

Electronic Supplementary Information For

Iron-Catalyzed Carboamination of Vinylarenes with Alkanes and Nitrogen Nucleophiles

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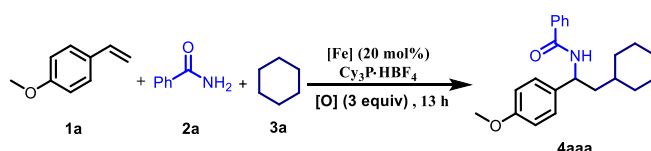
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1. General Methods

NMR spectra were recorded on Bruker Avance NEO 600 M and 400 M. Chemical shifts (ppm) are given relative to solvent: references for CDCl_3 were 7.26 ppm ($^1\text{H-NMR}$) and 77.0 ppm ($^{13}\text{C-NMR}$). ^{13}C NMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. Gas chromatography analysis was performed on a Shimadzu 2014 instrument with an FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using N_2 as carrier gas. HRMS was obtained on a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh. All reactions were carried out under N_2 atmosphere. All the reagents were purchased from Heowns, Rhawn, and Laajoo chemical company.

2. Optimization of Reaction Conditions

S-Table 1. Optimization of Reaction Conditions. ^[a]



Entry	[M]	[O]	T ($^{\circ}\text{C}$)	Yield (%)
1 ^{b)}	FeCl_3	DTBP	130	58
2	FeBr_2	DTBP	130	45
3	$\text{Fe}(\text{acac})_2$	DTBP	130	38
4	$\text{Fe}(\text{OTf})_2$	DTBP	130	34
5	$\text{Fe}(\text{BF}_4)_2$	DTBP	130	63
6	FeCl_2	TBHP	130	11 (6) ^b
7	FeCl_2	BPO	130	2 (-) ^b
8	FeCl_2	TBPB	130	12 (6) ^b
9	FeCl_2	TBPO	130	8 (2) ^b
10	FeCl_2	TBPA	130	14 (5) ^b

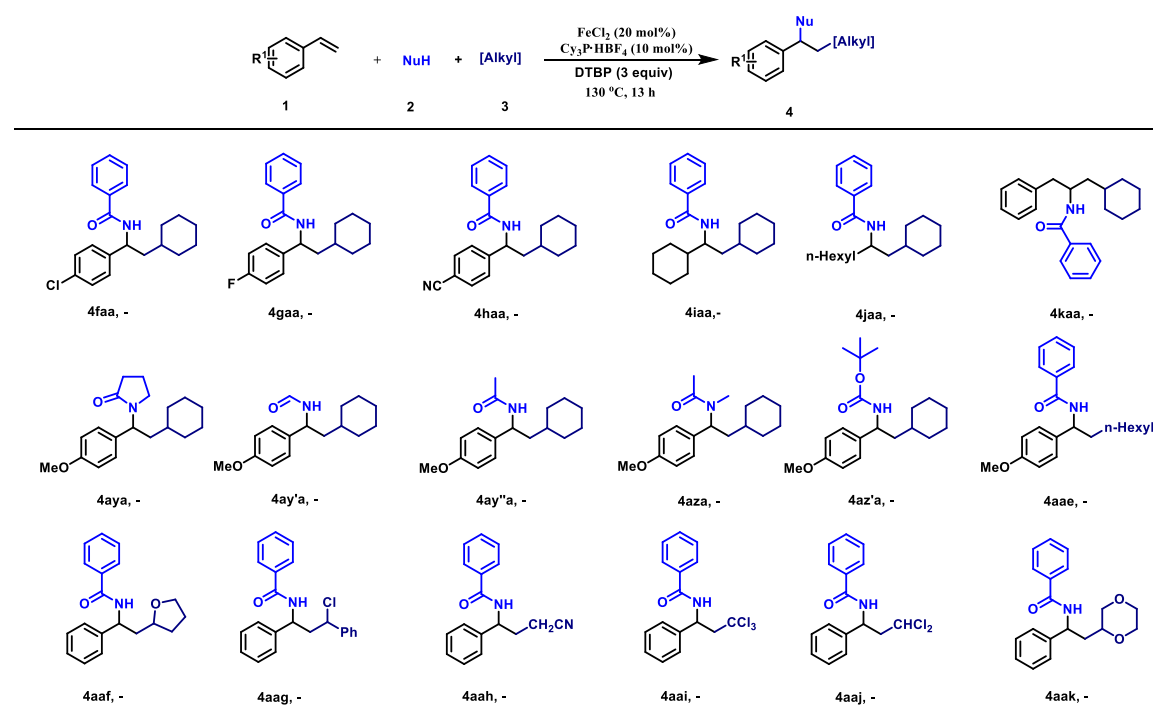
[a] Reaction conditions: **1a** (0.18 mmol, 1.8 equiv), **2a** (0.1 mmol, 1.0 equiv), DTBP (0.3 mmol, 3.0 equiv), $[\text{Fe}]$ (20 mol%), $\text{Cy}_3\text{P}\cdot\text{HBF}_4$ (10 mol%), cyclohexane (1 mL), 130 $^{\circ}\text{C}$, N_2 , and 13 h, yields were determined by GC analysis using hexadecane as internal standard. [b] 120 $^{\circ}\text{C}$. TBHP: tert-butyl hydroperoxide (5.5mol/L in decane (over molecular sieve 4A)). BPO: benzoyl peroxide. TBPB: tert-butyl peroxybenzoate. TBPO: tert-butyl peroxide. TBPA: tert-butyl peroxyacetate.

3. Typical reaction procedure for the synthesis of amines:

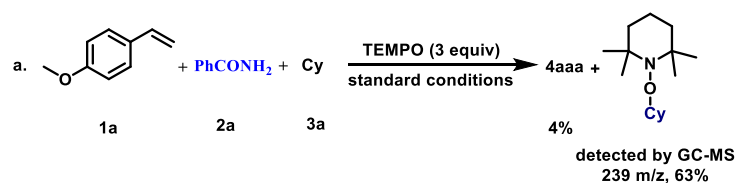
General procedure: To a 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added FeCl_2 (20 mol%) and $\text{Cy}_3\text{P}\cdot\text{HBF}_4$ (10 mol%). The reaction vessel was evacuated and filled with N_2 three times. Subsequently, degassed cyclohexane (1.0 mL), alkene **1** (0.18 mmol, 1.8 equiv), amine **2** (0.1 mmol, 1.0 equiv), and DTBP (0.3 mmol, 3 equiv) was added separately via syringe under N_2 at room temperature. The reaction mixture was heated with stirring at 130 °C (no need for preheating) in an oil bath for 13 hours. Upon completion, the yellow clear liquid was concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/AcOEt (20:1) as the eluent to give the corresponding products.

Scale up experiment: To a 50 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added FeCl_2 (20 mol%) and $\text{Cy}_3\text{P}\cdot\text{HBF}_4$ (10 mol%). The reaction vessel was evacuated and filled with N_2 three times. Subsequently, degassed cyclohexane (20 mL), alkene **1a** (5.4 mmol, 1.8 equiv), amine **2a** (3 mmol, 1.0 equiv), and DTBP (9 mmol, 3 equiv) was added separately via syringe under N_2 at room temperature. The reaction mixture was heated with stirring at 130 °C (no need for preheating) in an oil bath for 13 hours. Upon completion, the yellow clear liquid was concentrated under vacuum. The residue was purified by silica gel column chromatography using petroleum ether/AcOEt (20:1) as the eluent to give the corresponding products.

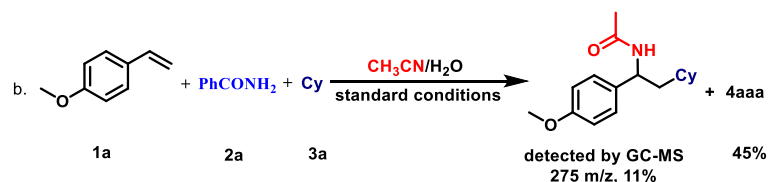
4. Unsuccessful examples



5. Control experiments



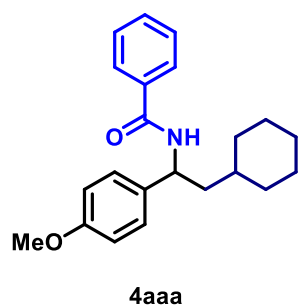
General procedure: To a 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added FeCl₂ (20 mol%) and Cy₃P·HBF₄ (10 mol%). The reaction vessel was evacuated and filled with N₂ three times. Subsequently, degassed cyclohexane (1.0 mL), alkene **1** (0.18 mmol, 1.8 equiv), amine **2** (0.1 mmol, 1.0 equiv), DTBP (0.3 mmol, 3 equiv) and TEMPO (0.3 mmol, 3 equiv) was added separately via syringe under N₂ at room temperature. The reaction mixture was heated with stirring at 130 °C (no need for preheating) in an oil bath for 13 hours. Upon completion, the reaction mixture was added hexadecane (20 mg) as internal standard. The reaction mixture was diluted with ethyl acetate (2 mL) and stir for 10 minutes. Finally, took 1 μL of the reaction solution and performed GC-MS detection. There was still a large amount of olefin remaining. Benzamide and its possible byproducts have not been discovered.



General procedure: To a 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was added FeCl₂ (20 mol%) and Cy₃P·HBF₄ (10 mol%). The reaction vessel was evacuated and filled with N₂ three times. Subsequently, degassed cyclohexane (1.0 mL), alkene **1** (0.18 mmol, 1.8 equiv), amine **2** (0.1 mmol, 1.0 equiv), DTBP (0.3 mmol, 3 equiv), CH₃CN (0.1 mL), and H₂O (0.2 mmol, 2 equiv) was added separately via syringe under N₂ at room temperature. The reaction mixture was heated with stirring at 130 °C (no need for preheating) in an oil bath for 13 hours. Upon completion, the reaction mixture was added hexadecane (20 mg) as internal standard. The reaction mixture was diluted with ethyl acetate (2 mL) and stir for 10 minutes. Finally, took 1 μL of the reaction solution and performed GC-MS detection.

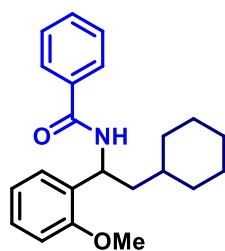
6. Characterization data for products

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)benzamide (4aaa)



Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (23.6 mg, 70%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.19 (d, *J* = 7.6 Hz, 1H), 5.17 (q, *J* = 7.8 Hz, 1H), 3.71 (s, 3H), 1.77 – 1.63 (m, 6H), 1.23 – 1.16 (m, 2H), 1.11 – 1.05 (m, 3H), 1.00 – 0.87 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 165.4, 157.8, 133.9, 133.8, 130.3, 127.5, 126.8, 125.9, 113.1, 54.3, 49.8, 43.0, 33.5, 32.3, 32.2, 25.5, 25.12, 25.09. GC-MS (EI-70 eV): *m/z* (%) 337 (5), 240 (63), 216 (12), 134 (18), 121 (15), 105 (100). HRMS (ESI): calcd for C₂₂H₂₇NNaO₂⁺ [M+Na]⁺ 360.1934, found: 360.1933.

N-(2-cyclohexyl-1-(2-methoxyphenyl)ethyl)benzamide (4baa)

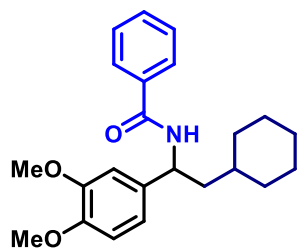


4baa

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (19.5 mg, 58%). ¹H NMR (400 MHz, Chloroform-*d*) δ 57.81 (d, *J* = 7.0 Hz, 2H), 7.51 (d, *J* = 7.1 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 9.2 Hz, 1H), 6.96 (t, *J* = 7.9 Hz, 2H), 5.47 (q, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 1.92 – 1.67 (m, 7H), 1.28 – 1.14 (m, 4H), 1.07 – 0.91 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 166.2, 157.3, 135.2, 131.3, 130.3, 129.0, 128.6, 128.4, 127.0, 121.0, 111.2, 55.5, 50.4, 43.4, 34.8, 33.5, 33.2, 26.6, 26.3, 26.2. GC-MS (EI-70 eV): *m/z* (%)

337 (5), 240 (99), 216 (3), 134 (5), 121 (8), 105 (100). HRMS (ESI): calcd for C₂₂H₂₇NNaO₂⁺ [M+Na]⁺ 360.1934, found: 360.1938.

N-(2-cyclohexyl-1-(3,4-dimethoxyphenyl)ethyl)benzamide (4caa)

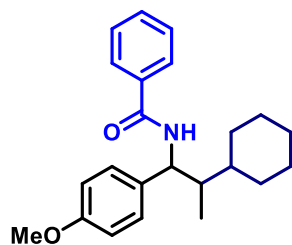


4caa

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (24.2 mg, 66%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.92 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.36 (d, *J* = 8.1 Hz, 1H), 5.27 (q, *J* = 7.9 Hz, 1H), 3.90 (d, *J* = 6.9 Hz, 6H), 1.88 – 1.71 (m, 7H), 1.35 – 1.27 (m, 1H), 1.23 – 1.15 (m, 3H), 1.11 – 0.92 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*)

δ 166.6, 149.0, 148.2, 135.5, 134.7, 131.5, 128.7, 127.0, 118.4, 111.2, 110.2, 55.98, 55.96, 51.2, 44.1, 34.6, 33.4, 33.2, 26.5, 26.23, 26.19. GC-MS (EI-70 eV): *m/z* (%) 367 (5), 270 (58), 246 (10), 121 (8), 105 (100), 77 (23). HRMS (ESI): calcd for C₂₃H₂₉NNaO₃⁺ [M+Na]⁺ 390.2040, found: 390.2045.

N-(2-cyclohexyl-1-(4-methoxyphenyl)propyl)benzamide (4daa)

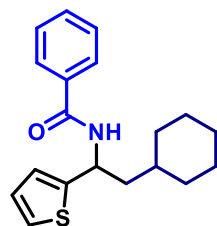


4daa

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (19.3 mg, 55%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.73 (m, 5H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.40 (m, 5H), 7.27 (t, *J* = 7.4 Hz, 4H), 6.89 (q, *J* = 7.9 Hz, 5H), 6.42 (t, *J* = 7.4 Hz, 2H), 5.28 (t, *J* = 7.4 Hz), 5.05 (t, *J* = 7.3 Hz), 3.82 (s, 6H), 1.83 – 1.68 (m, 12H), 1.37 – 1.29 (m, 6H), 1.19 – 1.08 (m, 9H), 0.93 – 0.86 (m, 3H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 131.5, 131.4,

128.7, 128.6, 128.4, 127.8, 127.0, 114.0, 55.9, 55.3, 55.1, 43.5, 39.5, 39.0, 32.4, 31.8, 28.1, 27.1, 26.8, 26.7, 26.6, 26.5, 12.5, 11.6. GC-MS (EI-70 eV): *m/z* (%) 351 (3), 240 (75), 137 (5), 121 (5), 105 (100), 77 (22). HRMS (ESI): calcd for C₂₃H₂₉NNaO₂⁺ [M+Na]⁺ 374.2091, found: 374.2091.

N-(2-cyclohexyl-1-(thiophen-2-yl)ethyl)benzamide (4eaa)

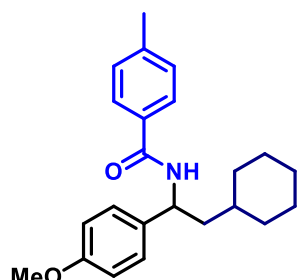


4eaa

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (18.5 mg, 59%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 5.0 Hz, 1H), 7.08 (d, *J* = 3.3 Hz, 1H), 7.00 (t, *J* = 8.1 Hz, 1H), 6.28 (d, *J* = 8.2 Hz, 1H), 5.66 (q, *J* = 7.9 Hz, 1H), 1.93 – 1.84 (m, 3H), 1.75 – 1.65 (m, 4H), 1.45 – 1.37 (m, 1H), 1.25 – 1.17 (m, 3H), 1.13 – 0.97 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 166.5, 146.7, 134.4, 131.7, 128.7, 127.03, 126.97, 124.6, 124.3, 46.9, 44.6, 34.6, 33.4, 33.0, 26.5, 26.21, 26.16.

GC-MS (EI-70 eV): m/z (%) 313 (11), 230 (2), 216 (40), 110 (13), 105 (100), 77 (27). HRMS (ESI): calcd for $C_{19}H_{23}NNaOS^+$ $[M+Na]^+$ 336.1393, found: 336.1395.

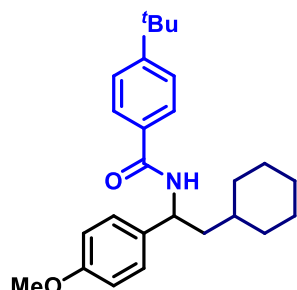
N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-methylbenzamide (4aba)



4aba

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (22.5 mg, 64%). 1H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.31 (d, J = 8.0 Hz, 1H), 5.27 (q, J = 7.8 Hz, 1H), 3.83 (s, 3H), 2.42 (s, 3H), 1.86 – 1.70 (m, 6H), 1.33 – 1.24 (m, 2H), 1.21 – 1.14 (m, 3H), 1.09 – 0.91 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 166.5, 158.7, 141.9, 135.0, 131.8, 129.2, 127.8, 127.0, 114.0, 55.3, 50.7, 44.1, 34.5, 33.3, 33.2, 26.6, 26.20, 26.17, 21.6. GC-MS (EI-70 eV): m/z (%) 351 (3), 254 (44), 216 (10), 134 (12), 119 (100), 91 (24). HRMS (ESI): calcd for $C_{23}H_{29}NNaO_2^+$ $[M+Na]^+$ 374.2091, found: 374.2094.

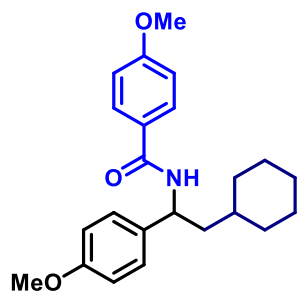
4-(tert-butyl)-N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)benzamide (4aca)



4aca

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (26.3 mg, 67%). 1H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.42 (d, J = 8.1 Hz, 1H), 5.29 (q, J = 7.9 Hz, 1H), 3.82 (s, 3H), 1.93 – 1.63 (m, 8H), 1.35 (s, 9H), 1.21 – 1.14 (m, 3H), 1.09 – 0.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 158.7, 154.9, 135.2, 131.8, 127.8, 126.9, 125.5, 114.0, 55.3, 50.7, 44.2, 35.0, 34.5, 33.4, 33.2, 31.2, 26.6, 26.24, 26.19. GC-MS (EI-70 eV): m/z (%) 393 (5), 296 (57), 216 (14), 161 (100), 134 (14), 118 (11). HRMS (ESI): calcd for $C_{26}H_{35}NNaO_2^+$ $[M+Na]^+$ 416.2560, found: 416.2563.

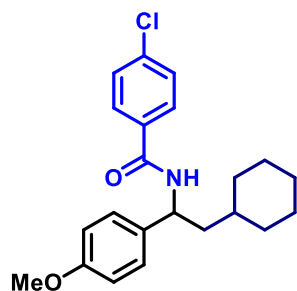
N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-methoxybenzamide (4ada)



4ada

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (28.6 mg, 78%). 1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.26 (d, J = 8.0 Hz, 1H), 5.25 (q, J = 7.8 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 1.85 – 1.67 (m, 7H), 1.29 – 1.24 (m, 1H), 1.21 – 1.14 (m, 3H), 1.07 – 0.93 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 166.1, 162.1, 158.7, 135.1, 128.8, 127.8, 127.0, 114.0, 113.7, 55.5, 55.4, 50.7, 44.1, 34.5, 33.32, 33.25, 26.6, 26.20, 26.17. GC-MS (EI-70 eV): m/z (%) 367 (3), 270 (33), 216 (11), 135 (100), 121 (8), 107 (7). HRMS (ESI): calcd for $C_{23}H_{29}NNaO_3^+$ $[M+Na]^+$ 390.2040, found: 390.2045.

4-chloro-N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)benzamide (4aea)

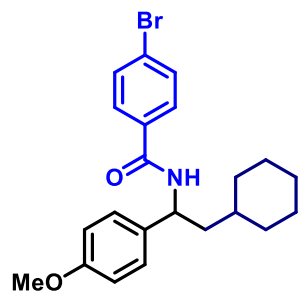


4aea

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (27.5 mg, 74%). 1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.59 (d, J = 8.0 Hz, 1H), 5.24 (q, J = 7.9 Hz, 1H), 3.82 (s, 3H), 1.87 – 1.61 (m, 7H), 1.27 – 1.23 (m, 1H), 1.23 – 1.15 (m, 3H), 1.05 – 0.90 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 165.6, 158.8, 137.6, 134.8, 133.1,

128.8, 128.5, 127.9, 114.1, 55.3, 51.0, 44.0, 34.5, 33.3, 26.5, 26.2. GC-MS (EI-70 eV): m/z (%) 371 (3), 274 (84), 216 (16), 139 (100), 134 (20), 111 (22). HRMS (ESI): calcd for C₂₂H₂₆CINNaO₂⁺ [M+Na]⁺ 394.1544, found: 394.1539.

4-bromo-N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)benzamide (4afa)

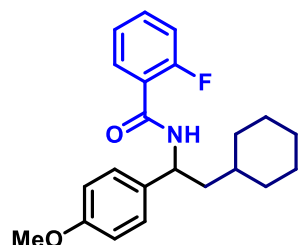


4afa

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (27.8 mg, 67%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.24 (q, *J* = 7.8 Hz, 1H), 3.82 (s, 3H), 1.87 – 1.64 (m, 7H), 1.27 – 1.24 (m, 1H), 1.21 – 1.14 (m, 3H), 1.06 – 0.90 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 165.8, 158.8, 134.8, 133.6, 131.7, 128.8, 127.9, 126.0, 114.1, 55.3, 51.0, 44.0, 34.5, 33.3, 26.6, 26.2. GC-MS (EI-70 eV): m/z (%) 415 (5), 320 (91), 216 (41), 185 (100), 173 (14), 134 (49).

HRMS (ESI): calcd for C₂₂H₂₆BrNNaO₂⁺ [M+Na]⁺ 438.1039, found: 438.1041.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-2-fluorobenzamide (4aga)

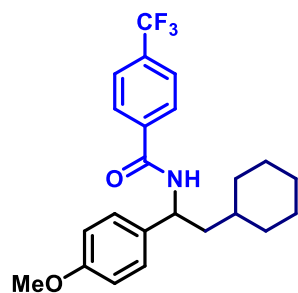


4aga

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (19.9 mg, 56%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (t, *J* = 8.8 Hz, 1H), 7.49 (q, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 9.8 Hz, 1H), 7.14 (m, 1H), 6.98 (m, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.28 (q, *J* = 8.8, 8.1 Hz, 1H), 3.83 (s, 3H), 1.88 – 1.80 (m, 3H), 1.77 – 1.66 (m, 4H), 1.33 – 1.26 (m, 1H), 1.23 – 1.14 (m, 3H), 1.09 – 0.91 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 162.4, 160.7 (d, *J* = 247.5 Hz), 158.7, 135.0, 133.3 (d, *J* = 9.1

Hz), 132.3 (d, *J* = 2.0 Hz), 127.8, 124.9 (d, *J* = 3.0 Hz), 121.2 (d, *J* = 12.1 Hz), 116.0 (d, *J* = 25.3 Hz), 114.1, 55.3, 51.1, 44.5, 34.5, 33.4, 33.2, 26.6, 26.21, 26.16. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -106.28. GC-MS (EI-70 eV): m/z (%) 355 (3), 258 (91), 216 (5), 137 (11), 123 (100), 95 (13). HRMS (ESI): calcd for C₂₂H₂₆FNNaO₂⁺ [M+Na]⁺ 378.1840, found: 378.1839.

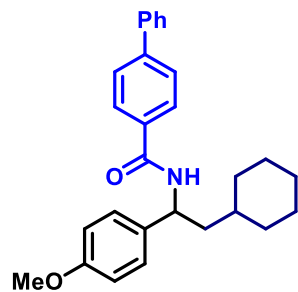
N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-(trifluoromethyl)benzamide (4aha)



4aha

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (28.4 mg, 70%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.26 (q, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 1.89 – 1.73 (m, 5H), 1.71 – 1.64 (m, 2H), 1.32 – 1.25 (m, 1H), 1.22 – 1.15 (m, 3H), 1.08 – 0.90 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 165.5, 158.9, 138.0, 134.6, 133.1 (q, *J* = 33.3 Hz), 127.9, 127.5, 125.6 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 273.7 Hz), 114.1, 55.3, 51.2, 43.9, 34.5, 33.3, 33.2, 26.5, 26.2. GC-MS (EI-70 eV): m/z (%) 405 (5), 308 (100), 216 (10), 173 (88), 145 (26), 121 (10). HRMS (ESI): calcd for C₂₃H₂₆F₃NNaO₂⁺ [M+Na]⁺ 428.1808, found: 428.1803.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-[1,1'-biphenyl]-4-carboxamide (4aia)

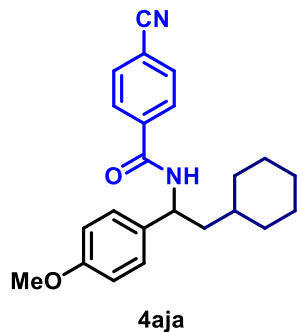


4aia

Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (30.1 mg, 73%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.3

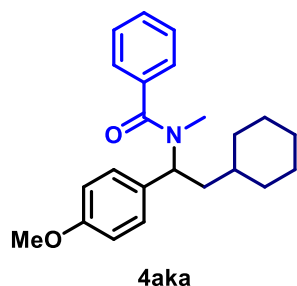
Hz, 2H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 7.2$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 2H), 7.43 (d, $J = 7.3$ Hz, 1H), 7.35 (d, $J = 8.6$ Hz, 2H), 6.92 (d, $J = 8.7$ Hz, 2H), 6.40 (d, $J = 7.9$ Hz, 1H), 5.31 (q, $J = 7.9$ Hz, 1H), 3.83 (s, 3H), 1.90 – 1.76 (m, 4H), 1.74 – 1.66 (m, 3H), 1.34 – 1.31 (m, 1H), 1.23 – 1.16 (m, 3H), 1.11 – 0.96 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 140.1, 133.4, 129.0, 128.1, 127.9, 127.5, 127.3, 114.1, 55.4, 50.9, 44.1, 34.6, 33.34, 33.27, 26.6, 26.22, 26.19. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{31}\text{NNaO}_2^+$ $[\text{M}+\text{Na}]^+$ 436.2247, found: 436.2245.

4-cyano-N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)benzamide (4aja)



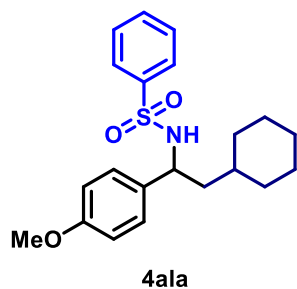
Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (13.8 mg, 38%). ^1H NMR (400 MHz, Chloroform- d) δ 7.87 (d, $J = 8.3$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 1.6$ Hz, 2H), 6.92 (d, $J = 8.6$ Hz, 2H), 6.36 (d, $J = 8.0$ Hz, 1H), 5.26 (q, $J = 7.8$ Hz, 1H), 3.84 (s, 3H), 1.89 – 1.78 (m, 4H), 1.76 – 1.69 (m, 3H), 1.27 – 1.24 (m, 1H), 1.21 – 1.17 (m, 3H), 1.09 – 0.96 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 159.0, 138.7, 134.2, 132.5, 127.9, 127.7, 118.2, 115.0, 114.2, 55.4, 51.3, 43.8, 34.5, 33.3, 33.2, 29.8, 26.5, 26.2. GC-MS (EI-70 eV): m/z (%) 362 (4), 265 (98), 216 (21), 173 (8), 134 (28), 130 (100). HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{NaO}_2^+$ $[\text{M}+\text{Na}]^+$ 385.1886, found: 385.1888.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-N-methylbenzamide (4aka)



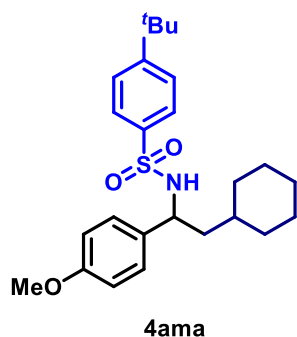
Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (15.4 mg, 44%). ^1H NMR (400 MHz, Chloroform- d) δ 7.45 – 7.39 (m, 6H), 7.19 (d, $J = 8.3$ Hz, 1H), 6.93 (d, $J = 8.7$ Hz, 2H), 6.16 (q, $J = 7.8$ Hz, 0.5H), 4.95 (t, $J = 7.8$ Hz, 0.5H), 3.85 (s, 3H), 2.89 (s, 1.5H), 2.61 (s, 1.5H), 2.08 – 1.61 (m, 7H), 1.94 – 1.61 (m, 4H), 1.04 – 0.75 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 158.9, 129.5, 129.4, 129.2, 128.6, 128.5, 128.3, 126.9, 126.7, 114.0, 113.8, 58.3, 55.4, 51.6, 39.6, 37.1, 34.8, 34.2, 34.0, 33.6, 33.4, 33.0, 31.6, 28.1, 26.63, 26.56, 26.4, 26.3, 26.0. GC-MS (EI-70 eV): m/z (%) 351 (6), 254 (19), 216 (37), 173 (11), 134 (45), 105 (100). HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{29}\text{NNaO}_2^+$ $[\text{M}+\text{Na}]^+$ 374.2091, found: 374.2090.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)benzenesulfonamide (4ala)



Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (26.5 mg, 71%). ^1H NMR (400 MHz, Chloroform- d) δ 7.67 (d, $J = 7.9$ Hz, 2H), 7.47 (t, $J = 7.4$ Hz, 1H), 7.35 (t, $J = 7.7$ Hz, 2H), 6.95 (d, $J = 8.6$ Hz, 2H), 6.68 (d, $J = 8.6$ Hz, 2H), 5.20 (d, $J = 7.3$ Hz, 1H), 4.37 (q, $J = 7.5$ Hz, 1H), 3.77 (s, 3H), 1.68 – 1.58 (m, 5H), 1.57 – 1.45 (m, 2H), 1.18 – 1.03 (m, 4H), 0.93 – 0.79 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 158.7, 140.7, 133.4, 132.2, 128.7, 127.7, 127.0, 113.8, 55.3, 45.5, 33.9, 33.1, 32.9, 26.4, 26.1, 26.0. GC-MS (EI-70 eV): m/z (%) 373 (3), 276 (100), 216 (9), 134 (24), 121 (11), 77 (41). HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{27}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$ 396.1604, found: 396.1606.

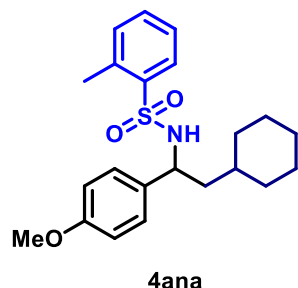
4-(tert-butyl)-N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)benzenesulfonamide (4ama)



Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (35.6 mg, 83%). ^1H NMR (400 MHz, Chloroform- d) δ 7.59 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 6.94 (d, $J = 8.6$ Hz, 2H), 6.65 (d, $J = 8.6$ Hz,

2H), 5.18 (d, $J = 7.6$ Hz, 1H), 4.36 (q, $J = 7.6$ Hz, 1H), 3.77 (s, 3H), 1.66 – 1.58 (m, 6H), 1.52 – 1.45 (m, 1H), 1.33 (s, 9H), 1.17 – 1.07 (m, 4H), 0.92 – 0.77 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 158.6, 155.8, 137.5, 133.5, 127.6, 127.0, 125.6, 113.6, 55.17, 55.19, 45.7, 35.0, 33.8, 33.2, 32.8, 31.1, 26.4, 26.11, 26.05. GC-MS (EI-70 eV): m/z (%) 429 (3), 232 (100), 216 (13), 198 (24), 134 (25), 121 (14). HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{35}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$ 452.2230, found: 452.2236.

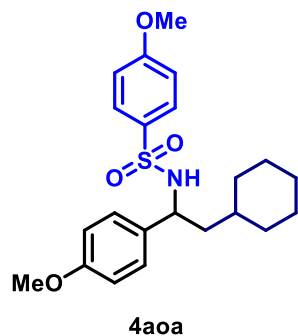
N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-2-methylbenzenesulfonamide (4ana)



Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (22.4 mg, 58%). ^1H NMR (400 MHz, Chloroform- d) δ 7.84 (d, $J = 7.9$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.16 (d, $J = 7.5$ Hz, 1H), 6.92 (d, $J = 8.6$ Hz, 2H), 6.66 (d, $J = 8.6$ Hz, 2H), 5.20 (d, $J = 7.4$ Hz, 1H), 4.29 (q, $J = 7.7$ Hz, 1H), 3.76 (s, 3H), 2.50 (s, 3H), 1.71 – 1.54 (m, 7H), 1.16 – 1.05 (m, 4H), 0.92 – 0.78 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 158.7, 138.5, 136.8, 133.3, 132.5, 132.2, 129.6, 127.6, 126.0, 113.7, 55.3, 55.2,

45.2, 33.9, 33.02, 32.98, 26.5, 26.11, 26.05, 20.3. GC-MS (EI-70 eV): m/z (%) 387 (5), 290 (100), 216 (16), 173 (7), 134 (29), 121 (17). HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{29}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$ 410.1760, found: 410.1756.

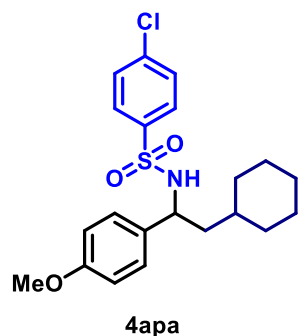
N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-methoxybenzenesulfonamide (4aoa)



Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (24.6 mg, 61%). ^1H NMR (400 MHz, Chloroform- d) δ 7.58 (d, $J = 8.8$ Hz, 2H), 6.95 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.9$ Hz, 2H), 6.70 (d, $J = 8.6$ Hz, 2H), 4.99 (d, $J = 7.1$ Hz, 1H), 4.33 (q, $J = 7.5$ Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 1.71 – 1.59 (m, 6H), 1.56 – 1.50 (m, 1H), 1.17 – 1.07 (m, 4H), 0.92 – 0.81 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 162.5, 158.7, 133.5, 132.4, 129.2, 127.7, 113.8, 113.8, 55.6, 55.3, 55.2, 45.6, 33.9, 33.1, 32.9, 26.5, 26.1, 26.0.

GC-MS (EI-70 eV): m/z (%) 403 (3), 306 (100), 216 (7), 171 (51), 134 (22), 121 (12). HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{29}\text{NNaO}_4\text{S}^+$ $[\text{M}+\text{Na}]^+$ 426.1710, found: 426.1708.

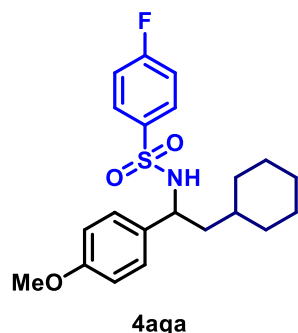
4-chloro-N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)benzenesulfonamide (4apa)



Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (23.6 mg, 58%). ^1H NMR (400 MHz, Chloroform- d) δ 7.53 (d, $J = 8.6$ Hz, 2H), 7.26 (d, $J = 8.6$ Hz, 2H), 6.91 (d, $J = 8.6$ Hz, 2H), 6.66 (d, $J = 8.6$ Hz, 2H), 5.46 (d, $J = 7.6$ Hz, 1H), 4.38 (q, $J = 7.7$ Hz, 1H), 3.77 (s, 3H), 1.68 – 1.61 (m, 6H), 1.55 – 1.48 (m, 1H), 1.20 – 1.06 (m, 4H), 0.93 – 0.80 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 158.8, 139.4, 138.4, 132.9, 128.8, 128.5, 127.7, 113.8, 55.5, 55.4, 45.4, 33.9, 33.1, 32.9, 26.4, 26.1, 26.0. GC-MS (EI-70 eV): m/z (%) 407 (2), 310 (100), 216 (13), 175 (18), 134 (14), 111 (25). HRMS

(ESI): calcd for $\text{C}_{21}\text{H}_{26}\text{ClNNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$ 430.1214, found: 430.1218.

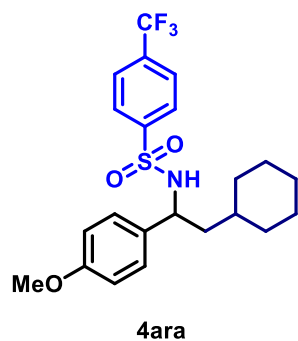
N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-fluorobenzenesulfonamide (4aqa)



Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (21.4 mg, 54%). ^1H NMR (400 MHz, Chloroform- d) δ 7.64 (d, $J = 5.1$ Hz, 1H), 7.62 (d, $J = 5.1$ Hz, 1H), 6.98 (t, $J = 8.5$ Hz, 2H), 6.93 (d, $J = 8.5$ Hz,

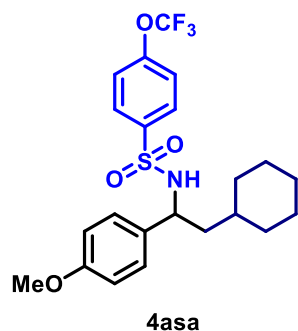
2H), 6.67 (d, $J = 8.5$ Hz, 2H), 5.42 (d, $J = 7.5$ Hz, 1H), 4.38 (q, $J = 7.6$ Hz, 1H), 3.77 (s, 3H), 1.68 – 1.61 (m, 6H), 1.56 – 1.49 (m, 1H), 1.18 – 1.10 (m, 4H), 0.93 – 0.81 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 164.7 (d, $J = 254.5$ Hz), 158.8, 137.0 (d, $J = 3.0$ Hz), 133.1, 129.8 (d, $J = 9.1$ Hz), 127.7, 115.8 (d, $J = 23.2$ Hz), 113.8, 55.5, 55.3, 45.5, 33.9, 33.1, 32.9, 26.4, 26.1, 26.0. ^{19}F NMR (376 MHz, Chloroform- d) δ -106.28. GC-MS (EI-70 eV): m/z (%) 391 (3), 294 (100), 216 (11), 159 (29), 134 (15), 121 (13). HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{26}\text{FNNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$ 414.1510, found: 414.1515.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-(trifluoromethyl)benzenesulfonamide (4ara)



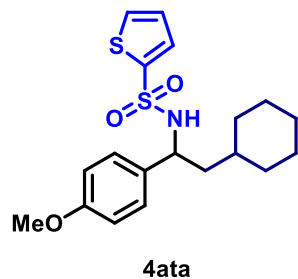
Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (28.7 mg, 65%). ^1H NMR (400 MHz, Chloroform- d) δ 7.69 (d, $J = 8.2$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 6.60 (d, $J = 8.6$ Hz, 2H), 5.41 (d, $J = 7.6$ Hz, 1H), 4.43 (q, $J = 7.7$ Hz, 1H), 3.73 (s, 3H), 1.73 – 1.61 (m, 6H), 1.55 – 1.48 (m, 1H), 1.20 – 1.07 (m, 4H), 0.96 – 0.86 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 158.9, 144.4, 133.6 (q, $J = 33.3$ Hz), 132.5, 127.7, 127.6, 125.7 (q, $J = 4.0$ Hz), 120.6 (q, $J = 274.7$ Hz), 113.7, 55.7, 55.2, 45.3, 33.9, 33.1, 32.9, 26.4, 26.1, 26.0. ^{19}F NMR (376 MHz, Chloroform- d) δ -63.09. GC-MS (EI-70 eV): m/z (%) 441 (4), 344 (100), 216 (6), 209 (7), 134 (25), 121 (10). HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{26}\text{F}_3\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$ 464.1478, found: 464.1481.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-(trifluoromethoxy)benzenesulfonamide (4asa)



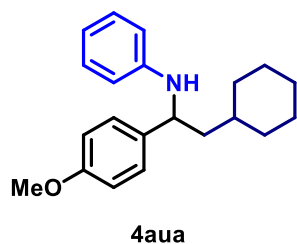
Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (27.4 mg, 60%). ^1H NMR (400 MHz, Chloroform- d) δ 7.65 (d, $J = 8.8$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 6.64 (d, $J = 8.6$ Hz, 2H), 5.56 (d, $J = 7.7$ Hz, 1H), 4.41 (q, $J = 7.7$ Hz, 1H), 3.74 (s, 3H), 1.71 – 1.59 (m, 6H), 1.54 – 1.46 (m, 1H), 1.20 – 1.06 (m, 4H), 0.95 – 0.82 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 158.9, 151.5, 139.3, 132.8, 131.2 (q, $J = 349.5$ Hz), 129.5, 129.2, 128.6, 127.7, 127.4, 120.6, 120.2 (q, $J = 260.6$ Hz), 113.7, 55.5, 55.2, 45.4, 33.9, 33.1, 32.9, 26.4, 26.1, 26.0. ^{19}F NMR (376 MHz, Chloroform- d) δ -57.77. GC-MS (EI-70 eV): m/z (%) 457 (3), 360 (100), 225 (19), 161 (15), 134 (22), 121 (8). HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{26}\text{F}_3\text{NNaO}_4\text{S}^+$ $[\text{M}+\text{Na}]^+$ 480.1427, found: 480.1222.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)thiophene-2-sulfonamide (4ata)



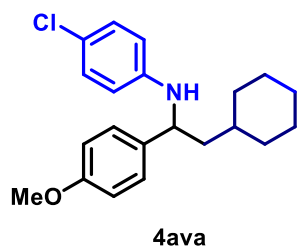
Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (15.5 mg, 41%). ^1H NMR (400 MHz, Chloroform- d) δ 7.48 (d, $J = 6.1$ Hz, 1H), 7.36 (d, $J = 4.9$ Hz, 1H), 7.03 (d, $J = 8.6$ Hz, 2H), 6.93 (t, $J = 7.8$ Hz, 1H), 6.75 (d, $J = 8.6$ Hz, 2H), 5.17 (d, $J = 7.4$ Hz, 1H), 4.44 (q, $J = 7.5$ Hz, 1H), 3.79 (s, 3H), 1.72 – 1.56 (m, 7H), 1.21 – 1.09 (m, 4H), 0.94 – 0.81 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 158.8, 141.8, 133.4, 132.3, 131.7, 127.6, 127.1, 113.9, 55.6, 55.4, 45.6, 33.9, 33.1, 33.0, 26.5, 26.13, 26.09. GC-MS (EI-70 eV): m/z (%) 379 (3), 282 (100), 216 (9), 173 (3), 147 (28), 121 (14). HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{25}\text{NNaO}_3\text{S}_2^+$ $[\text{M}+\text{Na}]^+$ 402.1168, found: 402.1168.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)aniline^[1] (4aua)



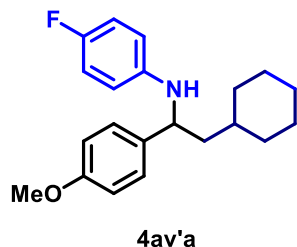
Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (16.4 mg, 53%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.5 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 2H), 4.41 (t, *J* = 7.9 Hz, 1H), 3.82 (s, 3H), 1.88 – 1.66 (m, 6H), 1.64 – 1.57 (m, 1H), 1.41 – 1.35 (m, 1H), 1.30 – 1.17 (m, 3H), 1.08 – 0.91 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.4, 147.5, 136.8, 129.2, 127.3, 117.06, 114.0, 113.3, 55.3, 54.7, 47.4, 34.5, 33.8, 33.1, 26.6, 26.3, 26.2. GC-MS (EI-70 eV): *m/z* (%) 309 (6), 216 (47), 212 (73), 173 (22), 134 (60), 121 (100).

4-chloro-N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)aniline (4ava)



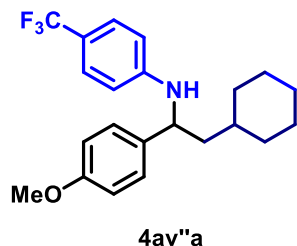
Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (23.3 mg, 68%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.46 (d, *J* = 8.7 Hz, 2H), 4.35 (t, *J* = 7.9 Hz, 1H), 3.82 (s, 3H), 1.79 – 1.66 (m, 6H), 1.63 – 1.56 (m, 1H), 1.34 – 1.27 (m, 1H), 1.24 – 1.16 (m, 3H), 1.05 – 0.91 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 158.5, 146.0, 136.2, 129.0, 127.3, 121.6, 114.4, 114.1, 55.3, 54.9, 47.2, 34.4, 33.8, 33.1, 26.6, 26.3, 26.1. GC-MS (EI-70 eV): *m/z* (%) 343 (5), 246 (22), 216 (56), 173 (24), 134 (72), 121 (100). HRMS (ESI): calcd for C₂₁H₂₆ClNNaO⁺ [M+Na]⁺ 366.1595, found: 366.1599.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-fluoroaniline (4av'a)



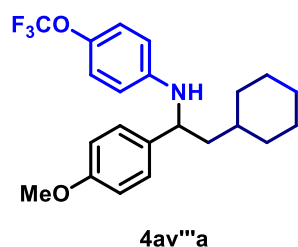
Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (21.6 mg, 66%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.83 (t, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 4.4 Hz, 1H), 6.46 (d, *J* = 4.4 Hz, 1H), 4.34 (t, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 1.86 – 1.66 (m, 6H), 1.63 – 1.56 (m, 1H), 1.34 – 1.28 (m, 1H), 1.25 – 1.17 (m, 3H), 1.07 – 0.91 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 158.5, 155.6 (d, *J* = 235.3 Hz), 143.9, 136.6, 127.4, 115.6 (d, *J* = 22.2 Hz), 114.1, 114.0, 55.4, 55.3, 47.4, 34.4, 33.8, 33.1, 26.6, 26.3, 26.2. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -128.57. GC-MS (EI-70 eV): *m/z* (%) 327 (4), 230 (26), 216 (64), 173 (29), 134 (94), 121 (100). HRMS (ESI): calcd for C₂₁H₂₆FNNaO⁺ [M+Na]⁺ 350.1891, found: 350.1887.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-(trifluoromethyl)aniline (4av''a)



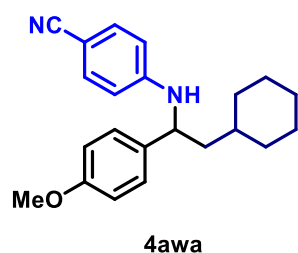
Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (29.4 mg, 78%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 2H), 4.44 (t, *J* = 7.9 Hz, 1H), 3.83 (s, 3H), 1.86 – 1.59 (m, 7H), 1.40 – 1.29 (m, 1H), 1.25 – 1.17 (m, 3H), 1.09 – 0.95 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 158.6, 149.9, 135.8, 127.2, 129.0 (q, *J* = 4.0 Hz), 125.1 (q, *J* = 260.6 Hz), 118.5 (q, *J* = 32.3 Hz), 114.1, 112.4, 55.3, 54.4, 47.1, 34.4, 33.8, 33.0, 26.5, 26.3, 26.1. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -60.88. GC-MS (EI-70 eV): *m/z* (%) 377 (5), 280 (86), 216 (16), 161 (47), 134 (67), 121 (100). HRMS (ESI): calcd for C₂₂H₂₆F₃NNaO⁺ [M+Na]⁺ 400.1859, found: 400.1856.

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-4-(trifluoromethoxy)aniline (4av'''a)



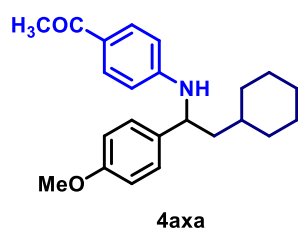
Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (31.4 mg, 80%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.49 (d, *J* = 8.9 Hz, 2H), 4.35 (t, *J* = 8.1 Hz, 1H), 3.83 (s, 3H), 1.83 – 1.66 (m, 6H), 1.64 – 1.57 (m, 1H), 1.40 – 1.33 (m, 1H), 1.27 – 1.16 (m, 3H), 1.07 – 0.91 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 158.6, 146.3, 140.1, 136.2, 127.3, 122.4, 120.7 (q, *J* = 256.5 Hz), 114.1, 113.4, 55.3, 55.0, 47.3, 34.4, 33.8, 33.1, 26.6, 26.3, 26.1. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -58.44. GC-MS (EI-70 eV): *m/z* (%) 393 (6), 296 (43), 216 (52), 177 (38), 134 (66), 121 (100). HRMS (ESI): calcd for C₂₂H₂₆F₃NNaO₂⁺ [M+Na]⁺ 416.1808, found: 416.1809.

4-((2-cyclohexyl-1-(4-methoxyphenyl)ethyl)amino)benzotrile (4awa)



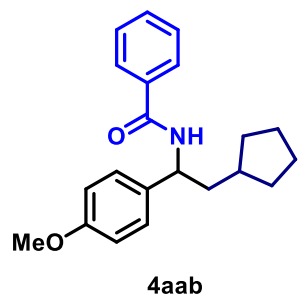
Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (27.7 mg, 83%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 2H), 4.61 (s, 1H), 4.43 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 1.83 – 1.64 (m, 7H), 1.38 – 1.32 (m, 1H), 1.26 – 1.15 (m, 3H), 1.07 – 0.94 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 158.7, 150.6, 135.1, 133.7, 127.2, 120.7, 114.2, 112.9, 98.5, 55.3, 54.4, 46.9, 34.3, 33.7, 33.0, 26.5, 26.2, 26.1. GC-MS (EI-70 eV): *m/z* (%) 334 (3), 237 (29), 216 (59), 173 (26), 134 (79), 118 (100). HRMS (ESI): calcd for C₂₂H₂₆NNaO⁺ [M+Na]⁺ 357.1937, found: 357.1934.

1-(4-((2-cyclohexyl-1-(4-methoxyphenyl)ethyl)amino)phenyl)ethan-1-one (4axa)



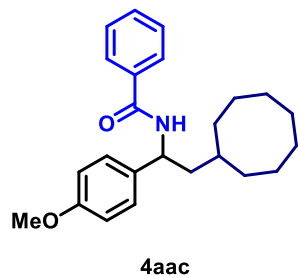
Purification by flash column chromatography (petroleum ether/EtOAc = 50:1). Colorless oil (21.4 mg, 61%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.63 (s, 1H), 4.49 (t, *J* = 7.1 Hz, 1H), 3.82 (s, 3H), 2.48 (s, 3H), 1.81 – 1.59 (m, 7H), 1.42 – 1.33 (m, 1H), 1.26 – 1.14 (m, 3H), 1.08 – 0.92 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 196.5, 158.6, 151.4, 135.6, 130.8, 127.2, 126.5, 114.2, 112.1, 55.3, 54.3, 47.0, 34.4, 33.7, 33.0, 26.5, 26.2, 26.13, 26.10. GC-MS (EI-70 eV): *m/z* (%) 351 (5), 254 (39), 216 (61), 173 (28), 134 (77), 121 (100). HRMS (ESI): calcd for C₂₃H₂₉NNaO₂⁺ [M+Na]⁺ 374.2091, found: 374.2096.

N-(2-cyclopentyl-1-(4-methoxyphenyl)ethyl)benzamide (4aab)



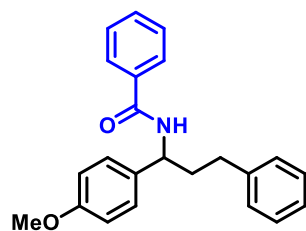
Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (21.0 mg, 65%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.1 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.51 (s, 1H), 5.19 (q, *J* = 7.7 Hz, 1H), 3.83 (s, 3H), 2.02 – 1.92 (m, 2H), 1.85 – 1.73 (m, 3H), 1.67 – 1.60 (m, 2H), 1.57 – 1.48 (m, 2H), 1.29 – 1.14 (m, 2H). ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 166.6, 158.8, 134.8, 134.7, 131.5, 128.6, 127.9, 127.0, 114.1, 55.4, 52.9, 42.7, 37.1, 33.0, 32.6, 25.3, 25.1. GC-MS (EI-70 eV): *m/z* (%) 323 (5), 240 (61), 202 (12), 134 (11), 121 (15), 105 (100). HRMS (ESI): calcd for C₂₁H₂₅NNaO₂⁺ [M+Na]⁺ 346.1778, found: 346.1781.

N-(2-cyclooctyl-1-(4-methoxyphenyl)ethyl)benzamide (4aac)



Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). Colorless oil (24.8 mg, 68%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.40 (d, J = 8.0 Hz, 1H), 5.25 (q, J = 7.8 Hz, 1H), 3.83 (s, 3H), 1.92 – 1.60 (m, 7H), 1.59 – 1.51 (m, 3H), 1.47 – 1.35 (m, 6H), 1.34 – 1.27 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 166.6, 158.8, 134.9, 134.8, 131.5, 128.6, 127.9, 127.0, 114.1, 55.4, 51.4, 44.3, 34.0, 31.9, 31.8, 27.49, 27.46, 26.2, 25.3, 25.1. GC-MS (EI-70 eV): m/z (%) 365 (6), 240 (82), 134 (14), 121 (10), 105 (100), 77 (23). HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{37}\text{NNaO}_2^+$ $[M+\text{Na}]^+$ 388.2247, found: 388.2251.

N-(1-(4-methoxyphenyl)-3-phenylpropyl)benzamide (4aad)^[2]



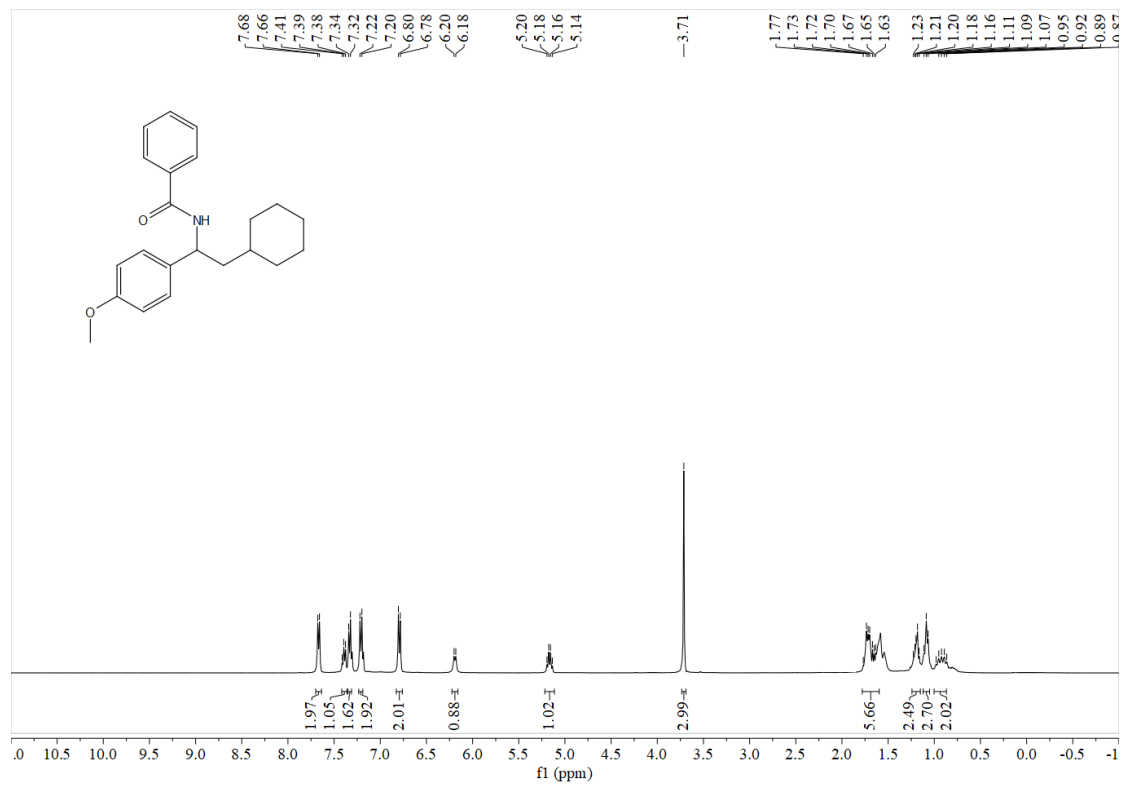
Purification by flash column chromatography (petroleum ether/EtOAc = 15:1). White solid (24.6 mg, 71%). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, J = 7.5 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.21 (t, J = 8.8 Hz, 3H), 6.91 (d, J = 8.6 Hz, 2H), 6.43 (d, J = 7.9 Hz, 1H), 5.22 (q, J = 7.5 Hz, 1H), 3.82 (s, 3H), 2.75 – 2.63 (m, 2H), 2.37 – 2.31 (m, 1H), 2.25 – 2.19 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 166.6, 159.0, 141.5, 134.6, 134.0, 131.4, 128.54, 128.52, 128.4, 127.9, 126.9, 126.0, 55.3, 53.3, 37.6, 32.7. GC-MS (EI-70 eV): m/z (%) 345 (5), 254 (10), 240 (35), 224 (11), 105 (100), 77 (28).

7. References

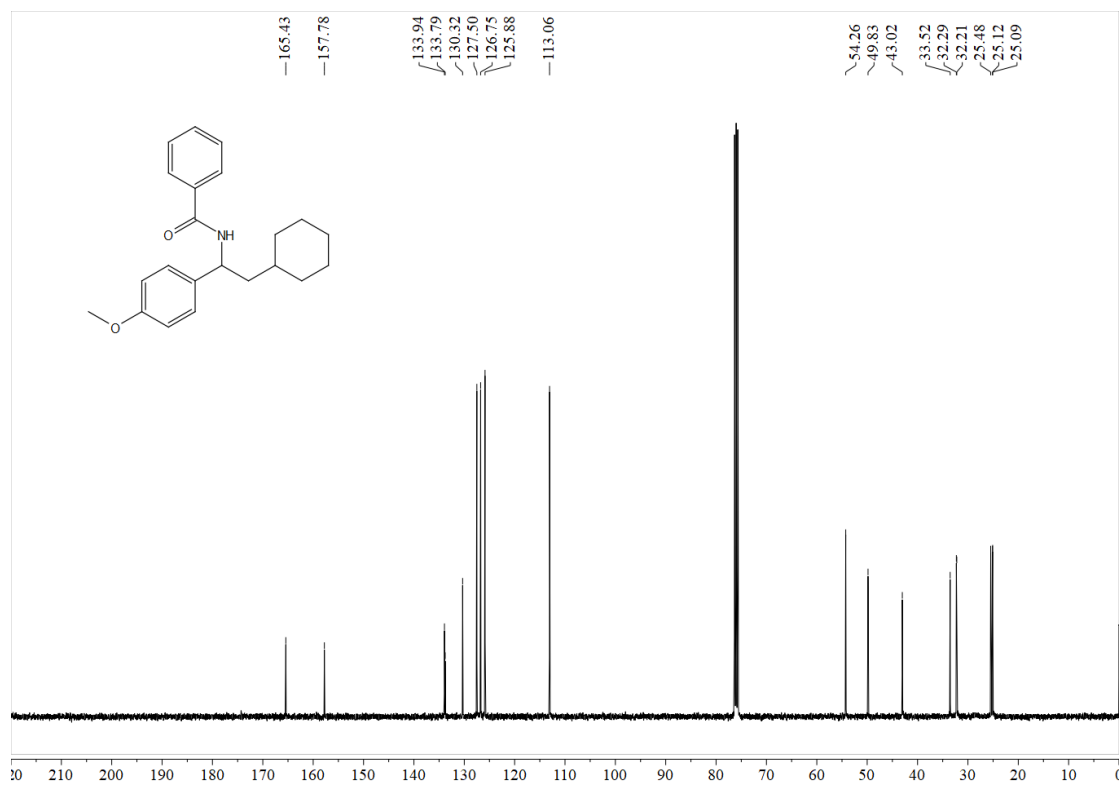
- [1] S. N. Gockel, S. Lee, B. L. Gay, K. L. Hull, Oxidative Three-Component Carboamination of Vinylarenes with Alkylboronic Acids. *ACS Catal.*, 2021, **11**, 5166–5171.
- [2] J. J. Kennedy-Ellis, E. D. Boldt, S. R. Chemler, Synthesis of Benzylureas and Related Amine Derivatives via Copper-Catalyzed Three-Component Carboamination of Styrenes, *Org. Lett.*, 2020, **22**, 8365–8369.

8. NMR Spectrum Copies

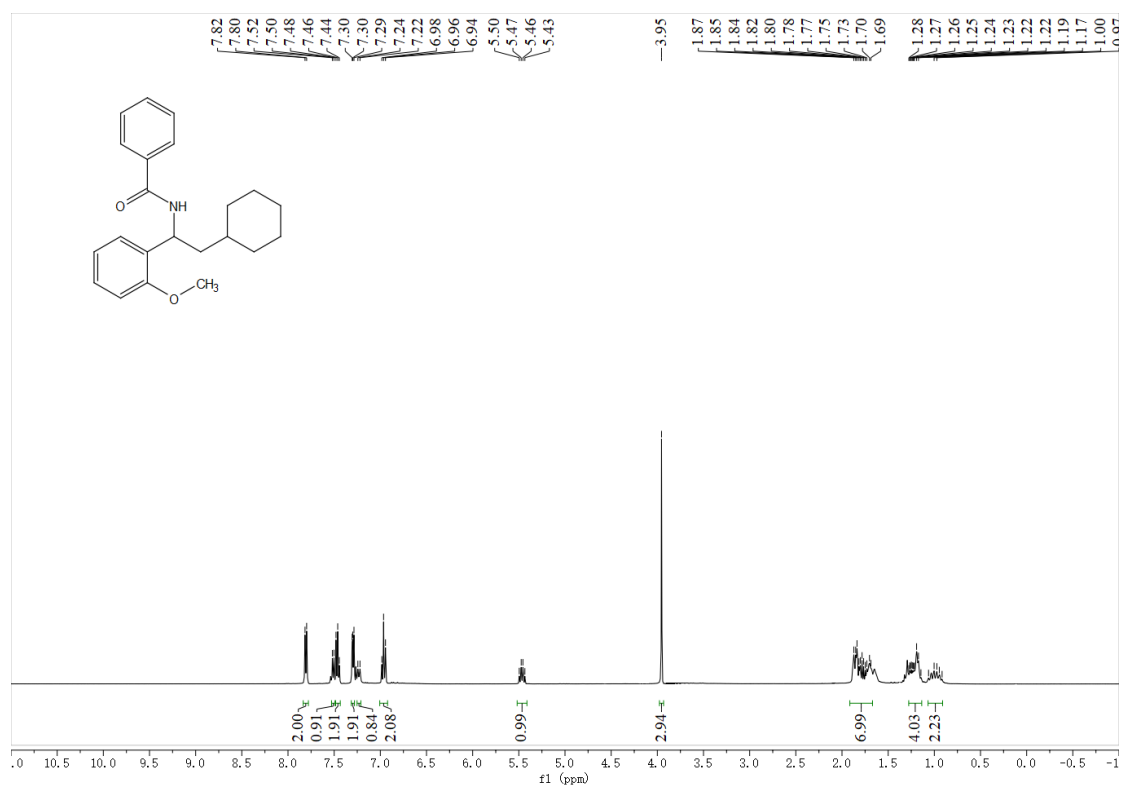
^1H NMR (400 MHz) Spectrum of **4aaa** in CDCl_3



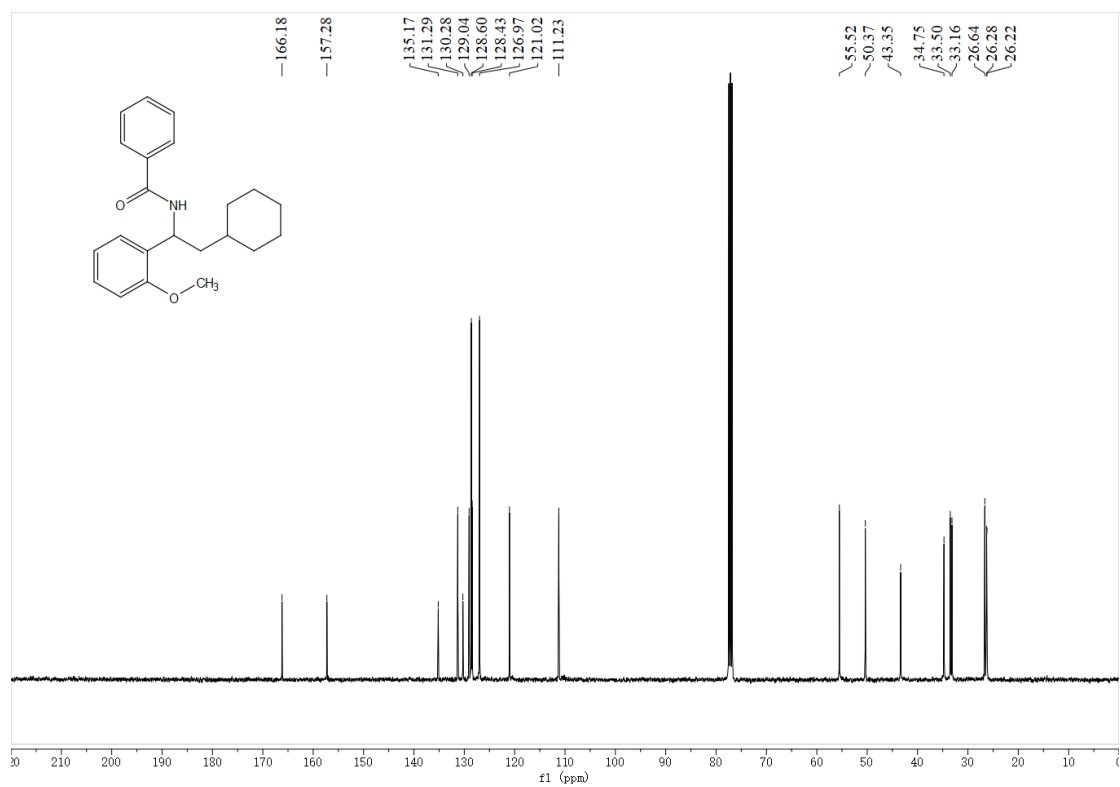
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4aaa** in CDCl_3



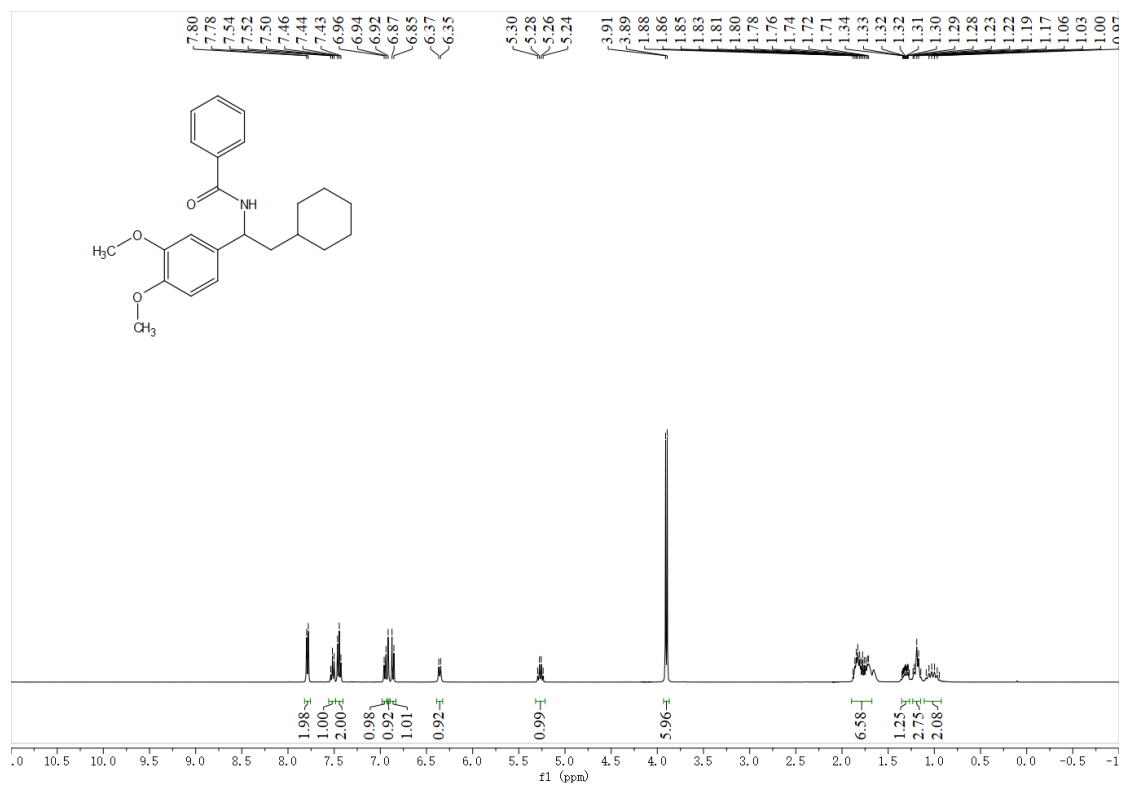
^1H NMR (400 MHz) Spectrum of **4baa** in CDCl_3



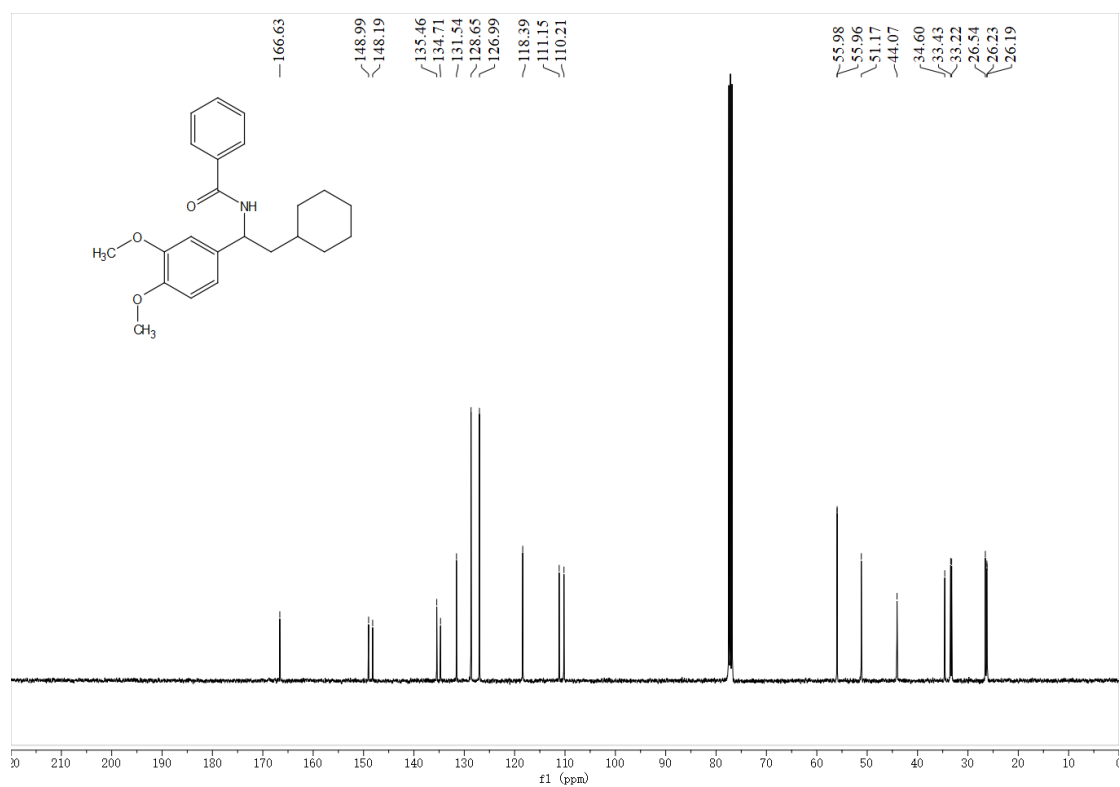
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4baa** in CDCl_3



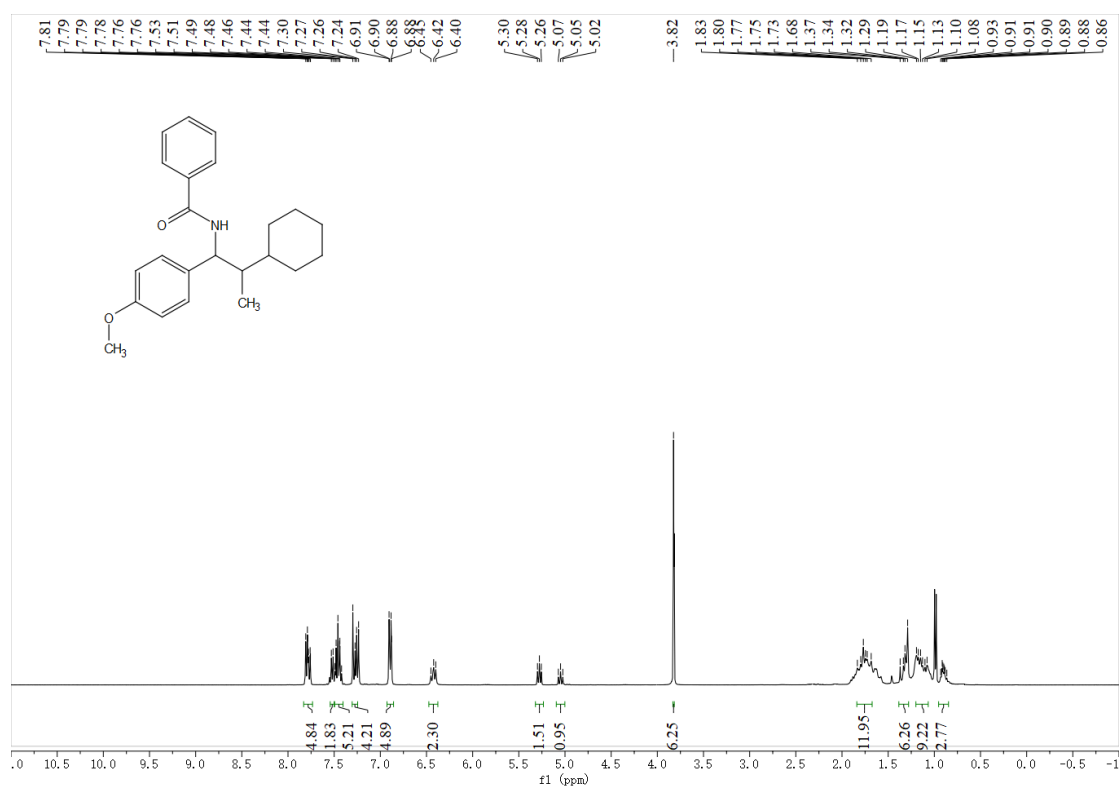
^1H NMR (400 MHz) Spectrum of **4caa** in CDCl_3



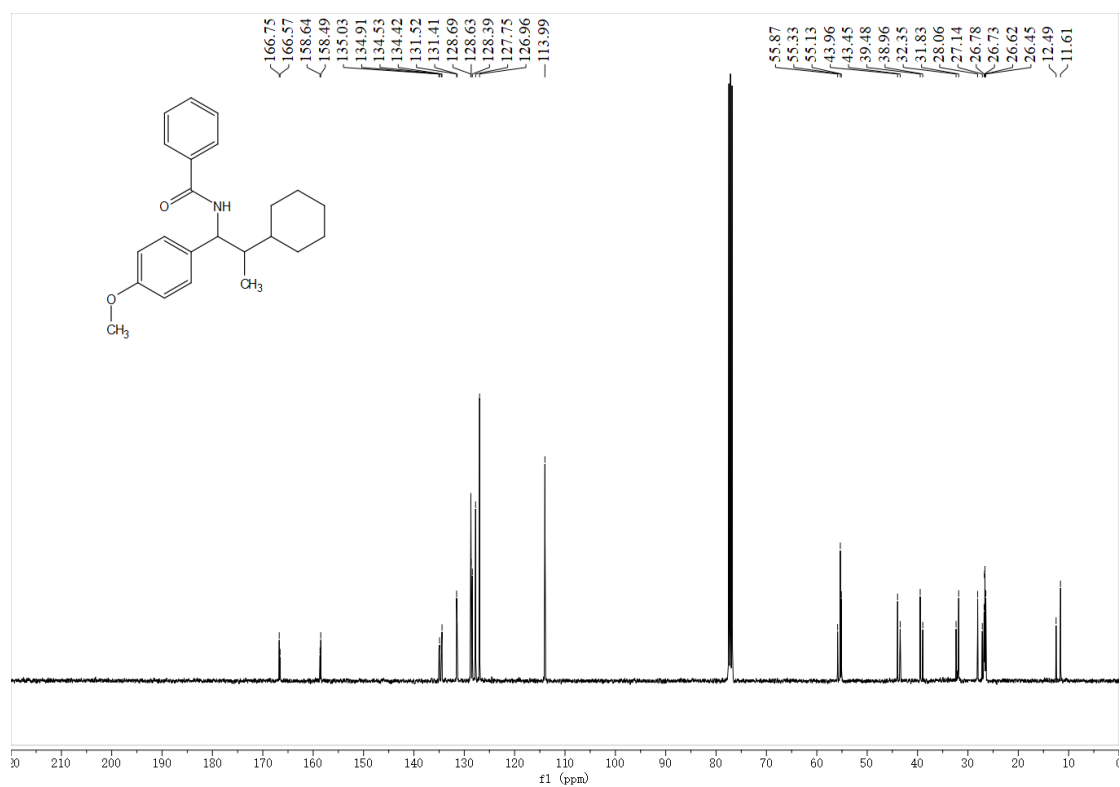
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4caa** in CDCl_3



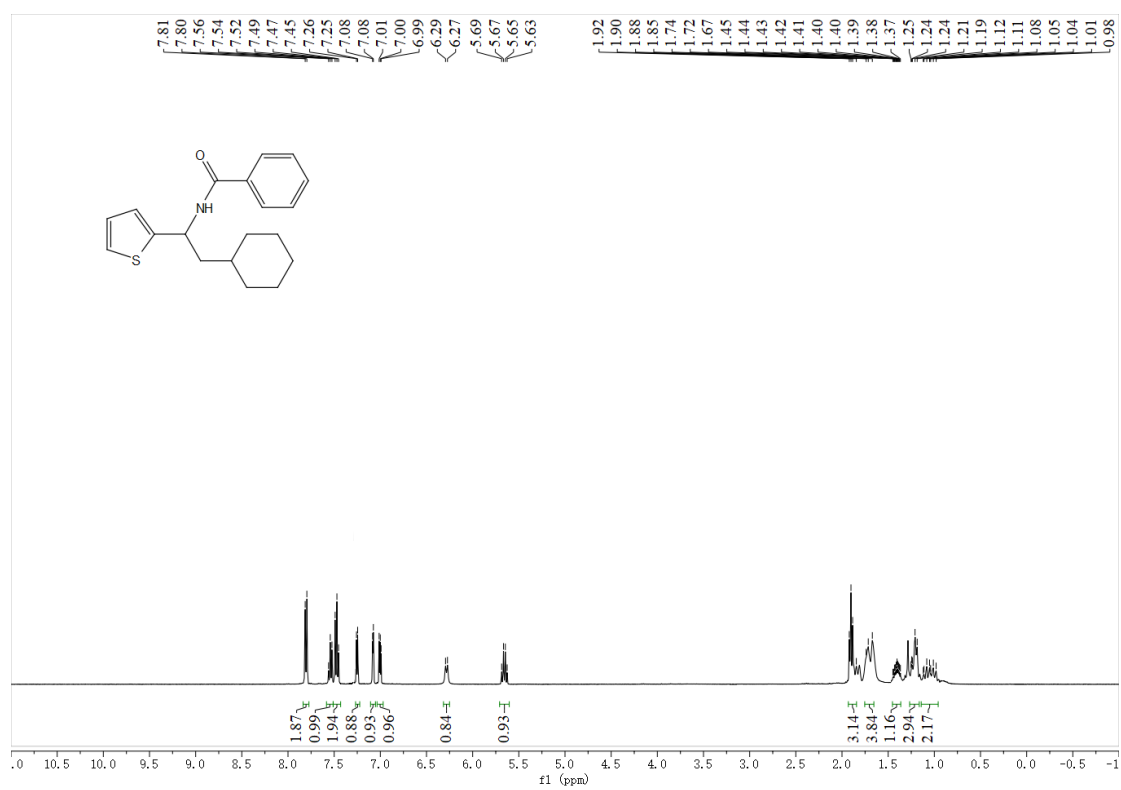
¹H NMR (400 MHz) Spectrum of **4daa** in CDCl₃



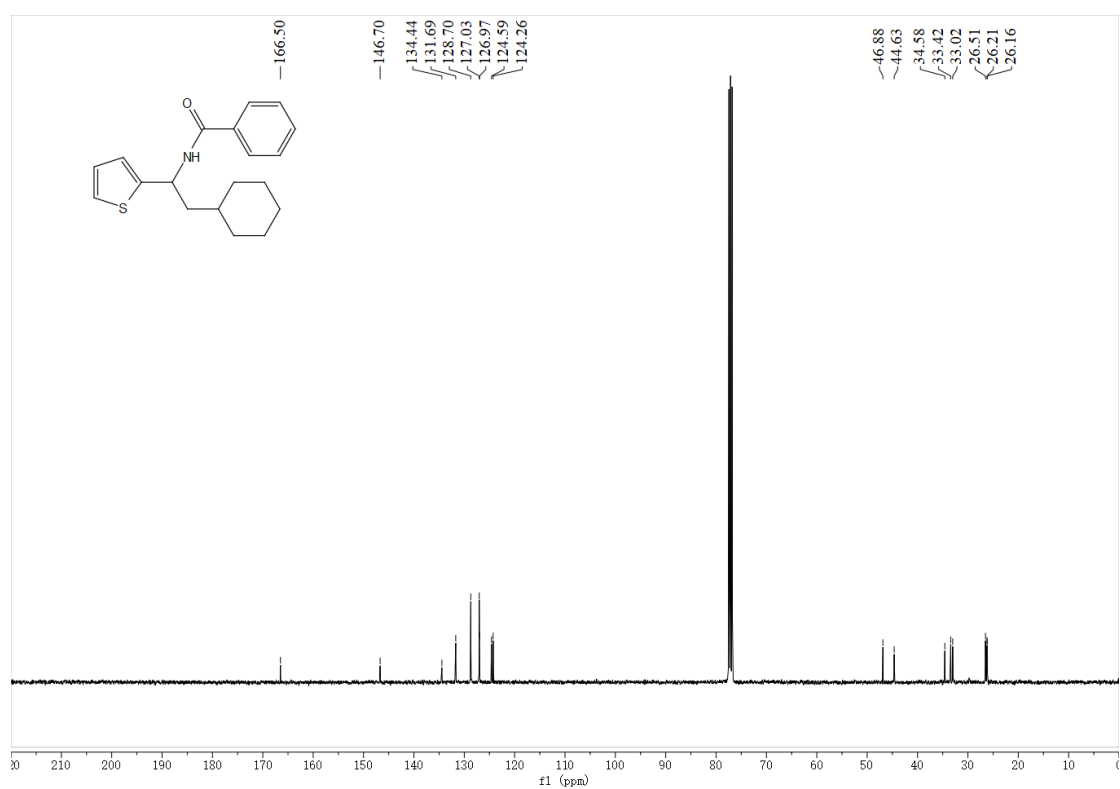
¹³C{¹H} NMR (101 MHz) Spectrum of **4daa** in CDCl₃



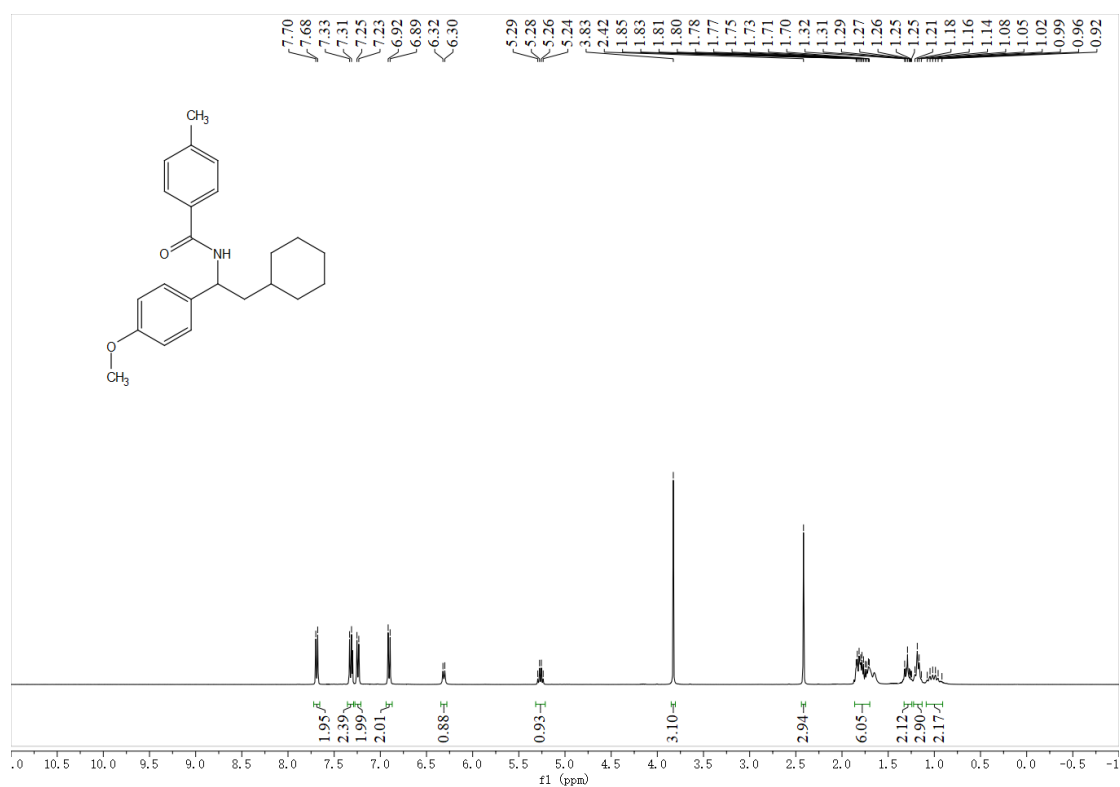
^1H NMR (400 MHz) Spectrum of **4eaa** in CDCl_3



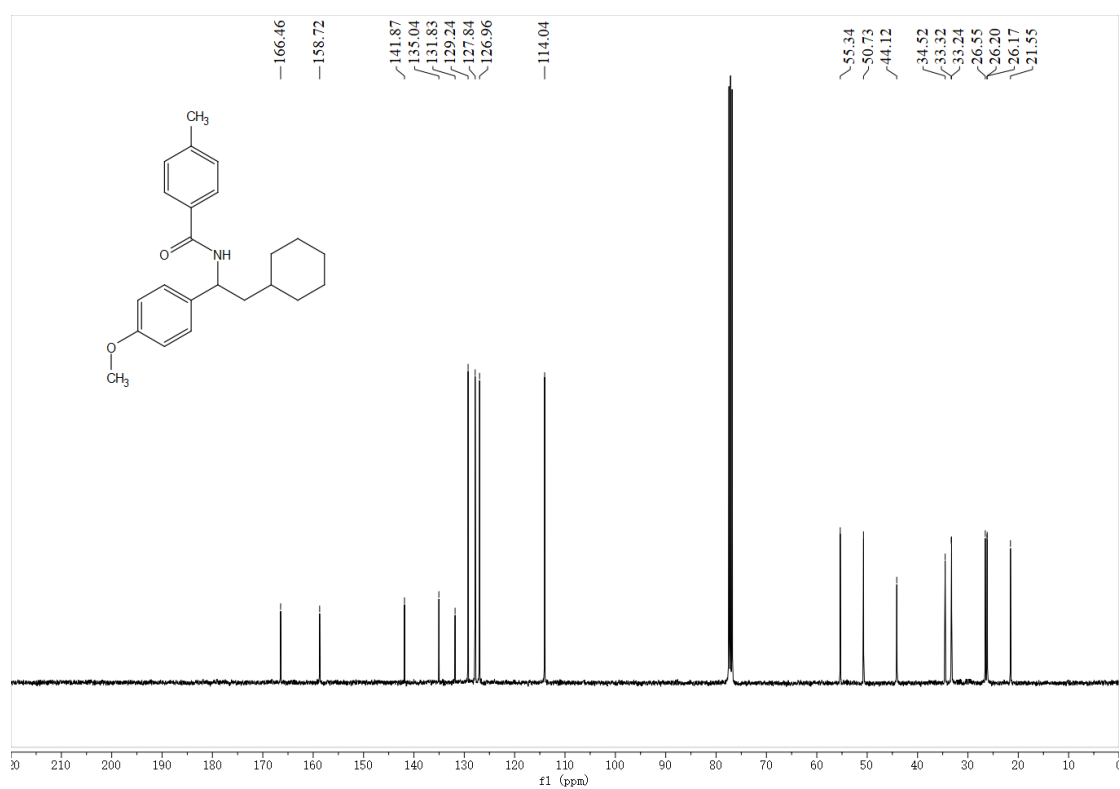
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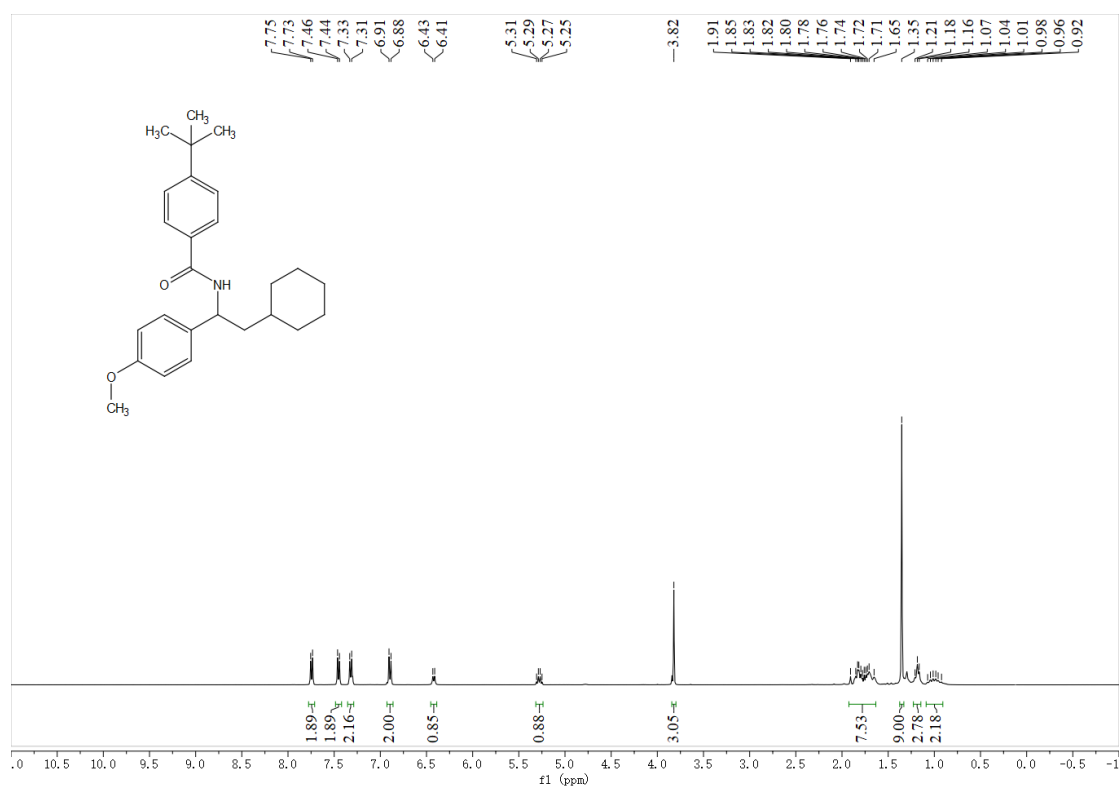
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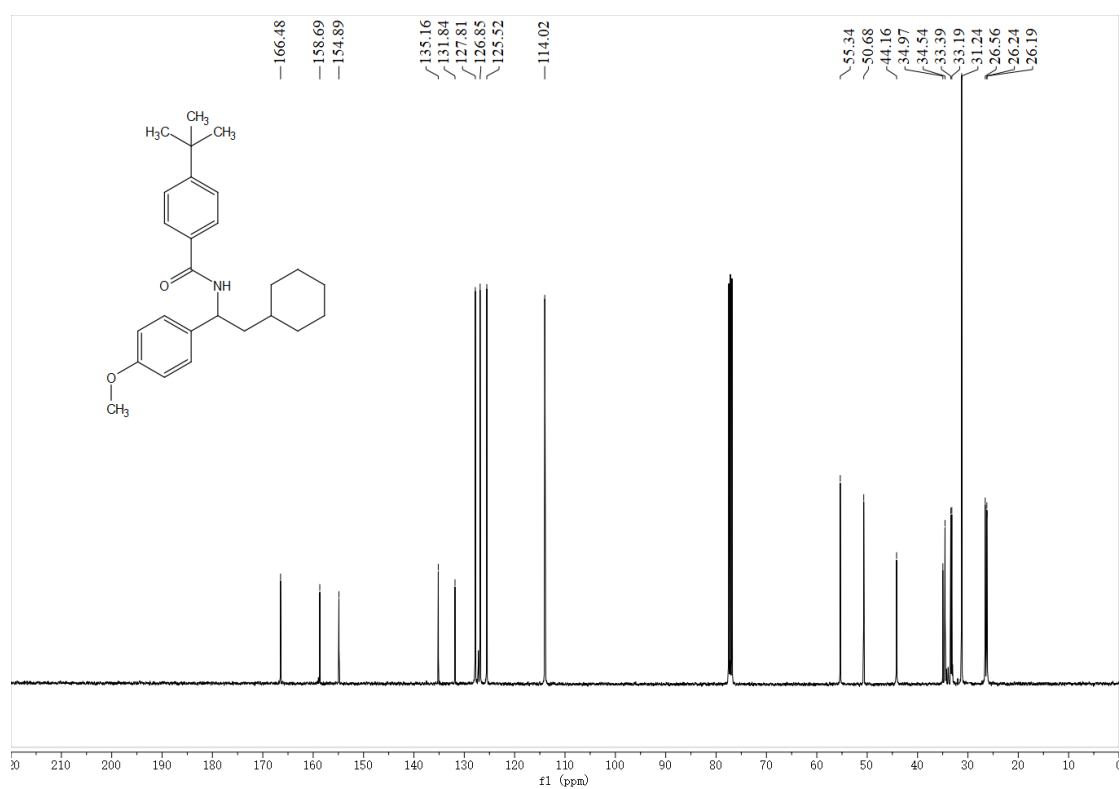
¹³C{¹H} NMR (101 MHz) Spectrum of **4aba** in CDCl₃



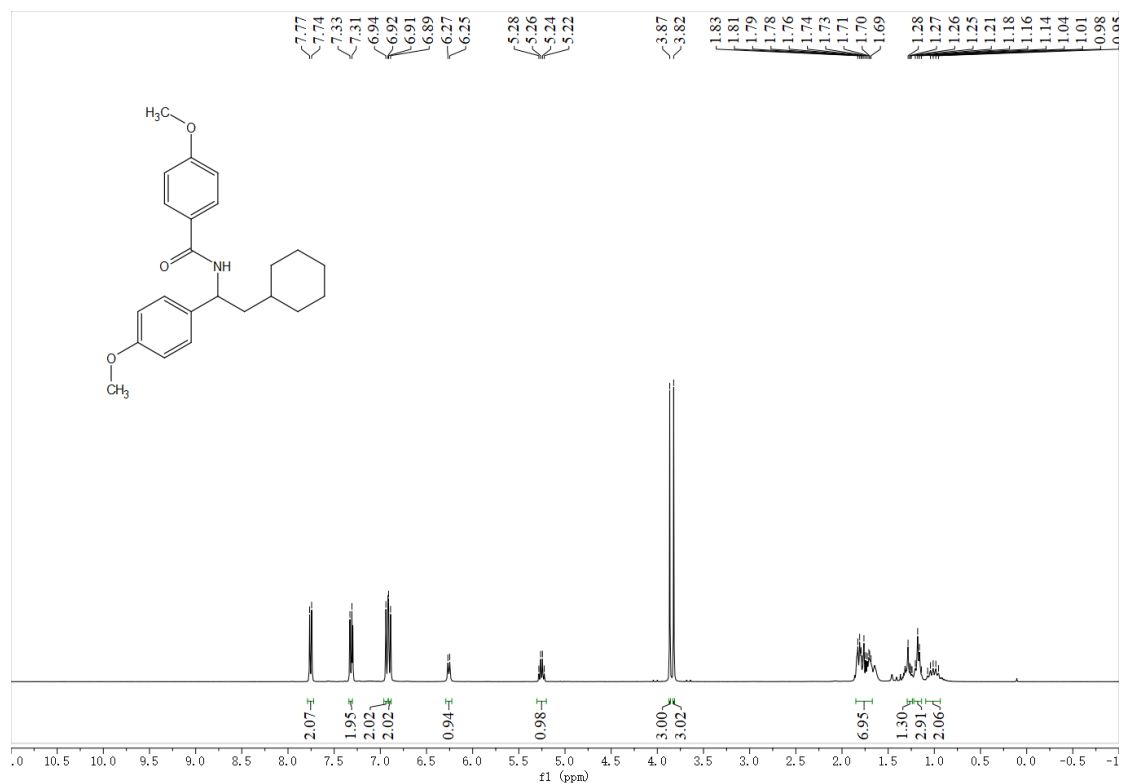
^1H NMR (400 MHz) Spectrum of **4aca** in CDCl_3



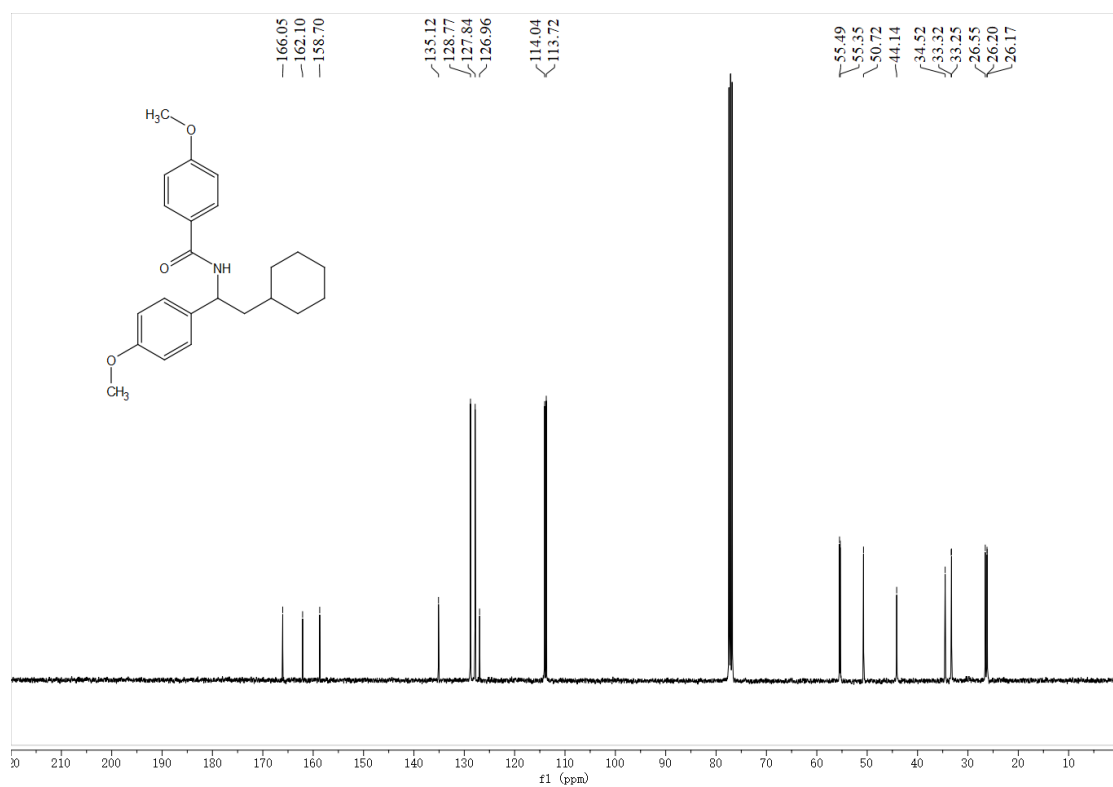
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4aca** in CDCl_3



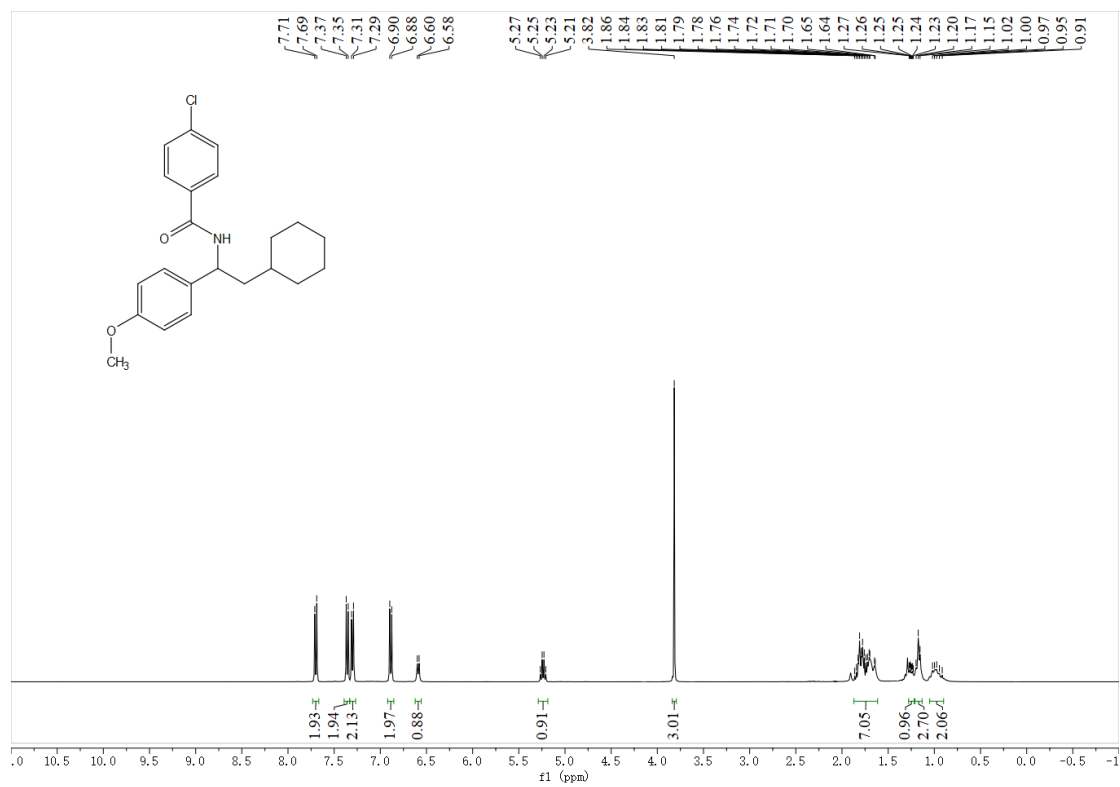
¹H NMR (400 MHz) Spectrum of **4ada** in CDCl₃



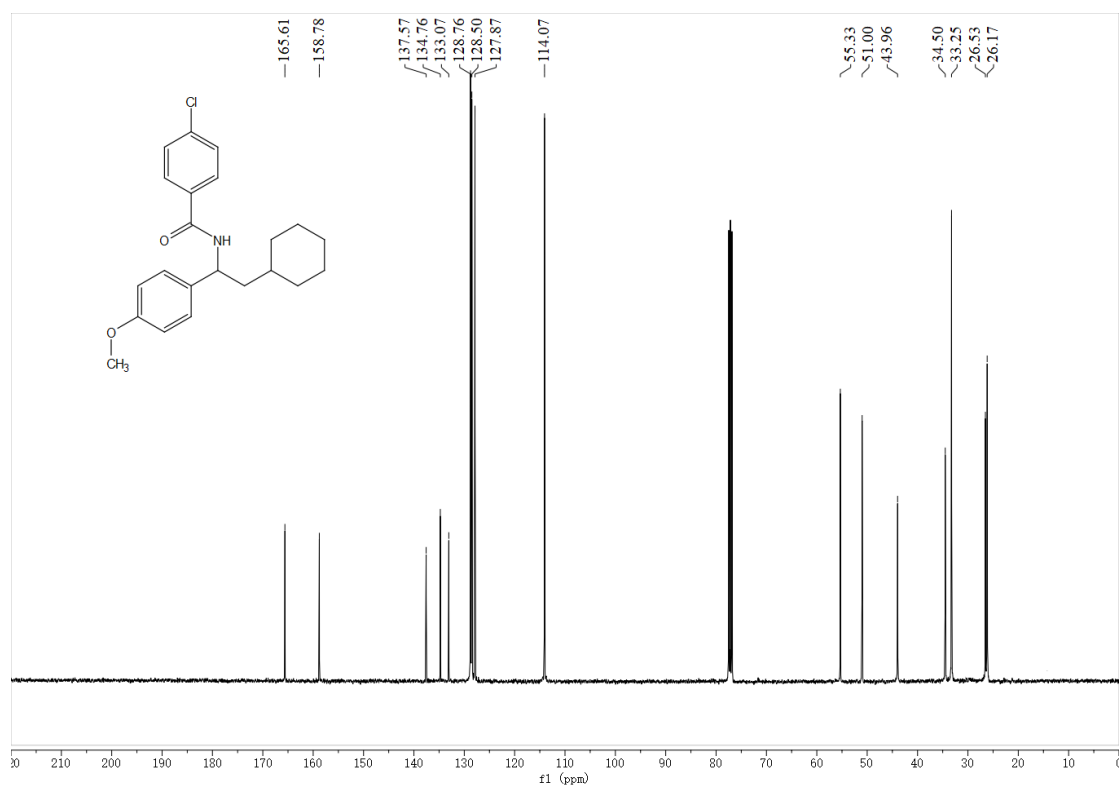
¹³C{¹H} NMR (101 MHz) Spectrum of **4ada** in CDCl₃



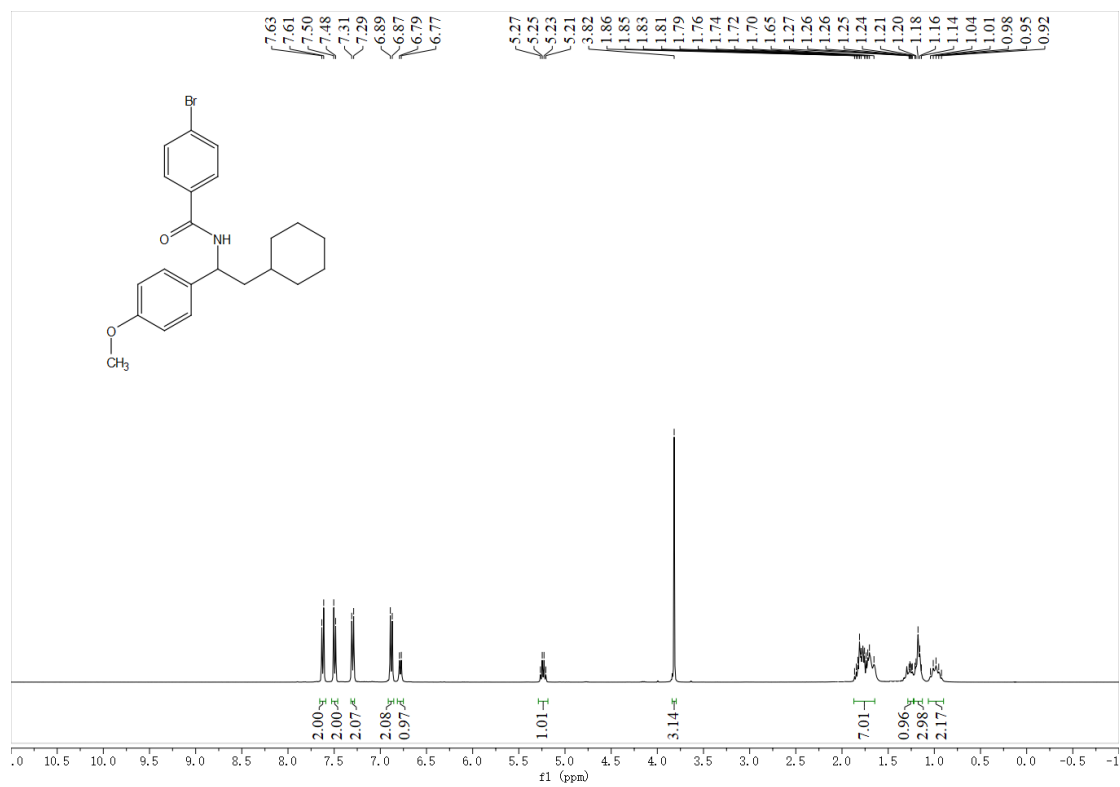
¹H NMR (400 MHz) Spectrum of **4aea** in CDCl₃



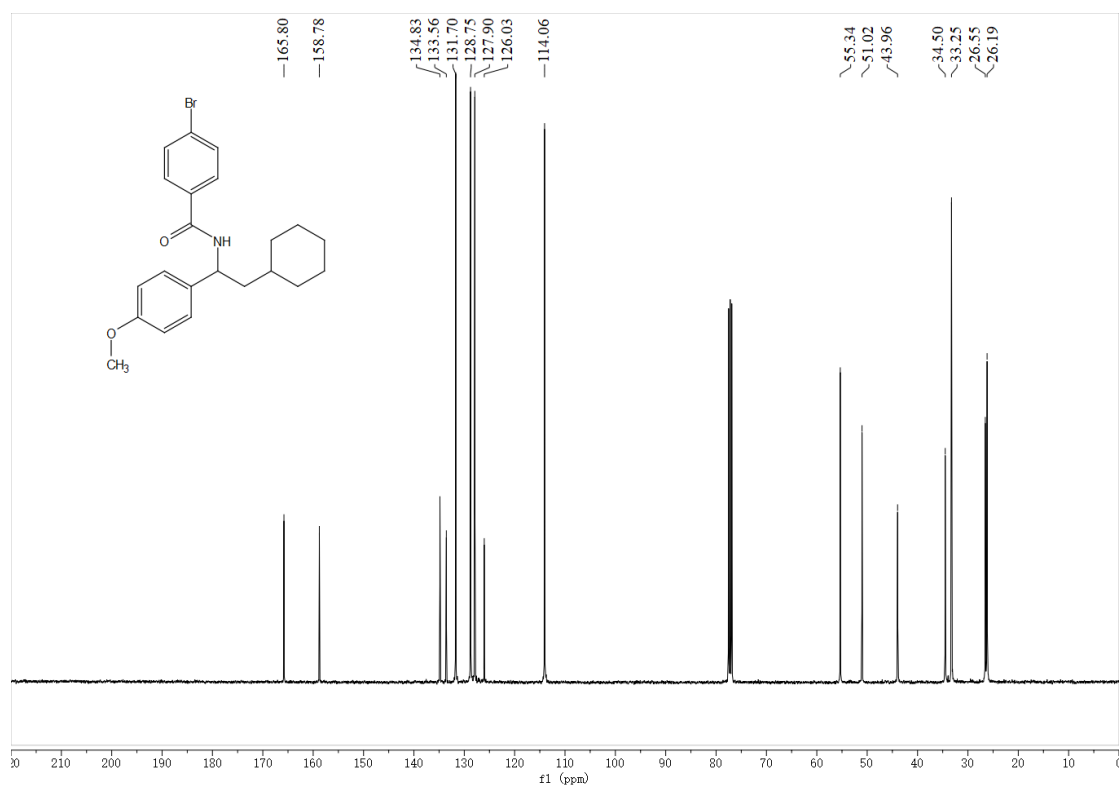
¹³C{¹H} NMR (101 MHz) Spectrum of **4aea** in CDCl₃



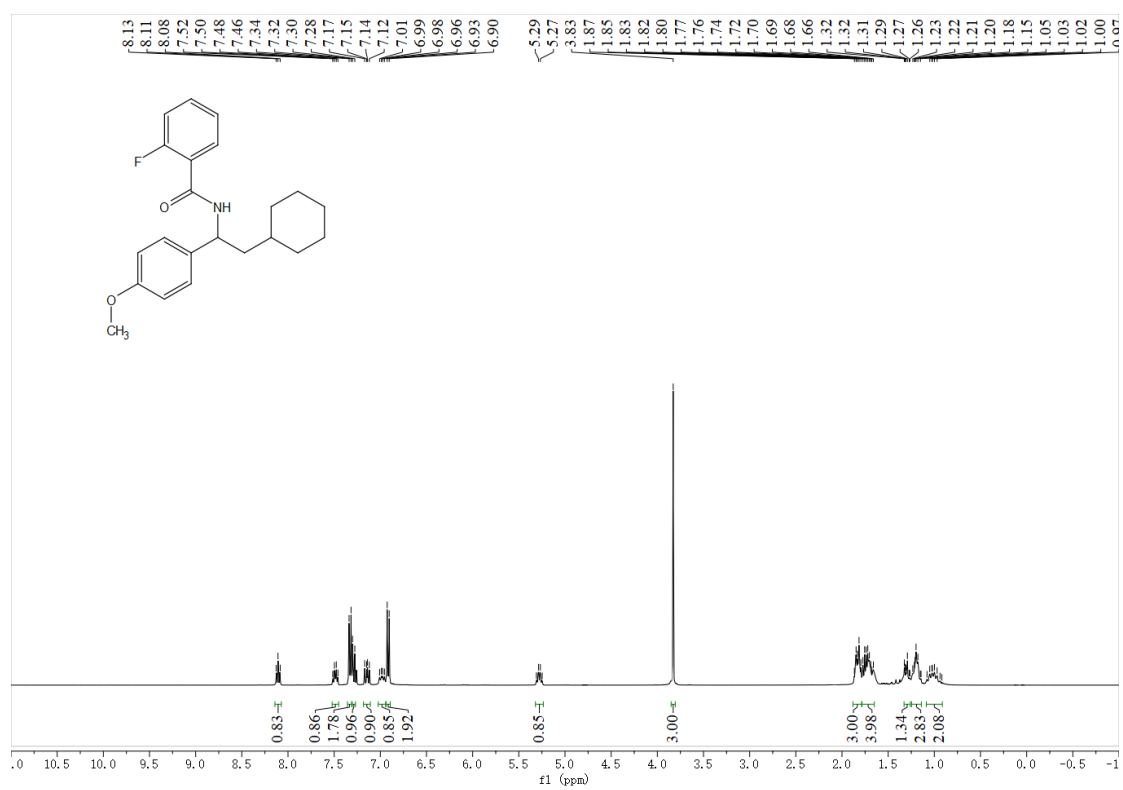
¹H NMR (400 MHz) Spectrum of **4afa** in CDCl₃



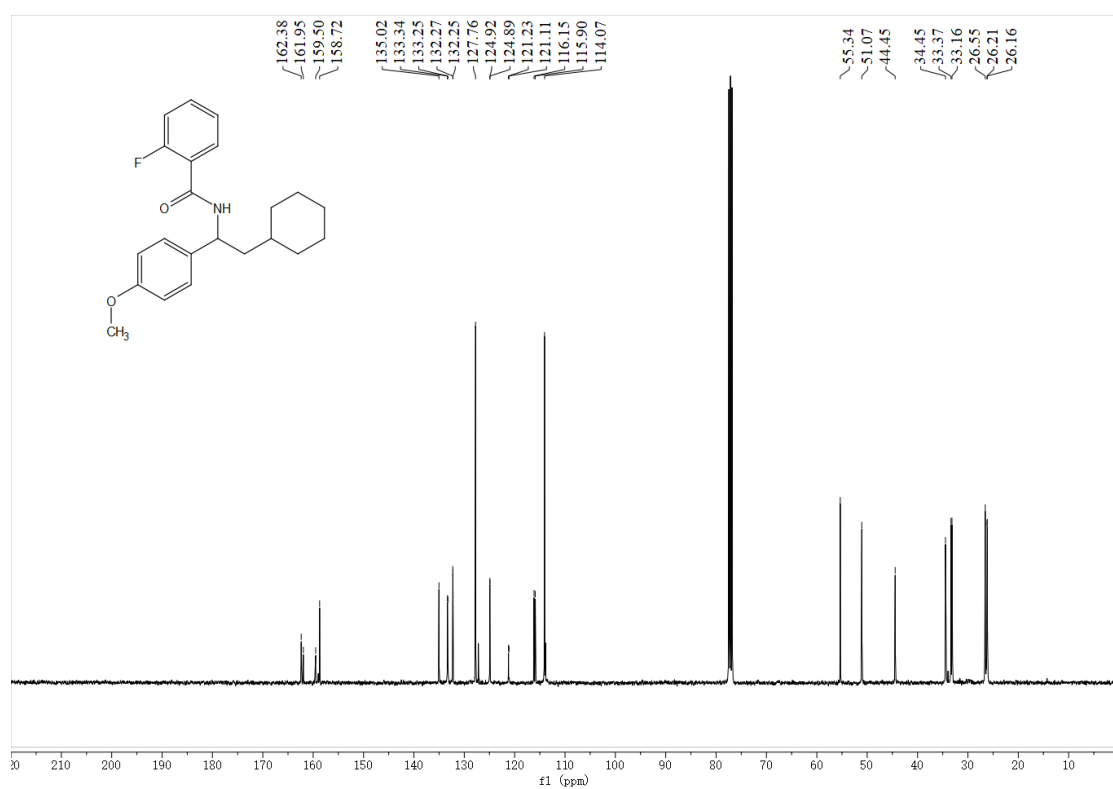
¹³C{¹H} NMR (101 MHz) Spectrum of **4afa** in CDCl₃



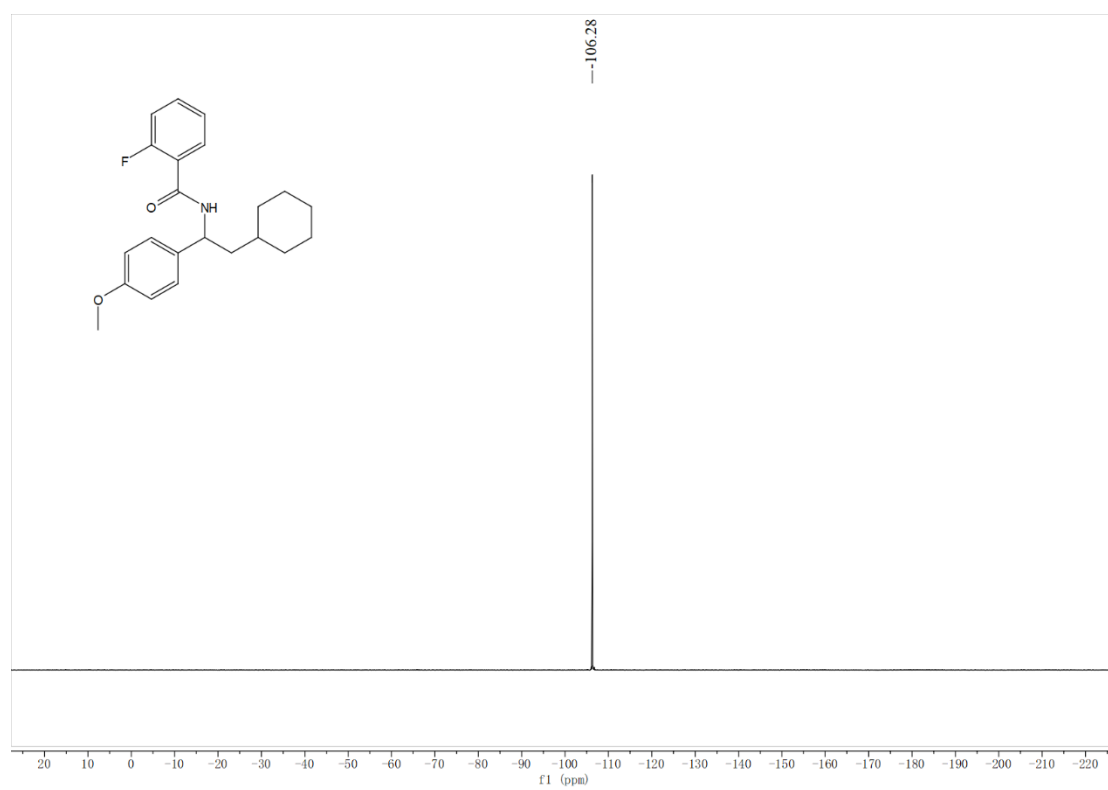
^1H NMR (400 MHz) Spectrum of **4aga** in CDCl_3



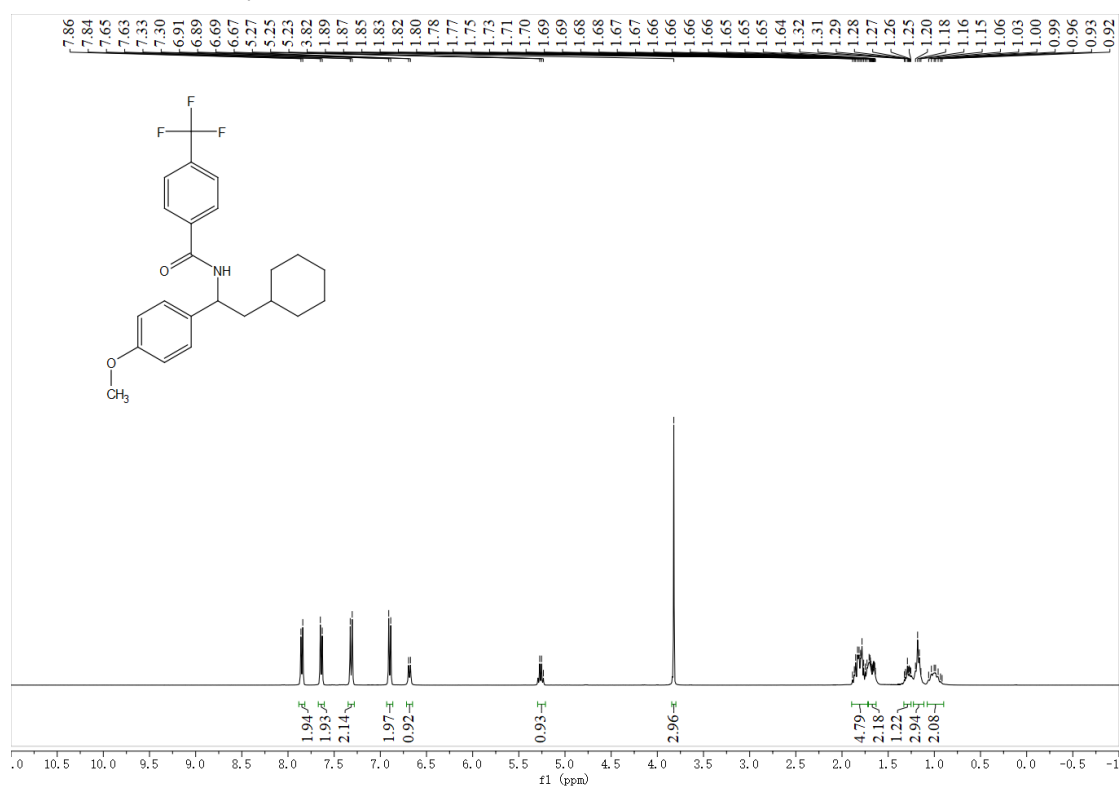
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4aga** in CDCl_3



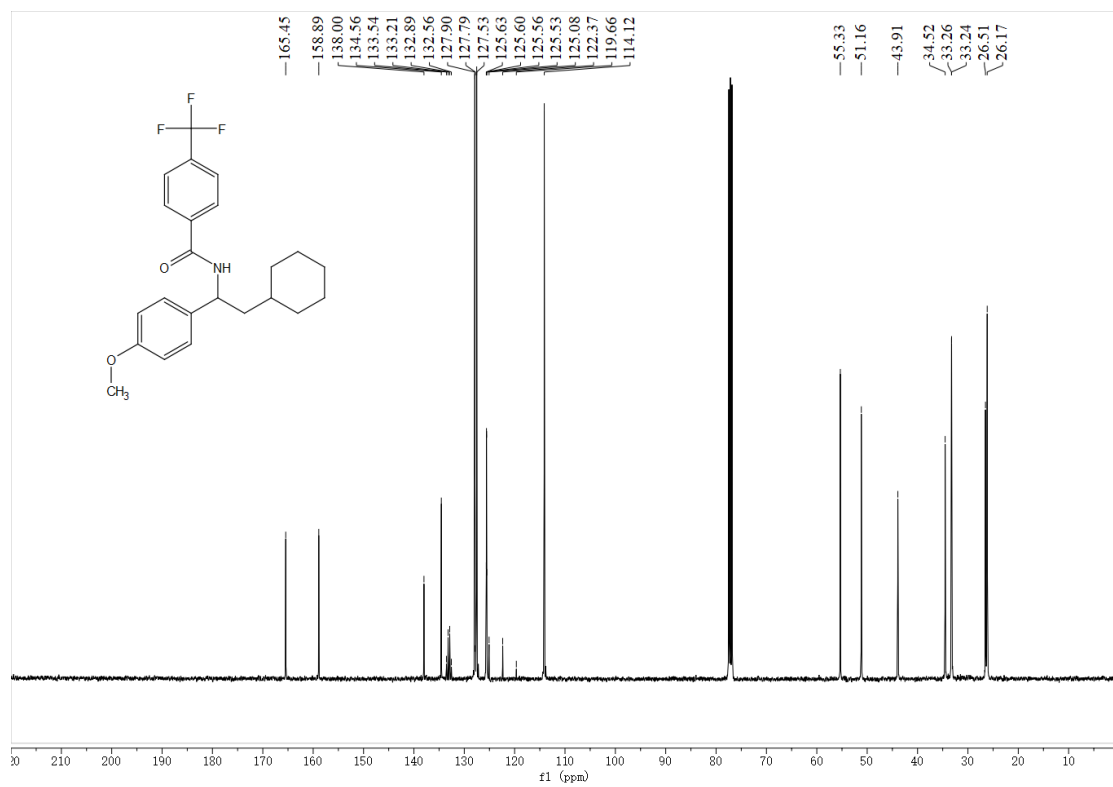
¹⁹F NMR (376 MHz) Spectrum of **4aga** in CDCl₃



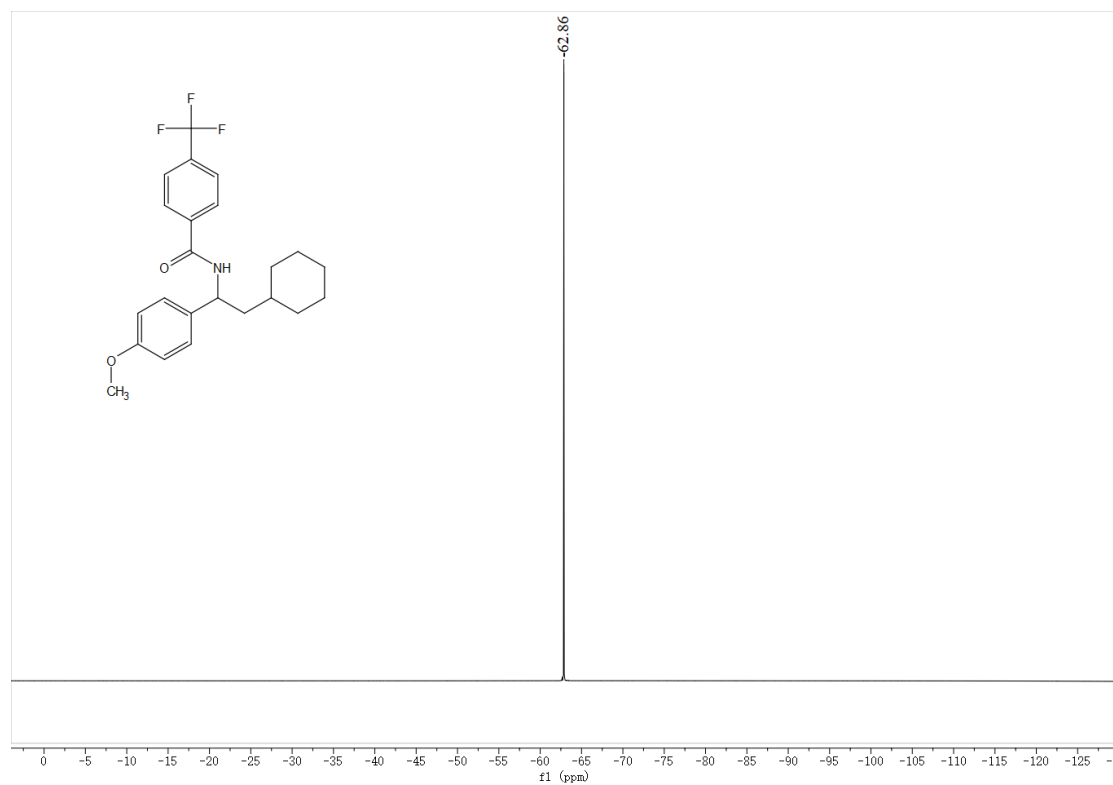
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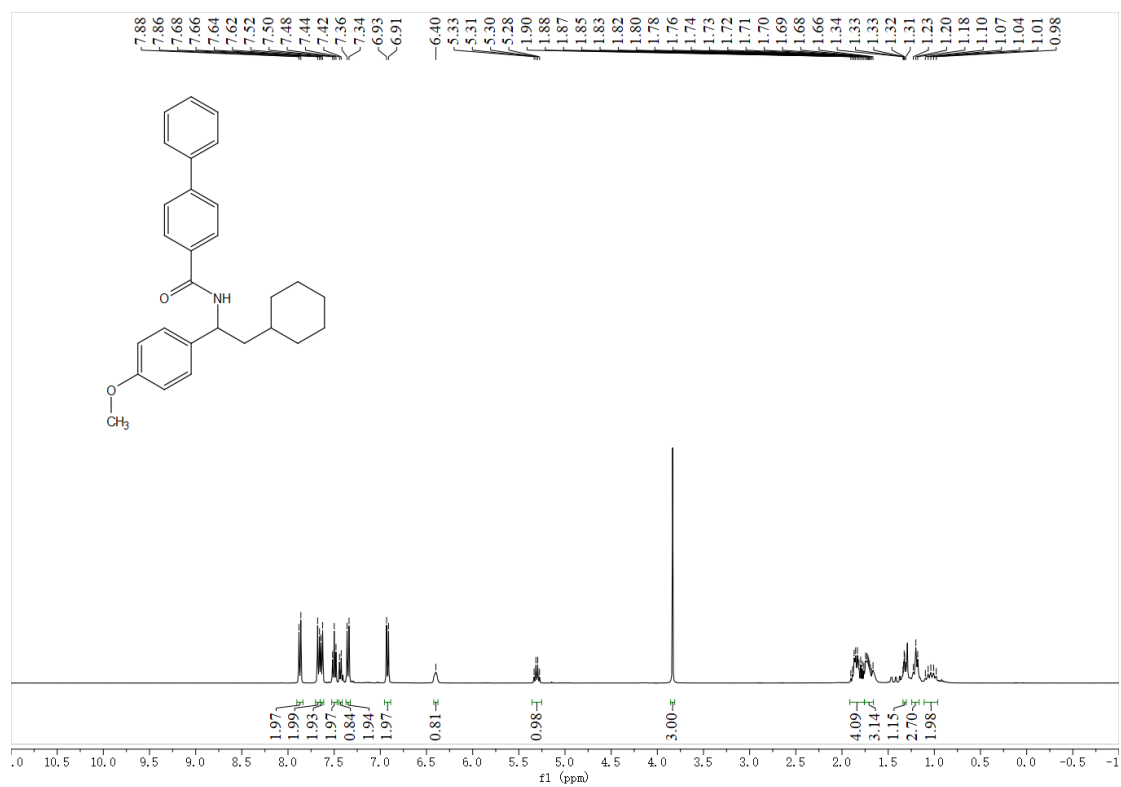
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4aha** in CDCl_3



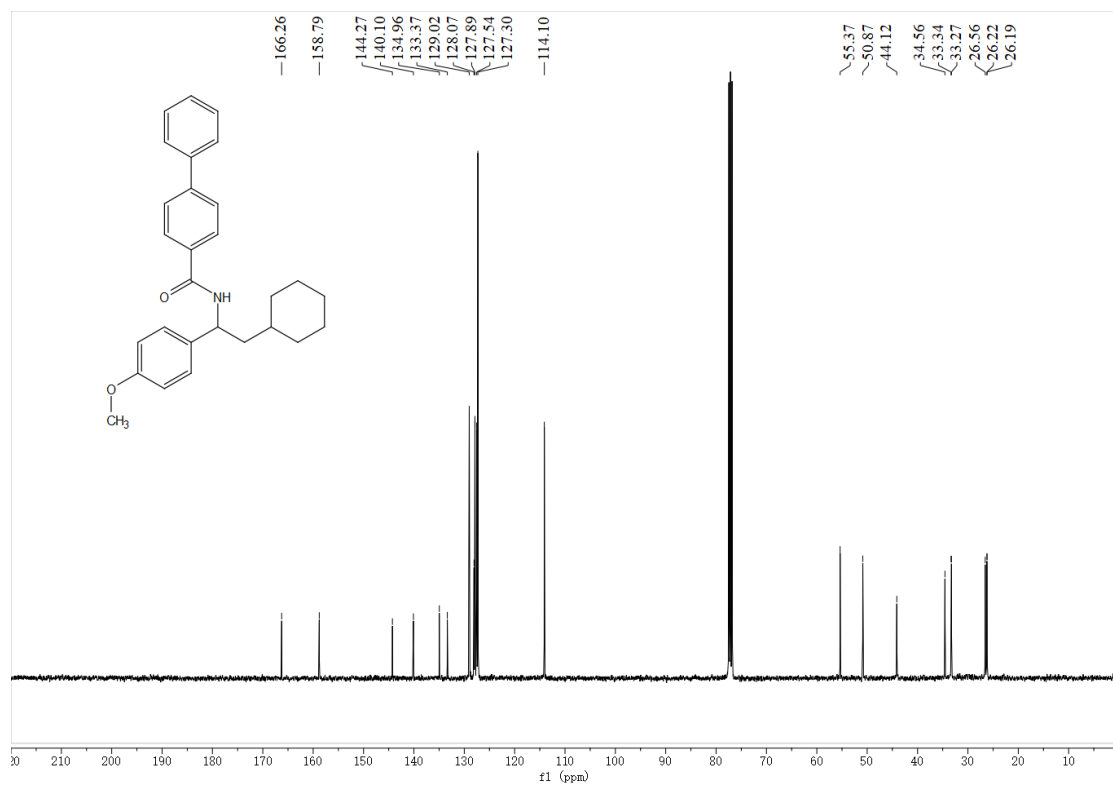
^{19}F NMR (376 MHz) Spectrum of **4aha** in CDCl_3



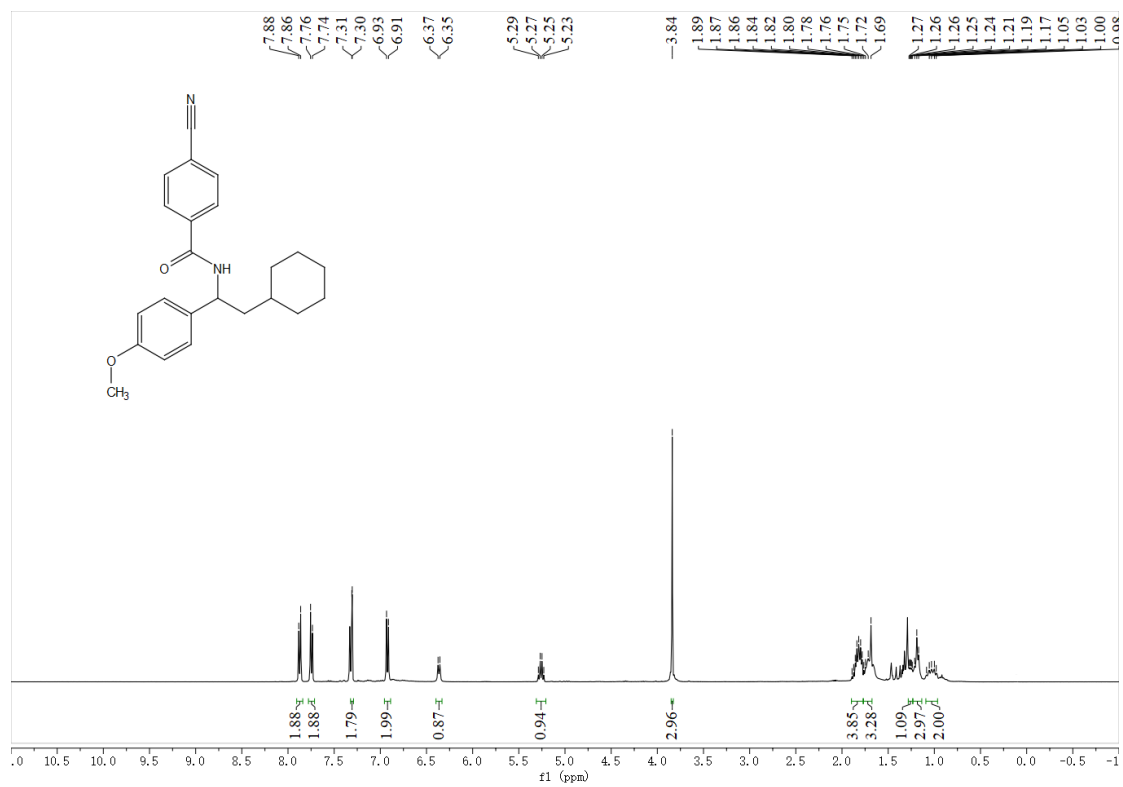
¹H NMR (400 MHz) Spectrum of **4aia** in CDCl₃



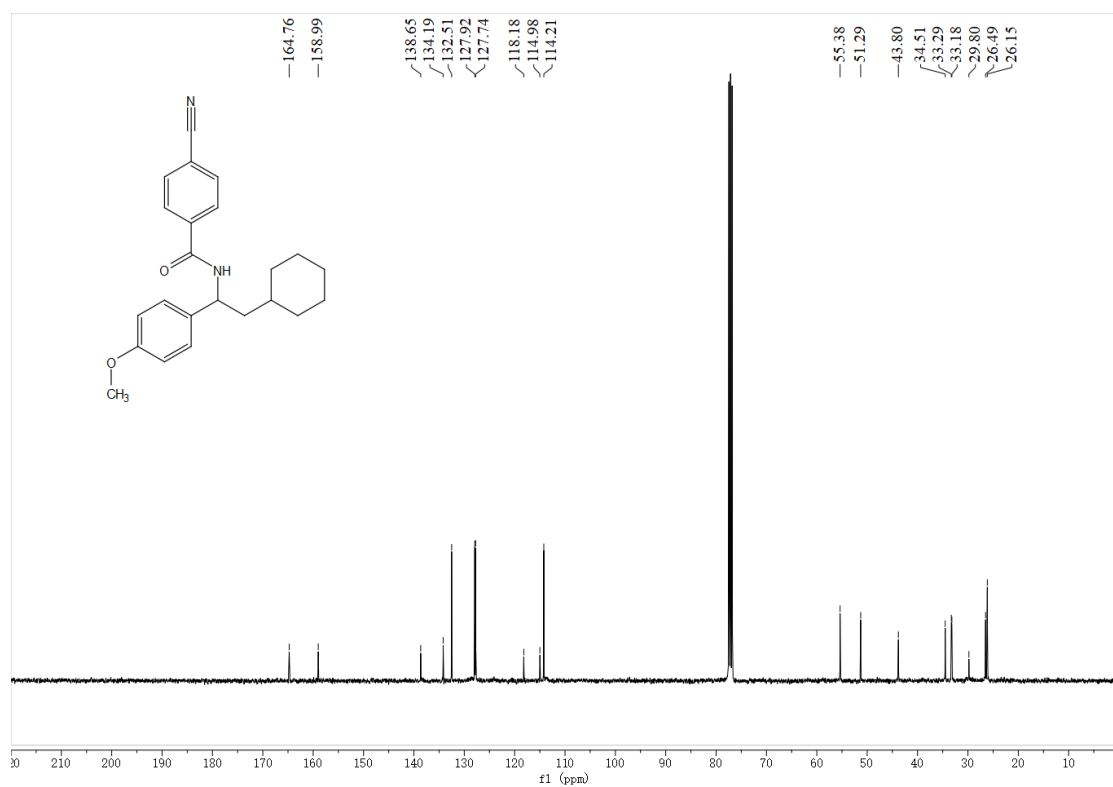
¹³C{¹H} NMR (101 MHz) Spectrum of **4aia** in CDCl₃



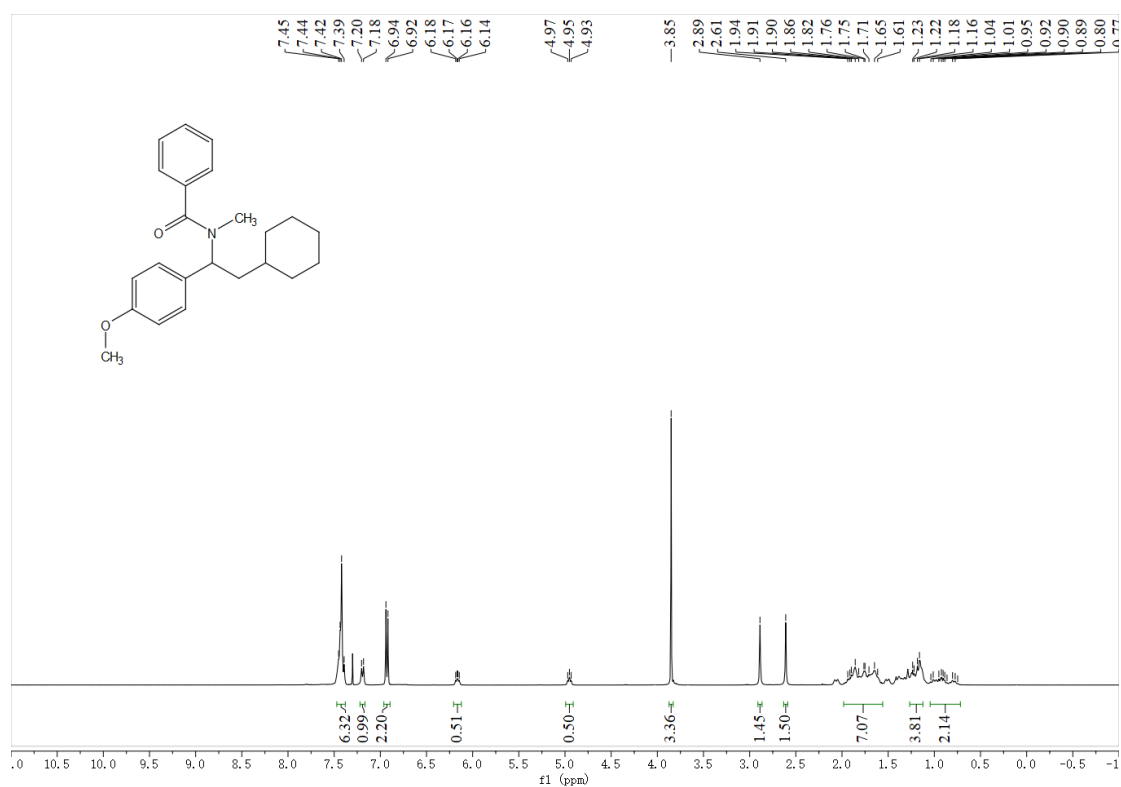
¹H NMR (400 MHz) Spectrum of **4aja** in CDCl₃



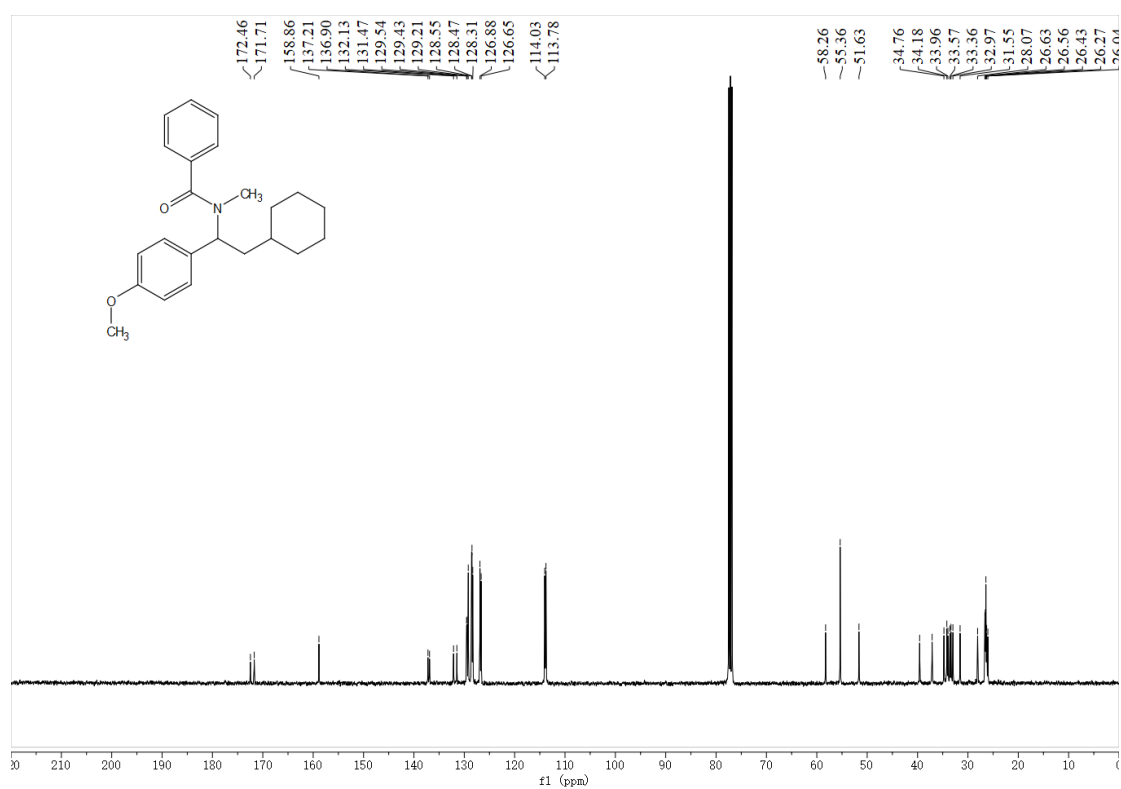
¹³C{¹H} NMR (101 MHz) Spectrum of **4aja** in CDCl₃



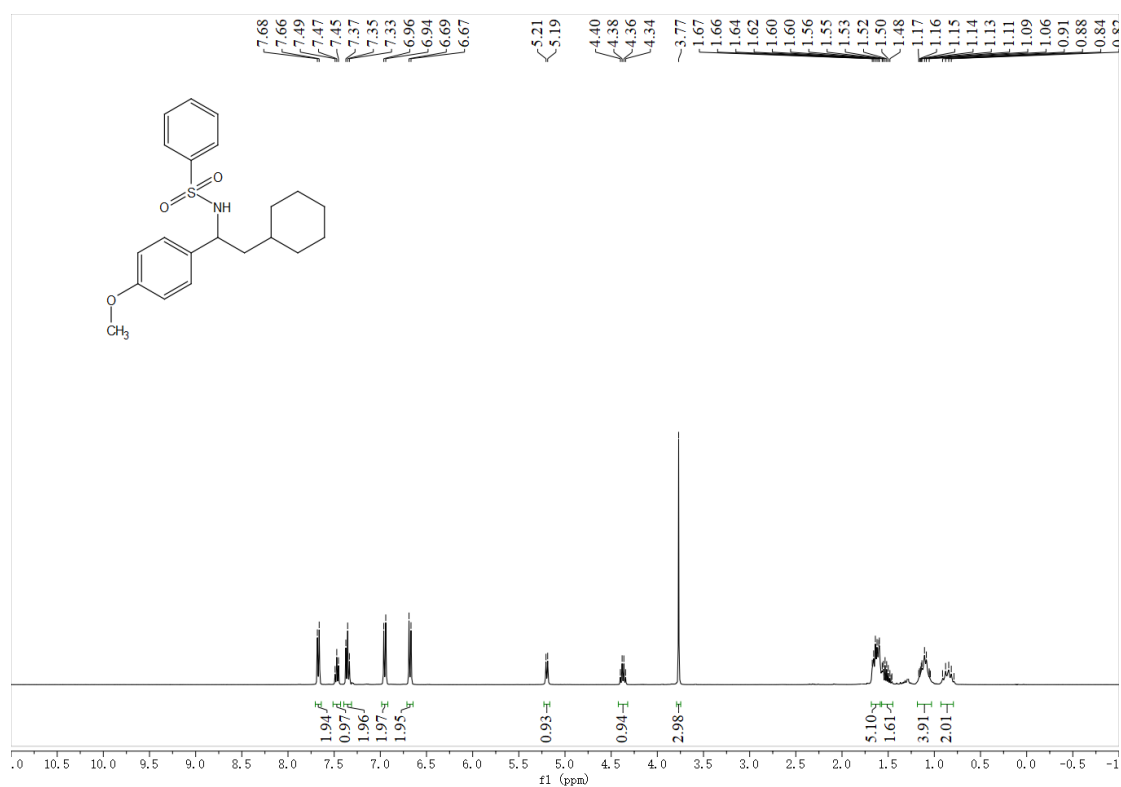
¹H NMR (400 MHz) Spectrum of **4aka** in CDCl₃



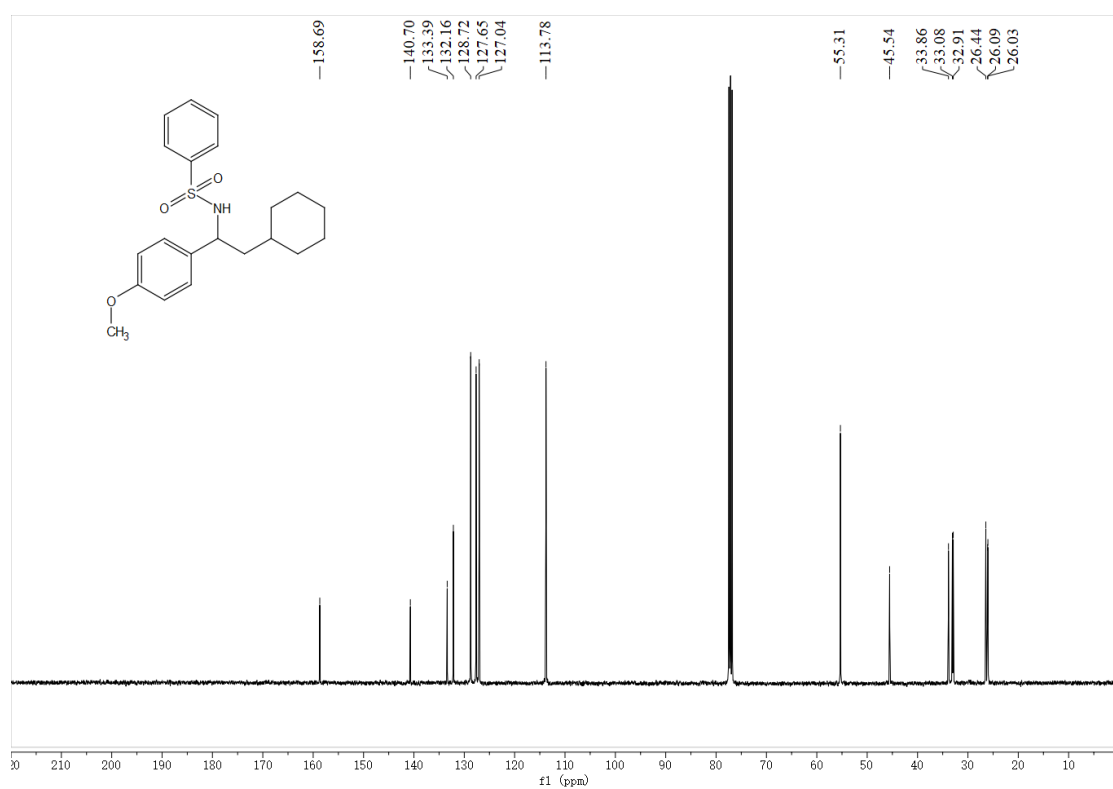
¹³C{¹H} NMR (101 MHz) Spectrum of **4aka** in CDCl₃



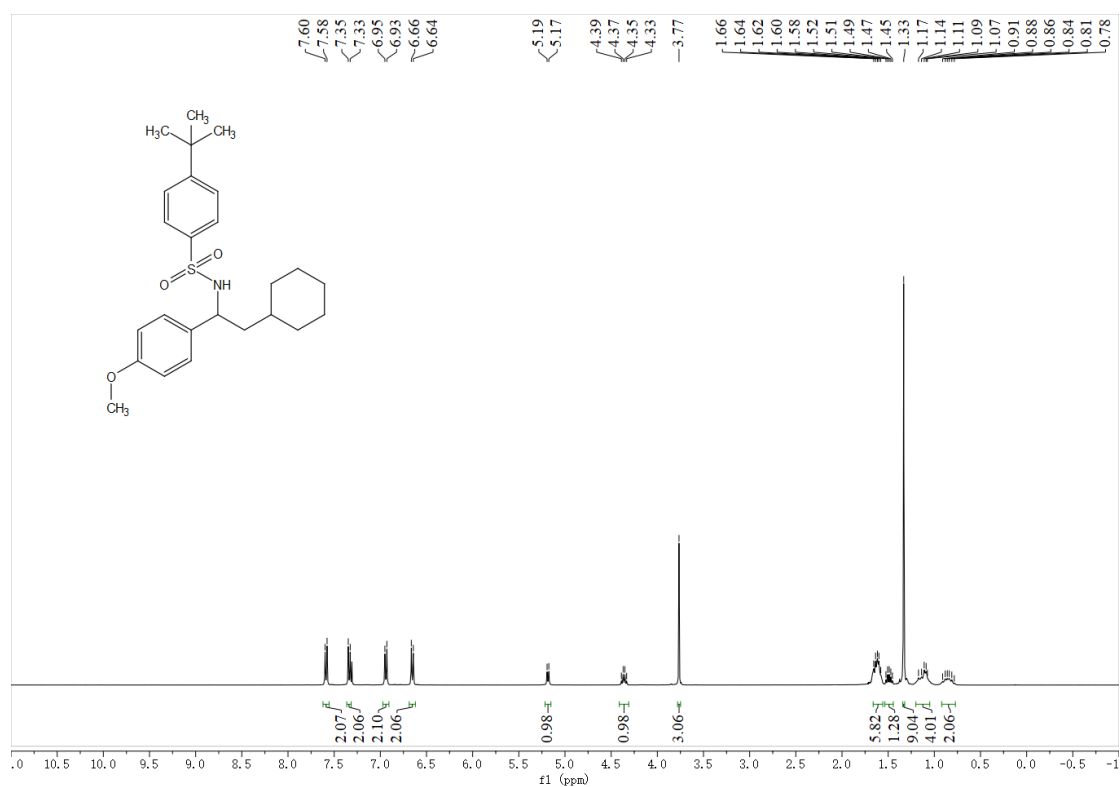
¹H NMR (400 MHz) Spectrum of **4a1a** in CDCl₃



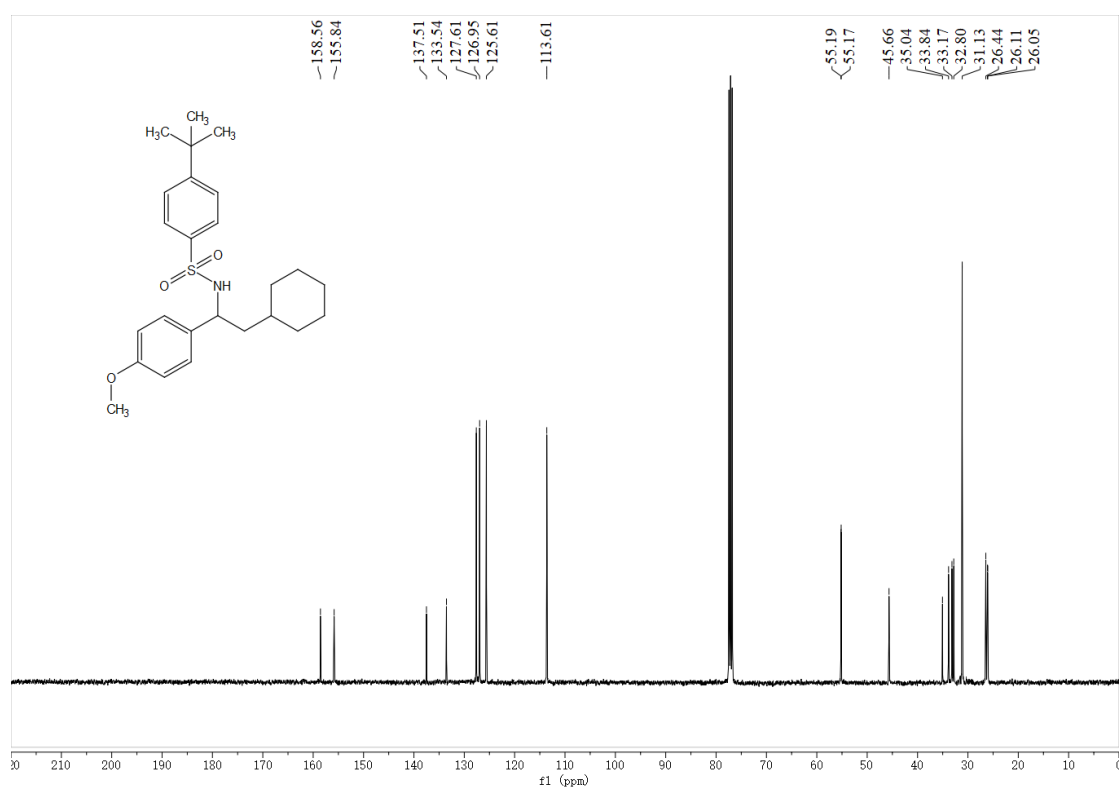
¹³C{¹H} NMR (101 MHz) Spectrum of **4a1a** in CDCl₃



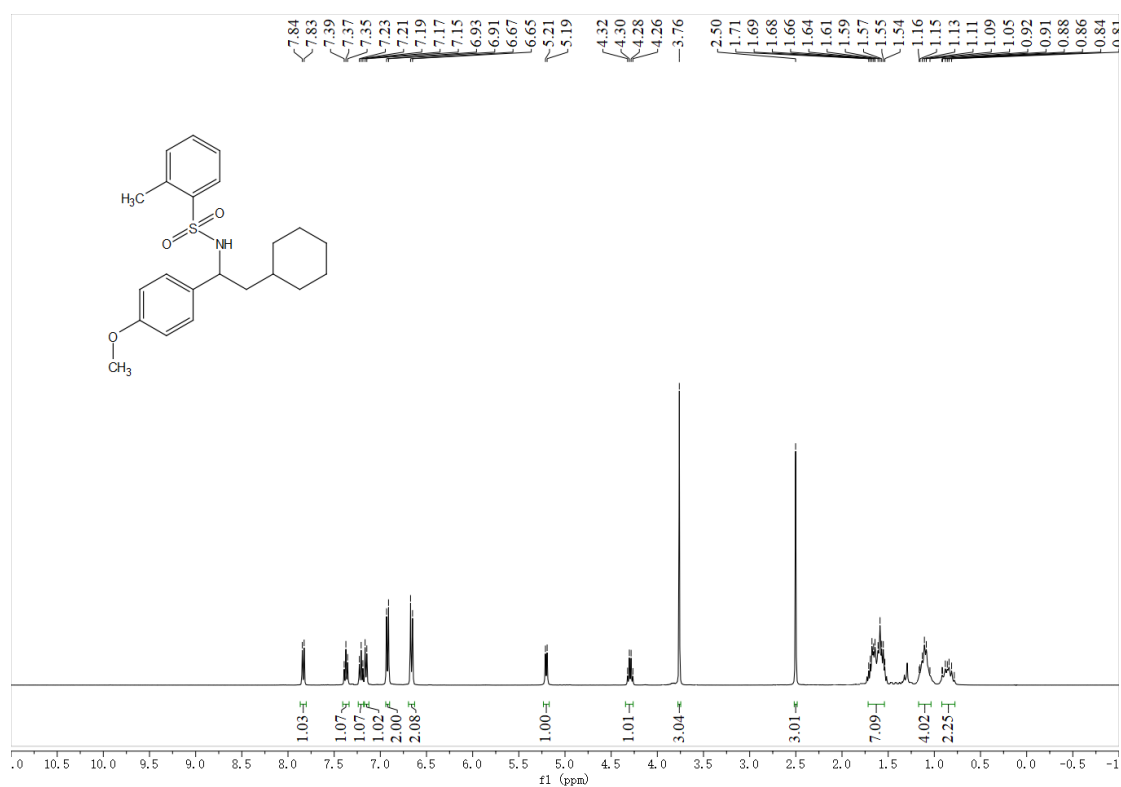
^1H NMR (400 MHz) Spectrum of **4ama** in CDCl_3



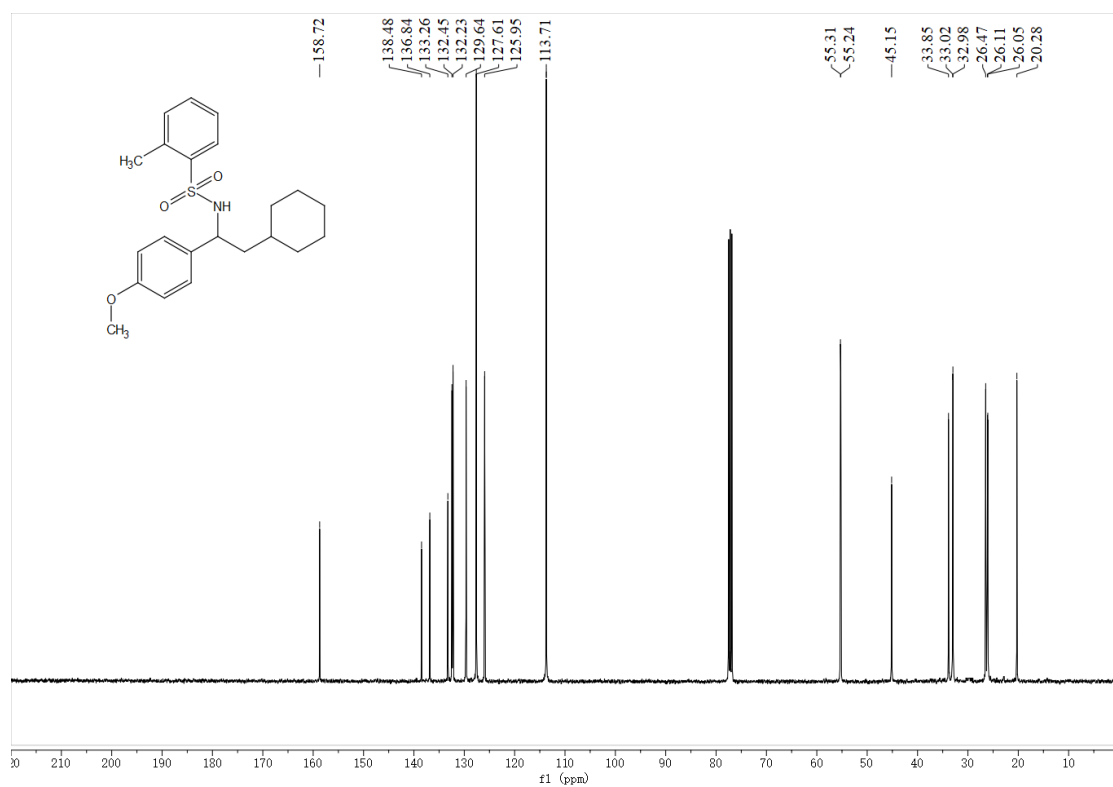
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4ama** in CDCl_3



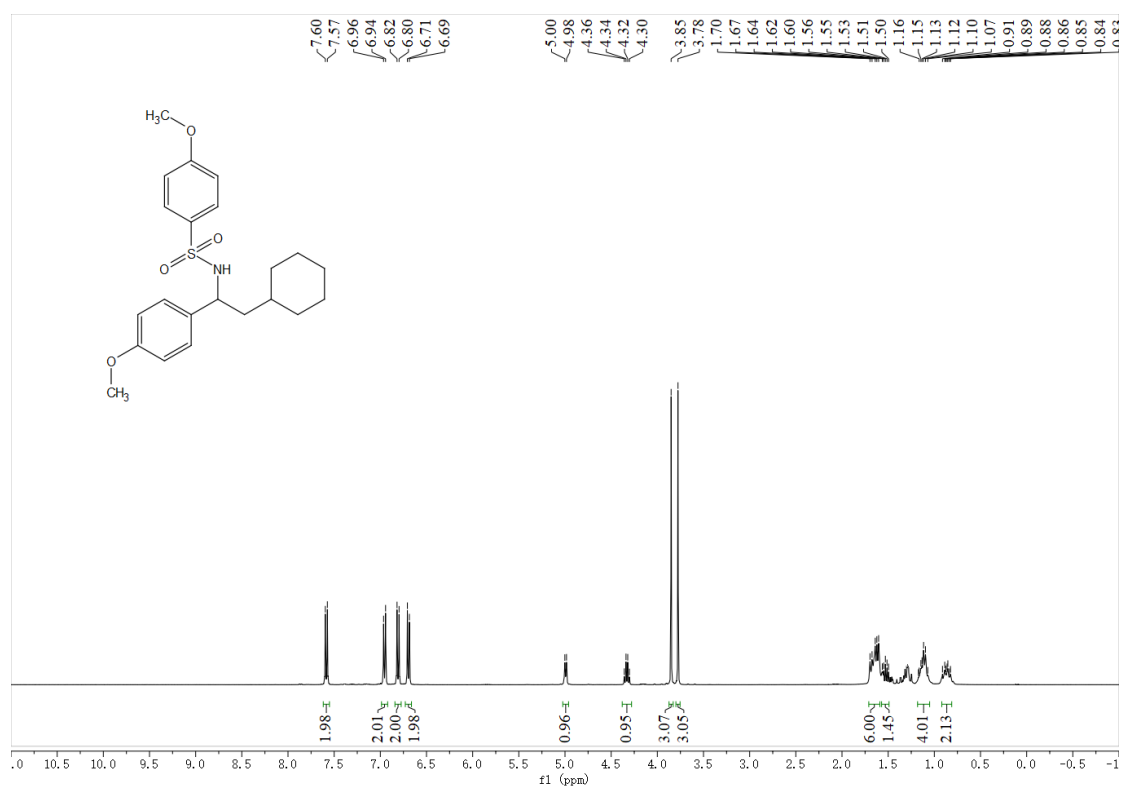
¹H NMR (400 MHz) Spectrum of **4ana** in CDCl₃



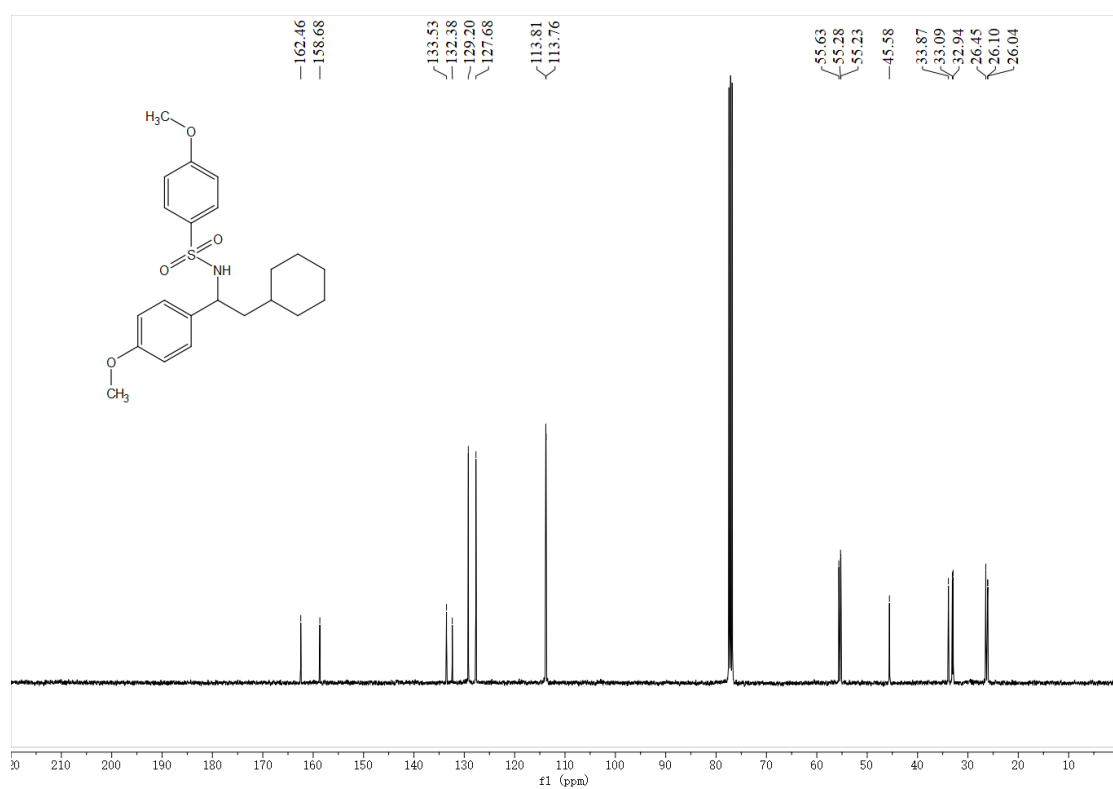
¹³C{¹H} NMR (101 MHz) Spectrum of **4ana** in CDCl₃



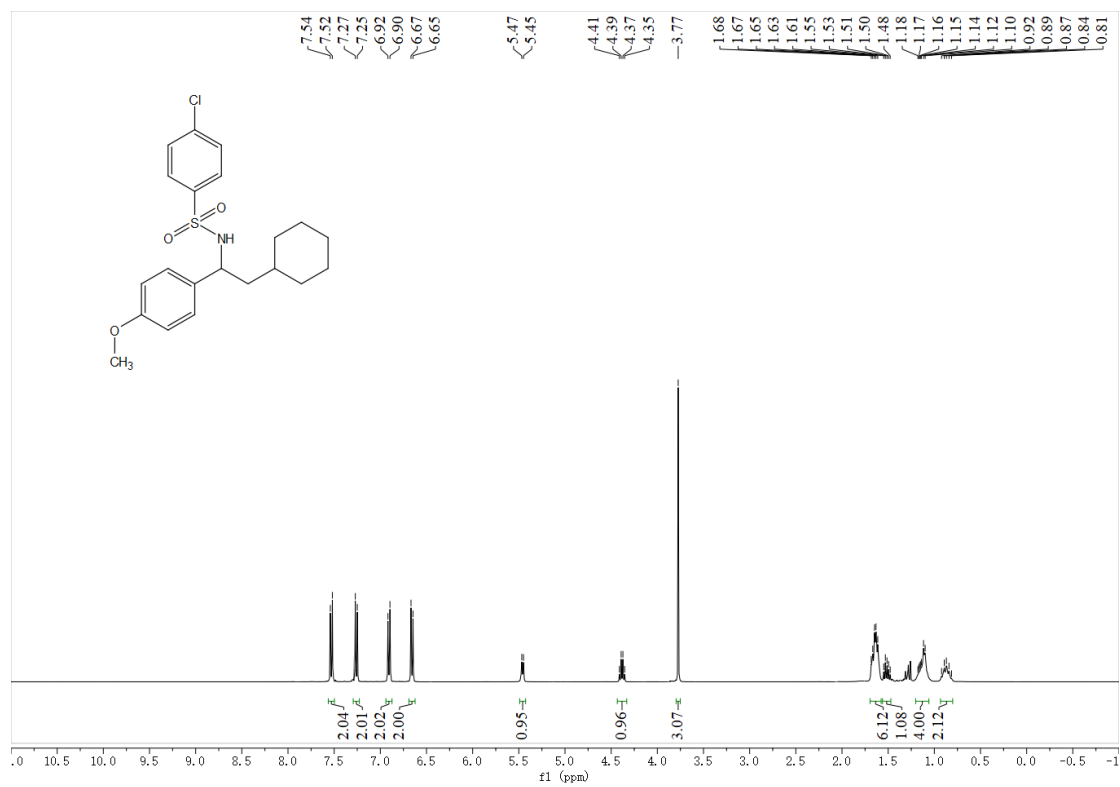
¹H NMR (400 MHz) Spectrum of **4a0a** in CDCl₃



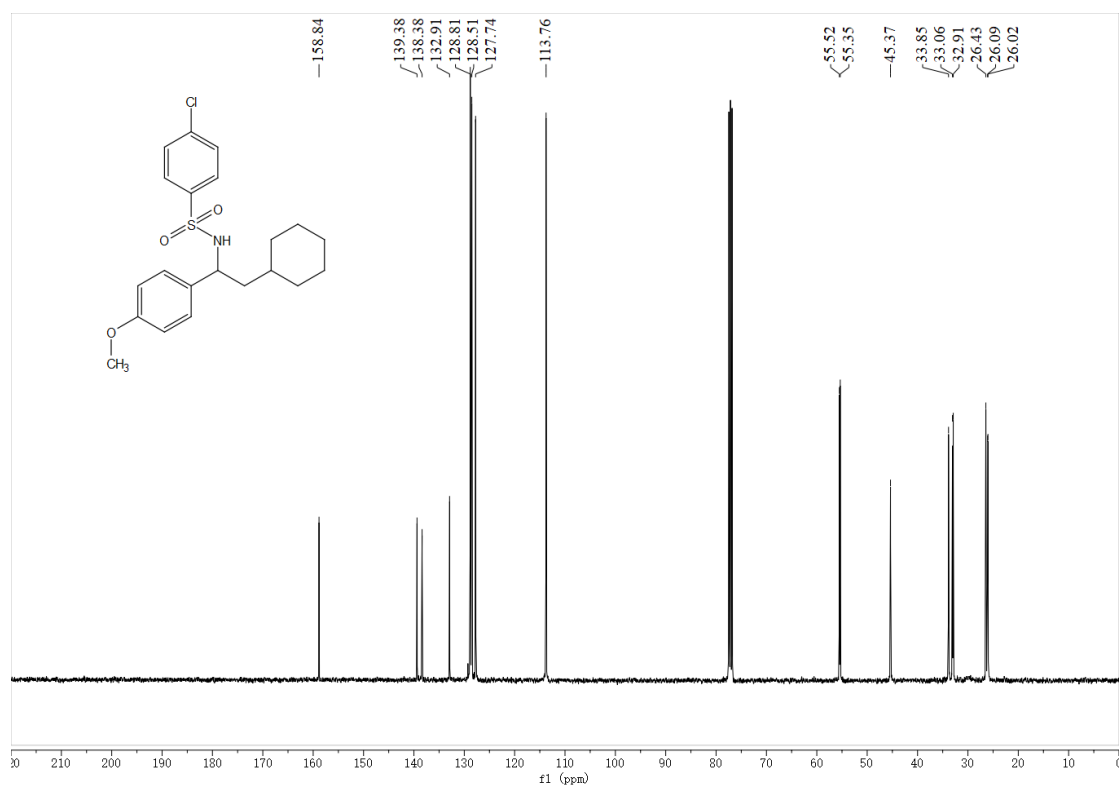
¹³C{¹H} NMR (101 MHz) Spectrum of **4a0a** in CDCl₃



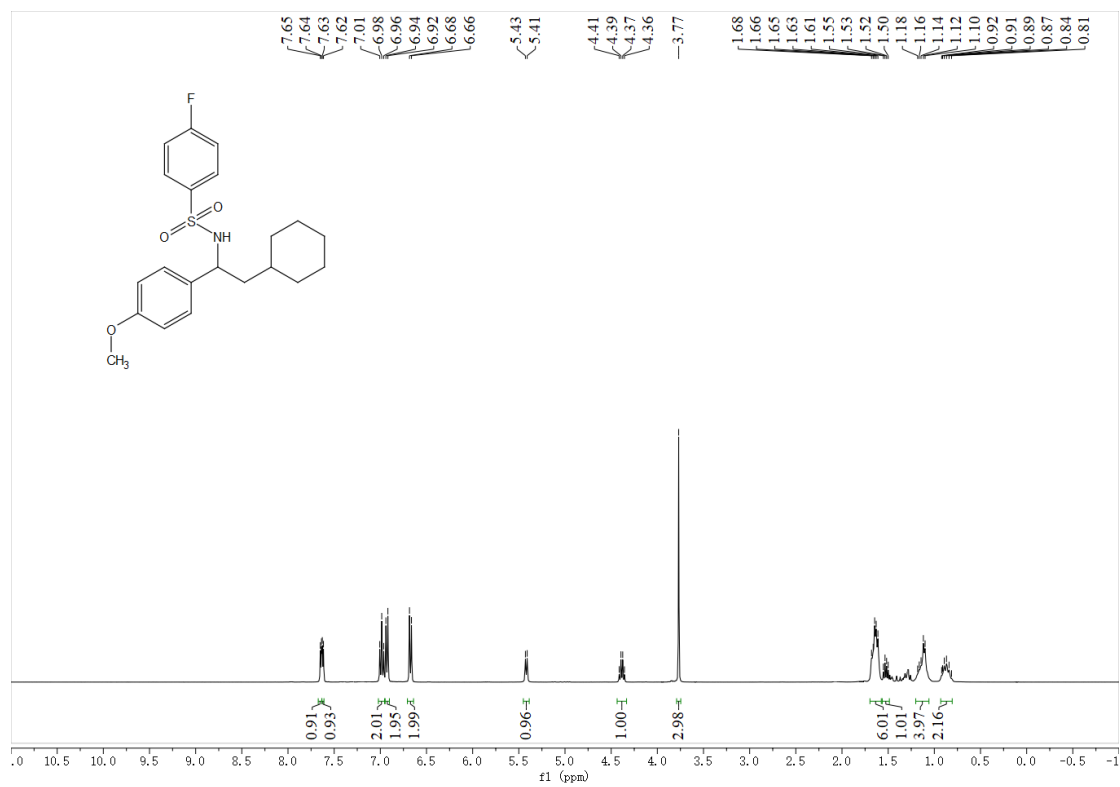
¹H NMR (400 MHz) Spectrum of **4apa** in CDCl₃



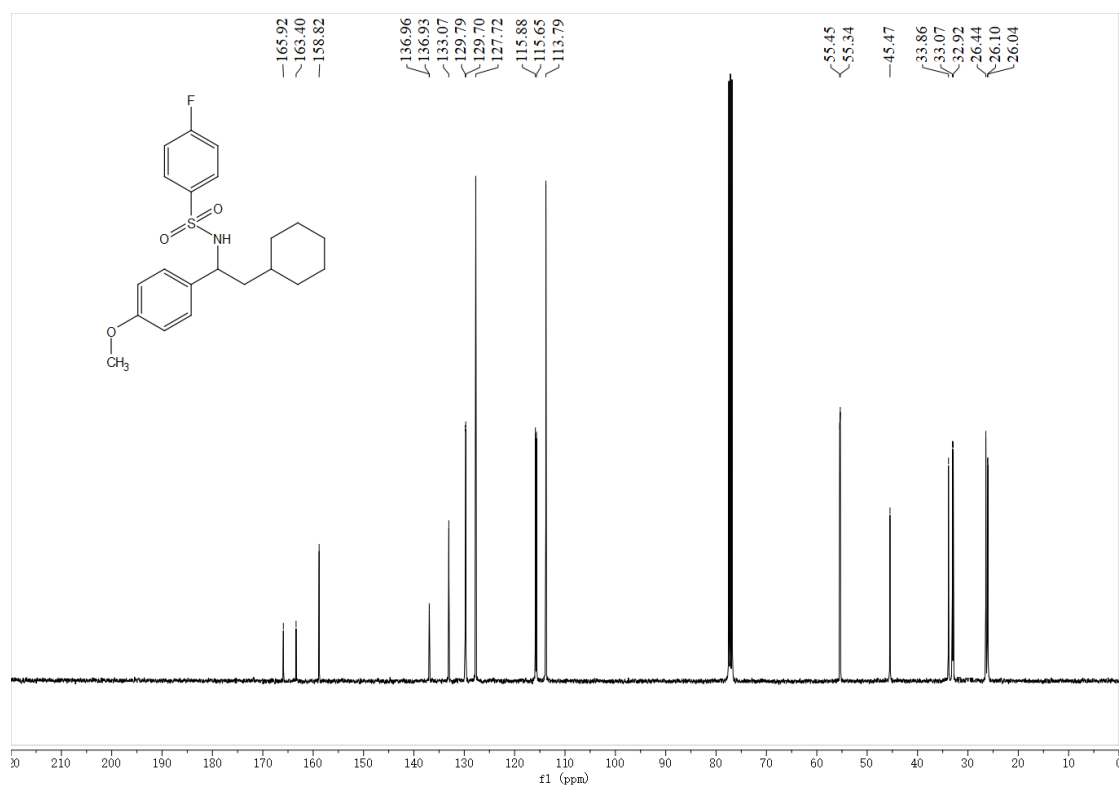
¹³C{¹H} NMR (101 MHz) Spectrum of **4apa** in CDCl₃



¹H NMR (400 MHz) Spectrum of **4aqa** in CDCl₃



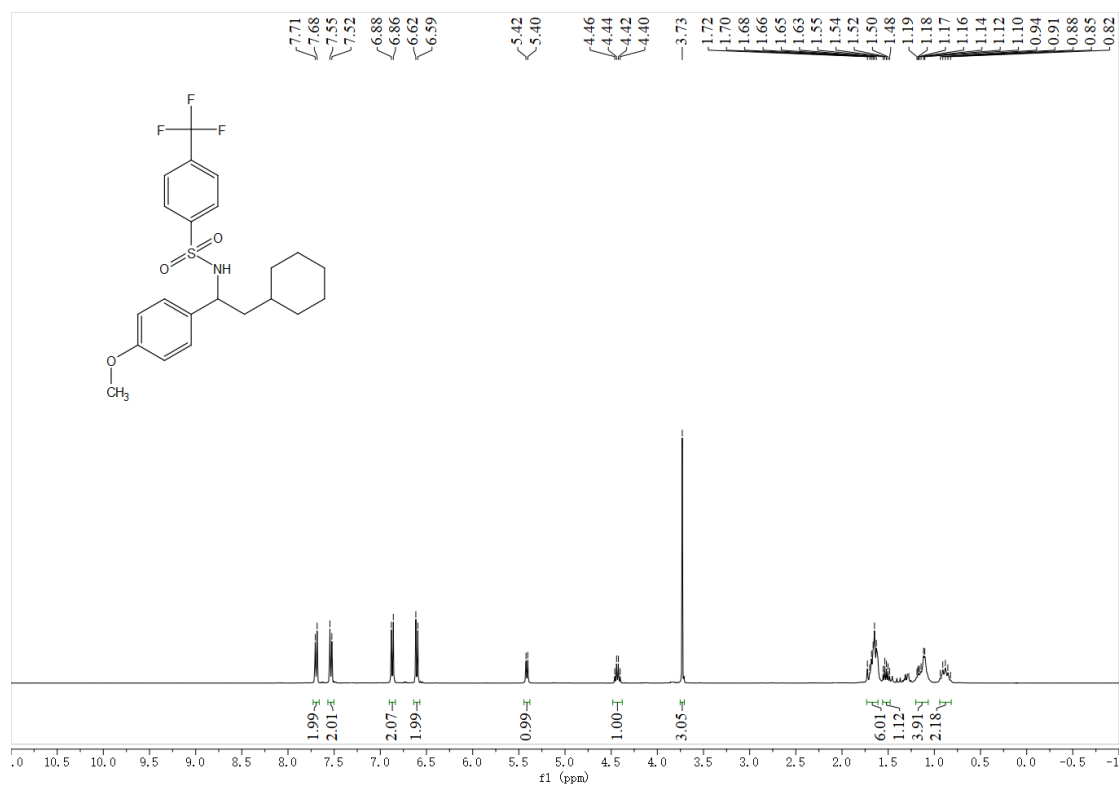
¹³C{¹H} NMR (101 MHz) Spectrum of **4aqa** in CDCl₃



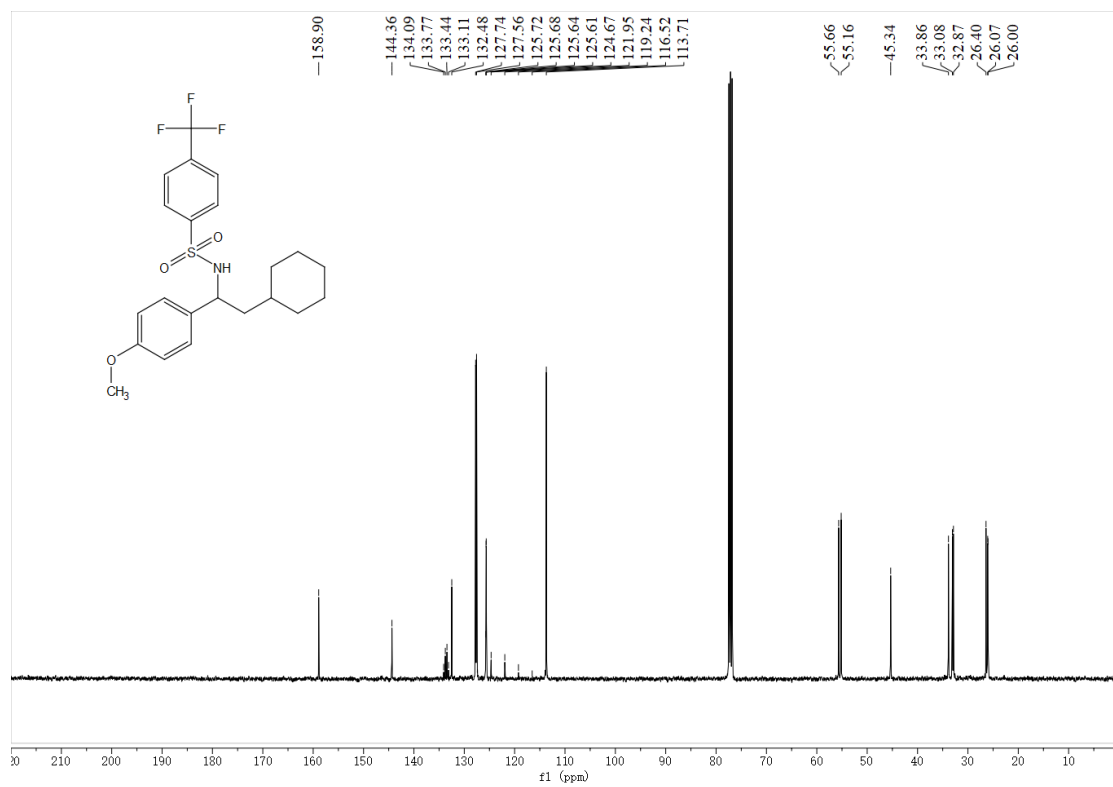
¹⁹F NMR (376 MHz) Spectrum of **4aqa** in CDCl₃



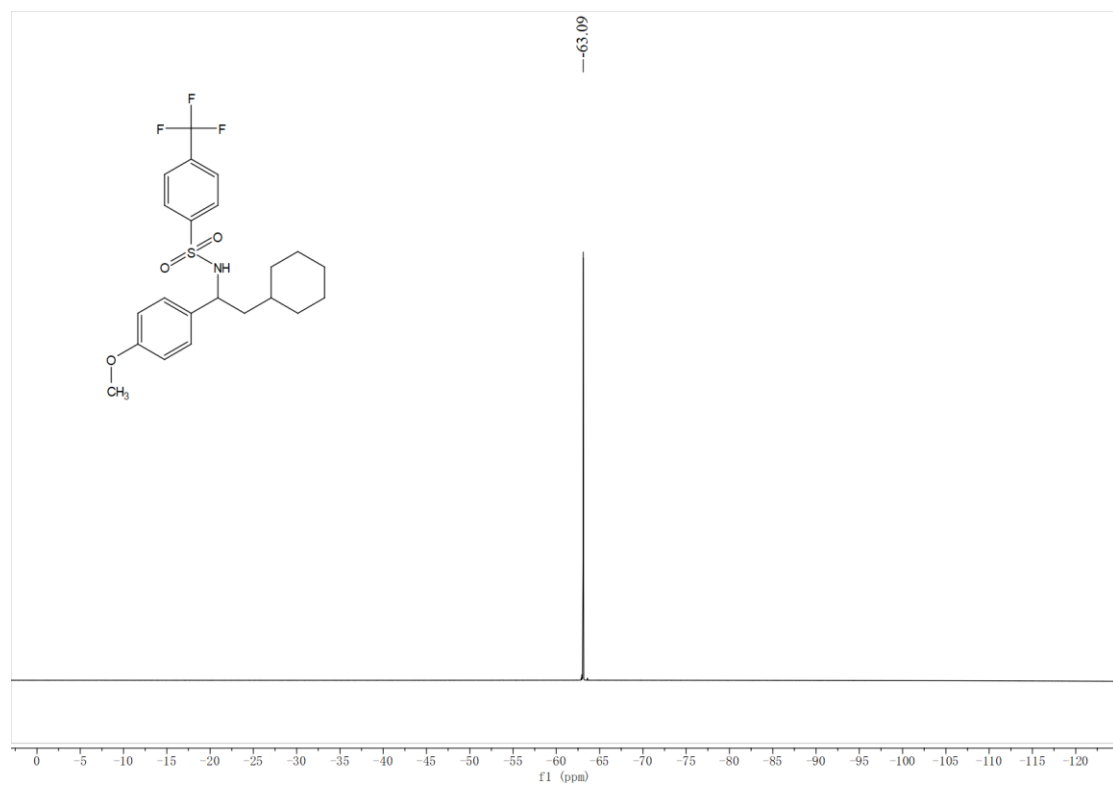
¹H NMR (400 MHz) Spectrum of **4ara** in CDCl₃



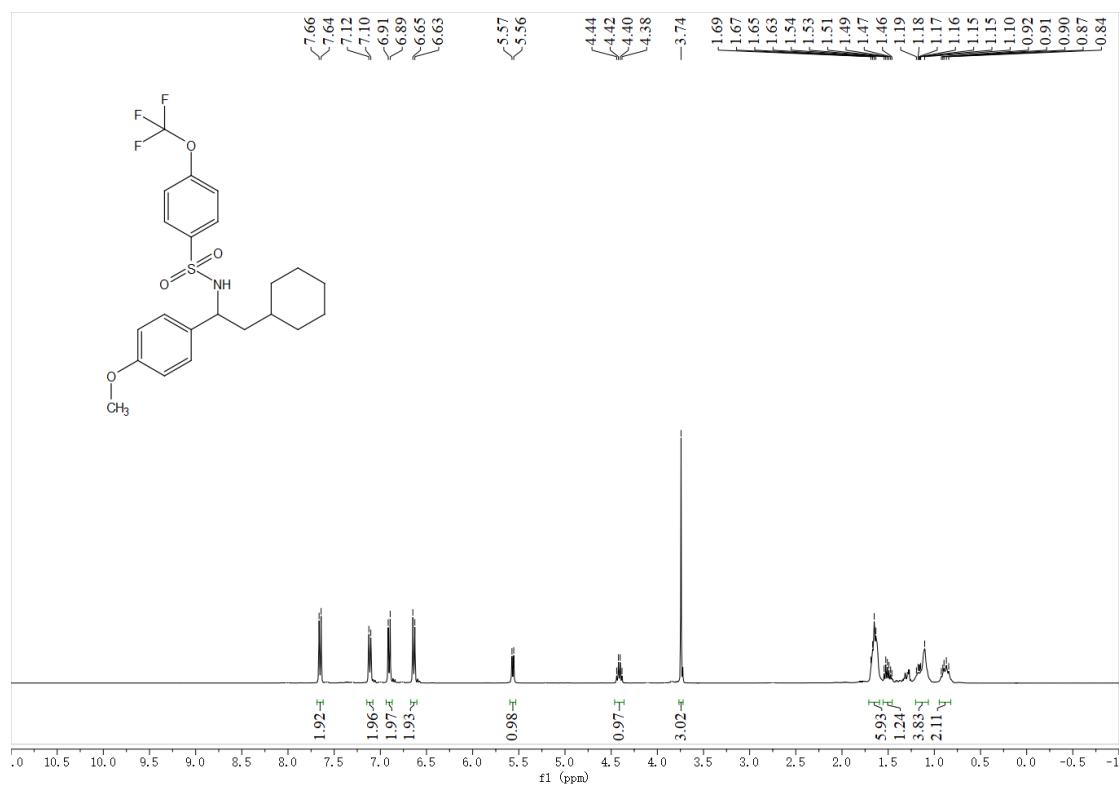
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4ara** in CDCl_3



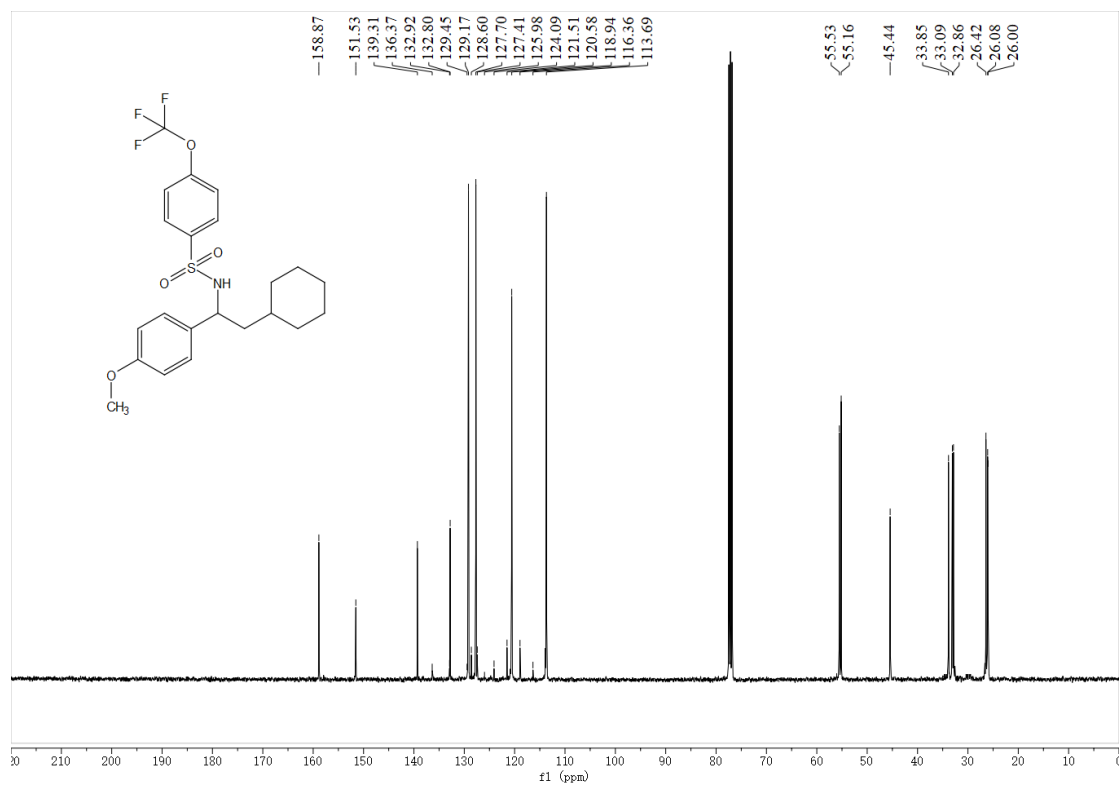
^{19}F NMR (376 MHz) Spectrum of **4ara** in CDCl_3



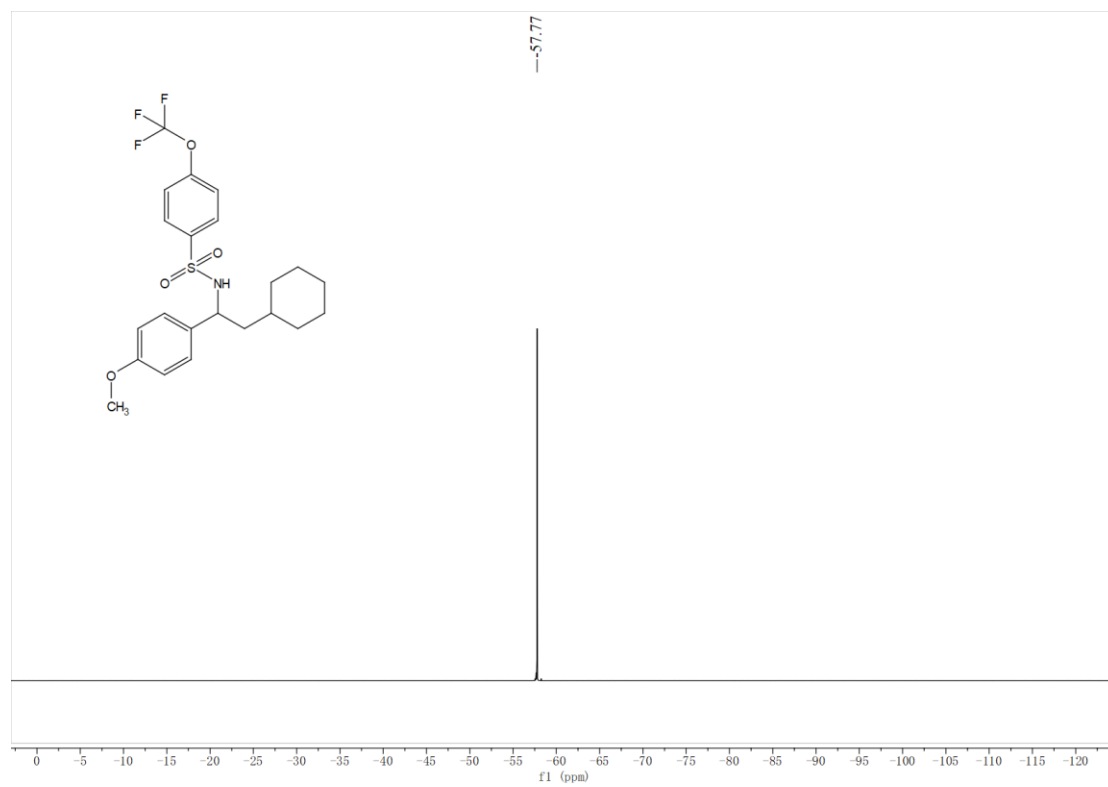
¹H NMR (400 MHz) Spectrum of **4asa** in CDCl₃



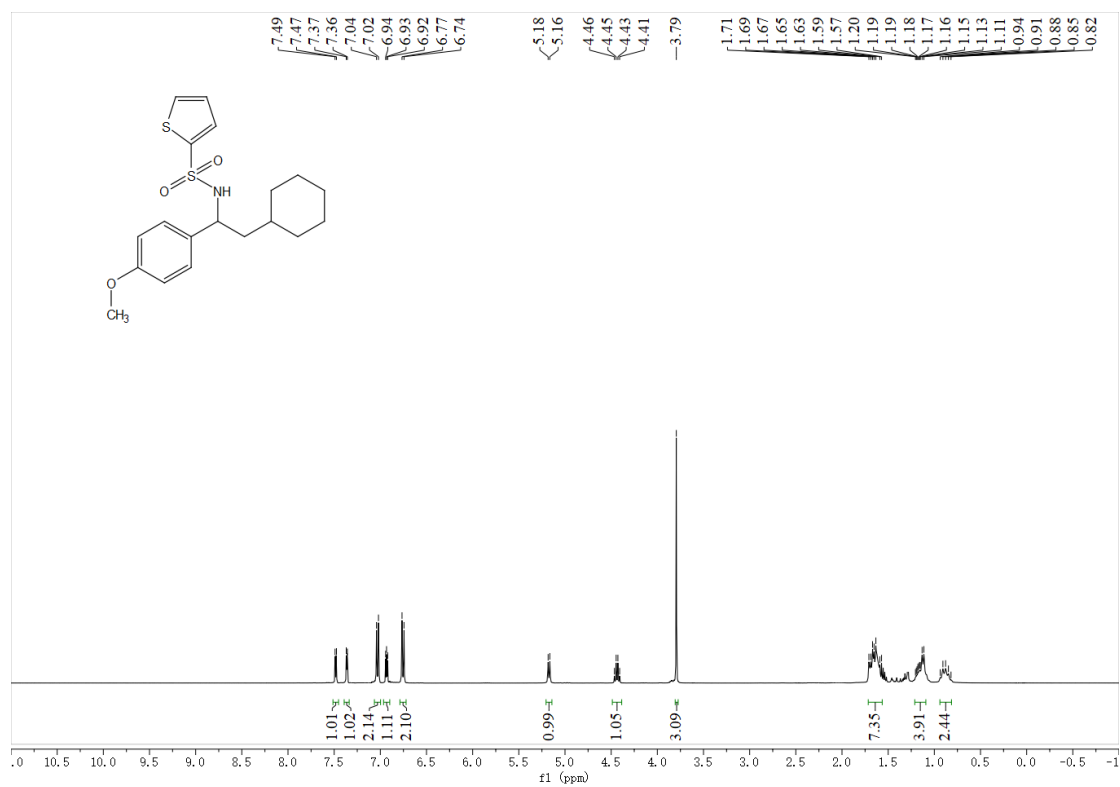
¹³C{¹H} NMR (101 MHz) Spectrum of **4asa** in CDCl₃



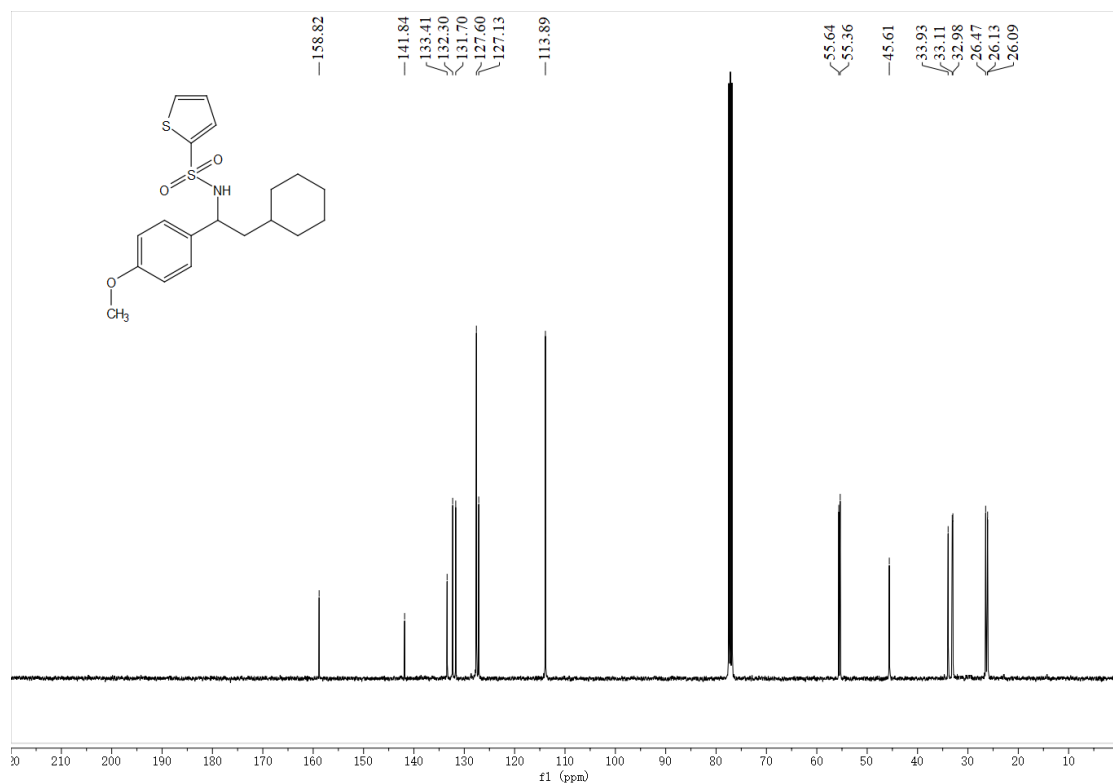
¹⁹F NMR (376 MHz) Spectrum of **4asa** in CDCl₃



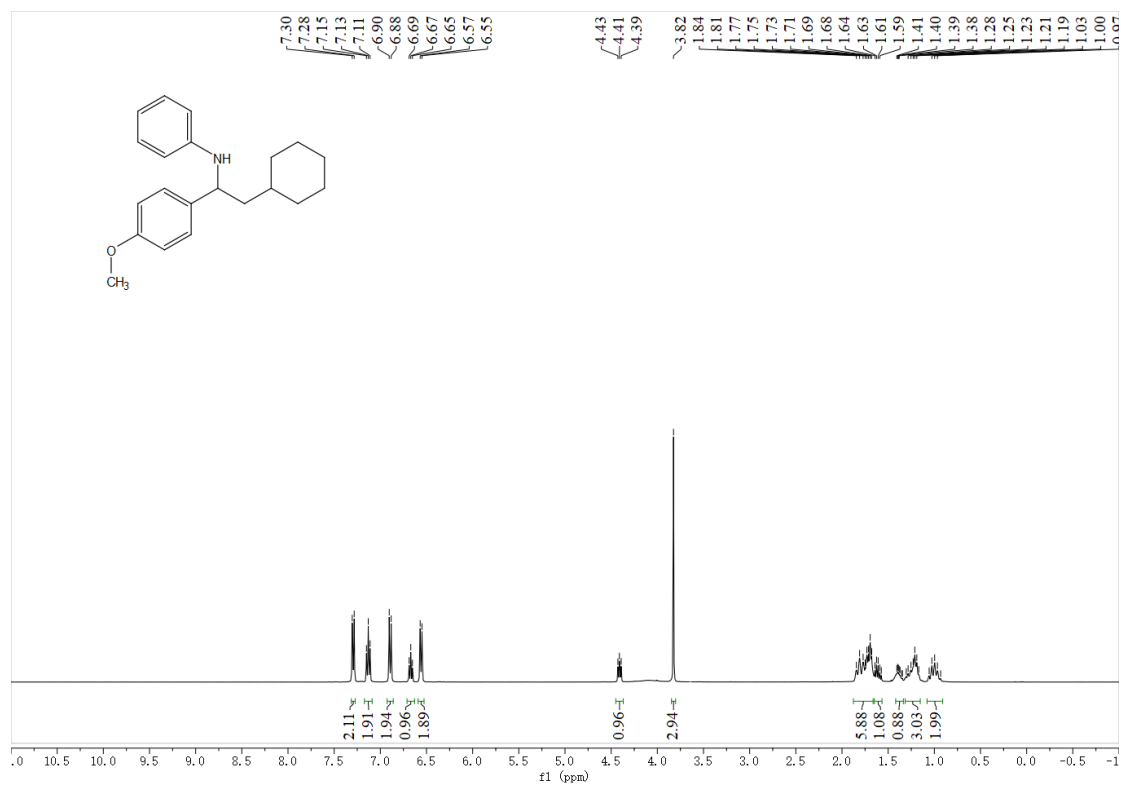
¹H NMR (400 MHz) Spectrum of **4ata** in CDCl₃



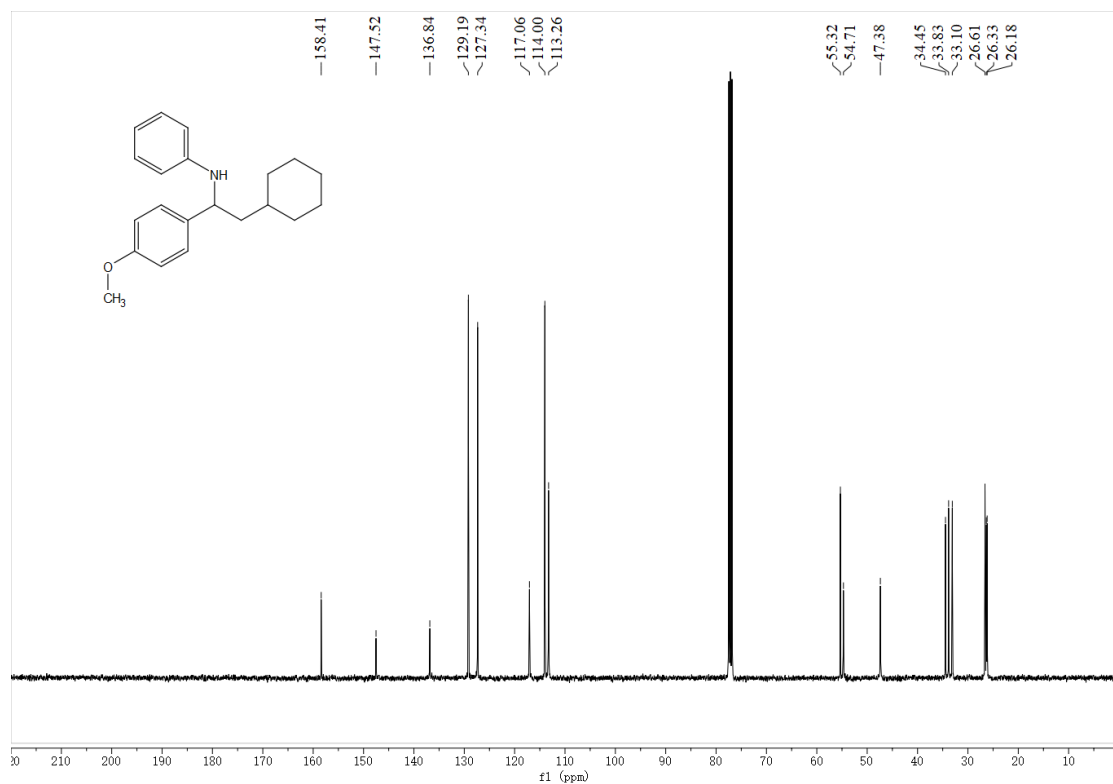
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4ata** in CDCl_3



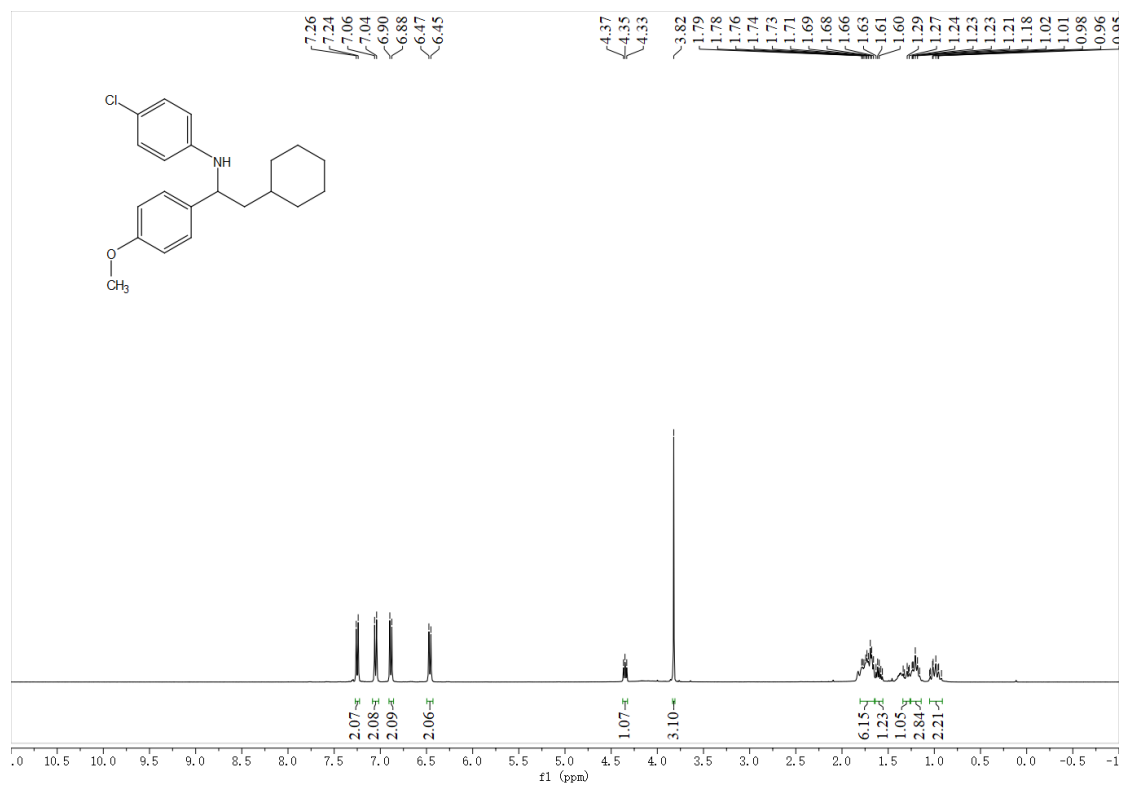
^1H NMR (400 MHz) Spectrum of **4aua** in CDCl_3



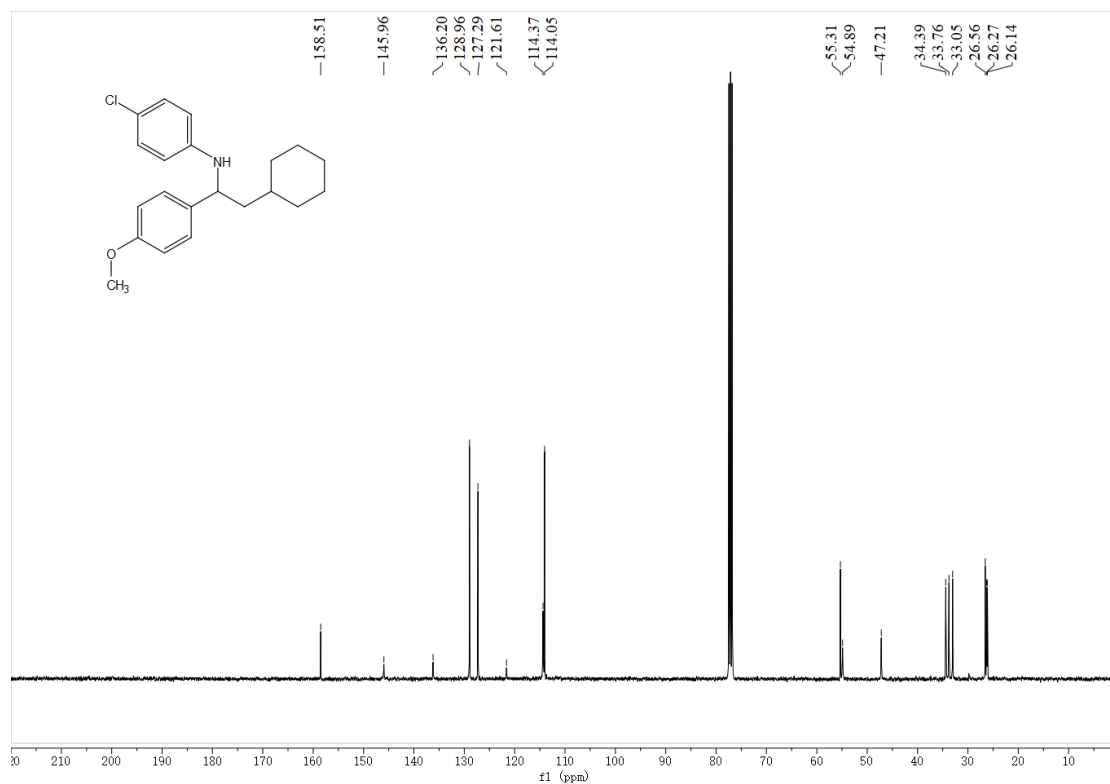
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4aua** in CDCl_3



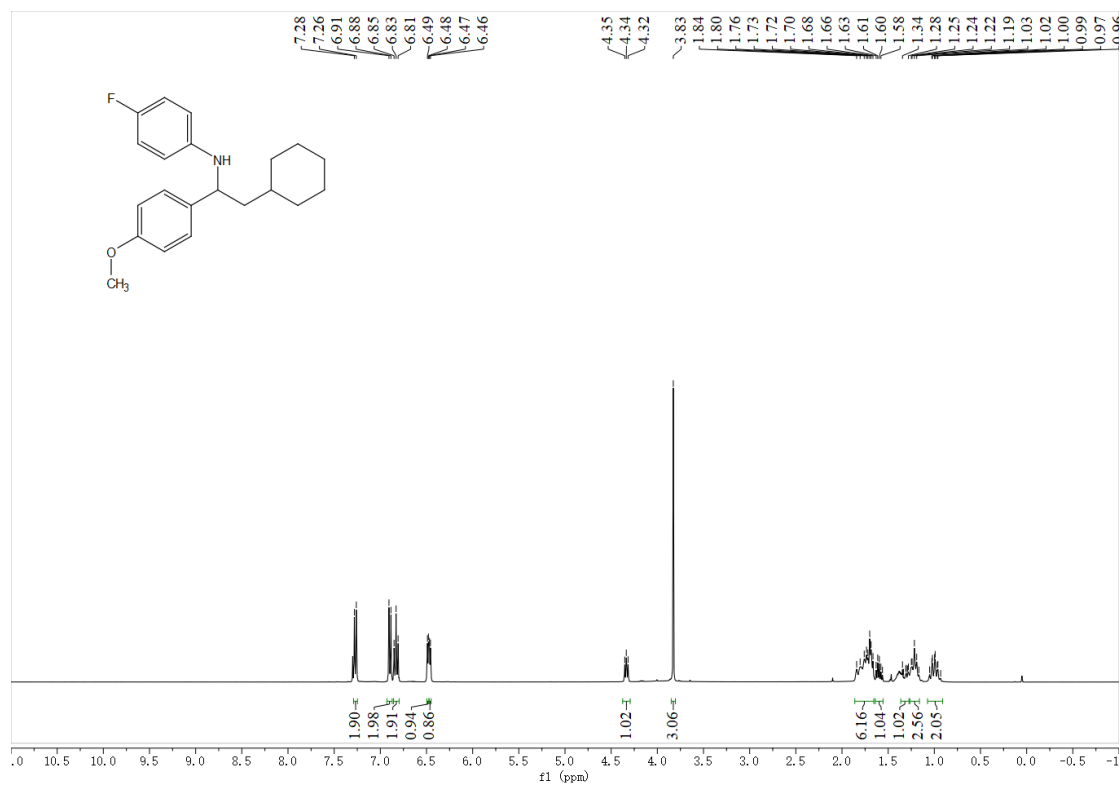
^1H NMR (400 MHz) Spectrum of **4ava** in CDCl_3



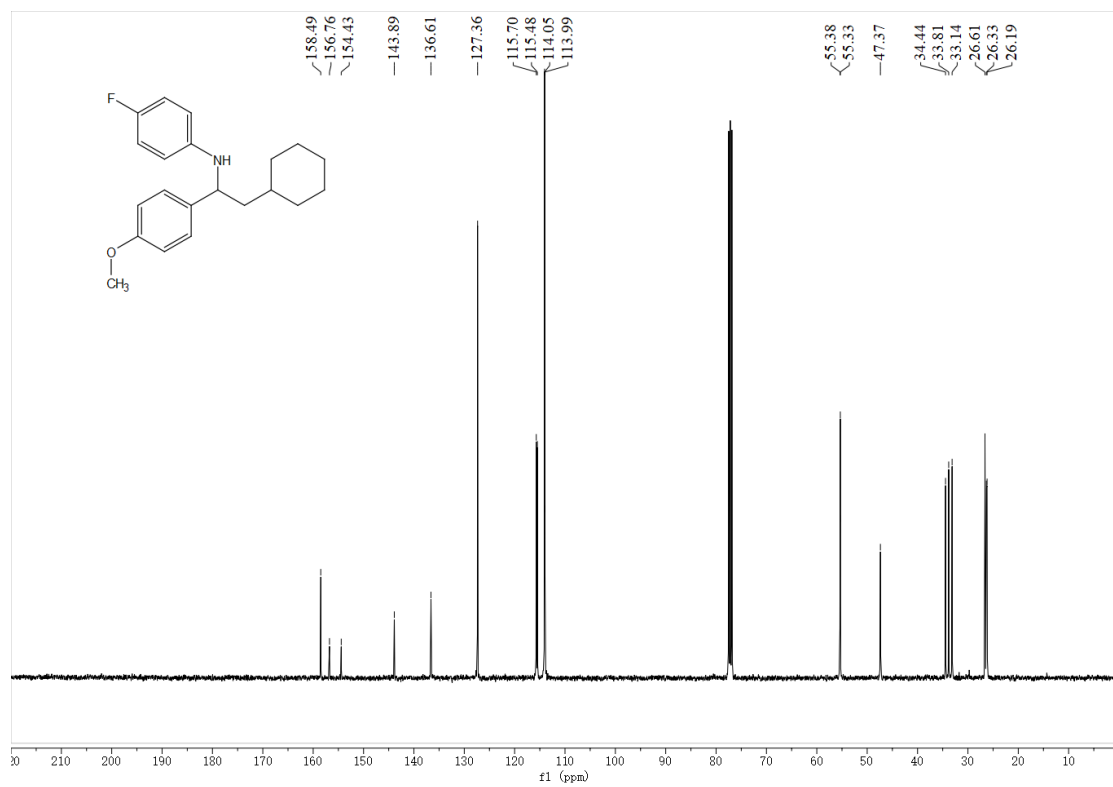
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4ava** in CDCl_3



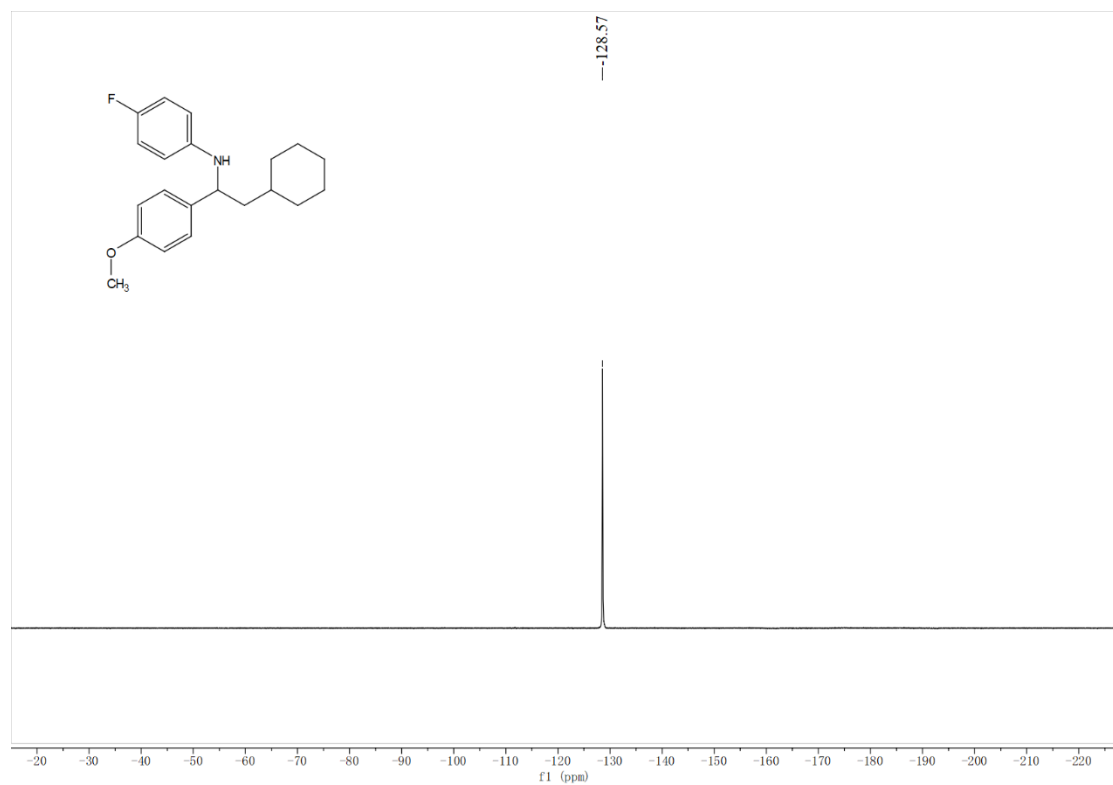
^1H NMR (400 MHz) Spectrum of **4av'a** in CDCl_3



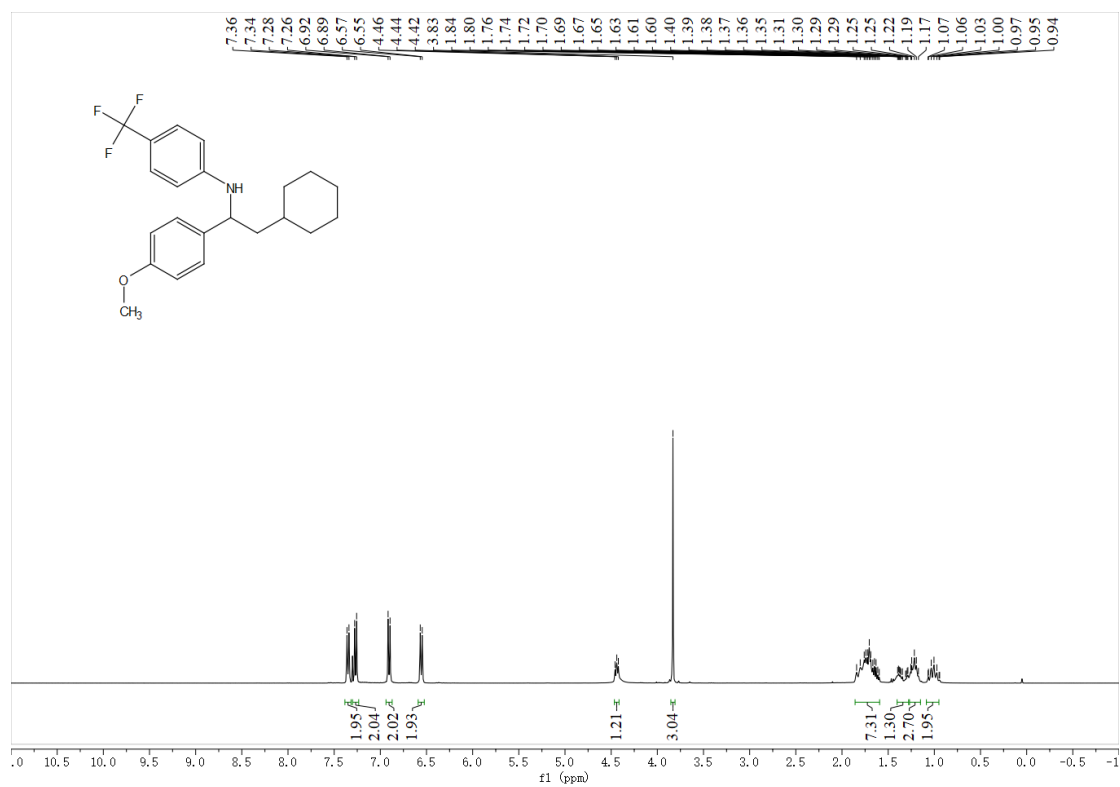
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4av'a** in CDCl_3



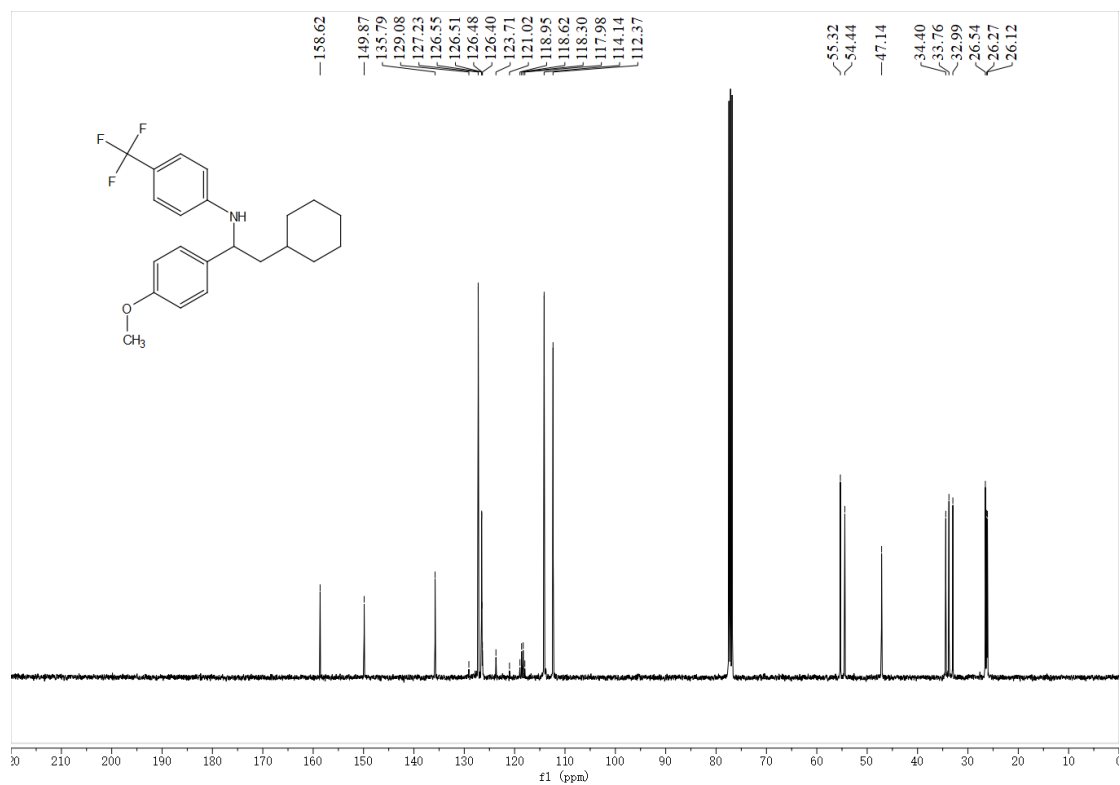
^{19}F NMR (376 MHz) Spectrum of **4av'a** in CDCl_3



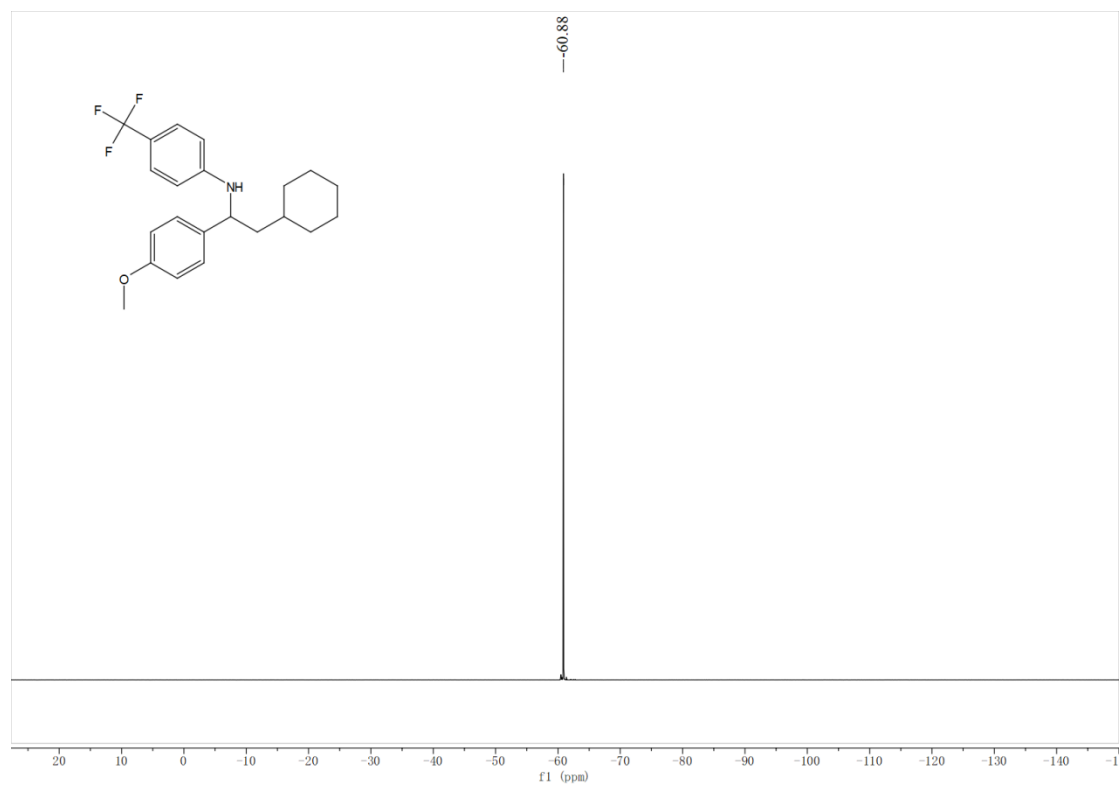
¹H NMR (400 MHz) Spectrum of **4av''a** in CDCl₃



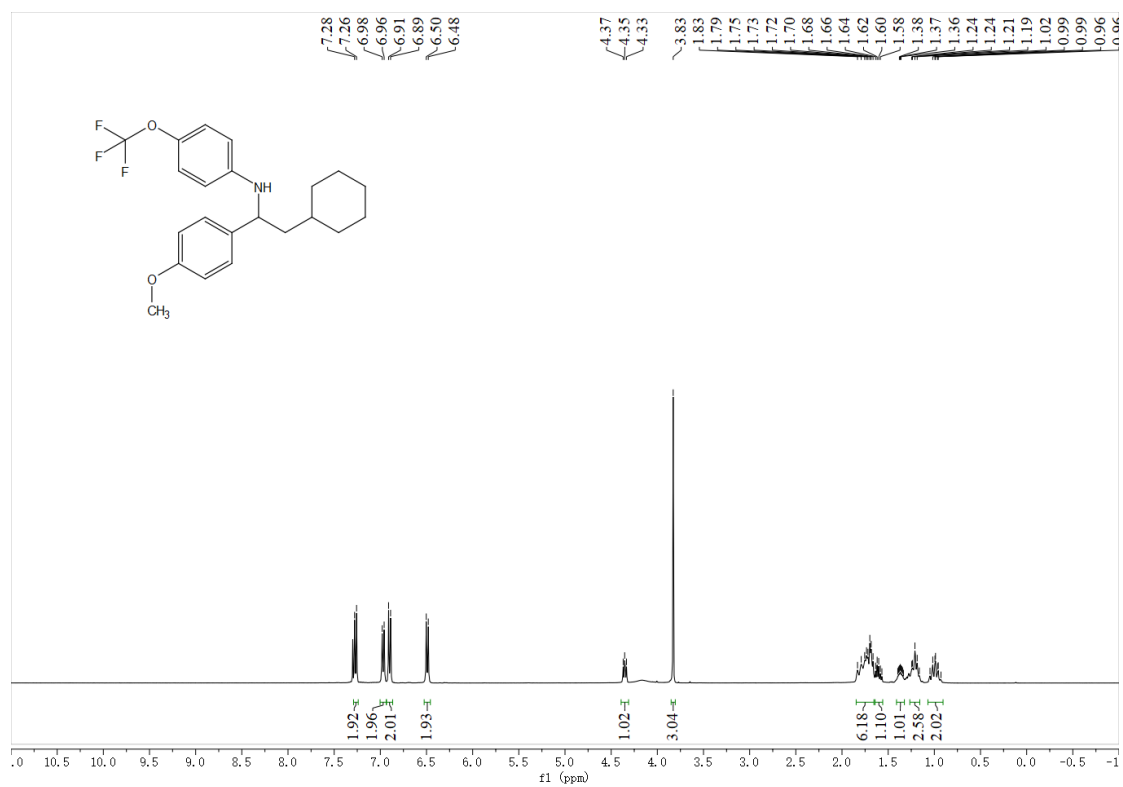
¹³C{¹H} NMR (101 MHz) Spectrum of **4av''a** in CDCl₃



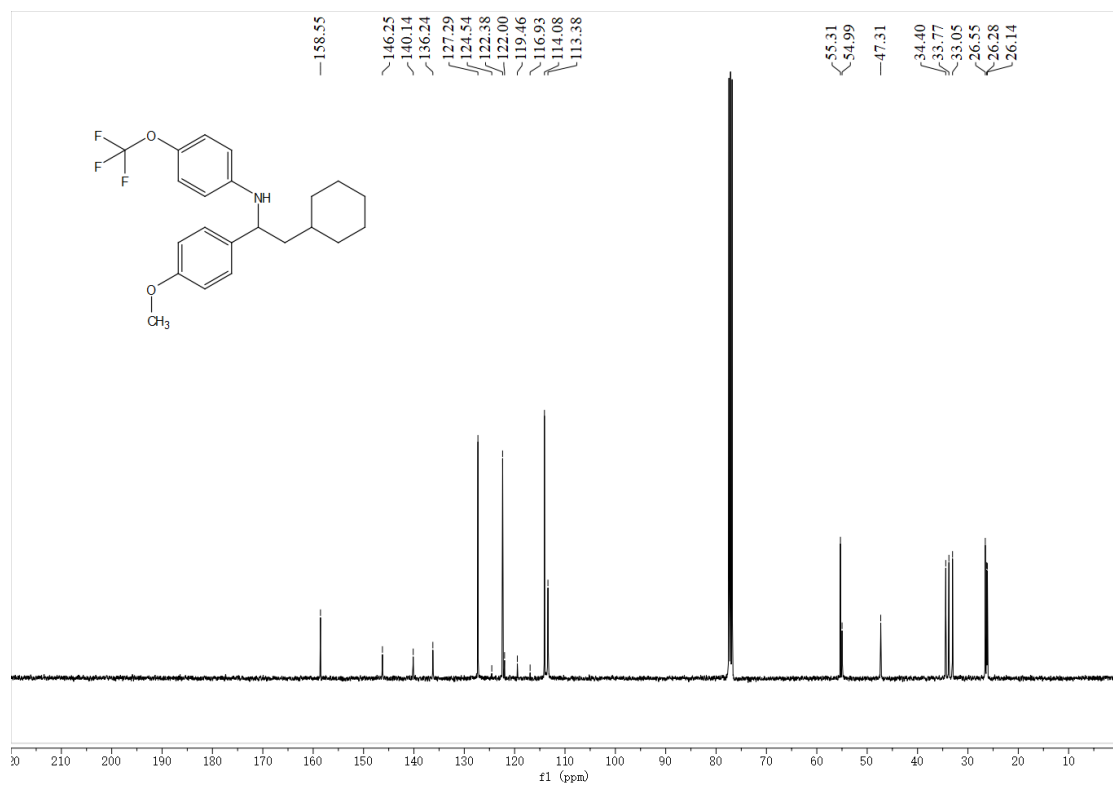
¹⁹F NMR (376 MHz) Spectrum of **4av''a** in CDCl₃



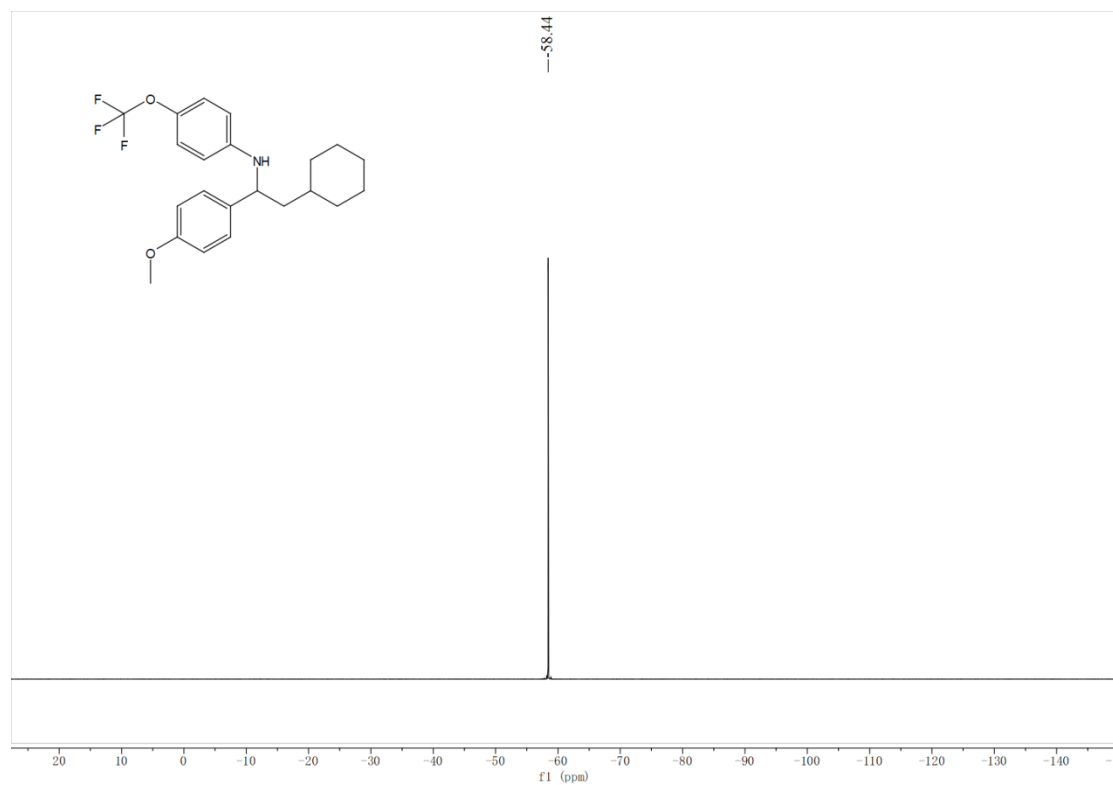
¹H NMR (400 MHz) Spectrum of **4av'''a** in CDCl₃



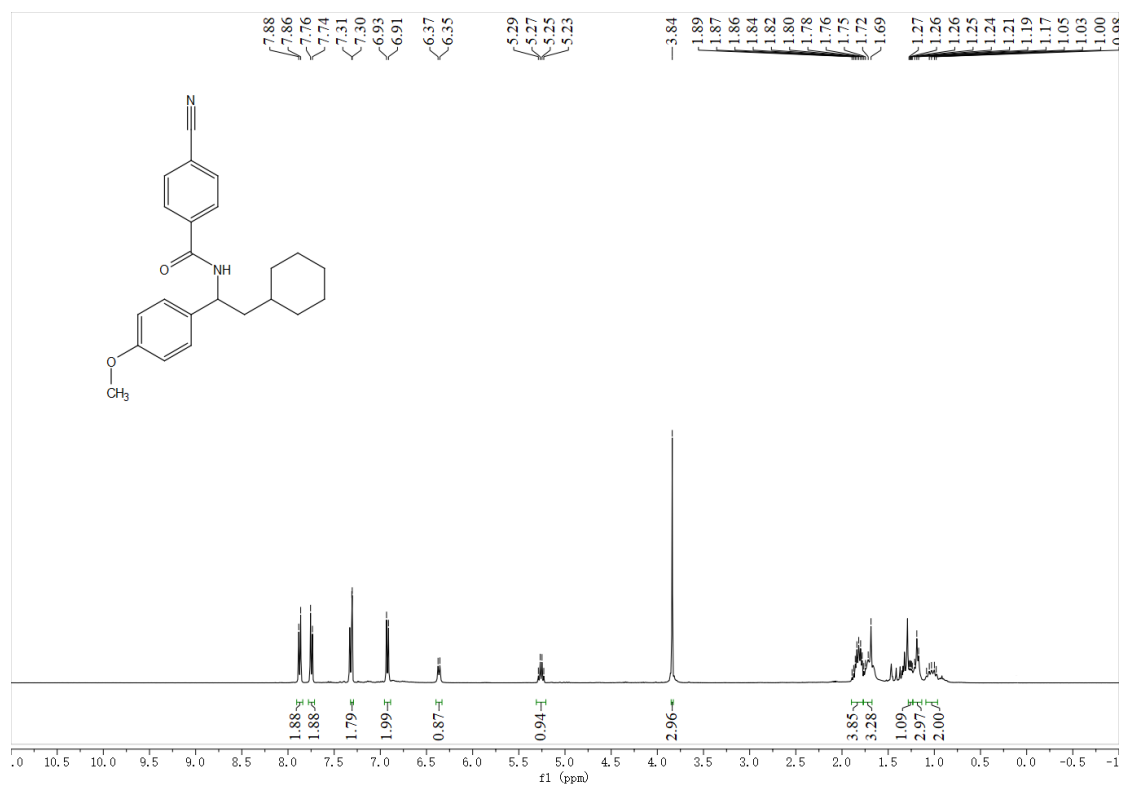
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4av'''a** in CDCl_3



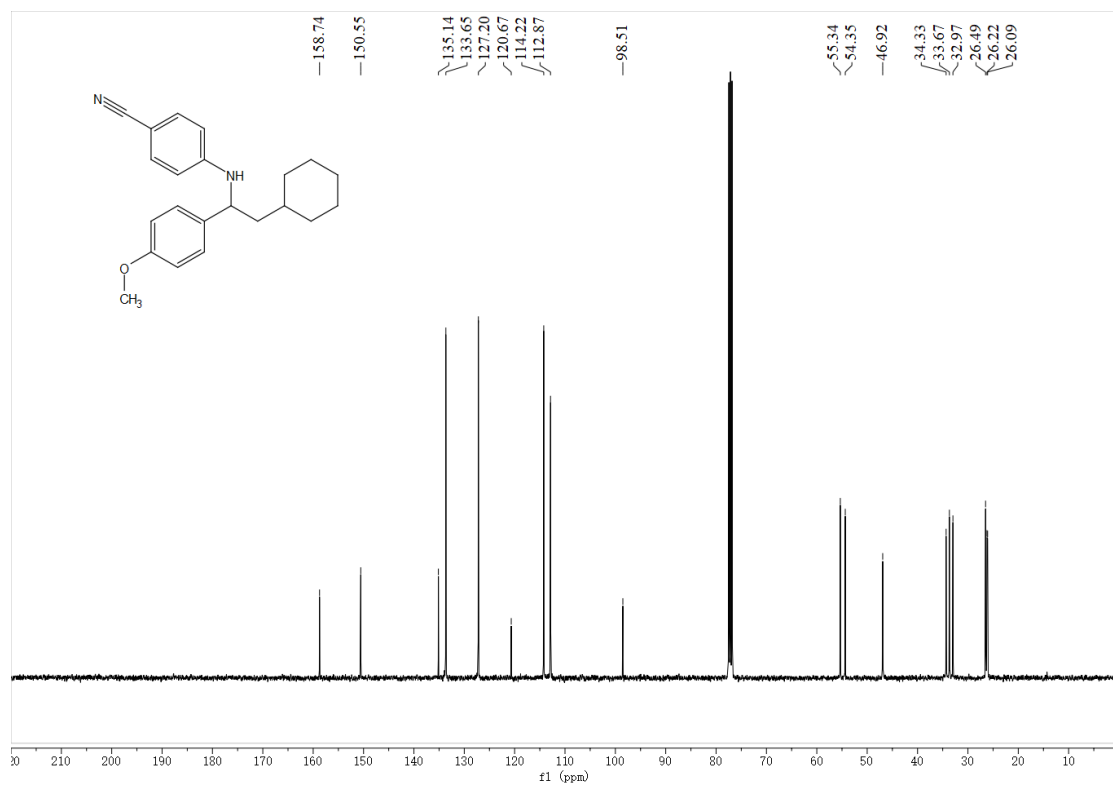
^{19}F NMR (376 MHz) Spectrum of **4av'''a** in CDCl_3



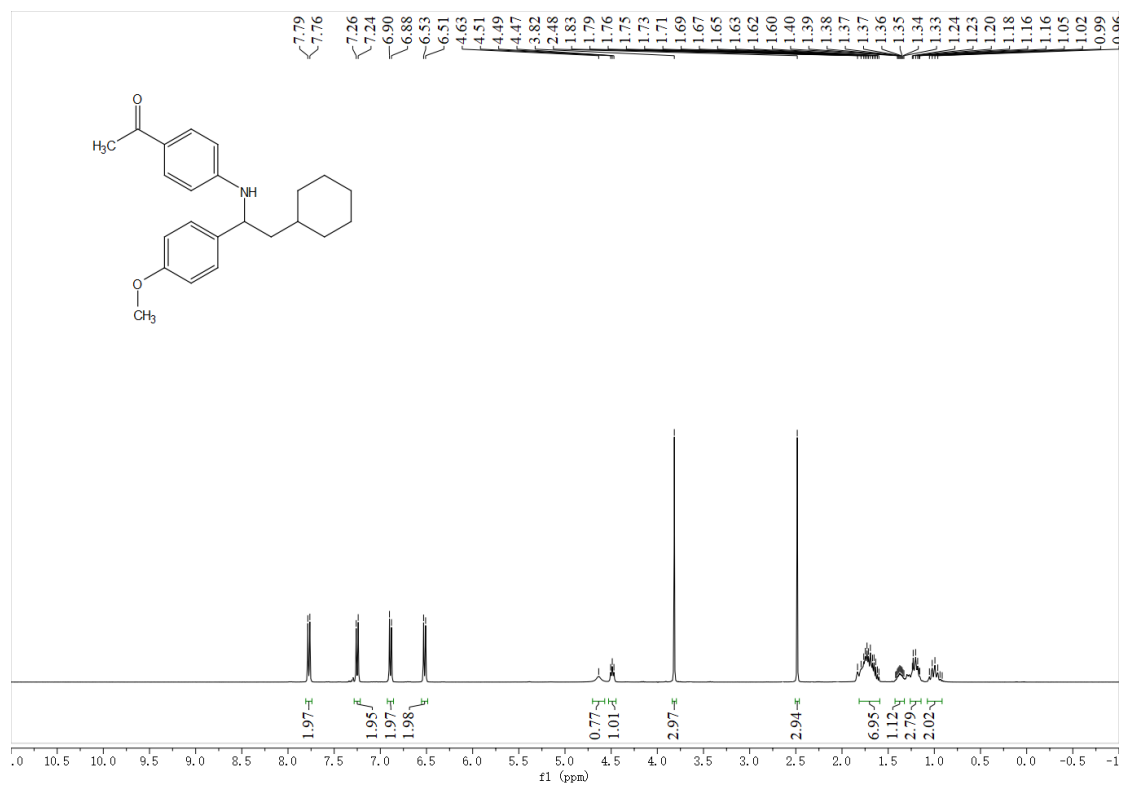
^1H NMR (400 MHz) Spectrum of **4awa** in CDCl_3



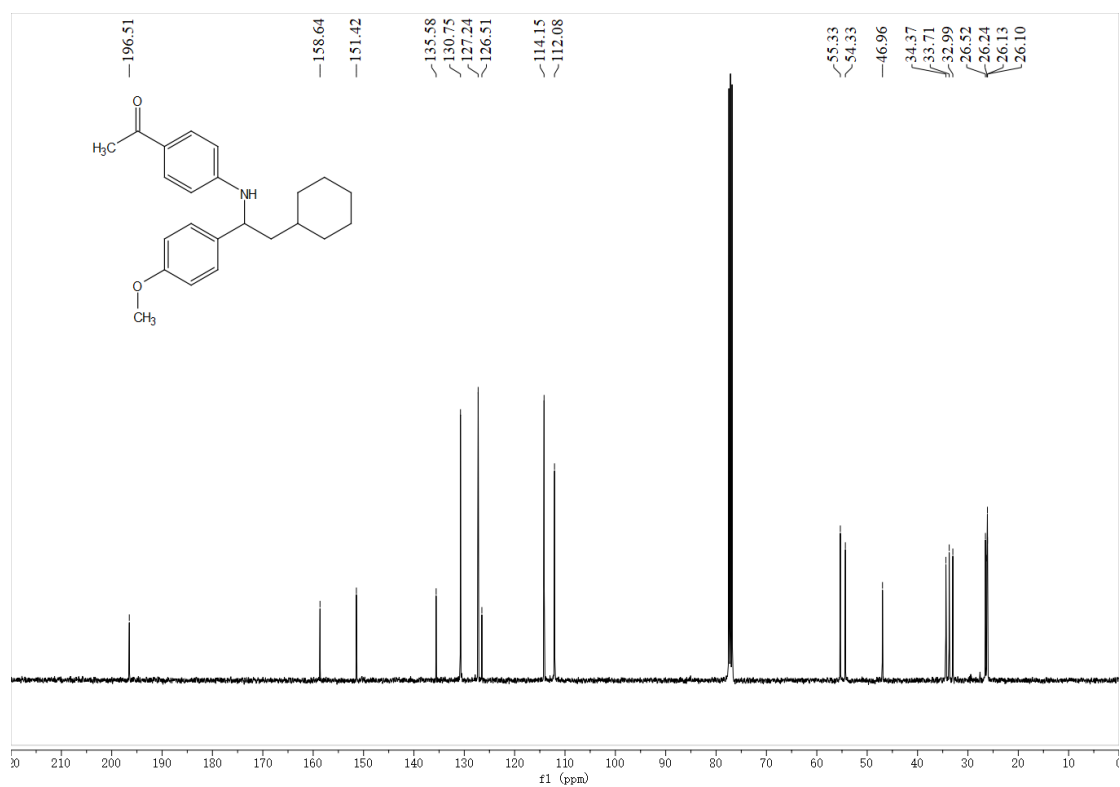
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4awa** in CDCl_3



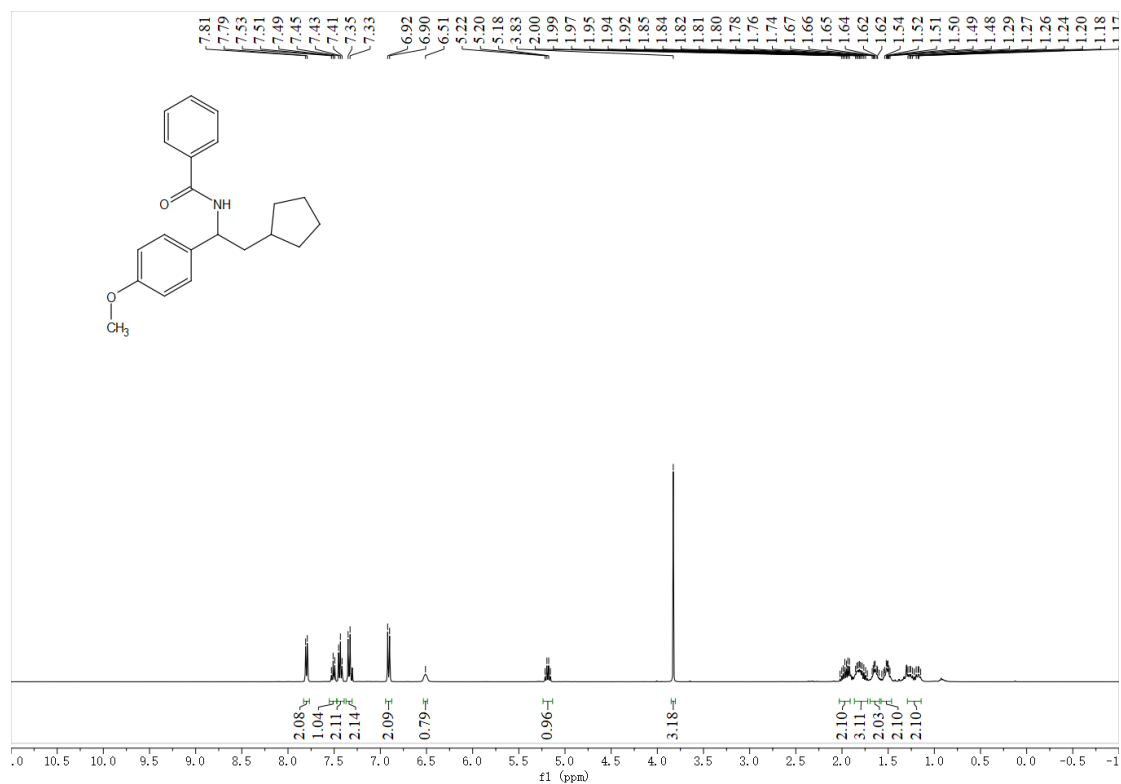
¹H NMR (400 MHz) Spectrum of **4axa** in CDCl₃



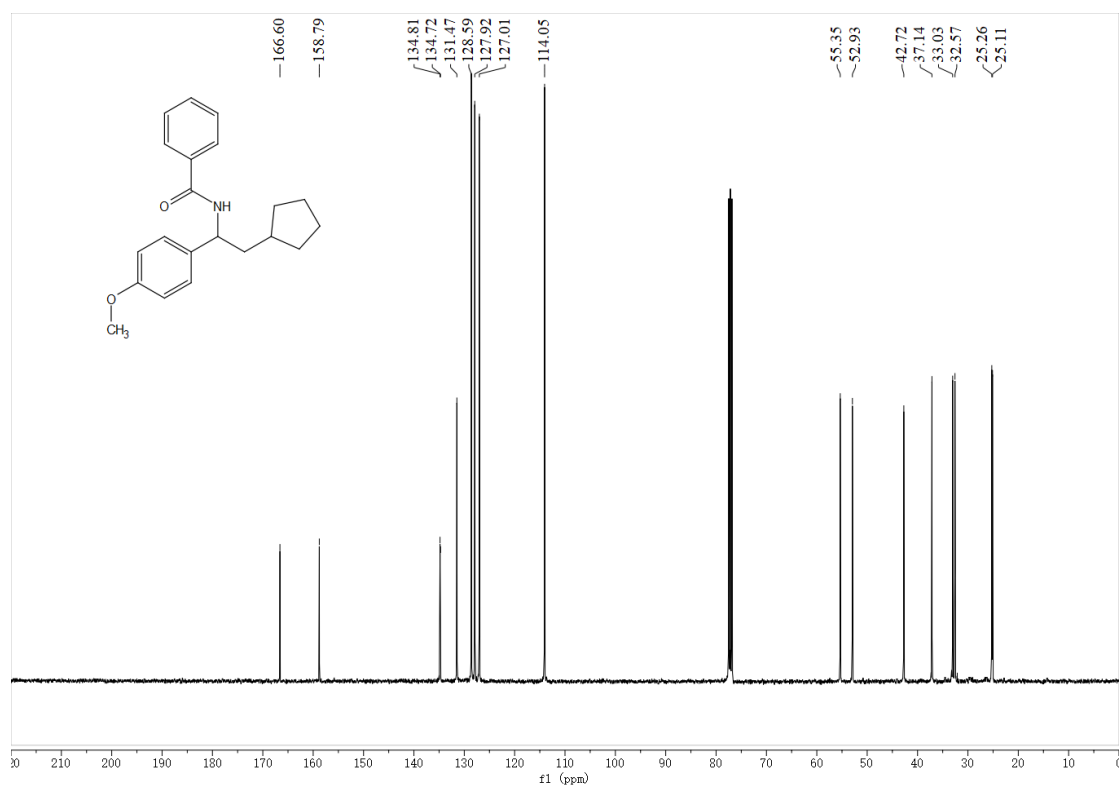
¹³C{¹H} NMR (101 MHz) Spectrum of **4axa** in CDCl₃



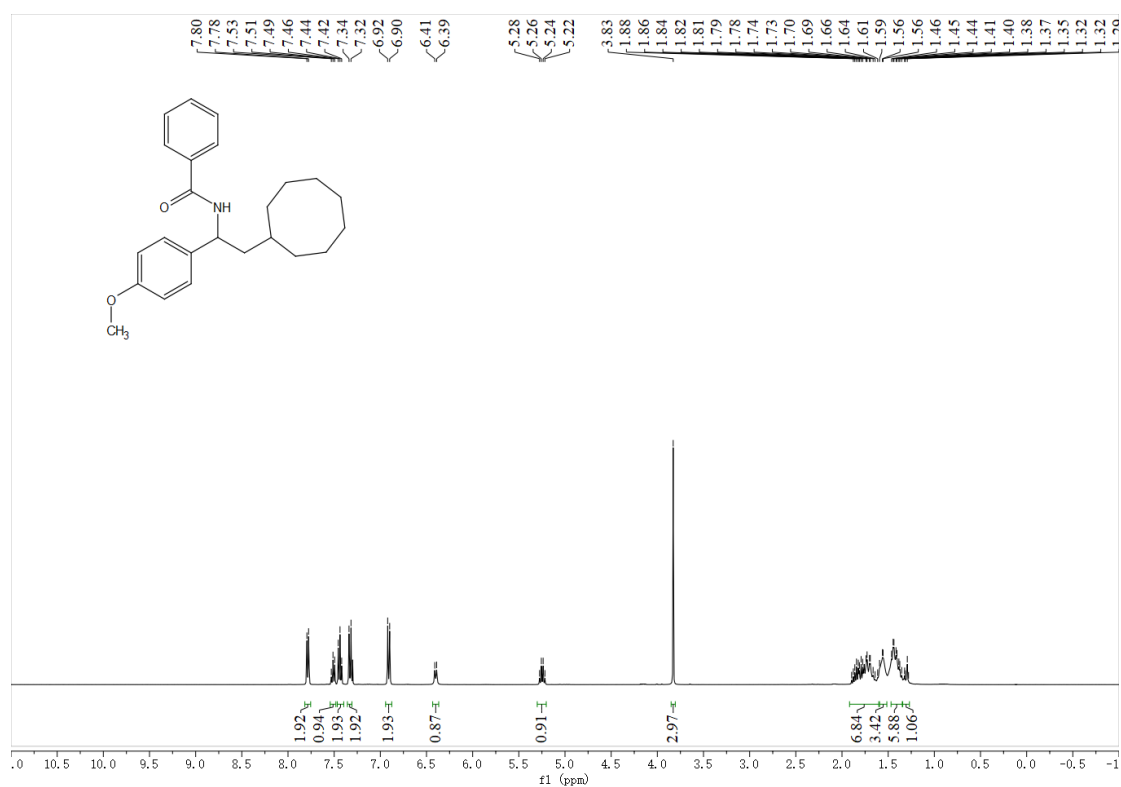
^1H NMR (400 MHz) Spectrum of **4aab** in CDCl_3



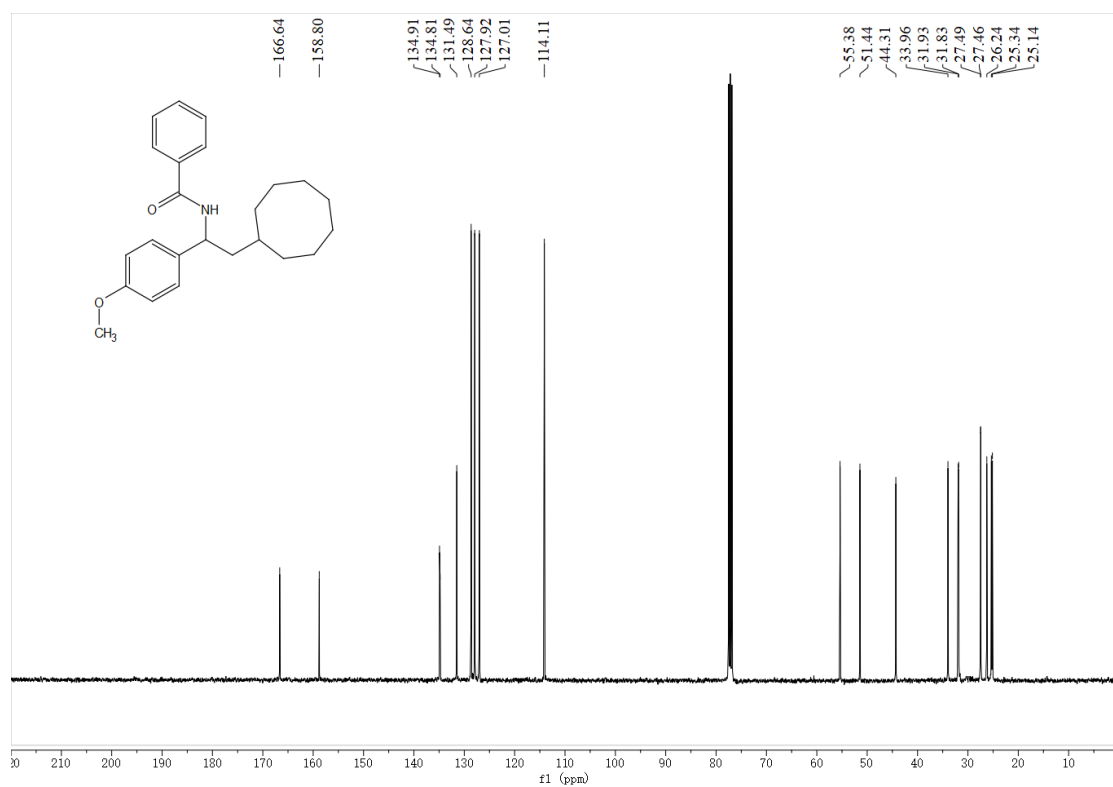
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4aab** in CDCl_3



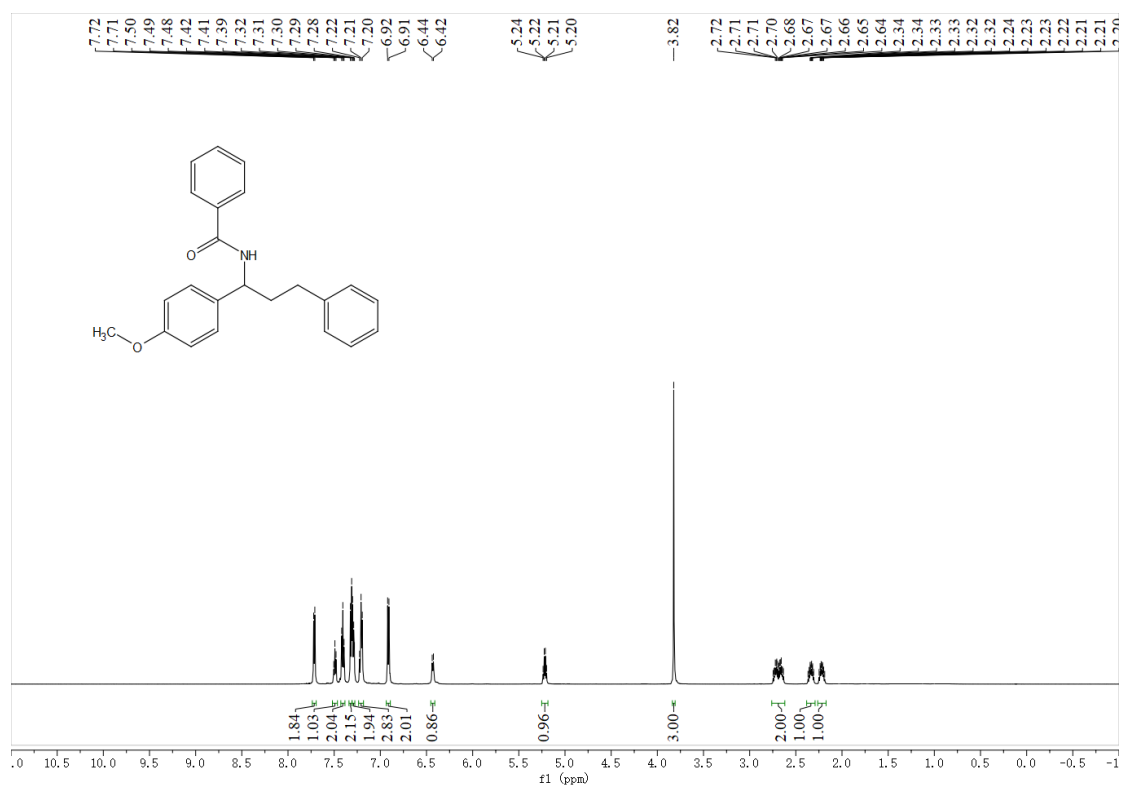
^1H NMR (400 MHz) Spectrum of **4aac** in CDCl_3



$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) Spectrum of **4aac** in CDCl_3



^1H NMR (600 MHz) Spectrum of **4aad** in CDCl_3



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz) Spectrum of **4aad** in CDCl_3

