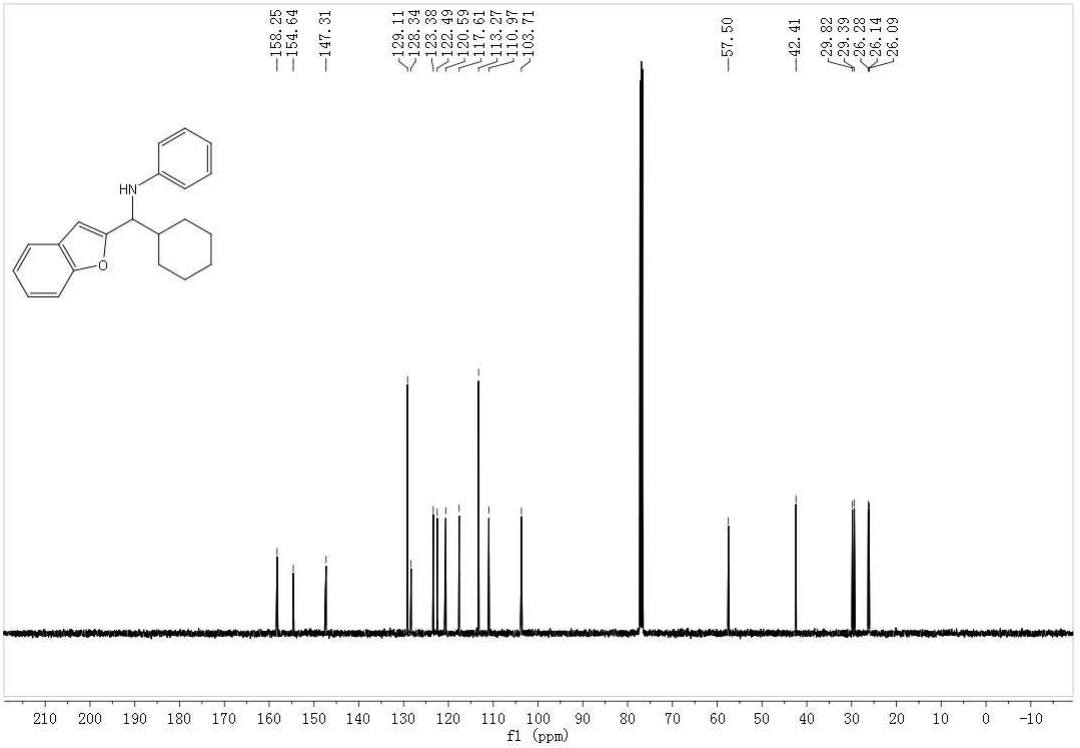
^{13}C NMR spectrum of compound **41** ($CDCl_3$, 126 MHz).



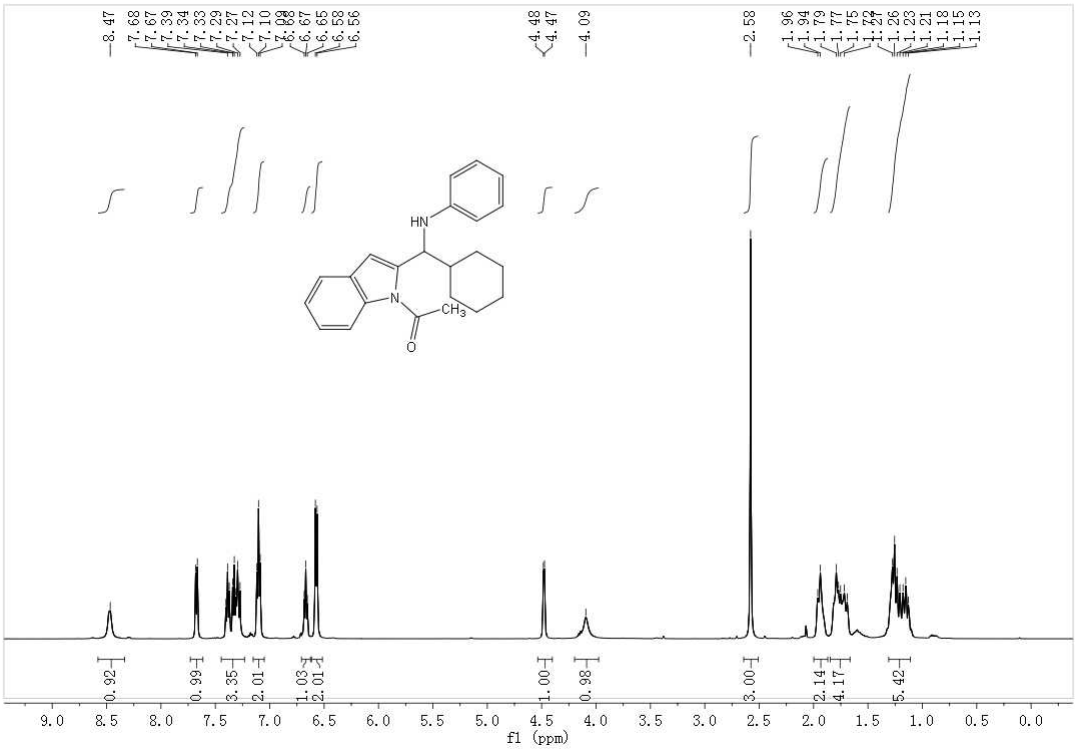
^{1}H NMR spectrum of compound **42** ($CDCl_3$, 500 MHz).



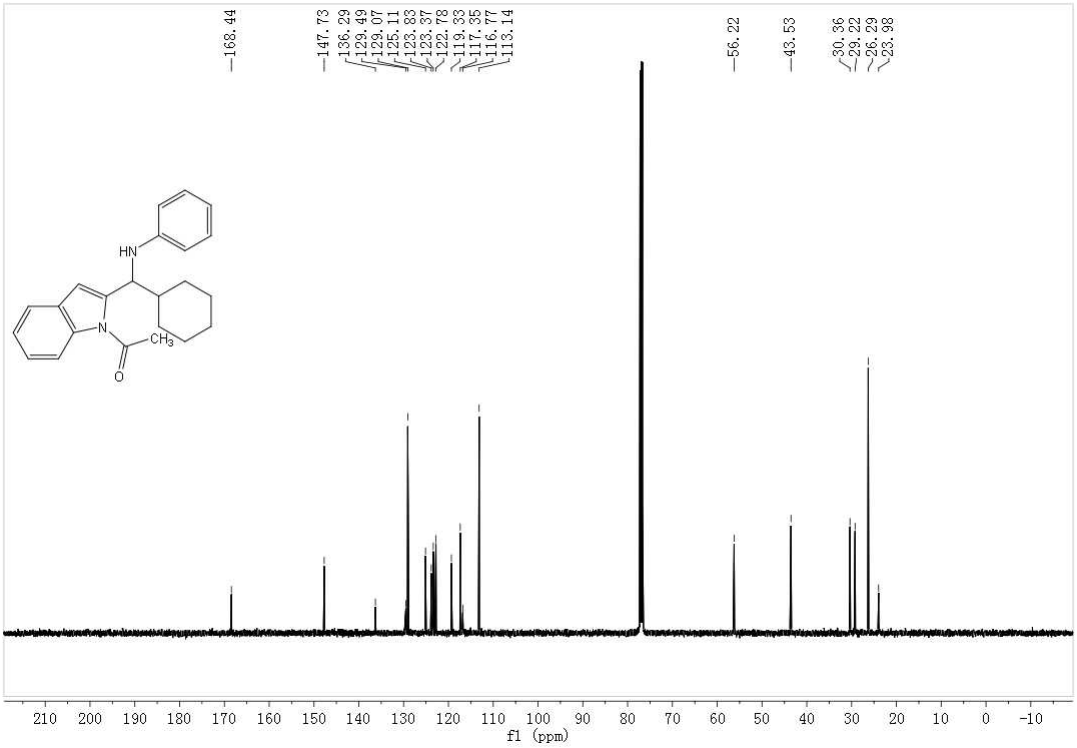
^{13}C NMR spectrum of compound **42** ($CDCl_3$, 126 MHz).



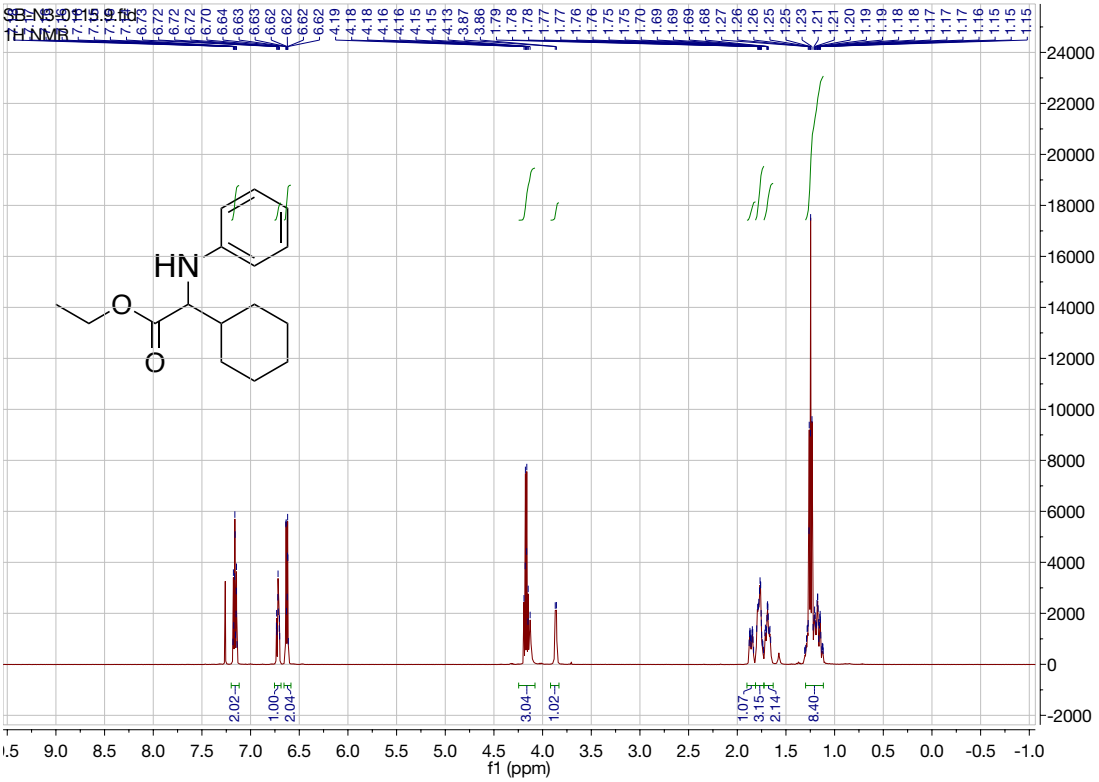
^{1}H NMR spectrum of compound **43** ($CDCl_3$, 500 MHz).



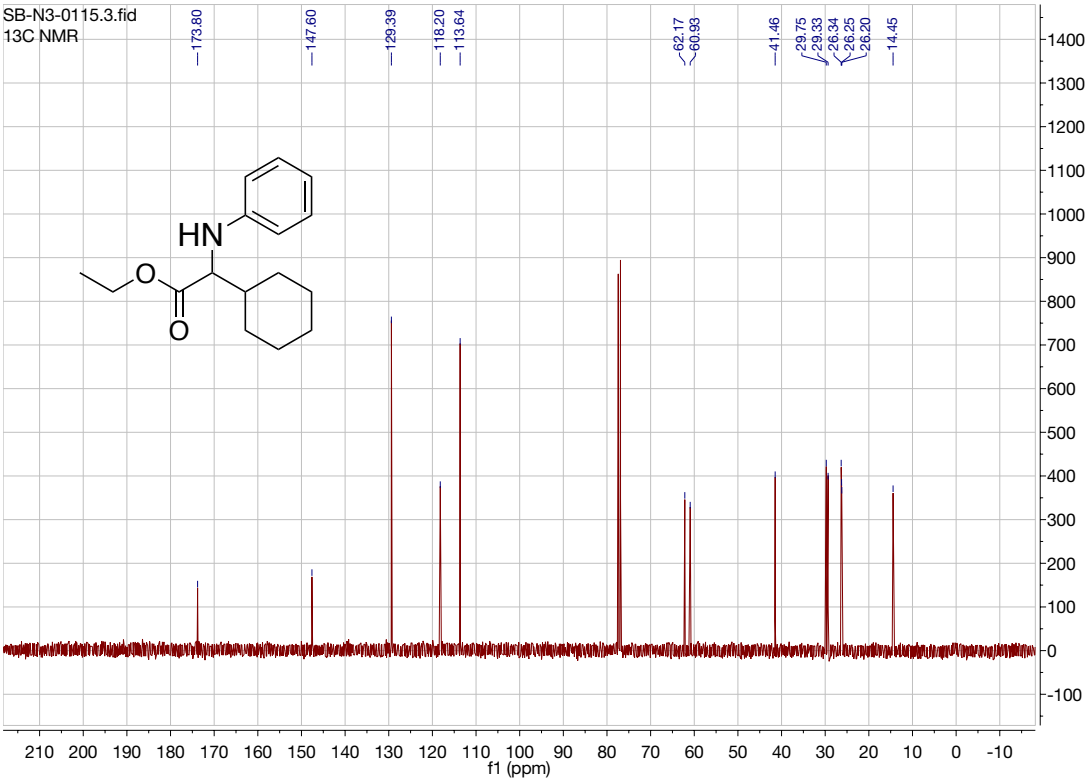
^{13}C NMR spectrum of compound **43** ($CDCl_3$, 126 MHz).



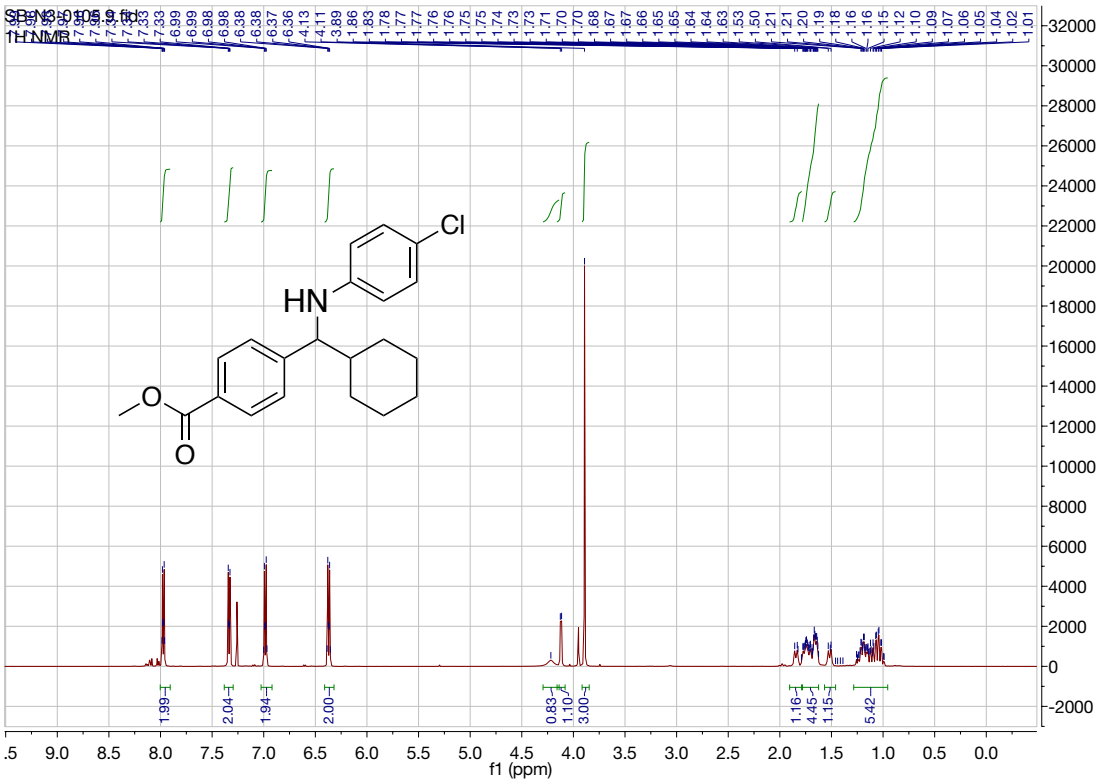
^{1}H NMR spectrum of compound **44** ($CDCl_3$, 500 MHz).



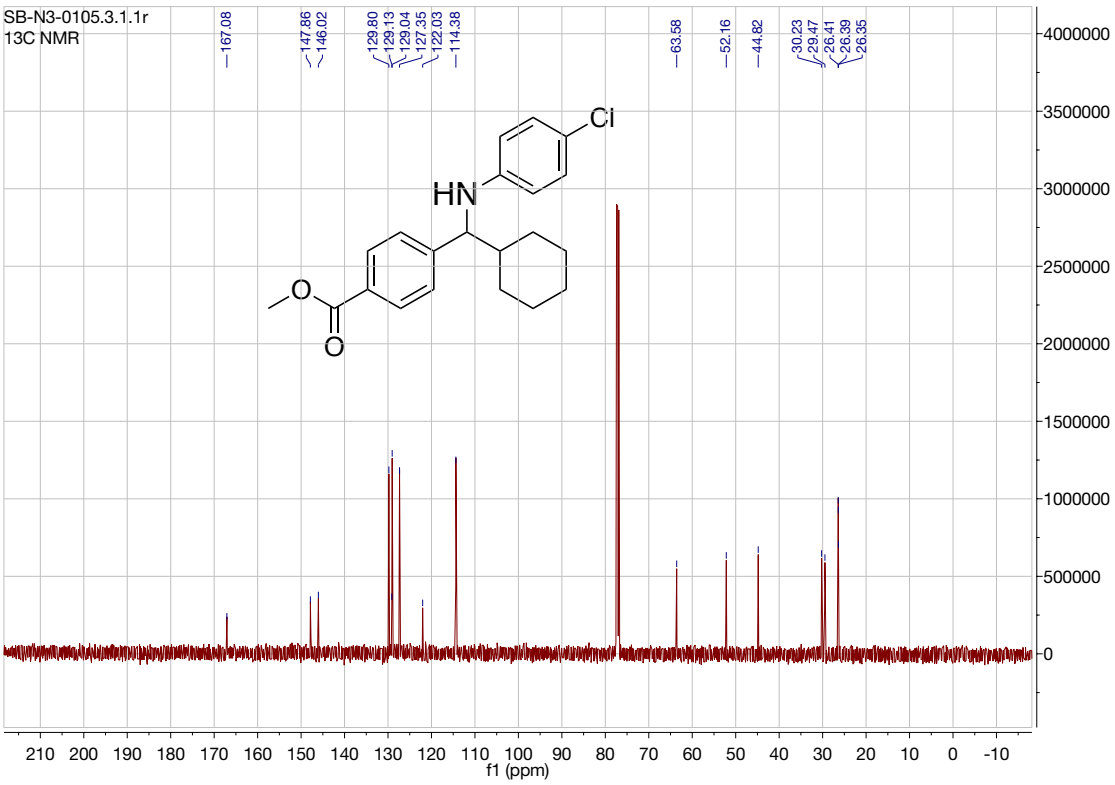
^{13}C NMR spectrum of compound **44** ($CDCl_3$, 126 MHz).



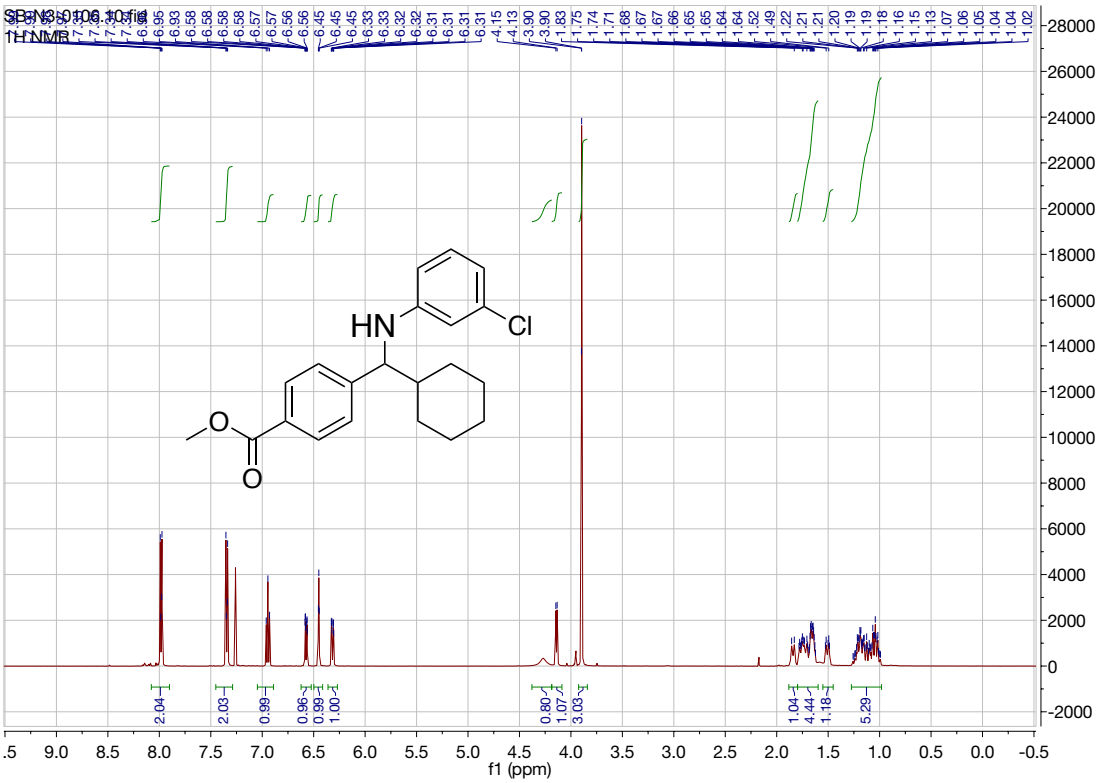
^{1}H NMR spectrum of compound **45** ($CDCl_3$, 500 MHz).



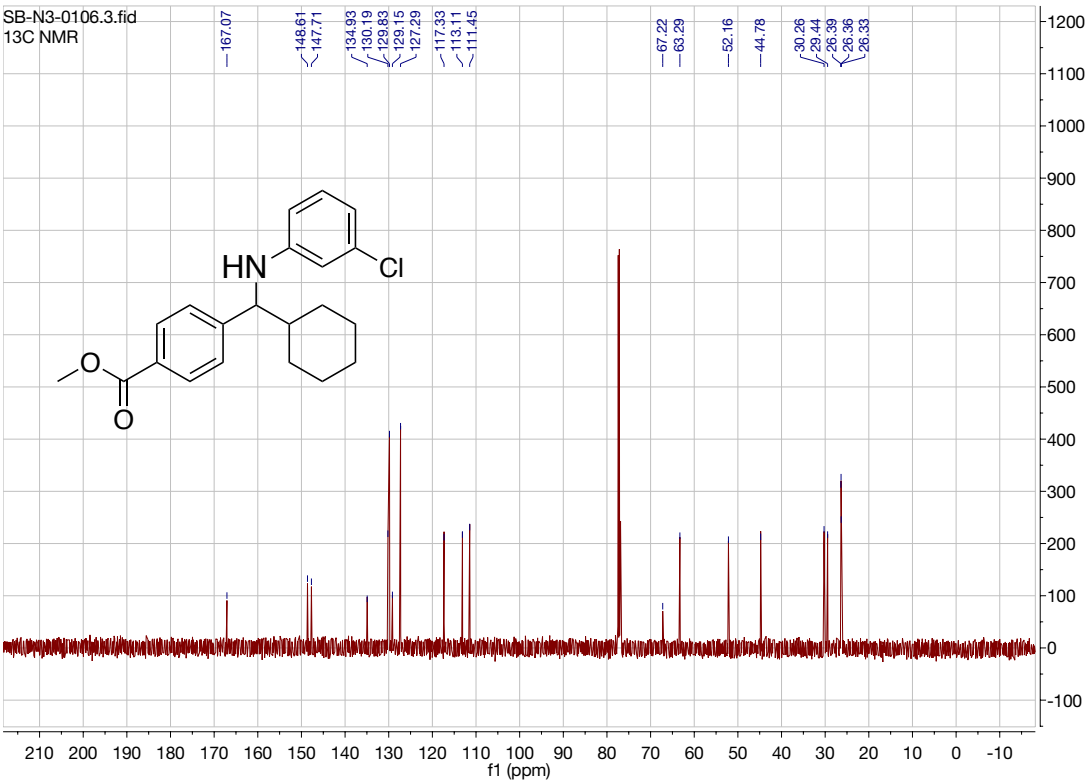
^{13}C NMR spectrum of compound **45**($CDCl_3$, 126 MHz).



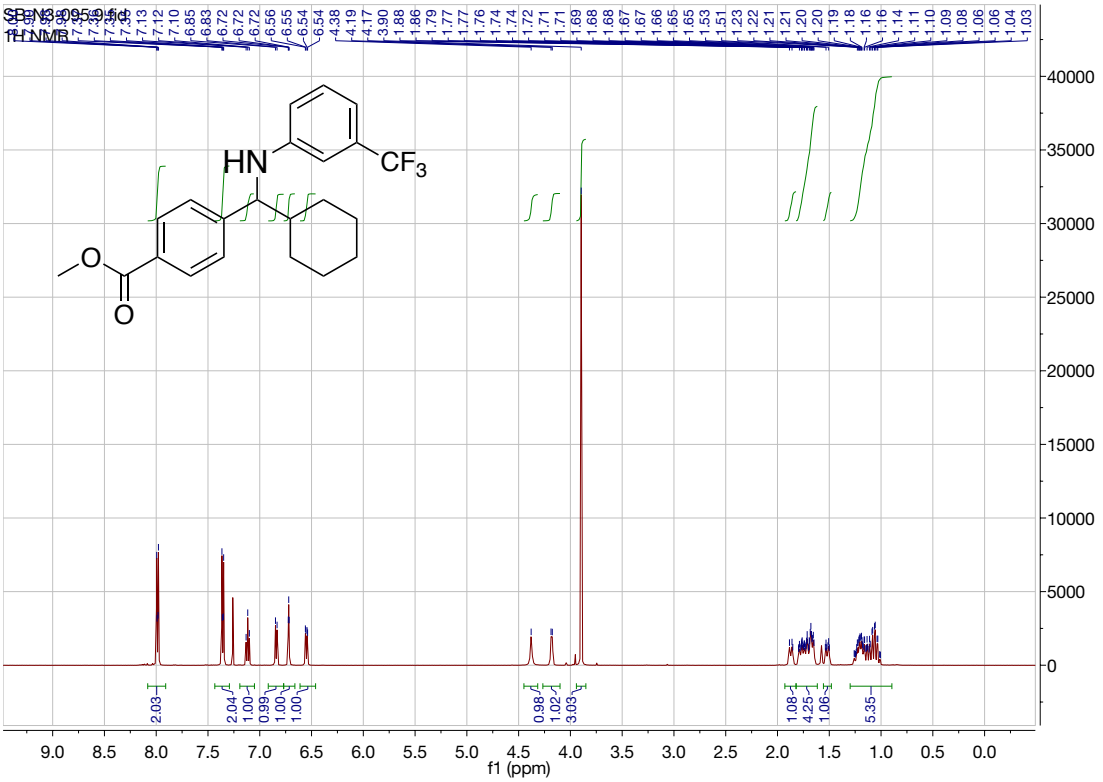
^{1}H NMR spectrum of compound **46** ($CDCl_3$, 500 MHz).



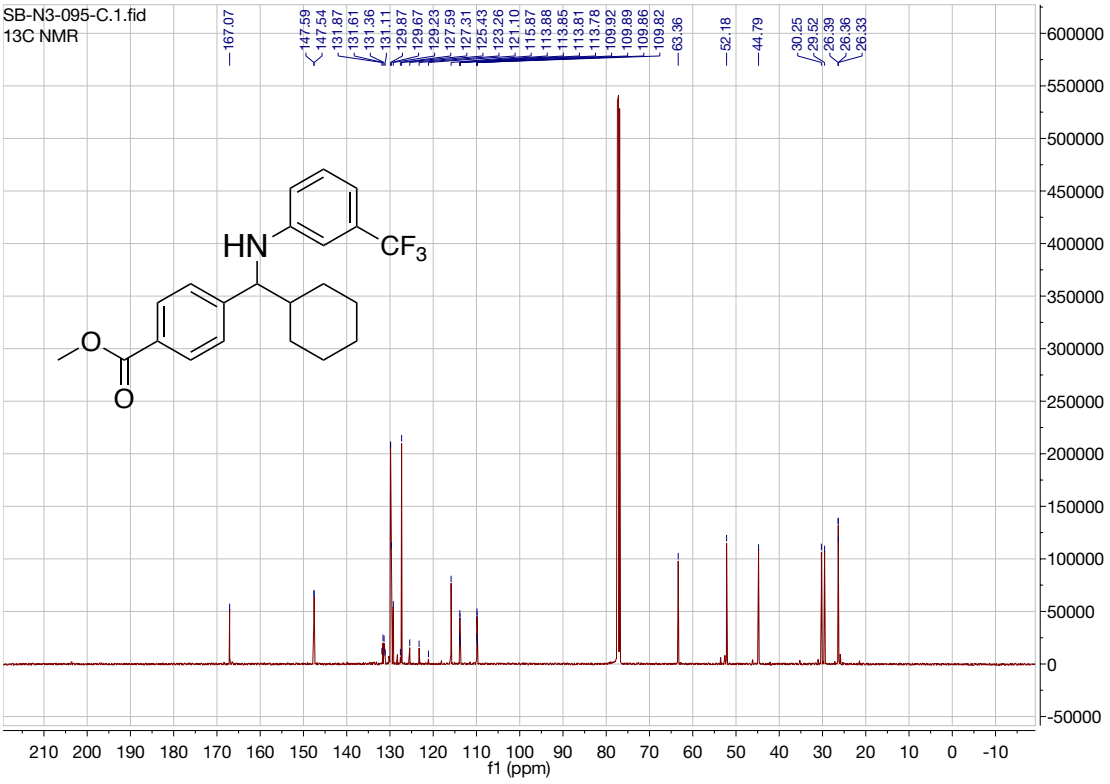
^{13}C NMR spectrum of compound **46** ($CDCl_3$, 126 MHz).



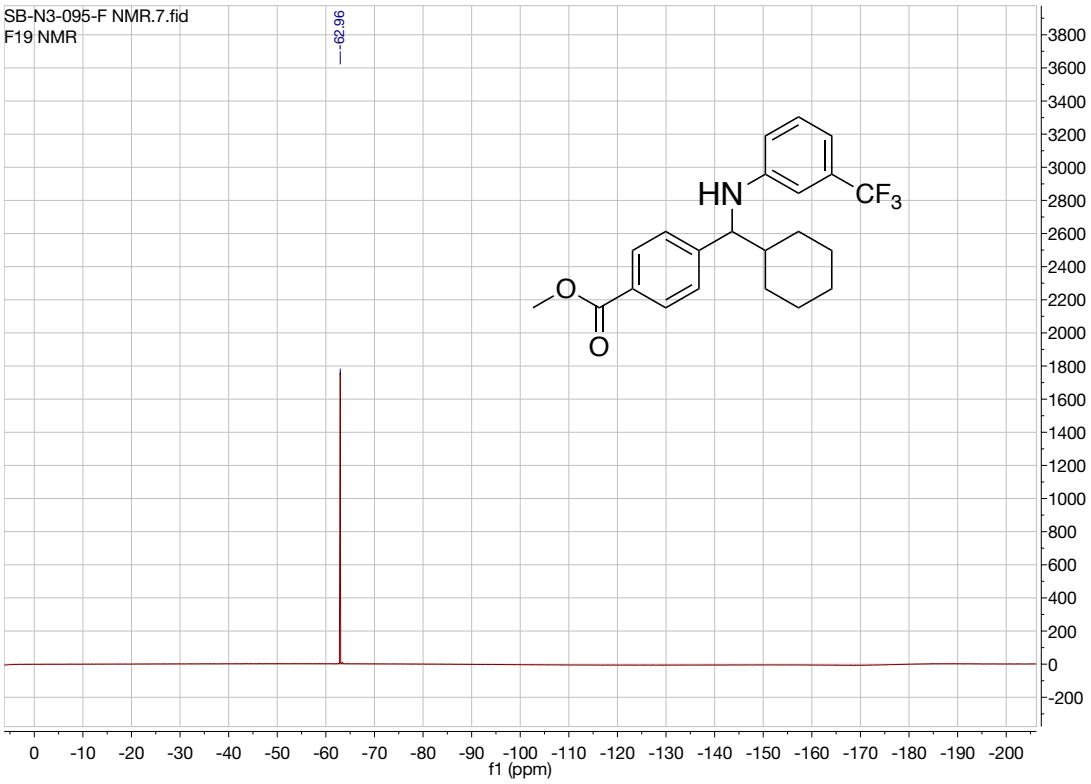
^{1}H NMR spectrum of compound **47** ($CDCl_3$, 500 MHz).



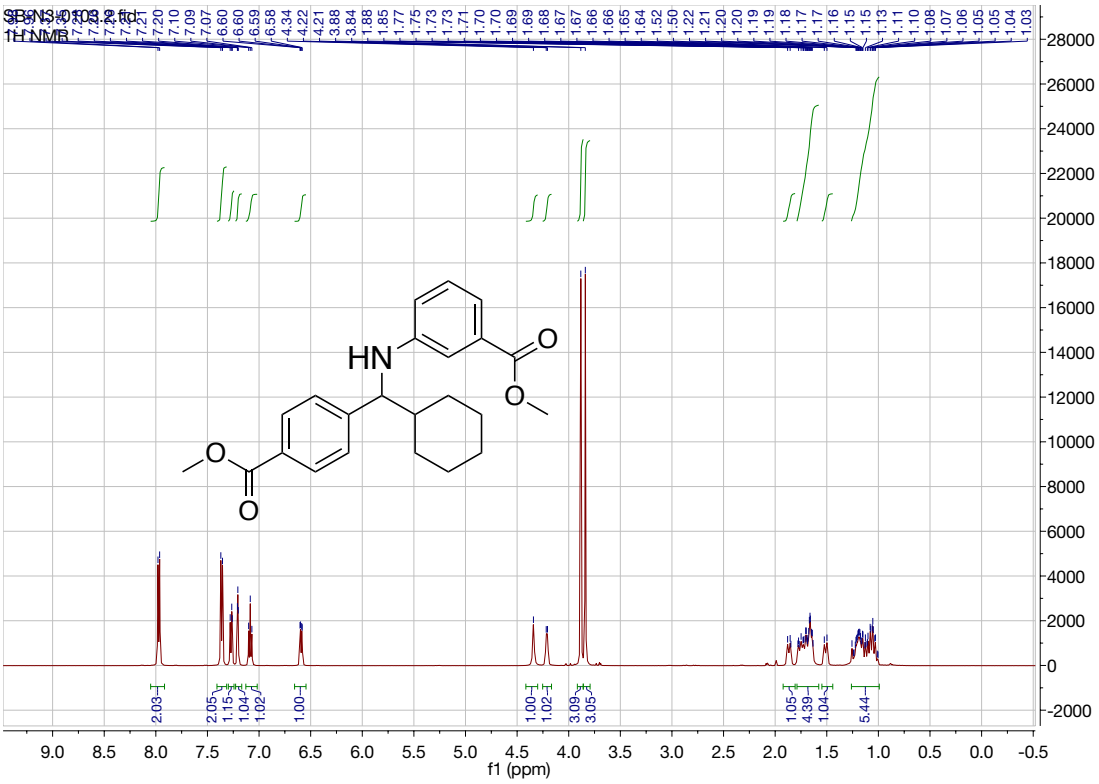
^{13}C NMR spectrum of compound **47** ($CDCl_3$, 126 MHz).



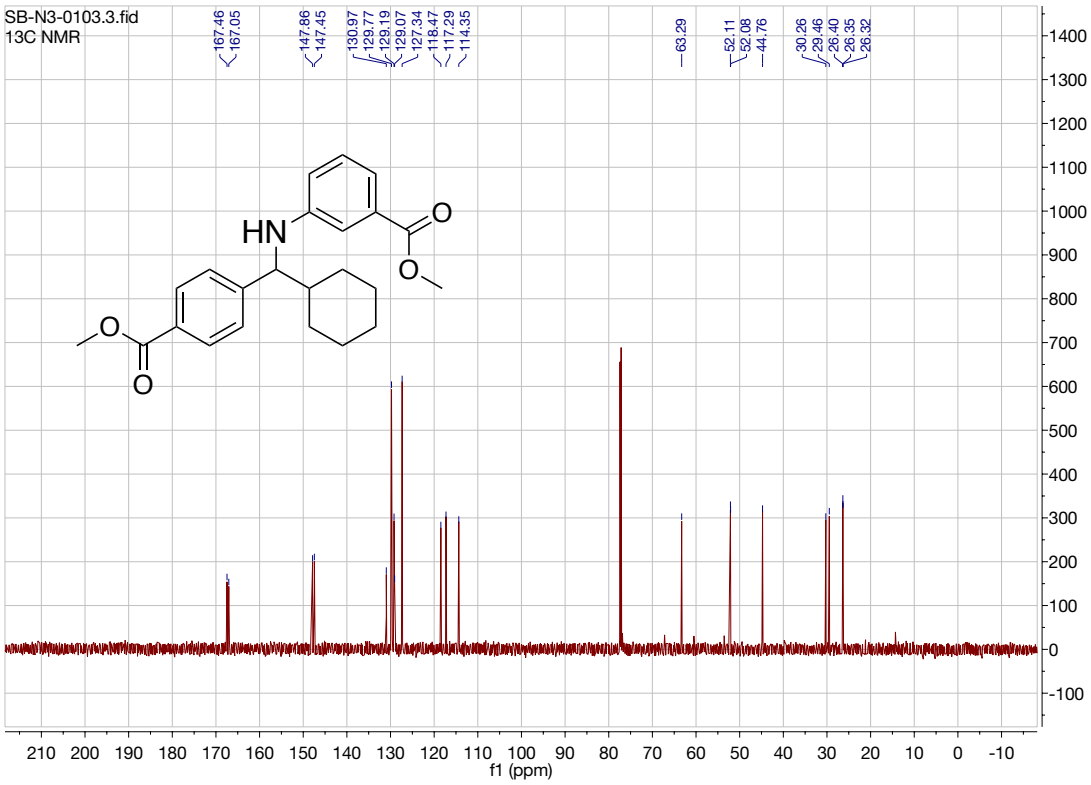
^{19}F NMR spectrum of compound **47** ($CDCl_3$, 471 MHz).



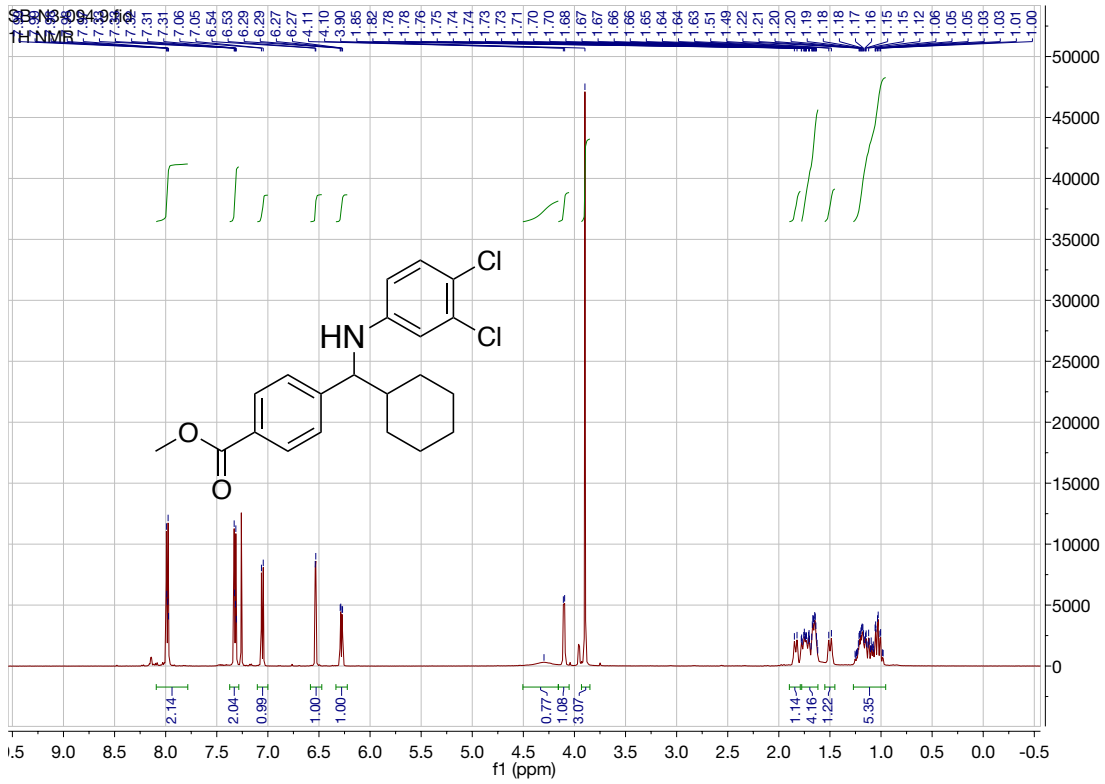
^{1}H NMR spectrum of compound **48** ($CDCl_3$, 500 MHz).



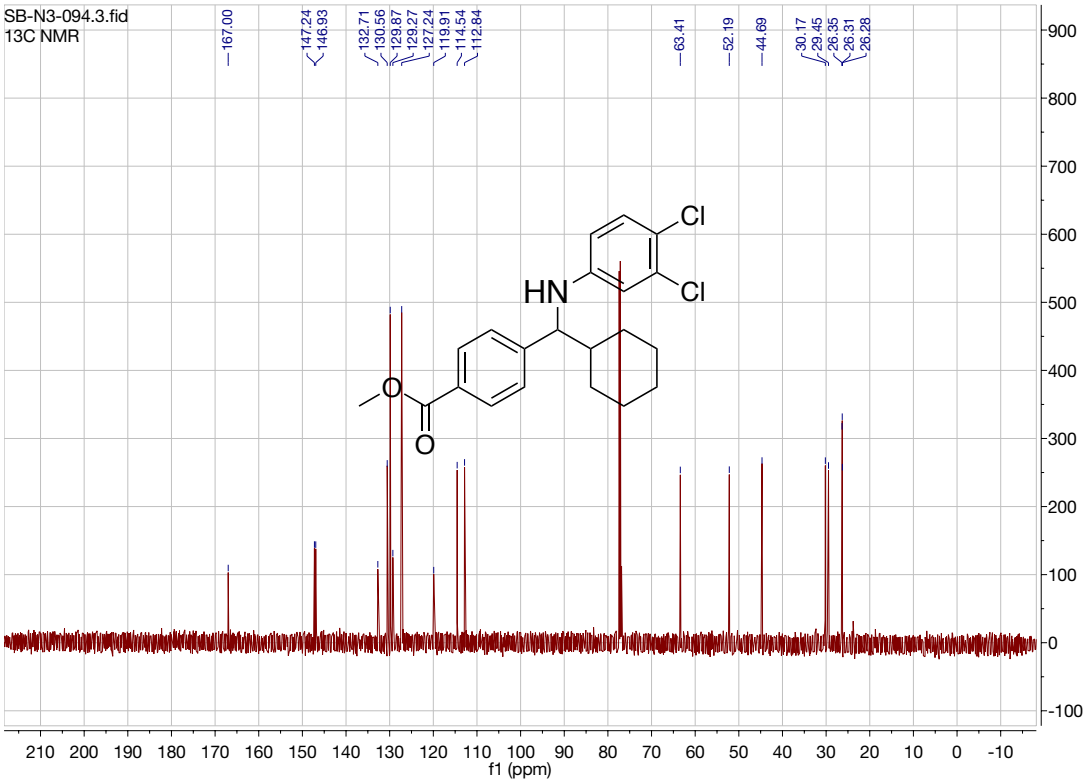
^{13}C NMR spectrum of compound **48** ($CDCl_3$, 126 MHz).



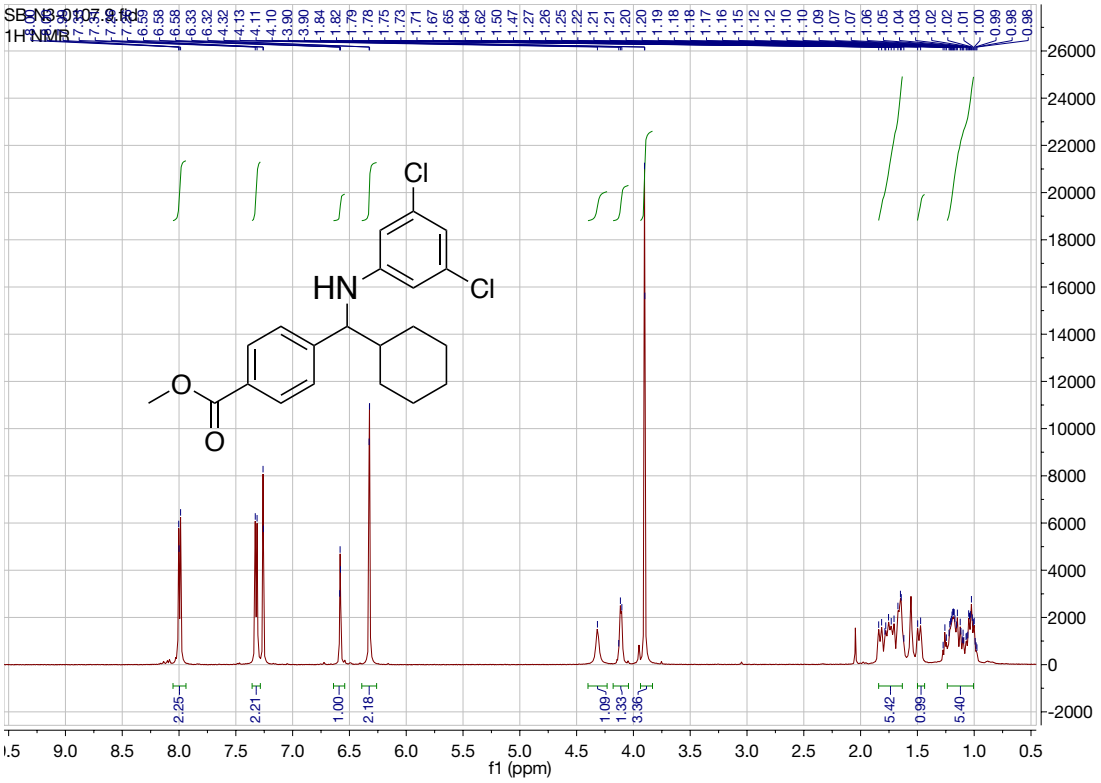
^{1}H NMR spectrum of compound **49** ($CDCl_3$, 500 MHz).



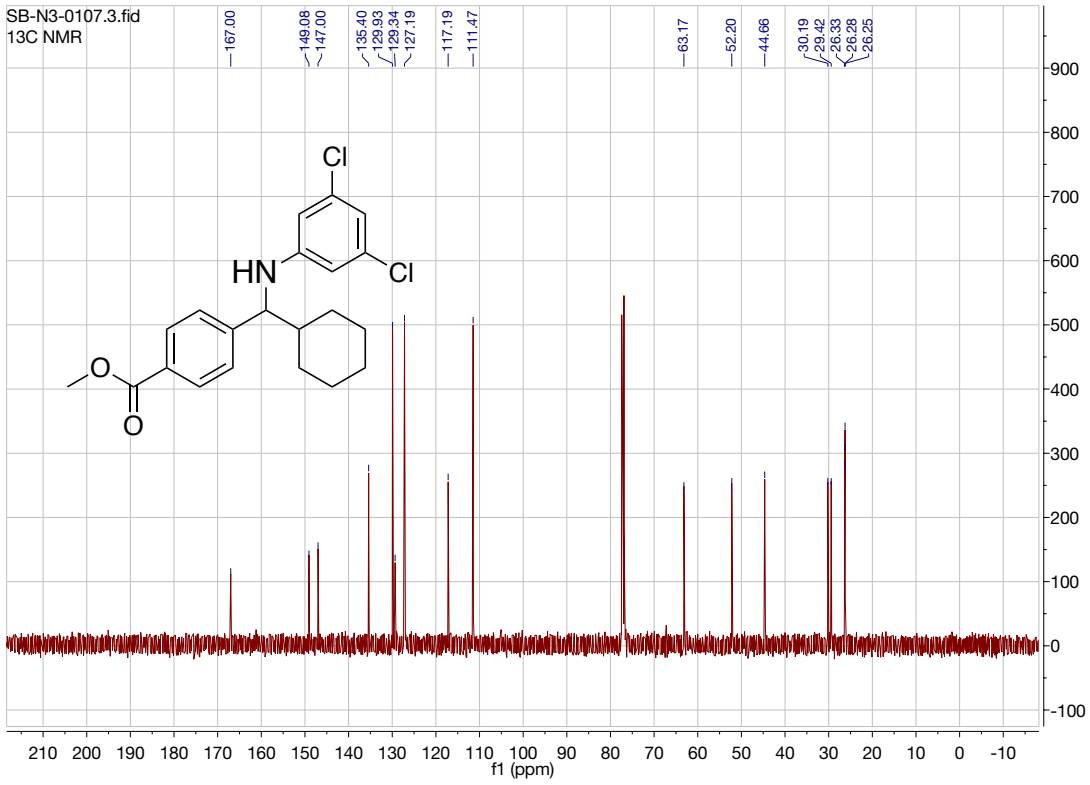
^{13}C NMR spectrum of compound **49** ($CDCl_3$, 126 MHz).



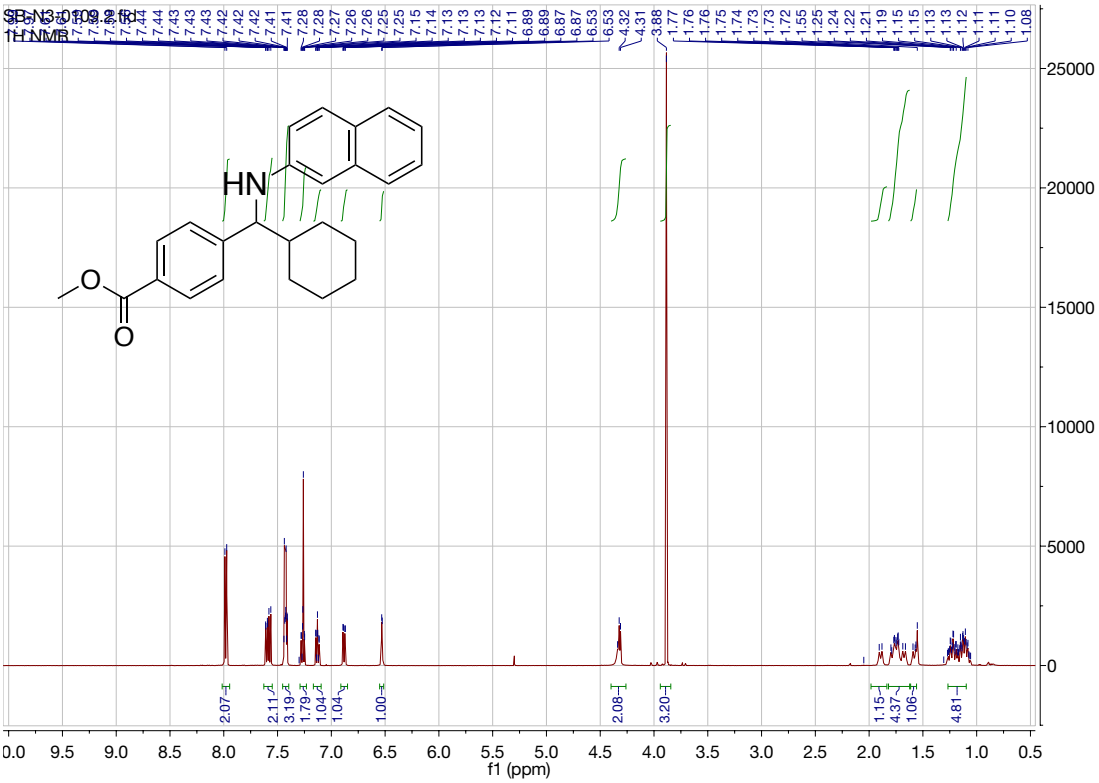
^{1}H NMR spectrum of compound **50** ($CDCl_3$, 500 MHz).



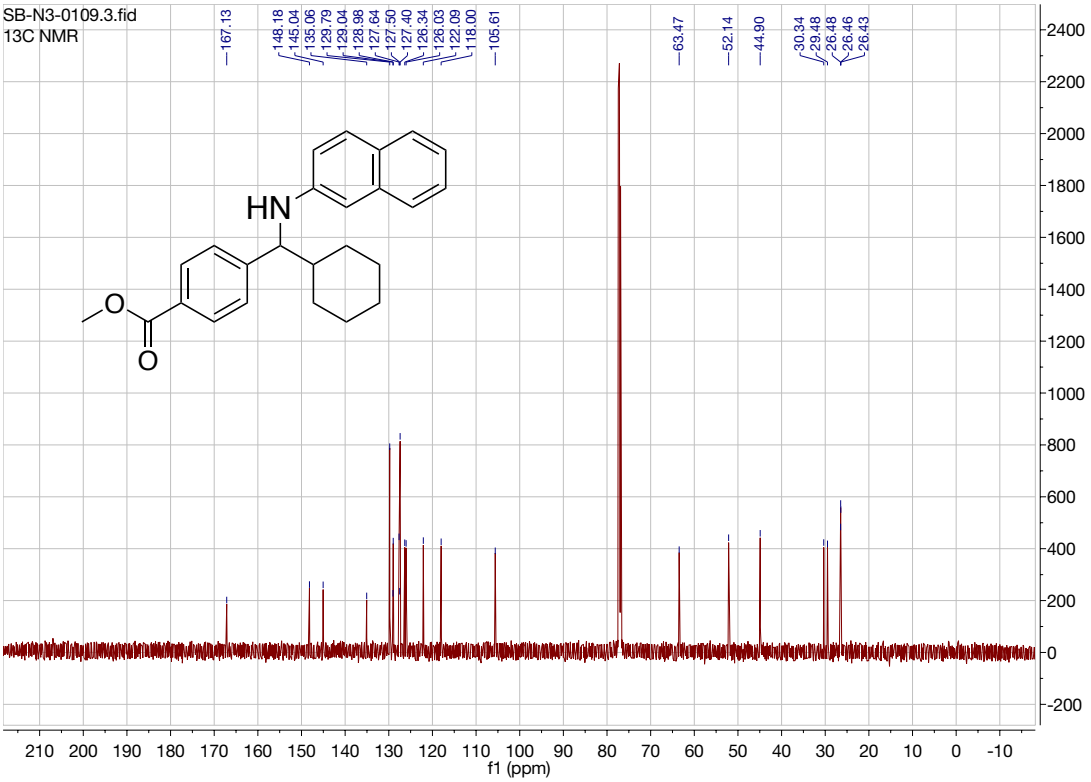
^{13}C NMR spectrum of compound **50** ($CDCl_3$, 126 MHz).



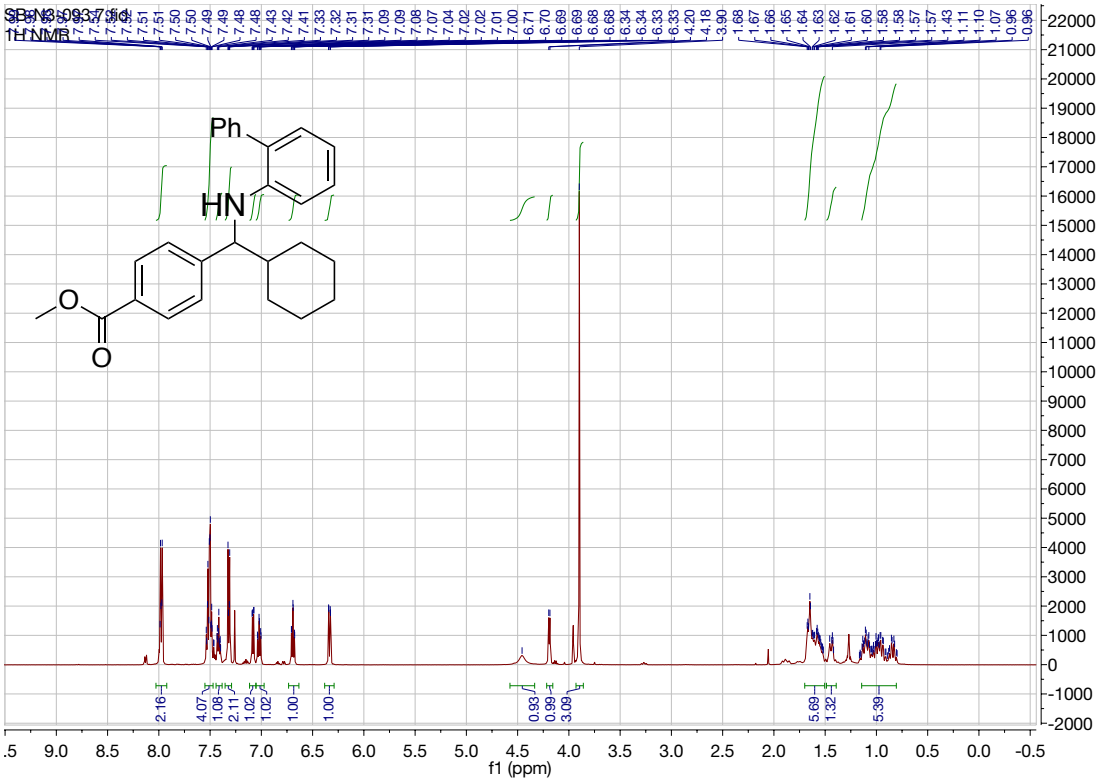
^{1}H NMR spectrum of compound **51** ($CDCl_3$, 500 MHz).



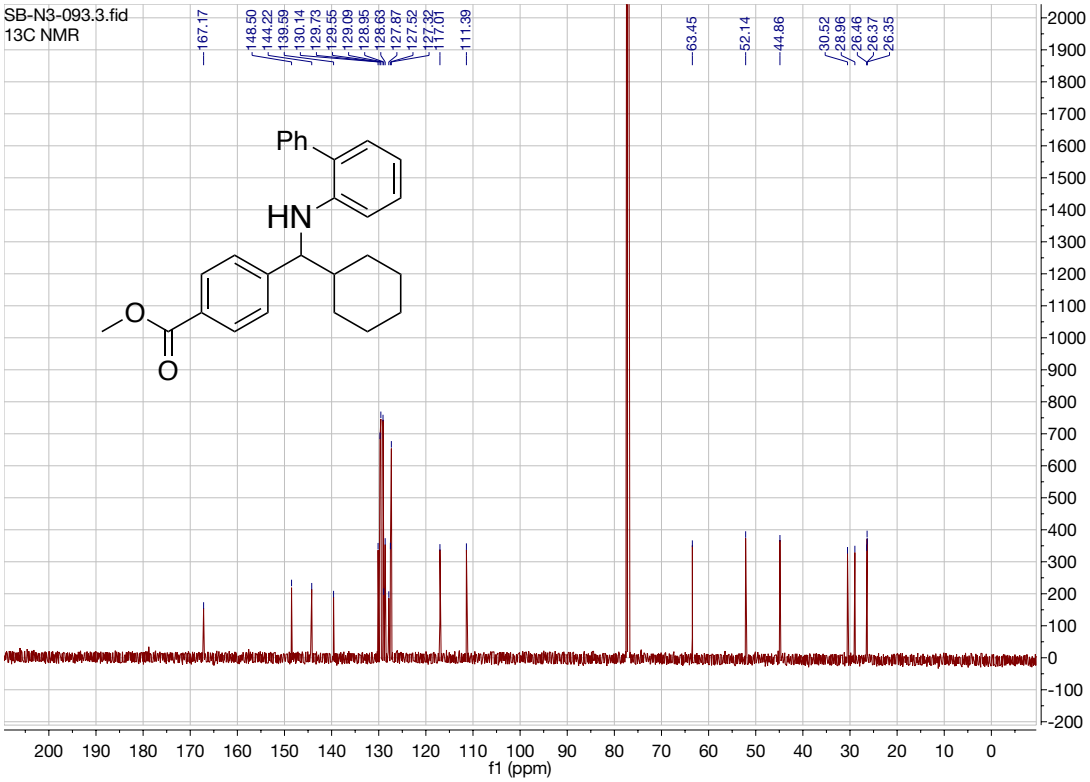
^{13}C NMR spectrum of compound **51** ($CDCl_3$, 126 MHz).



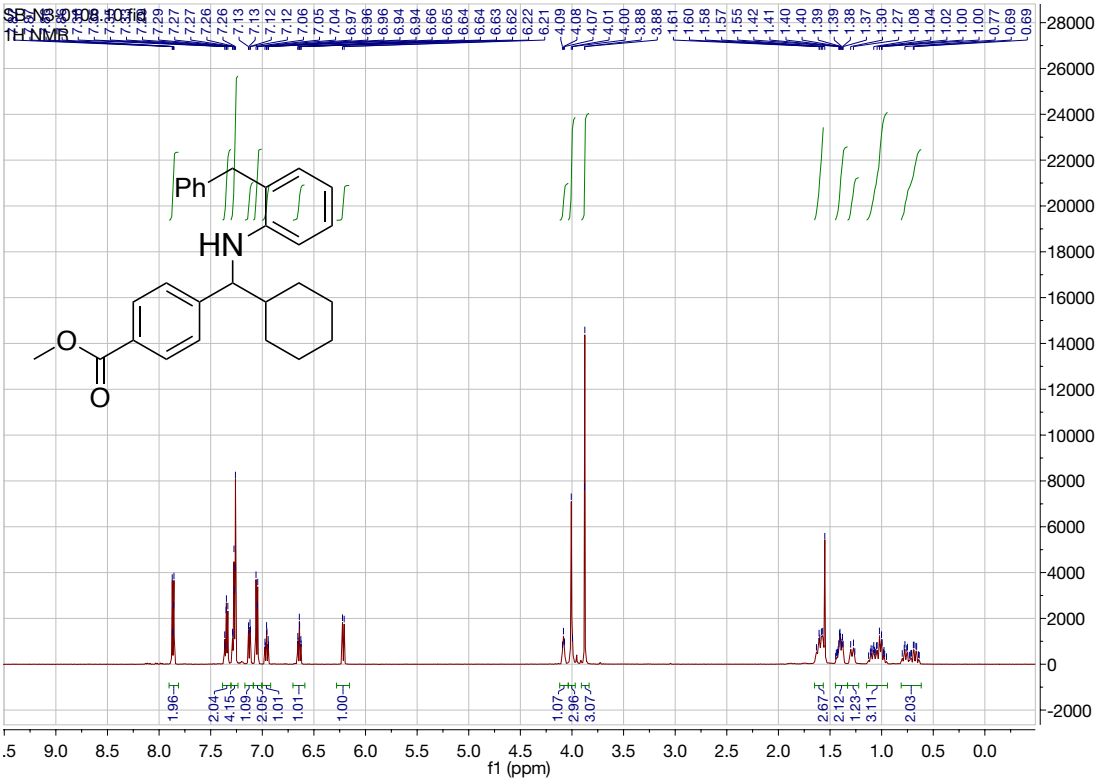
^{1}H NMR spectrum of compound **52** ($CDCl_3$, 500 MHz).



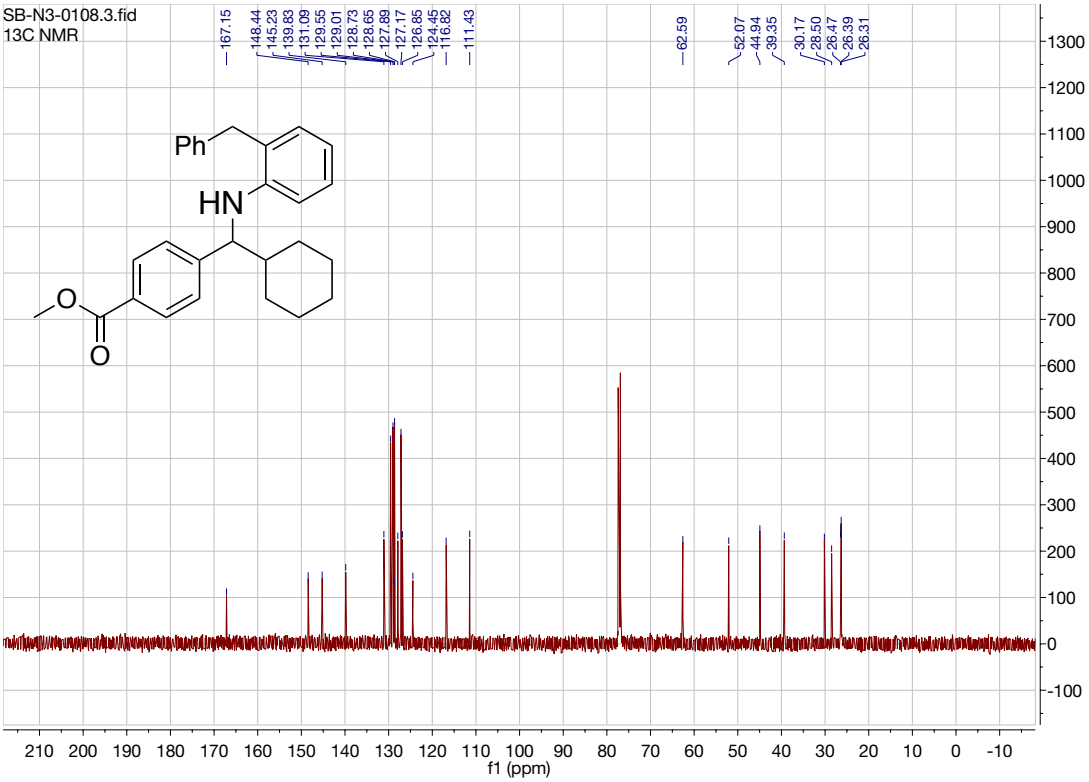
^{13}C NMR spectrum of compound **52** ($CDCl_3$, 126 MHz).



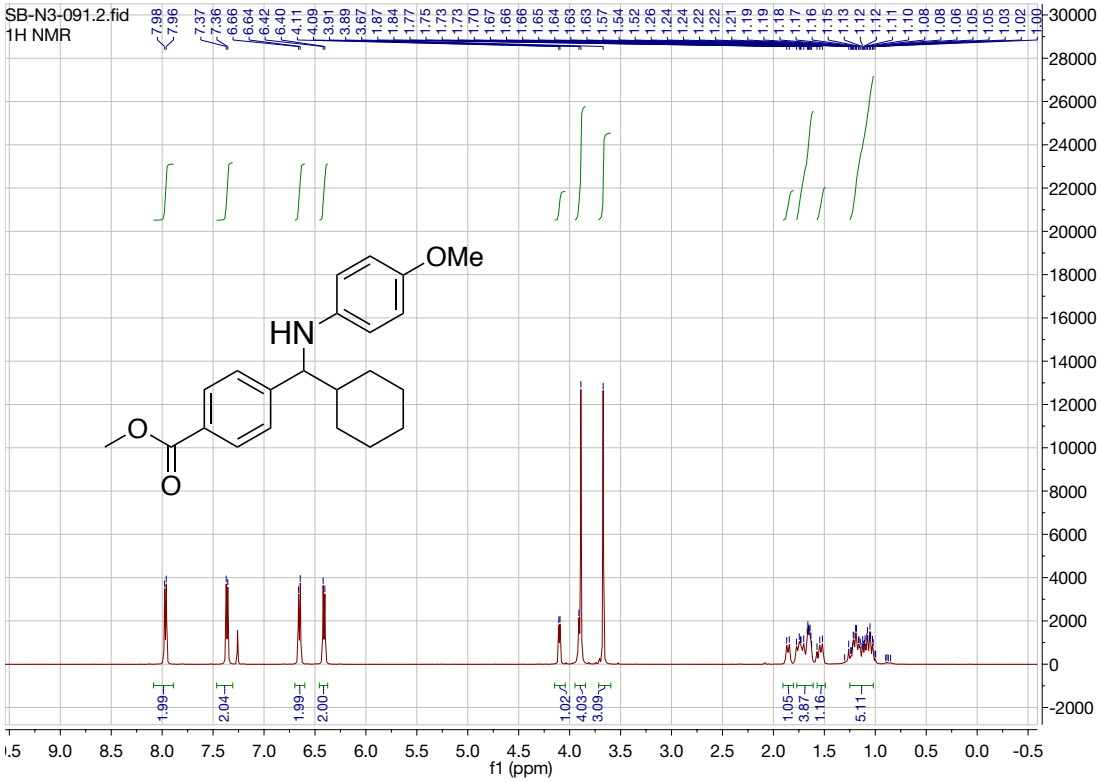
^{1}H NMR spectrum of compound **53** ($CDCl_3$, 500 MHz).



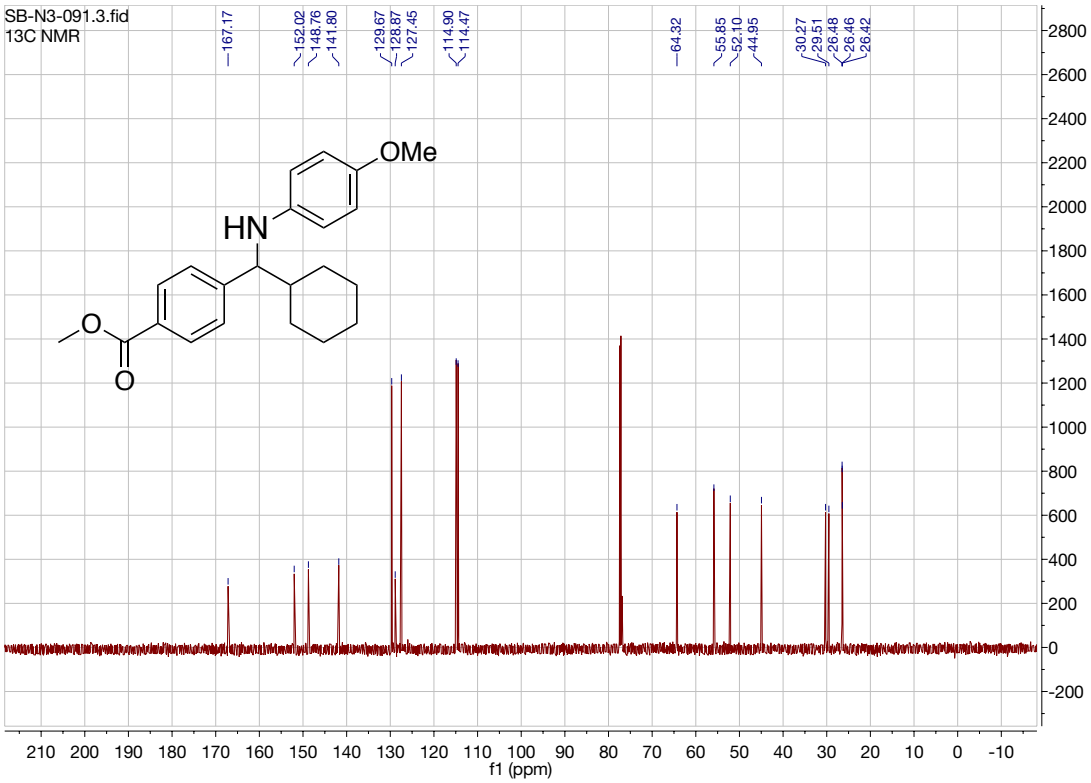
^{13}C NMR spectrum of compound **53** ($CDCl_3$, 126 MHz).



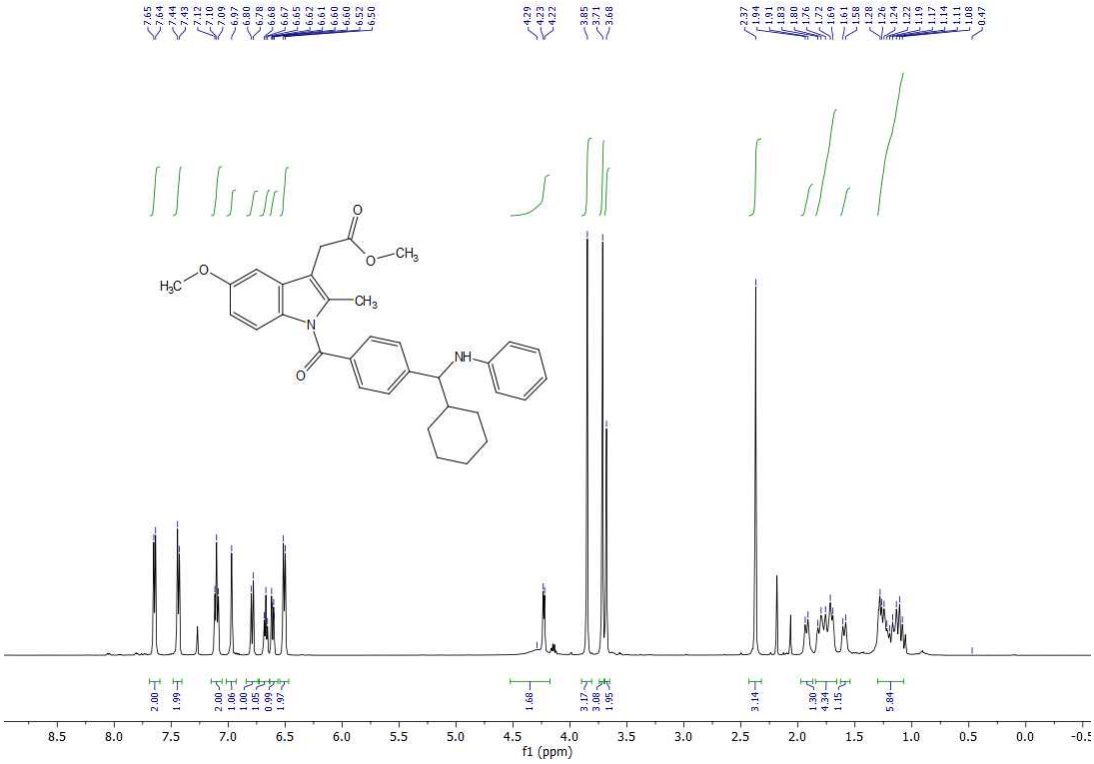
^{1}H NMR spectrum of compound **54** ($CDCl_3$, 500 MHz).



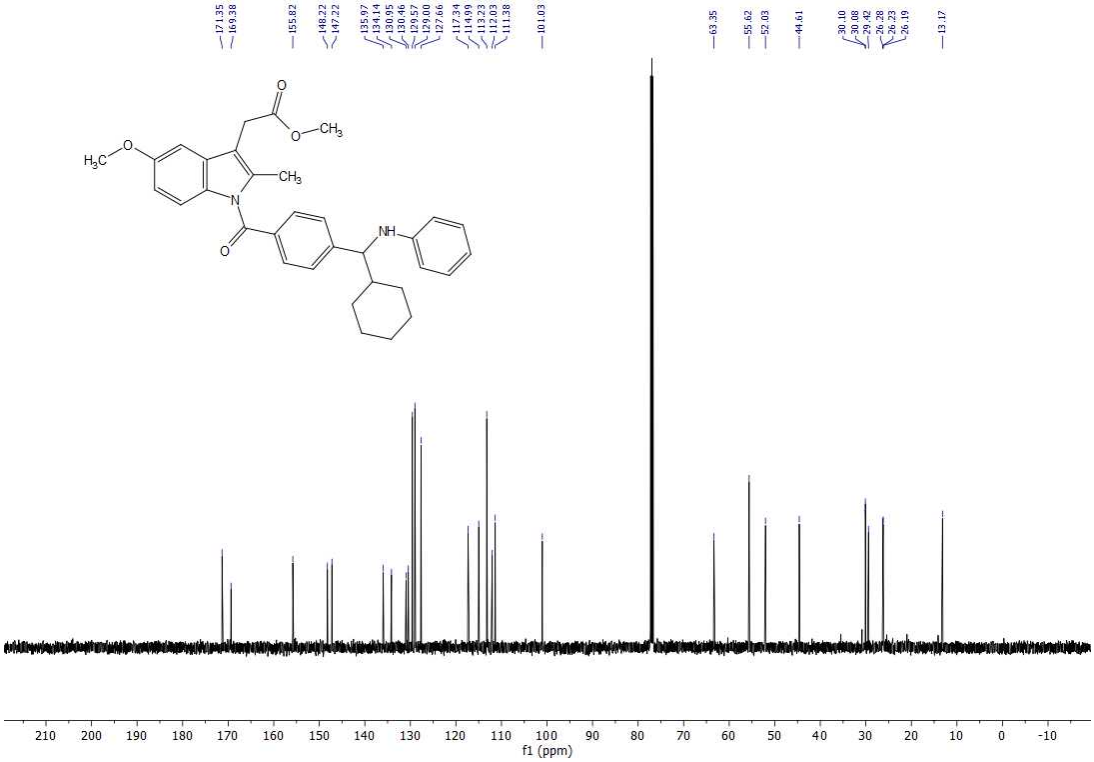
^{13}C NMR spectrum of compound **54** ($CDCl_3$, 126 MHz).



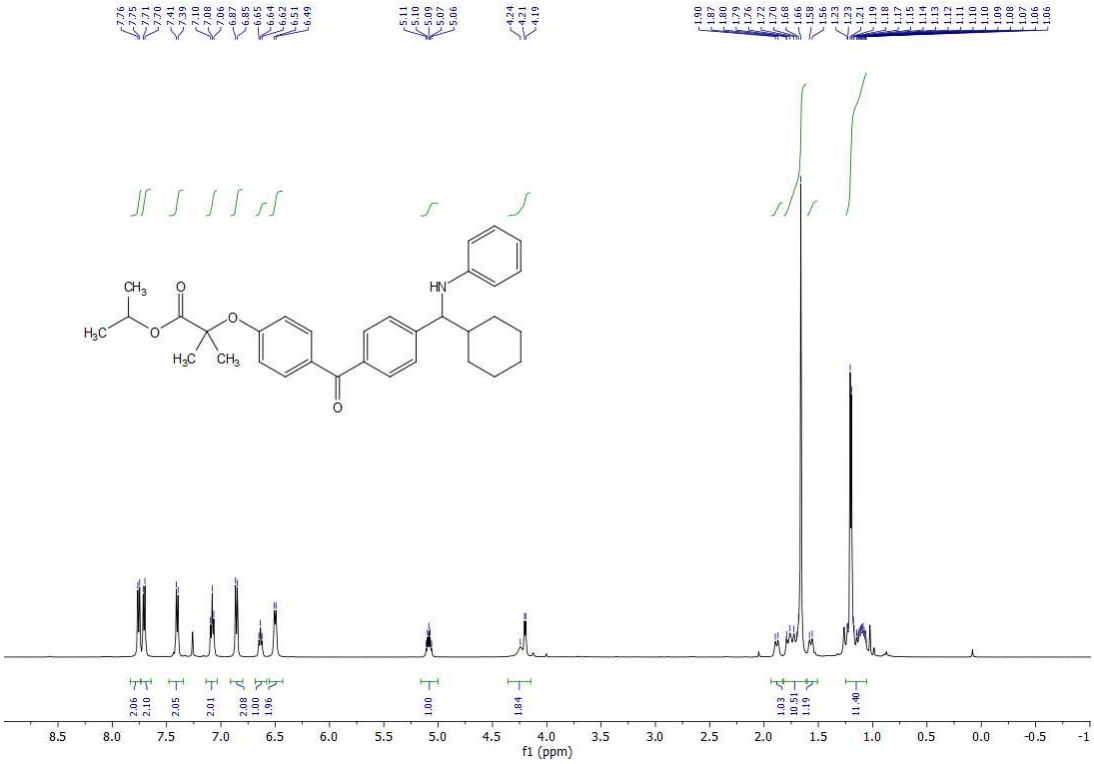
^{1}H NMR spectrum of compound **55** ($CDCl_3$, 500 MHz).



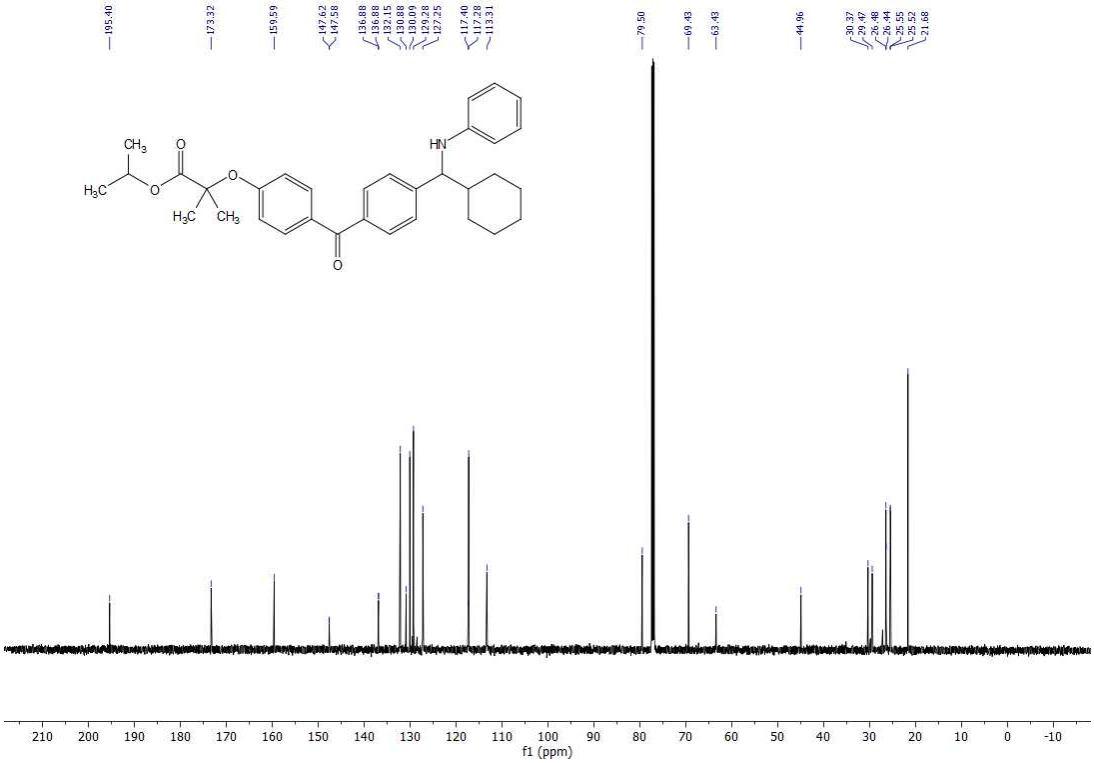
^{13}C NMR spectrum of compound **55** ($CDCl_3$, 126 MHz).



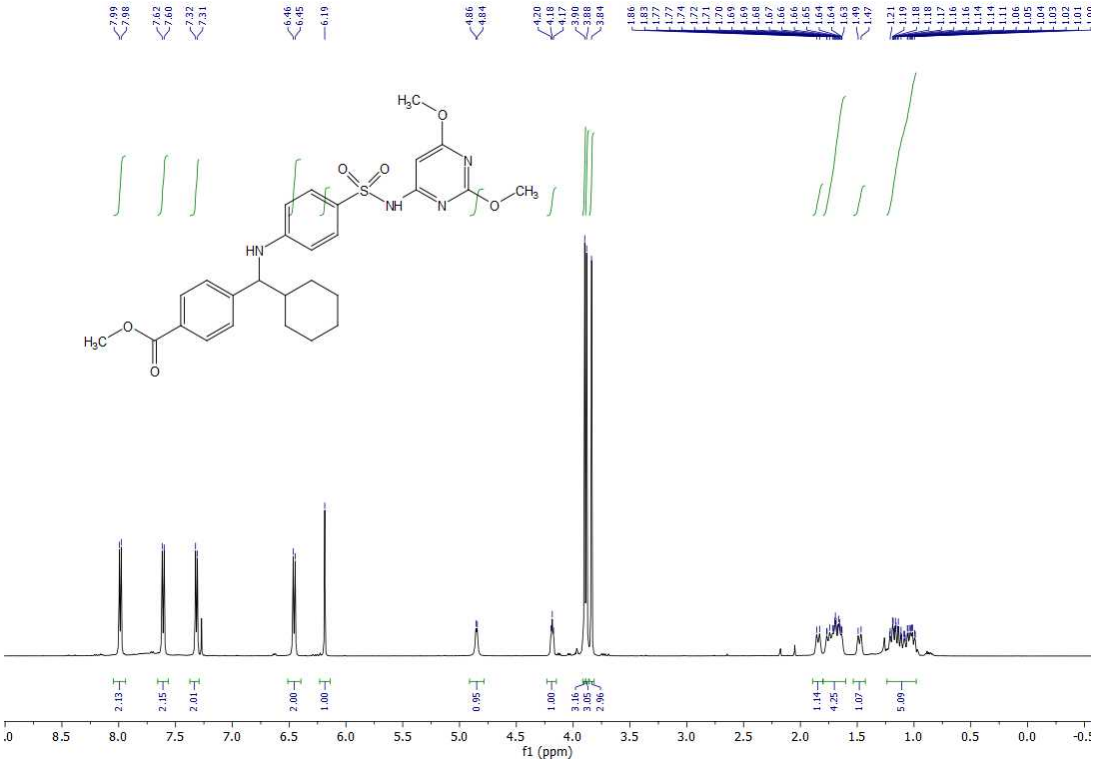
^{1}H NMR spectrum of compound **56** ($CDCl_3$, 500 MHz).



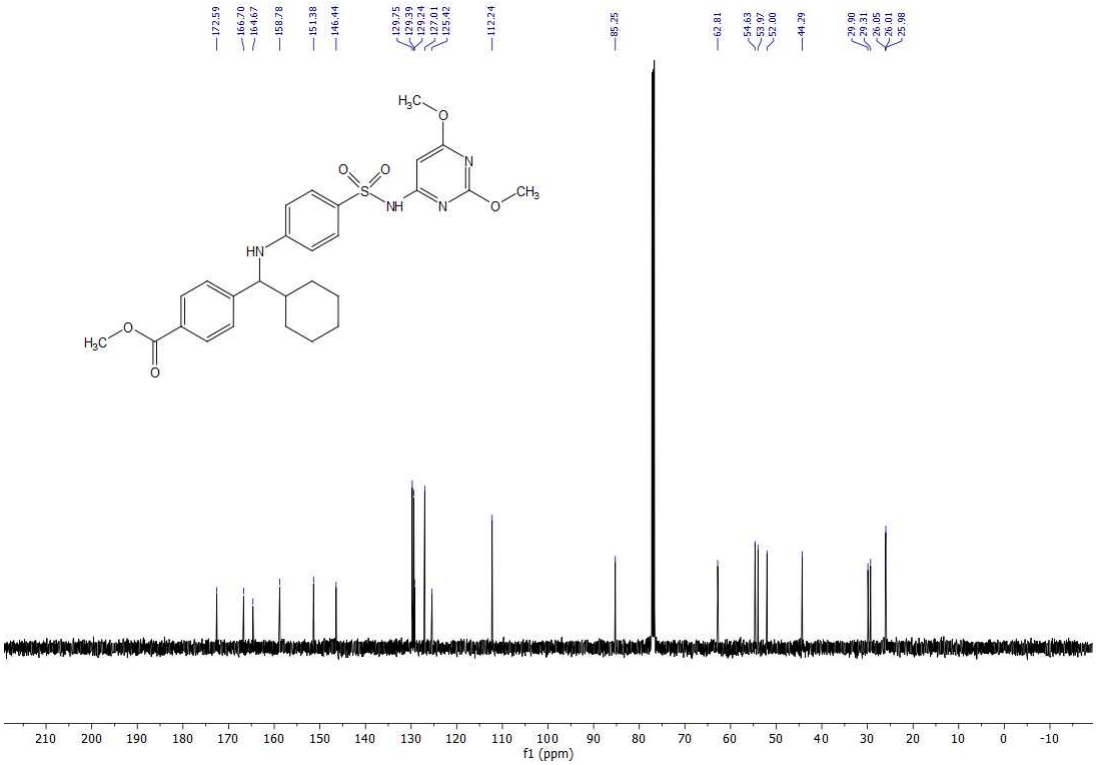
^{13}C NMR spectrum of compound **56** ($CDCl_3$, 126 MHz).



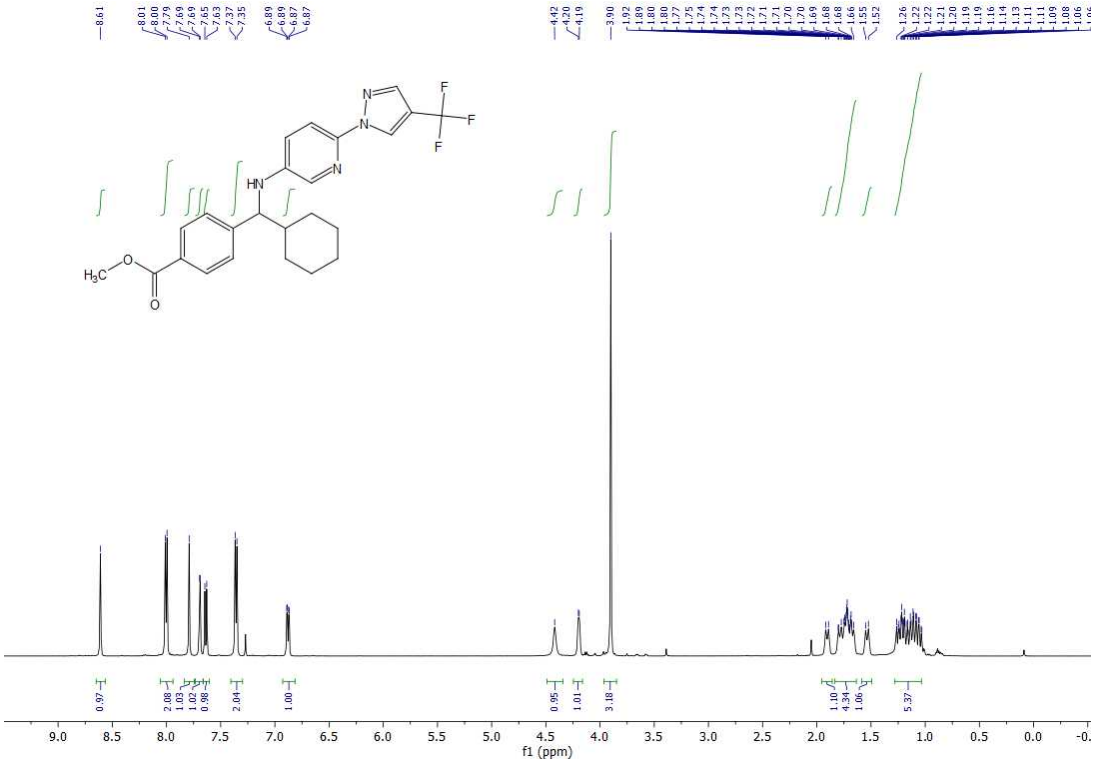
^{1}H NMR spectrum of compound **57** ($CDCl_3$, 500 MHz).



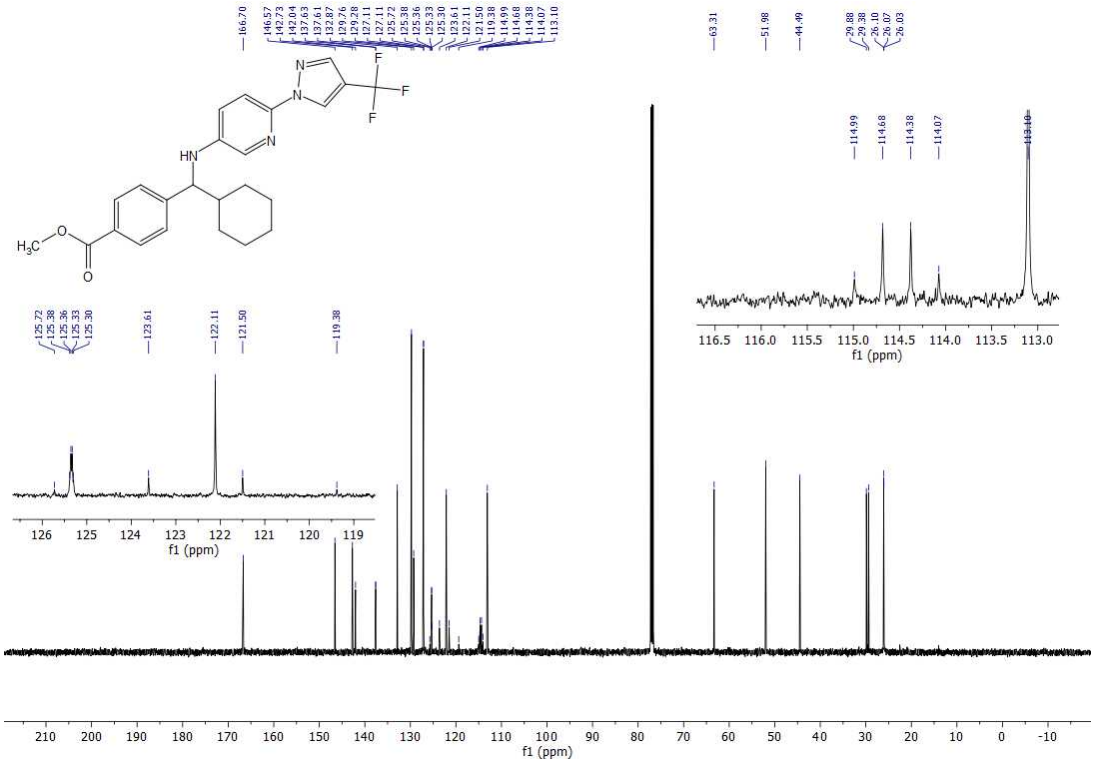
^{13}C NMR spectrum of compound **57** ($CDCl_3$, 126 MHz).



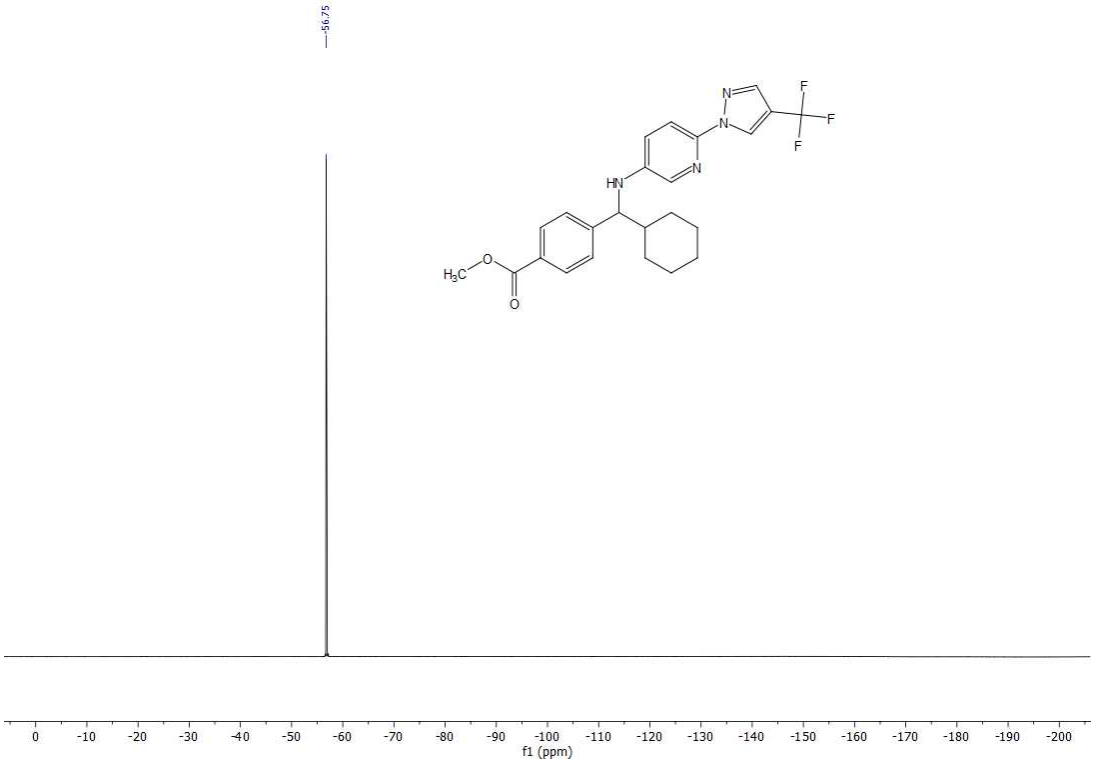
^{1}H NMR spectrum of compound **60** ($CDCl_3$, 500 MHz).



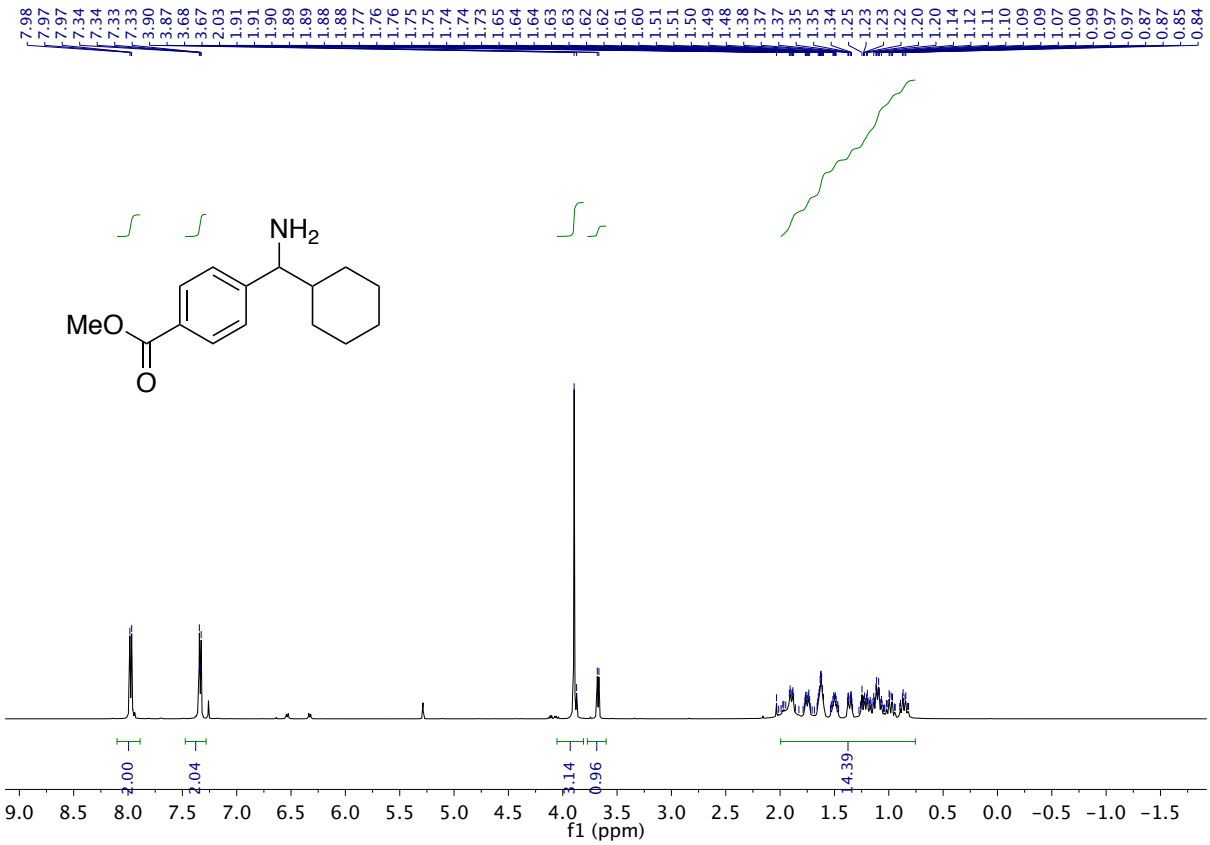
^{13}C NMR spectrum of compound **60** ($CDCl_3$, 126 MHz).



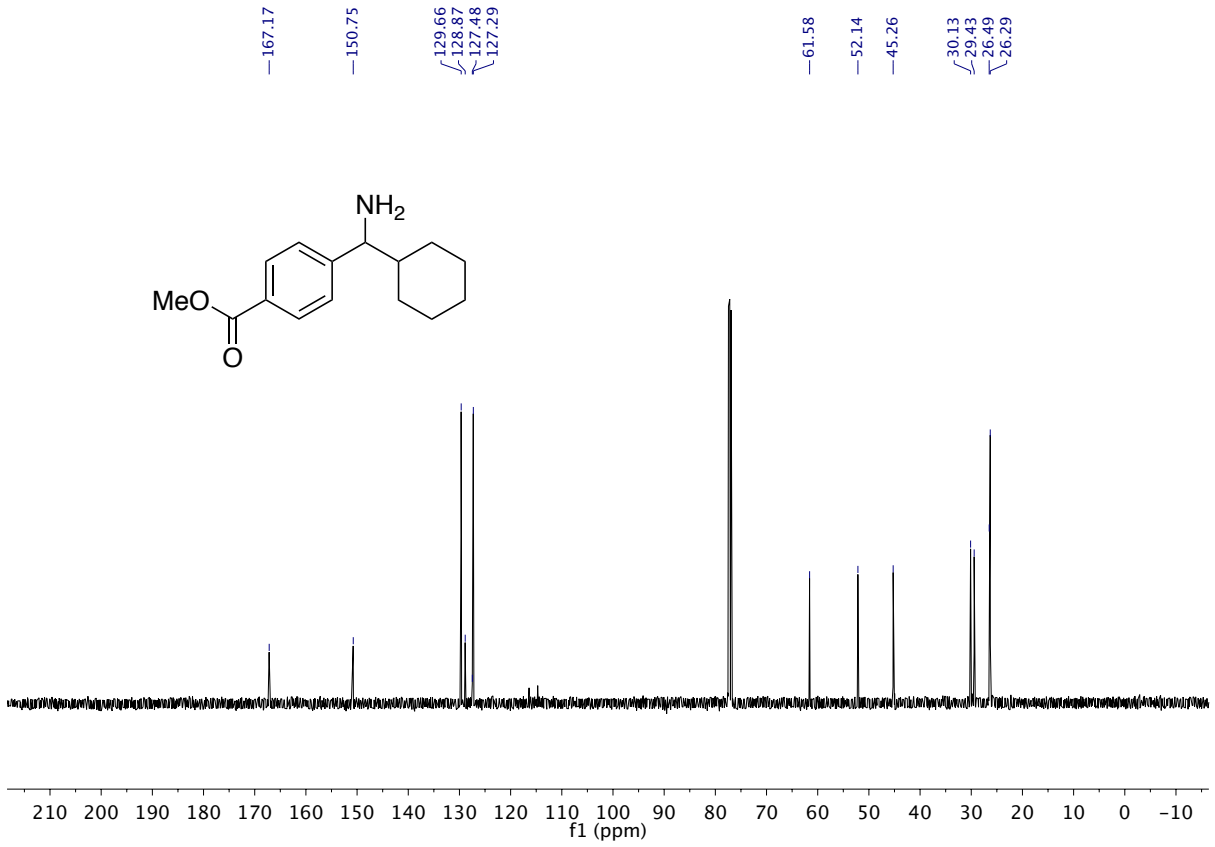
^{19}F NMR spectrum of compound **60** ($CDCl_3$, 471 MHz).



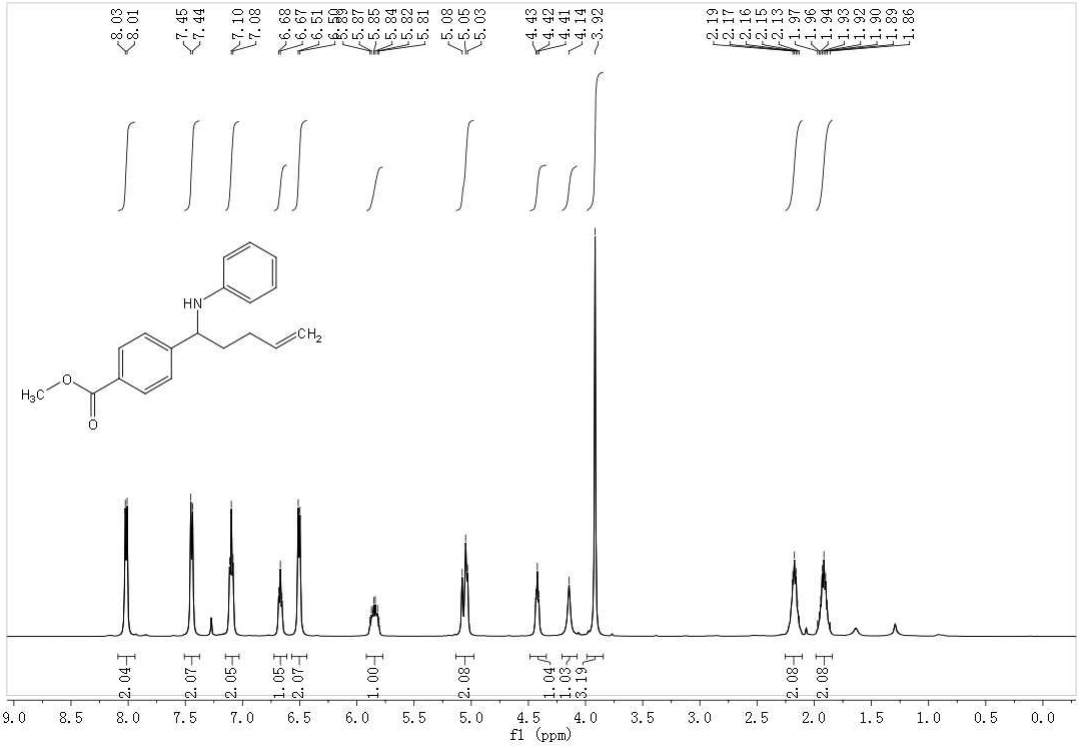
^{1}H NMR spectrum of compound **61** ($CDCl_3$, 500 MHz).



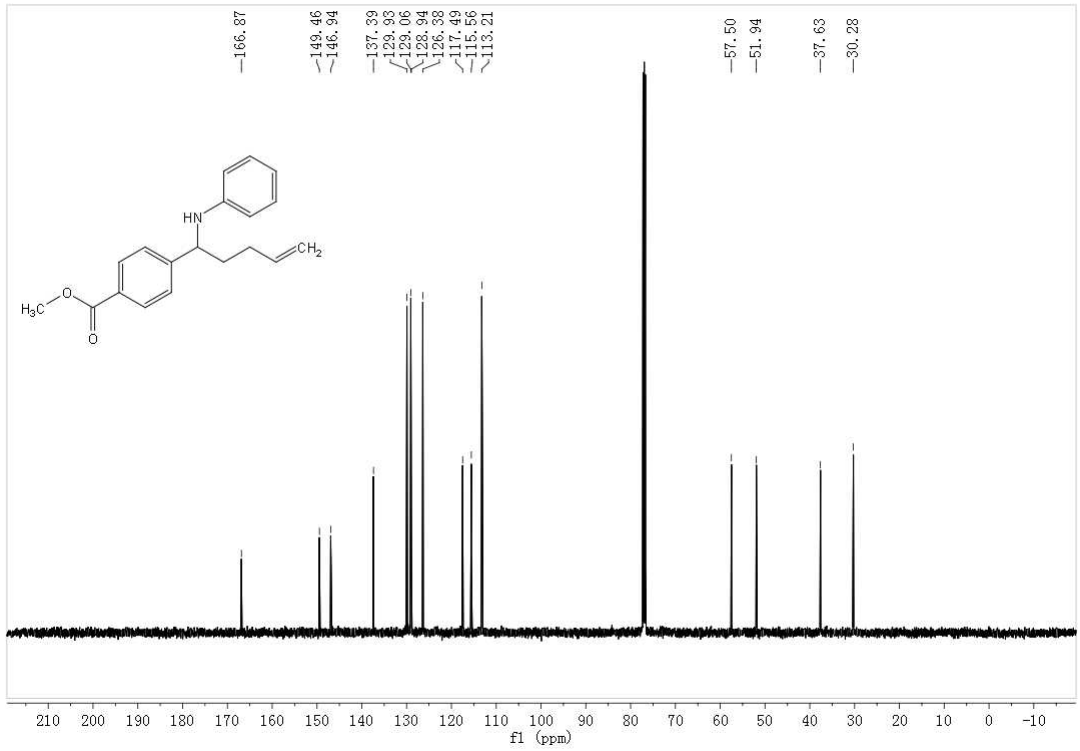
^{13}C NMR spectrum of compound **61** ($CDCl_3$, 126 MHz).



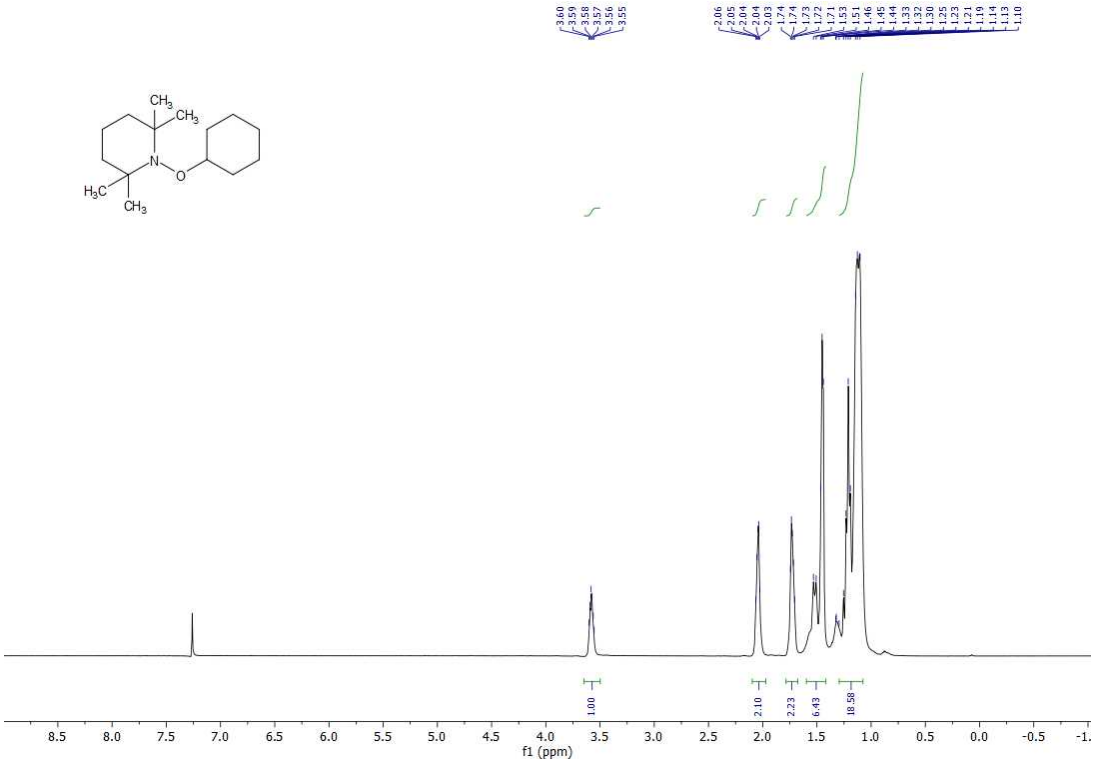
^{1}H NMR spectrum of compound **62** ($CDCl_3$, 500 MHz).



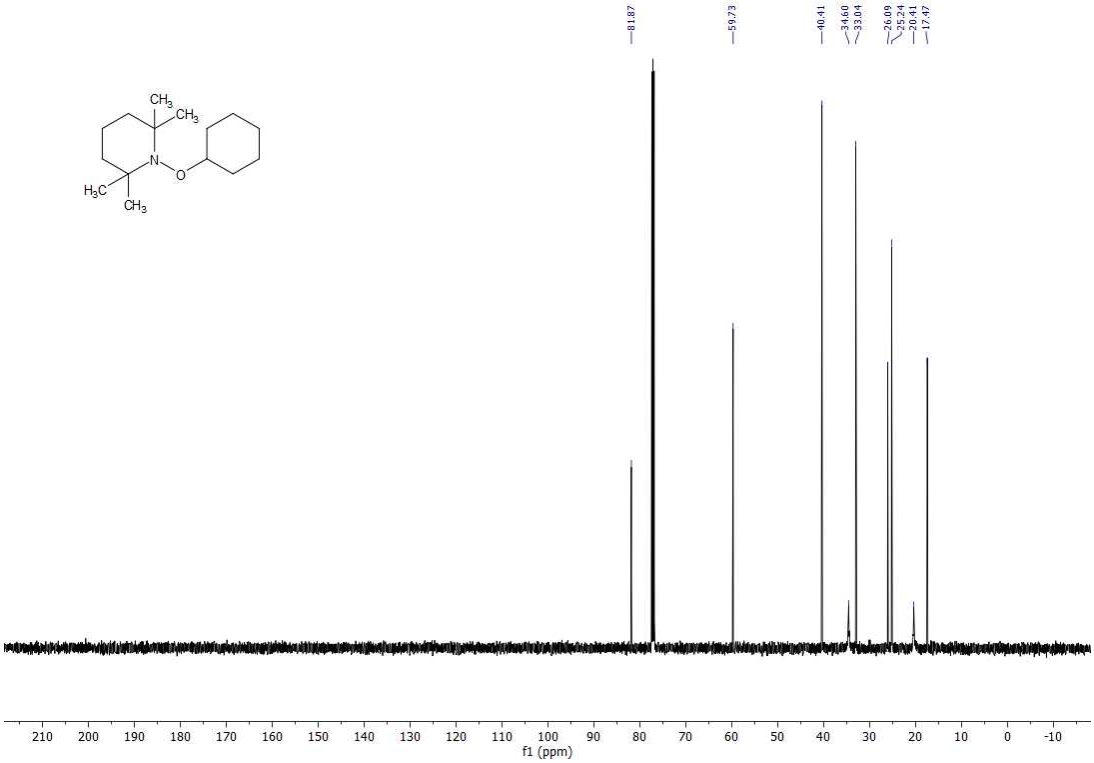
^{13}C NMR spectrum of compound **62** ($CDCl_3$, 126 MHz).



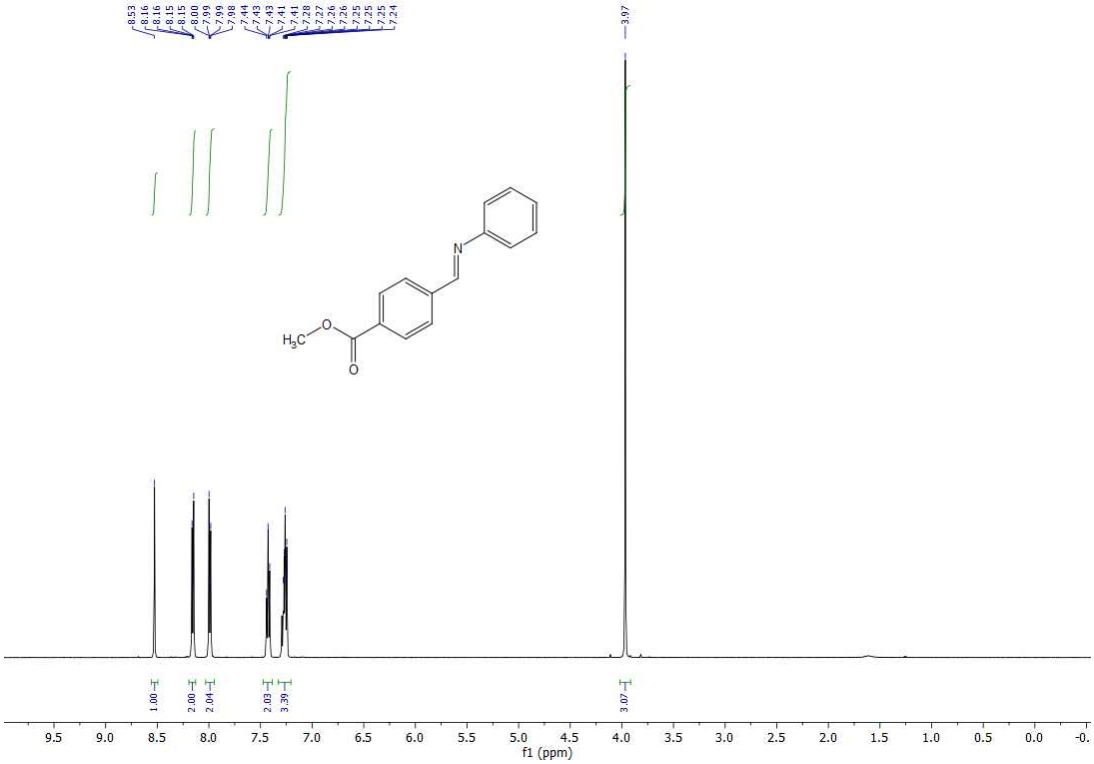
^{1}H NMR spectrum of compound **63** ($CDCl_3$, 500 MHz).



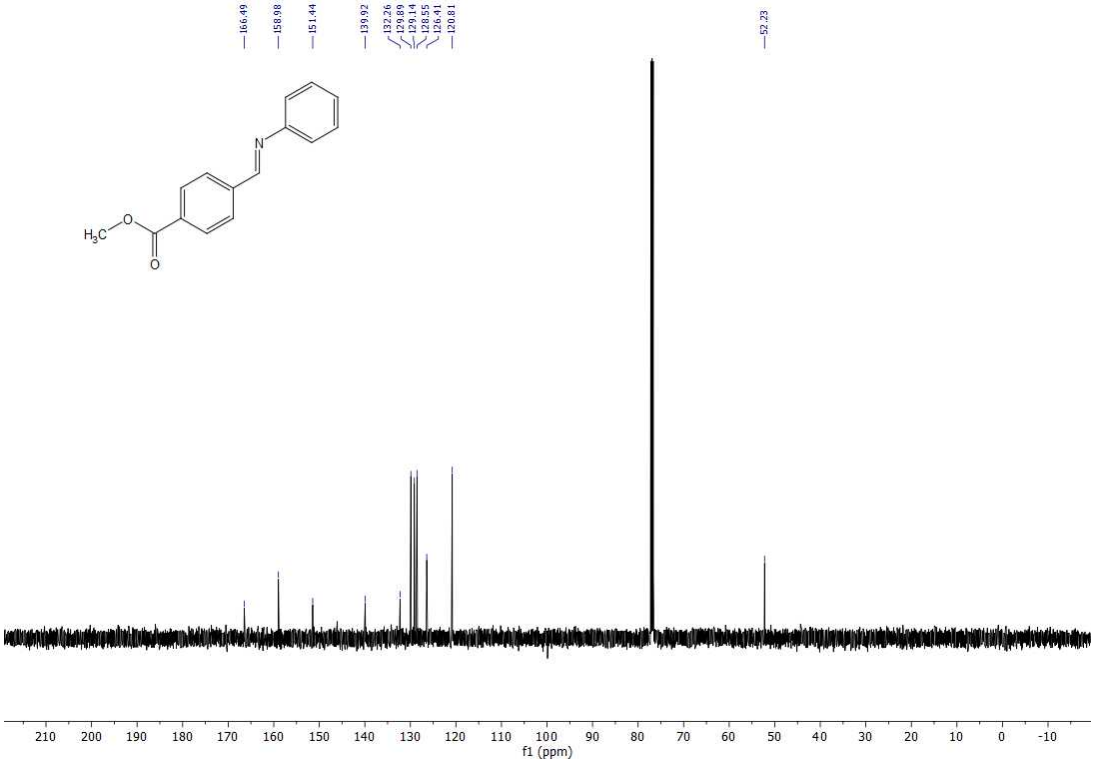
^{13}C NMR spectrum of compound **63** ($CDCl_3$, 126 MHz).



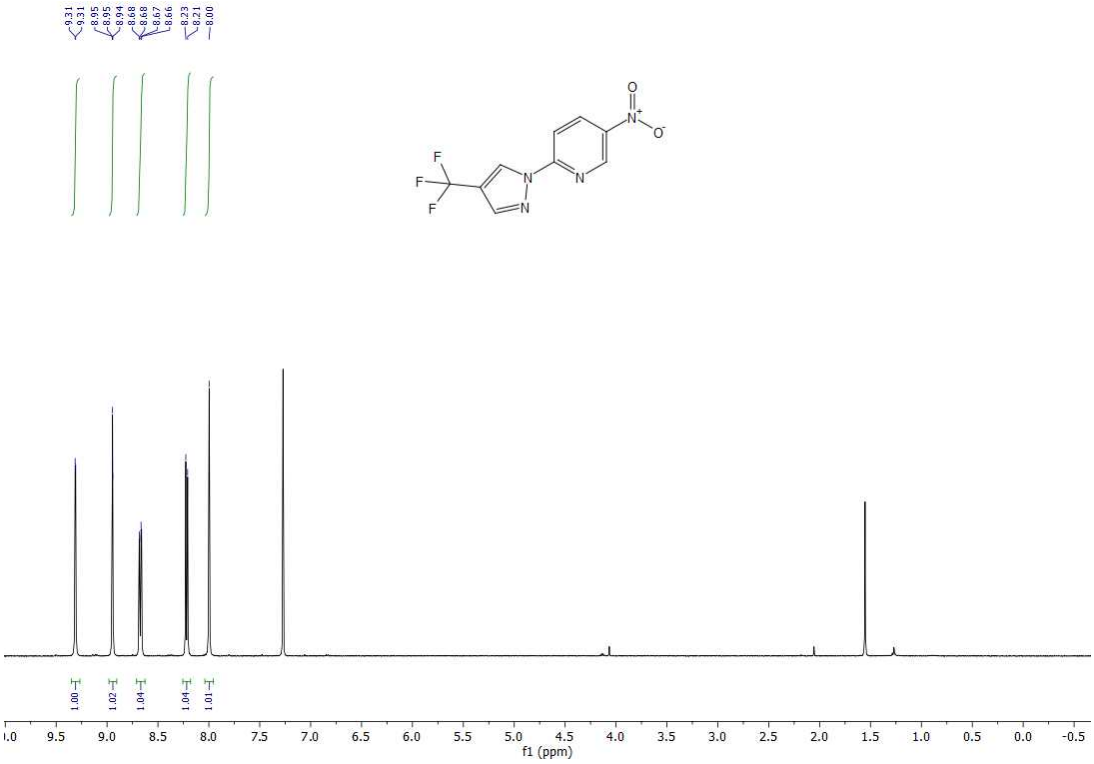
^{1}H NMR spectrum of compound **64** ($CDCl_3$, 500 MHz).



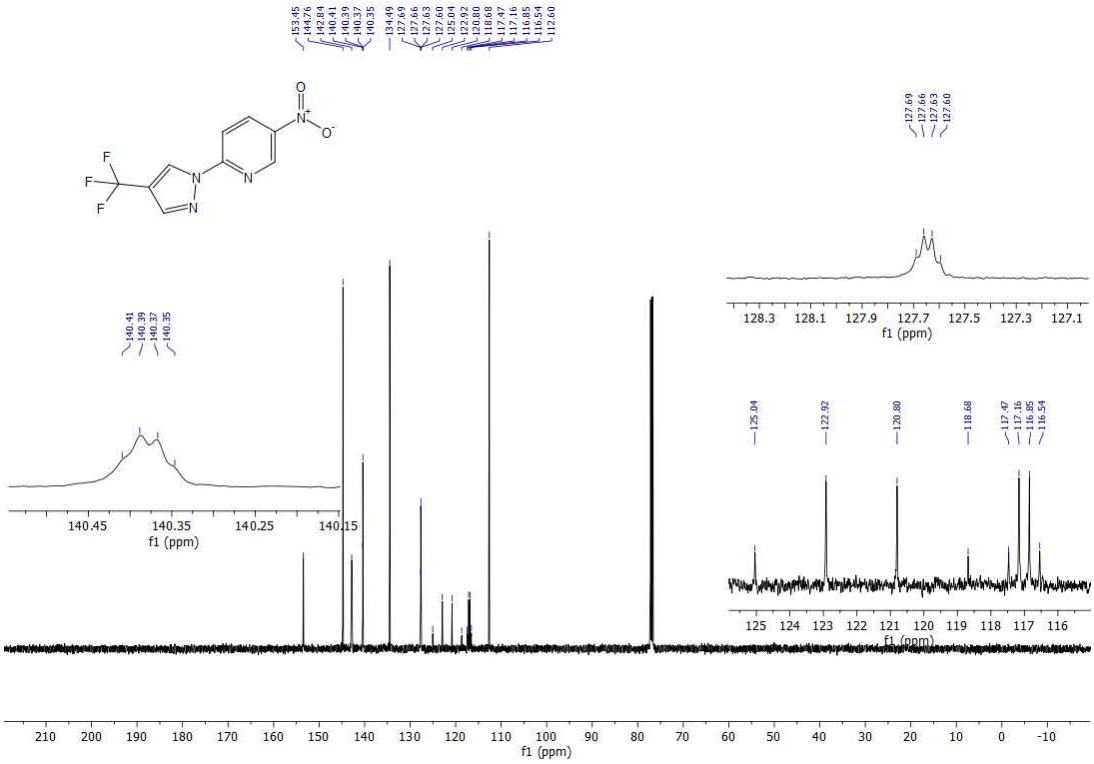
^{13}C NMR spectrum of compound **64** ($CDCl_3$, 126 MHz).



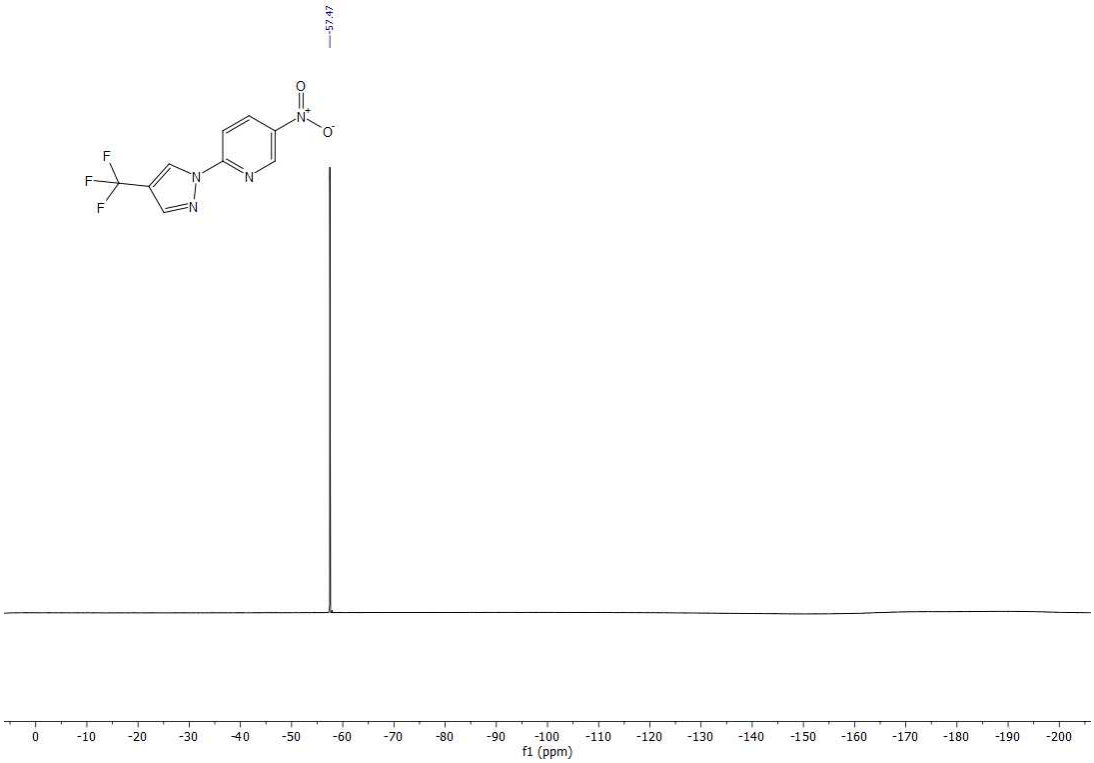
^{1}H NMR spectrum of compound **58** ($CDCl_3$, 500 MHz).



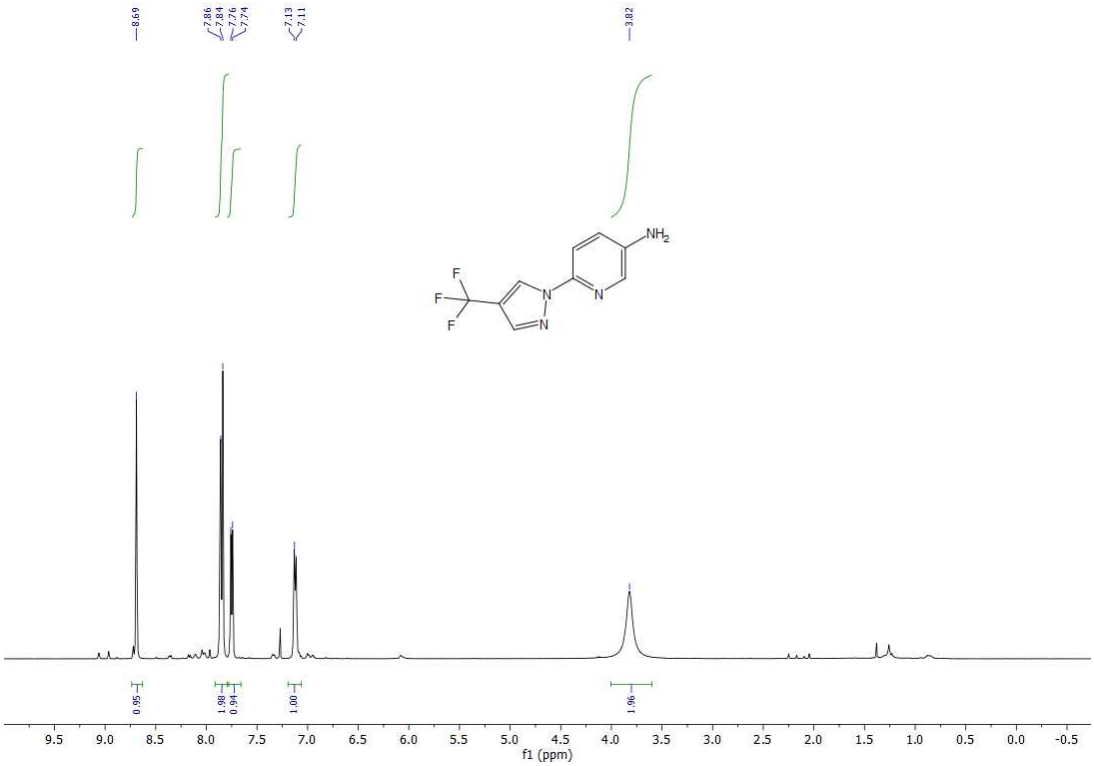
^{13}C NMR spectrum of compound **58** ($CDCl_3$, 126 MHz).



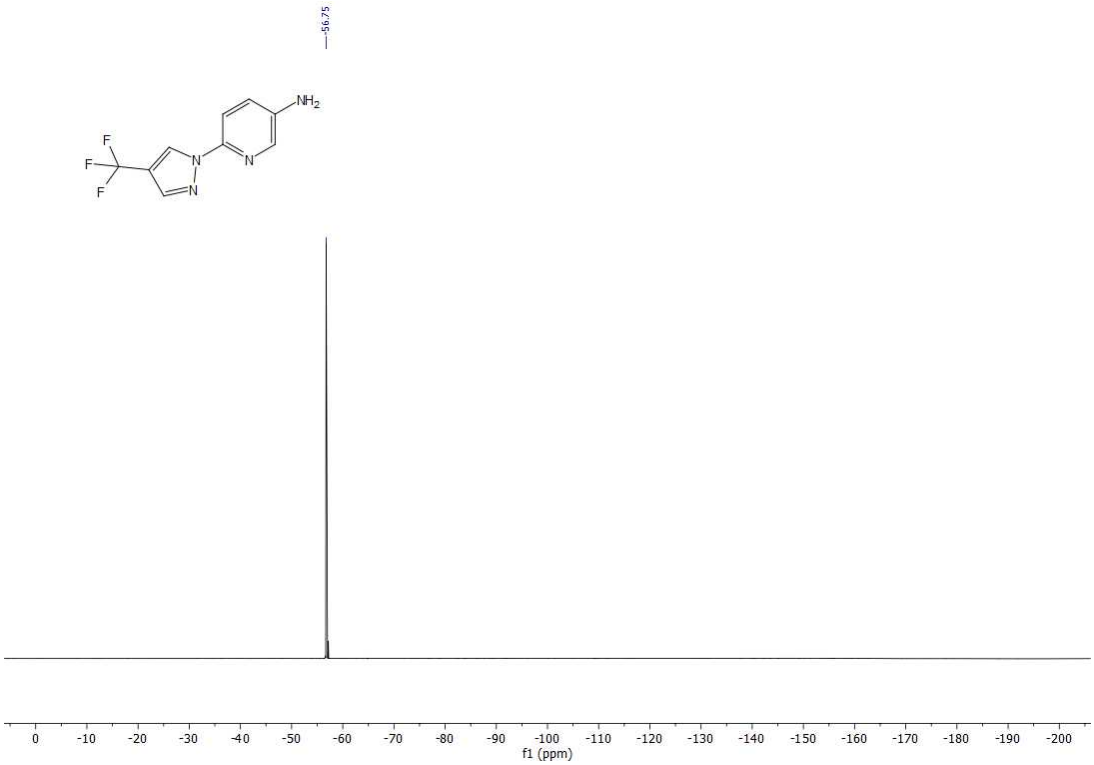
^{19}F NMR spectrum of compound **58** ($CDCl_3$, 471 MHz).



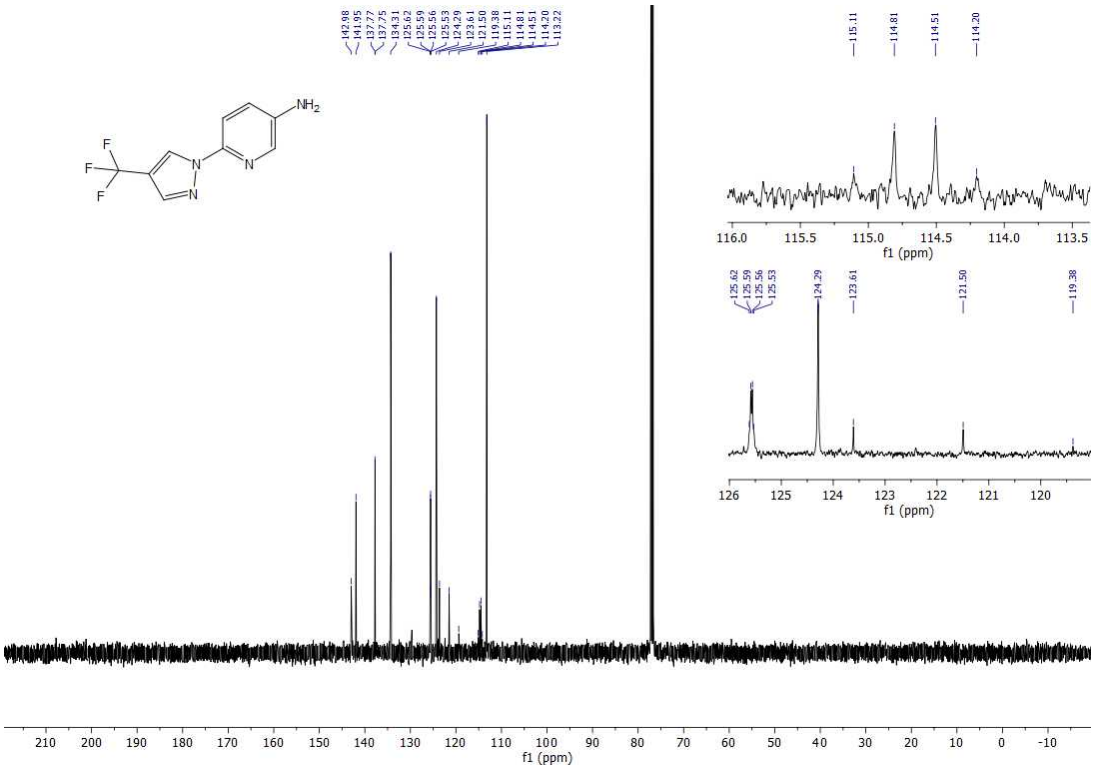
^{1}H NMR spectrum of compound **59** ($CDCl_3$, 500 MHz).



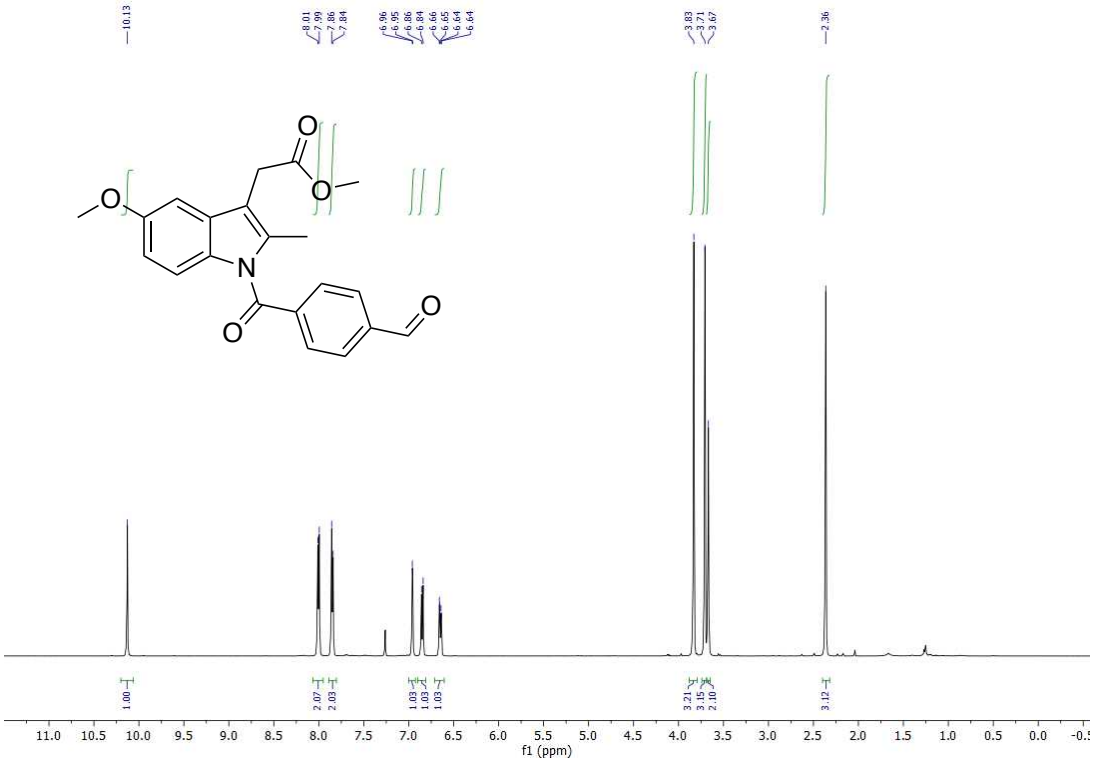
^{13}C NMR spectrum of compound **59** ($CDCl_3$, 126 MHz).



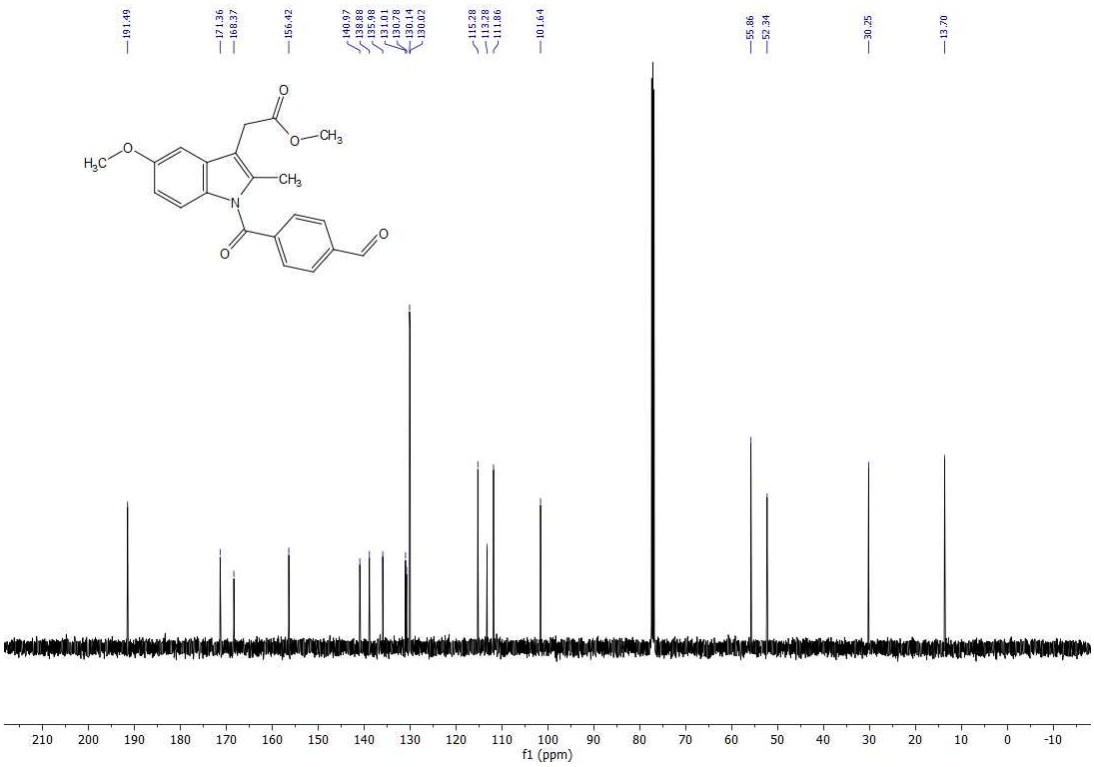
^{19}F NMR spectrum of compound **59** ($CDCl_3$, 471 MHz).



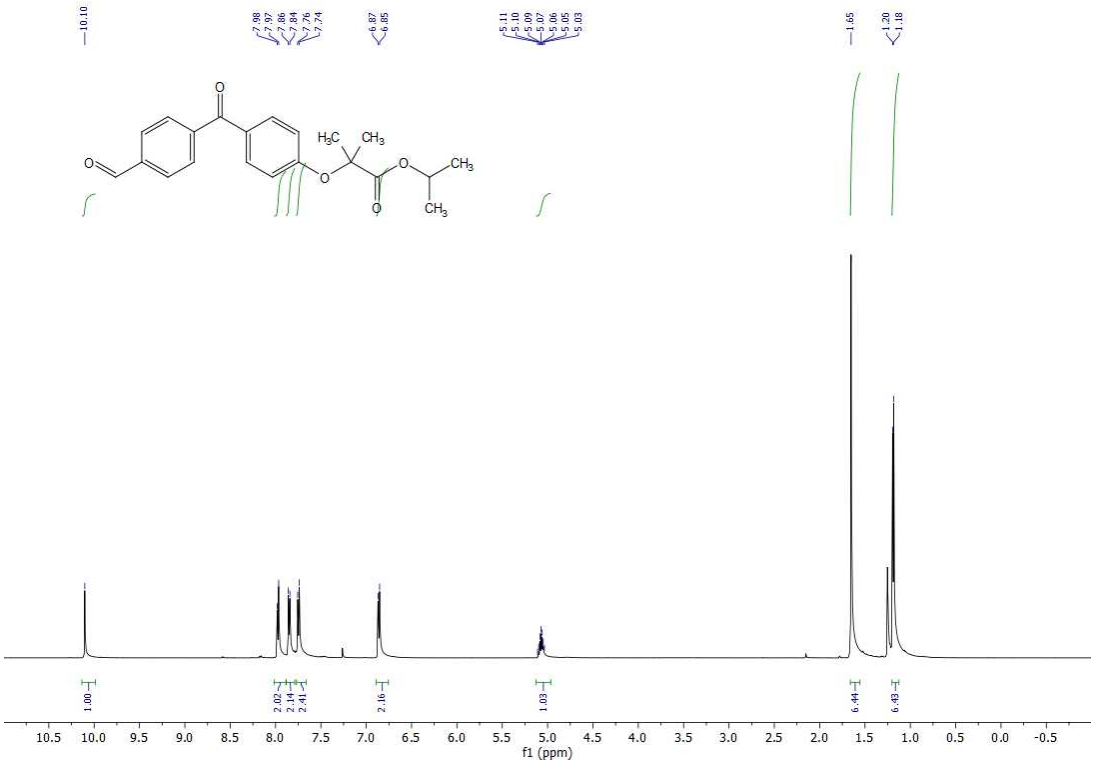
[1] H NMR spectrum of compound of aldehyde corresponding to **55** ($CDCl_3$, 500 MHz).



[13] C NMR spectrum of compound aldehyde corresponding to **55** ($CDCl_3$, 126 MHz).



^{1} H NMR spectrum of compound of aldehyde corresponding to **56** ($CDCl_3$, 500 MHz).



^{13} C NMR spectrum of compound of aldehyde corresponding to **56** ($CDCl_3$, 126 MHz).