Electronic Supplementary Information for

Coordination Assembly Enables Highly Selective Catalytic Hydroaminomethylation of Olefins

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1. General

All commercial reagents were used directly without further purification, unless otherwise stated. Dry *N*,*N*-dimethylformamide (DMF) was purchased from Alfa Aesar, stored over 4 Å molecular sieves, and handled under N_2 atmosphere. All reaction vials were purchased from Beijing Synthware Glass. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. The chemical shifts (δ) for ^1H NMR are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent ($CHCl_3$ at δ 7.26 ppm); coupling constants are expressed in hertz (Hz). ^{13}C NMR spectra were referenced to the carbon signal of $CDCl_3$ (77.0 ppm). The following abbreviations are used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = mulitplet, dd = doublet of doublets, q = quartet. ESI-MS spectra were recorded on a Bruker microTOF II instrument. IR spectra were recorded on AVATAR FT-IR 360 instrument. Powder XRD studies were performed on a Bruker AXS D8. SEM experiments were carried out on a Philips XL30 microscope operated at 20 kV. TEM experiments were carried out on a JEOL JEM-2010 transmission electron microscope. The AC-HAADF-STEM images was collected on a JEOL JEM-ARM200F operated at 300 kV, with a guaranteed resolution of 80 pm. The X-ray photoemission spectroscopy (XPS) was performed in a PHI 5000C ESCA system. BET experiments were performed on a Quantachrome AUTOSORB-IQ. TGA were performed on a TA SDT Q600. The X-ray absorption spectra including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the K-edge of Rh of the samples were collected at the BL 14W1 of Shanghai Synchrotron Radiation Facility (SSRF), China.

2. Synthesis of catalysts and substrates

2.1 Synthesis of NHC-Rh complexes

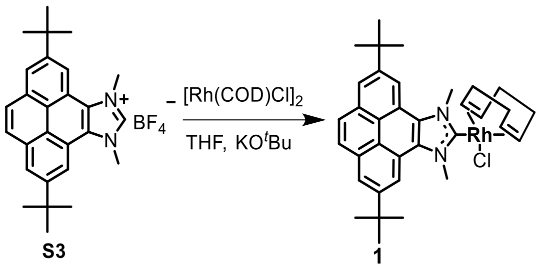


Fig. S1. Synthesis of mono-NHC-Rh complex **1**

Slat **S3** was synthesized according to the literature reports [1].

S3 (brown solid, 73 % yield).**^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.73 (s, 1H), 8.85 (d, J = 1.7 Hz, 2H), 8.56 (d, J = 1.6 Hz, 2H), 8.29 (s, 2H), 4.70 (s, 6H), 1.61 (s, 18H) ppm;

^{19}F NMR (376 MHz, DMSO-d_6) δ = -148.27 ppm.

Synthesis of mono-NHC-Rh complex **1:** A Schlenk tube was charged with salt **S3** (178.7 mg, 0.380 mmol), KO^{t}Bu (47.0 mg, 0.419 mmol), [Rh(COD)Cl]$_2$ (93.8 mg, 0.190 mmol), THF (3 mL) and stirred for 12 hours at ambient temperature under nitrogen atmosphere. After reaction completion, solvent was removed under vacuum, and the residue was purified over flash chromatography on silica gel (CH_2Cl_2/methanol = 800:1) to obtain yellow solid (212.4 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 1.8 Hz, 2H), 8.18 (d, J = 1.7 Hz, 2H), 8.04 (s, 2H), 5.25-5.20 (m, 2H), 5.12 (s, 6H), 3.50 (t, J = 4.3 Hz, 2H), 2.61-2.50 (m, 4H), 2.11-2.01 (m, 4H), 1.61 (s, 18H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4 (d, J = 51.4 Hz), 190.1, 148.7, 131.7, 129.3, 128.2, 122.0, 121.1, 120.8, 116.0, 99.4, 99.3, 68.7, 68.5, 40.2, 35.4, 33.0, 31.9, 29.0 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{35}H_{42}N_2Rh$ 593.2403; Found: 593.2422.

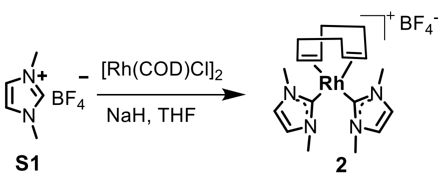


Fig. S2. Synthesis of bis-NHC-Rh complexes **2**

Synthesis of bis-NHC-Rh complex **2:** A Schlenk tube was charged with salt **S1** (184 mg, 1 mmol), [Rh(COD)Cl]$_2$ (123 mg, 0.25 mmol), NaH (60%, 52 mg ,1.3 mmol), dry THF (10 mL) and stirred for 12 hours at ambient temperature under nitrogen atmosphere. After reaction completion, solvent was removed under vacuum, and the residue was purified over flash chromatography on silica gel using CH_2Cl_2/methanol (100:1) mixture as eluent to obtain yellow solid (55 mg, 45% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.26 (s, 4H), 4.18 (s, 4H), 3.94 (s, 12H), 2.41 (d, J = 10.1 Hz, 4H), 2.10 (q, J = 7.6

Hz, 4H) ppm;

^{13}C NMR (101 MHz, DMSO-d_6) δ 180.2 (d, J = 53.9 Hz), 123.6, 88.4, 88.3, 38.3, 30.8 ppm;

^{19}F NMR (376 MHz, DMSO-d_6) δ = -148.26 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{18}H_{28}N_4Rh$ 403.1369; Found: 403.1367.

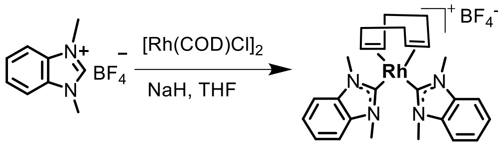


Fig. S3. Synthesis of bis-NHC-Rh complex **3**

Synthesis of bis-NHC-Rh complex **3:** A Schlenk tube using salt **S2** (234 mg, 1 mmol), $[Rh(COD)Cl]_2$ (123 mg, 0.25 mmol), NaH (60%, 52 mg ,1.3 mmol), dry THF (10 mL) and stirred for 12 hours at ambient temperature under nitrogen atmosphere. After reaction completion, solvent was removed under vacuum, and the residue was purified over flash chromatography on silica gel using CH_2Cl_2/methanol (80:1) mixture as eluent to obtain yellow solid (102 mg, 69% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 (dd, J = 6.0, 3.1 Hz, 4H), 7.28 (dd, J = 6.1, 3.1 Hz, 4H), 4.48 (s, 4H), 4.29 (s, 12H), 2.62-2.54 (m, 4H), 2.26 (d, J = 8.6 Hz, 4H) ppm;

^{13}C NMR (101 MHz, DMSO-d_6) δ 193.6 (d, J = 53.9 Hz), 135.3, 123.0, 110.7, 91.0, 55.4, 36.0, 30.8 ppm;

^{19}F NMR (376 MHz, DMSO-d_6) δ = -148.32 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{26}H_{32}N_4Rh$ 503.1682; Found: 503.1677.

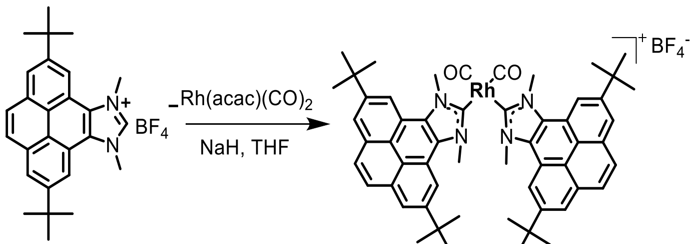


Fig. S4. Synthesis of bis-NHC-Rh complex **4a.**

Synthesis of bis-NHC-Rh complex **4a：** A Schlenk tube using salt **S3** (470 mg, 1 mmol), $[Rh(acac)(CO)_2]$ (65 mg, 0.25 mmol), NaH (60%, 52 mg, 1.3 mmol), dry THF (10 mL) and stirred for 12 hours at ambient temperature under nitrogen atmosphere. After reaction completion, solvent was removed under vacuum, and the residue was purified over flash chromatography on silica gel using CH_2Cl_2/methanol (80:1) mixture as eluent to obtain yellow solid (159 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 4H), 8.22 (s, 4H), 8.03 (s, 4H), 4.96 (s, 12H), 1.58 (s, 36H) ppm;

^{13}C NMR (101 MHz, DMSO-d_6) δ 180.3 (d, J = 15.2 Hz), 171.9, 149.3, 131.7, 129.7, 128.7, 123.6, 120.9, 120.7, 117.4, 41.3, 35.7, 32.0 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ = -152.33 ppm;

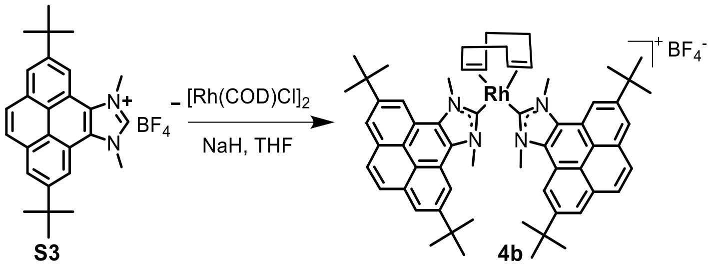


Fig. S5. Synthesis of bis-NHC-Rh complex **4b.**

Synthesis of bis-NHC-Rh complex **4b**： A Schlenk tube using salt **S3** (470 mg, 1 mmol), $[Rh(COD)Cl]_2$ (123 mg, 0.25 mmol), NaH (60%, 52 mg, 1.3 mmol), dry THF (10 mL) and stirred for 12 hours at ambient temperature under nitrogen atmosphere. After reaction completion, solvent was removed under vacuum, and the residue was purified over flash chromatography on silica gel using CH_2Cl_2/methanol (80:1) mixture as eluent to obtain yellow solid (185 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 1.7 Hz, 4H), 8.17 (d, J = 1.6 Hz, 4H), 7.99 (s, 4H), 5.25 (s, 12H), 4.60 (s, 4H), 2.79 (d, J = 10.4 Hz, 4H), 2.30 (d, J = 8.9 Hz, 4H), 1.62 (s, 36H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0 (d, J = 55.1 Hz), 149.2, 131.6, 129.6, 128.1, 122.6, 120.9, 120.7, 116.3, 91.1, 91.0, 41.7, 35.4, 31.8, 30.8 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ = -153.21 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{62}H_{72}N_4Rh$ 975.4812; Found: 975.4841.

2.2 General synthetic procedure of NHC-Rh coordination assemblies

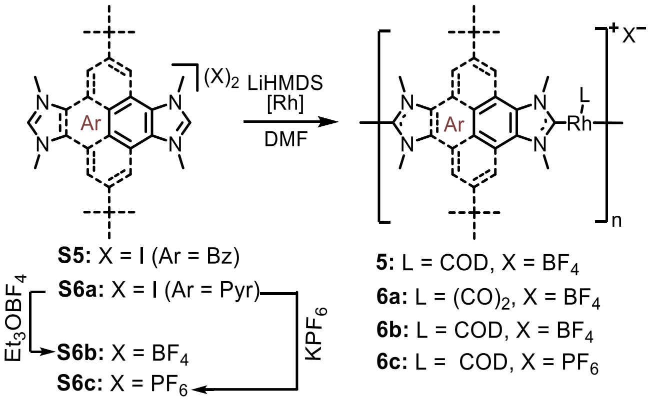


Fig. S6. General synthetic procedure of NHC-Rh coordination assemblies.

Bis-imidazolium salts **S5, S6a** were synthesized according to the literature reports [2].

S5 (brown solid, 84 % yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.89 (s, 2H), 8.80 (s, 2H), 4.18 (s, 12H) ppm.

S6a (brown solid, 63 % yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.83 (s, 2H), 9.03 (s, 4H), 4.74 (s, 12H), 1.67 (s, 18H) ppm.

S6b: A Schlenk tube was charged with **S6a** (184 mg, 0.26 mmol), triethyloxonium tetrafluoroborate (117 mg, 1.04 mmol), dry CH_2Cl_2 (5 mL), and stirred at ambient temperature for 12 hours, methanol (3 mL) was then added. The resulting reaction mixture was stirred for an additional hour and then poured into excess diethyl ether (50 mL). After precipitation completed, the solids were collected via filtration and dried under reduced pressure to afford the desired salts as a white powder in 94% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.88 (s, 2H), 9.04 (s, 4H), 4.77 (s, 12H), 1.69 (s, 18H) ppm;

^{13}C NMR (101 MHz, DMSO-d_6) δ = 150.8, 143.6, 127.5, 121.4, 120.4, 118.9, 54.8, 36.1, 31.6 ppm;

^{19}F NMR (376 MHz, DMSO-d_6) δ = -148.29 ppm.

Salt **S6c**: To a solution of salt **S6a** (184 mg, 0.26 mmol) in 5 mL H_2O was added KPF_6 (191 mg, 1.04 mmol) and reaction mixture was stirred for 3 hours at ambient temperature. After precipitation completed, the solids were collected via filtration and dried under reduced pressure to afford the desired salts as a white powder, 86% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.88 (s, 2H), 9.04 (s, 4H), 4.77 (s, 12H), 1.69 (s, 18H) ppm;

^{19}F NMR (376 MHz, DMSO-d_6) δ = -69.21, -71.11 ppm.

NHC-Rh coordination assemblies **5 and 6a-6c**: bis-imidazolium salts **S5** or **S6a-6c** (0.5 mmol) and corresponding rhodium precursor ([Rh(acac)(CO)$_2$] (0.5 mmol) or [Rh(COD)Cl]$_2$ (0.25 mmol) were dissolved in DMF (5 mL) under N_2 at room temperature, LiHMDS (1 mmol) solution in THF was added dropwise. The resulting mixture was stirred at 80 ^{o}C for 24 h. After cooling to room temperature, the precipitate was washed by DMF, deionized water and methanol successively. Further purification of the solid was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 60 ^{o}C to give dark-brown solid.

NHC-Rh coordination assembly **5**: dark-brown solid, 99% yield;

IR (KBr pellet) ν 446.75, 662.39, 745.33, 828.32, 867.96, 1104.61, 1256.68, 1384.47, 1463.08, 1589.98, 1655.98, 1947.24, 2929.90, 3396.47 cm^{-1};

Elemental analysis (%) Calcd. for $(C_{20}H_{26}BF_4N_4Rh)_n$: C, 46.90; H, 5.12; N, 10.94; found: C, 46.75; H, 5.31; N, 10.81.

NHC-Rh coordination assembly **6a**: dark-brown solid, 92% yield;

IR (KBr pellet) ν 440.98, 660.64, 726.70, 747.54, 812.93, 844.41, 862.07, 923.34, 1092.44, 1246.78, 1371.43, 1472.66, 1613.14, 1663.55, 1965.51, 2121.69, 2954.90, 3416.58 cm^{-1};

Elemental analysis (%) Calcd. for $(C_{32}H_{35}RhN_4O_2{\cdot}BF_4{}^{\cdot})_n$: C, 55.09; H, 5.02; N,8.03; *found:* C, 54.97; H, 5.62; N, 8.21.

NHC-Rh coordination assembly **6b**: dark-brown solid, 97% yield;

IR (KBr pellet) *ν* 436.72, 727.09, 744.28, 816.01, 861.10, 923.91, 948.90, 1058.91, 1247.16, 1372.27, 1471.17, 1612.26, 1659.73, 1950.07, 2953.16, 3405.68 cm^{-1};

Solid ^{13}C NMR (101 MHz) δ = 187.3, 168.7, 149.5, 129.7, 121.4, 62.4, 55.3, 40.4, 36.0, 31.7 ppm;

Elemental analysis (%) *Calcd. for* $(C_{38}H_{47}RhN_4BF_4\cdot)_n$: C, 60.88; H, 7.28; N, 7.48; *found:* C, 60.72; H,7.83; N, 7.23.

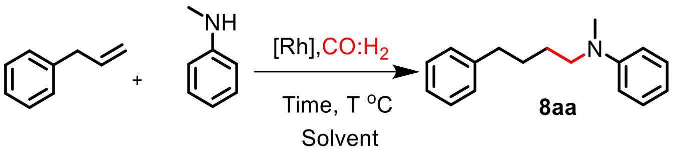
NHC-Rh coordination assembly **6c**: dark-brown solid, 93% yield;

IR (KBr pellet) *v* 446.63, 726.43, 747.38, 817.65, 862.32, 924.07, 1087.50, 1246.70, 1372.80, 1470.27, 1612.15, 1663.47, 1950.29, 2953.95, 3417.64 cm^{-1};

Elemental analysis (%) *Calcd. for* $(C_{38}H_{47}RhN_4PF_6)_n$: C, 56.51; H, 5.82; N, 6.94; *found:* C, 56.23; H, 5.96; N, 6.76.

3. Optimization of reaction conditions

Table S1. Optimization for hydroaminomethylation of allylbenzene [a]



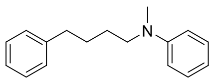
Entry	[Cat.] (mol %)	CO/H₂ (bar)	Solvent (4 mL)	Temp (°C)	Time (h)	Yield[b] (%)	l/b[c]
1	**5** (1.0)	60bar (1:5)	THF	100	12	51	64/36
2	**5** (1.0)	60bar (1:5)	THF	120	1	48	58/42
3	**5** (1.0)	60bar (1:5)	THF	130	12	47	54/46
4	**5** (1.0)	60bar (1:5)	THF	140	12	50	55/45
5	**5** (1.0)	60bar (1:5)	Tol	140	12	20	88/12
6	**5** (1.0)	60bar (1:5)	anisole	140	12	58	65/35
7	**5** (1.0)	60bar (1:5)	dioxane	140	12	42	85/15
8	**5** (1.0)	60bar (1:5)	MeOH	140	12	36	89/11
9	**5** (1.0)	60bar (1:5)	THF/MeOH	140	12	40	73/27
10	**5** (1.0)	60bar (1:5)	Tol/MeOH	140	12	54	63/37
11	**5** (1.0)	60bar (1:5)	THF	140	18	53	55/45
12	**5** (1.0)	60bar (1:5)	THF	140	24	52	55/45
13	**5** (1.0)	70bar (1:5)	THF	140	18	59	66/34
14	**5** (1.0)	80bar (1:5)	THF	140	18	70	77/23
15	**5** (1.0)	80bar (1:6)	THF	140	18	72	85/15
16	**5** (1.0)	80bar (1:7)	THF	140	18	72	89/11
17	**5** (1.0)	80bar (1:8)	THF	140	18	66	91/9
18	**5** (1.0)	80bar (1:9)	THF	140	18	72	91/9
19	**5 (1.0)**	80bar (1:12)	THF	140	18	67	97/3
20	**5** (1.0)	80bar (1:9)	THF	150	18	77	88/12
21	**6a** (1.0)	80bar (1:9)	THF	150	18	89	97/3
22	**6b (1.0)**	**80bar (1:9)**	**THF**	**150**	**18**	**95**	**97/3**
23	**6b (1.0)**	**80bar (1:9)**	**THF**	**150**	**18**	**96**	**98/2**
24	**6b (1.0)**	**80bar (1:9)**	**THF**	**150**	**18**	**95**	**97/3**
25	**6c (1.0)**	80bar (1:9)	THF	150	18	86	93/7
26	**1 (1.0)**	80bar (1:9)	THF	150	18	50	67/33
27	**2** (1.0)	80bar (1:9)	THF	150	18	20	58/42
28	**3** (1.0)	80bar (1:9)	THF	150	18	50	63/37
29	**4b** (1.0)	80bar (1:9)	THF	150	18	71	84/16
30	**6b** (0.5)	80bar (1:9)	THF	150	18	65	86/14
31	**6b** (0.3)	80bar (1:9)	THF	150	18	52	83/17
32	/	80bar (1:9)	THF	150	18	NR	N/A
33	**6b** (1.0)	70bar (1:9)	THF	150	18	88	92/8
34	**6b** (1.0)	80bar (1:9)	THF	140	18	89	95/5
35	**6b** (1.0)	60bar (1:9)	THF	150	18	76	91/9

36	**6b** (1.0)	80bar (1:9)	THF	130	18	79	95/5

[a] 1.25 mmol of allylbenzene, 0.5 mmol *N*-methylaniline. [b]Isolated yields. [c] Regioselectivities were determined by ^{1}H NMR of the crude reaction mixture.

4. General procedure for the hydroaminomethylation of olefins

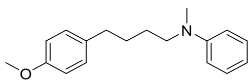
The hydroaminomethylation reactions were carried out in a Parr stainless steel autoclave (125 mL). In a typical experiment, the autoclave was loaded with a mixture of **6b** (1.0 mol %), 1.25 mmol olefins, 0.5 mmol amines and 4.0 mL THF. Subsequently, the autoclave was pressurized with CO (8 bar) and hydrogen (72 bar) and heated to 150 ºC. After 18 h, the autoclave was allowed to cool to room temperature and the gases were vented. The solvent was removed under vacuum, regioselectivities were determined by ^{1}H NMR of the crude reaction mixture. And then the product was purified by column chromatography and the product was analyzed by NMR spectroscopy.



9aa.[3] Yellow oil (114 mg, 95% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (m, 7H), 6.71 (t, *J* = 7.5 Hz, 3H), 3.35 (t, *J* = 6.8 Hz, 2H), 2.94 (s, 3H), 2.67 (t, *J* = 7.0 Hz, 2H), 1.72-1.63 (m, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 142.3, 129.1, 128.4, 128.3, 125.7, 115.9, 112.1, 52.6, 38.3, 35.8, 29.0, 26.4 ppm.

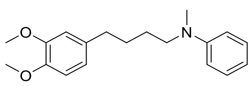


9ba. Yellow oil (121 mg, 90% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 100:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.82-6.74 (m, 3H), 3.87 (s, 3H), 3.42 (d, *J* = 6.7 Hz, 2H), 2.99 (s, 3H), 2.72-2.64 (m, 2H), 1.72 (q, *J* = 3.7 Hz, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 149.4, 134.5, 129.3, 129.2, 115.9, 113.8, 112.2, 55.3, 52.7, 38.4, 35.0, 29.3, 26.4 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{18}H_{23}NO$ [M+H]+ 270.1852; Found: 270.1844.

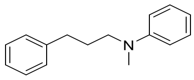


9ca. Yellow oil (145 mg, 97% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 50:1).

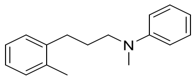
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.79-6.70 (m, 5H), 3.91 (d, *J* = 3.3 Hz, 6H), 3.39 (t, *J* = 5.2 Hz, 2H), 2.96 (s, 3H), 2.68-2.59 (m, 2H), 1.69 (q, *J* = 3.8 Hz, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 148.8, 147.2, 135.0, 129.2, 120.2, 115.9, 112.1, 111.7, 111.3, 56.0, 55.9, 52.7, 38.4, 35.5, 29.3, 26.5 ppm.

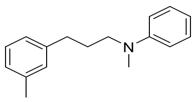
HR-MS (ESI/TOF) m/z: Calcd. for $C_{19}H_{26}NO_2$ [M+H]+ 300.1958; Found: 300.1949.



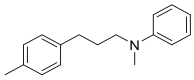
9da.[4] Yellow oil (93 mg, 92% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.30-7.22 (m, 5H), 6.73 (d, *J* = 8.0 Hz, 3H), 3.43-3.36 (m, 2H), 2.97 (s, 3H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.02-1.92 (m, 2H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 141.8, 129.2, 128.39, 128.36, 125.9, 116.0, 112.2, 52.3, 38.3, 33.4, 28.2 ppm.



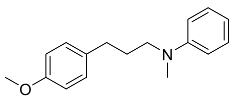
9ea-*o*. Yellow oil (113 mg, 94% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.5, 3.9 Hz, 2H), 7.25 (dd, *J* = 8.6, 4.2 Hz, 4H), 6.81-6.75 (m, 3H), 3.56-3.43 (m, 2H), 3.06 (s, 3H), 2.80-2.69 (m, 2H), 2.43 (s, 3H), 2.05-1.91 (m, 2H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 140.1, 135.9, 130.3, 129.3, 128.7, 126.12, 126.08, 116.2, 112.4, 52.6, 38.4, 30.8, 27.2, 19.4 ppm;
HR-MS (ESI/TOF) m/z: Calcd. for $C_{17}H_{22}N$ $[M+H]^+$ 240.1752; Found: 240.1762.



9ea-*m*.[5] Yellow oil (108 mg, 90% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.19 (m, 3H), 7.09-7.02 (m, 3H), 6.73 (dd, *J* = 7.8, 6.2 Hz, 3H), 3.42-3.35 (m, 2H), 2.97 (s, 3H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 2.01-1.87 (m, 2H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 141.8, 137.9, 129.19, 129.16, 128.3, 126.6, 125.4, 116.0, 112.3, 52.3, 38.3, 33.3, 28.2, 21.4 ppm.



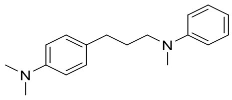
9ea-*p*.[6] Yellow oil (108 mg, 90% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.21 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 4H), 6.75 -6.66 (m, 3H), 3.37 (q, *J* = 7.9 Hz, 2H), 2.96 (s, 3H), 2.65 (q, *J* = 7.9 Hz, 2H), 2.37 (s, 3H), 1.98-1.86 (m, 2H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 138.7, 135.3, 129.13, 129.05, 128.2, 116.0, 112.2, 52.3, 38.3, 32.9, 28.3, 21.0 ppm.



9fa.[7] Yellow oil (111 mg, 87% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 100:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 2H), 7.20-7.14 (m, 2H), 6.93-6.87 (m, 2H), 6.77-6.71 (m, 3H), 3.86 (s, 3H), 3.39 (t, J = 7.5 Hz, 2H), 2.98 (s, 3H), 2.67 (t, J = 7.7 Hz, 2H), 2.00-1.90 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 149.4, 133.9, 129.3, 129.2, 116.0, 113.8, 112.3, 55.3, 52.2, 38.3, 32.5, 28.4 ppm.

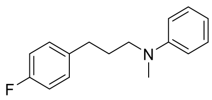


9ga. Yellow oil (114 mg, 85% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 40:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 2H), 7.15-7.08 (m, 2H), 6.78-6.69 (m, 5H), 3.41-3.33 (m, 2H), 2.96 (s, 9H), 2.62 (t, J = 7.7 Hz, 2H), 1.97-1.86 (m, 2H) ppm;

^{13}C NMR δ 149.4, 149.1, 130.0, 129.1, 128.9, 115.9, 113.1, 112.2, 52.3, 41.0, 38.3, 32.3, 28.4 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{18}H_{25}N_2$ [M+H]+ 269.2012; Found: 269.1993.

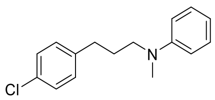


9ha.[6] Yellow oil (105 mg, 87% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 2H), 7.18 (t, J = 4.4 Hz, 2H), 7.06-6.97 (m, 2H), 6.73 (t, J = 7.1 Hz, 3H), 3.41-3.33 (m, 2H), 2.97 (s, 3H), 2.67 (t, J = 7.7 Hz, 2H), 1.99-1.87 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 160.1, 149.3, 137.4, 129.7, 129.6, 129.2, 116.1, 115.2, 115.0, 112.2, 52.1, 38.3, 32.5, 28.3 ppm;

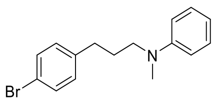
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.58 ppm.



9ia.[8] Yellow oil (110 mg, 85% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 4H), 7.18 (d, J = 8.4 Hz, 2H), 6.75 (t, J = 7.6 Hz, 3H), 3.39 (t, J = 7.4 Hz, 2H), 2.98 (s, 3H), 2.69 (t, J = 7.8 Hz, 2H), 2.01-1.89 (m, 2H) ppm;

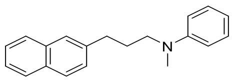
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 140.3, 131.6, 129.7, 129.2, 128.5, 116.2, 112.3, 52.2, 38.4, 32.7, 28.2 ppm.



9ja.[8] Yellow oil (134 mg, 88% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.41 (m, 2H), 7.32-7.22 (m, 2H), 7.14-7.07 (m, 2H), 6.78-6.67 (m, 3H), 3.41-3.33 (m, 2H), 2.96 (s, 3H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.98-1.88 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 140.8, 131.4, 130.1, 129.2, 119.6, 116.2, 112.3, 52.1, 38.3, 32.8, 28.1 ppm.

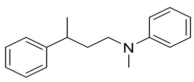


9ka. Yellow oil (120 mg, 84% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.78 (m, 3H), 7.70 (d, *J* = 4.4 Hz, 1H), 7.52 (q, *J* = 7.0 Hz, 2H), 7.44 -7.36 (m, 1H), 7.35-7.24 (m, 2H), 6.76 (dd, *J* = 7.7, 5.1 Hz, 3H), 3.46 (t, *J* = 7.4 Hz, 2H), 3.00 (d, *J* = 3.6 Hz, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.15-2.02 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 139.3, 133.6, 132.1, 129.2, 128.0, 127.6, 127.4, 127.2, 126.4, 126.0, 125.2, 116.1, 112.3, 52.3, 38.3, 33.5, 28.0 ppm;

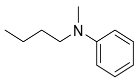
HR-MS (ESI/TOF) m/z: Calcd. for $C_{20}H_{22}N$ [M+H]+ 276.1747; Found: 276.1711.



9la.[9] Yellow oil (118 mg, 99% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.2 Hz, 2H), 7.34-7.24 (m, 5H), 6.75 (dd, *J* = 6.5, 2.8 Hz, 1H), 6.71-6.64 (m, 2H), 3.38-3.17 (m, 2H), 2.94 (s, 3H), 2.86-2.74 (m, 1H), 2.00-1.90 (m, 2H), 1.38 (d, *J* = 3.3 Hz, 3H) ppm;

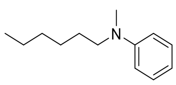
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 147.1, 129.4, 128.8, 127.2, 126.4, 116.2, 112.5, 51.3, 38.4, 38.2, 34.6, 23.1 ppm.



9ma-2.[10] Yellow oil (65 mg, 80% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 6.96 – 6.86 (m, 3H), 3.56 – 3.47 (m, 2H), 3.12 (s, 3H), 1.85 – 1.72 (m, 2H), 1.65 – 1.52 (m, 2H), 1.18 (t, *J* = 7.3 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 129.3, 116.0, 112.3, 52.7, 38.4, 29.1, 20.6, 14.2.



9ma-4.[11] Yellow oil (81 mg, 85% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 2H), 6.79-6.71 (m, 3H), 3.40-3.34 (m, 2H), 2.99 (s, 3H), 1.64 (t, *J* = 7.4 Hz, 2H), 1.39 (s, 6H), 1.00-0.95 (m, 3H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 129.2, 115.9, 112.2, 52.9, 38.3, 31.9, 27.0, 26.7, 22.8, 14.1 ppm.
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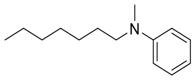
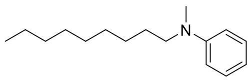
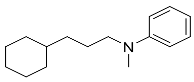


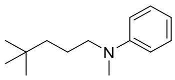
9ma-5.[12] Yellow oil (96 mg, 93% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 6.82-6.73 (m, 3H), 3.41-3.34 (m, 2H), 3.00 (s, 3H), 1.66 (t, *J* = 7.8 Hz, 2H), 1.45-1.33 (m, 8H), 1.03-0.94 (m, 3H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 129.2, 115.9, 112.2, 52.9, 38.4, 32.0, 29.4, 27.3, 26.8, 22.8, 14.2 ppm.



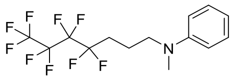
9ma-7.[12] Yellow oil (107 mg, 92% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 2H), 6.83-6.76 (m, 3H), 3.44-3.36 (m, 2H), 3.02 (s, 3H), 1.68 (t, *J* = 7.5 Hz, 2H), 1.45-1.38 (m, 12H), 1.03-0.99 (m, 3H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 129.2, 115.9, 112.2, 52.9, 38.3, 32.0, 29.74, 29.69, 29.4, 27.3, 26.8, 22.8, 14.2 ppm.



9na. [13] Yellow oil (99 mg, 86% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 2H), 6.77 (dd, *J* = 8.6, 2.9 Hz, 3H), 3.35 (dd, *J* = 8.9, 6.5 Hz, 2H), 2.99 (d, *J* = 2.1 Hz, 3H), 1.84-1.73 (m, 5H), 1.65 (d, *J* = 7.7 Hz, 2H), 1.36 (s, 2H), 1.31-1.26 (m, 4H), 0.99-0.92 (m, 2H) ppm ;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 129.2, 115.8, 112.1, 53.2, 38.3, 37.7, 34.9, 33.5, 26.7, 26.5, 24.0 ppm.



9oa.[14] White oil (104 mg, 98% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.1 Hz, 2H), 6.84 (dd, *J* = 8.8, 2.2 Hz, 3H), 3.41 (t, *J* = 7.5 Hz, 2H), 3.07 (s, 3H), 1.76-1.65 (m, 2H), 1.38-1.28 (m, 2H), 1.05 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 129.3, 116.0, 112.2, 53.8, 41.5, 38.3, 30.4, 29.5, 22.0 ppm.

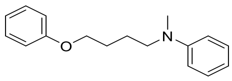


9pa.[14] Yellow oil (185 mg, 92% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.7, 7.4 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 3H), 3.46 (t, *J* = 7.3 Hz, 2H), 3.00 (s, 3H), 2.25-2.10 (m, 2H), 2.02-1.92 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 129.3, 116.9, 112.6, 52.0, 38.2, 28.6, 28.4, 28.1, 18.0 ppm.

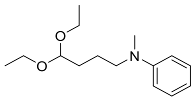
^{19}F NMR (376 MHz, $CDCl_3$) δ -81.14, -114.22, -124.49, -126.07 ppm.



9qa.[14] Yellow oil (73 mg, 57% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 200:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 4H), 6.96 (dd, *J* = 22.7, 7.7 Hz, 3H), 6.75 (dd, *J* = 16.7, 7.9 Hz, 3H), 4.01 (t, *J* = 5.8 Hz, 2H), 3.43 (t, *J* = 7.0 Hz, 2H), 2.98 (s, 3H), 1.89-1.76 (m, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 129.5, 129.3, 120.7, 116.3, 114.5, 112.4, 67.6, 52.7, 38.5, 29.8, 27.0, 23.6 ppm.

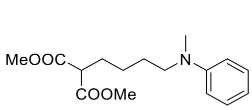


9ra. Yellow oil (67 mg, 53% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 200:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 15.5, 6.7 Hz, 2H), 6.69 (dd, *J* = 14.9, 7.7 Hz, 3H), 4.51 (s, 1H), 3.65 (dd, *J* = 9.4, 7.0 Hz, 2H), 3.55-3.44 (m, 2H), 3.38-3.30 (m, 2H), 2.93 (s, 3H), 1.66 (d, *J* = 2.8 Hz, 4H), 1.21 (t, *J* = 7.0 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 129.1, 115.9, 112.1, 102.8, 61.1, 52.5, 38.2, 31.1, 22.0, 15.3 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{15}H_{26}NO_2$ [M+H]+ 252.1958; Found: 252.1960.

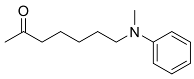


9sa.Yellow oil (103 mg, 71% yield) was obtained after column chromatography (petroleum ether / ethyl acetate= 10:1).

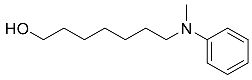
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.7, 7.2 Hz, 2H), 6.73-6.67 (m, 3H), 3.75 (s, 6H), 3.39 (t, *J* = 7.5 Hz, 1H), 3.35-3.29 (m, 2H), 2.93 (s, 3H), 1.96 (q, *J* = 7.6 Hz, 2H), 1.67-1.58 (m, 2H), 1.41-1.33 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 149.2, 129.1, 116.0, 112.1, 52.5 , 52.4, 51.6, 38.3, 28.7, 26.3, 24.9 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{16}H_{24}NO_4$ $[M+H]^+$ 294.1700; Found: 294.1691.



9ta. Yellow oil (70 mg, 63% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 50:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 2H), 6.77 -6.69 (m, 3H), 3.38-3.31 (m, 2H), 2.96 (s, 3H), 2.47 (t, *J* = 7.3 Hz, 2H), 2.17 (s, 3H), 1.68-1.61 (m, 4H), 1.40-1.32 (m, 2H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 149.3, 129.2, 116.0, 112.2, 52.6, 43.6, 38.3, 29.9, 26.8, 26.6, 23.7 ppm;
HR-MS (ESI/TOF) m/z: Calcd. for $C_{14}H_{22}NO$ $[M+H]^+$ 220.1696; Found: 220.1689.



9ua. White oil (91 mg, 82% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 2H), 6.76-6.64 (m, 3H), 3.66 (t, *J* = 6.6 Hz, 2H), 3.36-3.29 (m, 2H), 2.94 (s, 3H), 1.64-1.57 (m, 4H), 1.46-1.34 (m, 6H), 1.27 (s, 1H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 129.1, 115.8, 112.1, 63.0, 52.8, 38.3, 32.7, 29.3, 27.2, 26.6, 25.8 ppm
HR-MS (ESI/TOF) m/z: Calcd. for $C_{14}H_{24}NO$ $[M+H]^+$ 222.1852; Found: 222.1846.

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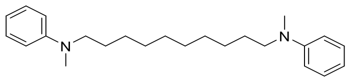
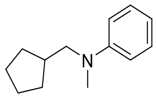
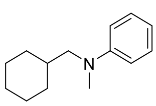


.

9va.[14] Yellow oil (126 mg, 72% yield) was obtained after column chromatography (petroleum ether / ethyl acetate= 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.21 (m, 4H), 6.76-6.65 (m, 6H), 3.31 (t, *J* = 7.6 Hz, 4H), 2.94 (s, 6H), 1.58 (t, *J* = 7.4 Hz, 4H), 1.31 (d, *J* = 5.4 Hz, 12H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 129.1, 115.8, 112.1, 52.8, 38.3, 29.61, 29.56, 27.2, 26.7 ppm.



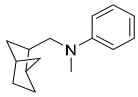
9wa-5.[15] Yellow oil (83 mg, 88% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 6.81-6.69 (m, 3H), 3.31 (d, *J* = 7.3 Hz, 2H), 3.02 (s, 3H), 2.29-2.40 (m, 1H), 1.86-1.56 (m, 6H), 1.36-1.22 (m, 2H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 129.1, 115.7, 112.0, 57.8, 39.05, 38.97, 30.9, 25.1 ppm.



9wa-6.[16] Yellow oil (77 mg, 76% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.9 Hz, 2H), 6.78-6.69 (m, 3H), 3.19 (d, J = 6.7 Hz, 2H), 3.02 (d, J = 3.1 Hz, 3H), 1.83-1.75 (m, 5H), 1.40-1.23 (m, 5H), 1.01 (d, J = 12.0 Hz, 1H) ppm;

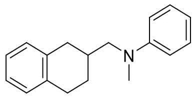
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 129.1, 115.4, 111.6, 59.7, 39.6, 36.9, 31.3, 26.6, 26.1 ppm.



9xa [14]. Yellow oil (89 mg, 83% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 2H), 6.84 (dd, J = 14.9, 7.7 Hz, 3H), 3.29-3.15 (m, 2H), 3.09 (s, 3H), 2.43-2.37 (m, 1H), 2.27 (d, J = 3.1 Hz, 1H), 2.08-1.99 (m, 1H), 1.69-1.61 (m, 2H), 1.58-1.51 (m, 2H), 1.33-1.25 (m, 3H), 1.24-1.17 (m, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 129.2, 115.9, 112.1, 58.1, 41.0, 39.3, 39.1, 36.7, 35.5, 35.3, 30.0, 29.1 ppm.

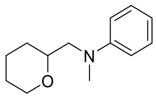


9ya. Yellow oil (78 mg, 62% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 2H), 7.13 (q, J = 5.9 Hz, 4H), 6.75 (dd, J = 17.5, 7.8 Hz, 3H), 3.43-3.28 (m, 2H), 3.06 (s, 3H), 2.96-2.81 (m, 3H), 2.55 (dd, J = 16.3, 10.7 Hz, 1H), 2.37-2.22 (m, 1H), 2.11-2.01 (m, 1H), 1.57-1.44 (m, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 136.6, 136.0, 129.2, 129.1, 128.9, 125.7, 125.6, 115.9, 111.9, 58.8, 39.6, 34.0, 33.6, 28.9, 27.5 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{18}H_{22}N$ $[M+H]^+$ 252.1747; Found: 252.1738.

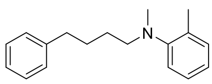


9za. Yellow oil (58 mg, 57% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 100:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.21 (m, 2H), 6.71 (d, J = 8.6 Hz, 3H), 5.29 (d, J = 3.5 Hz, 1H), 3.70 -3.60 (m, 2H), 3.32 (t, J = 7.7 Hz, 2H), 2.92 (d, J = 3.1 Hz, 3H), 1.60 (d, J = 7.1 Hz, 6H) ppm;

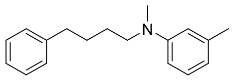
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 129.2, 116.0, 112.2, 62.8, 52.8, 38.3, 32.6, 29.7, 26.5, 23.4 ppm.

HR-MS (ESI/TOF) m/z: Calcd. for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1539; Found: 206.1528.

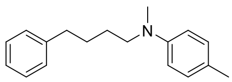


9ab. Yellow oil (114 mg, 90% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

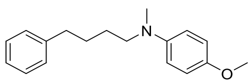
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 5H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.3 Hz, 1H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.69 (s, 3H), 2.65 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H), 1.74-1.61 (m, 4H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 142.6, 133.2, 131.0, 128.4, 128.3, 126.3, 125.6, 122.8, 120.0, 56.0, 41.8, 35.8, 29.0, 27.3, 18.3 ppm;
HR-MS (ESI/TOF) m/z: Calcd. for $C_{18}H_{24}N$ $[M+H]^+$ 254.1903; Found: 254.1894.



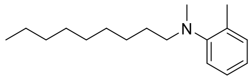
9ac [16]. Yellow oil (114 mg, 93% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 2H), 7.20 (dd, *J* = 7.6, 5.6 Hz, 3H), 7.15-7.09 (m, 1H), 6.52 (d, *J* = 7.3 Hz, 3H), 3.32 (t, *J* = 6.8 Hz, 2H), 2.91 (s, 3H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.71 -1.61 (m, 4H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 142.4, 138.8, 129.1, 128.44, 128.37, 125.8, 117.0, 112.9, 109.5, 52.7, 38.4, 35.9, 29.1, 26.6, 22.0 ppm.



9ad [16]. Yellow oil (112 mg, 91% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 2H), 7.30-7.24 (m, 3H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.75-6.68 (m, 2H), 3.37 (t, *J* = 6.9 Hz, 2H), 2.95 (s, 3H), 2.72 (t, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.72 (dd, *J* = 4.4, 2.3 Hz, 4H) ppm;
^{13}C NMR (101 MHz, CDCl3) δ 147.5, 142.4, 129.7, 128.5, 128.4, 125.8, 125.3, 112.7, 53.1, 38.6, 35.9, 29.2, 26.4, 20.3 ppm.



9ae. Yellow oil (123 mg, 92% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.5, 6.5 Hz, 2H), 7.25 (dd, *J* = 8.0, 6.3 Hz, 3H), 6.93-6.87 (m, 2H), 6.79-6.73 (m, 2H), 3.82 (s, 3H), 3.30 (t, *J* = 7.0 Hz, 2H), 2.90 (s, 3H), 2.70 (t, *J* = 7.3 Hz, 2H), 1.74-1.62 (m, 4H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 144.5, 142.4, 128.4, 128.3, 125.8, 114.8, 114.5, 55.8, 53.9, 39.0, 35.9, 29.1, 26.4 ppm;
HR-MS (ESI/TOF) m/z: Calcd. for $C_{18}H_{24}NO$ $[M+H]^+$ 270.1852; Found: 270.1843.

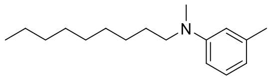


9mb. Yellow oil (102 mg, 83% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.17 (m, 2H), 7.10 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.01 (t, *J* = 7.1 Hz, 1H), 2.94-2.87 (m, 2H), 2.71 (s, 3H), 2.37 (s, 3H), 1.62-1.52 (m, 2H), 1.37-1.31 (m, 12H), 0.94 (t, *J* = 6.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 133.1, 131.0, 126.2, 122.6, 119.9, 56.4, 41.7, 31.9, 29.65, 29.58, 29.3, 27.7, 27.2, 22.7, 18.3, 14.1 ppm.

HR-MS (ESI/TOF) m/z: Calcd. for $C_{17}H_{30}N$ $[M+H]^+$ 248.2373; Found: 248.2365.

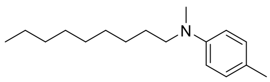


9mc. Yellow oil (113 mg, 91% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.12 (m, 1H), 6.55 (d, *J* = 6.2 Hz, 3H), 3.32 (t, *J* = 7.6 Hz, 2H), 2.95 (s, 3H), 2.36 (s, 3H), 1.61 (s, 2H), 1.34 (d, *J* = 13.0 Hz, 12H), 0.93 (t, *J* = 6.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 138.7, 129.0, 116.8, 112.9, 109.4, 52.9, 38.3, 31.9, 29.65, 29.59, 29.3, 27.2, 26.7, 22.7, 22.0, 14.1 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{17}H_{30}N$ $[M+H]^+$ 248.2373; Found: 248.2365.

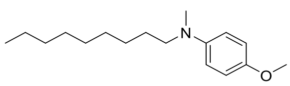


9md. Yellow oil (112 mg, 91% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.27-3.17 (m, 2H), 2.86 (s, 3H), 1.55 (t, *J* = 7.4 Hz, 2H), 1.30 (d, *J* = 10.2 Hz, 12H), 0.90 (t, *J* = 6.6 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 144.6, 114.7, 114.4, 55.8, 54.0, 38.9, 31.9, 29.60, 29.56, 29.3, 27.2, 26.5, 22.7, 14.1 ppm.

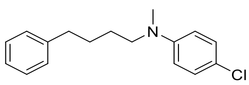
HR-MS (ESI/TOF) m/z: Calcd. for $C_{17}H_{30}N$ $[M+H]^+$ 248.2373; Found: 248.2365.



9me.[14] Yellow oil (119 mg, 91% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 100:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87-6.80 (m, 2H), 6.70 (d, *J* = 9.1 Hz, 2H), 3.77 (s, 3H), 3.26-3.17 (m, 2H), 2.86 (s, 3H), 1.54 (t, *J* = 7.4 Hz, 2H), 1.29 (d, *J* = 9.9 Hz, 12H), 0.89 (t, *J* = 6.6 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 144.6, 114.7, 114.4, 55.8, 54.0, 38.9, 31.9, 29.6, 29.5, 29.3, 27.2, 26.5, 22.6, 14.1 ppm.

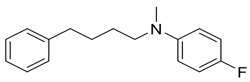


9af. Yellow oil (120 mg, 88% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.29-7.18 (m, 5H), 6.67-6.61 (m, 2H), 3.34 (t, *J* = 6.9 Hz, 2H), 2.93 (s, 3H), 2.70 (t, *J* = 7.1 Hz, 2H), 1.75-1.62 (m, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 142.2, 128.9, 128.41, 128.38, 125.9, 120.6, 113.2, 52.7, 38.5, 35.8, 29.0, 26.3 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{17}H_{21}ClN$ [M+H]$^+$ 274.1357; Found: 274.1349.



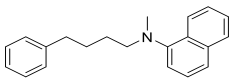
9ag. Yellow oil (118 mg, 92% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 2H), 7.26 (dd, *J* = 9.1, 7.2 Hz, 3H), 7.04-6.95 (m, 2H), 6.72 -6.64 (m, 2H), 3.34 (t, *J* = 6.9 Hz, 2H), 2.93 (d, *J* = 1.5 Hz, 3H), 2.72 (t, *J* = 7.3 Hz, 2H), 1.78-1.64 (m, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 154.1, 146.3, 142.3, 128.43, 128.39, 125.9, 115.6, 115.4, 113.53, 113.46, 53.5, 38.8, 35.8, 29.0, 26.3 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -129.81 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{17}H_{21}FN$ [M+H]$^+$ 258.1653; Found: 258.1644.

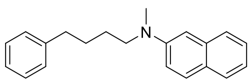


9ah. Yellow oil (126 mg, 87% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 200:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40-8.33 (m, 1H), 7.96-7.87 (m, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.57 (dd, *J* = 6.5, 3.7 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.30-7.17 (m, 4H), 3.21 (t, *J* = 6.7 Hz, 2H), 2.94 (s, 3H), 2.76-2.67 (m, 2H), 1.80 (t, *J* = 3.9 Hz, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 142.6, 134.9, 129.7, 128.5, 128.3, 125.77, 125.76, 125.74, 125.2 , 124.1, 123.1, 115.6, 56.9, 42.6, 35.8, 29.8, 29.1, 27.2 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{21}H_{24}N$ [M+H]$^+$ 290.1903; Found: 290.1894.

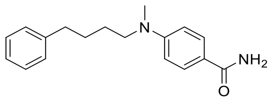


9ai. Yellow oil (128 mg, 89% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 200:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 18.0, 8.5 Hz, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.34 (dd, *J* = 8.4, 6.4 Hz, 2H), 7.28-7.20 (m, 4H), 7.17 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.92 (d, *J* = 2.6 Hz, 1H), 3.52-3.43 (m, 2H), 3.05 (s, 3H), 2.70 (d, *J* = 7.2 Hz, 2H), 1.77-1.67 (m, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 142.3, 135.2, 128.7, 128.40, 128.35, 127.4, 126.5, 126.2, 126.0, 125.8, 121.8, 116.1, 105.9, 52.9, 38.6, 35.8, 29.0, 26.6 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{21}H_{24}N$ [M+H]$^+$ 290.1903; Found: 290.1892.

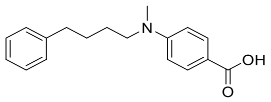


9aj. White solid (133 mg, 94% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$)δ 7.75-7.68 (m, 2H), 7.34-7.26 (m, 2H), 7.24-7.16 (m, 3H), 6.68-6.61 (m, 2H), 5.88 (s, 2H), 3.40 (t, *J* = 6.7 Hz, 2H), 3.00 (s, 3H), 2.68 (t, *J* = 7.0 Hz, 2H), 1.68 (dd, *J* = 7.2, 3.6 Hz, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 151.7, 142.0, 129.2, 128.4, 125.9, 119.6, 110.7, 52.3, 38.4, 35.7, 28.8, 26.5 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{18}H_{23}N_2O$ $[M+H]^+$ 283.1805; Found: 283.1784.

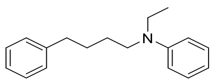


9ak. White solid (131 mg, 92% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 1:1).

^{1}H NMR (400 MHz, DMSO-*d$_6$)* δ 12.02 (s, 1H), 7.72-7.66 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.20-7.11 (m, 3H), 6.68-6.60 (m, 2H), 3.39 (t, *J* = 7.1 Hz, 2H), 2.92 (s, 3H), 2.59 (t, *J* = 7.3 Hz, 2H), 1.61-1.47 (m, 4H) ppm;

^{13}C NMR (101 MHz, DMSO-*d$_6$)* δ 168.0, 152.4, 142.5, 131.5, 128.72, 128.69, 126.1, 117.0, 110.9, 51.6, 38.4, 35.4, 28.7, 26.3 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645; Found: 284.1625.

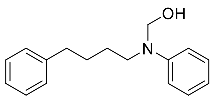


9al. Yellow oil (145 mg, 96% yield) was obtained after column chromatography (petroleum ether / ethyl acetate= 400:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 2H), 7.31-7.20 (m, 5H), 6.73 (d, *J* = 8.2 Hz, 3H), 3.41 (q, *J* = 6.5 Hz, 2H), 3.36-3.30 (m, 2H), 2.77-2.67 (m, 2H), 1.80-1.66 (m, 4H), 1.20 (q, *J* = 5.9 Hz, 3H) ppm;

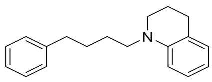
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 142.4, 129.3, 128.4, 128.3, 125.8, 115.4, 111.9, 50.3, 45.0, 35.9, 29.1, 27.3, 12.3 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{18}H_{24}N$ $[M+H]^+$ 254.1903; Found: 254.1900.

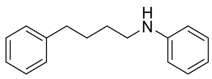


9am. Yellow oil (88 mg, 72% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 5:1).

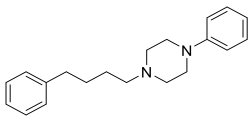
¹H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 2H), 7.28-7.20 (m, 5H), 6.80-6.75 (m, 3H), 3.78 (t, *J* = 5.9 Hz, 2H), 3.48 (t, *J* = 5.9 Hz, 2H), 3.37 (t, *J* = 6.9 Hz, 2H), 2.69 (t, *J* = 6.9 Hz, 2H), 2.01 (s, 1H), 1.75-1.65 (m, 4H) ppm;
¹³C NMR (101 MHz, $CDCl_3$) δ 148.3, 142.2, 129.3, 128.38, 128.36, 125.8, 116.8, 113.0, 60.0, 53.2, 51.7, 35.8, 28.9, 26.5 ppm;
HR-MS (ESI/TOF) m/z: Calcd. for $C_{17}H_{22}NO$ $[M+H]^+$ 256.1696; Found: 256.1663.



9an. Yellow oil (133 mg, 96% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 200:1).
¹H NMR (400 MHz, $CDCl_3$) δ 7.43-7.35 (m, 2H), 7.30 (dd, *J* = 8.0, 4.0 Hz, 3H), 7.15 (t, *J* = 6.6 Hz, 1H), 7.04 (t, *J* = 5.6 Hz, 1H), 6.70-6.60 (m, 2H), 3.40-3.32 (m, 4H), 2.86 (t, *J* = 5.8 Hz, 2H), 2.80-2.72 (m, 2H), 2.08-1.99 (m, 2H), 1.84-1.70 (m, 4H) ppm;
¹³C NMR (101 MHz, $CDCl_3$) δ 145.3, 142.4, 129.2, 128.44, 128.37, 127.1, 125.8, 122.2, 115.3, 110.5, 51.4, 49.6, 35.9, 29.2, 28.3, 26.1, 22.3 ppm;
HR-MS (ESI/TOF) m/z: Calcd. for $C_{19}H_{24}N$ $[M+H]^+$ 266.1903; Found: 266.1885.



9ao.[17] Yellow oil (73 mg, 65% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 50:1).
¹H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.24-7.15 (m, 5H), 6.75-6.68 (m, 1H), 6.65-6.58 (m, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.79-1.64 (m, 4H) ppm;
¹³C NMR (101 MHz, $CDCl_3$) δ 148.3, 142.2, 129.2, 128.4, 128.3, 125.8, 117.2, 112.7, 43.9, 35.6, 29.1, 28.9 ppm.



9ap.Yellow oil (131 mg, 89% yield) was obtained after column chromatography (petroleum ether / ethyl acetate = 2:1).
¹H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 4H), 7.22 (dd, *J* = 7.2, 2.3 Hz, 3H), 6.986.93 (m, 2H), 6.90 -6.84 (m, 1H), 3.23 (t, *J* = 3.7 Hz, 4H), 2.68 (t, *J* = 6.4 Hz, 2H), 2.62 (t, *J* = 4.8 Hz, 4H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.73-1.57 (m, 4H) ppm;
¹³C NMR (101 MHz, $CDCl_3$) δ 151.3, 142.4, 129.1, 128.4, 128.3, 125.7, 119.6, 116.0, 58.5, 53.3, 49.1, 35.8, 29.4, 26.5 ppm;
HR-MS (ESI/TOF) m/z: Calcd. for $C_{20}H_{27}N_2$ $[M+H]^+$ 295.2169; Found: 295.2149.

Preparation of aripiprazole (13a)

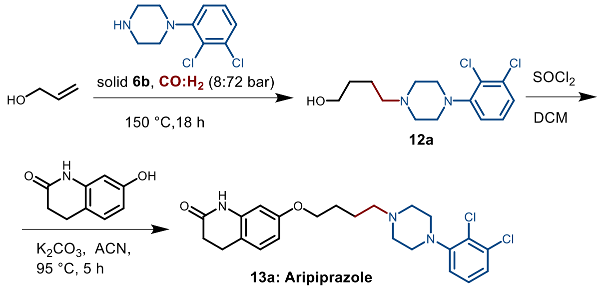
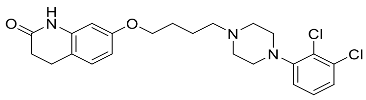


Fig. S7. Preparation of aripiprazole.

In a typical experiment, a Parr stainless steel autoclave (125 mL) was loaded with a mixture of **6b** (1.0 mol %), 10.0 mmol allyl alcohol, 5.0 mmol 1-(2,3-dichlorophenyl)piperazine and 20.0 mL THF. Subsequently, the autoclave was pressurized with CO (8 bar) and hydrogen (72 bar) and heated to 150 ^{o} C. After 18 h, the autoclave was allowed to cool to room temperature and the gases were vented. The solvent was removed under vacuum, the resulting crude **12a** (63% as determined by ^{1}HNMR of the crude with 1,3,5-methoxybenzene as the internal standard, *l:b* = 96/4) was then filtered through a plug of silica (CH_2Cl_2/MeOH = 40:1) and concentrated *in vacuo*. This linear amino alcohol (302 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (4.0 mL) followed by addition of sulfoxide chloride (0.6 mL, 1.5 mmol). After stirring at 60 ^{o}C for 3.5 h, the resulting reaction mixture was cooled to 0 ℃ and stirred for 2 h, the solvent was removed under vacuum, the resulting crude was then filtered through a plug of silica (CH_2Cl_2/MeOH = 100:1) and concentrated in vacuo. This resulting crude (297 mg, 0.93 mmol) was dissolved in acetonitrile (4.0 mL) followed by addition of of 7-hydroxy-3,4-dihydroquinolin-2(1*H*)-one (152 mg, 0.93 mmol, 1.0 equiv.), K_2CO_3 (139 mg, 1.02 mmol, 1.1 equiv.). After stirring at 95 ℃ overnight, the solvent was removed under vacuum, and then filtered through a plug of silica (petroleum ether / ethyl acetate= 1:1) and concentrated in vacuo to give aripiprazole (**13a**, 391 mg, 94 %) as a white solid.



13a.[18] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.15-7.09 (m, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.94 (dd, *J* = 6.3, 3.2 Hz, 1H), 6.51 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.39 (d, *J* = 2.4 Hz, 1H), 3.95 (t, *J* = 6.2 Hz, 2H), 3.06 (t, *J* = 4.8 Hz, 4H), 2.88 (dd, *J* = 8.5, 6.5 Hz, 2H), 2.72-2.53 (m, 6H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.85 -1.75 (m, 2H), 1.73-1.64 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 158.7, 151.3, 138.3, 134.0, 128.6, 127.4, 124.5, 118.6, 115.6, 108.8, 102.3, 67.9, 58.2, 53.3, 51.4, 31.1, 27.3, 24.6, 23.4 ppm.

Preparation of laurel aripiprazole (13b)

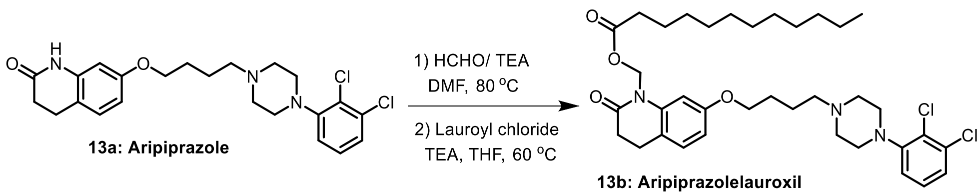
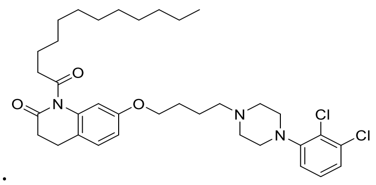


Fig. S8. Preparation of aripiprazolelauroxil.

A Schlenk tube was charged with aripiprazole (448 mg, 1 mmol), formaldehyde aqueous solution (37%, 1.6 mL), triethylamine (0.50 eq, 52 mg, 0.5 mmol,) and DMF (1.5 mL), and stirred at 80 °C for 2.5

hours. After reaction completion, solvent was removed under vacuum, and the residue was purified over flash chromatography on silica gel to give hydroxymethylaripiprazole (444 mg, 93%) as a white solid. This hydroxymethylaripiprazole (239 mg, 0.5 mmol), triethylamine (52 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (2.5 mL), and stirred at room temperature for 5 min, followed by addition of lauryl chloride (219 mg, 1 mmol) at 30 ℃. After stirring for 1.0 h, the resulting reaction mixture was diluted CH_2Cl_2 (30 mL) and quenched by addition of brine (50 mL), the organic layer was separated, and the aqueous layer was further extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was recrystallized from isopropanol to give aripiprazolelauroxil (**13b**, 245 mg, 78%) as white powder.



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13b. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.14 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 1H), 7.03-6.98 (m, 1H), 6.83 (d, *J* = 3.1 Hz, 1H), 6.63 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.98 (t, *J* = 5.7 Hz, 2H), 3.64 (dd, *J* = 12.8, 8.3 Hz, 4H), 3.37 (d, *J* = 12.6 Hz, 2H), 3.10 (dd, *J* = 13.6, 5.7 Hz, 5H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.82 (dd, *J* = 8.3, 5.3 Hz, 2H), 2.68 (dd, *J* = 8.3, 5.2 Hz, 2H), 2.23-2.11 (m, 2H), 1.88 (t, *J* = 6.8 Hz, 2H), 1.77-1.66 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 2H), 1.34-1.17 (m, 16H), 0.86 (t, *J* = 6.6 Hz, 3H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 173.0, 157.2, 149.0, 137.4, 134.2, 128.1, 127.9, 127.6, 126.1, 121.8, 119.3, 111.1, 109.3, 67.1, 57.2, 52.2, 47.9, 45.8, 40.4, 35.1, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.5, 25.1, 24.8, 22.7, 20.8, 14.1, 8.6 ppm;
HR-MS (ESI/TOF) m/z: Calcd. for $C_{35}H_{50}Cl_2N_3O_3$ $[M+H]^+$ 630.3229; Found: 630.3278.

Preparation of NGB2904 (14)

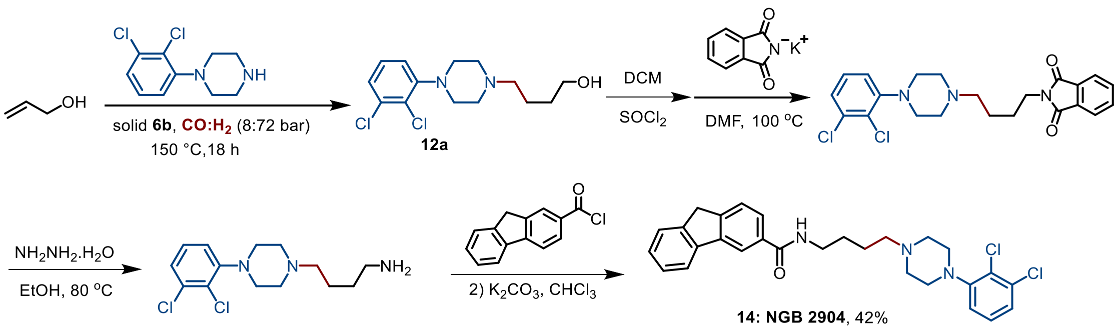
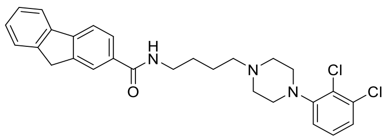


Fig. S9. Preparation of NGB2904.

In a typical experiment, a Parr stainless steel autoclave (125 mL) was loaded with a mixture of **6b** (1.0 mol %), 10.0 mmol allyl alcohol, 5.0 mmol 1-(2,3-dichlorophenyl)piperazine and 20.0 mL THF. Subsequently, the autoclave was pressurized with CO (8 bar) and hydrogen (72 bar) and heated to 150 °C. After 18 h, the autoclave was allowed to cool to room temperature and the gases were vented. The solvent was removed under vacuum, the resulting crude **12a** (63% as determined by ^{1}H NMR of the crude with 1,3,5-methoxybenzene as the internal standard, l:b = 96/4) was then filtered through a plug of silica (CH_2Cl_2/MeOH = 40:1) and concentrated in vacuo. This linear amino alcohol (302 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (4.0 mL) followed by addition of sulfoxide chloride (0.6 ml, 1.5 mmol). After stirring at 60 ^{o}C for 3.5 h, the resulting reaction mixture was cooled to 0 ℃ and stirred for 2 h , the solvent was removed under vacuum, the resulting crude was then filtered through a plug of silica (CH_2Cl_2 / MeOH = 100:1) and concentrated in vacuo, followed by the addition of potassium phthalimide (266 mg, 1.8 mmol). The reagents were suspended in 4.0 mL of dry DMF and allowed to reflux at 100 ^{o}C for 3 hours. Reaction was cooled, quenched with addition of water, and extracted with EtOAc (4 x 20 mL). The organic phases were combined, dried over Na_2SO_4, filtered, concentrated, and purified by flash column chromatography in CH_2Cl_2, 397 mg of yellow solid was obtained with a 92% yield. This intermediate was dissolved in 4.0 mL EtOH, followed by the addition of hydrazine monohydrate. The reaction mixture was allowed to mix for 5 hours at 80 ^{o}C then allowed to cool to rt. The solvent was removed under vacuum, the resulting crude was then filtered through a plug of silica (CH_2Cl_2 / MeOH = 10:1) and concentrated in vacuo. This 4-(4-(2, 3-dichlorophenyl)piperazin-1-yl)butan-1-amine (250 mg, 0.83 mmol) was dissolved in 4.0 mL chloroform, and 115 mg K_2CO_3 was added. The 9*H*-fluorene-2-carbonyl chloride (189 mg, 0.83 mmol) was dissolved in proper amount of chloroform, and then dropped into a three-way flask of 10.0 mL with a constant pressure drop funnel. Titration reaction 1h, extraction, mother solution decompression concentration to obtain a light yellow solid, ether recrystallization to obtain *N*-(4-(4-(2,3-dichlorophenyl)piperazin-1-yl)butyl)-9*H*-fluorene-3-carboxamide (**14**, 289 mg, 95 %) as a white solid.



14 **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.84-7.73 (m, 3H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.43-7.30 (m, 2H), 7.11 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 5.5 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.89 (s, 2H), 3.50 (q, *J* = 6.2 Hz, 2H), 3.09-2.89 (m, 4H), 2.61 (s, 4H), 2.46 (t, *J* = 6.8 Hz, 2H), 1.79-1.59 (m, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 151.1, 144.7, 143.9, 143.4, 140.7, 134.0, 133.4, 127.6, 127.5, 127.4, 127.0, 125.8, 125.2, 124.6, 123.9, 120.5, 119.7, 118.5, 58.1, 53.3, 51.1, 40.1, 36.9, 27.6, 24.5 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{28}H_{30}Cl_2N_3O$ $[M+H]^+$ 494.1766; Found: 494.1772.

Preparation of brexpiprazole (15)

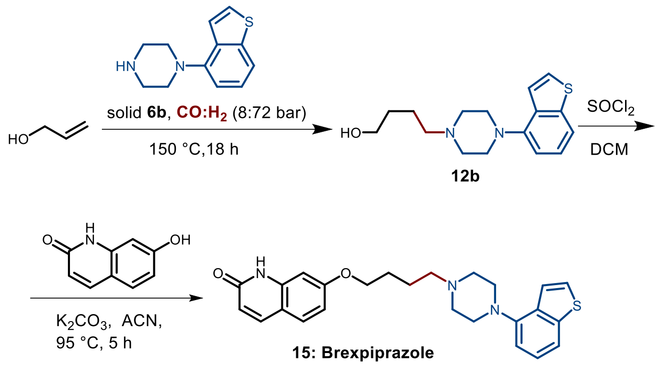
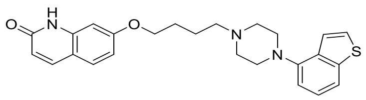


Fig. S10. Preparation of brexpiprazole.

In a typical experiment, a Parr stainless steel autoclave (125 mL) was loaded with a mixture of **6b** (1.0 mol %), 10.0 mmol allyl alcohol, 5.0 mmol 1-(benzo[*b*]thiophen-4-yl)piperazine and 20.0 mL THF. Subsequently, the autoclave was pressurized with CO (8 bar) and hydrogen (72 bar) and heated to 150 ^{o} C. After 18 h, the autoclave was allowed to cool to room temperature and the gases were vented. The solvent was removed under vacuum, the resulting crude **12b** (56% as determined by ^{1}H NMR of the crude with 1,3,5-methoxybenzene as the internal standard, *l:b* = 96/4) was then filtered through a plug of silica (CH_2Cl_2/MeOH = 20:1) and concentrated *in vacuo*. This linear amino alcohol (290 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (4.0 mL) followed by addition of sulfoxide chloride (0.6 ml, 1.5 mmol). After stirring at 60 ^{o}C for 3.5 h, the resulting reaction mixture was cooled to 0 ℃ and stirred for 2 h , the solvent was removed under vacuum, the resulting crude was then filtered through a plug of silica (CH_2Cl_2/MeOH = 100:1) and concentrated in vacuo. This resulting crude (280, 0.91 mmol) was dissolved in acetonitrile (4.0 mL) followed by addition of of 7-(Allyloxy)quinolin-2(1*H*)-one (146 mg, 0.91 mmol, 1.0 equiv.), K_2CO_3 (136 mg, .1.01mmol, 1.1 equiv.). After stirring at 95 ℃ overnight, the solvent was removed under vacuum, and then filtered through a plug of silica (petroleum ether / ethyl acetate= 1:1) and concentrated in vacuo.to give brexpiprazole (**15**, 331 mg, 84 %) as a white solid.



15.[18] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.93 (s, 1H), 7.73 (d, *J* = 9.4 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.48-7.35 (m, 3H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.83 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.59 (d, *J* = 9.3 Hz, 1H), 4.12 (t, *J* = 6.3 Hz, 2H), 3.22 (t, *J* = 5.0 Hz, 4H), 2.84-2.62 (m, 4H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.98-1.84 (m, 2H), 1.83-1.67 (m, 2H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 161.4, 148.5, 141.1, 140.8, 140.5, 134.0, 128.9, 125.0, 124.9, 121.9, 117.8, 116.9, 114.1, 112.7, 112.1, 99.0, 68.1, 58.2, 53.6, 52.1, 27.2, 23.4 ppm.

Preparation of BP897 (16)

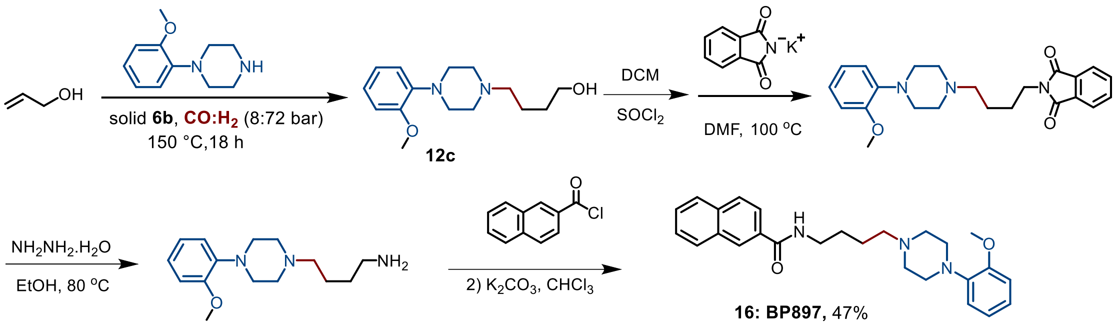
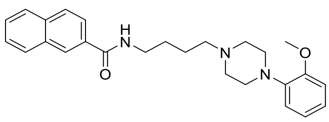


Fig. S11. Preparation of BP897.

In a typical experiment, a Parr stainless steel autoclave (125 mL) was loaded with a mixture of **6b** (1.0 mol %), 10.0 mmol allyl alcohol, 5.0 mmol 1-(2-methoxyphenyl)piperazine and 20.0 mL THF. Subsequently, the autoclave was pressurized with CO (8 bar) and hydrogen (72 bar) and heated to 150 ^{o} C. After 18 h, the autoclave was allowed to cool to room temperature and the gases were vented. The solvent was removed under vacuum, the resulting crude **12c** (55% as determined by ^{1}H NMR of the crude with 1,3,5-methoxybenzene as the internal standard, *l:b* = 96/4) was then filtered through a plug of silica (CH_2Cl_2/MeOH = 40:1) and concentrated *in vacuo*. This linear amino alcohol (264 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (4.0 mL) followed by addition of sulfoxide chloride (0.6 ml, 1.5 mmol). After stirring at 60 ^{o} C for 3.5 h, the resulting reaction mixture was cooled to 0 ℃ and stirred for 2 h , the solvent was removed under vacuum, the resulting crude was then filtered through a plug of silica (CH_2Cl_2/MeOH = 100:1) and concentrated in vacuo, followed by the addition of potassium phthalimide (266 mg, 1.8 mmol). The reagents were suspended in 4.0 mL of dry DMF and allowed to reflux at 100 ^{o}C for 3 hours. Reaction was cooled, quenched with addition of water, and extracted with EtOAc (4 x 20 mL). The organic phases were combined, dried over Na_2SO_4, filtered, concentrated, and purified by flash column chromatography in CH_2Cl_2. 366 mg of yellow solid was obtained with a 93% yield. This intermediate was dissolved in 4.0 mL EtOH, followed by the addition of hydrazine monohydrate. The reaction mixture was allowed to mix for 5 hours at 80 ^{o} C , then allowed to cool to rt. The solvent was removed under vacuum, the resulting crude was then filtered through a plug of silica (CH_2Cl_2 / MeOH = 10:1) and concentrated in vacuo. This 4-(4-(2-methoxy-phenyl) -piperazinyl) -butyl-1-primary amine (200 mg, 0.76 mmol) was dissolved in 4.0 mL chloroform, and 208 mg K_2CO_3 was added. The 2-naphthoyl chloride (144 mg, 0.76 mmol) was dissolved in proper amount of chloroform, and then dropped into a three-way flask of 10.0 mL with a constant pressure drop funnel. Titration reaction 1h, extraction, mother solution decompression concentration to obtain a light yellow solid, ether recrystallization to obtain *N*-[4-(2-methoxy-phenyl) -piperazinyl]-butyl-2-naphthoformamide (**16**, 307 mg, 97 %) as a white solid .



16. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.8 Hz, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.00-7.90 (m, 2H), 7.88-7.80 (m, 2H), 7.57-7.43 (m, 2H), 7.10-7.01 (m, 1H), 6.93-6.82 (m, 3H), 3.83 (s, 3H), 3.60

(q, J = 6.1 Hz, 4H), 3.43 (d, J = 4.7 Hz, 4H), 3.19-2.90 (m, 4H), 2.05 (q, J = 7.4 Hz, 2H), 1.80 (q, J = 6.5 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 152.0, 138.8, 134.7, 132.7, 131.4, 129.2, 128.14, 128.10, 127.6, 127.5, 126.4, 124.3, 124.2, 121.2, 118.8, 111.3, 56.4, 55.4, 52.3, 47.4, 38.1, 26.1, 20.7 ppm;

HR-MS (ESI/TOF) m/z: Calcd. for $C_{26}H_{32}N_3O_2$ $[M+H]^+$ 418.2495; Found: 418.2528.

Preparation of buspirone (18)

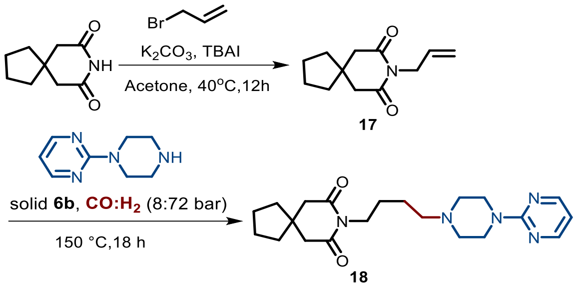
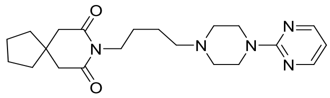


Fig. S12. Preparation of buspirone.

To a solution of 8-azaspiro[4.5]decane-7,9-dione (1.19 g, 7.11 mmol, 1.0 equiv.) in acetone (15 mL) was added allyl bromide (0.675 mL, 7.8 mmol, 1.1 equiv.), K_2CO_3 (1.96 g, 14.2 mmol, 2.0 equiv.) and TBAI (0.25 g, 0.68 mmol, 9.5 mol%). After stirring for 72 h at roomtemperature, the reaction mixture was filtered through Celite and the filtrate concentrated in vacuo to give the crude which was purified via column chromatography (pentane/EtOAc= 1/10) to give **17** (1.32 g, 6.35 mmol, 89%) as a colourless oil. In a typical experiment, a Parr stainless steel autoclave (125 mL) was loaded with a mixture of **6b** (1.0 mol %), 10.0 mmol **17**, 5.0 mmol 2-(piperazin-1-yl)pyrimidine and 20.0 mL THF. Subsequently, the autoclave was pressurized with CO (8 bar) and hydrogen (72 bar) and heated to 150 °C. After 18 h, the autoclave was allowed to cool to room temperature and the gases were vented. The solvent was removed under vacuum, the resulting crude **18** (63% as determined by ^{1}H NMR of the crude with 1,3,5-methoxybenzene as the internal standard, $l:b$ = 96/4) was then purified via column chromatography (CH_2Cl_2 / EtOAc =1:200) to give buspirone as a colourless solid.



18.[18] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, J = 4.7 Hz, 2H), 6.45 (t, J = 4.8 Hz, 1H), 3.82-3.74 (m, 6H), 2.57 (s, 4H), 2.47 (t, J = 5.1 Hz, 4H), 2.37 (t, J = 6.8 Hz, 2H), 1.72-1.67 (m, 4H), 1.54-1.45 (m, 8H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 161.7, 157.7, 109.7, 58.3, 53.1, 44.9, 43.7, 39.5, 39.4, 39.3, 37.6, 26.1, 24.25, 24.19 ppm.

5. SEM, TEM, EDX & HAADF-STEM images of coordination assemblies

5.1 SEM images of coordination assemblies

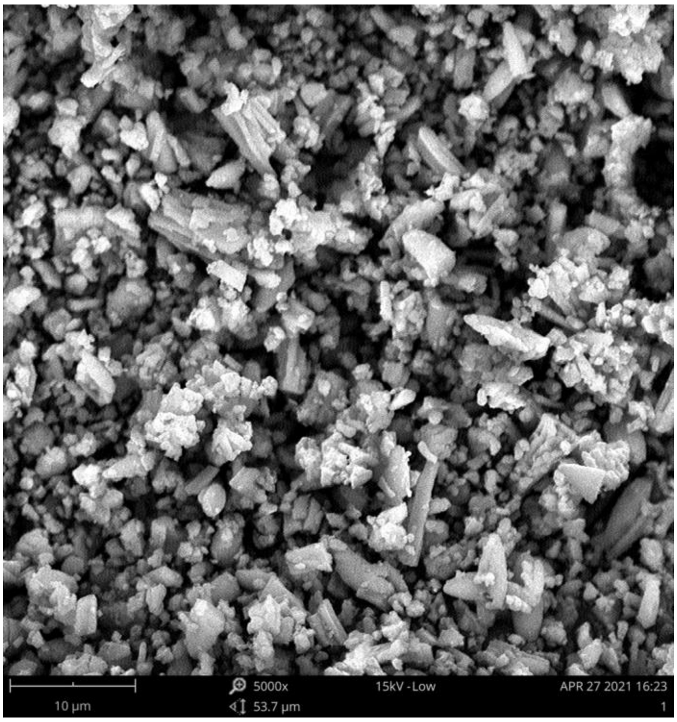


Fig. S13. SEM image of freshly prepared NHC-Rh coordination assembly **5** (scale bar 10 μm).

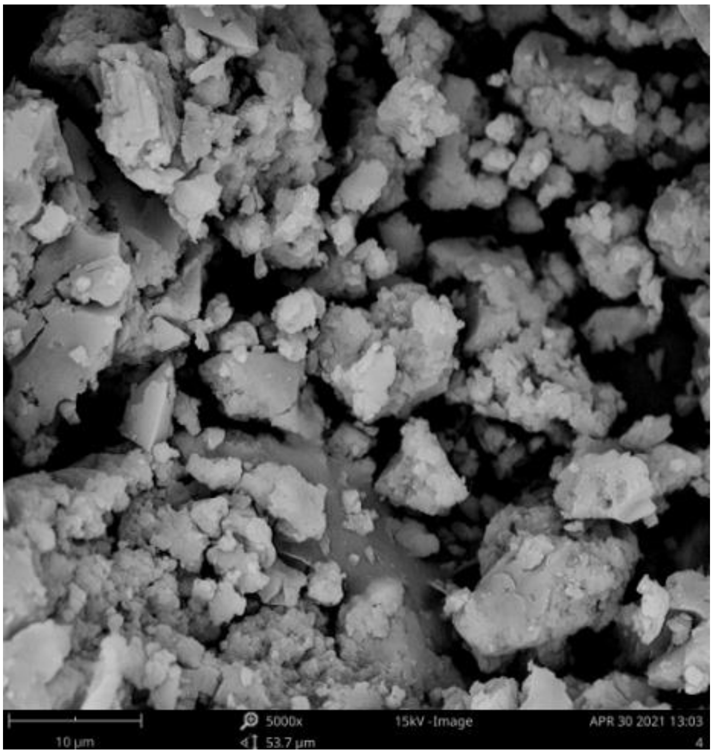


Fig. S14. SEM image of freshly prepared NHC-Rh coordination assembly **6a** (scale bar 10 μm).

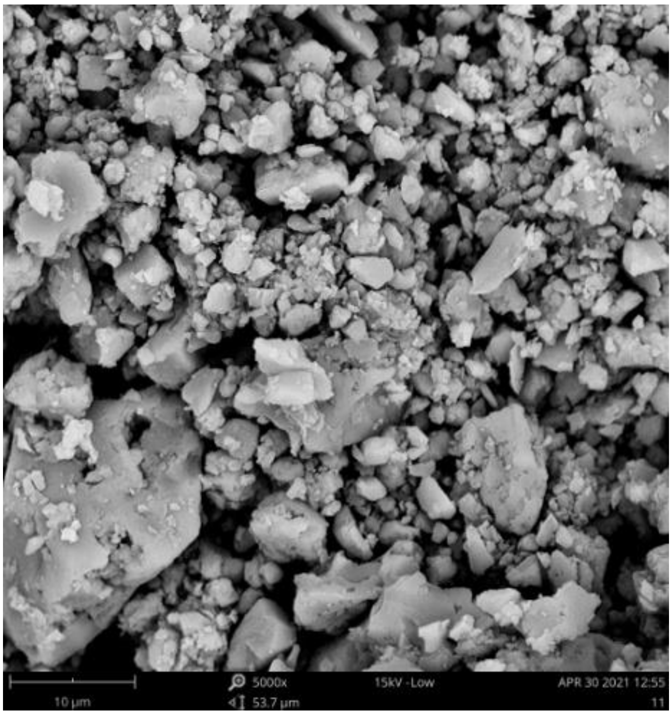


Fig. S15. SEM image of freshly prepared NHC-Rh coordination assembly **6b** (scale bar 10 µm).

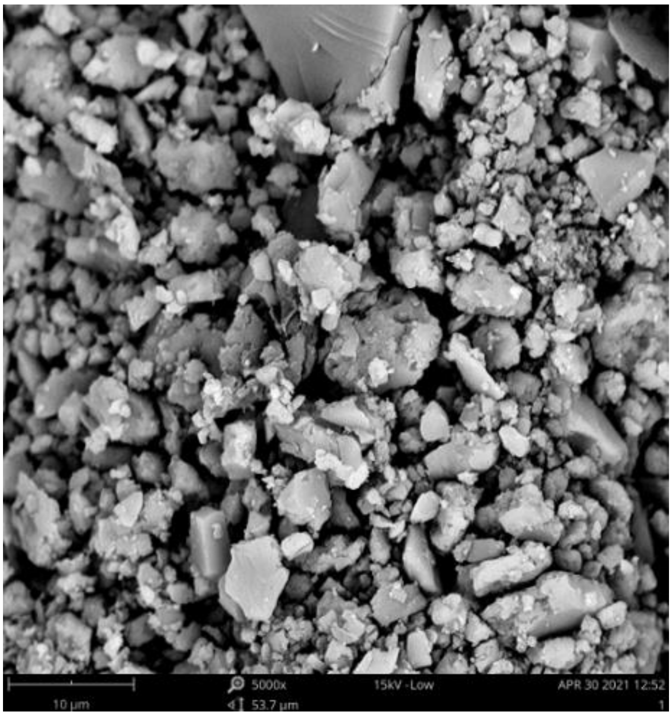


Fig. S16. SEM image of freshly prepared NHC-Rh coordination assembly **6c** (scale bar 10 µm).

5.2 EDX of coordination assemblies

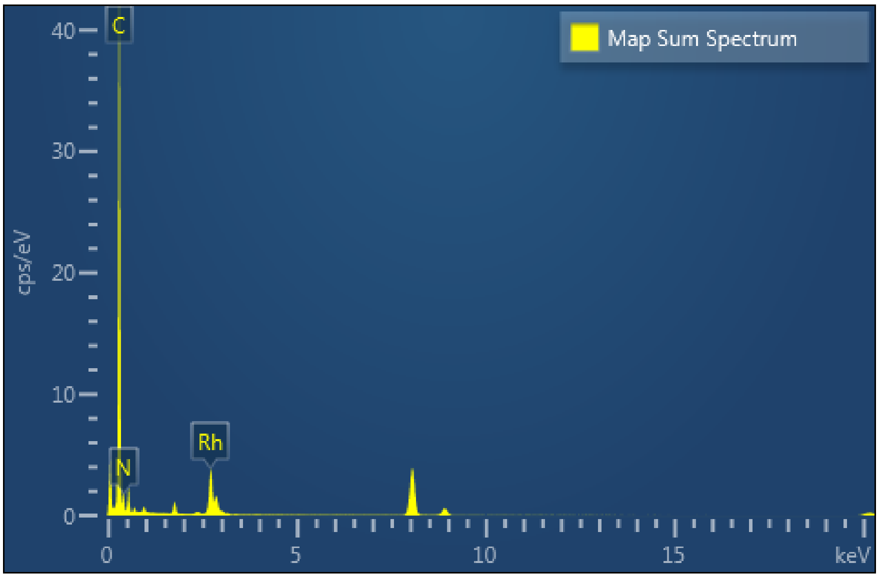


Fig. S17. EDX pattern of newly prepared NHC-Rh coordination assembly **6b** measured with TEM.

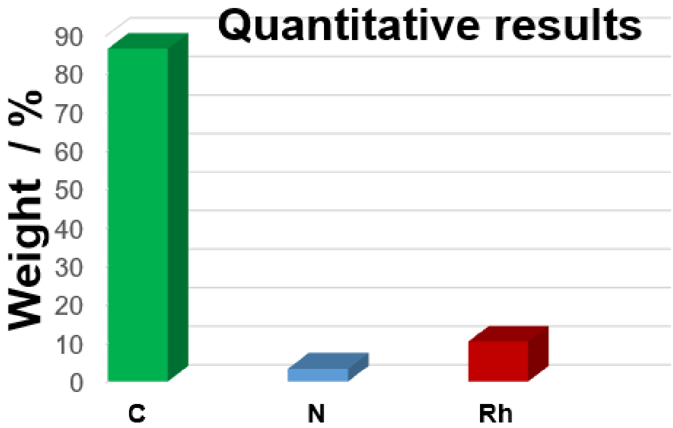


Fig. S18. EDX pattern in percentage of newly prepared NHC-Rh coordination assembly **6b** measured with TEM. The Cu signal originates from the microgate used.

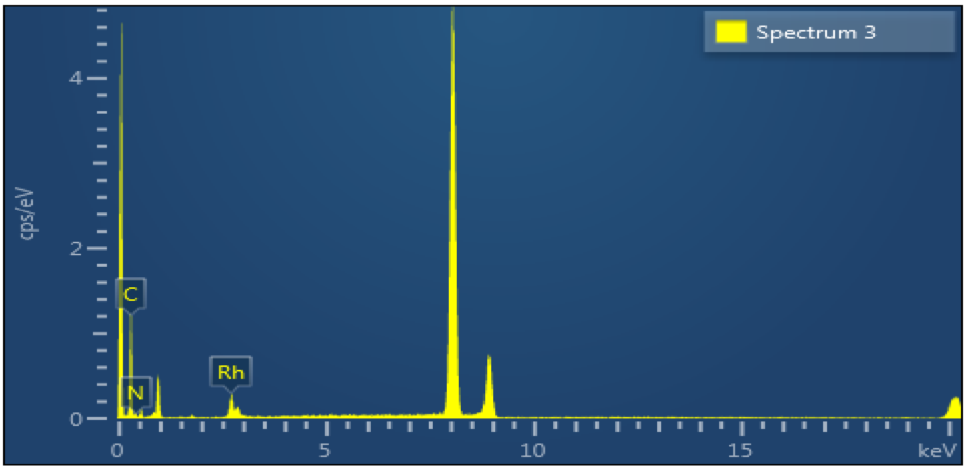


Fig. S19. EDX pattern of recovered NHC-Rh coordination assembly **6b** measured with TEM.

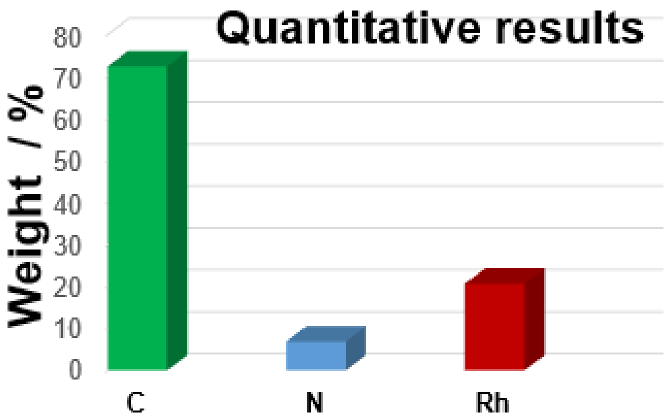


Fig. S20. EDX pattern in percentage of recovered NHC-Rh coordination assembly **6b** measured with TEM. The Cu signal originates from the microgate used.

5.3 Magnified HAADF-STEM images of NHC-Rh coordination assembly 6b

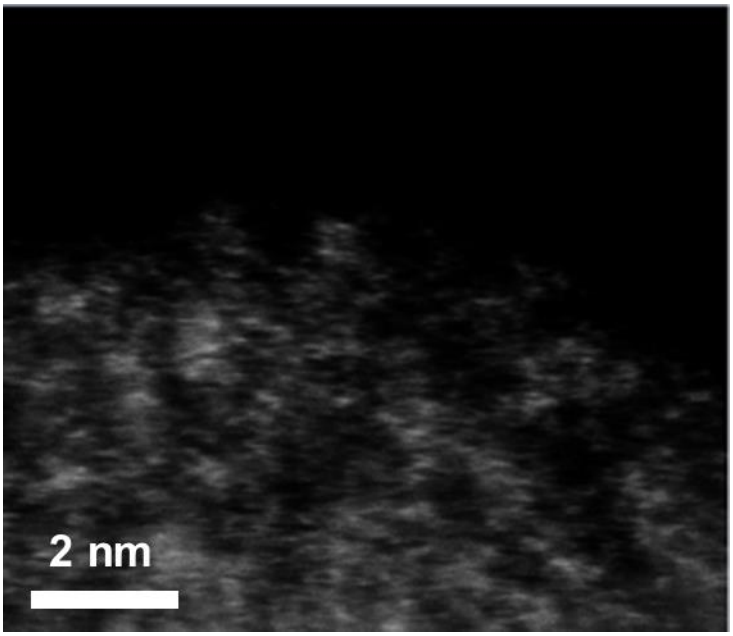


Fig. S21. Magnified HAADF-STEM image of freshly prepared NHC-Rh coordination assembly **6b** (scale bar 2 nm).

5.4 SEM, TEM, EDX & HAADF-STEM images of recovered NHC-Rh coordination assembly 6b

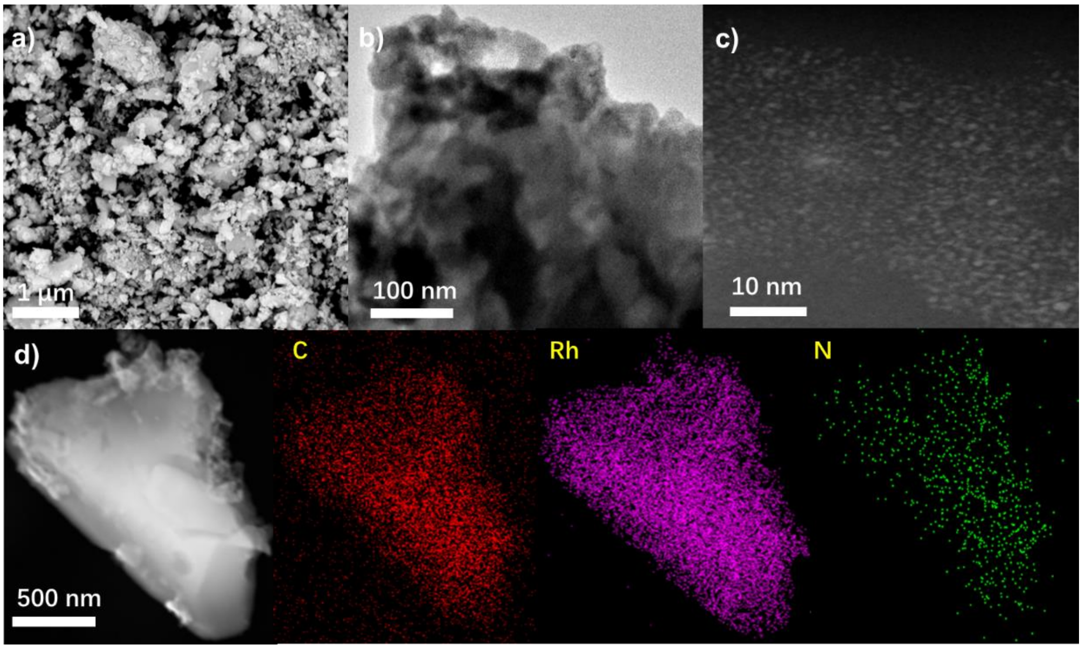


Fig. S22. (a) SEM, (b) TEM, and (c) magnified HAADF-STEM images of the recovered solid **6b** (white dots represent individual Rh atoms), respectively. (d) EDS mapping of the recovered solid **6b**.

6. XPS, PXRD, Solid-state ^{13}C NMR, FT-IR, TG & N_2 sorption studies

6.1 XPS spectra of coordination assemblies

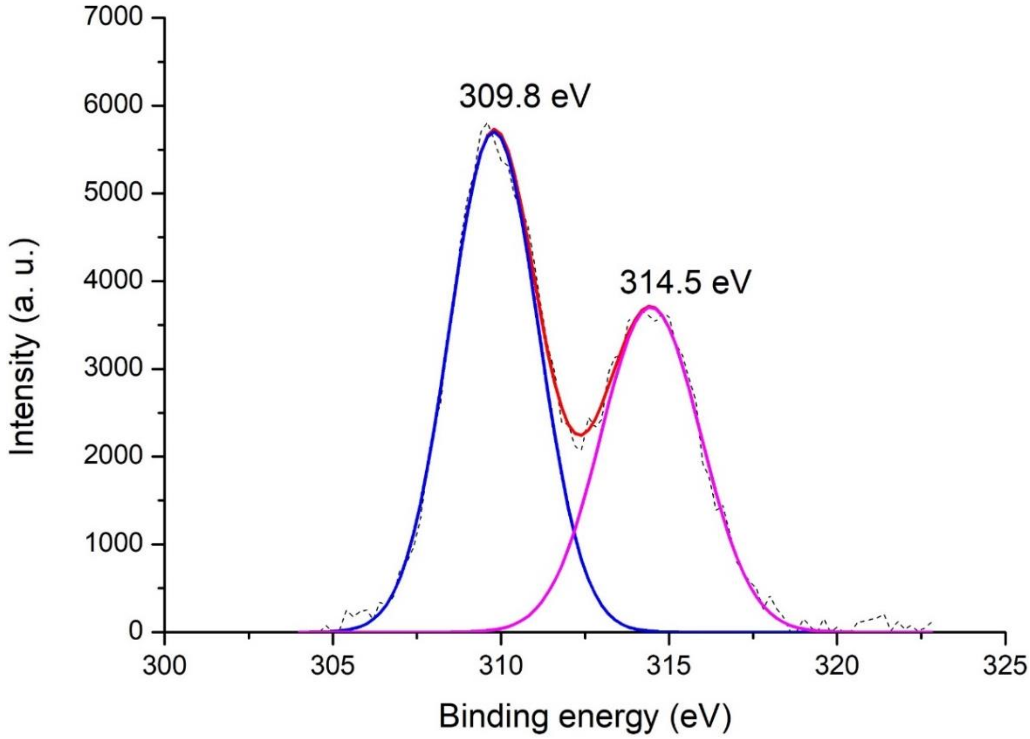


Fig. S23. XPS spectrum of freshly prepared NHC-Rh coordination assembly **5**.

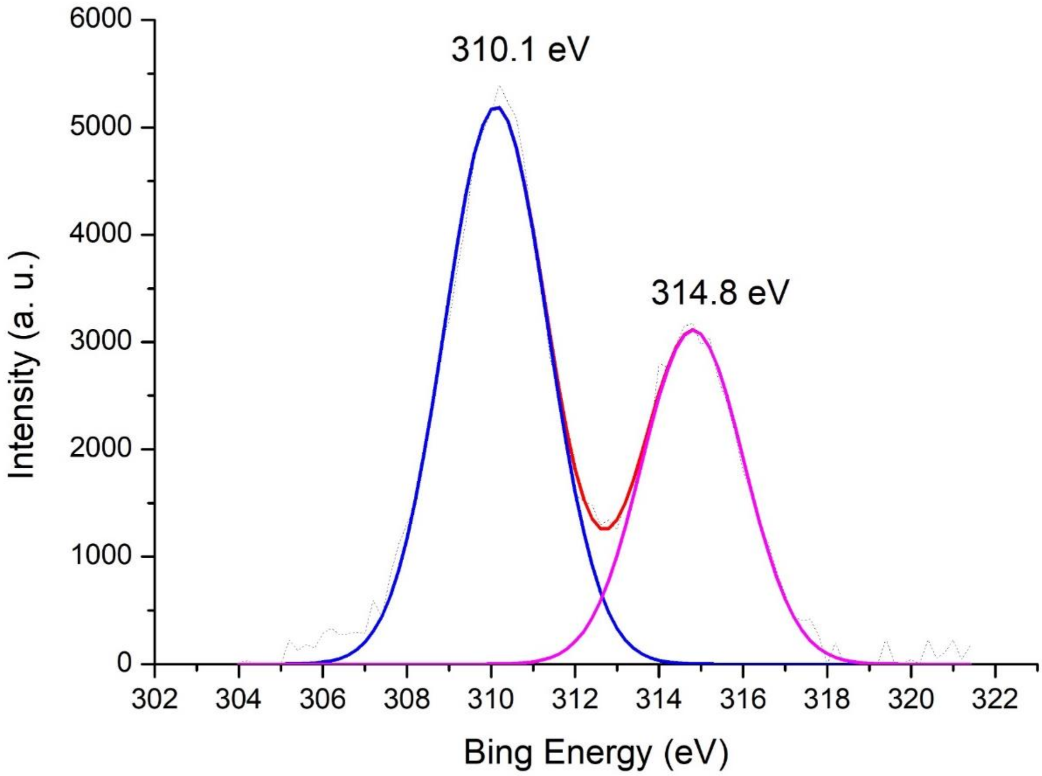


Fig. S24. XPS spectrum of freshly prepared NHC-Rh coordination assembly **6a**.

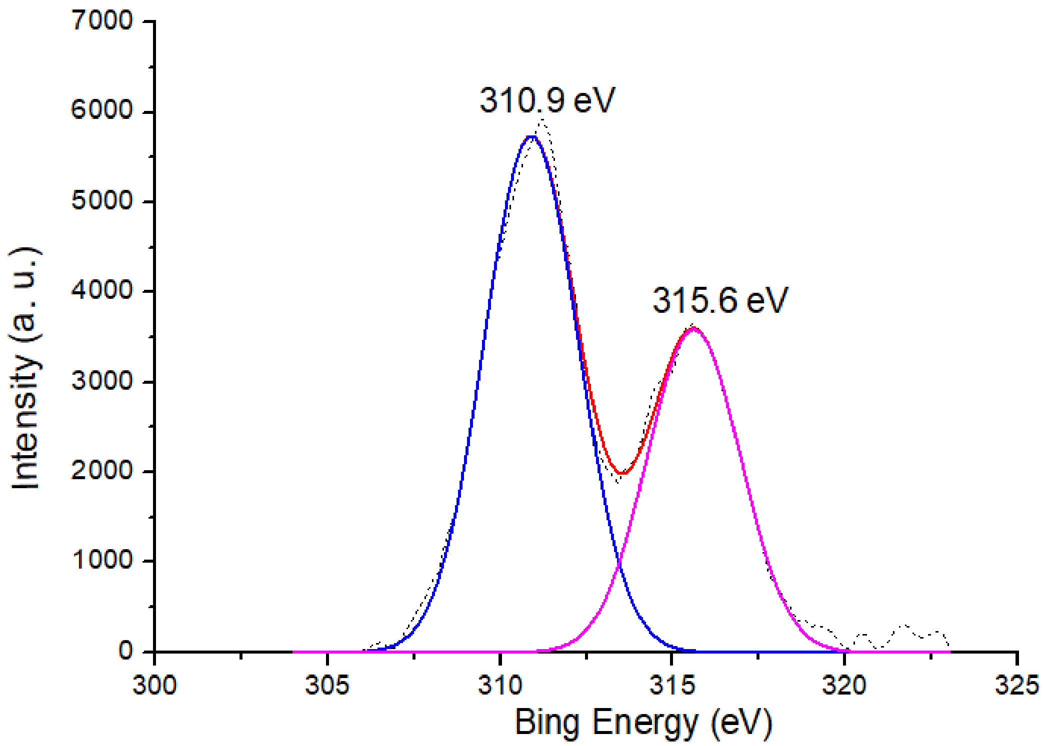


Fig. S25. XPS spectrum of freshly prepared NHC-Rh coordination assembly **6b**.

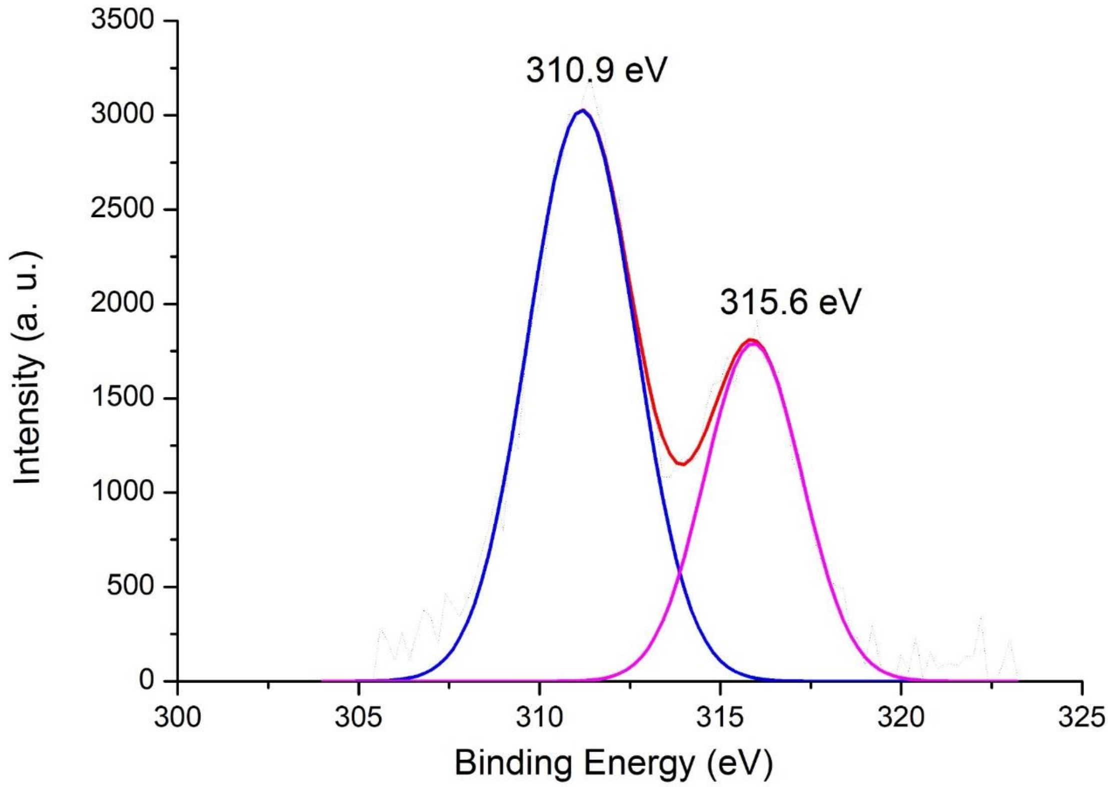


Fig. S26. XPS spectrum of freshly prepared NHC-Rh coordination assembly **6c**.

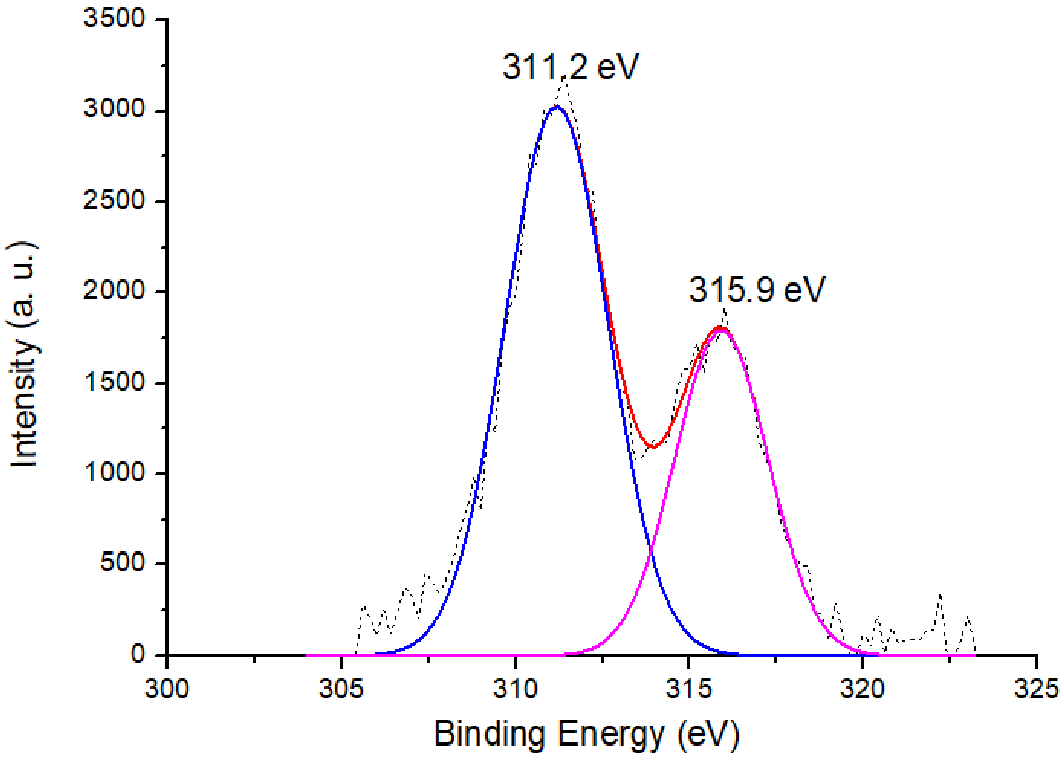


Fig. S27. XPS spectrum of homogeneous bis-NHC-Rh complex **4b**.

6.2 PXRD spectra of coordination assemblies

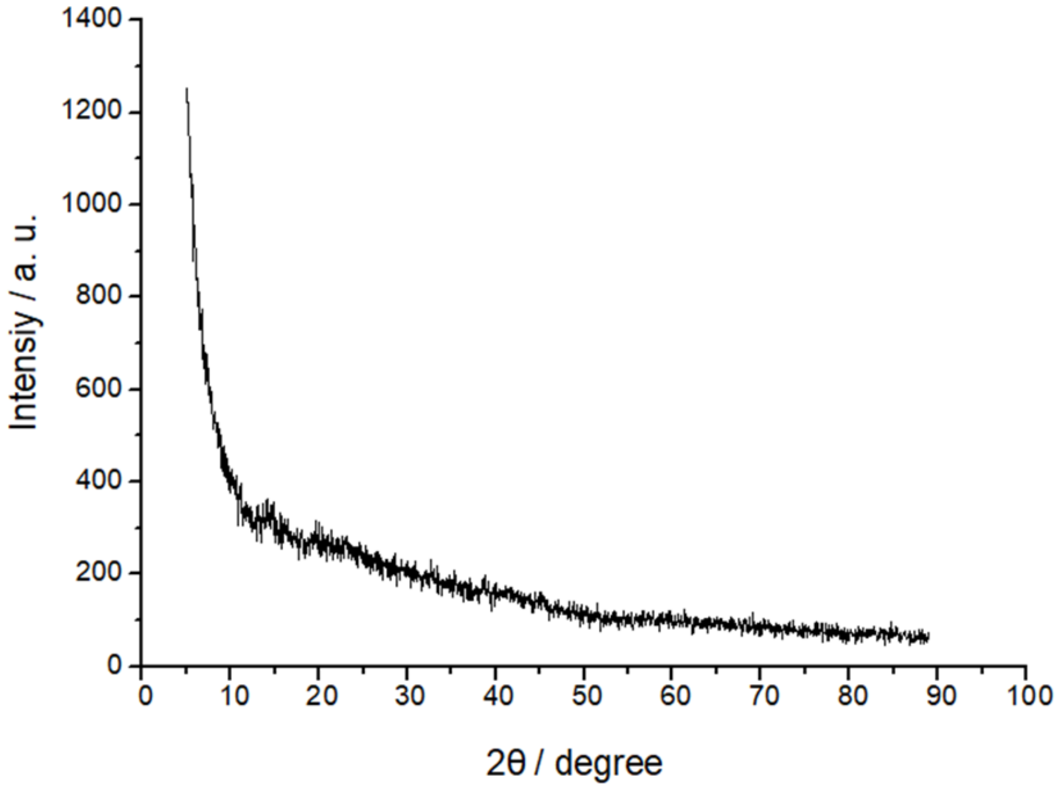


Fig. S28. PXRD spectrum of freshly prepared NHC-Rh coordination assembly **6b**.

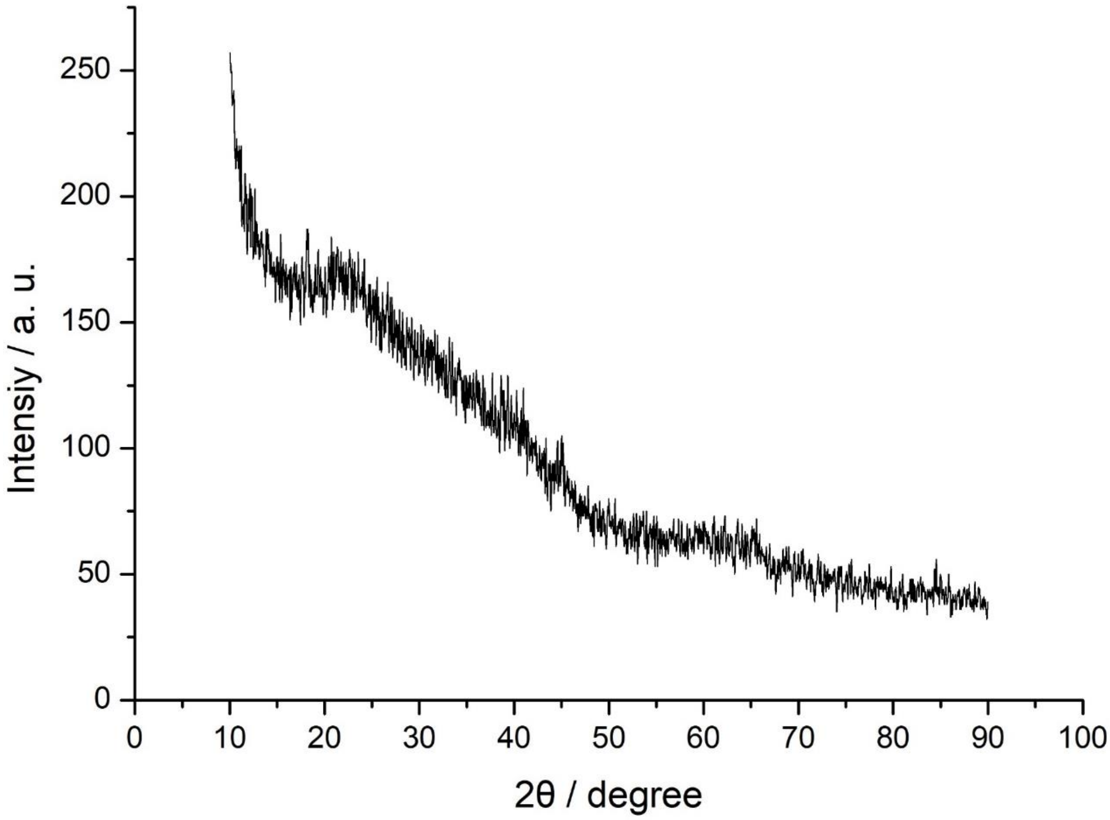


Fig. S29. PXRD spectrum of recovered NHC-Rh coordination assembly **6b**.

6.3 Solid-state ^{13}C NMR spectra

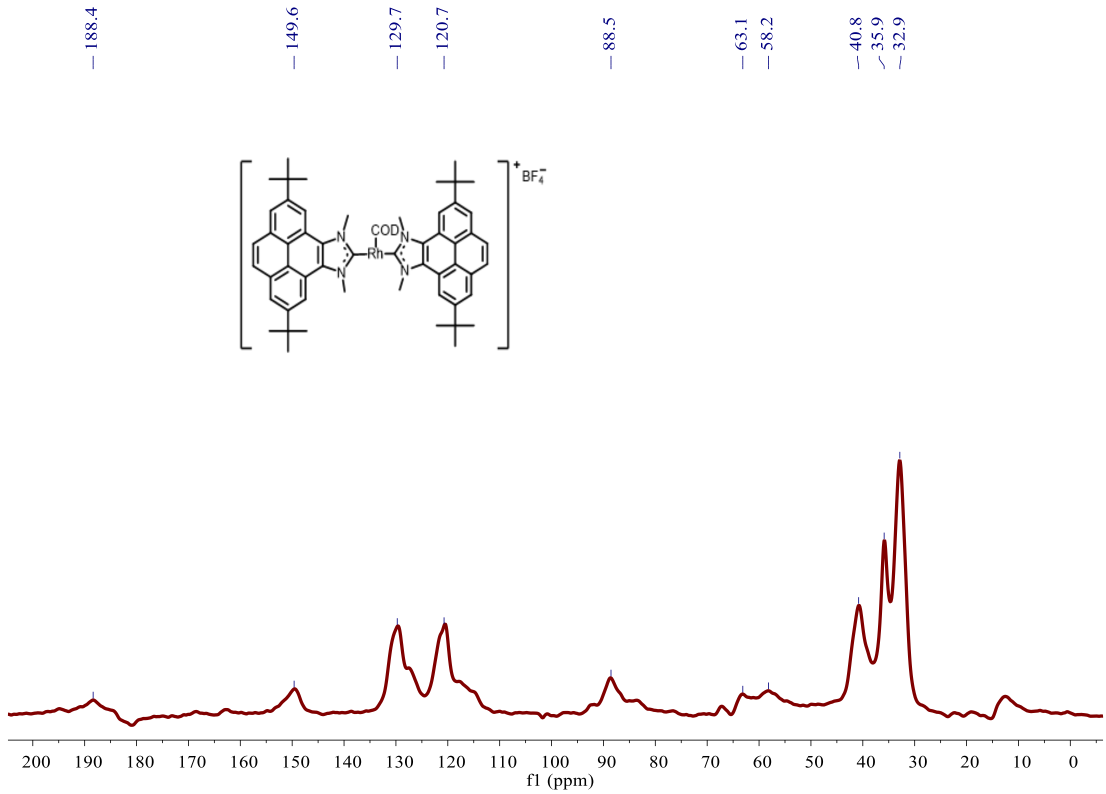


Fig. S30. Solid-state ^{13}C NMR spectrum of NHC-Rh complex **4b**.

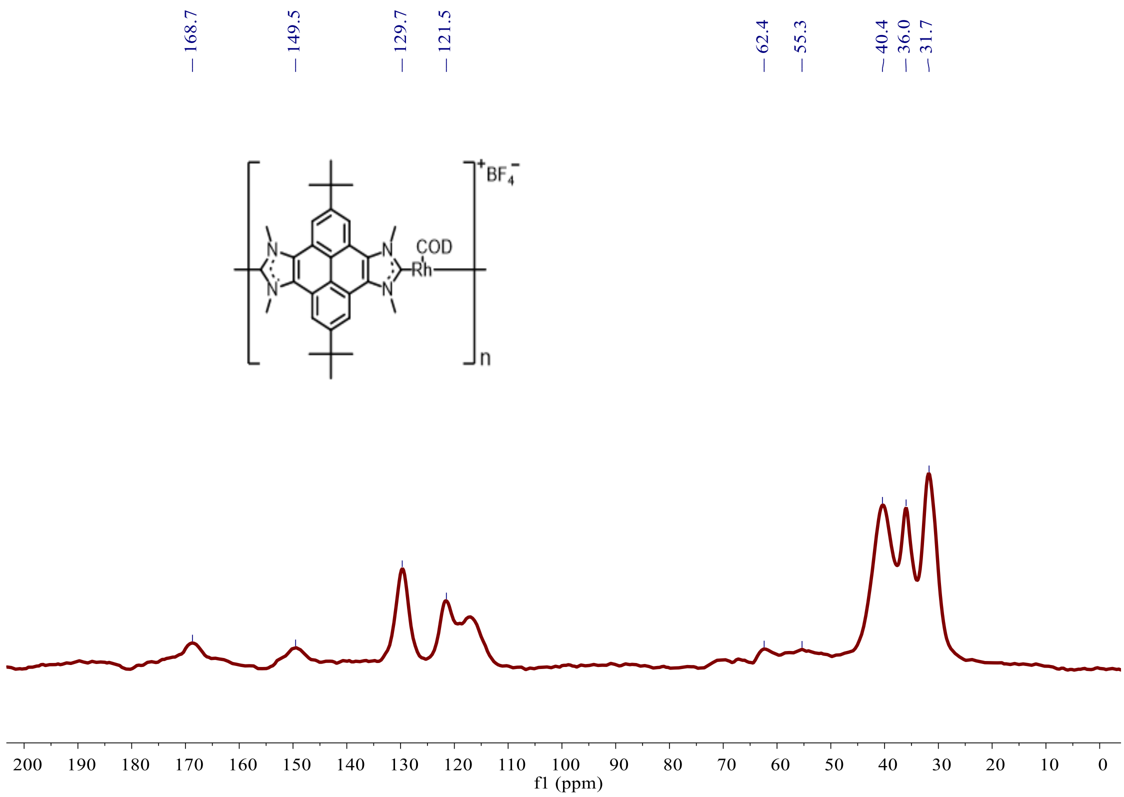


Fig. S31. Solid-state ^{13}C NMR spectrum of freshly prepared NHC-Rh coordination assembly **6b.**

6.4 FT-IR spectra of coordination assemblies

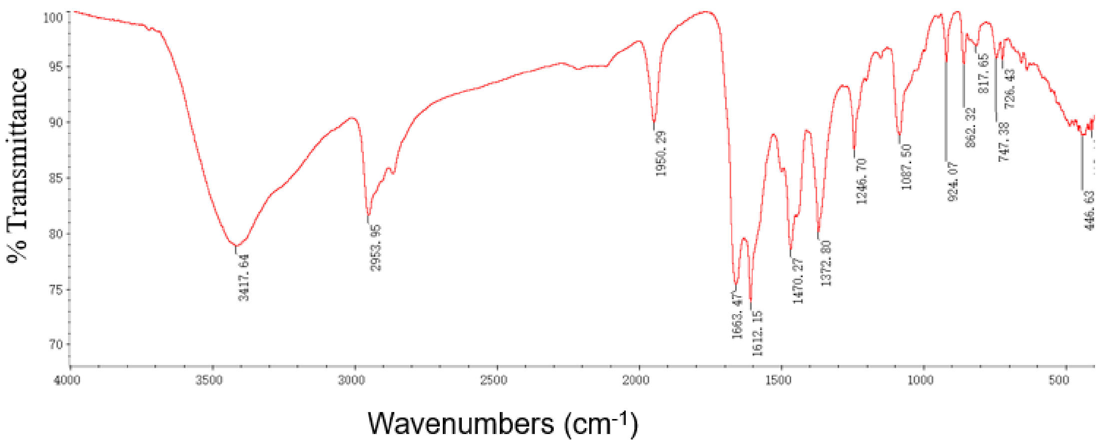


Fig. S32. FT-IR spectrum of freshly prepared NHC-Rh complex **4b.**

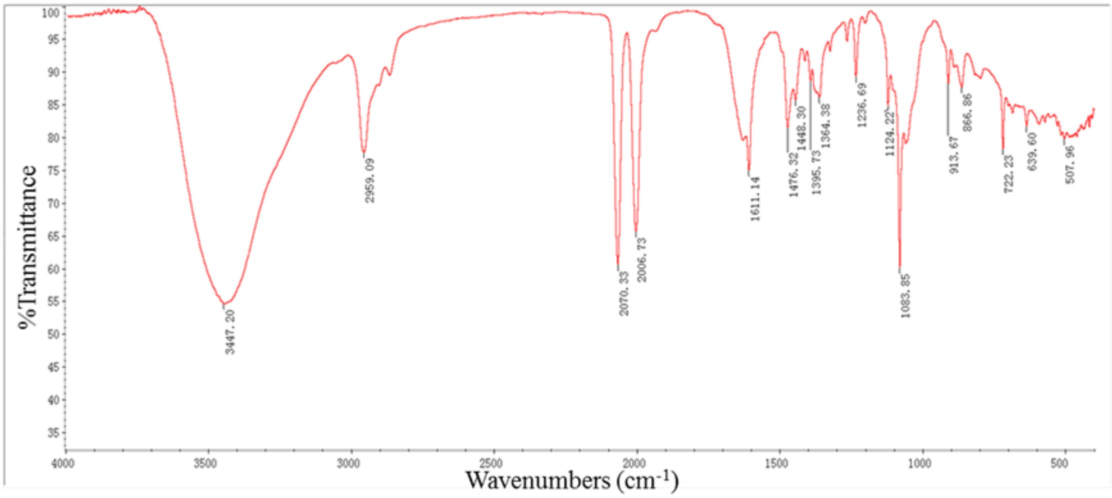


Fig. S33. FT-IR spectrum of freshly prepared NHC-Rh complex **4a.**

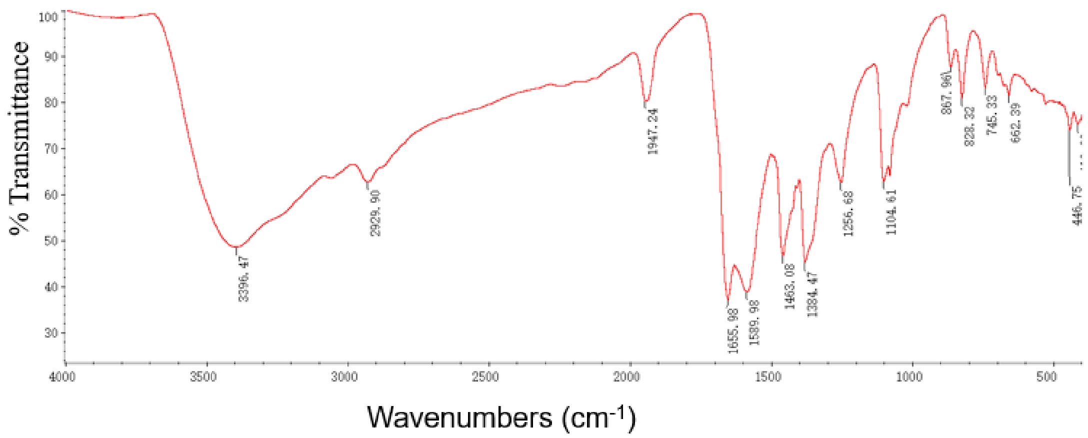


Fig. S34. FT-IR spectrum of freshly prepared NHC-Rh coordination assembly **5**.

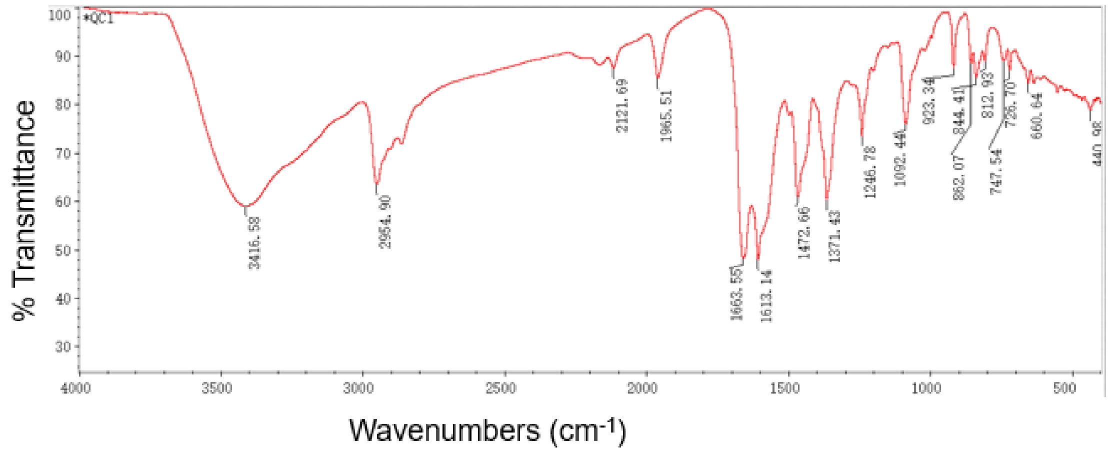


Fig. S35. FT-IR spectrum of freshly prepared NHC-Rh coordination assembly **6a**.

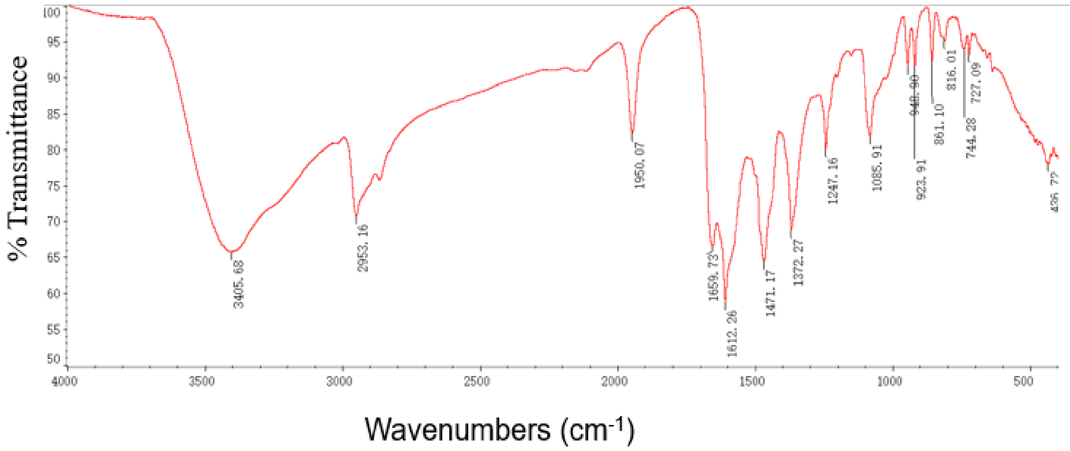


Fig. S36. FT-IR spectrum of freshly prepared NHC-Rh coordination assembly **6b**.

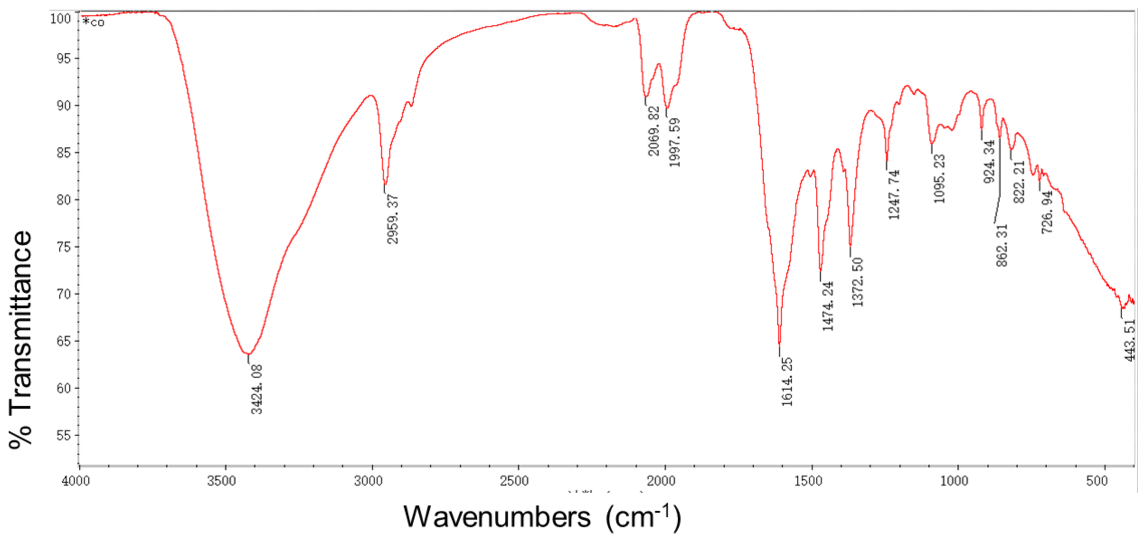


Fig. S37. FT-IR spectrum of recovered NHC-Rh coordination assembly **6b** after the 18th run.

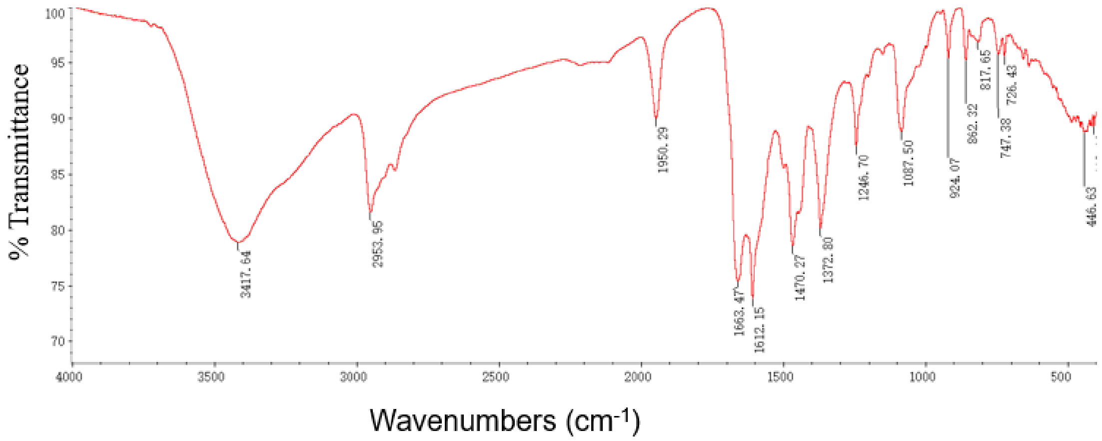


Fig. S38. FT-IR spectrum of freshly prepared NHC-Rh coordination assembly **6c**.

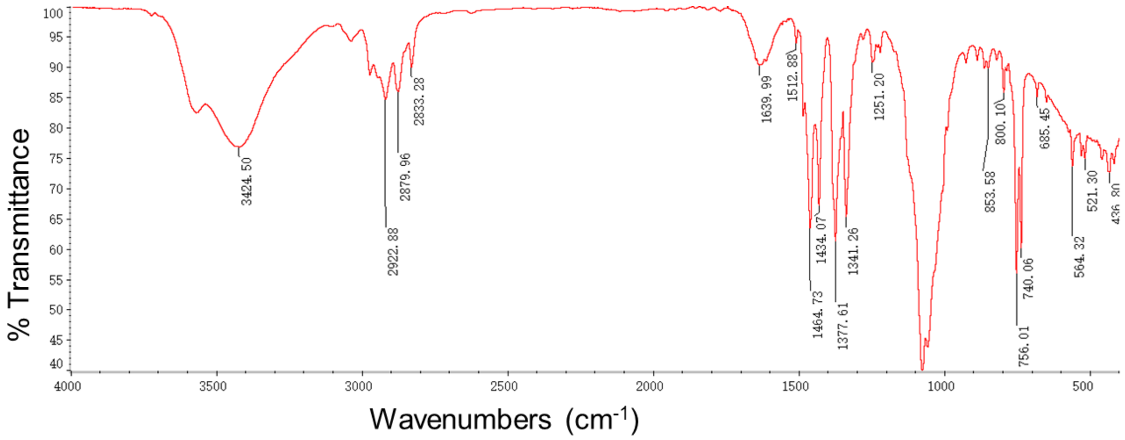


Fig. S39. FT-IR spectrum of freshly prepared NHC-Rh complex **6b** after 200 °C**.**

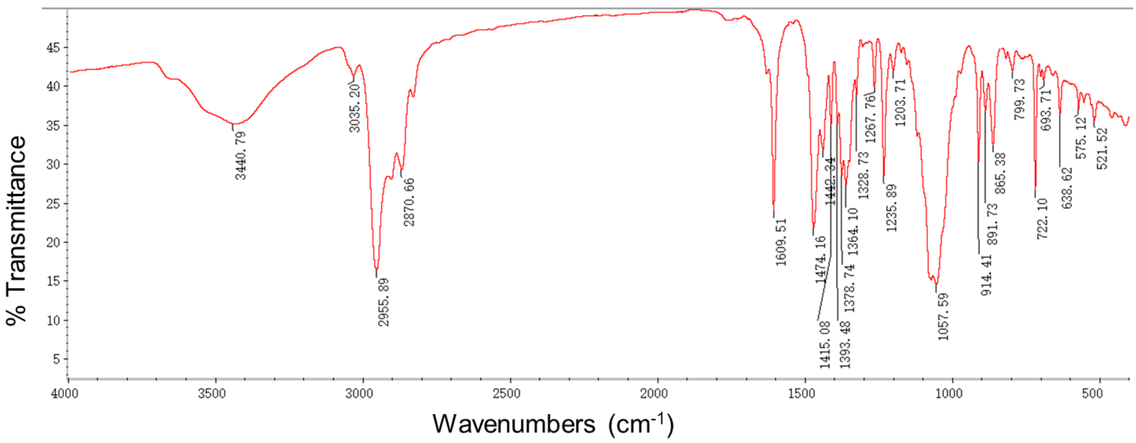


Fig. S40. FT-IR spectrum of freshly prepared NHC-Rh complex **6a** after 200 °C**.**

6.5 TG spectra of coordination assemblies

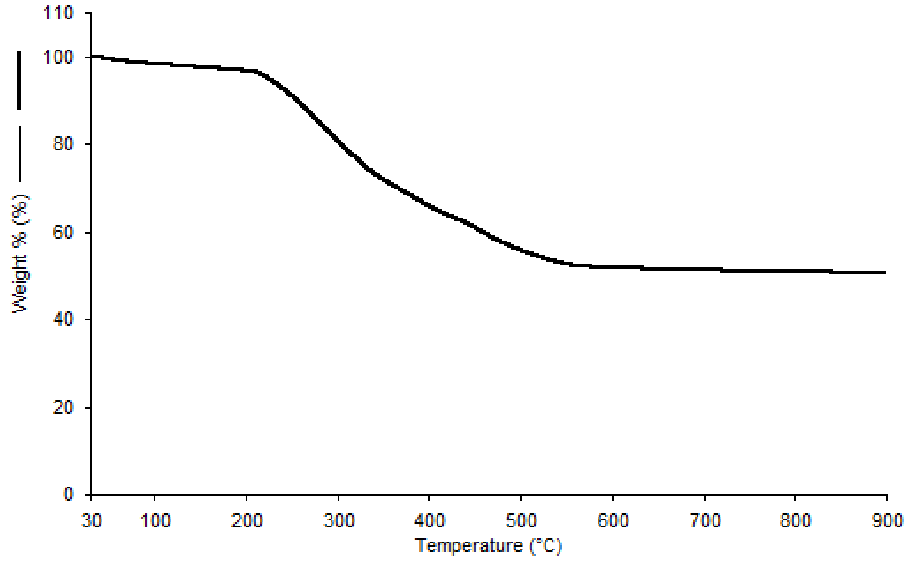


Fig. S41. TG spectrum of freshly prepared NHC-Rh coordination assembly **6a**.

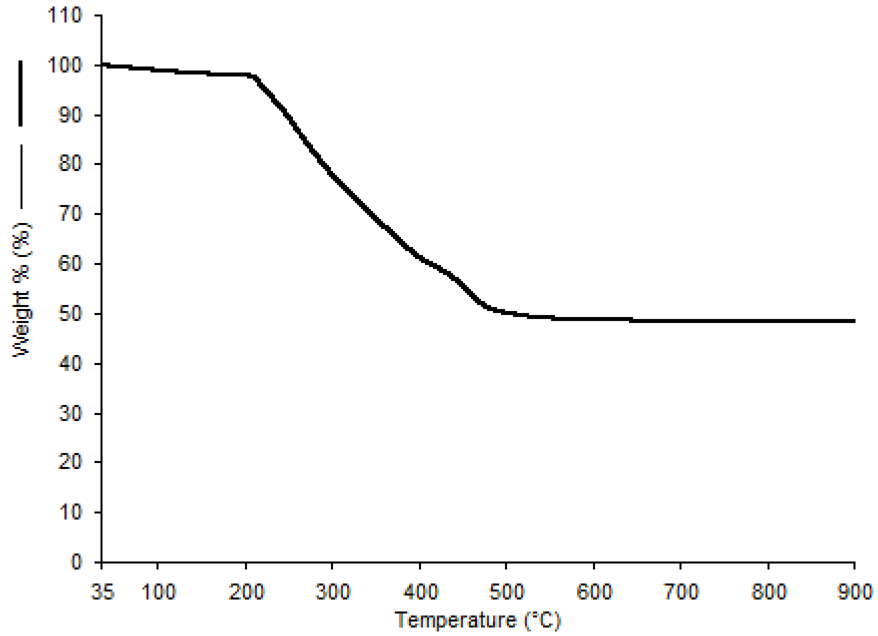


Fig. S42. TG spectrum of freshly prepared NHC-Rh coordination assembly **6b**.

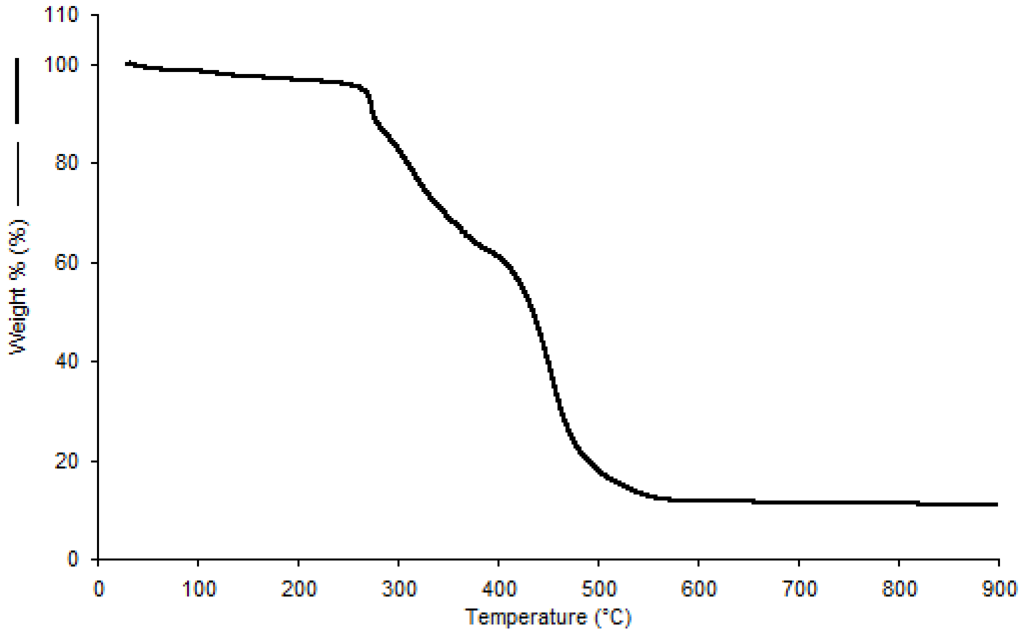


Fig. S43. TG spectrum of freshly prepared NHC-Rh coordination assembly **6c**.

6.6 N_2 sorption isotherm of NHC-Rh coordination assembly 6b

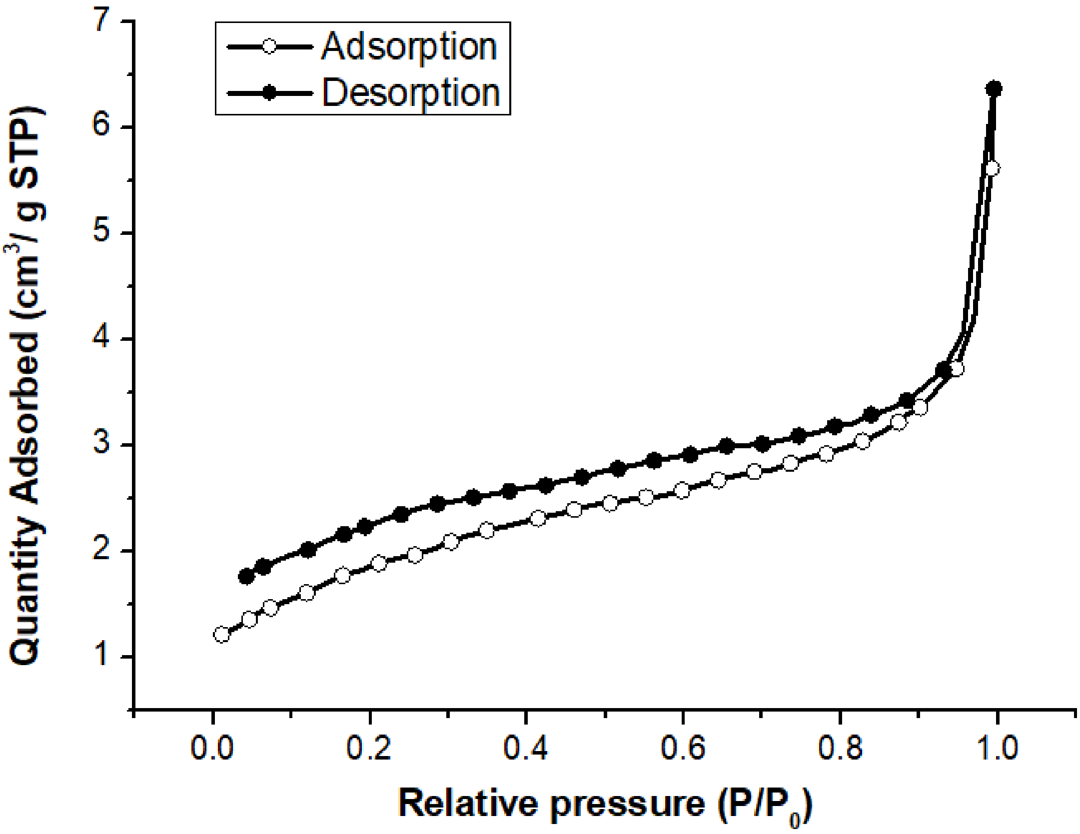


Fig. S44. N_2 sorption isotherm of NHC-Rh coordination assembly **6b**.

7. XANES, k^2-weighted EXAFS& Gel permeation chromatography studies

Table S2. The best-fifitted EXAFS results of Rh sample [a]

Sample	Shell	CN	R(Å)	σ^2 (10^{-2} Å^2)	ΔE_0 (eV)	r-factor (%)
Rh foil	Rh-Rh	12	2.69	0.4	-7.1	2
Solid 6b	Rh-C	3.1	2.11	0.05	-5.1	
Rh sample	Rh-C	7.7	2.06	0.2	-9.9	0.4

[a] CN is the coordination number for the absorber-backscatterer pair, R is the average absorber-backscatterer distance, σ^2 is the Debye-Waller factor, and ΔE0 is the inner potential correction. The accuracies of the above parameters are estimated as CN, ±20%; R, ±1%; σ^2, ± 20%; ΔE_0, ±20%. The data range used for data fitting in k-space (Δk) and R-space (ΔR) are 3.0-13.6 Å^{-1} and 1.0-1.9 Å, respectively.

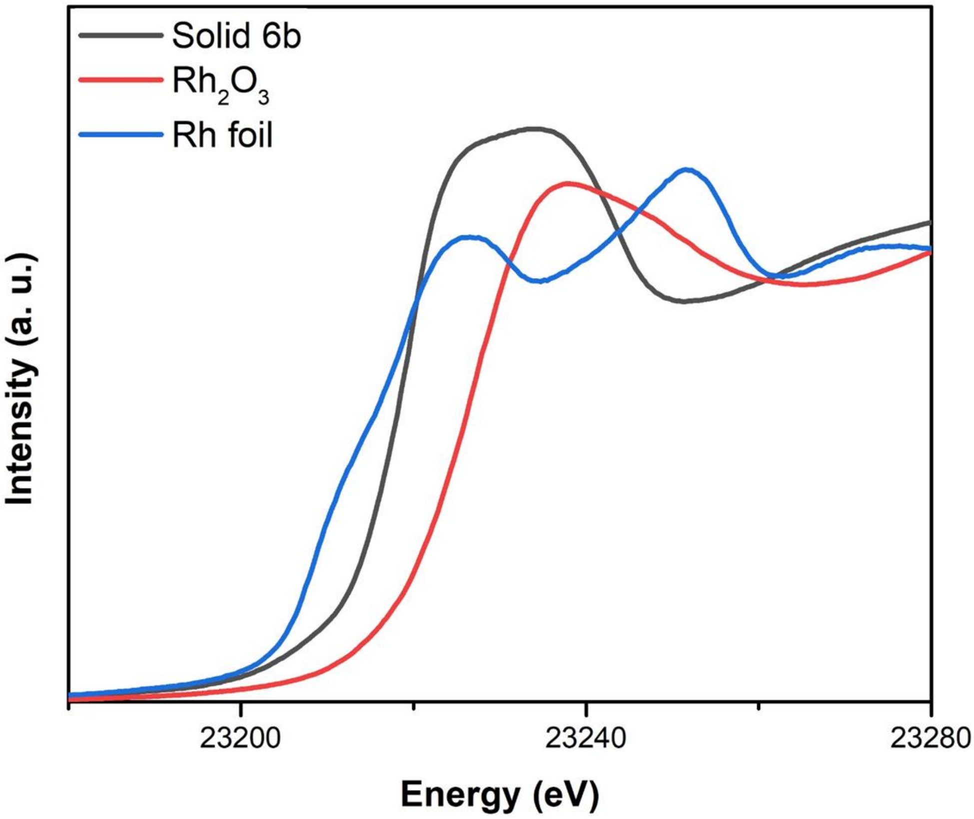


Fig. S45. The normalized XANES spectra at the Rh K-edge of the solid **6b**, Rh_2O_3 and Rh foil.

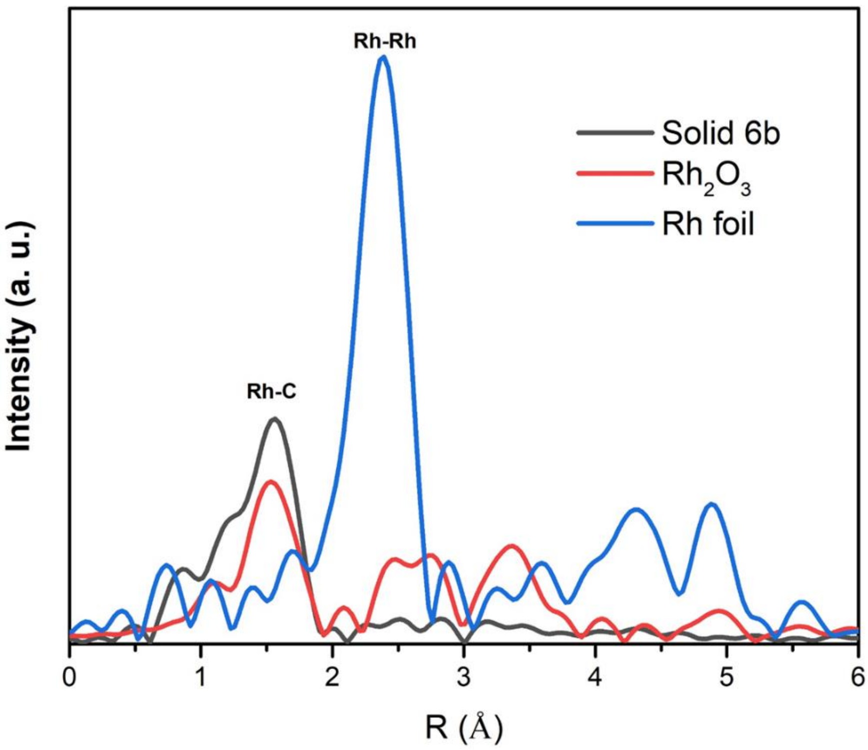


Fig. S46. The Fourier transform of k ^{2} -weighted EXAFS spectra at the K-edge of the solid **6b**, Rh_2O_3 and Rh foil

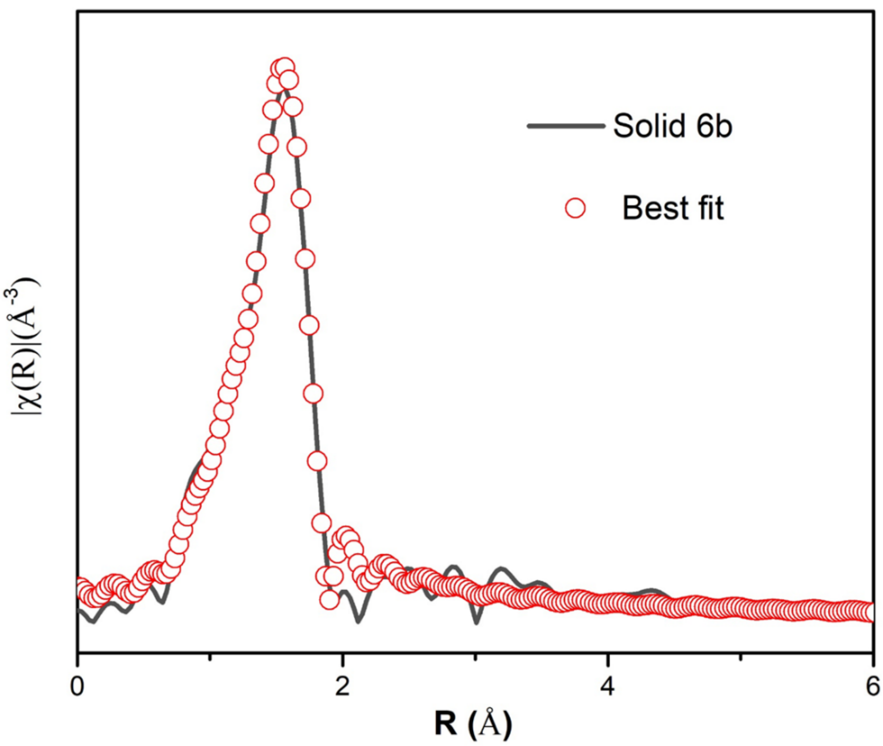
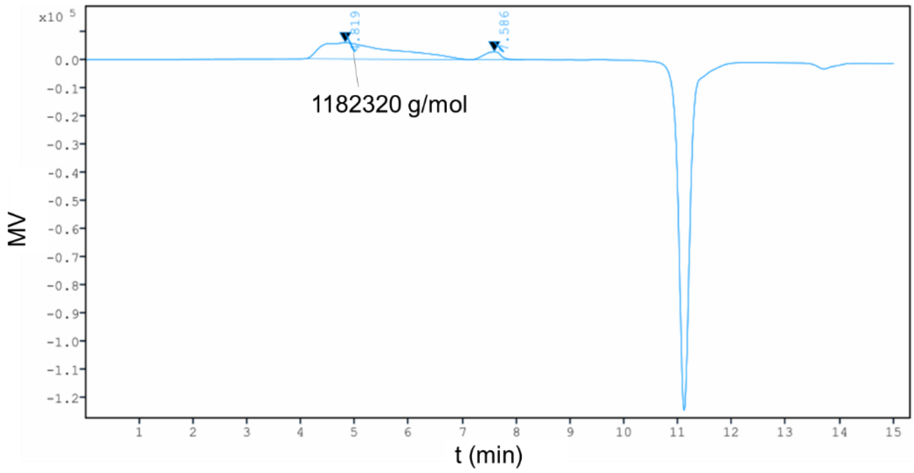


Fig. S47. The experimental Rh EXAFS spectra (black line) and the fitting curve of solid **6b** (red line)

8. Gel permeation chromatography (GPC) Study

Due to its insolubility of solid NHC-Rh coordination assembly **6b** even in hot DMF or DMSO, we performed GPC analysis on its oligomer **6b'**, which was prepared with bis-NHC ligand and rhodium precursor in a ratio of 20:21 under the otherwise identical preparation method. The obtained solid could be partially dissolved in hot DMSO, which make it is possible to be measured by GPC.



GPC result

	RT		Mn	Mw	Mz	Mz+1
1	4.819	8908501	1182320	9190058	24696017	35719546
2	7.586	45451	46756	49486	52078	54576

Fig. S48. GPC result of NHC-Rh coordination assembly **6b'**.

9. Metal-leaching tests with ICP-AES

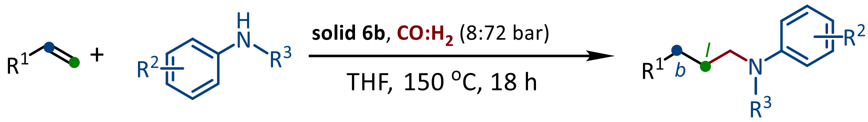
Table S3. Rhodium leaching tests with the filtrates of the reaction mixture after consecutive runs[a].

[Cat.]	Run	Conc. of Rh (mg/L)
6b	1	0.0856
6b	2	0.0741
6b	3	0.0631
6b	7	<0.03
6b	10	<0.03
6b	14	<0.03
6b	18	<0.03

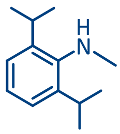
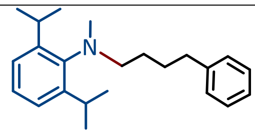
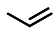
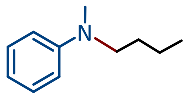
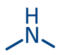
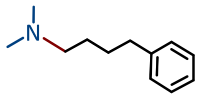
[a] ICP-AES analysis of the reaction filtrates after each consecutive run (reaction was carried at 1 mmol scale with 1 mol % **6b**). After filtration, the recovered catalyst was washed with 10 mL methanol and 10 mL dichloromethane then separated with centrifuging. After full volatilization of the dichloromethane at r.t, the residue was diluted to 500 mL as an alkaline or higher concentration will both cause a flameout of ICP-AES. The corresponding amount of Rh in the original mixture is 0.5 × the concentration measured with ICP-AES (mg).

Table S4. **Substrate scope of olefins and amines** [a]

Extremely bulky 2, 6-diisopropyl-*N*-methylaniline was selected as the amine substrate, no corresponding amine product was detected. We have applied propene as the smallest olefin in our study, one of the most important substrates in industry, the corresponding amine **9ma-2** was still produced 84% yield with 95/5 selectivity, demonstrating the high efficiency of our strategy. When *N*, *N*-dimethylamine, with better nucleophilicity than aromatic amines, was applied, no corresponding product was obtained.



7a or **7ma-2** **8a or 8q-r** **9aq-ar** or **9ma-2**

Entry 1	 **8q**	 **9aq**: 0%
Entry 2	 **7ma-2**	 **9ma-2**: 84%, *l*/*b*=95/5
Entry 3	 **8r**	 **9ar**: 0%

[a] Reaction conditions: 1.25 mmol olefin, 0.5 mmol amine, 1 mol % solid catalyst **6b**, 4.0 mL THF, $CO:H_2$ (80 bar, 1:9), 150 °C, 18 h (All yields reported are isolated yields and regioselectivities were determined by ^1H NMR of the crude reaction mixture)

10. ^{1}H, ^{13}C and ^{19}F NMR spectra

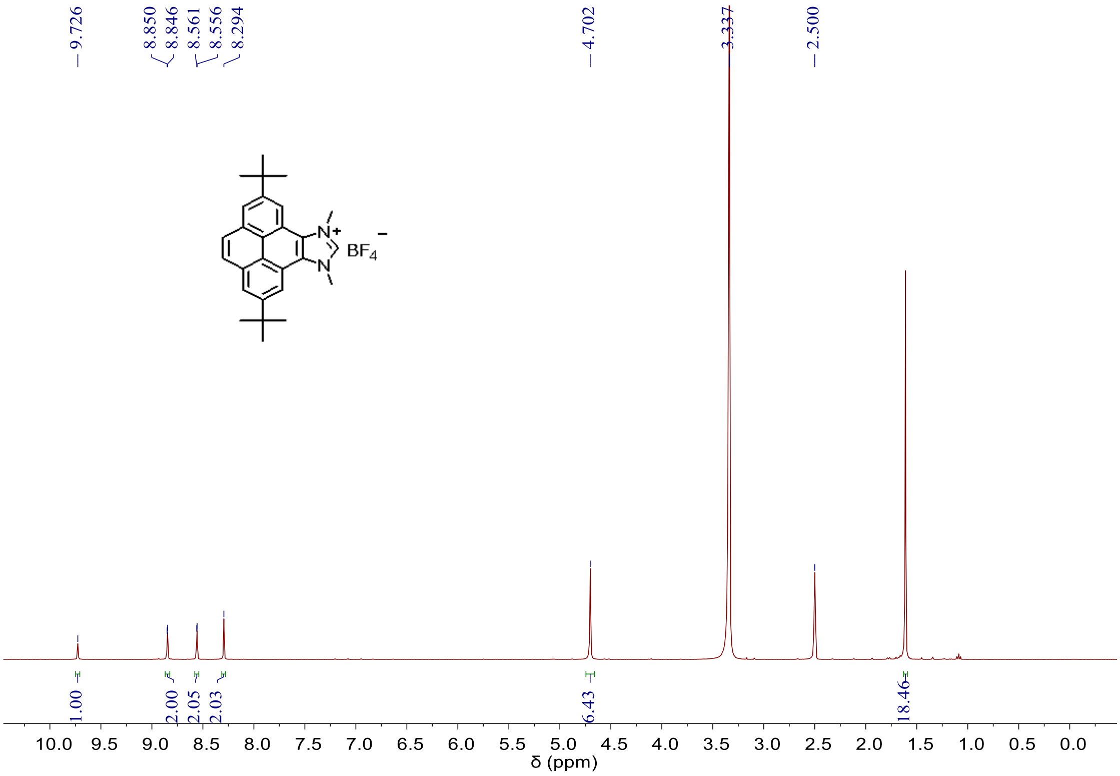


Fig. S49. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of compound **S3**.

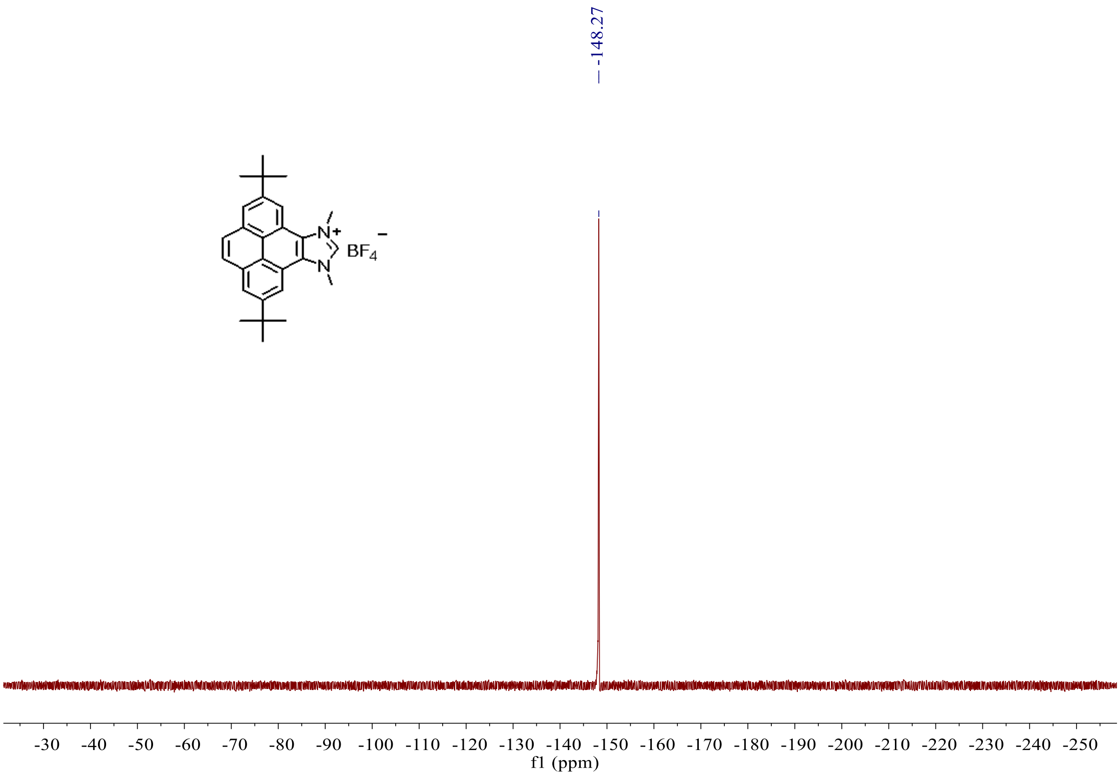


Fig. S50. ^{19}F NMR (376 MHz, DMSO-d_6, 298 K) spectrum of compound **S3**.

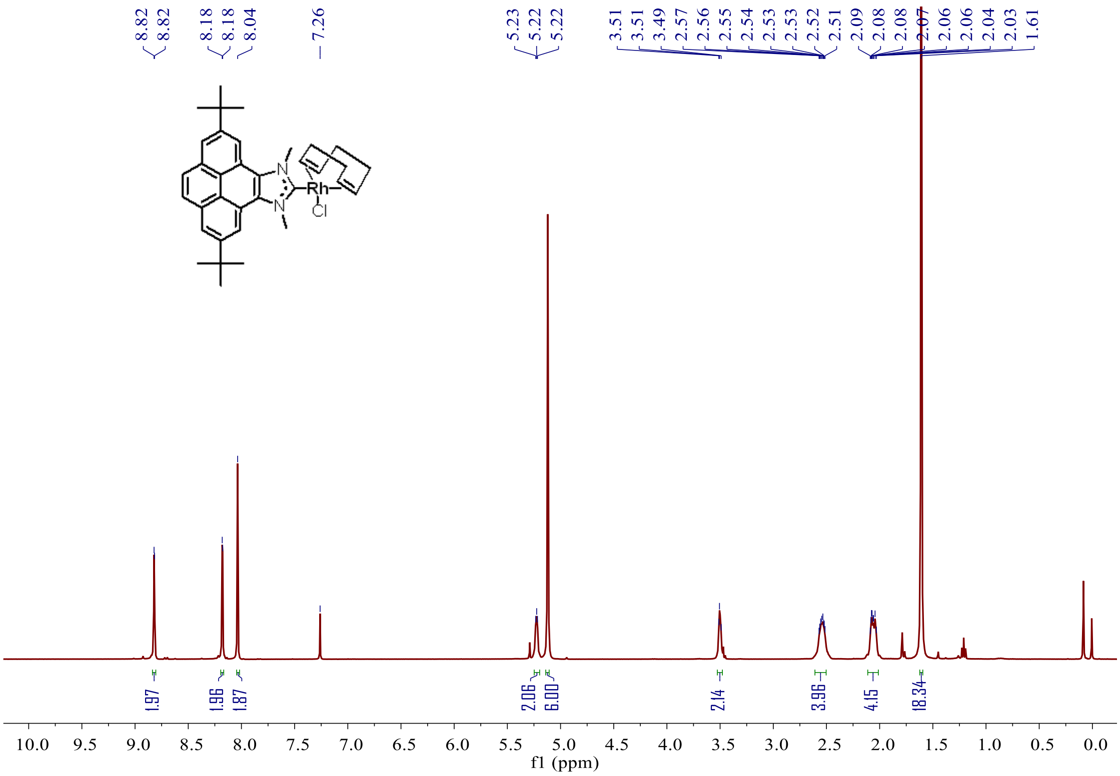


Fig. S51. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of NHC-Rh complex **1**.

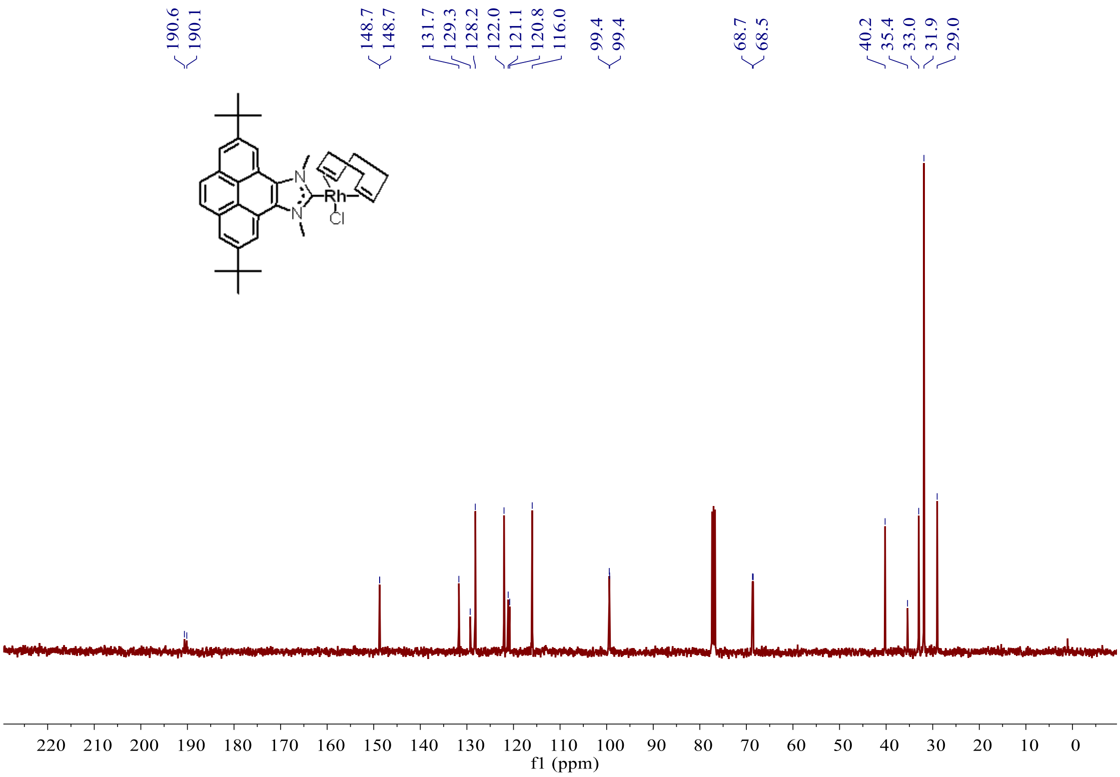


Fig. S52. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of NHC-Rh complex **1**.

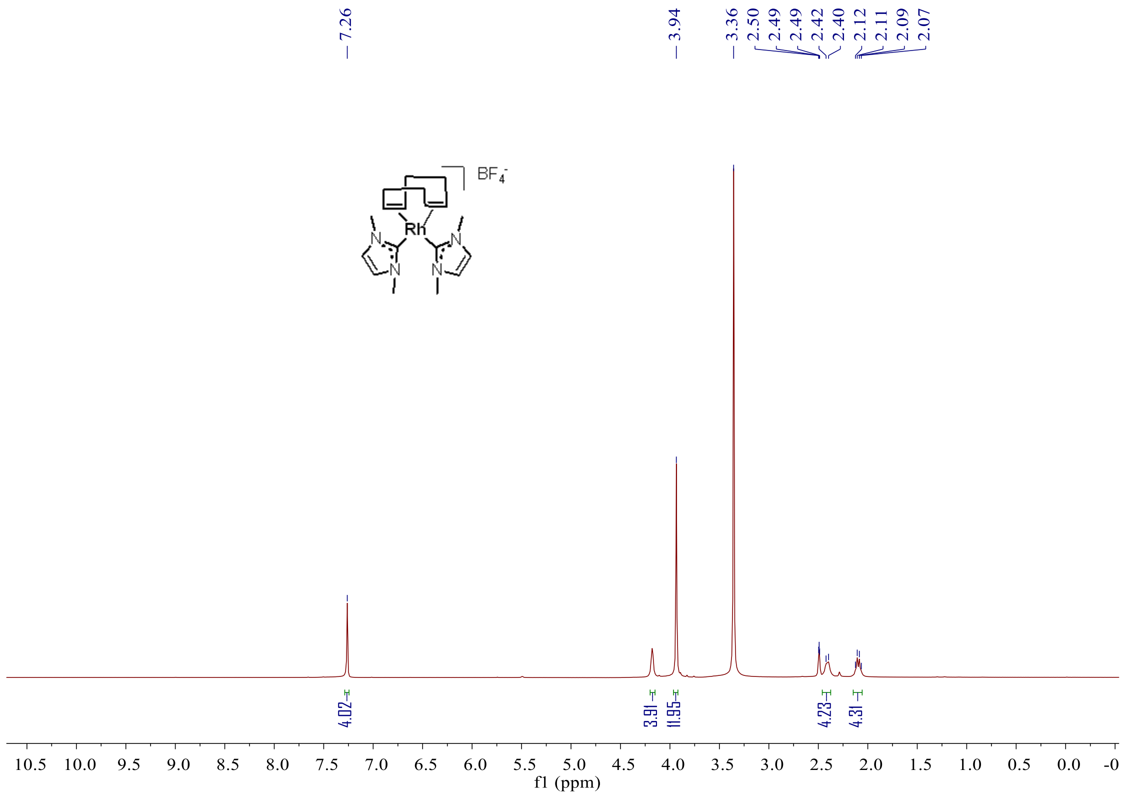


Fig. S53. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of NHC-Rh complex **2**.

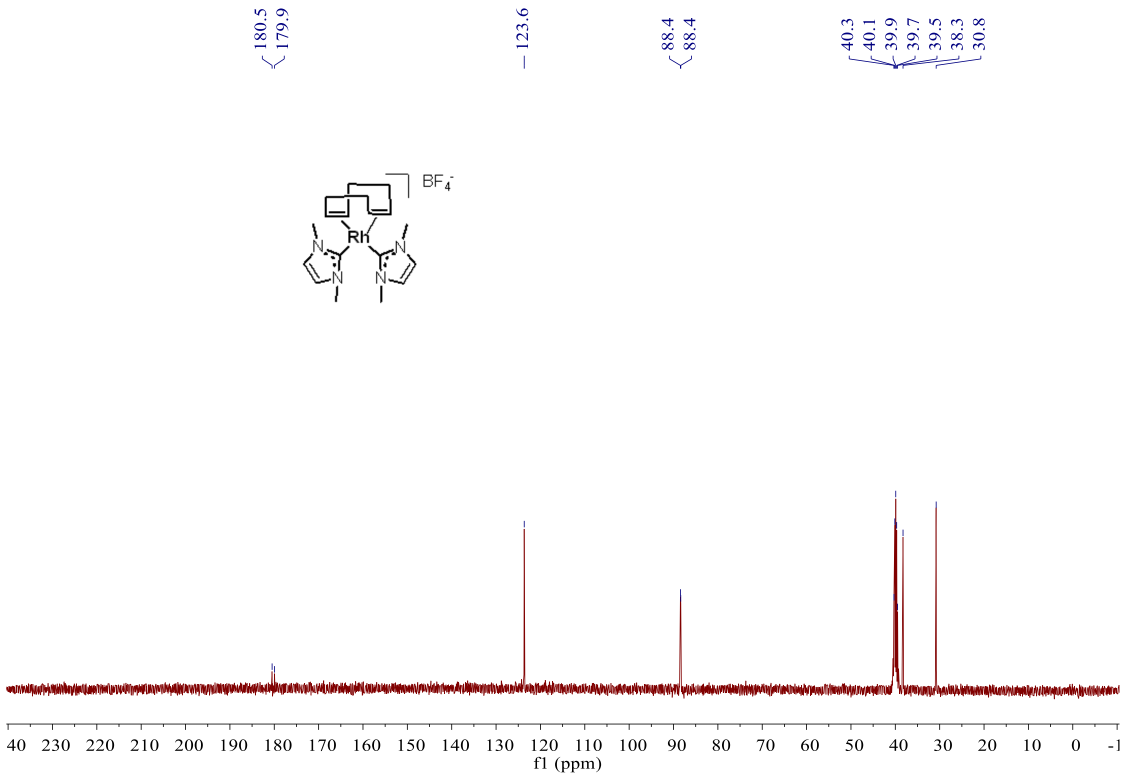


Fig. S54. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) spectrum of NHC-Rh complex **2**.

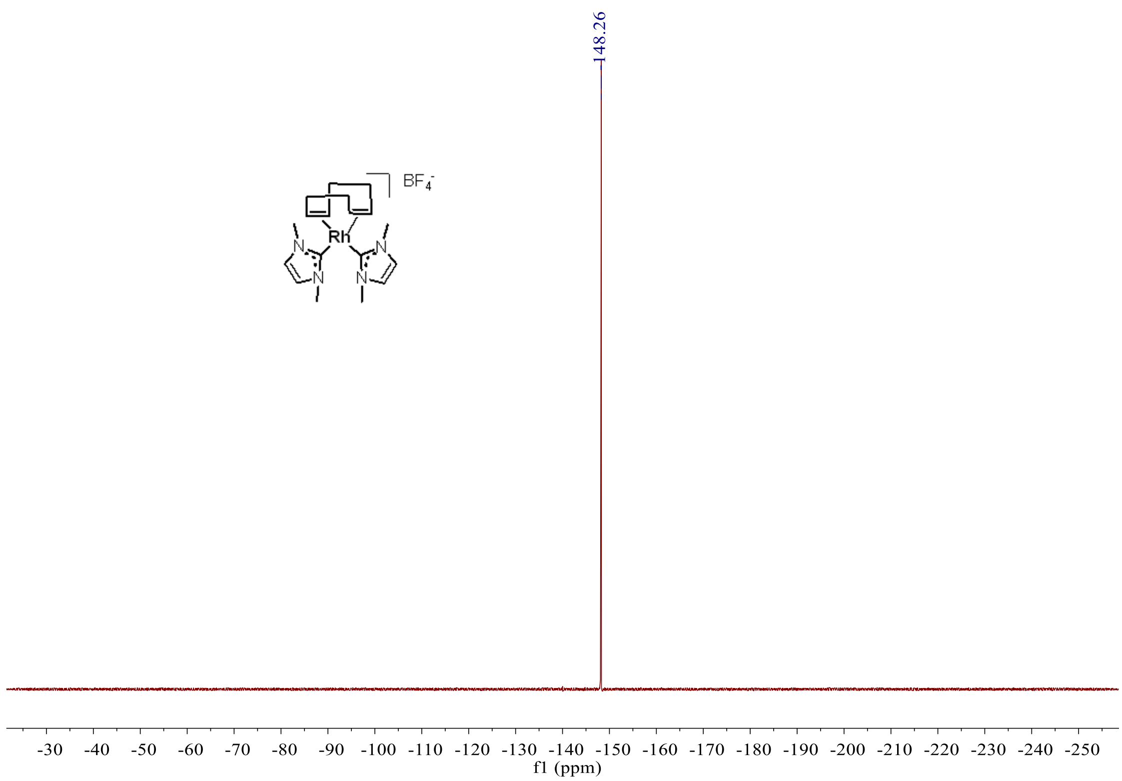


Fig. S55. ^{19}F NMR (376 MHz, DMSO-d_6, 298 K) spectrum of NHC-Rh complex **2**.

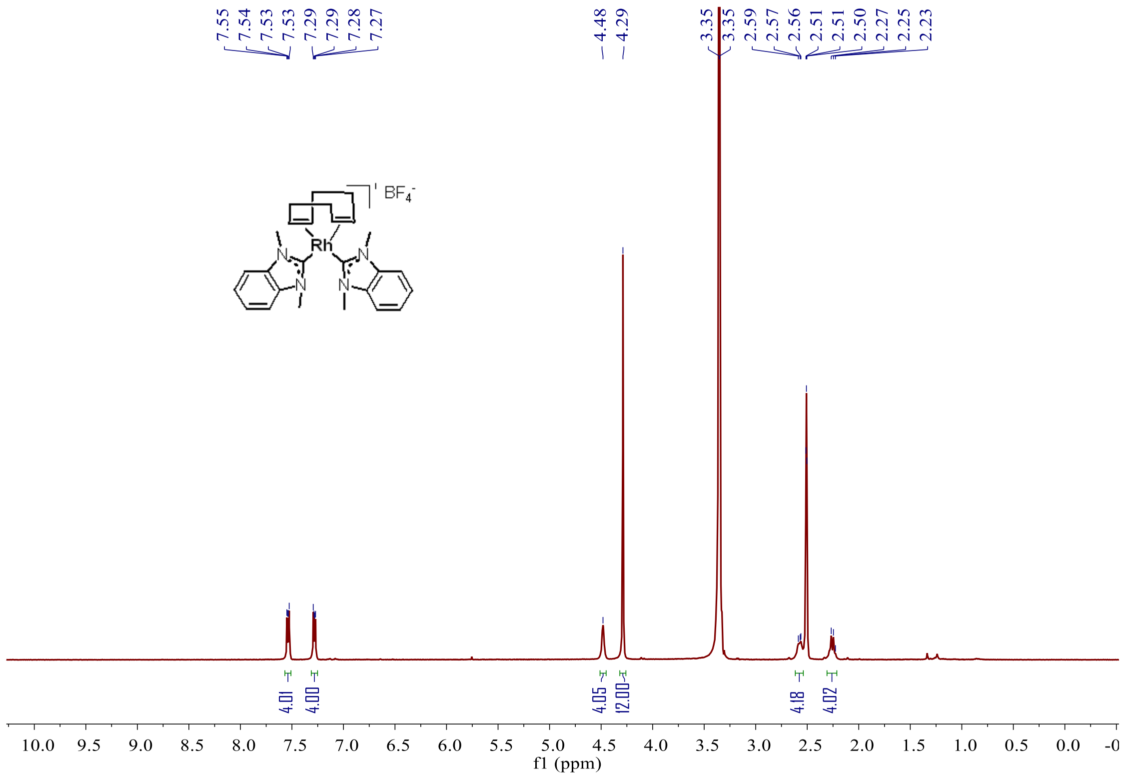


Fig. S56. ^{1}H NMR (400 MHz, DMSO-*d*6, 298 K) spectrum of NHC-Rh complex **3**.

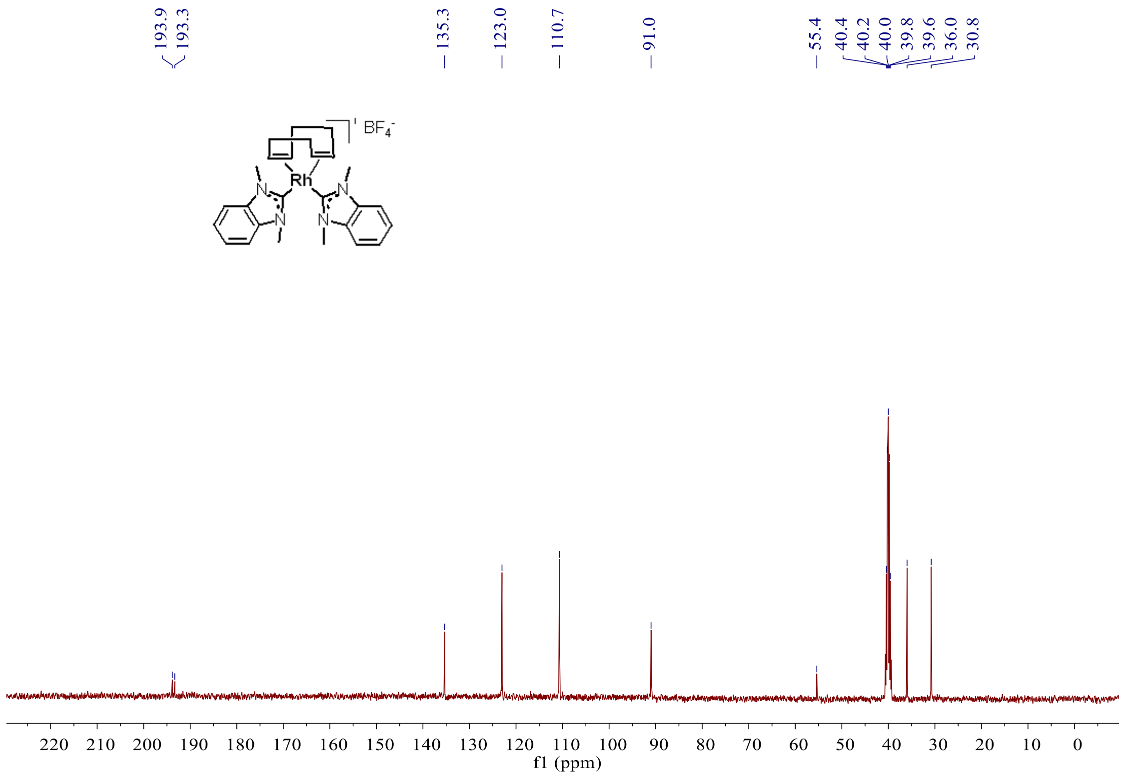


Fig. S57. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) spectrum of NHC-Rh complex **3**.

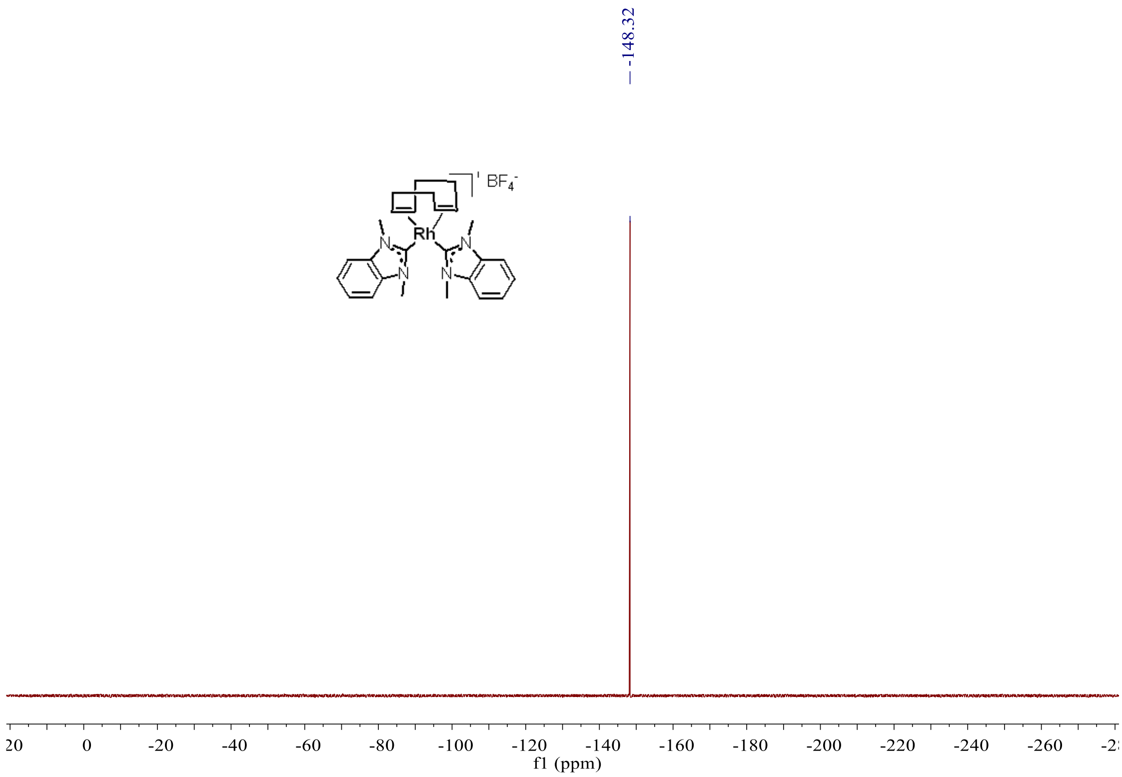


Fig. S58. ^{19}F NMR (376 MHz, DMSO-d_6, 298 K) spectrum of NHC-Rh complex **3**.

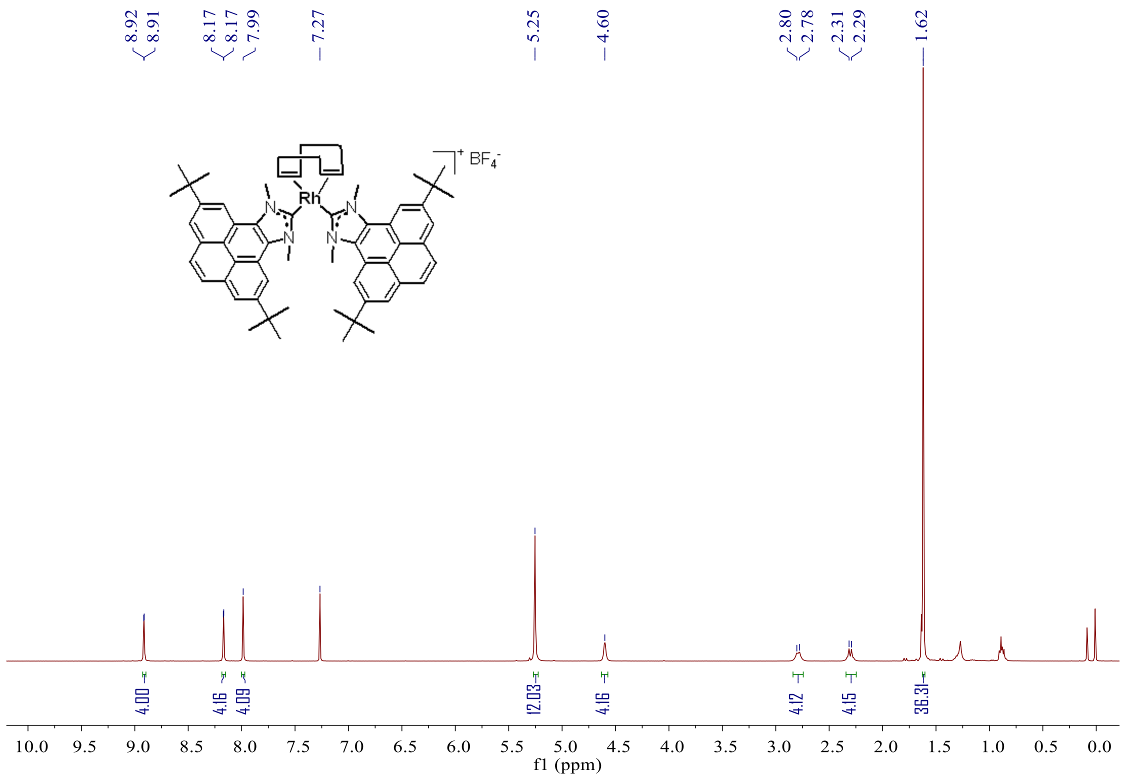


Fig. S59. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of NHC-Rh complex **4b**.

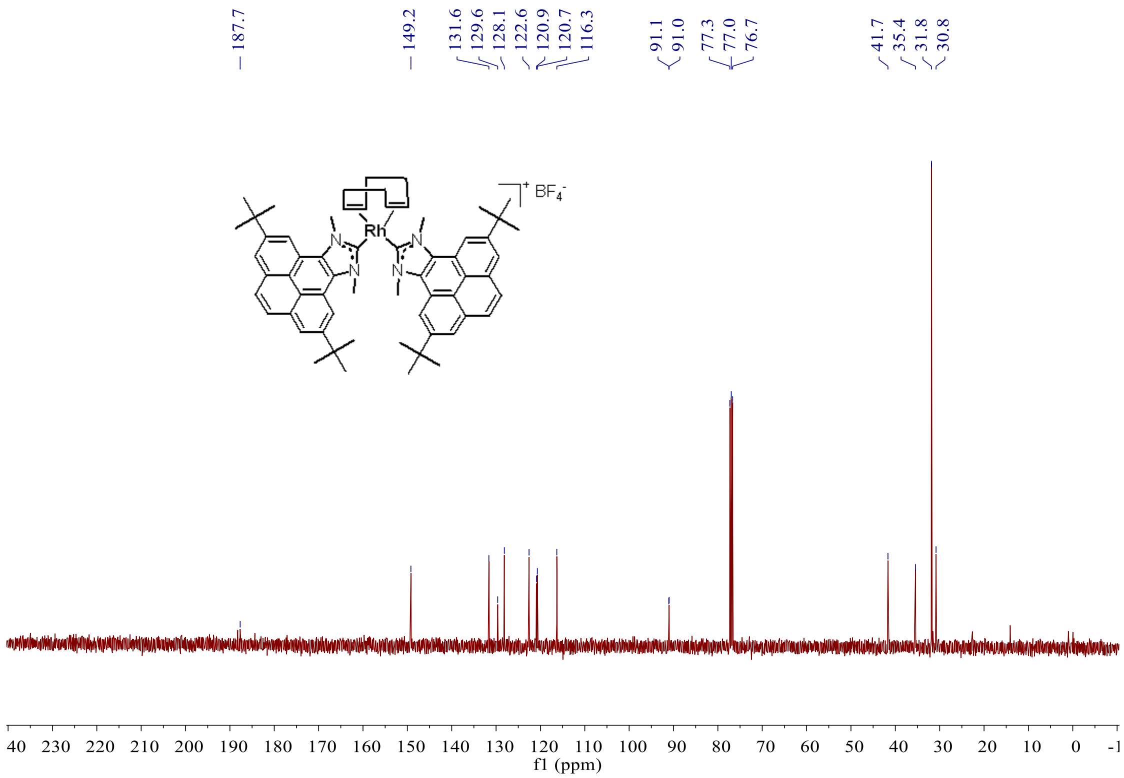


Fig. S60. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of spectrum of NHC-Rh complex **4b**.

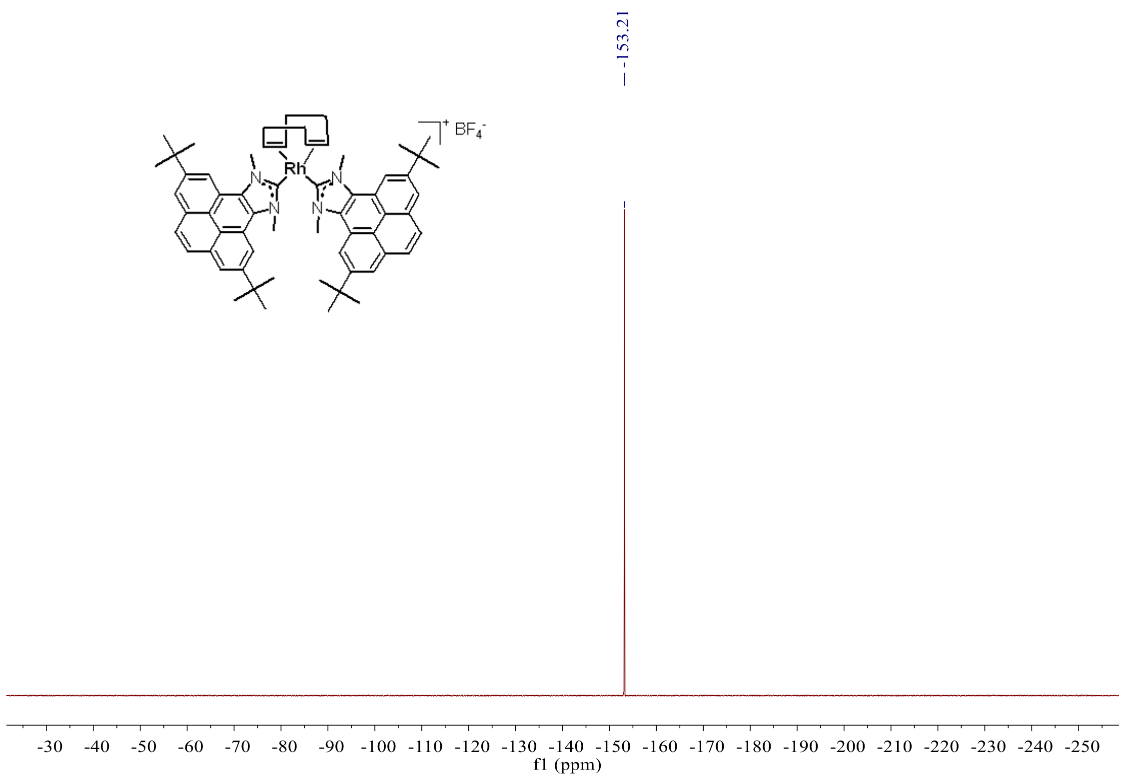


Fig. S61.[19]F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of NHC-Rh complex **4b**.

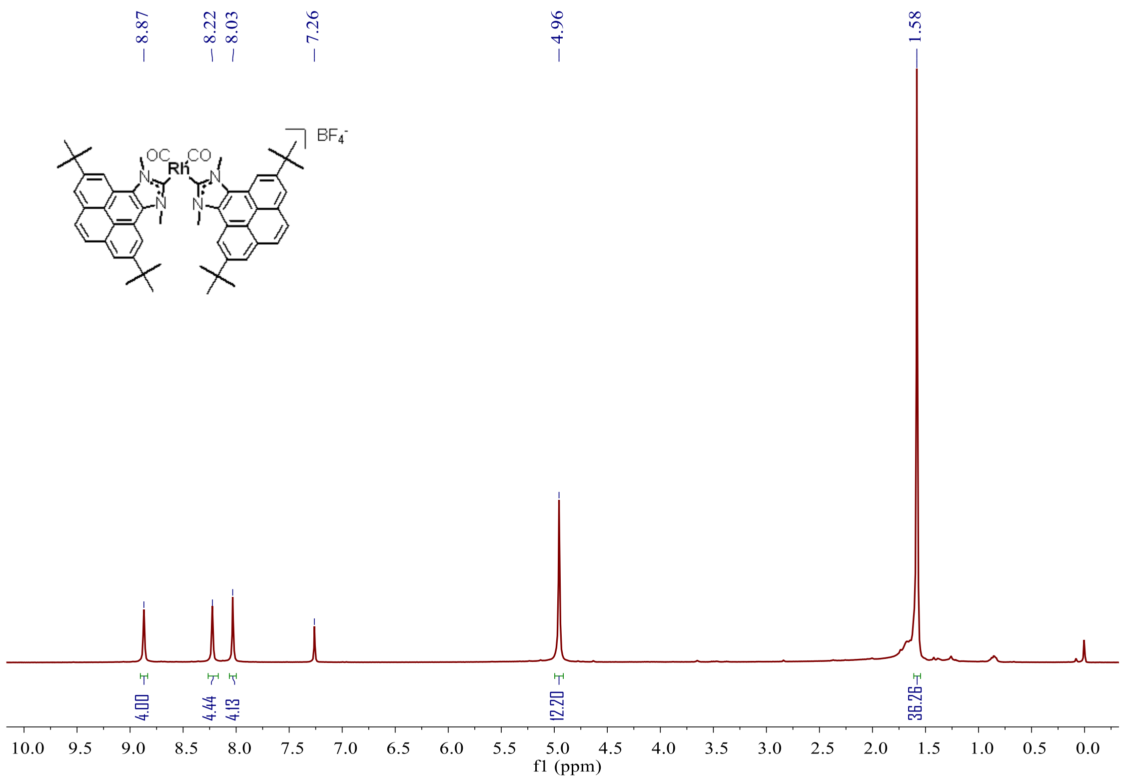


Fig. S62. [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of NHC-Rh complex **4a**.

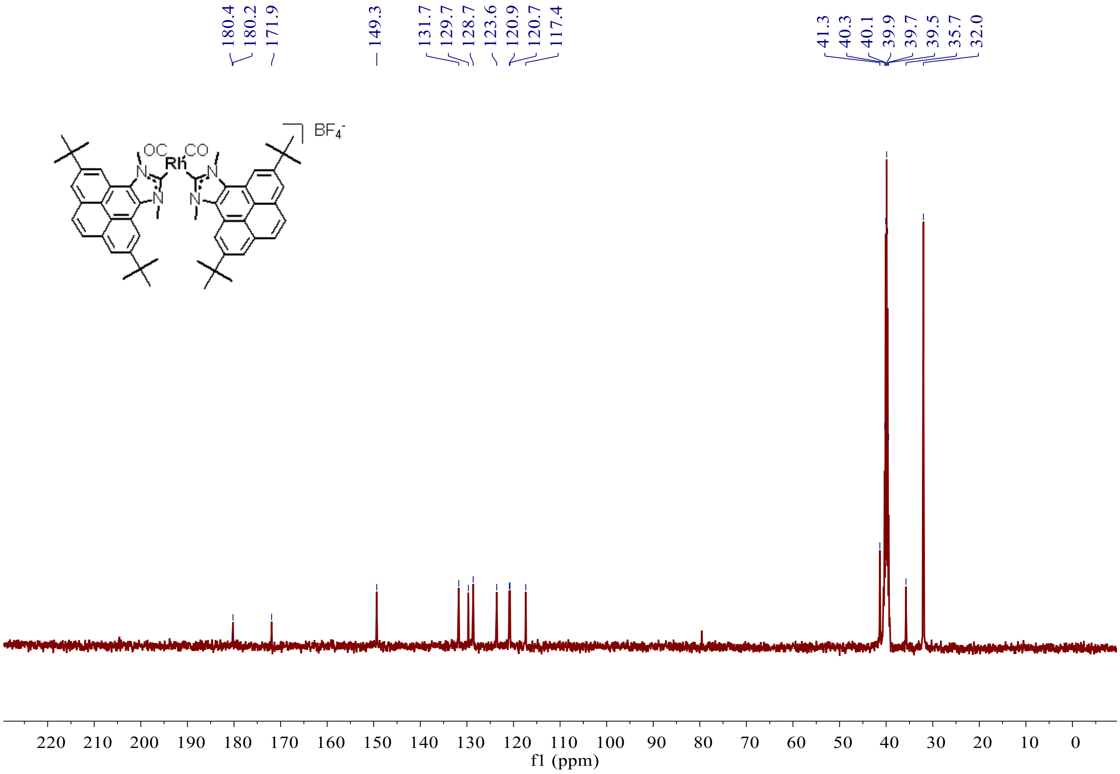


Fig. S63. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) spectrum of spectrum of NHC-Rh complex **4a**.

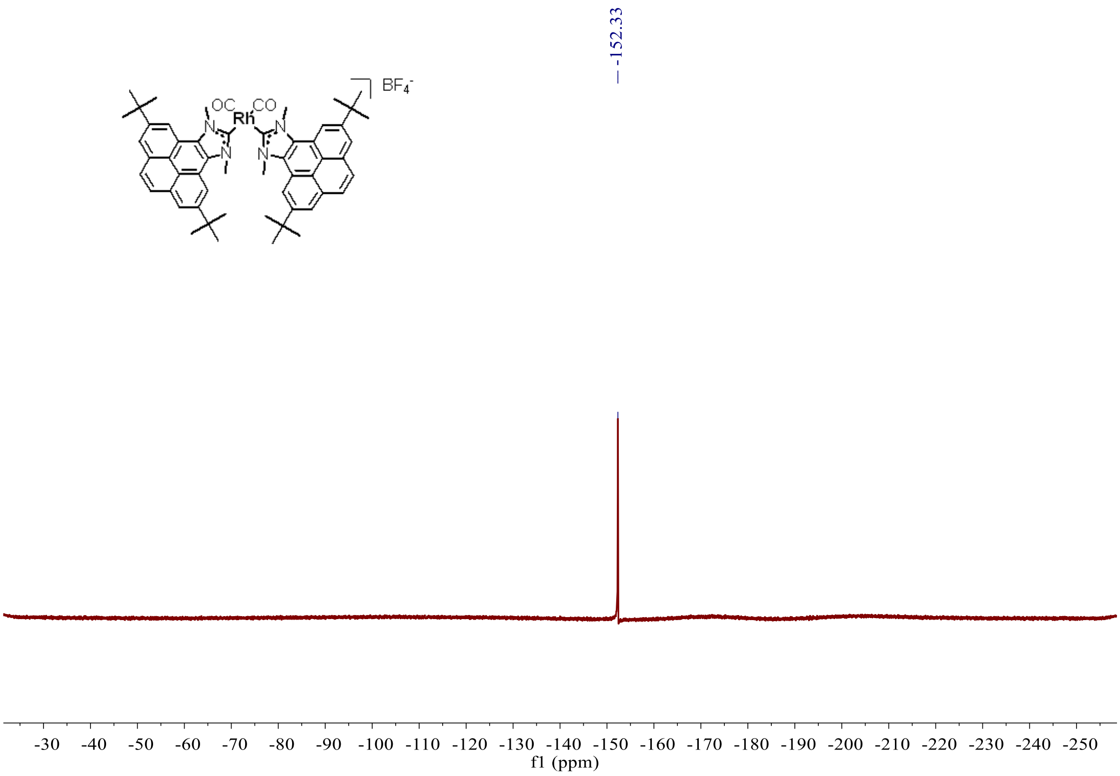


Fig. S64. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of NHC-Rh complex **4a**.

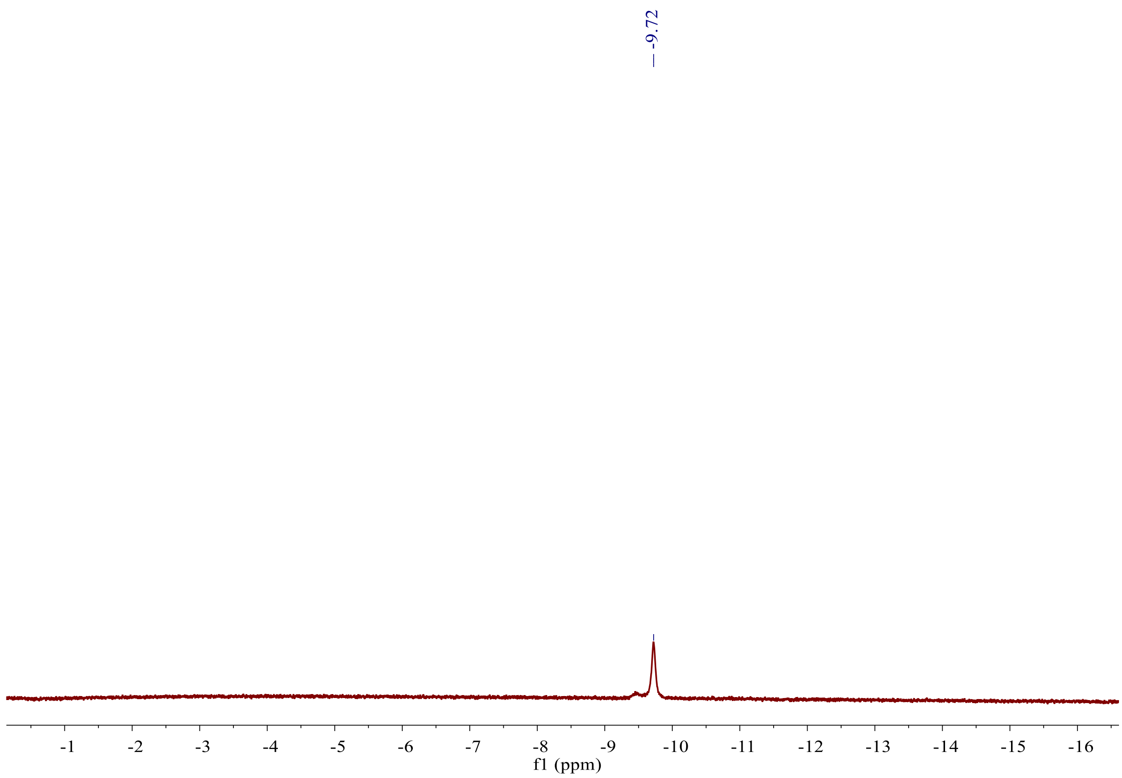


Fig. S65. [1]H NMR (400 MHz, CDCN-d_3, 298 K) spectrum of Rh-H moieties**.**

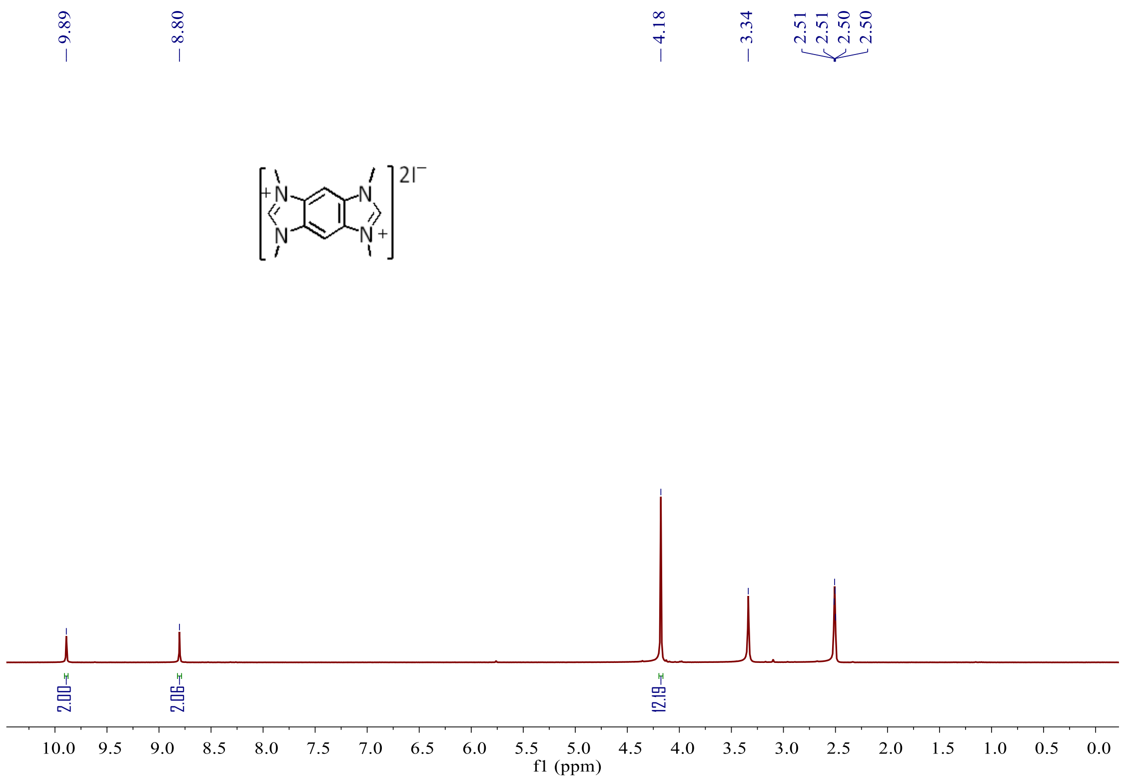


Fig. S66. [1]H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of compound **S5**.

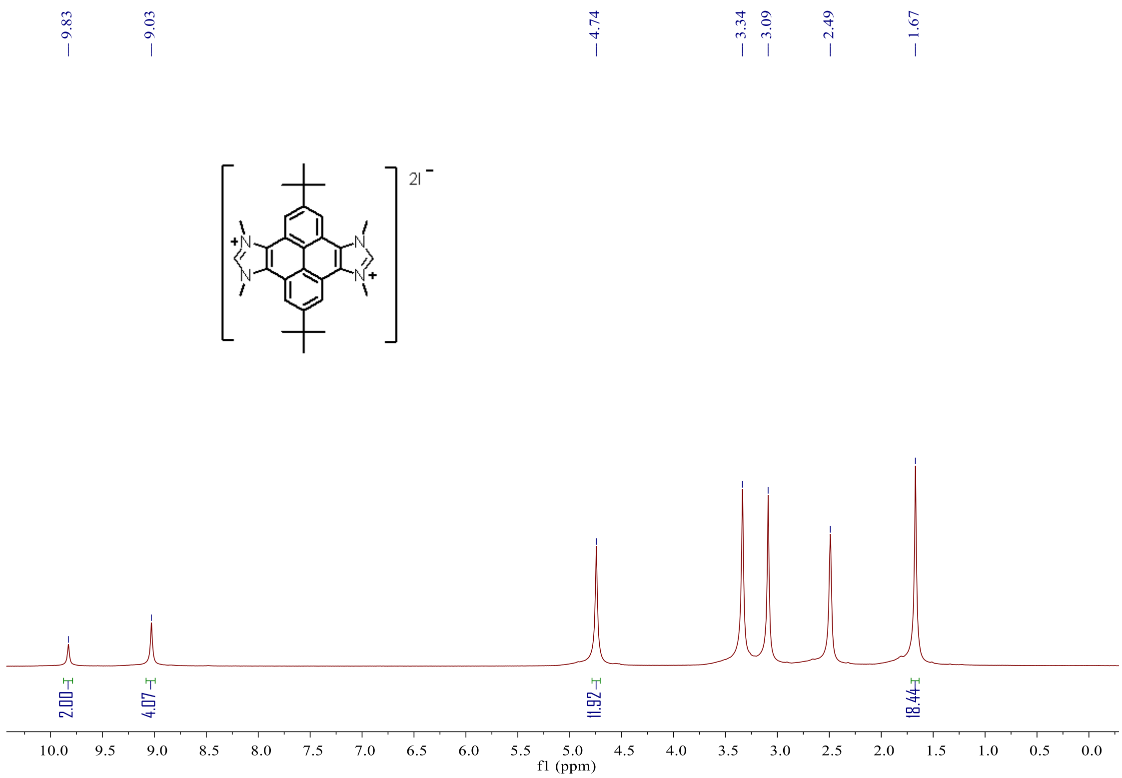


Fig. S67. [1]H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of compound **S6a**.

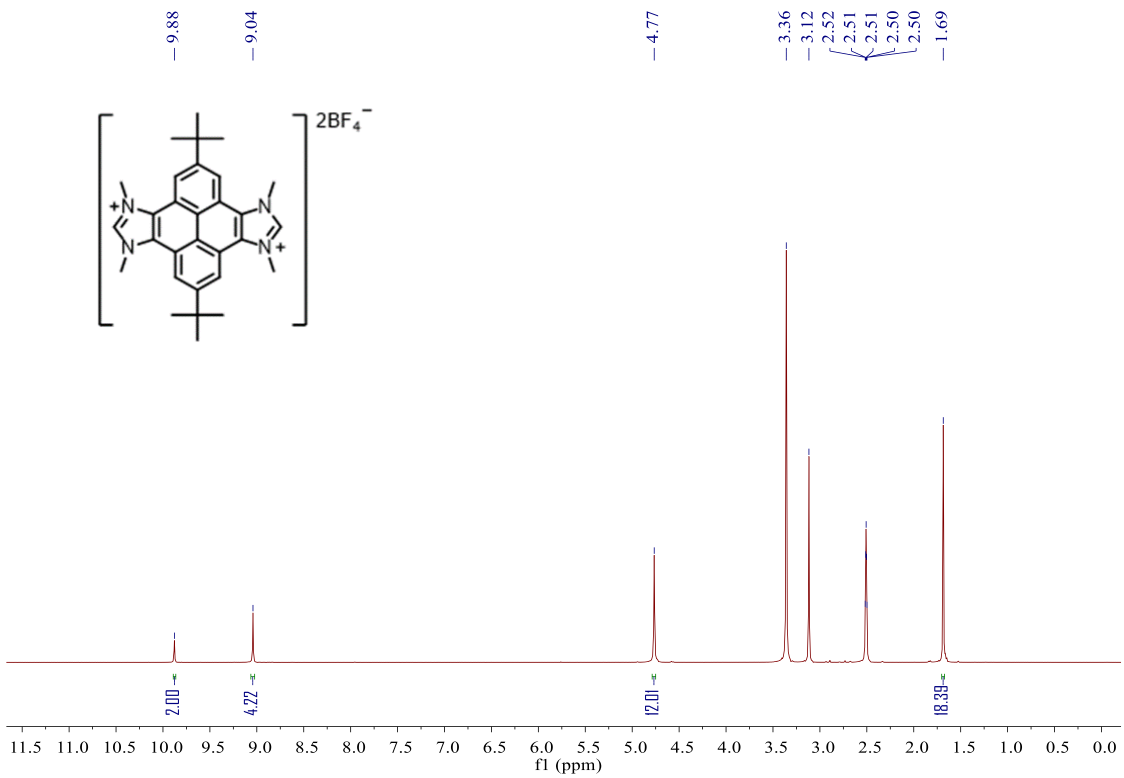


Fig. S68. [1]H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of compound **S6b**.

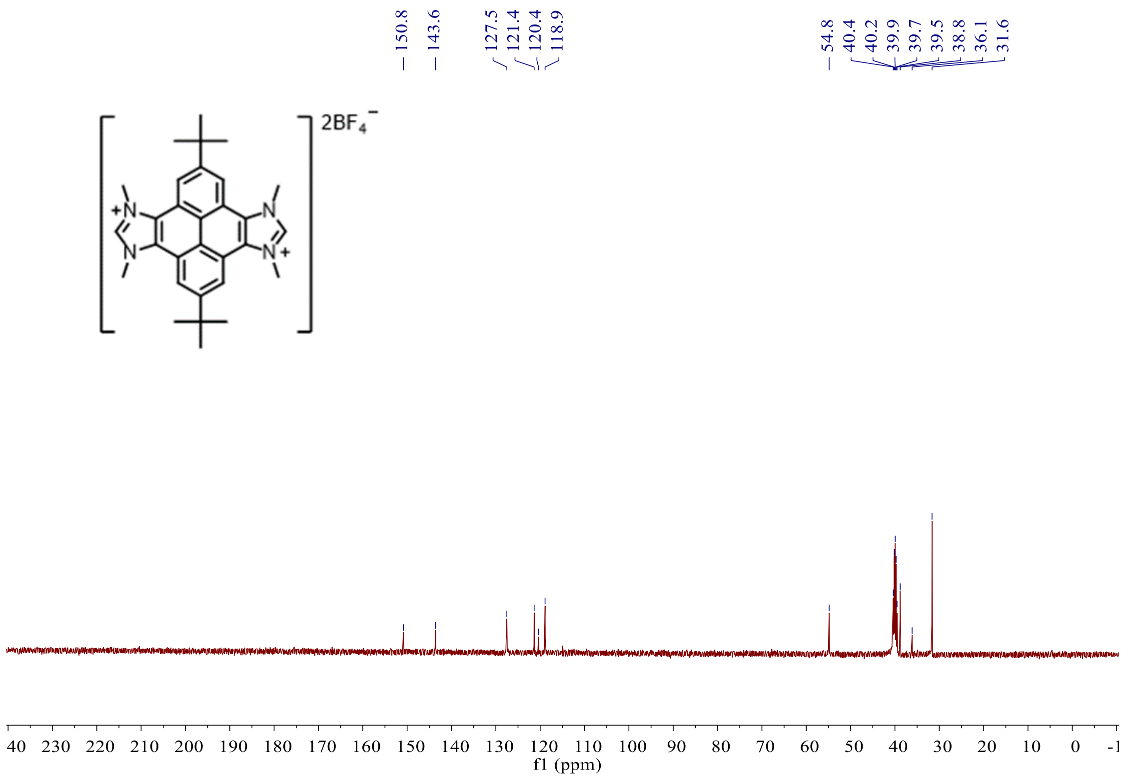


Fig. S69. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) spectrum of compound **S6b**.

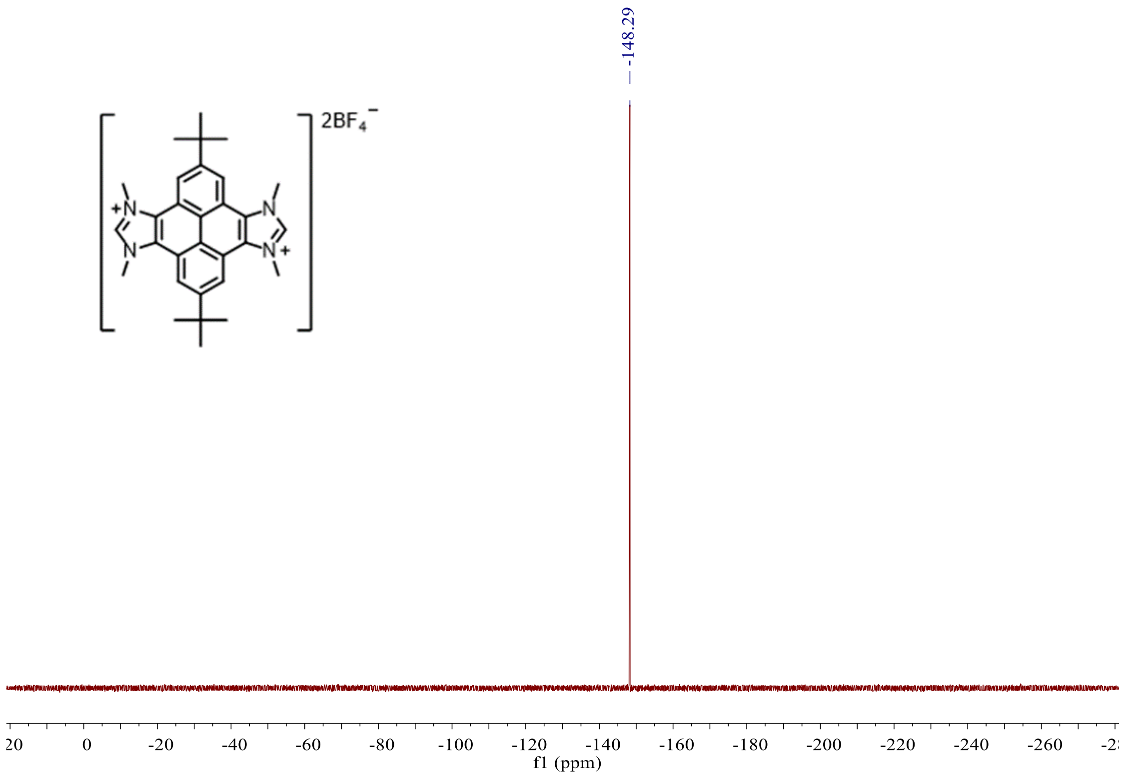


Fig. S70. ^{19}F NMR (376 MHz, DMSO-d_6, 298 K) spectrum of compound **S6b**.

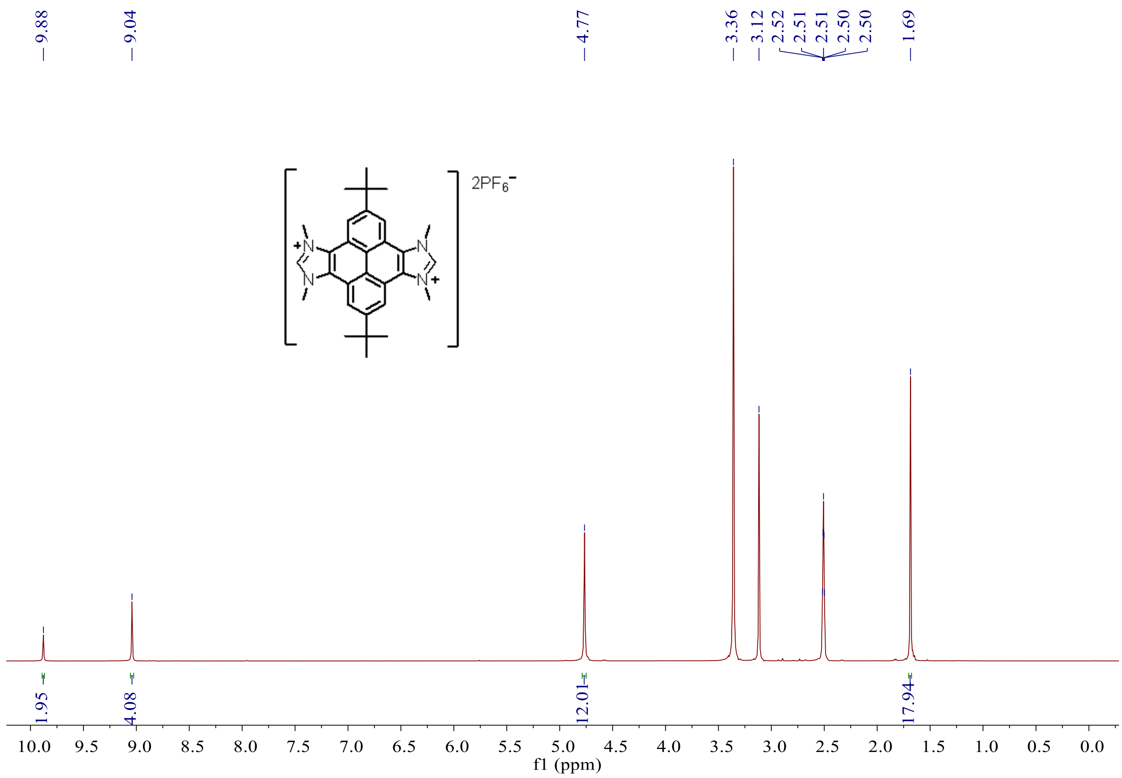


Fig. S71. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of compound **S6c**.

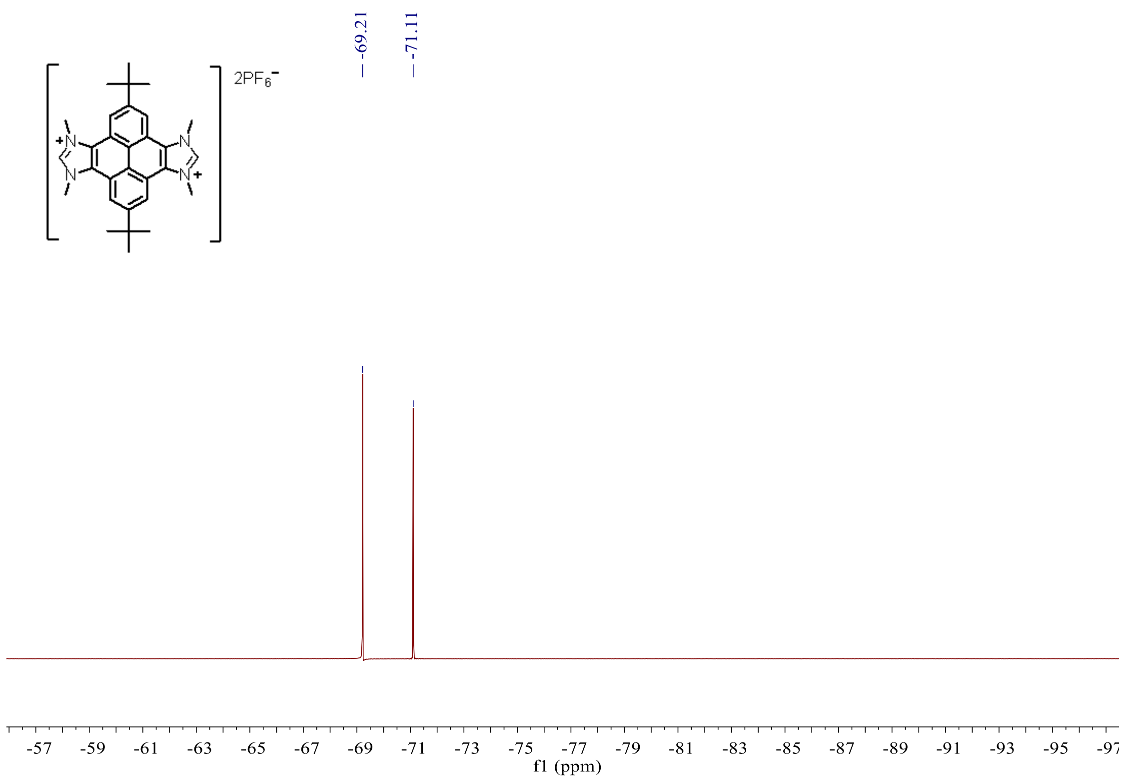


Fig. S72. ^{19}F NMR (376 MHz, DMSO-d_6, 298 K) spectrum of compound **S6c**.

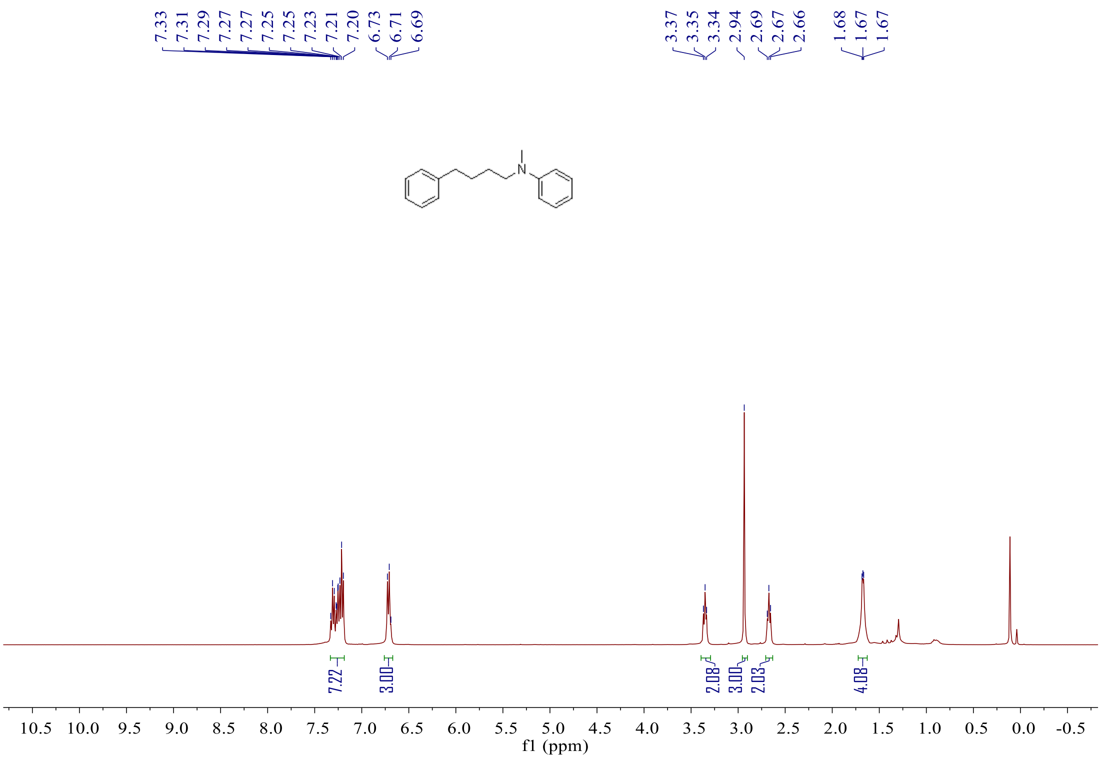


Fig. S73. [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9aa**.

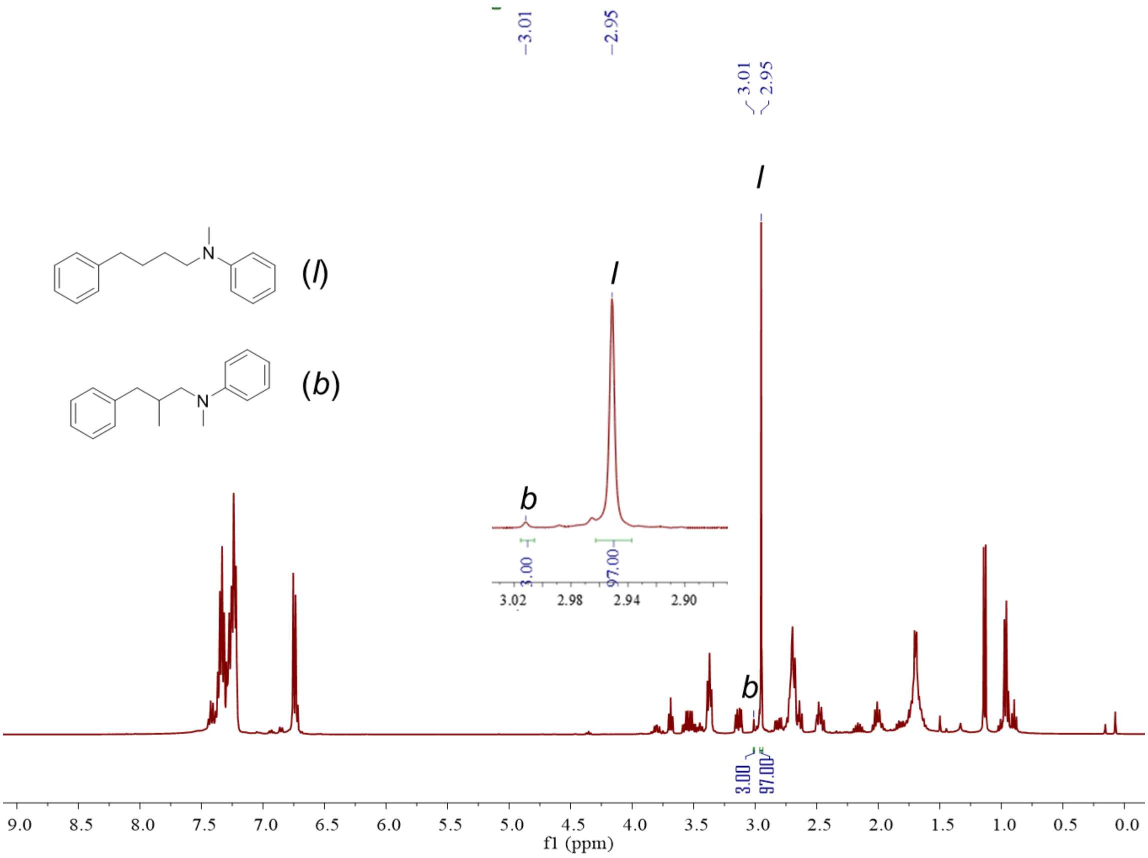


Fig. S74. [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of reaction mixture after reaction competition to generate **9aa**.

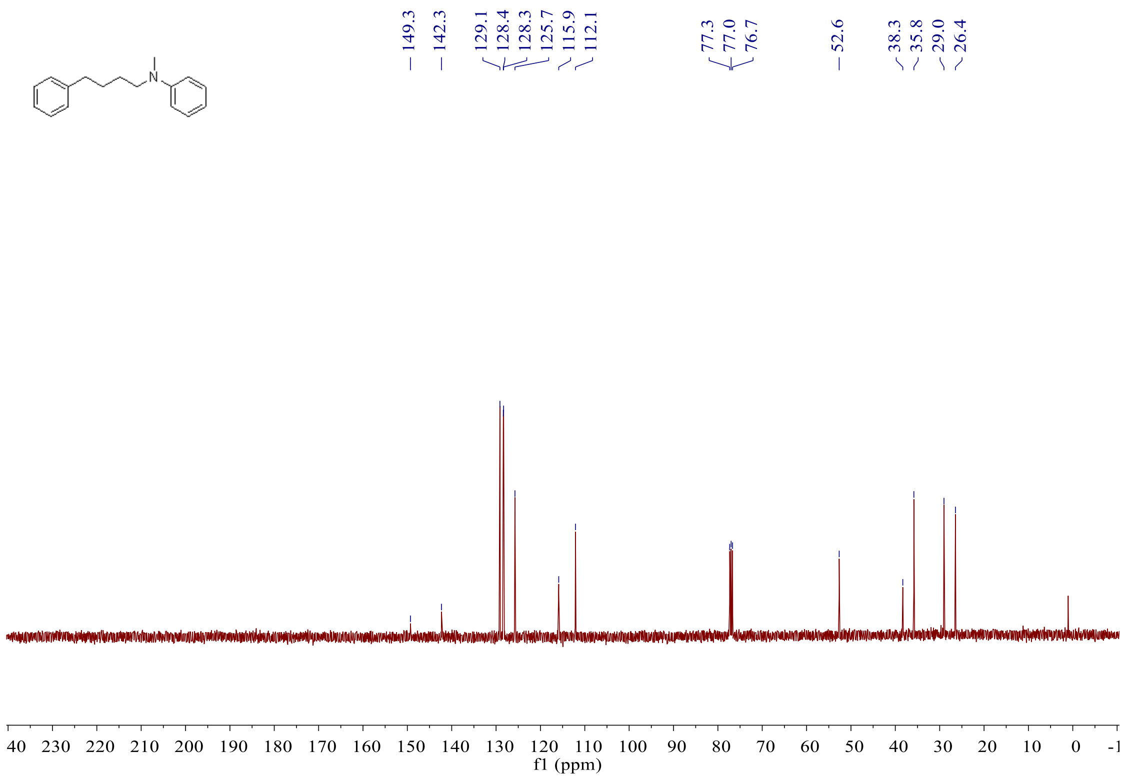


Fig. S75. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9aa**.

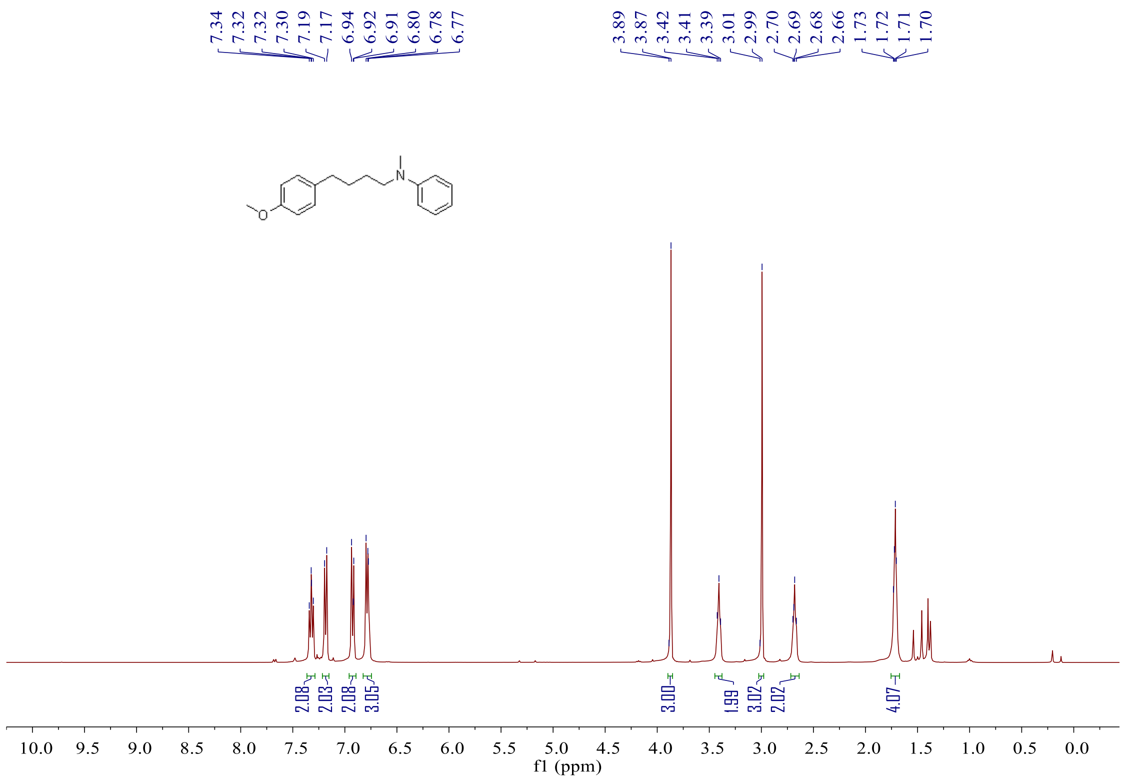


Fig. S76. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ba**.

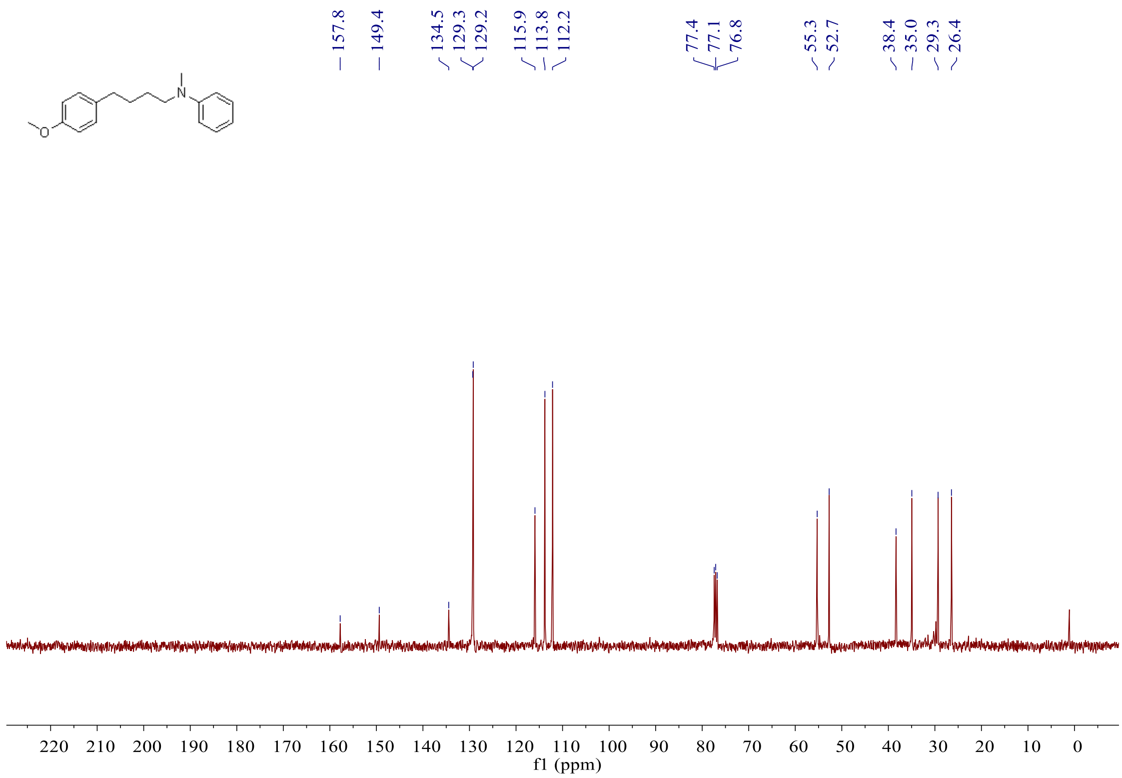


Fig. S77. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ba**.

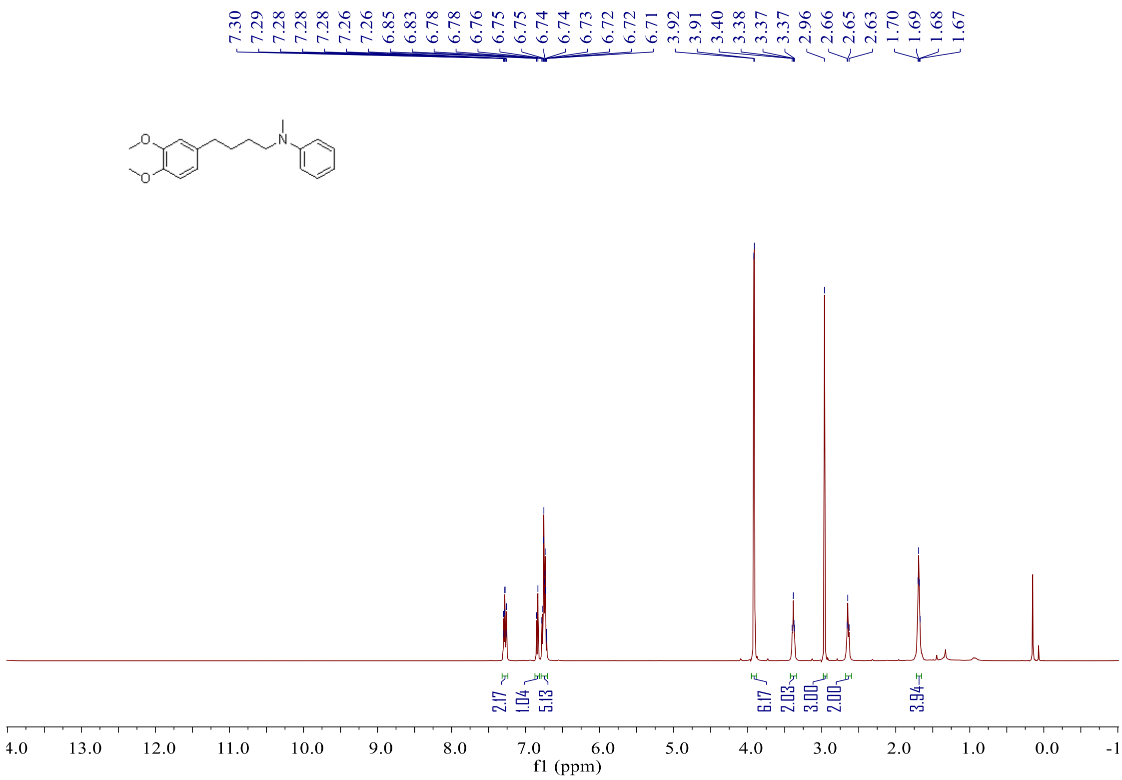


Fig. S78. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ca**.

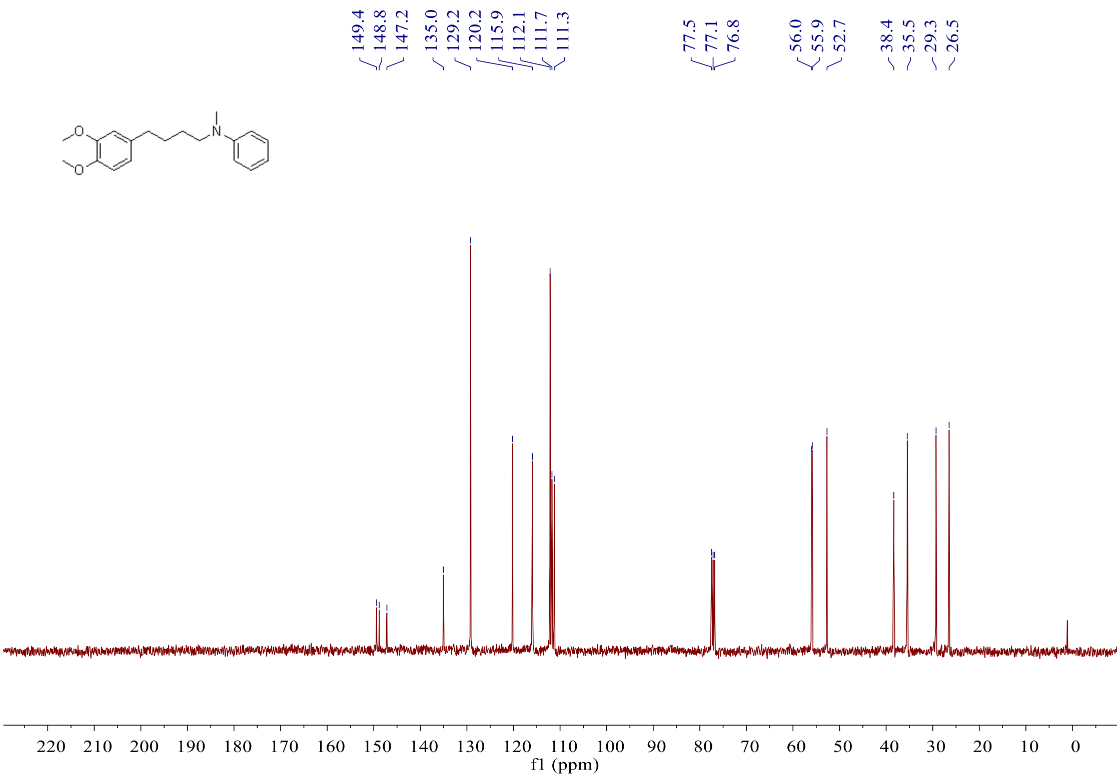


Fig. S79. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ca**.

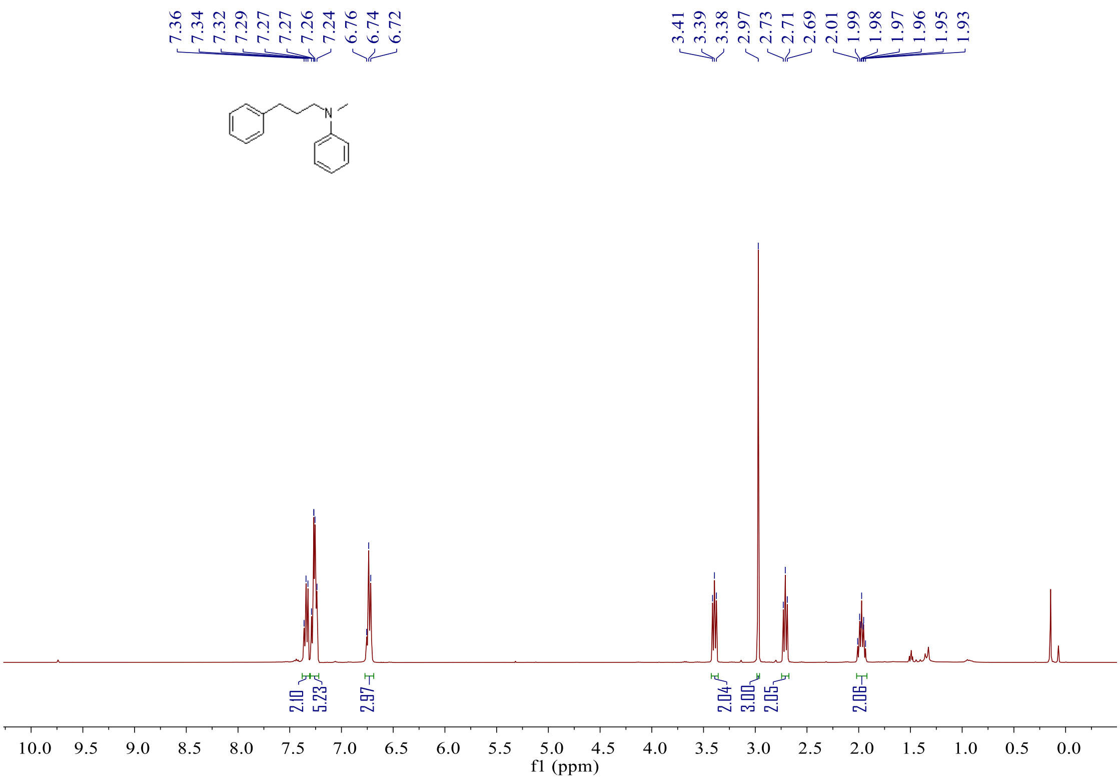


Fig. S80. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9da**.

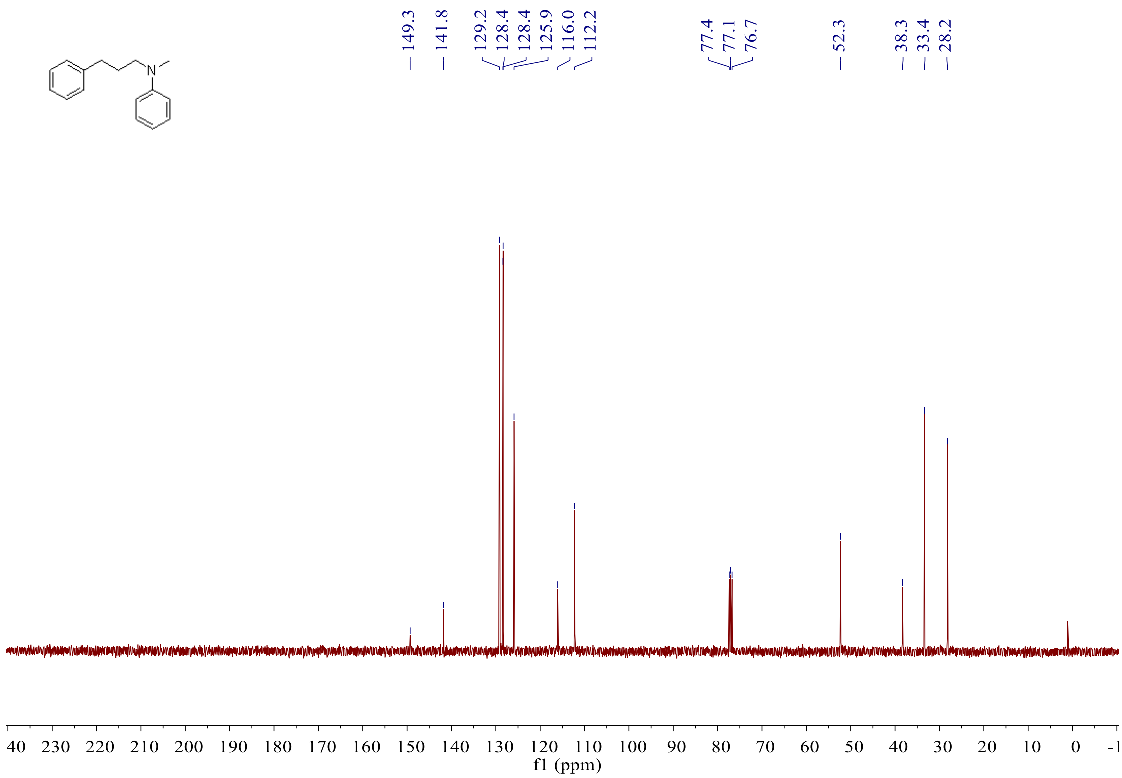


Fig. S81. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9da**.

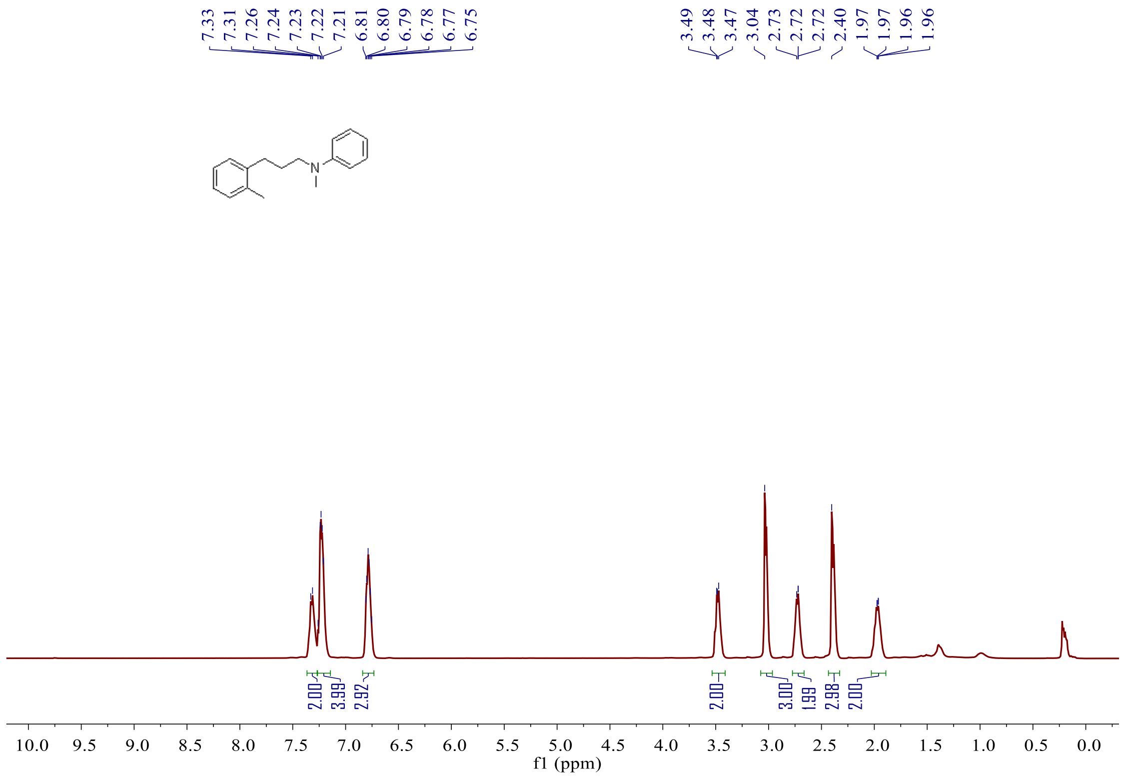


Fig. S82. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ea-*o***.

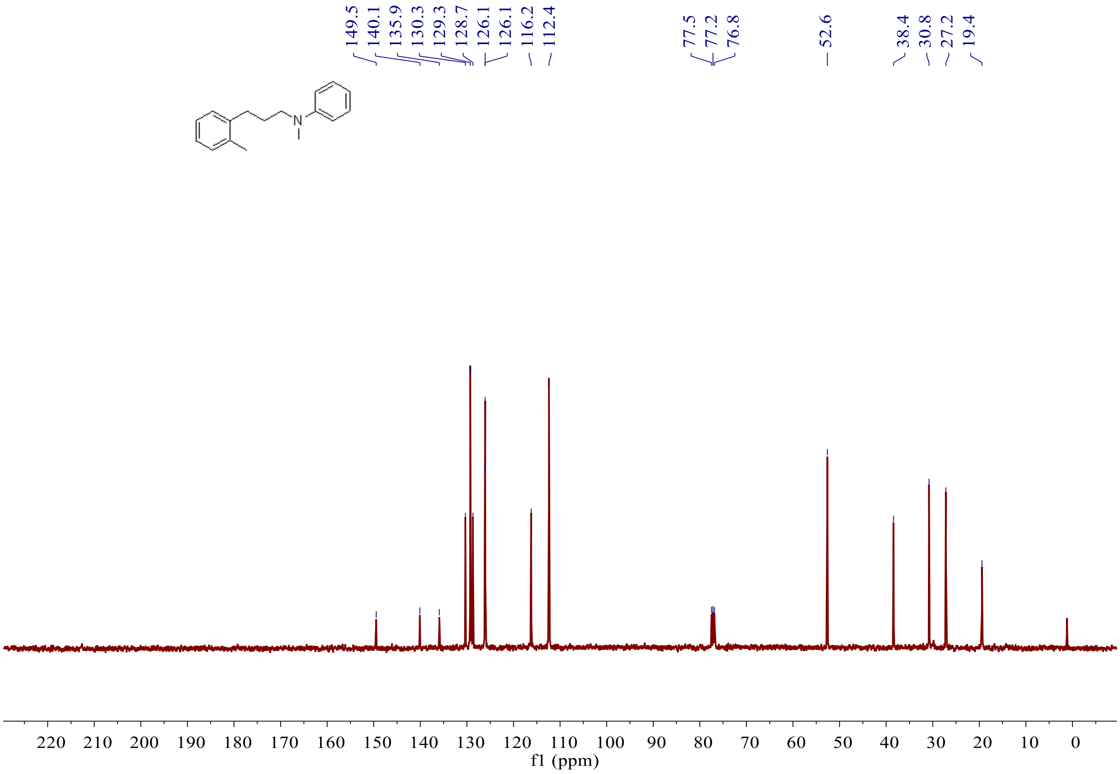


Fig. S83. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ea-*o***.

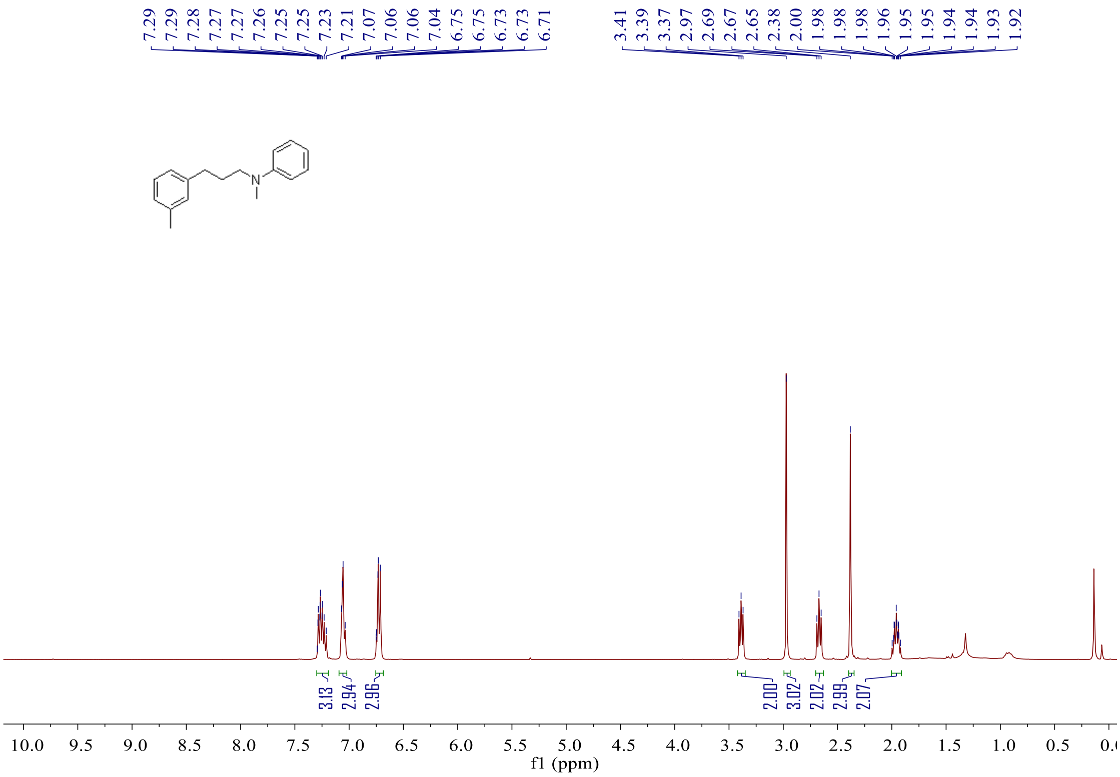


Fig. S84. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ea-*m***.

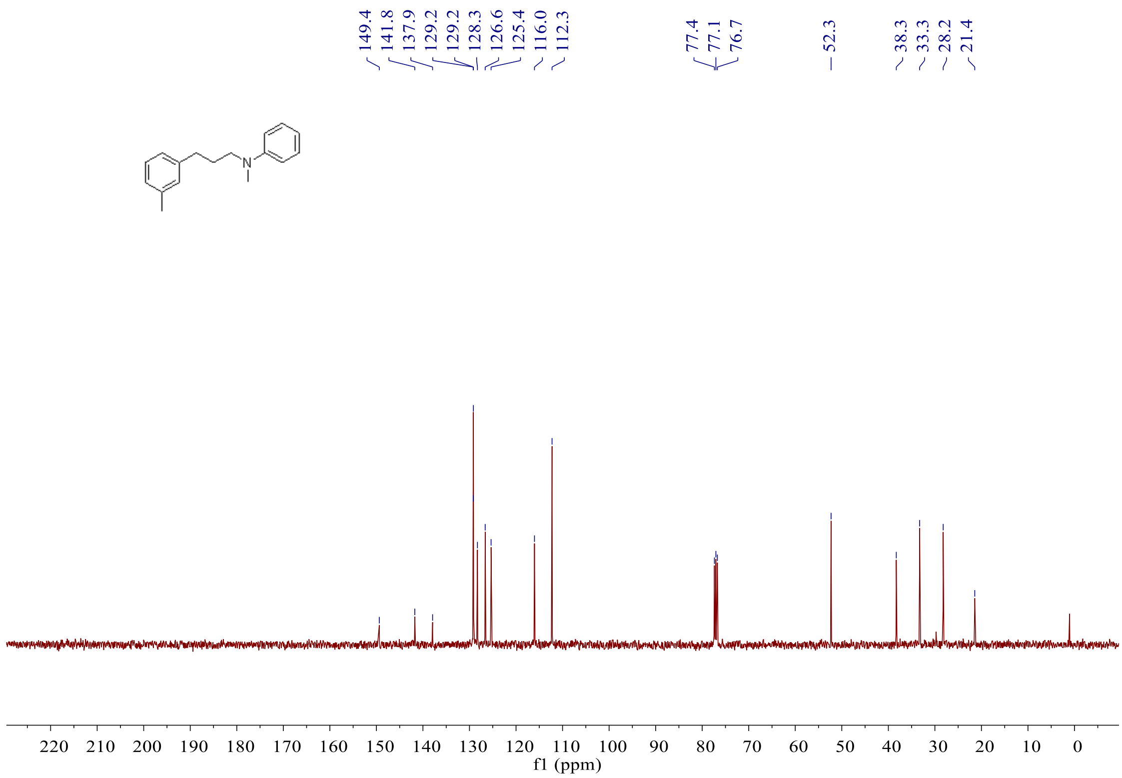


Fig. S85. [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ea-*m***.

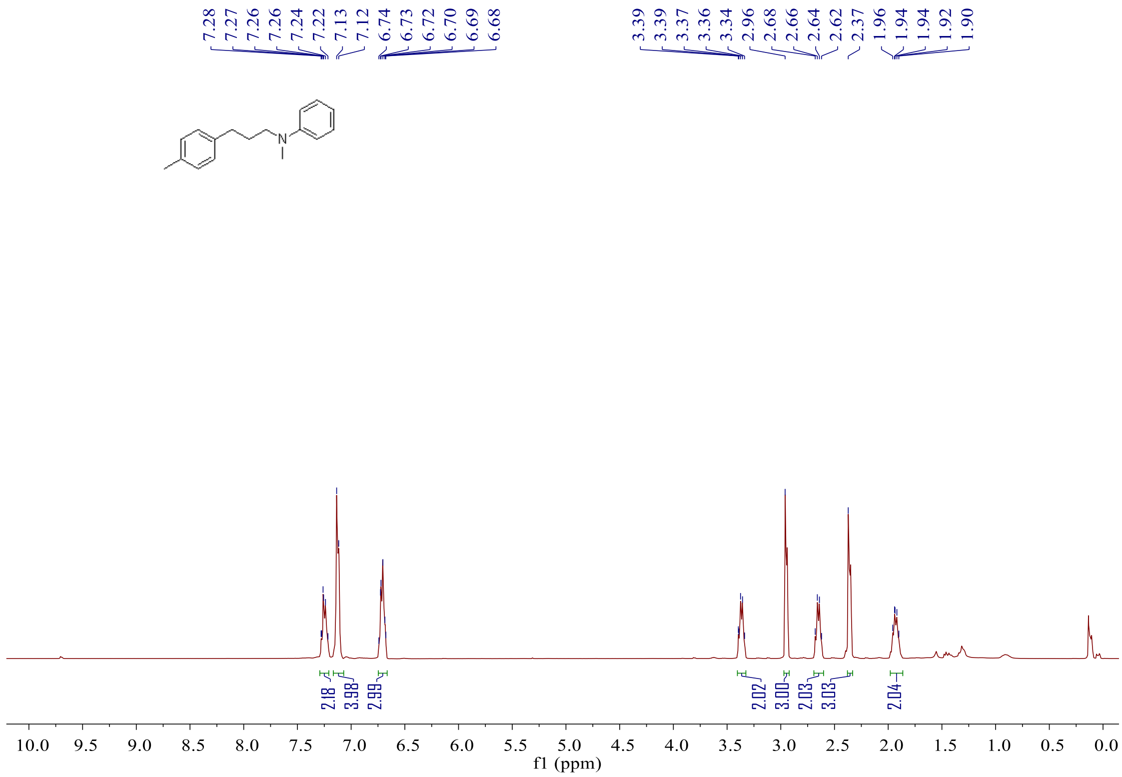


Fig. S86. [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ea-*p***.

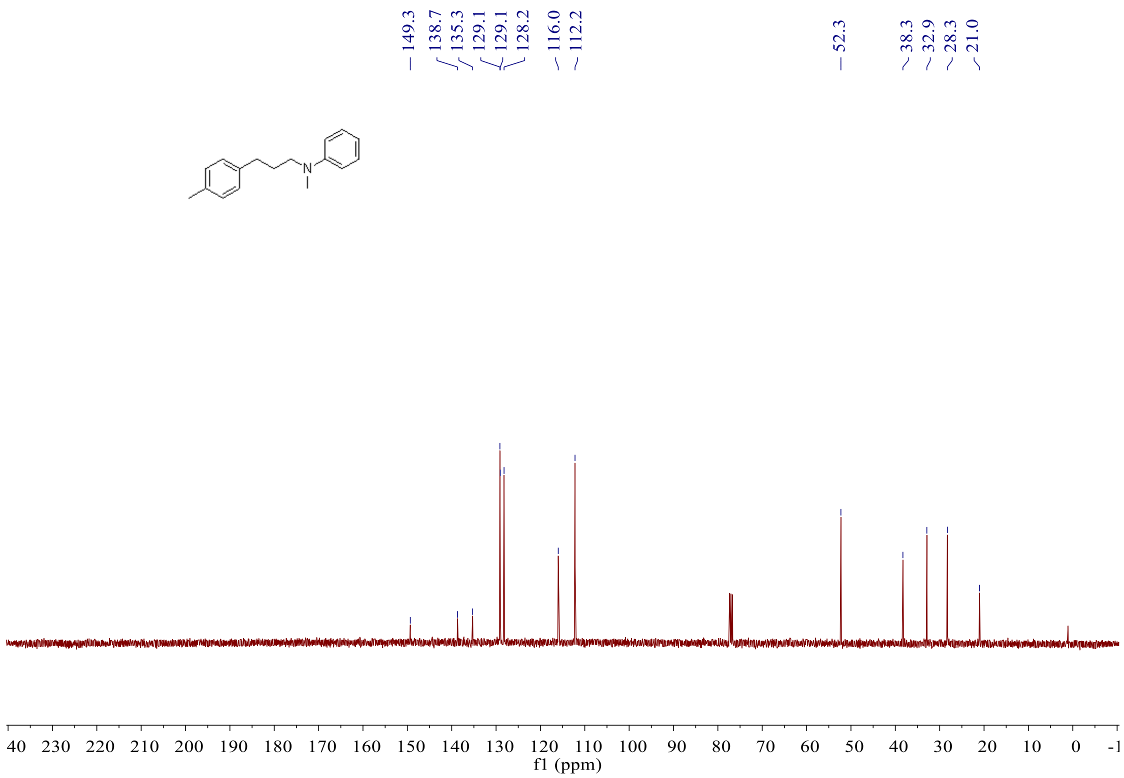


Fig. S87. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ea-*p***.

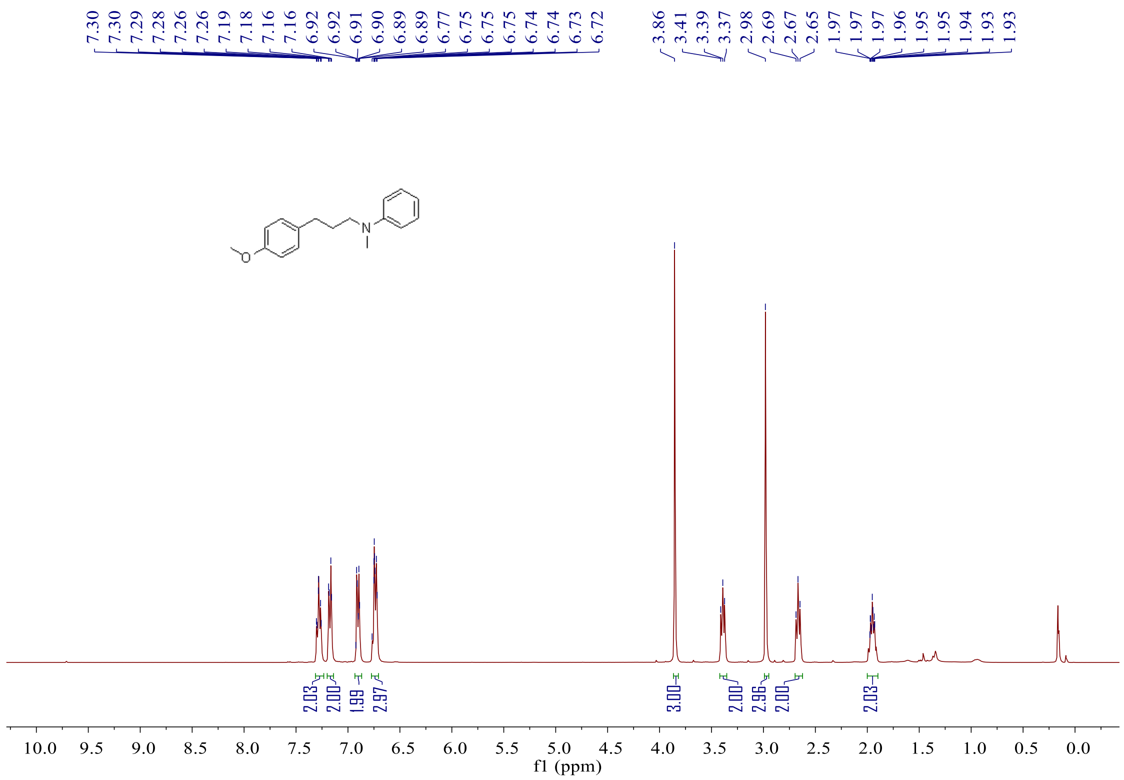


Fig. S88. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9fa**.

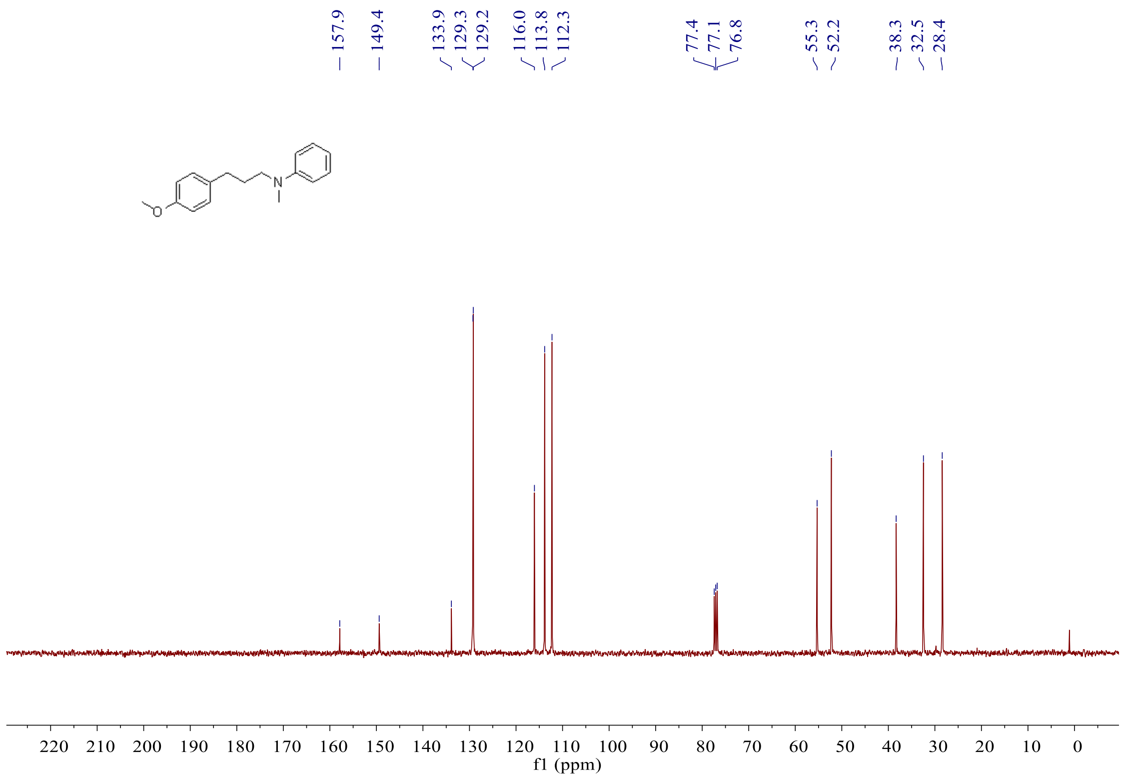


Fig. S89. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9fa**.

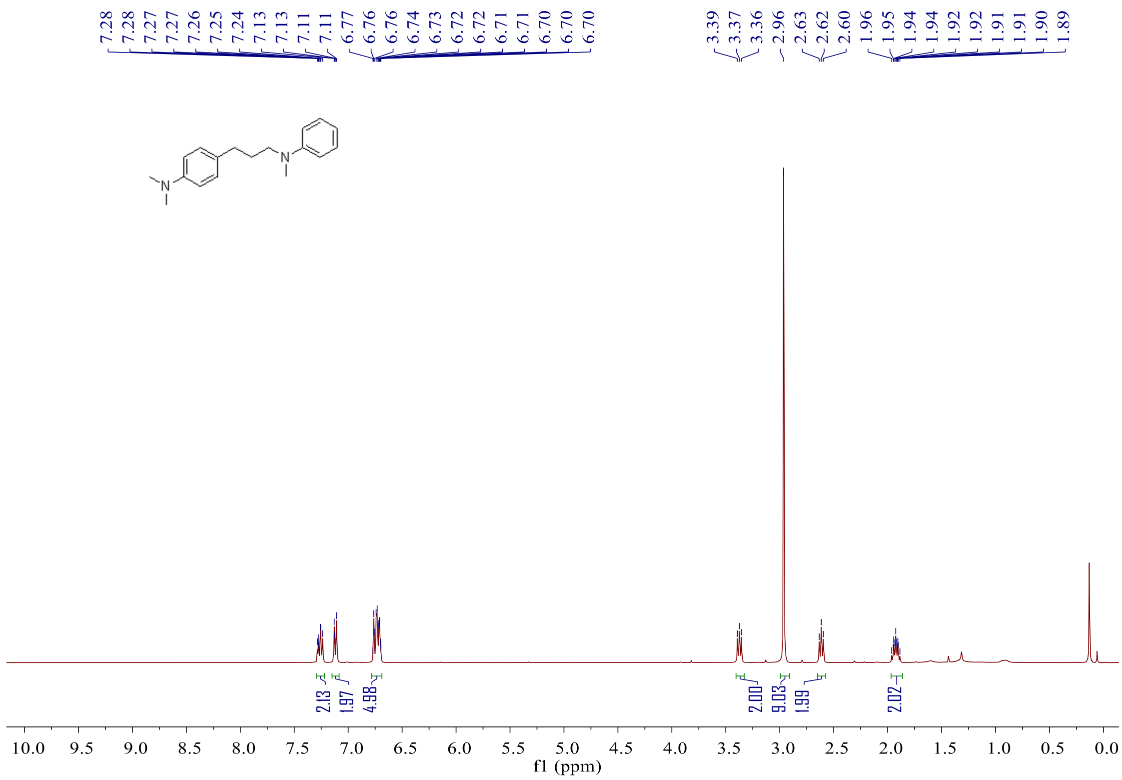


Fig. S90. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ga**.

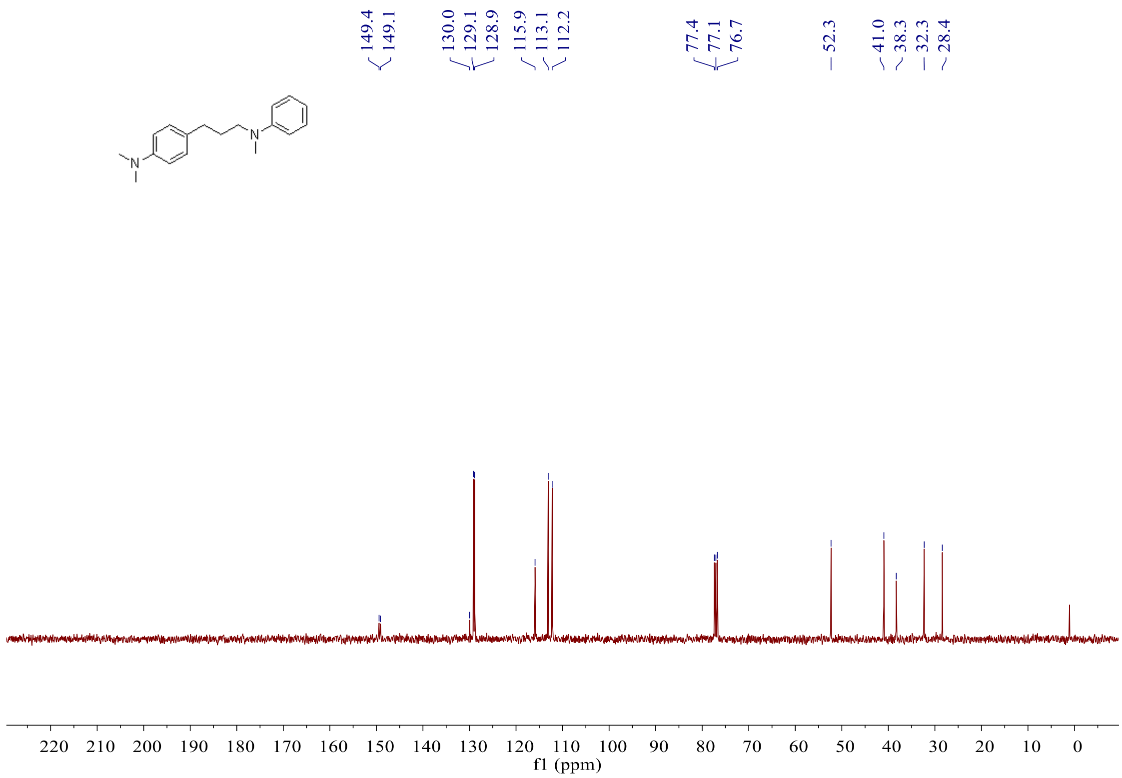


Fig. S91. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ga**.

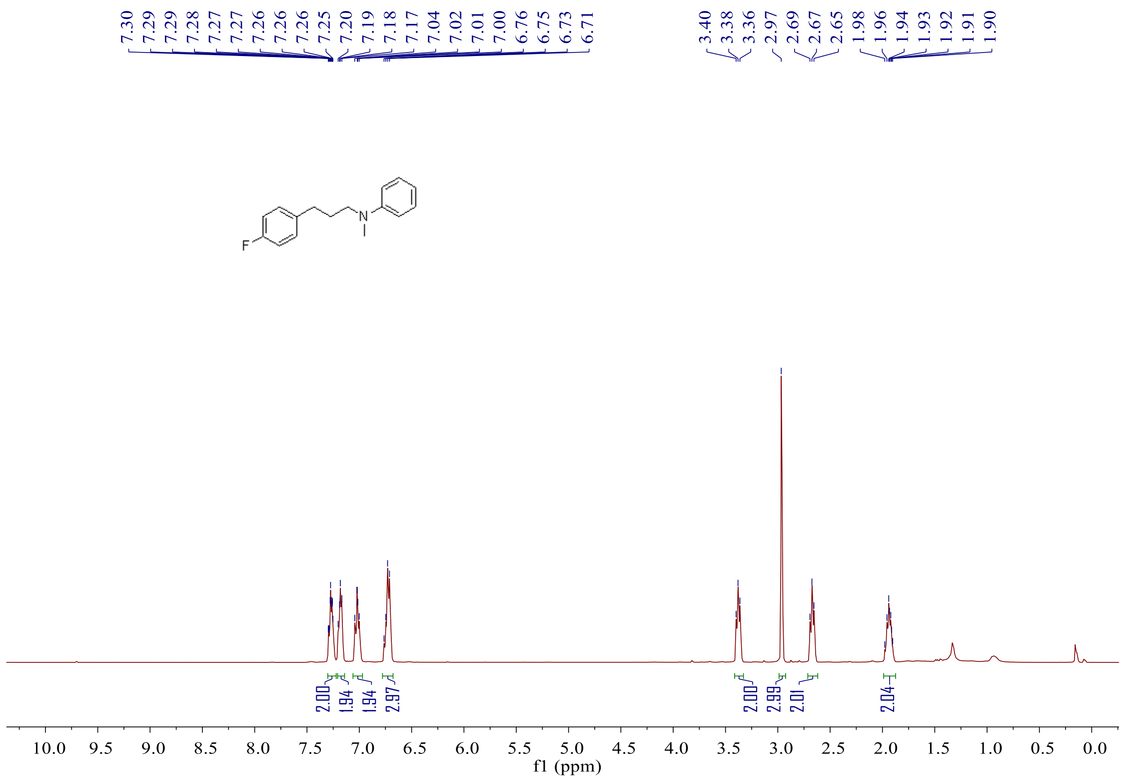


Fig. S92. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ha**.

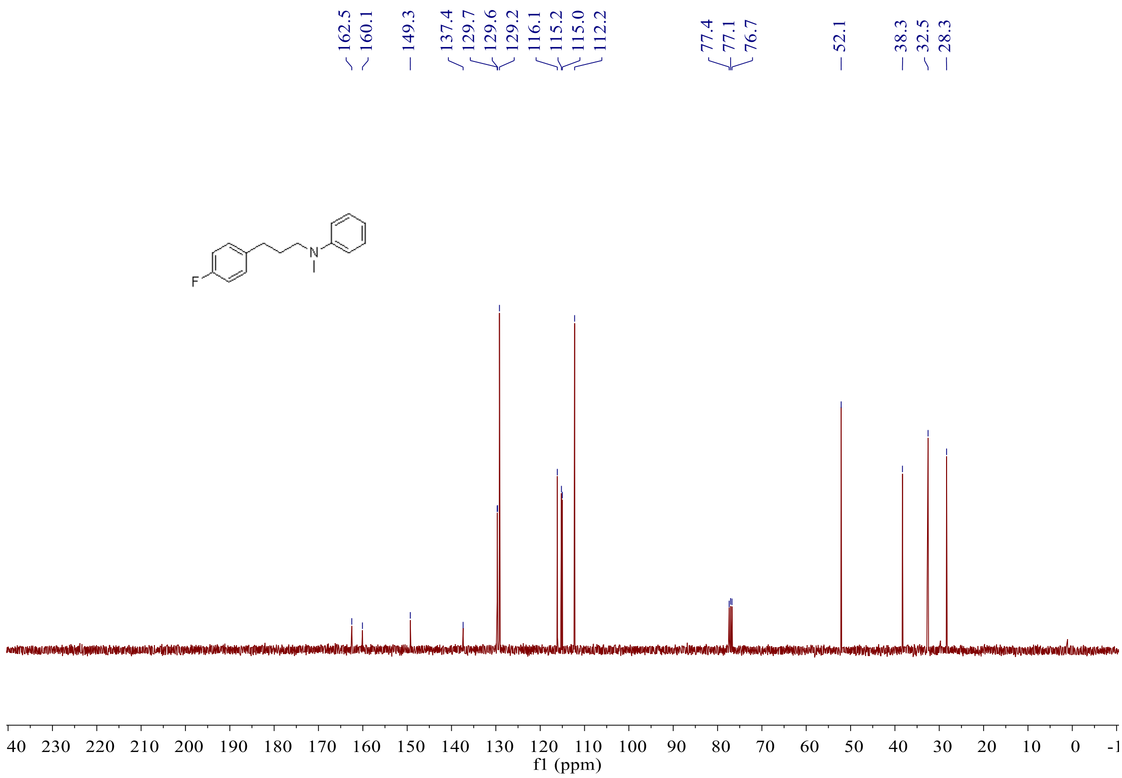


Fig. S93. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ha**.

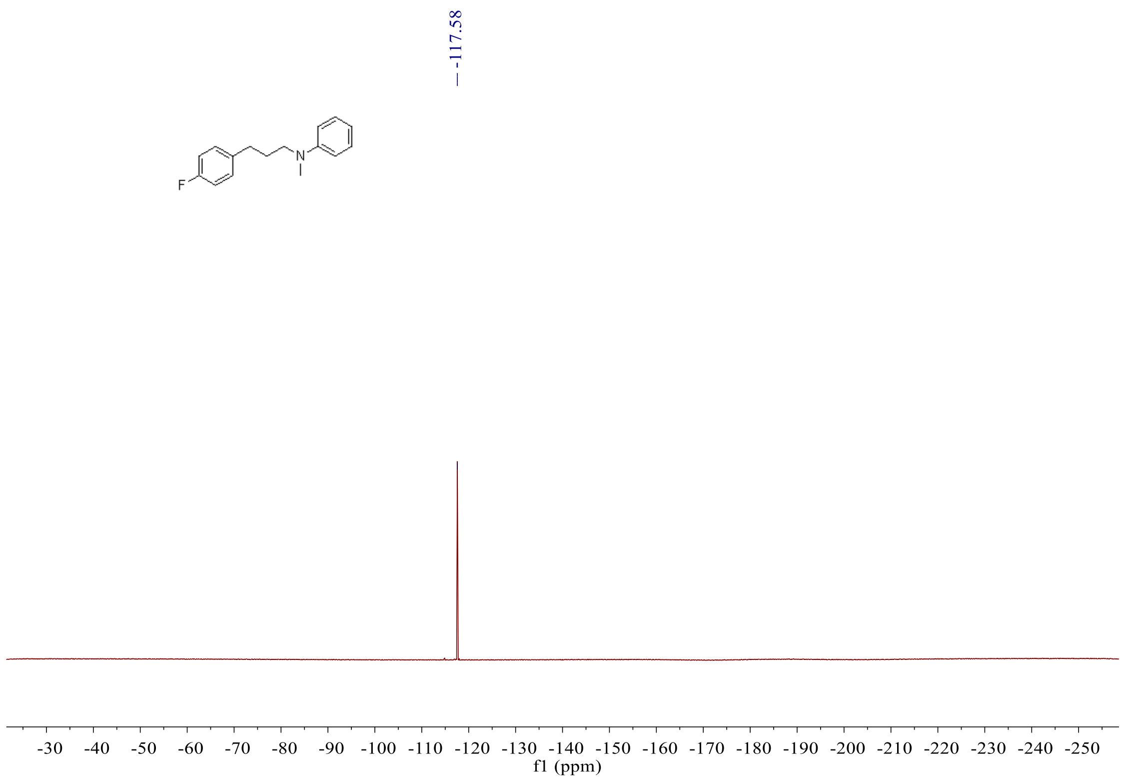


Fig. S94. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of compound **9ha**.

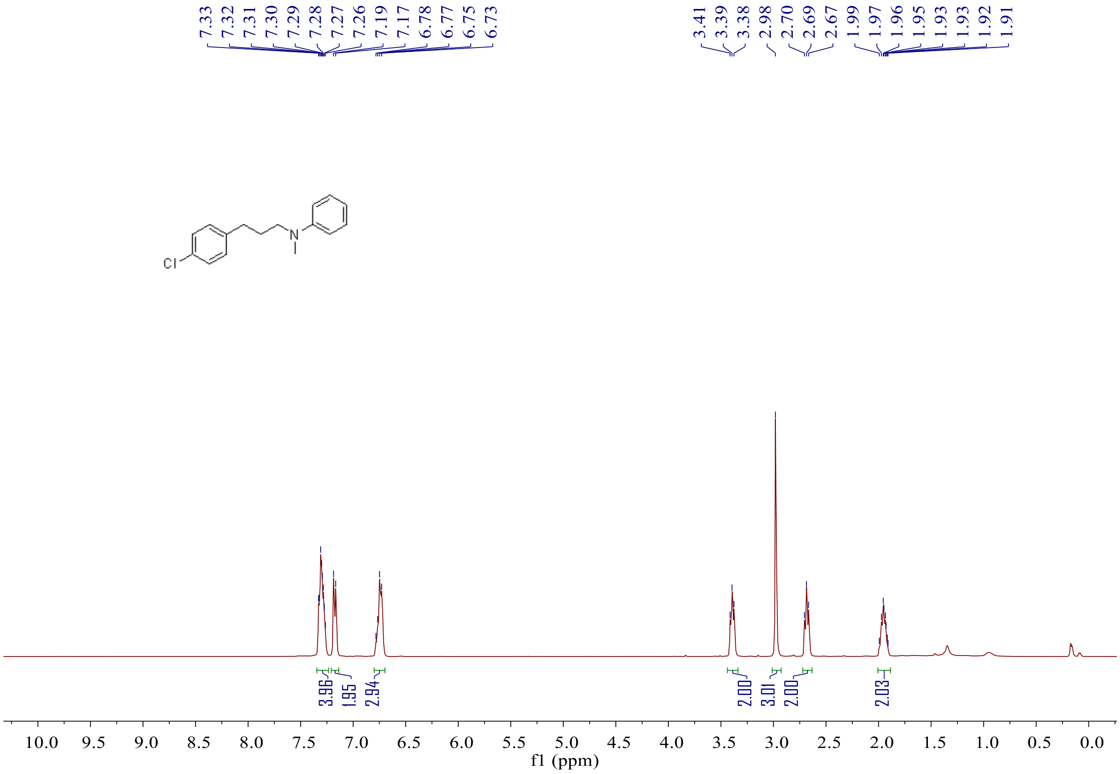


Fig. S95. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ia**.

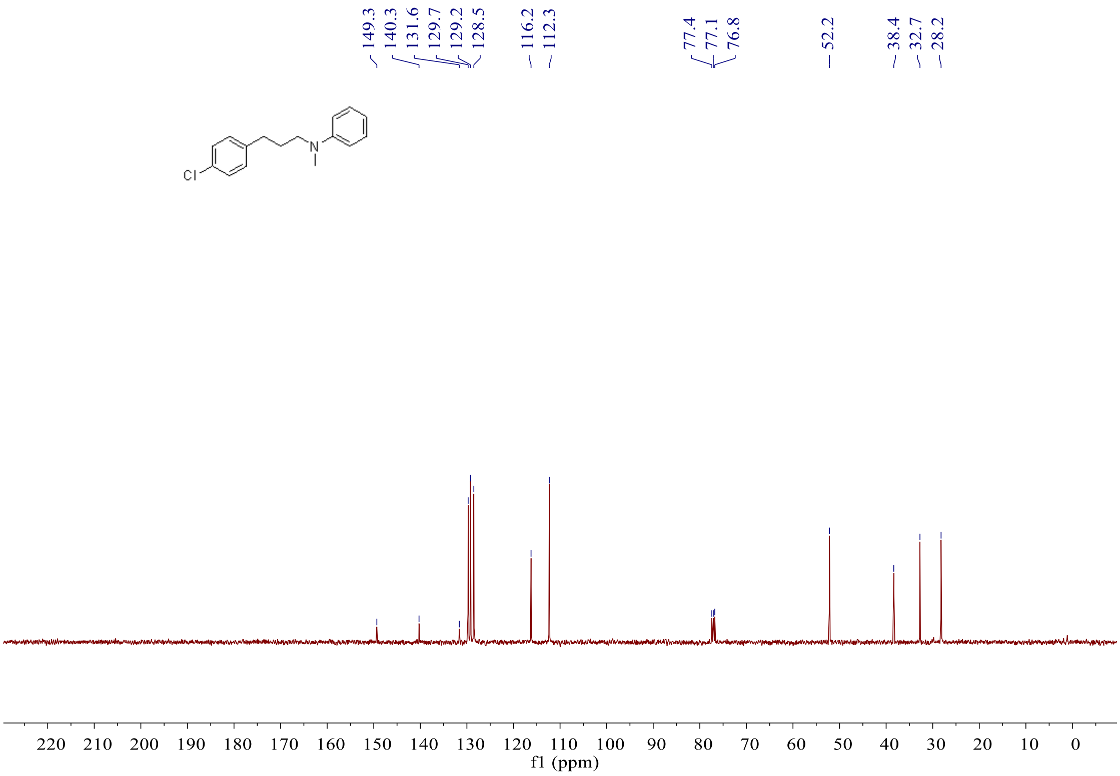


Fig. S96. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ia**.

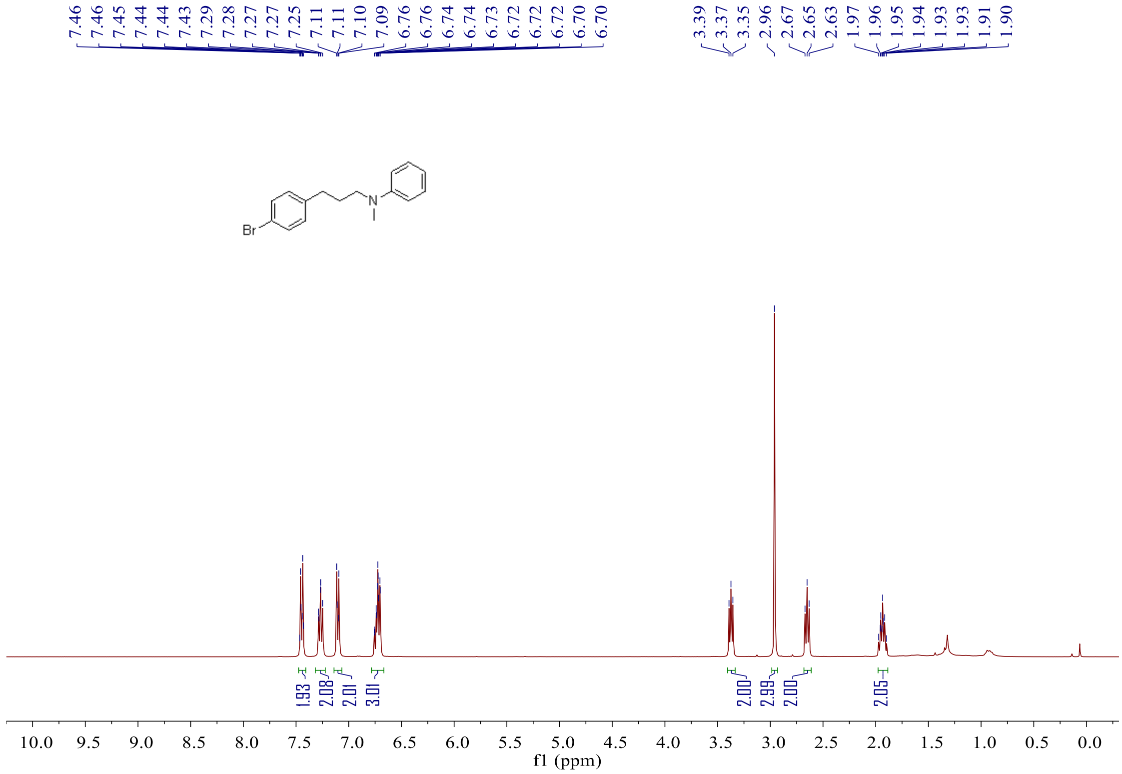


Fig. S97. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ja**.

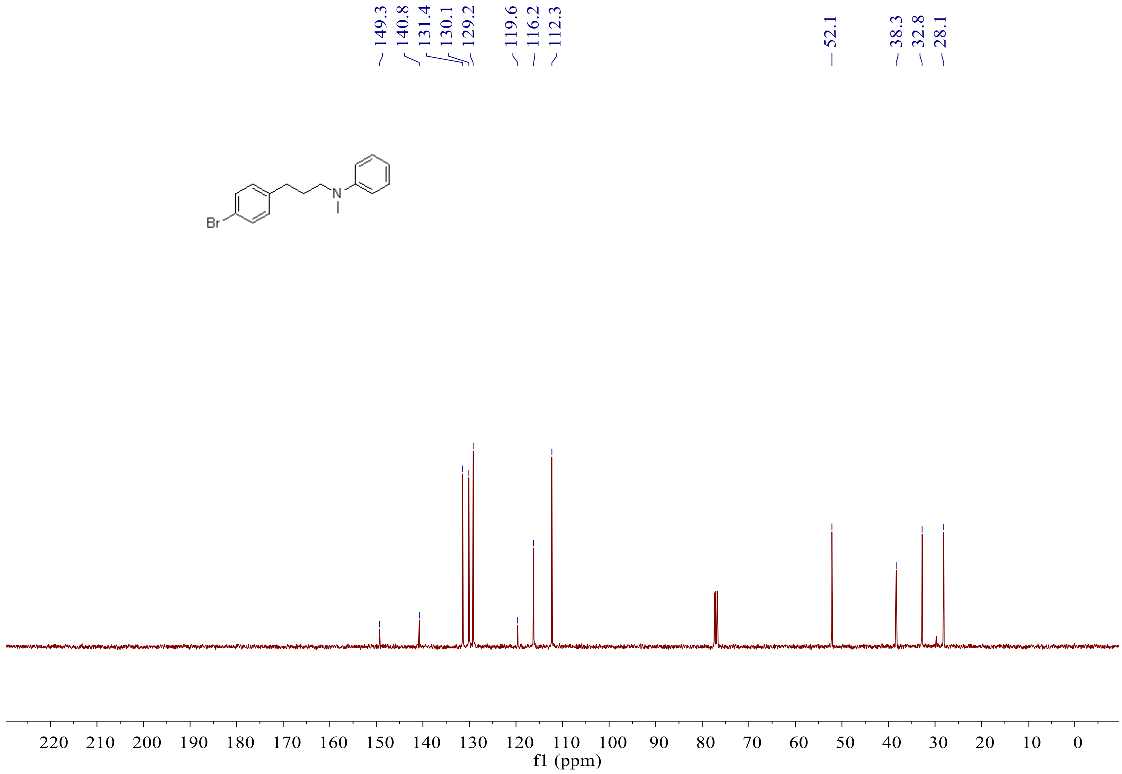


Fig. S98. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ja**.

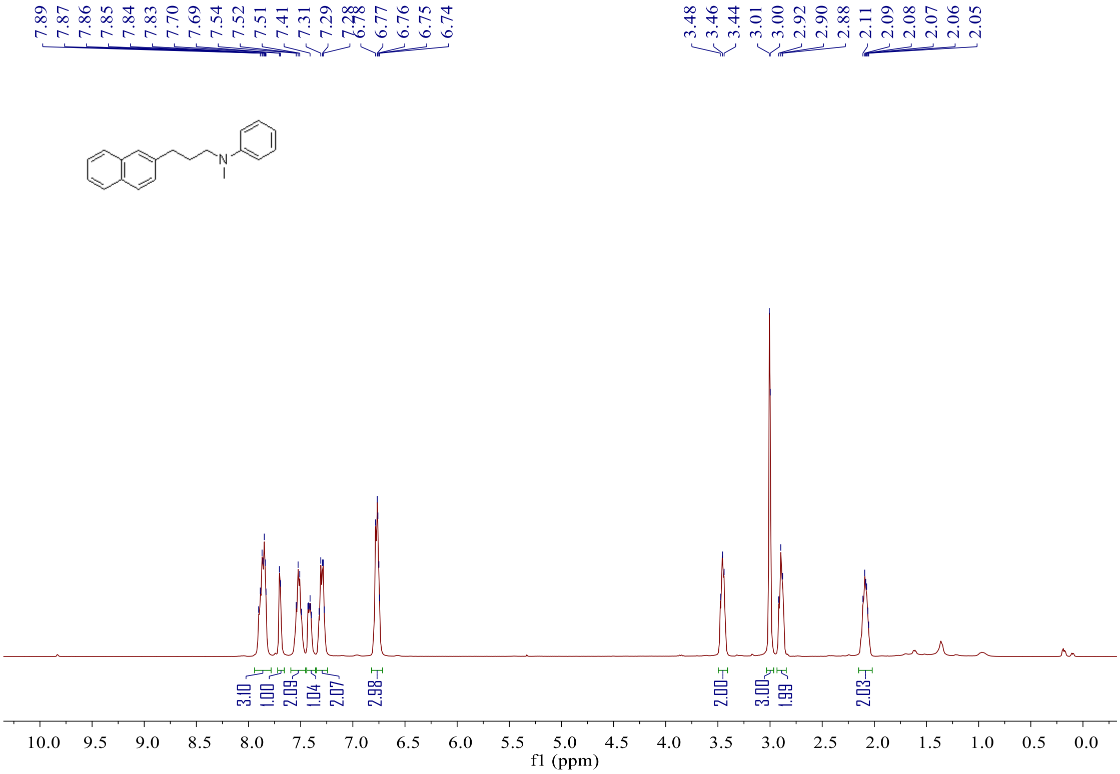


Fig. S99. [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ka.**

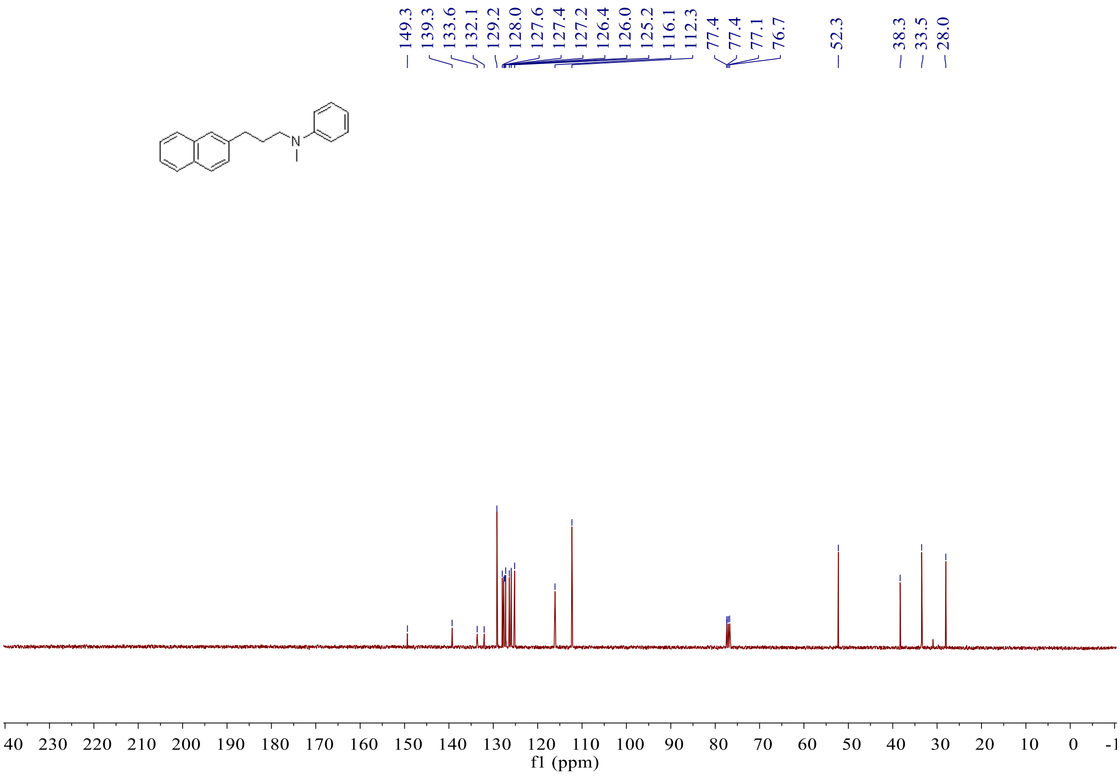


Fig. S100. [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ka**.

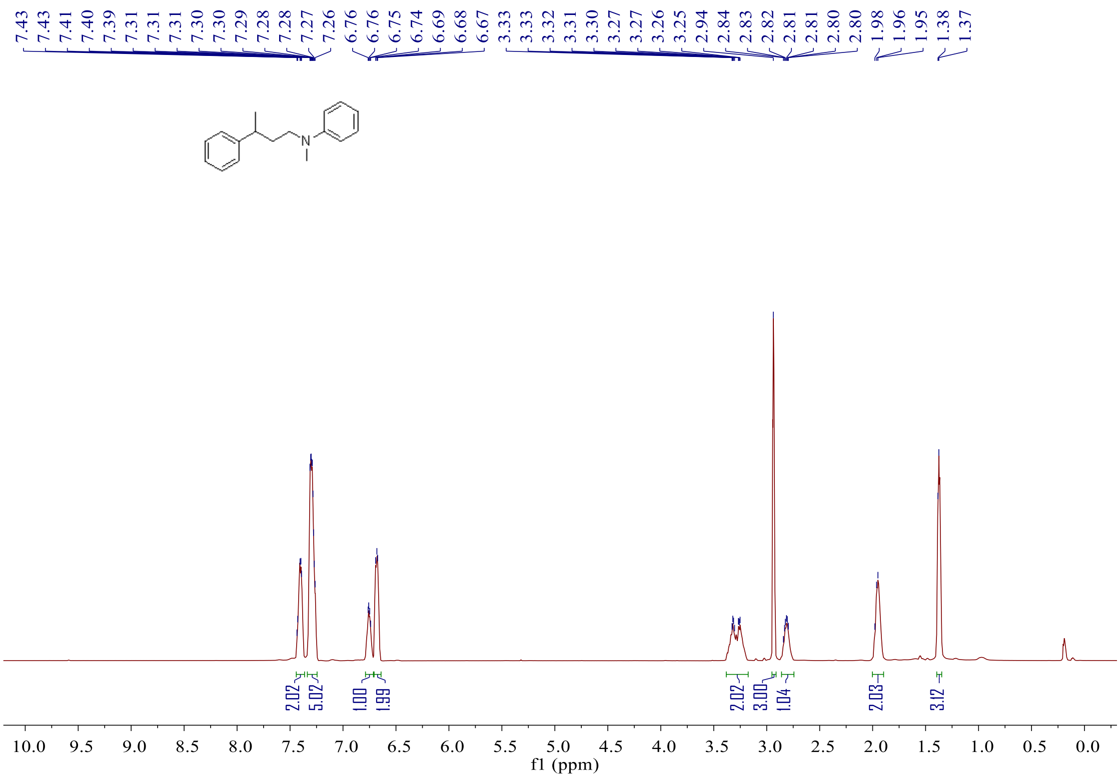


Fig. S101. [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9la**.

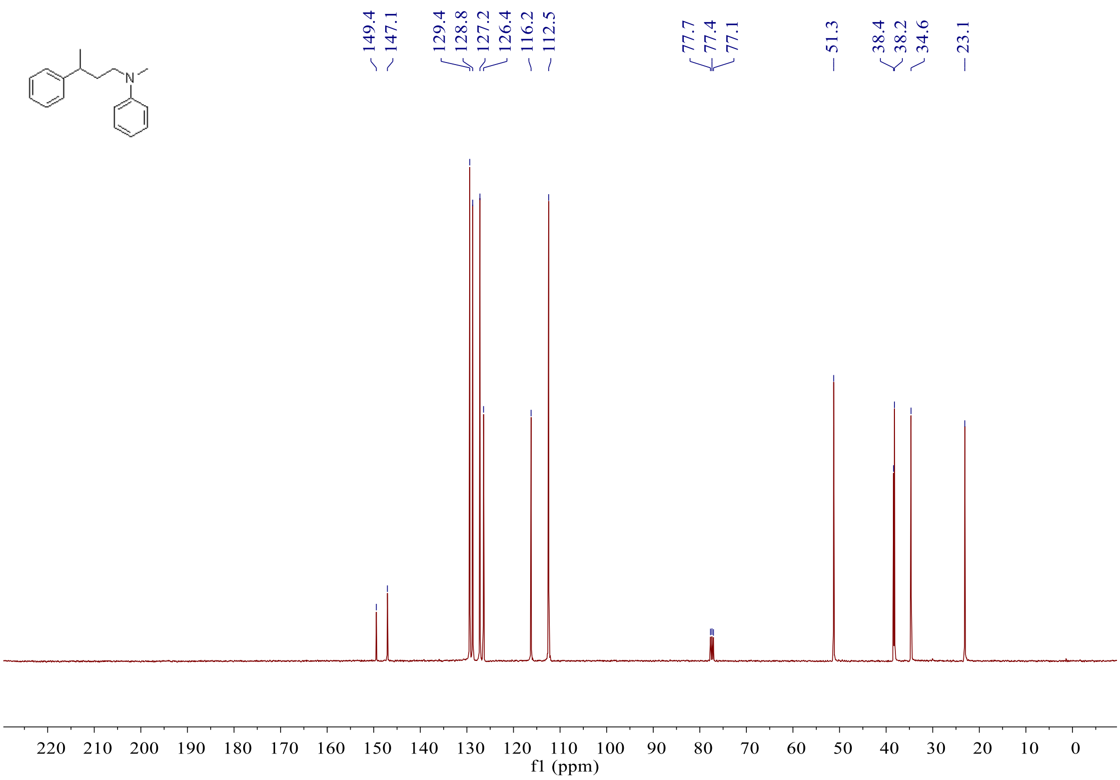


Fig. S102. [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9la**.

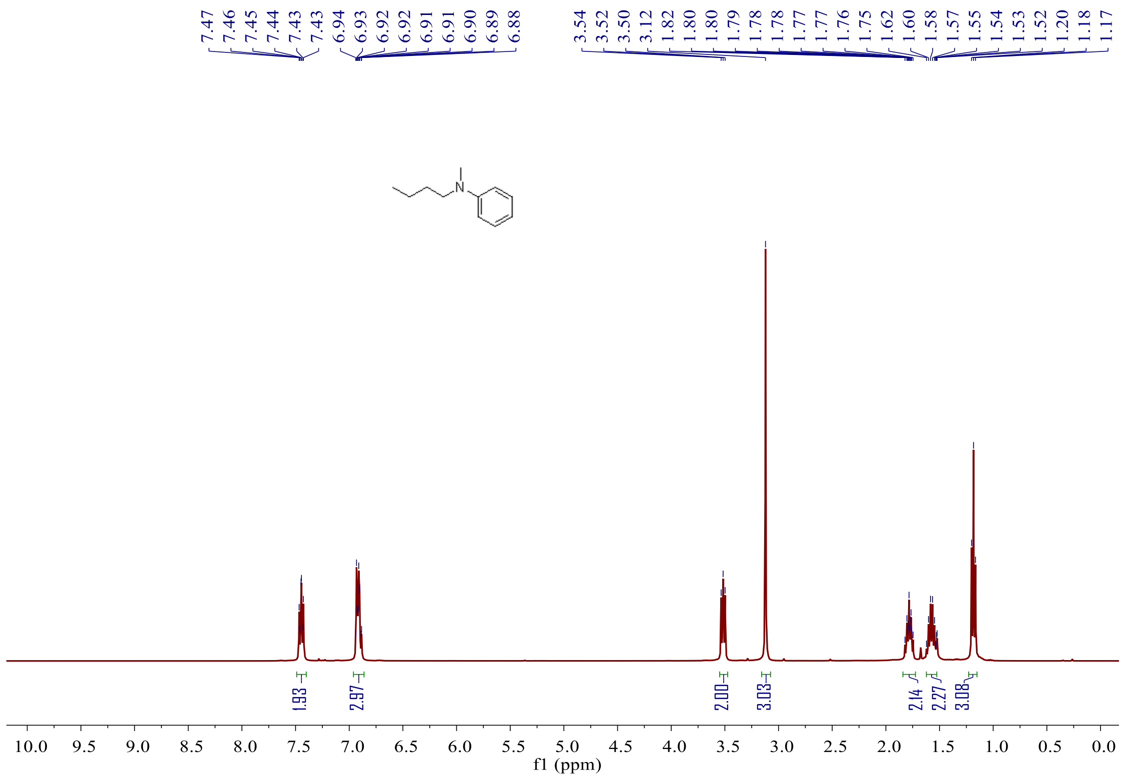


Fig. S103. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ma-2**.

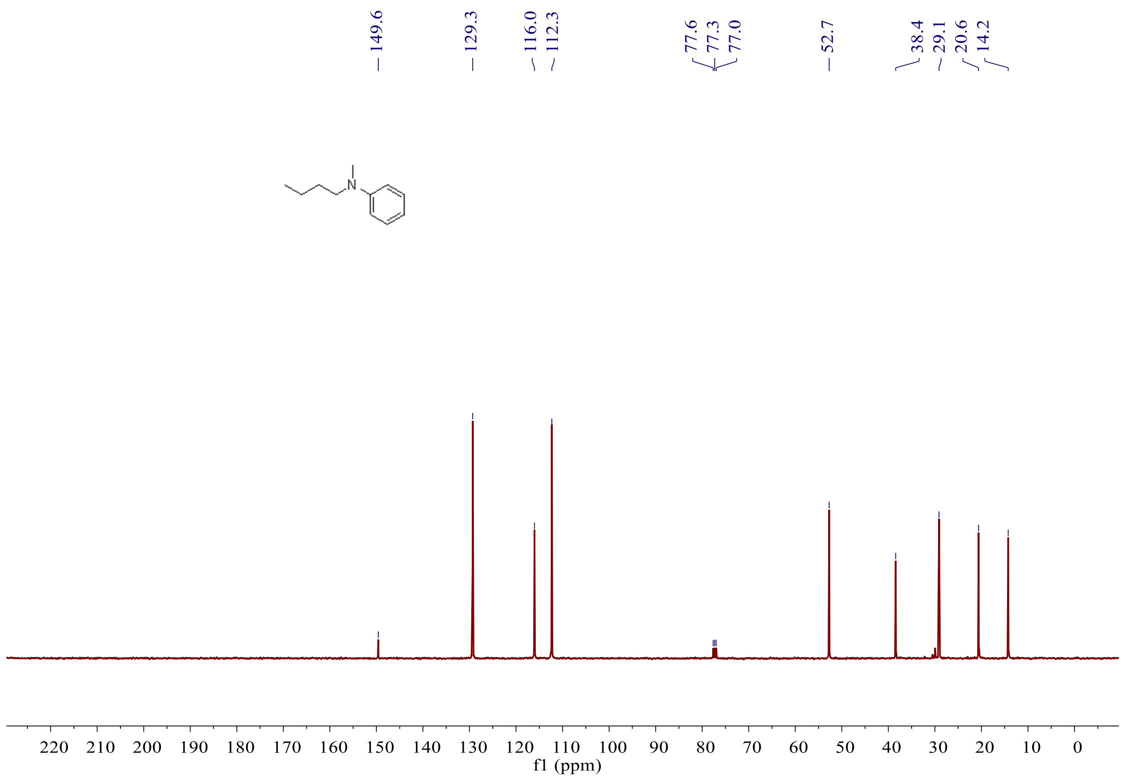


Fig. S104. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ma-2.**

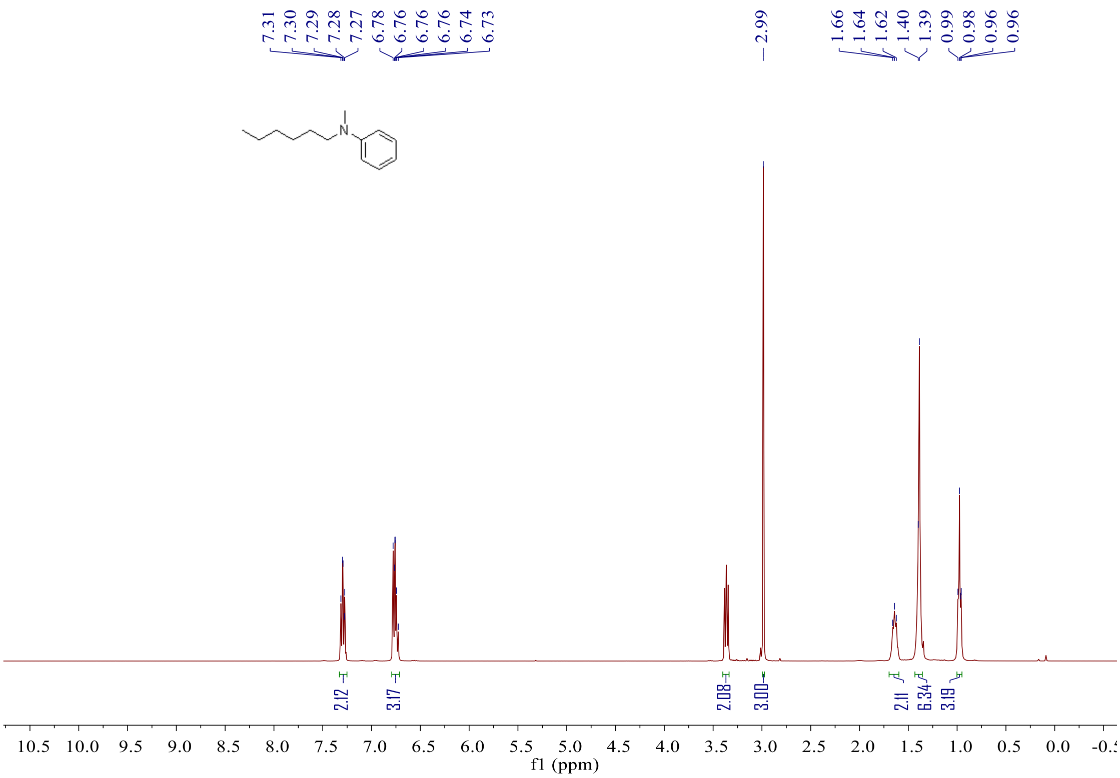


Fig. S105. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ma-4**.

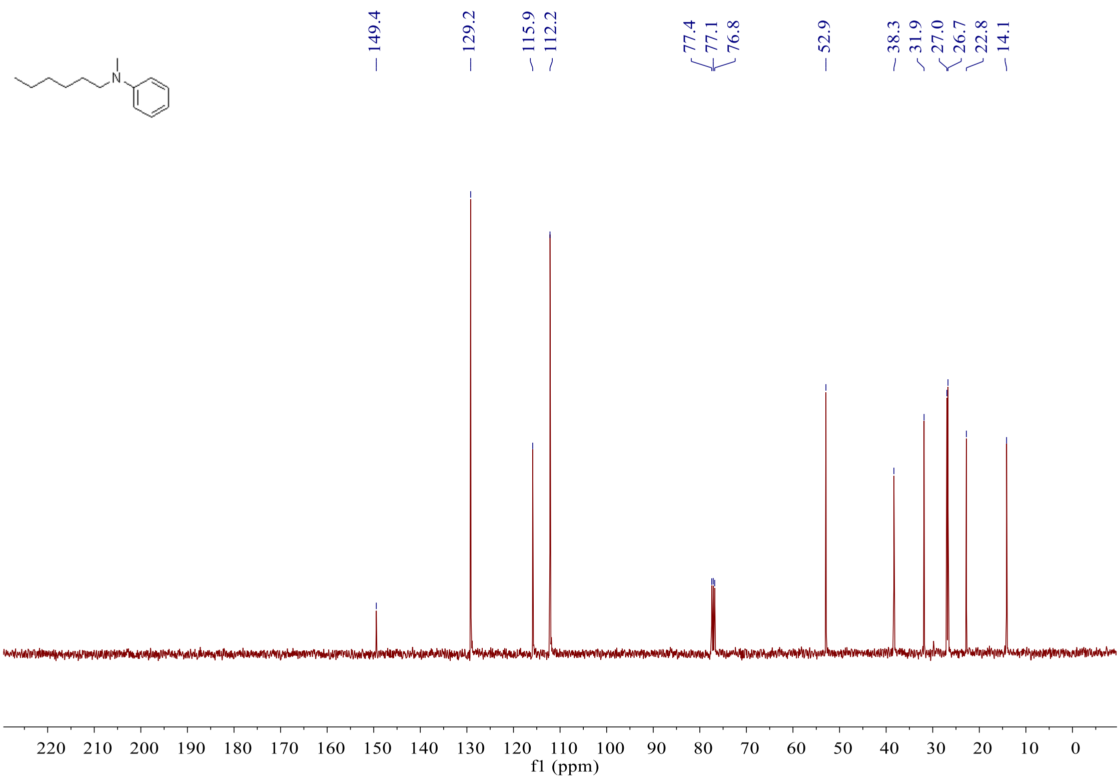


Fig. S106. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ma-4.**

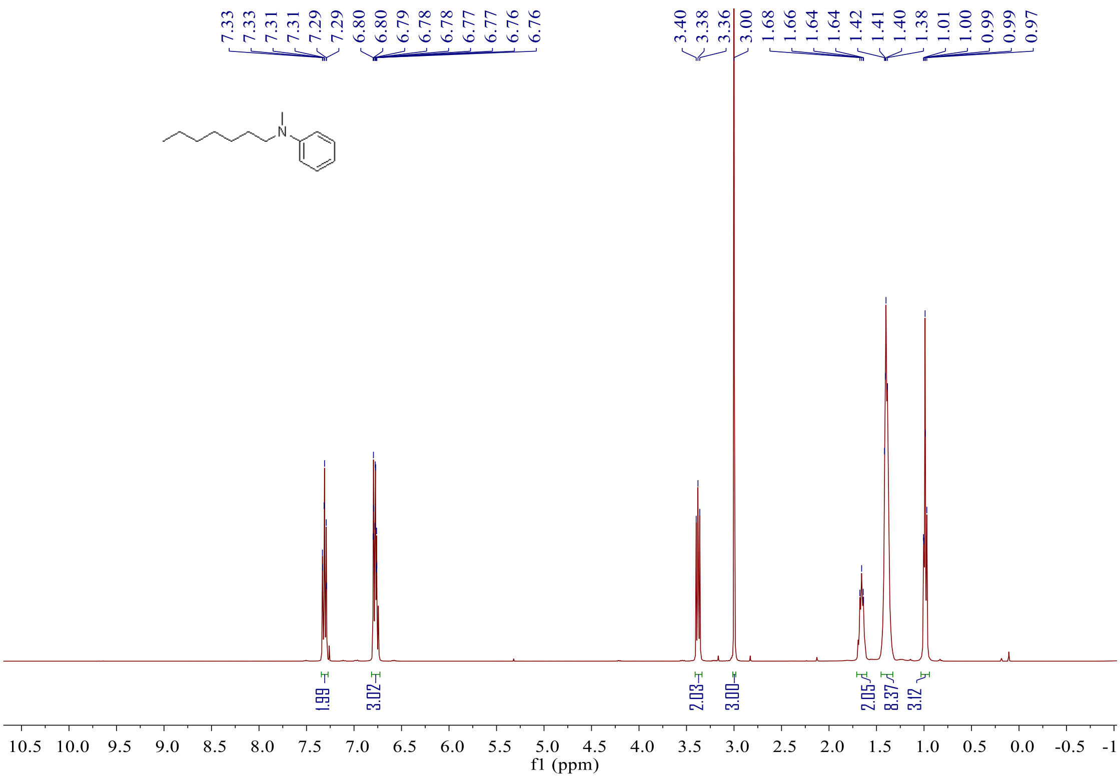


Fig. S107. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ma-5**.

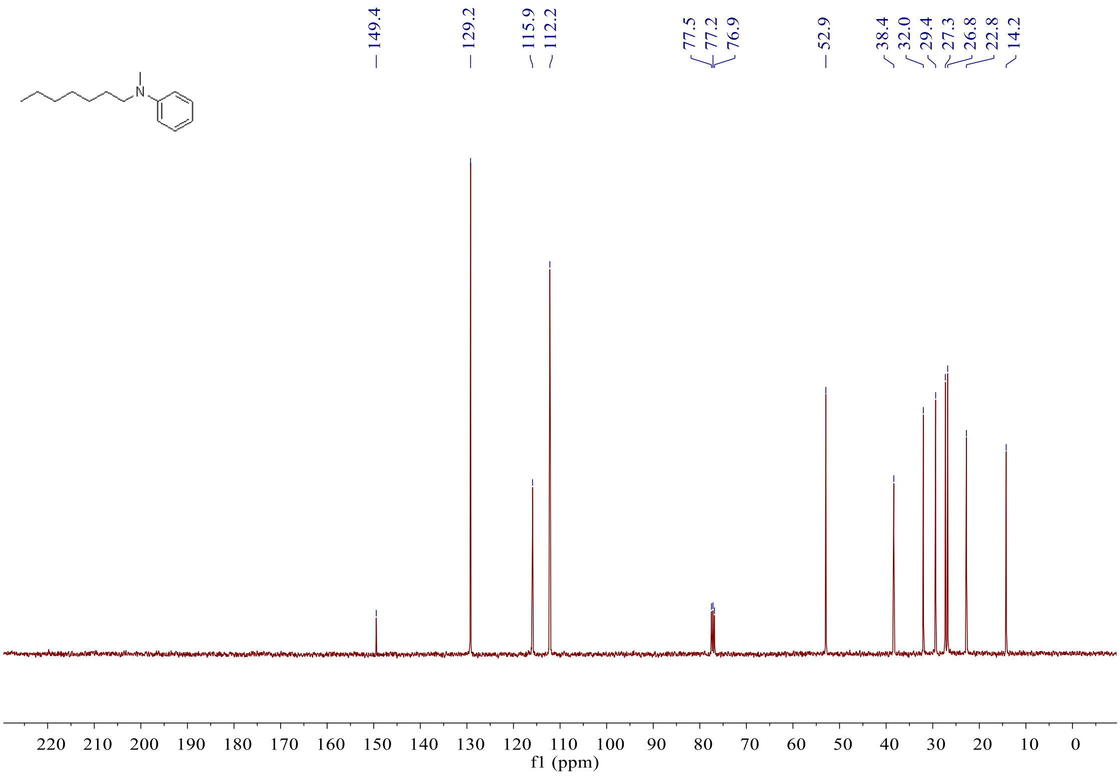


Fig. S108. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ma-5.**

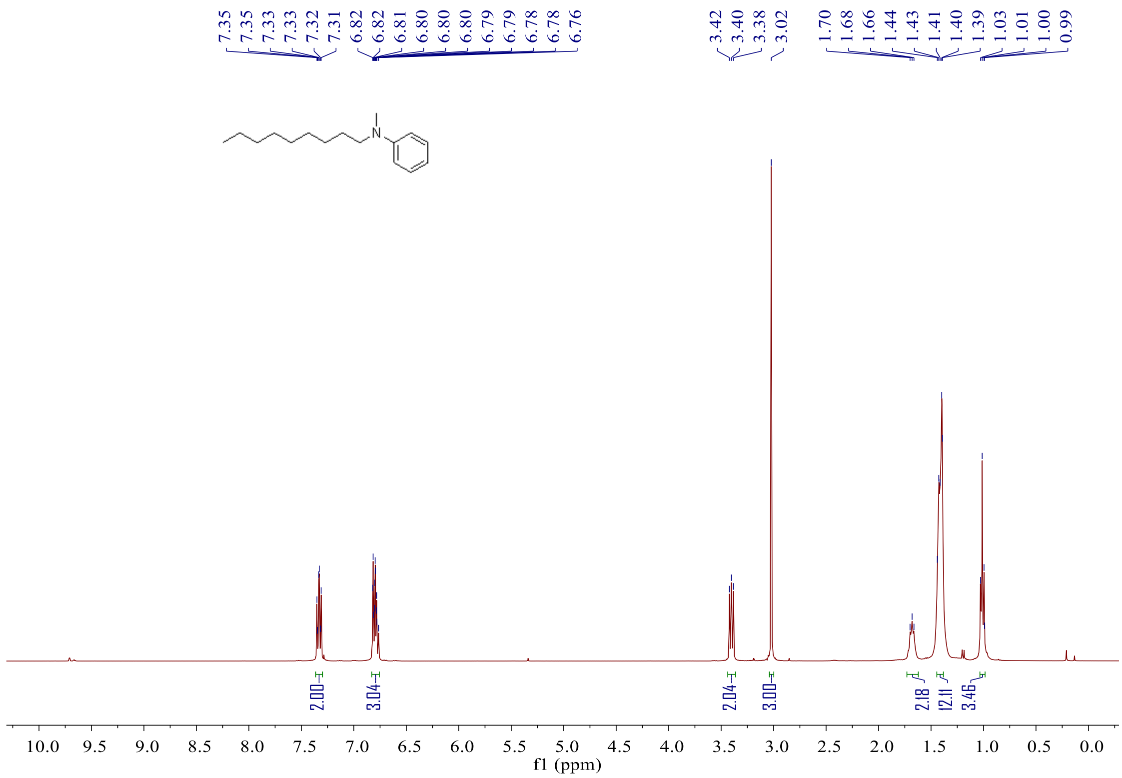


Fig. S109. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ma-7.**

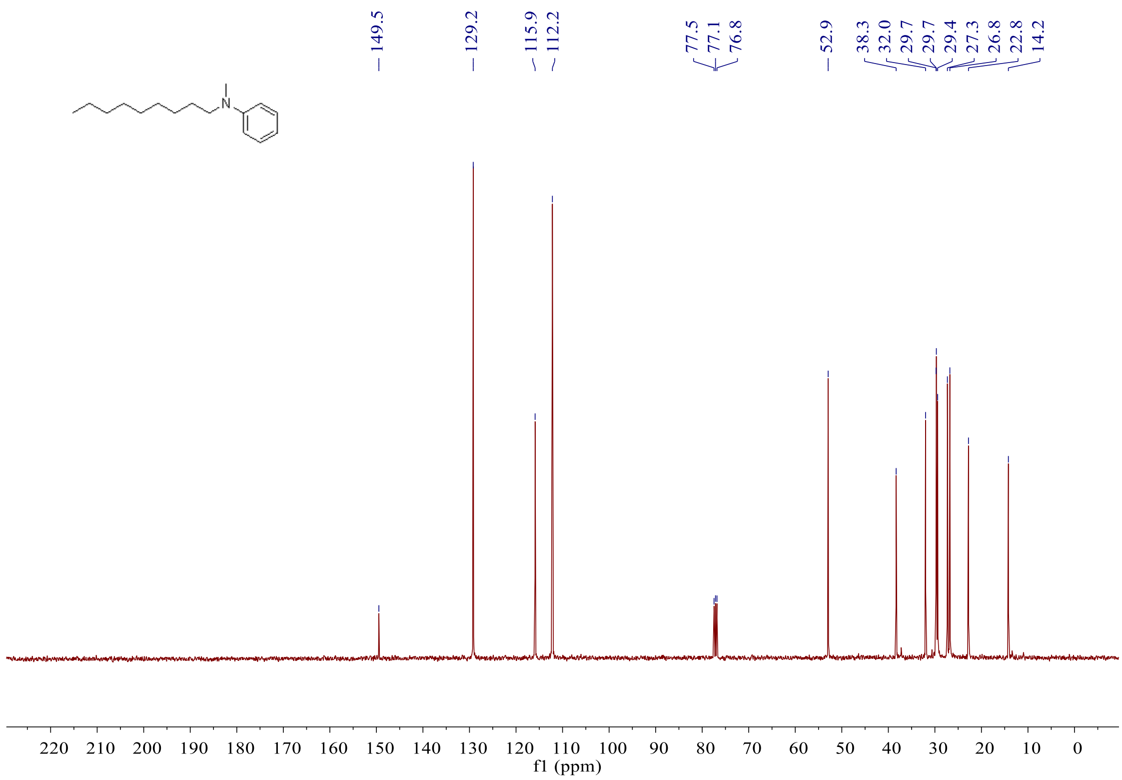


Fig. S110. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ma-7**.

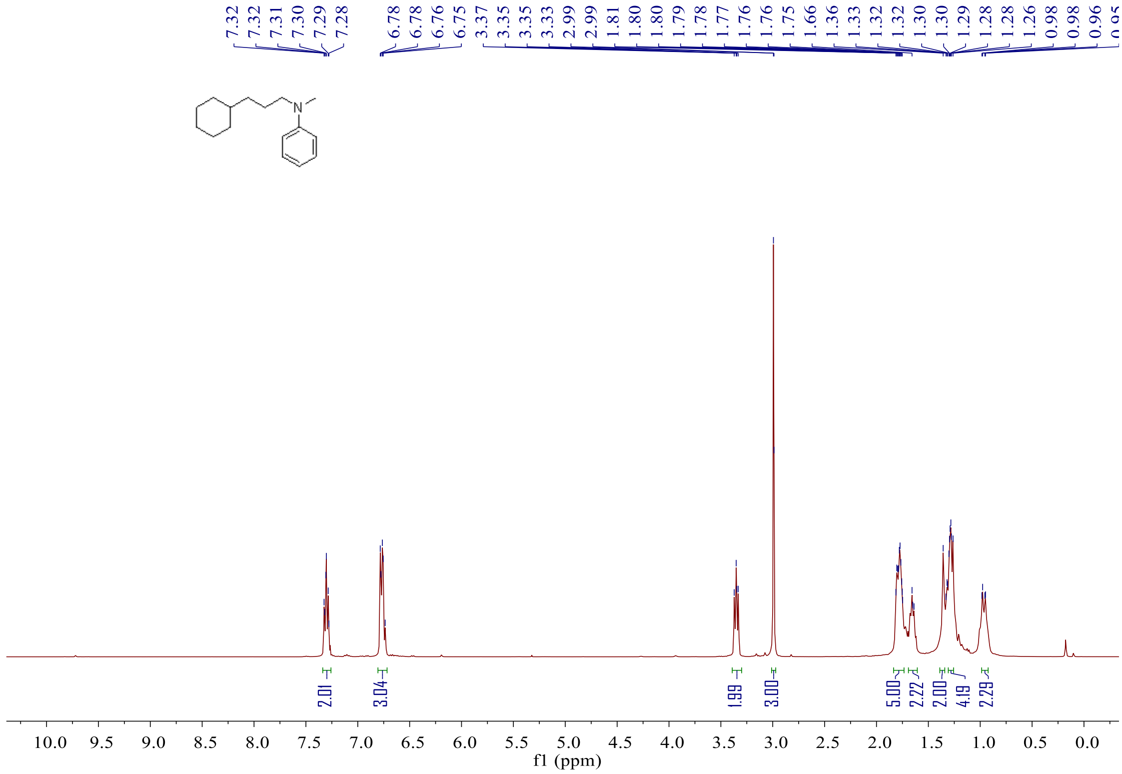


Fig. S111. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9na**.

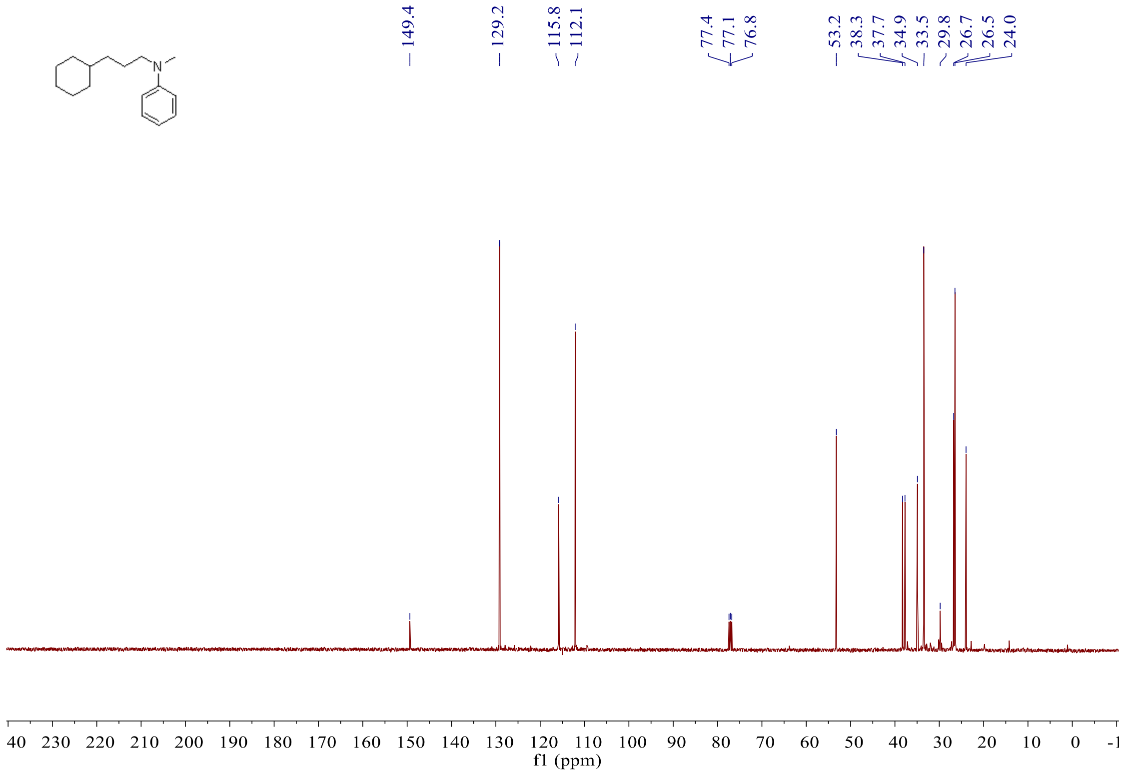


Fig. S112. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9na.**

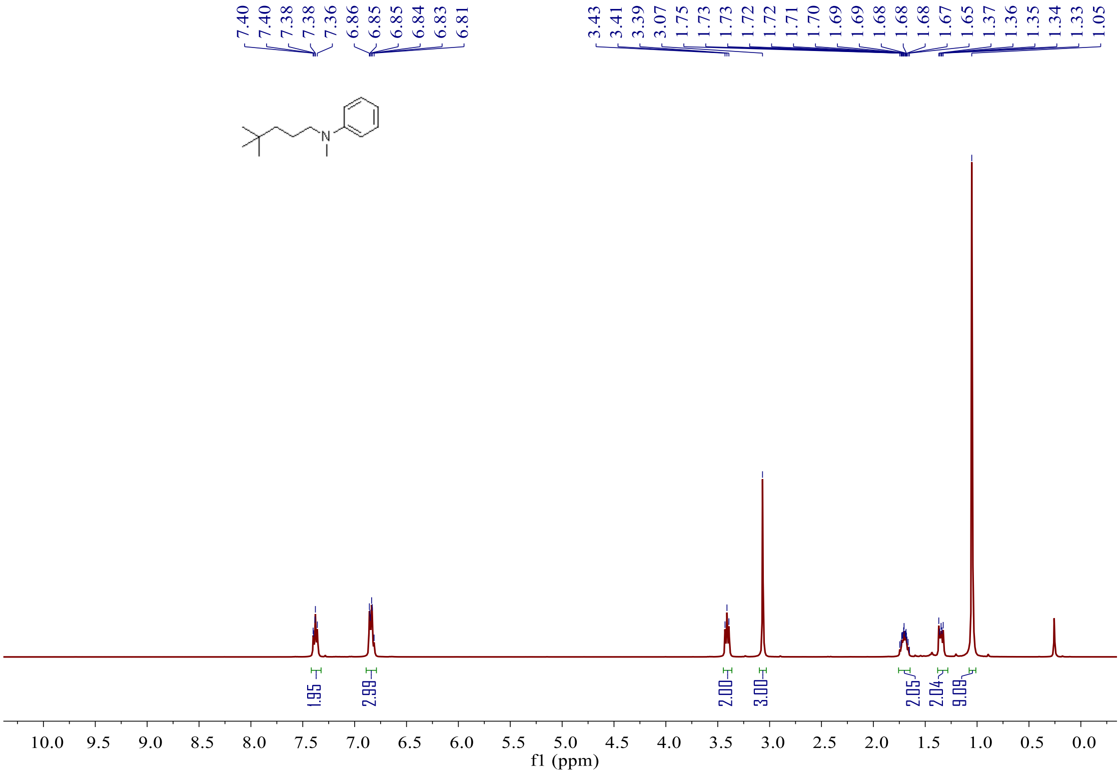


Fig. S113. [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9oa.**

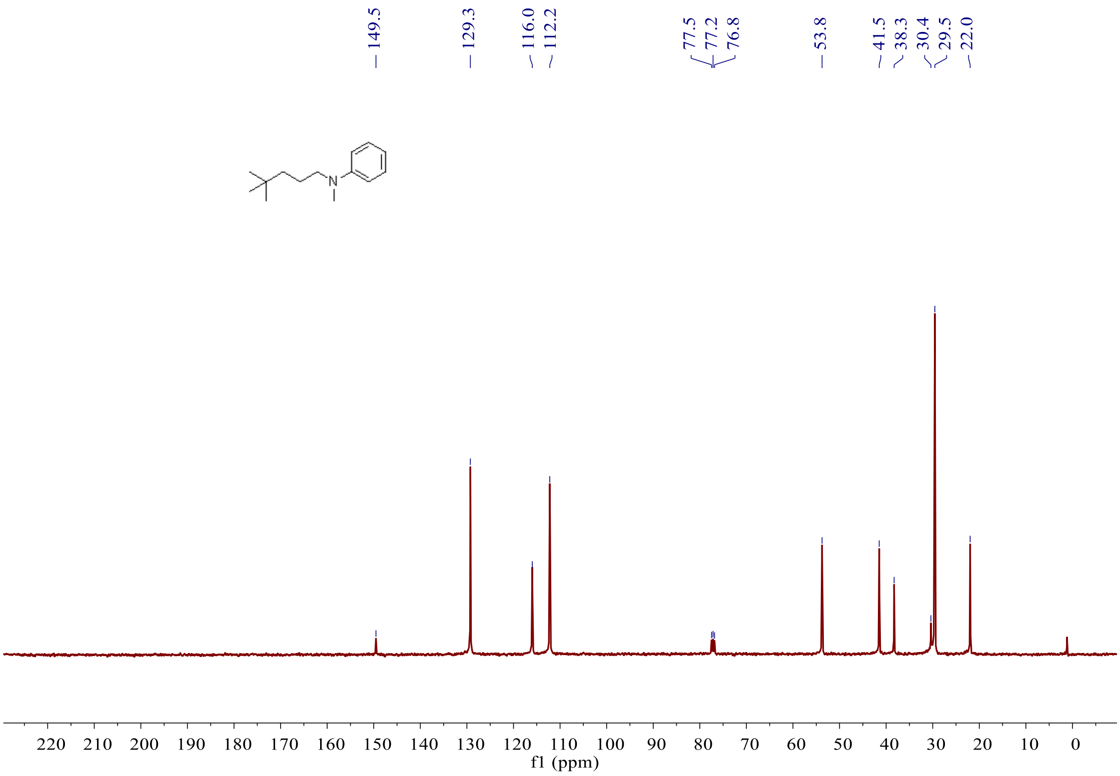


Fig. S114. [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9oa.**

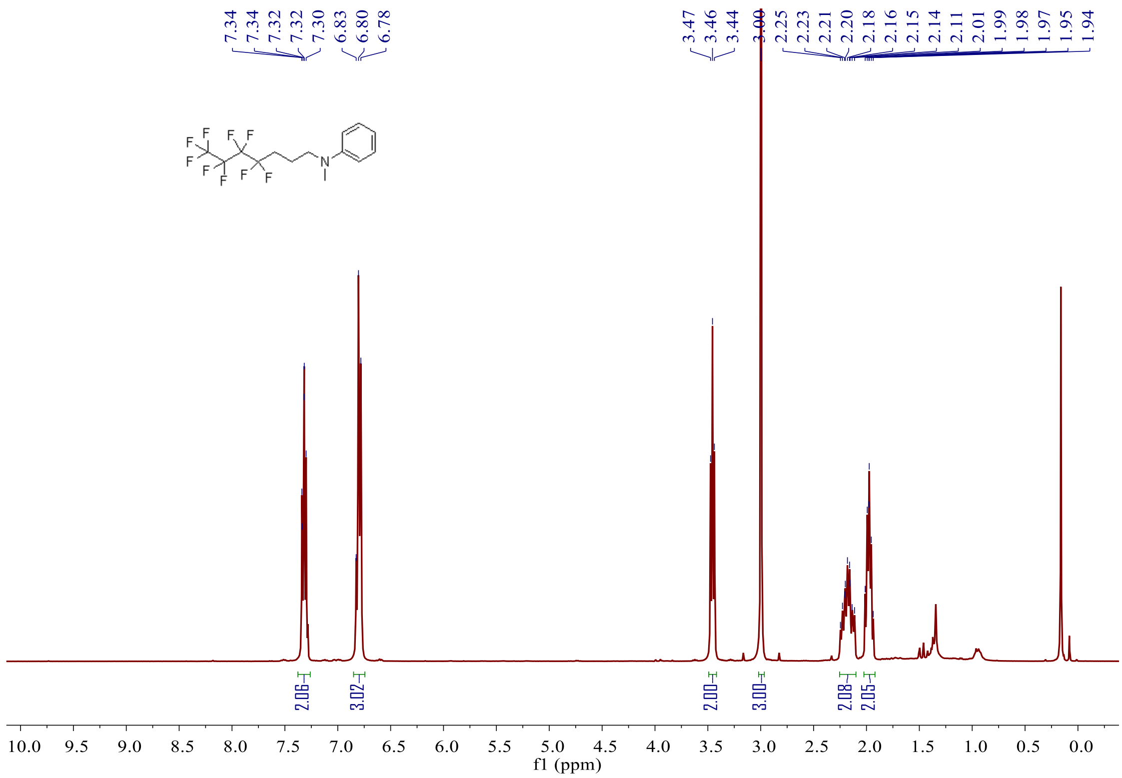


Fig. S115. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9pa**.

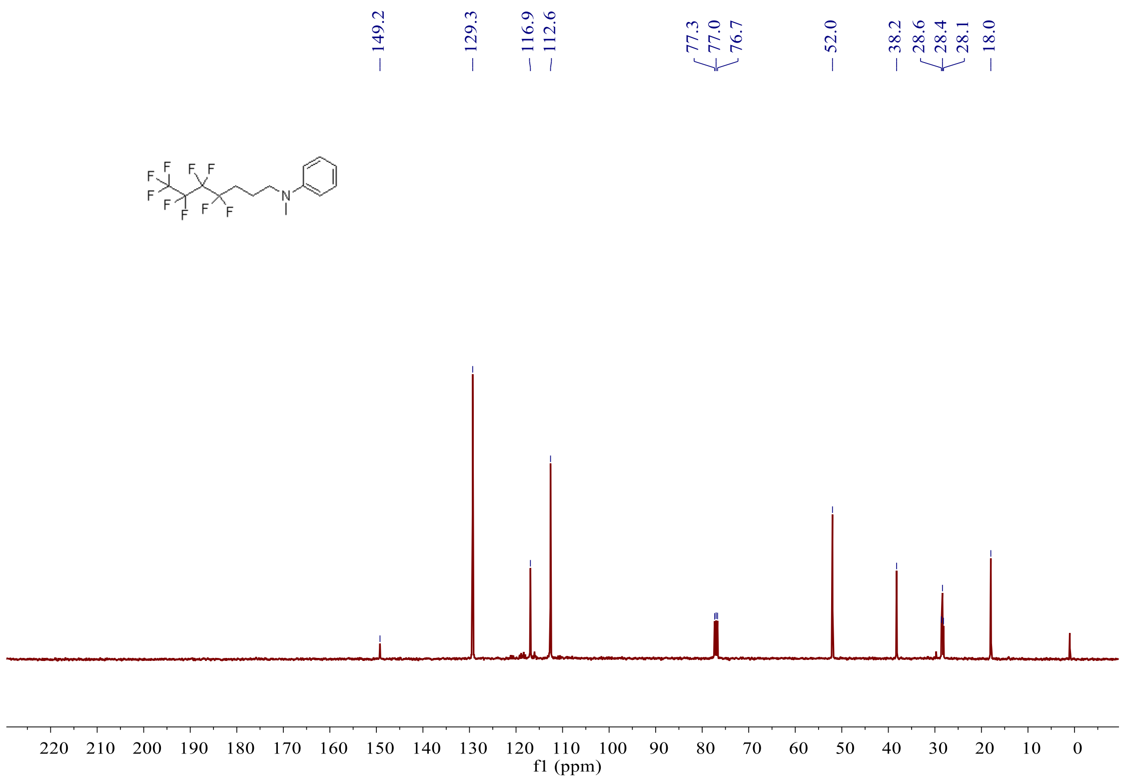


Fig. S116. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9pa**.

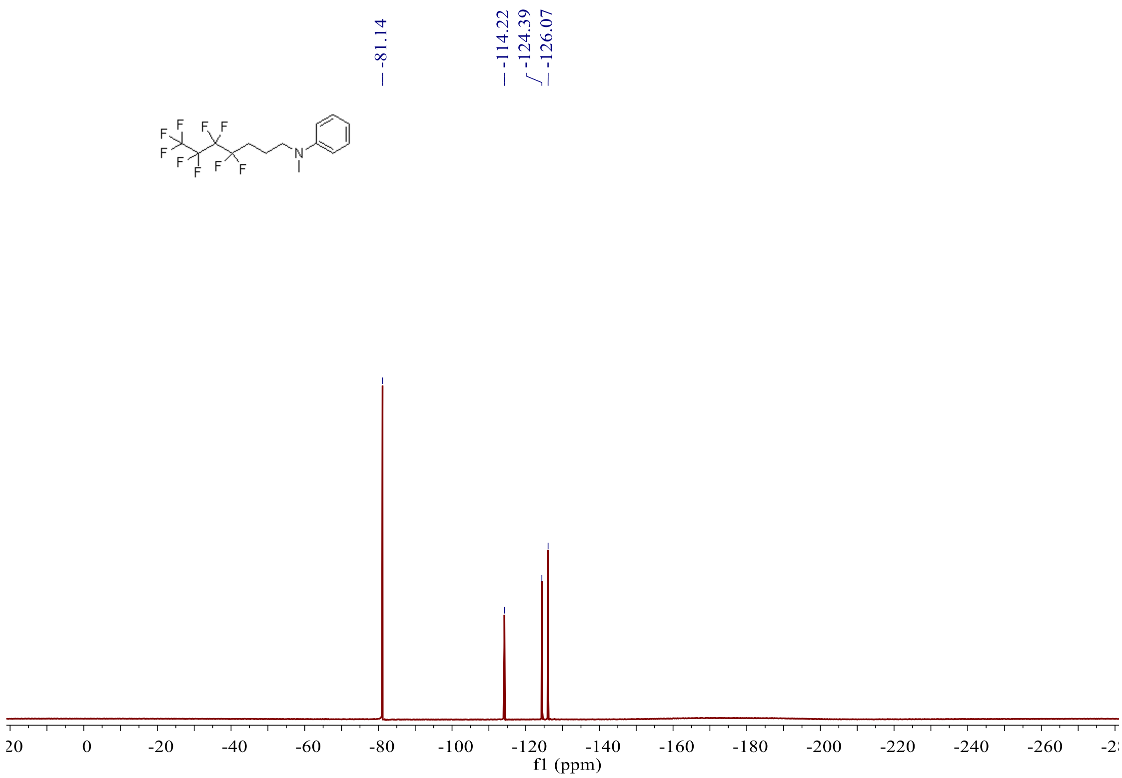


Fig. S117. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of compound **9pa**.

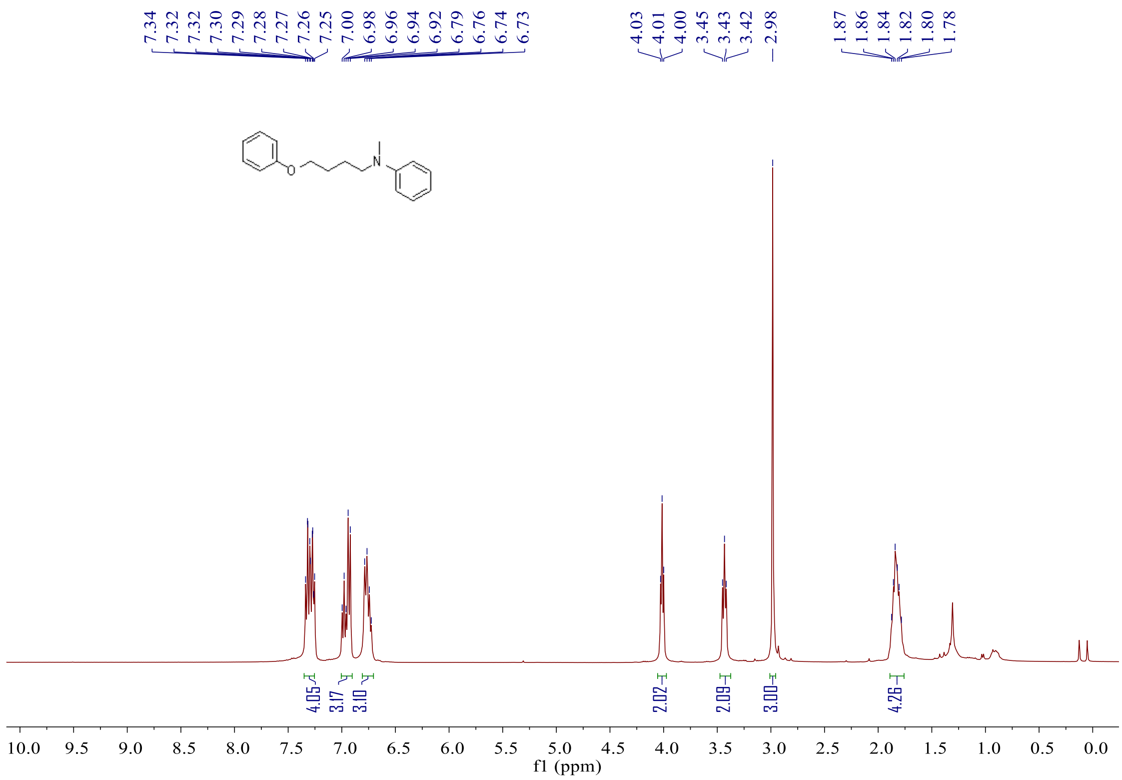


Fig. S118. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9qa.**

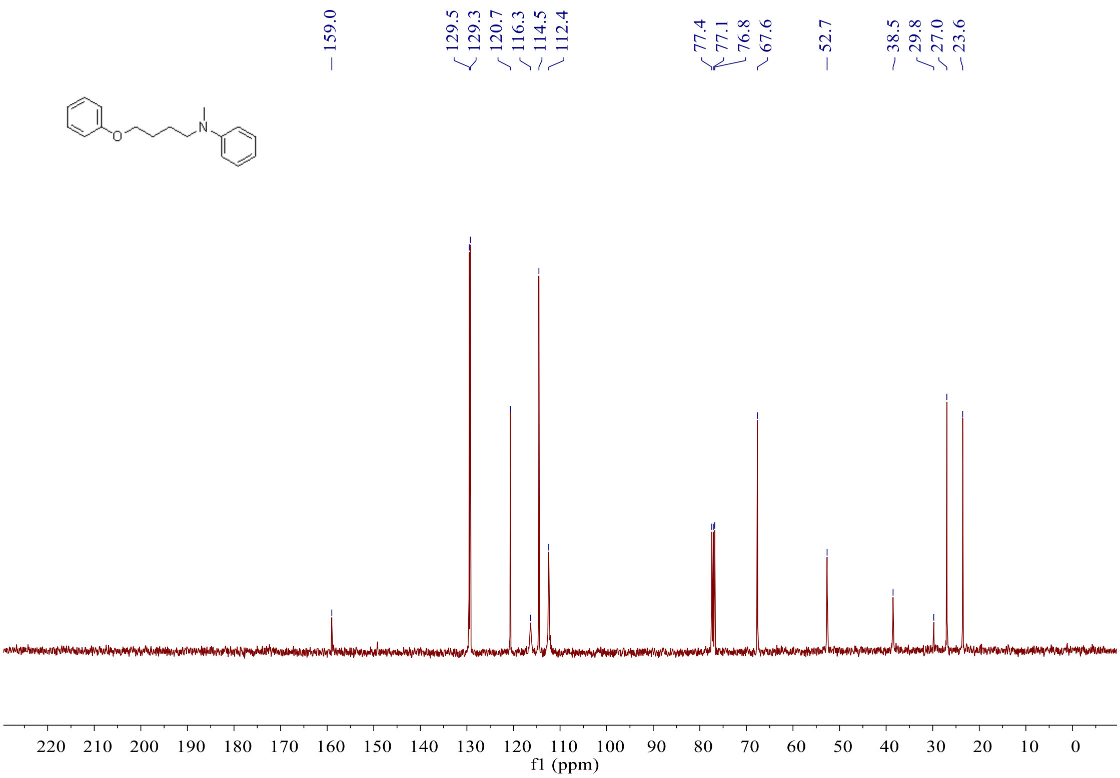


Fig. S119. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9qa.**

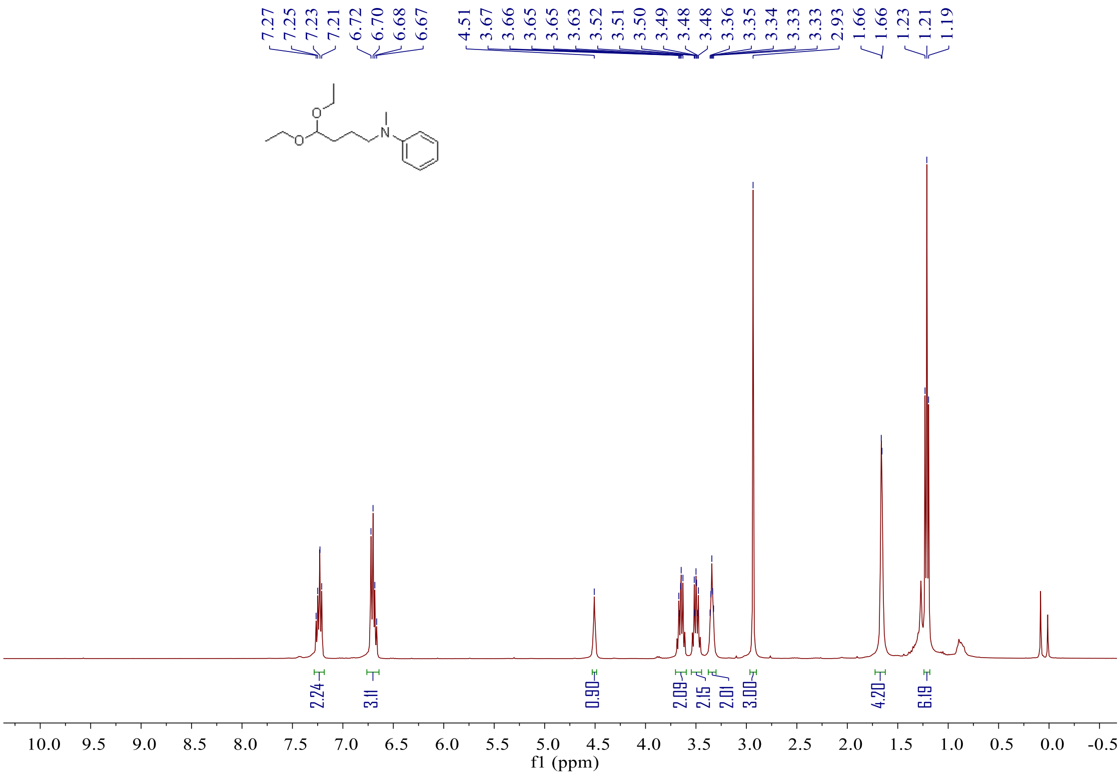


Fig. S120. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ra**.

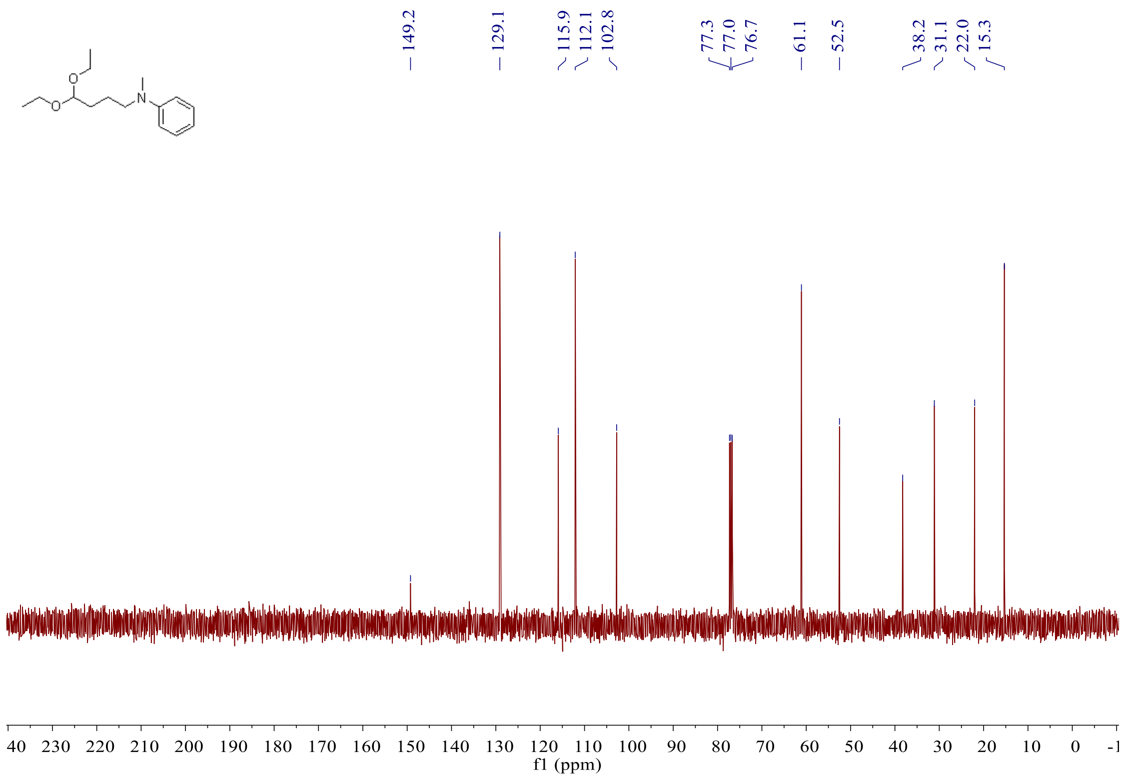


Fig. S121. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ra**.

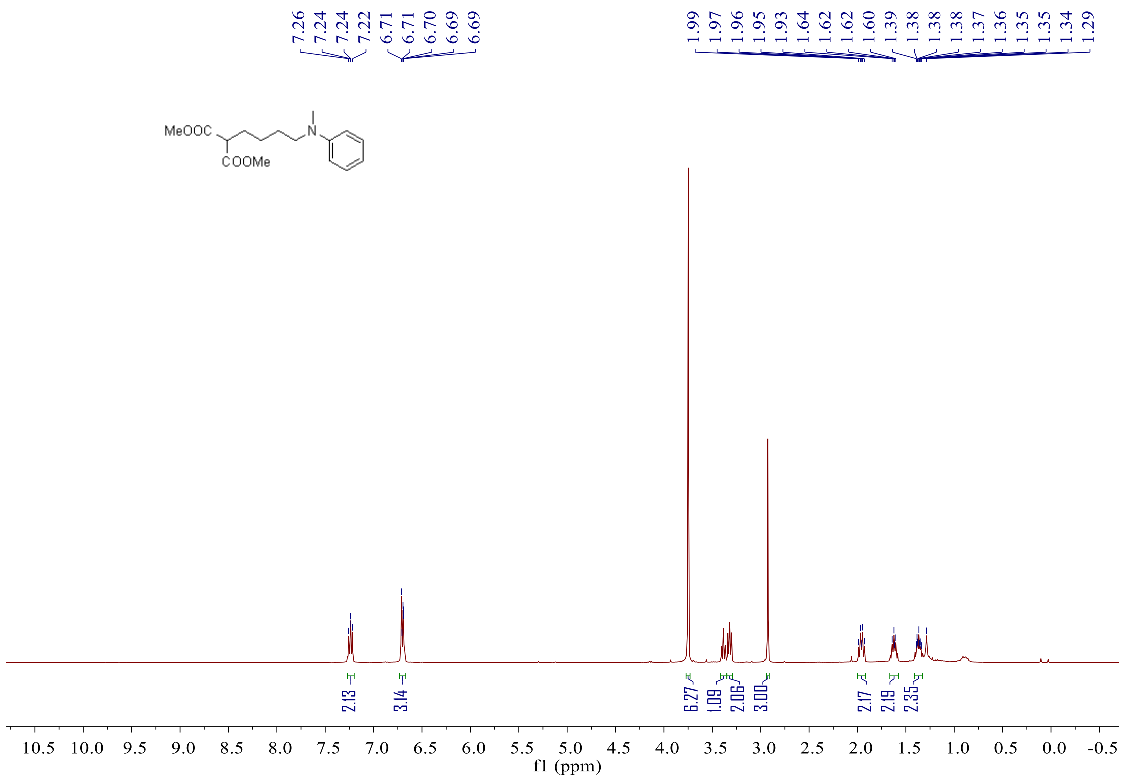


Fig. S122. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9sa**.

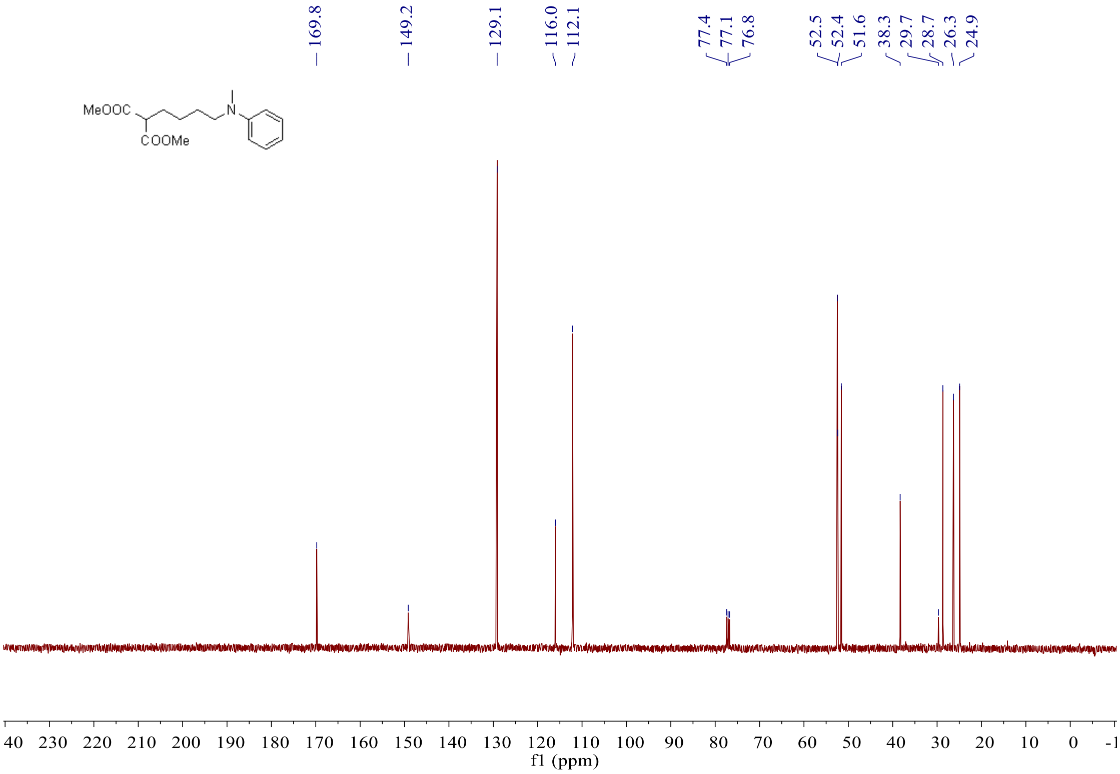


Fig. S123. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9sa**.

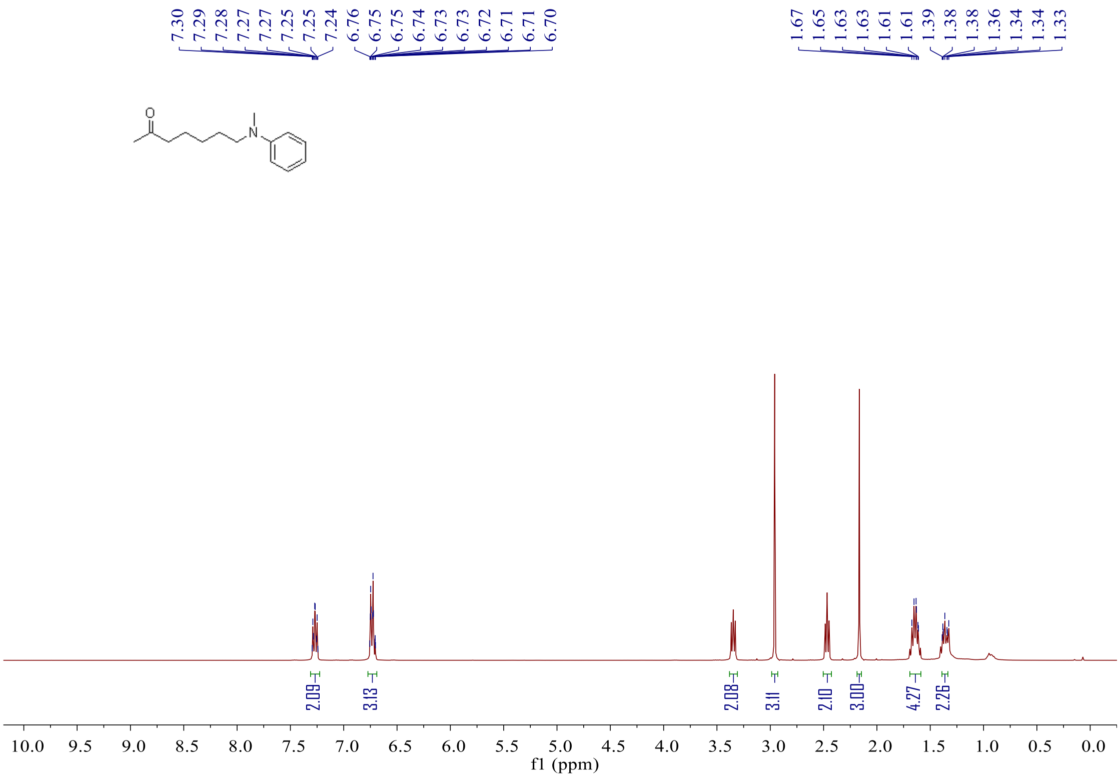


Fig. S124. ^{13}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ta**.

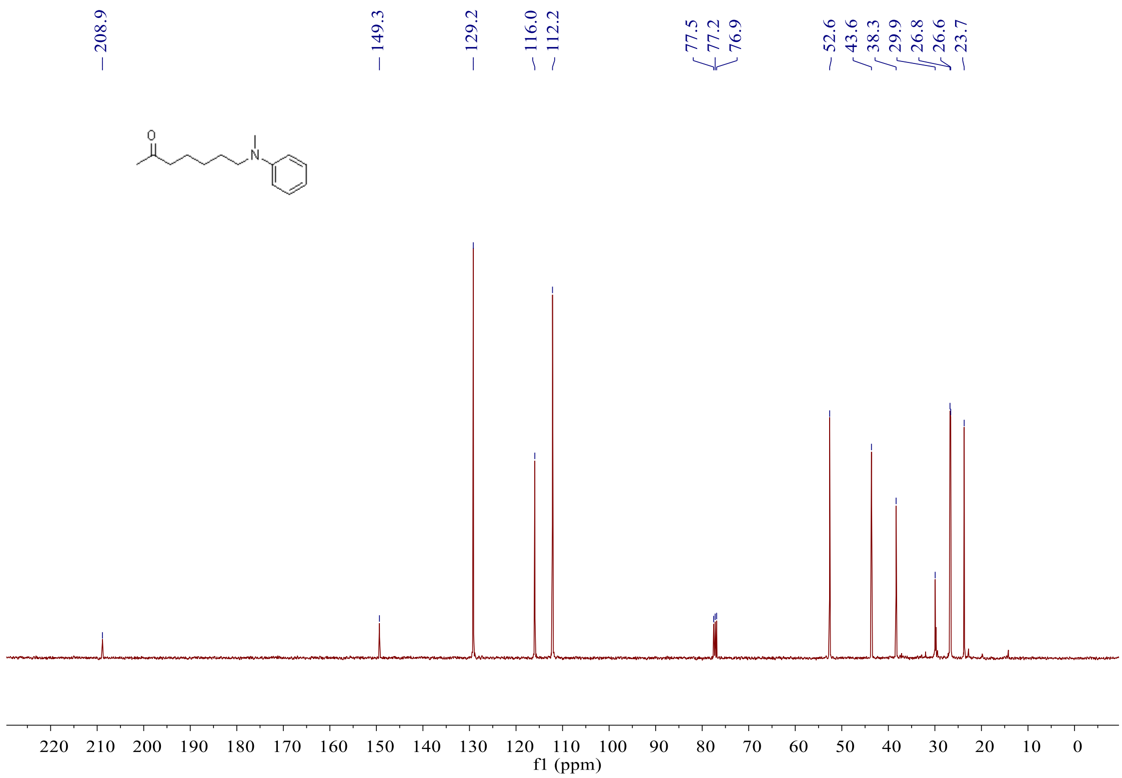


Fig. S125. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ta.**

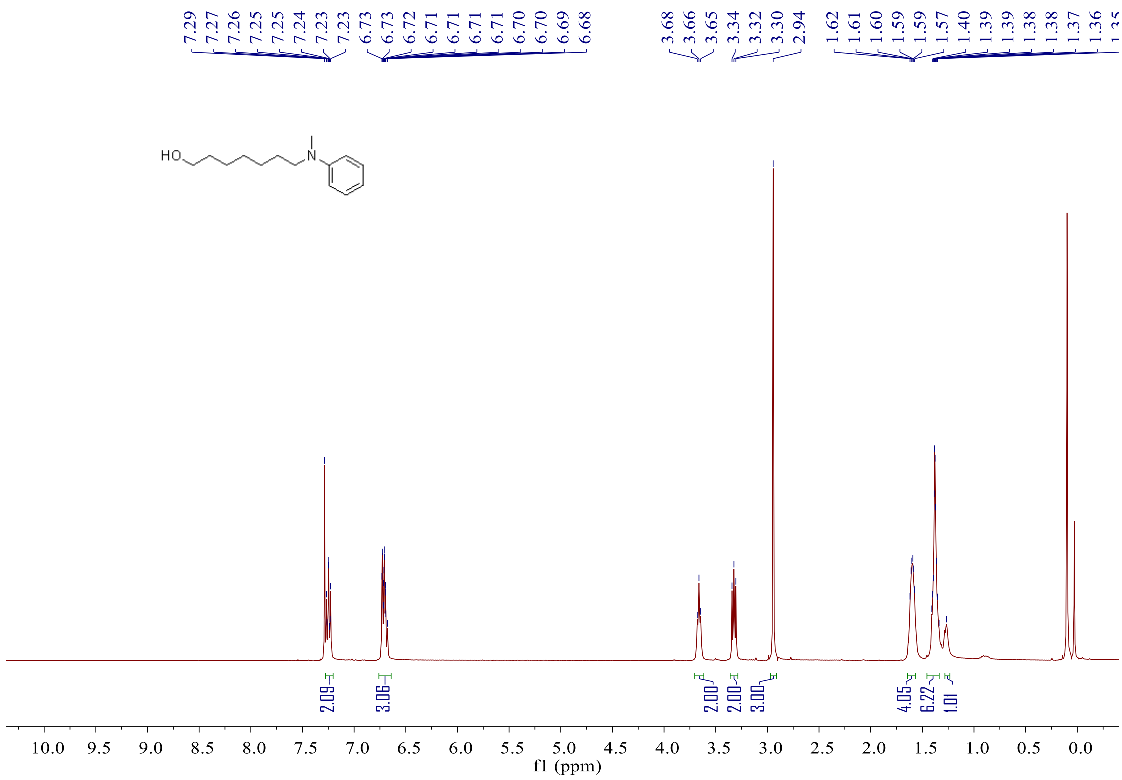


Fig. S126. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ua.**

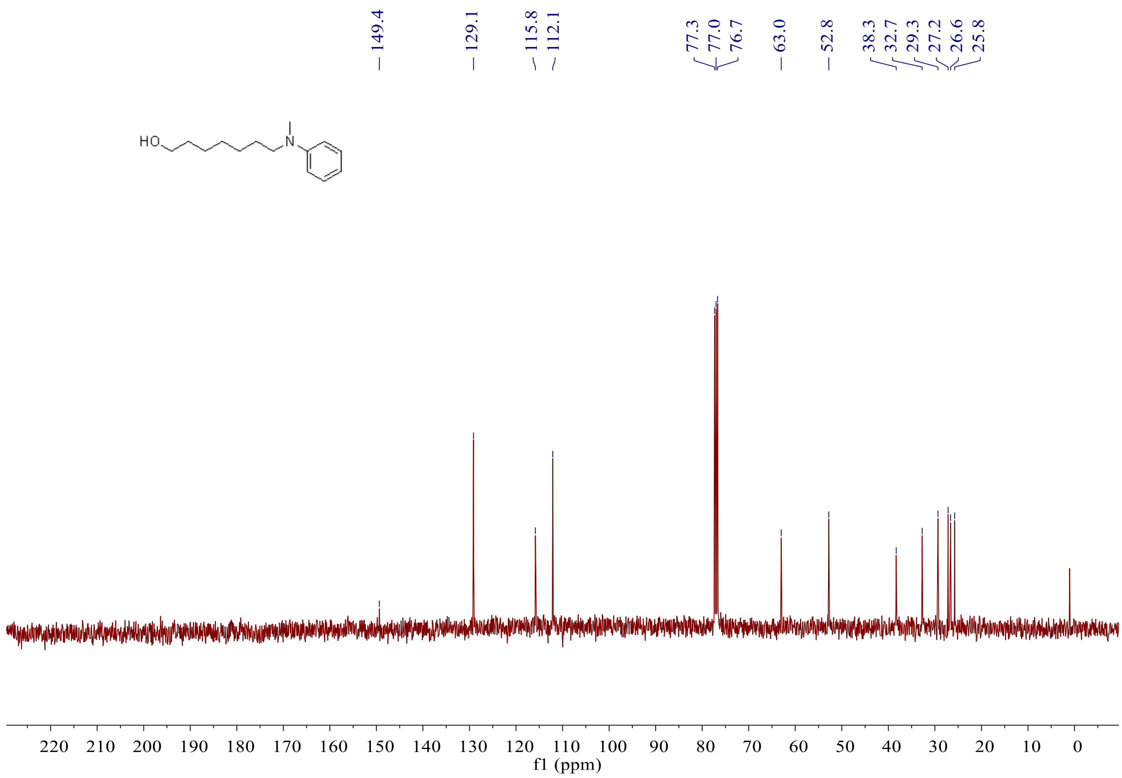


Fig. S127. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ua**.

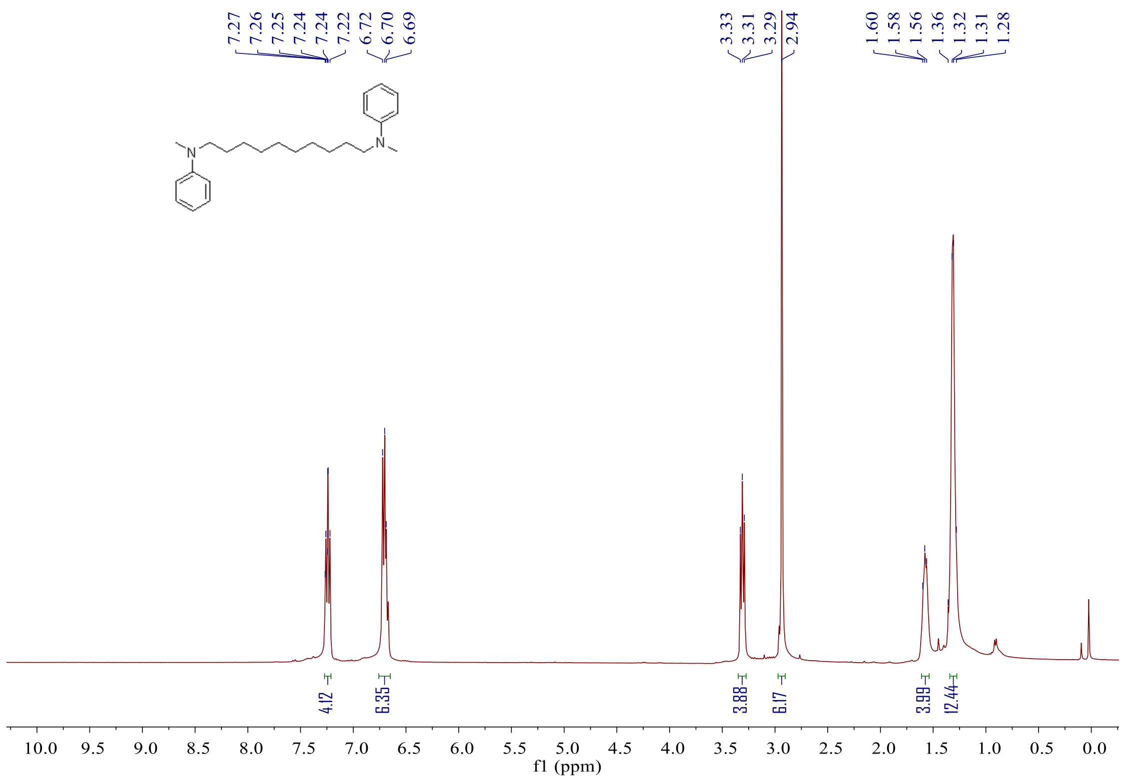


Fig. S128. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9va.**

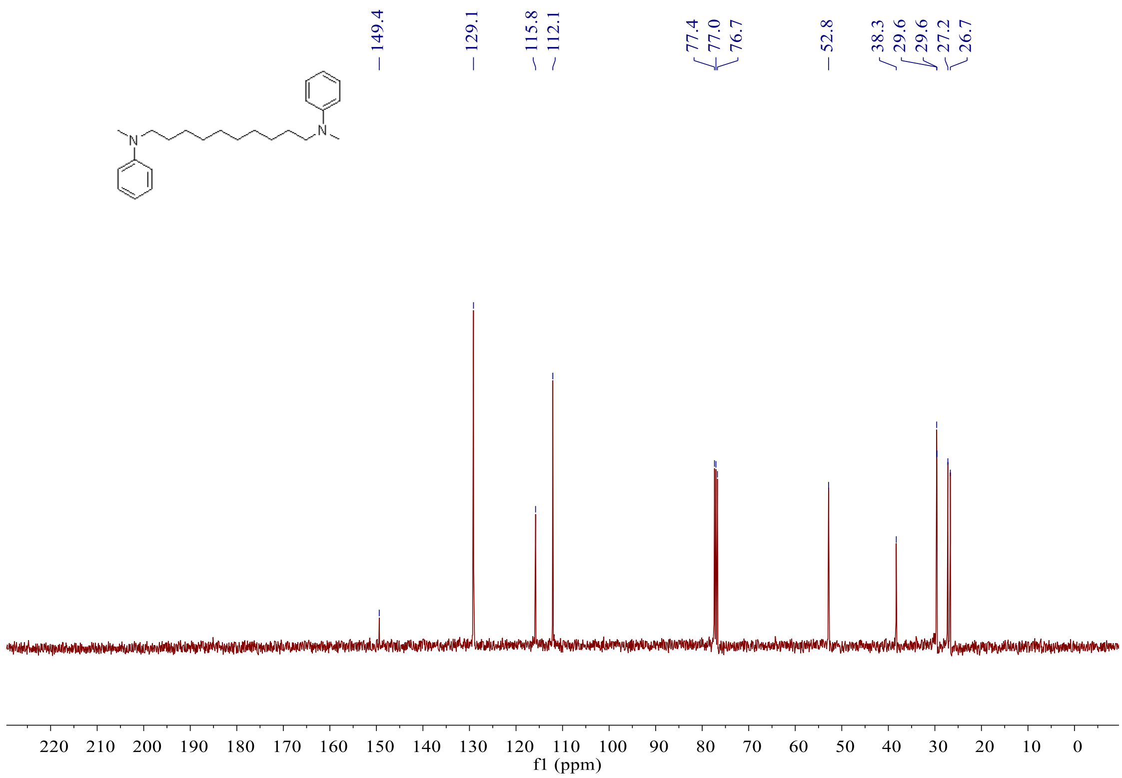


Fig. S129. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9va.**

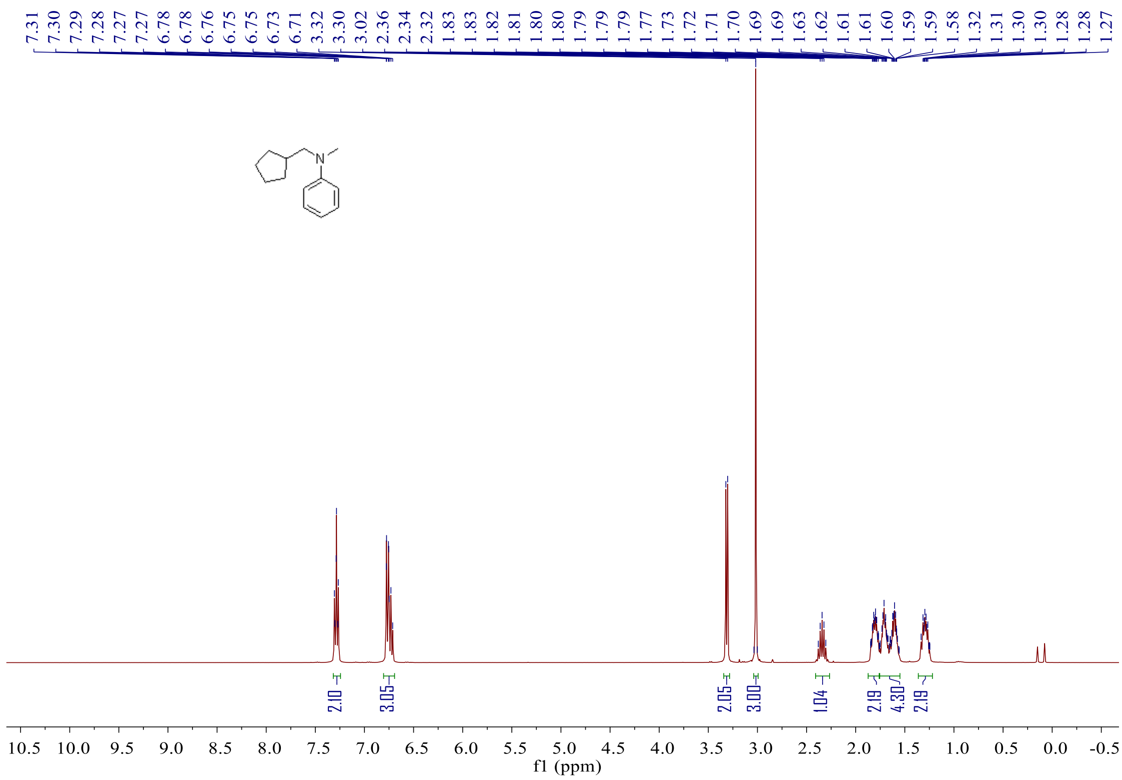


Fig. S130. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9wa-5**.

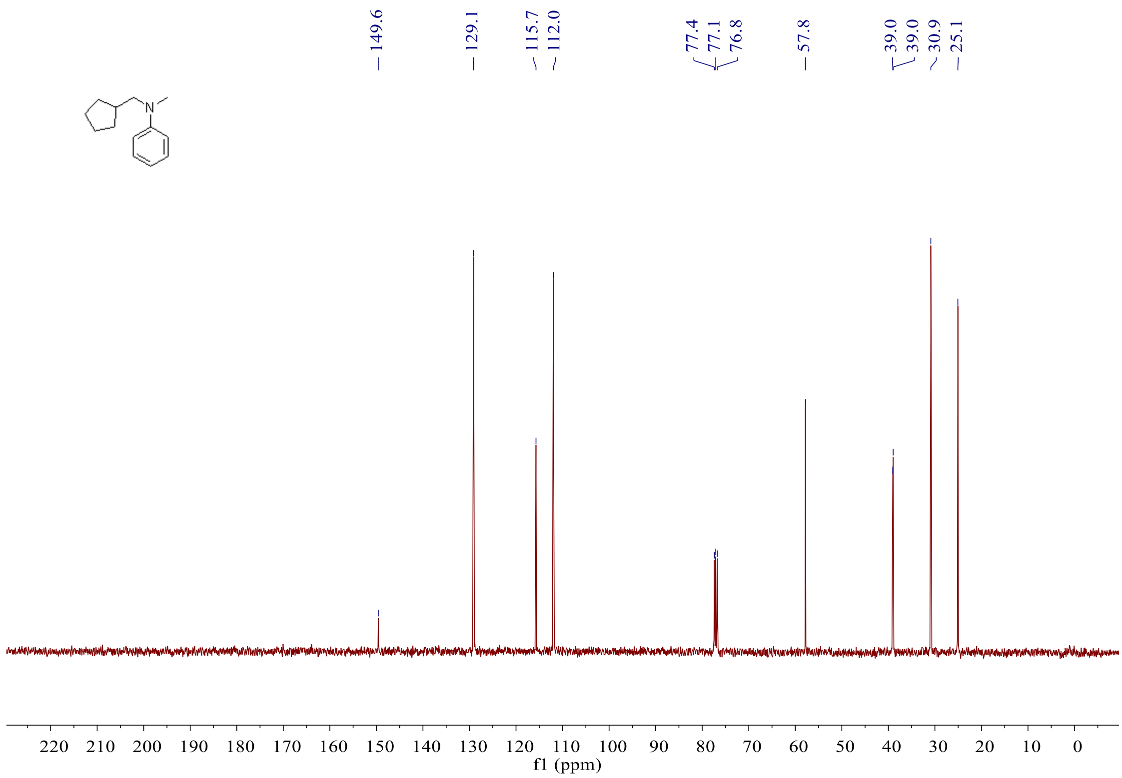


Fig. S131. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9wa-5**.

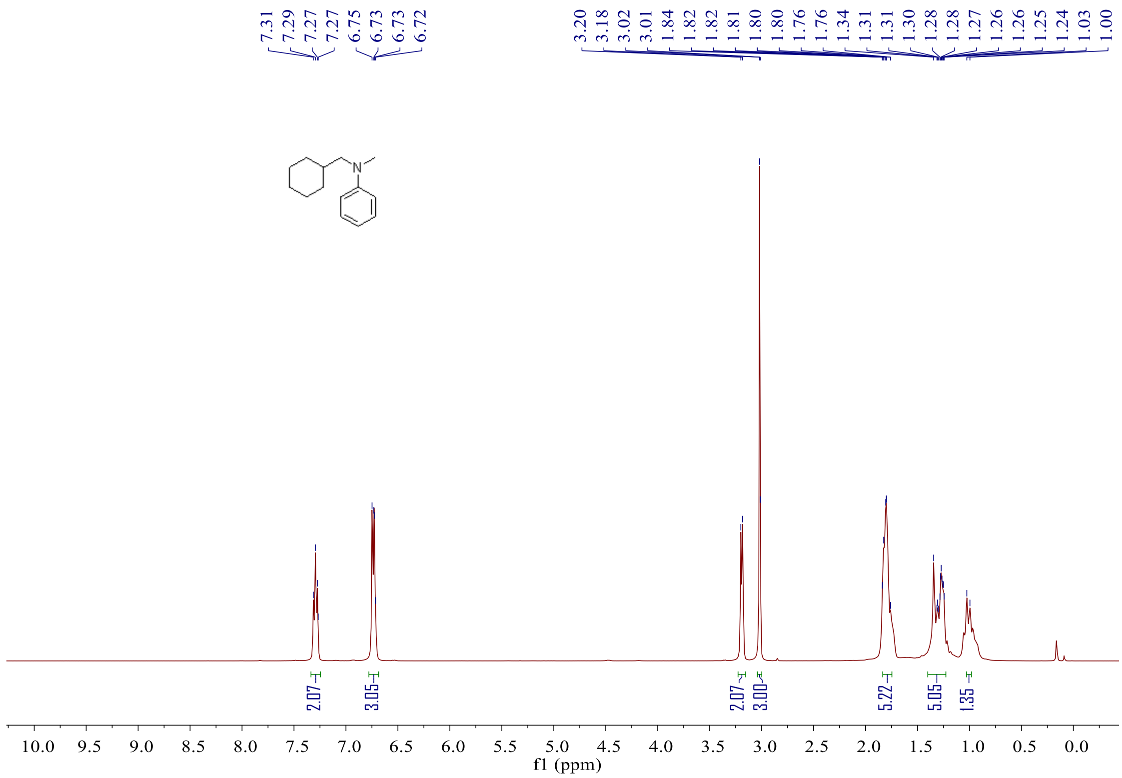


Fig. S132. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9wa-6**.

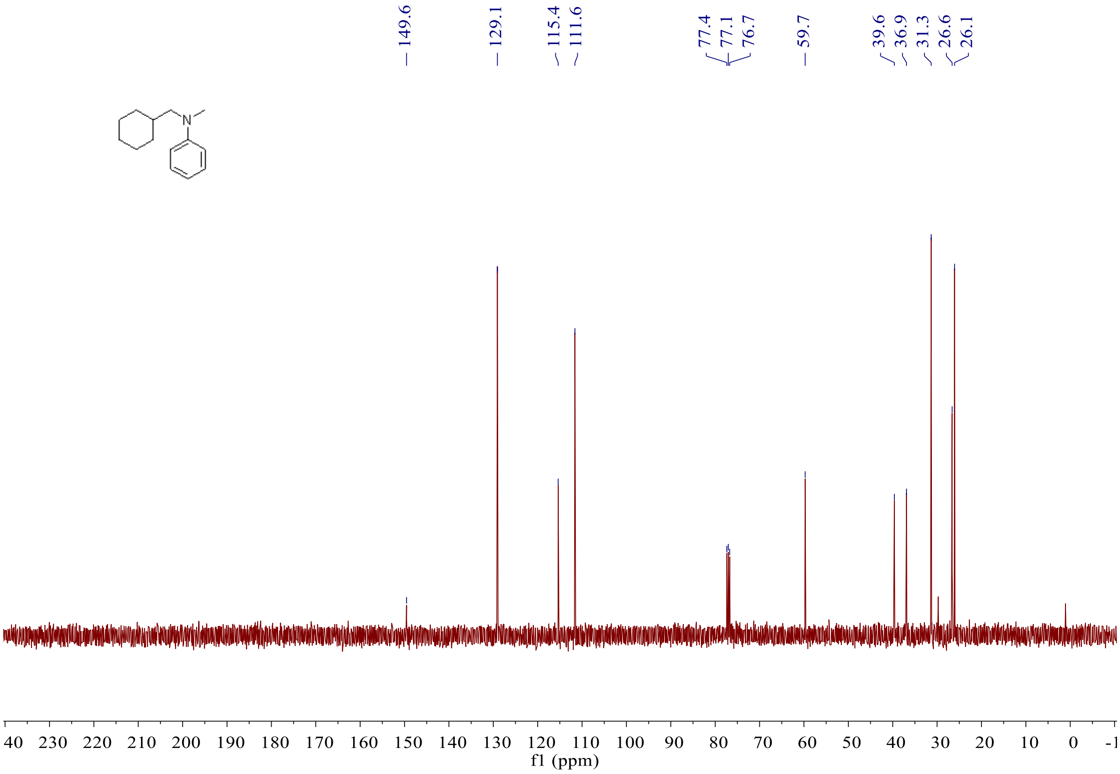


Fig. S133. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9wa-6**.

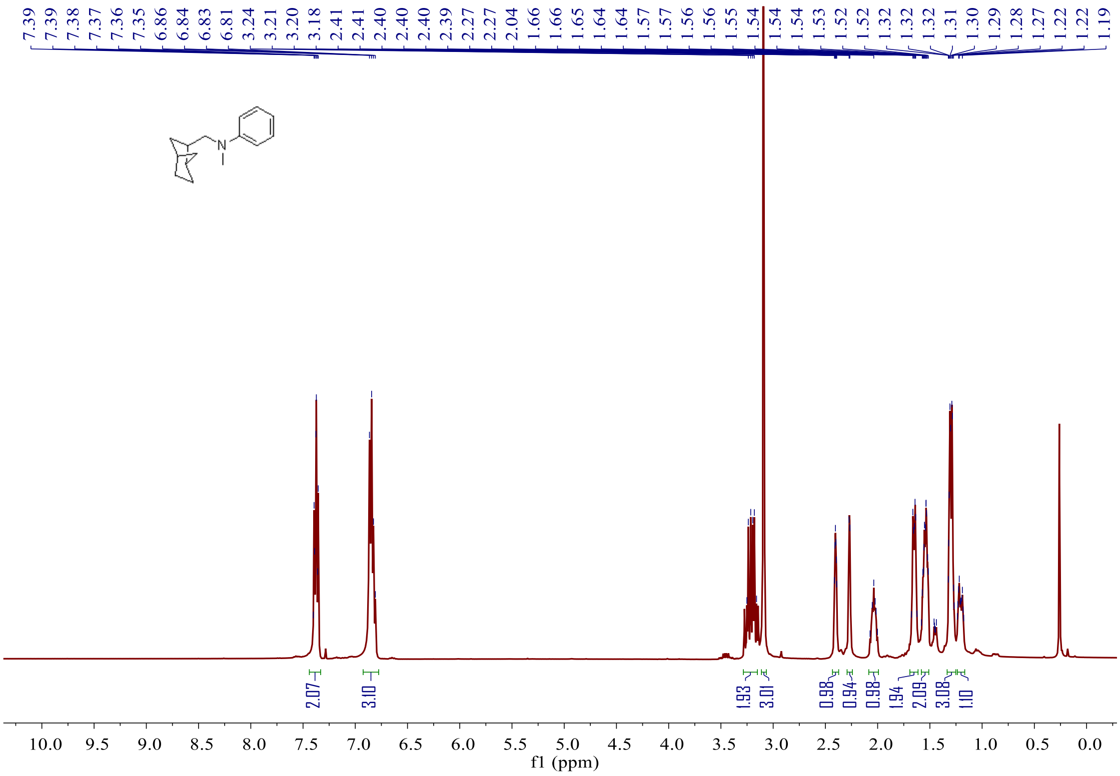


Fig. S134. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9xa**.

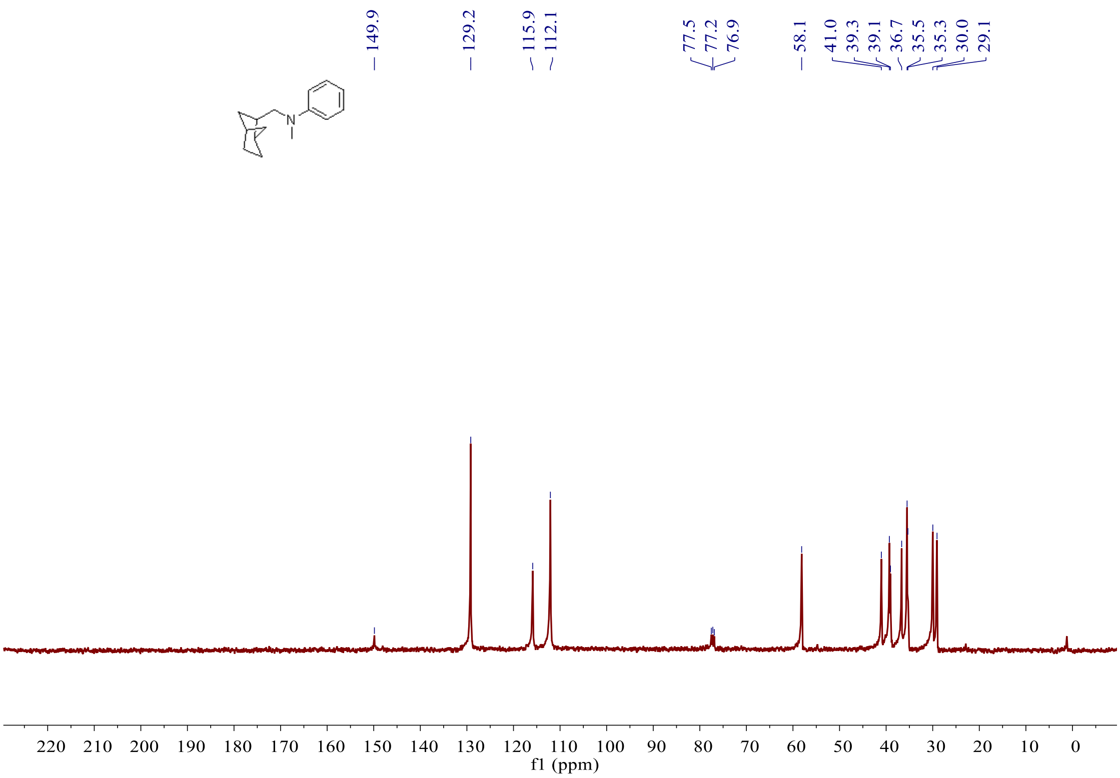


Fig. S135. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9xa**.

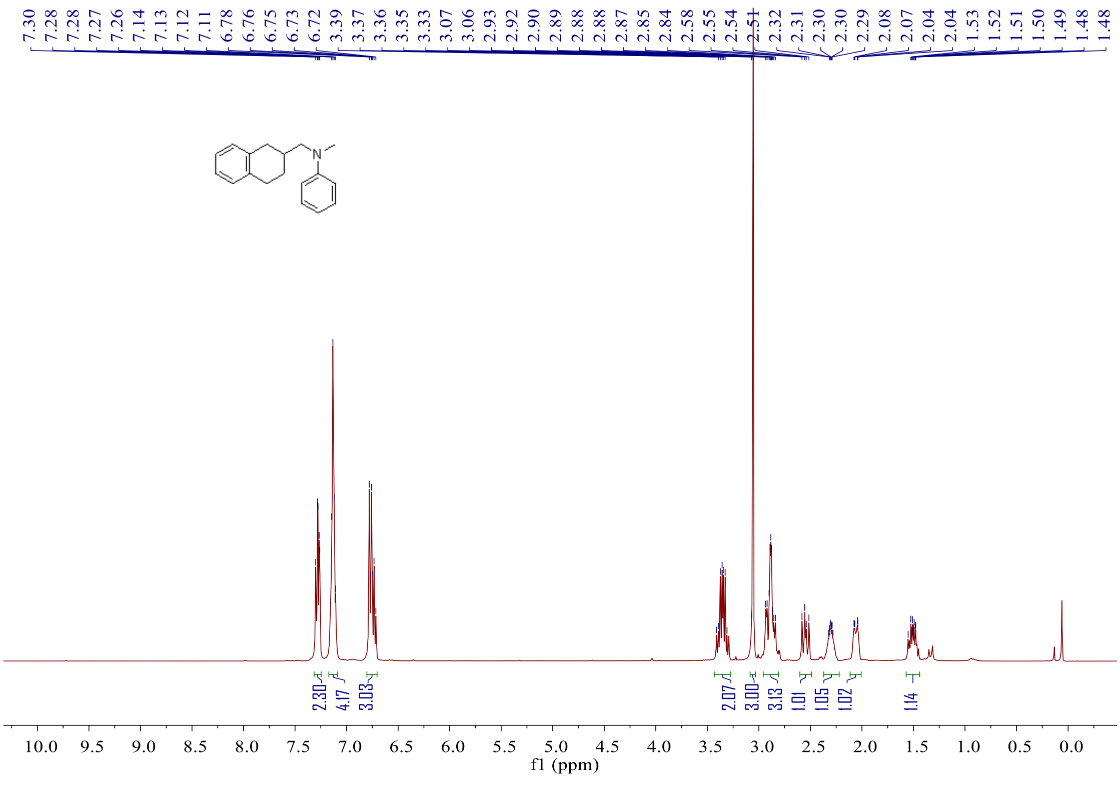


Fig. S136. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ya**.

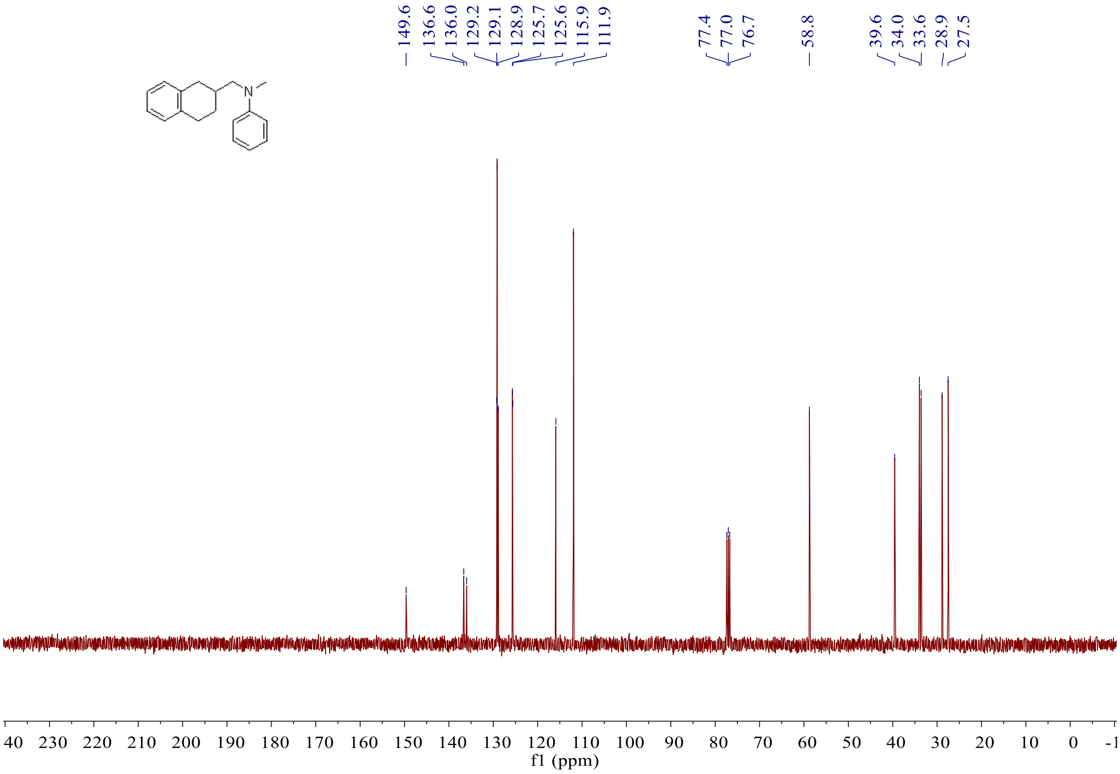


Fig. S137. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ya**.

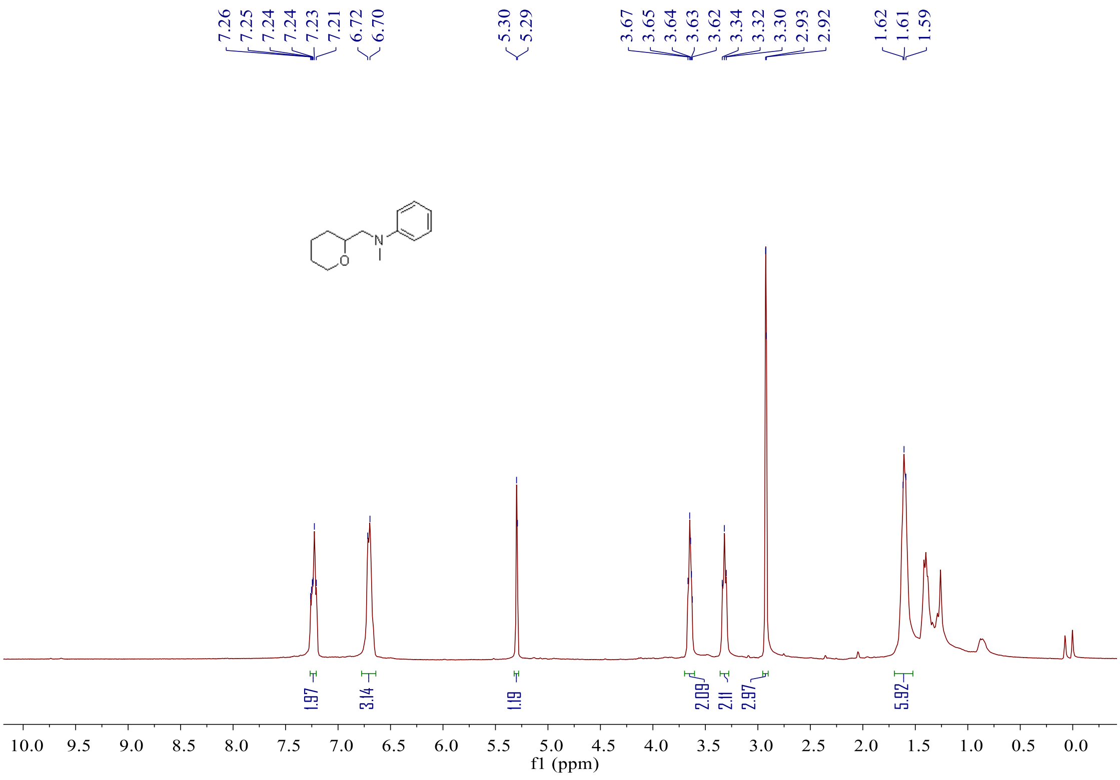


Fig. S138. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9za**.

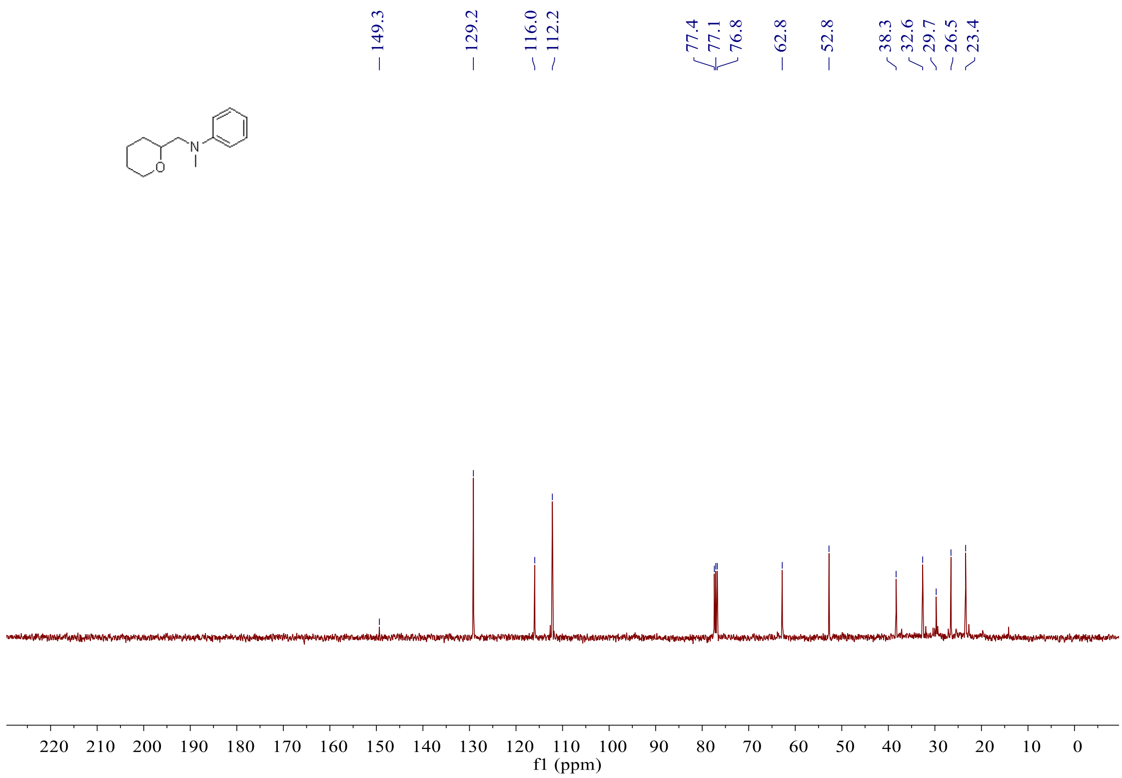


Fig. S139. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9za**.

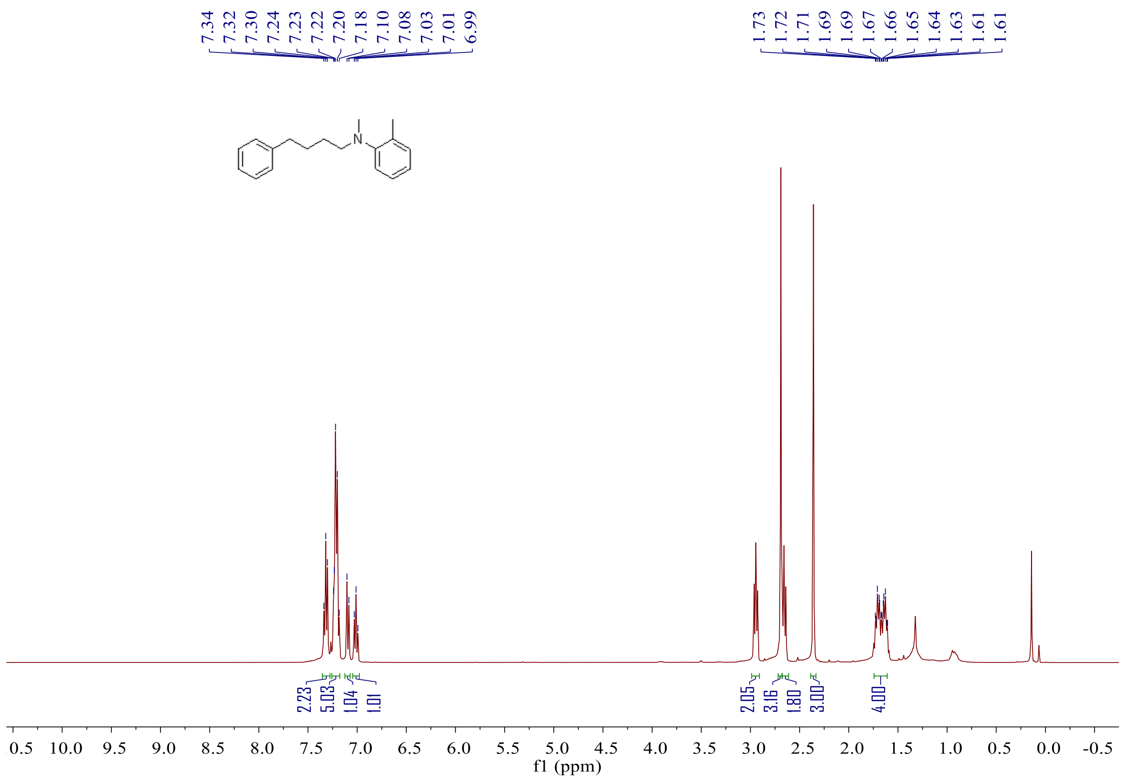


Fig. S140. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ab**.

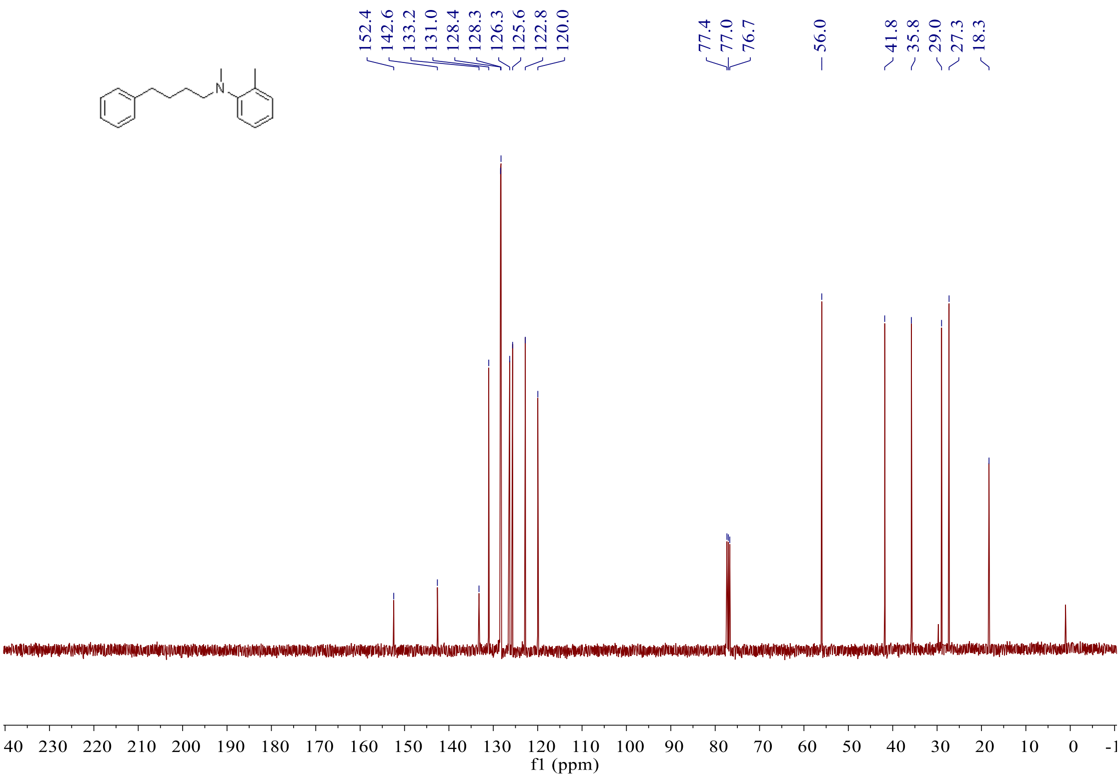


Fig. S141. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ab**.

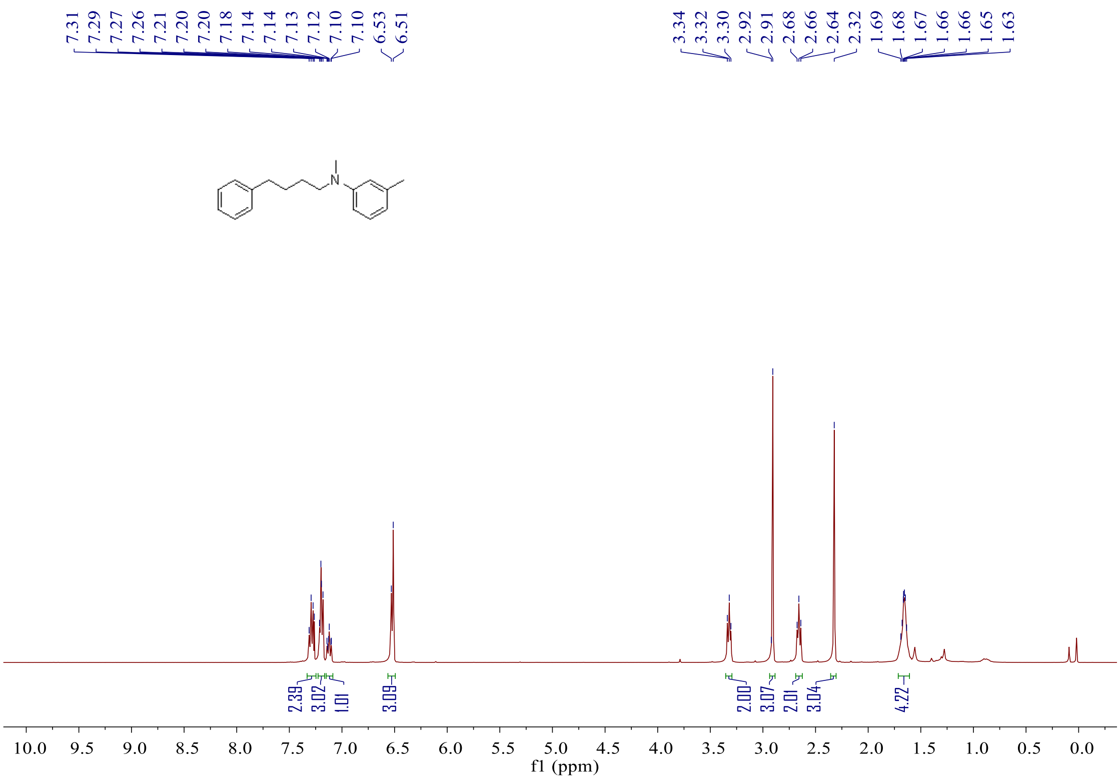


Fig. S142. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ac**.

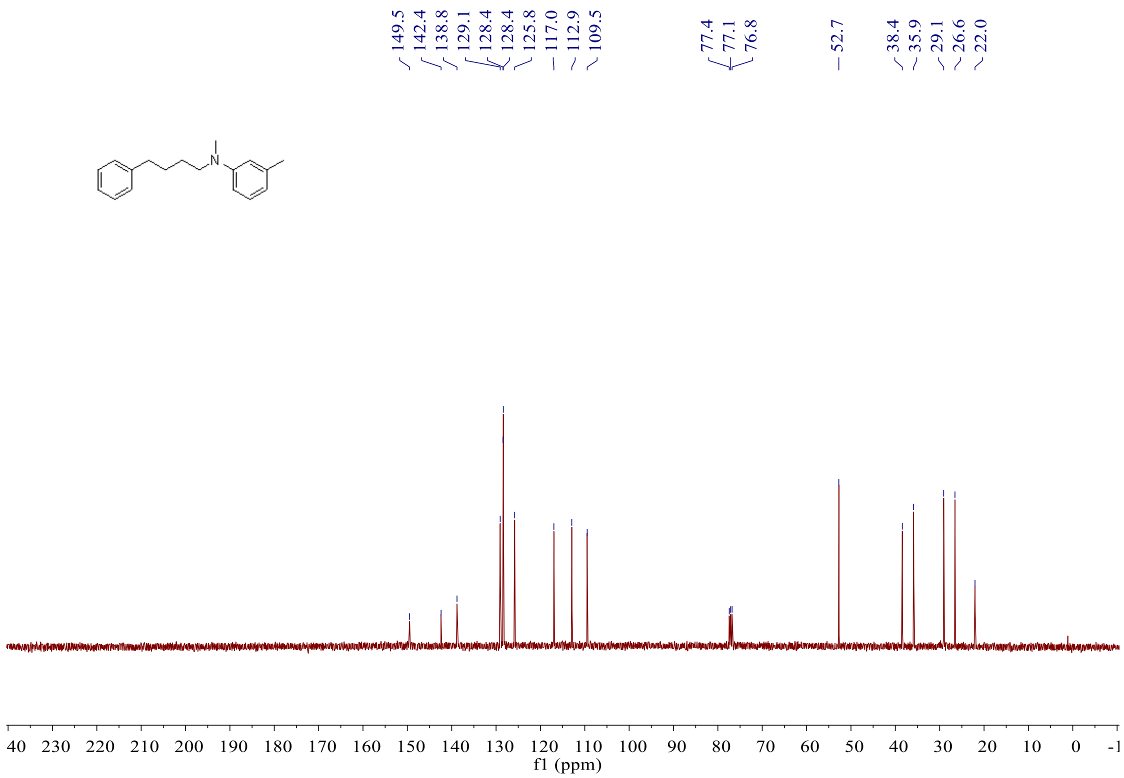


Fig. S143. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ac**.

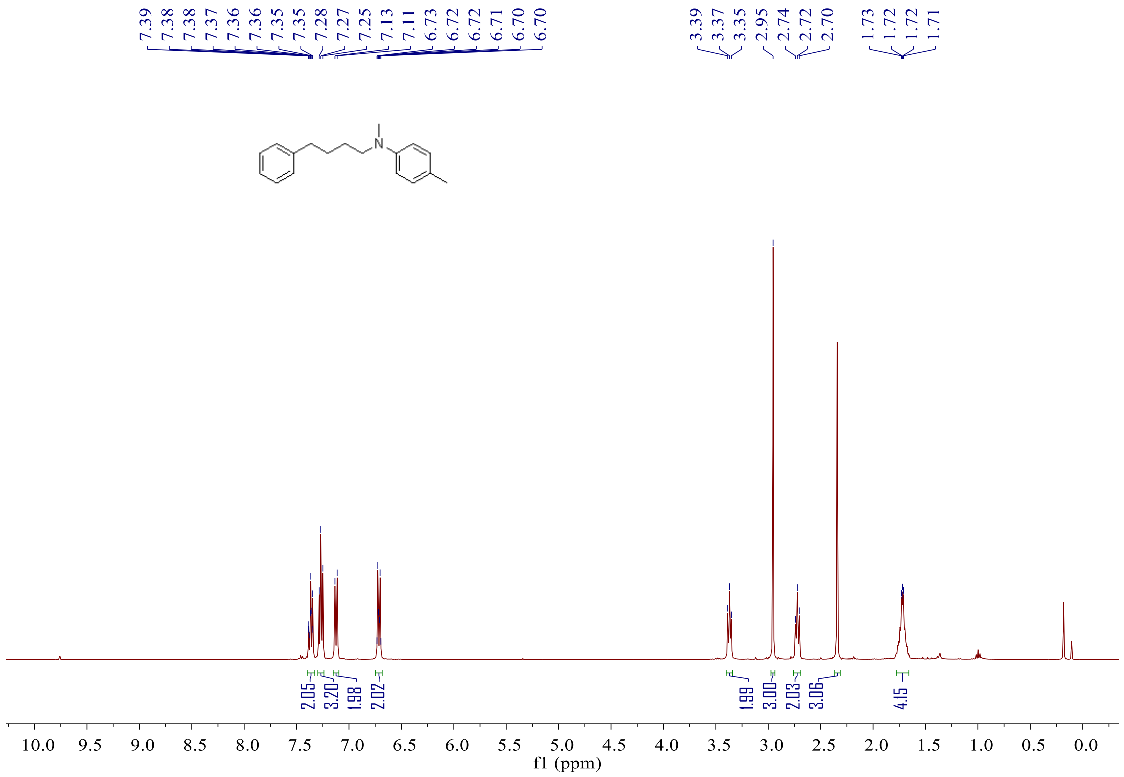


Fig. S144. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ad**.

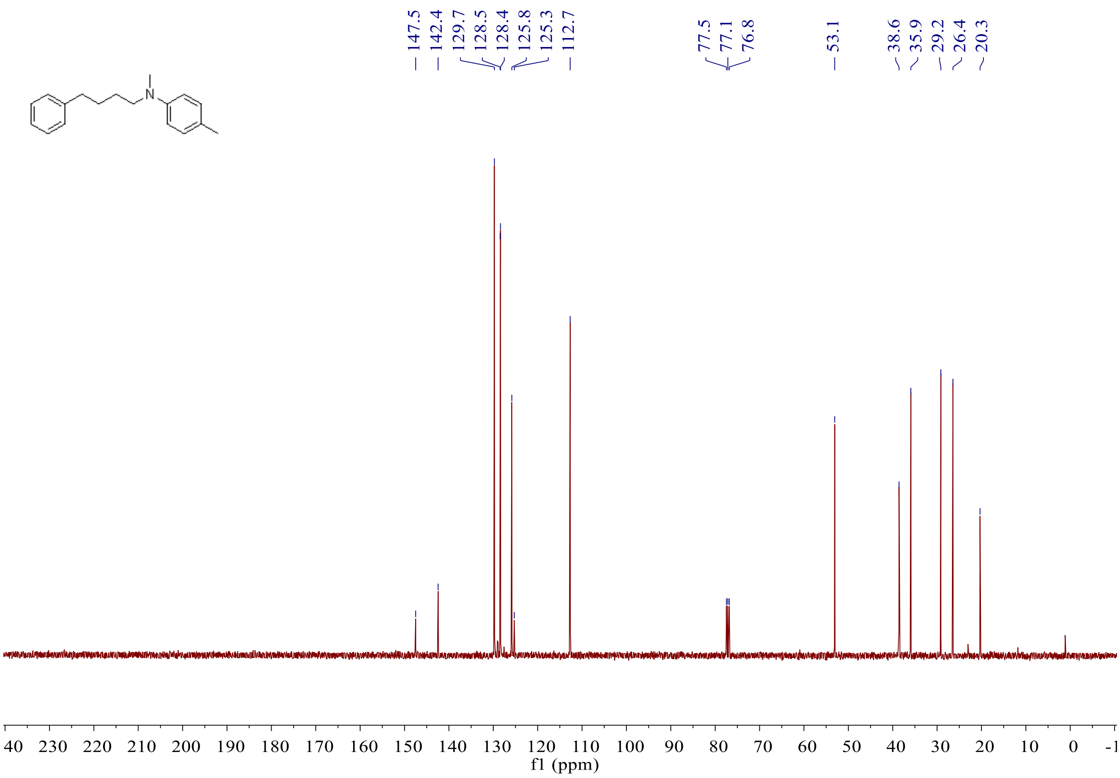


Fig. S145. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ad.**

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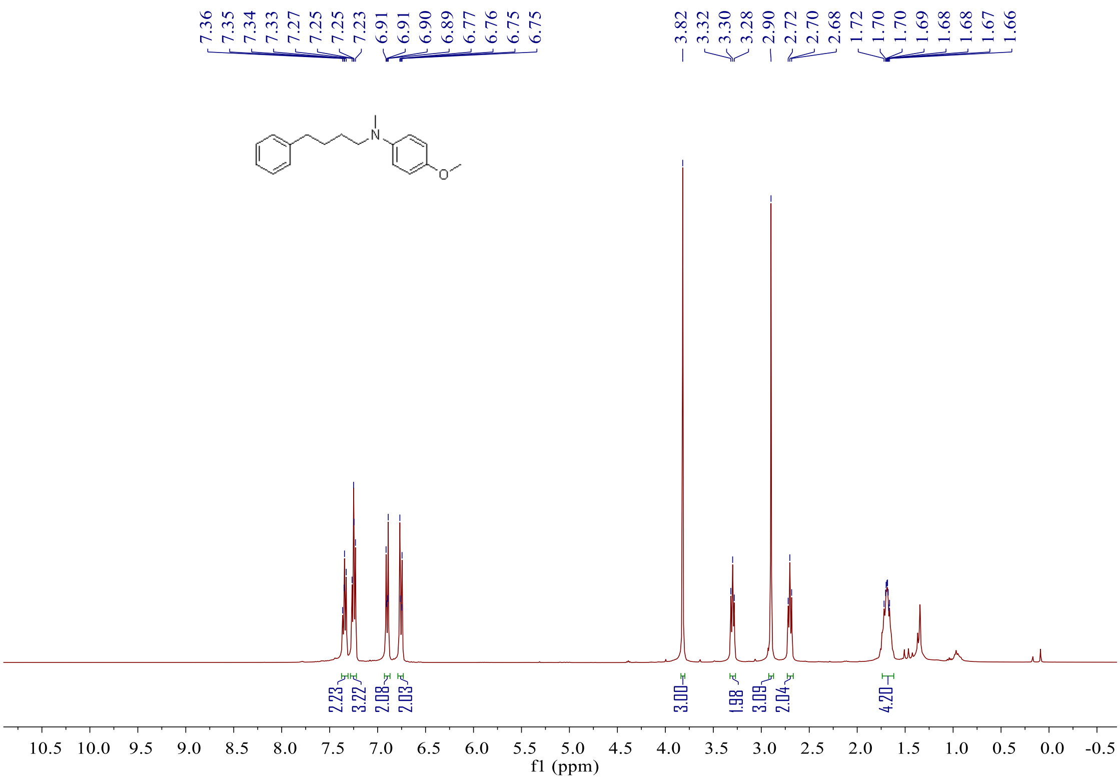

Fig. S146. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ae**.

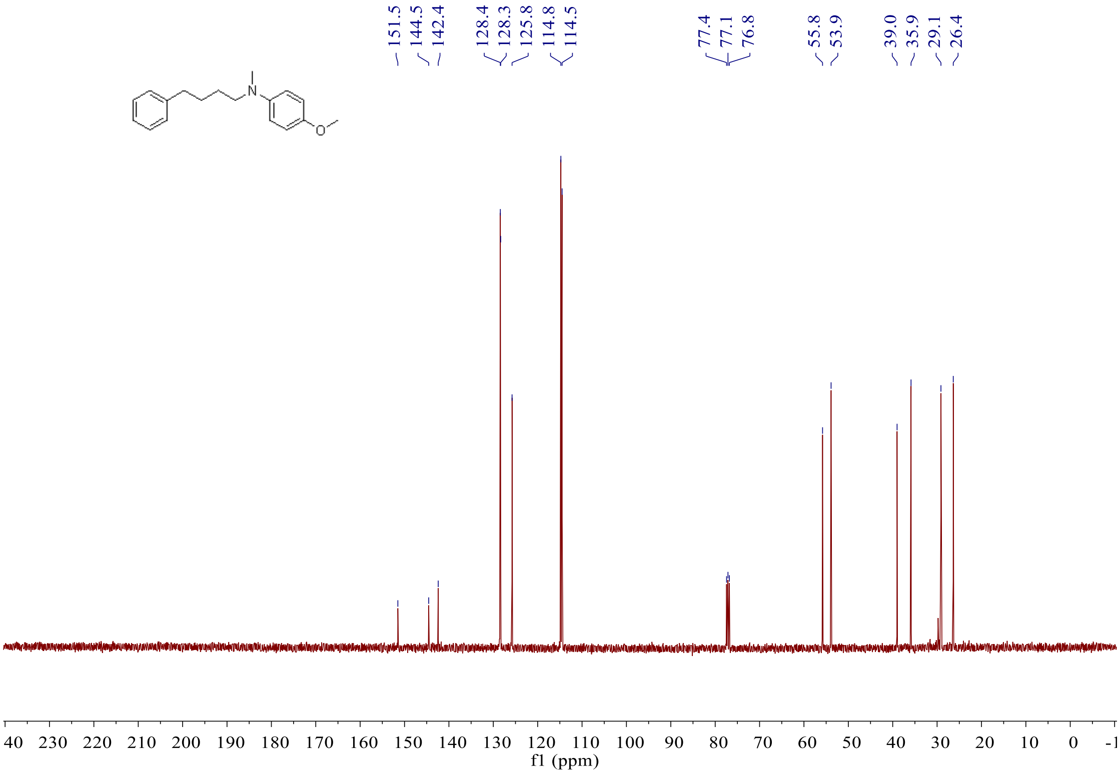

Fig. S147. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ae**.

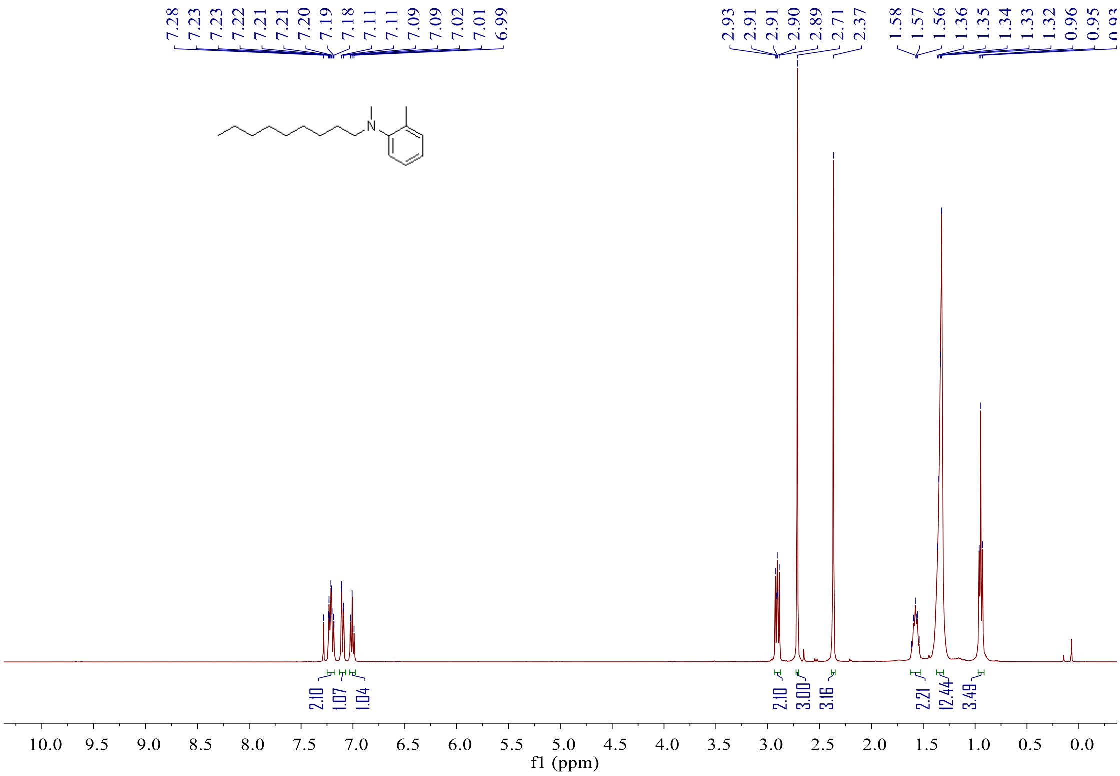

Fig. S148. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9mb**.

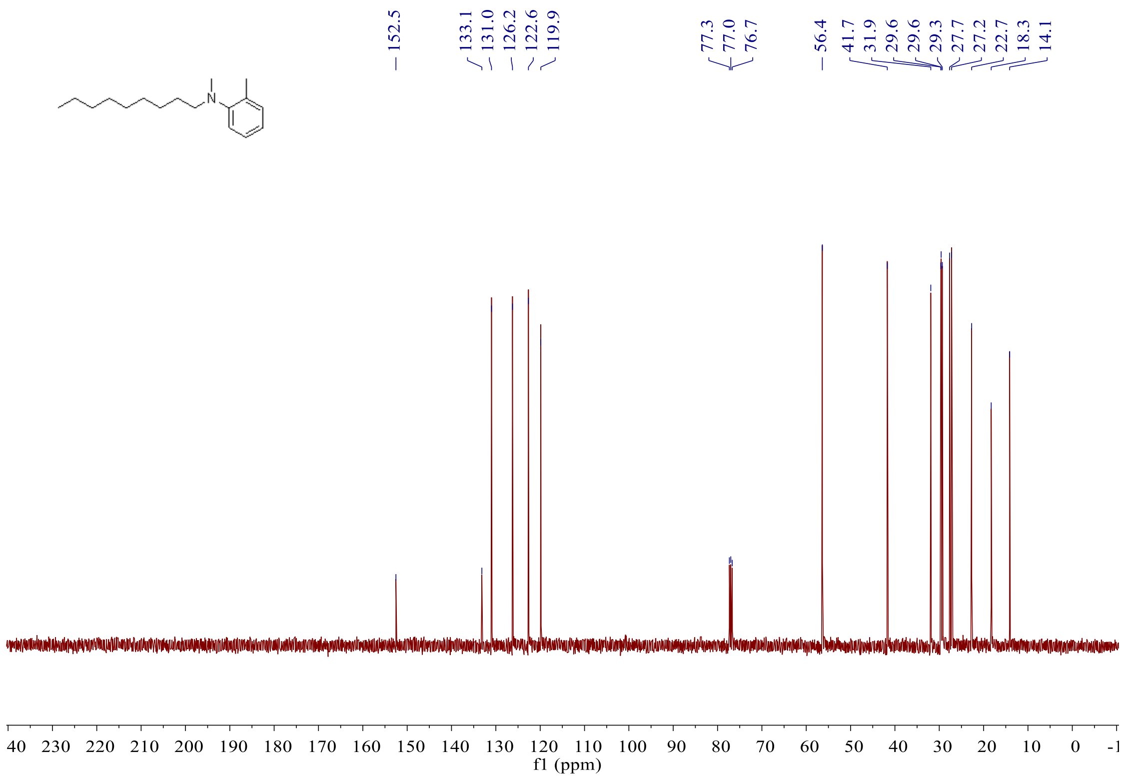

Fig. S149. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9mb**.

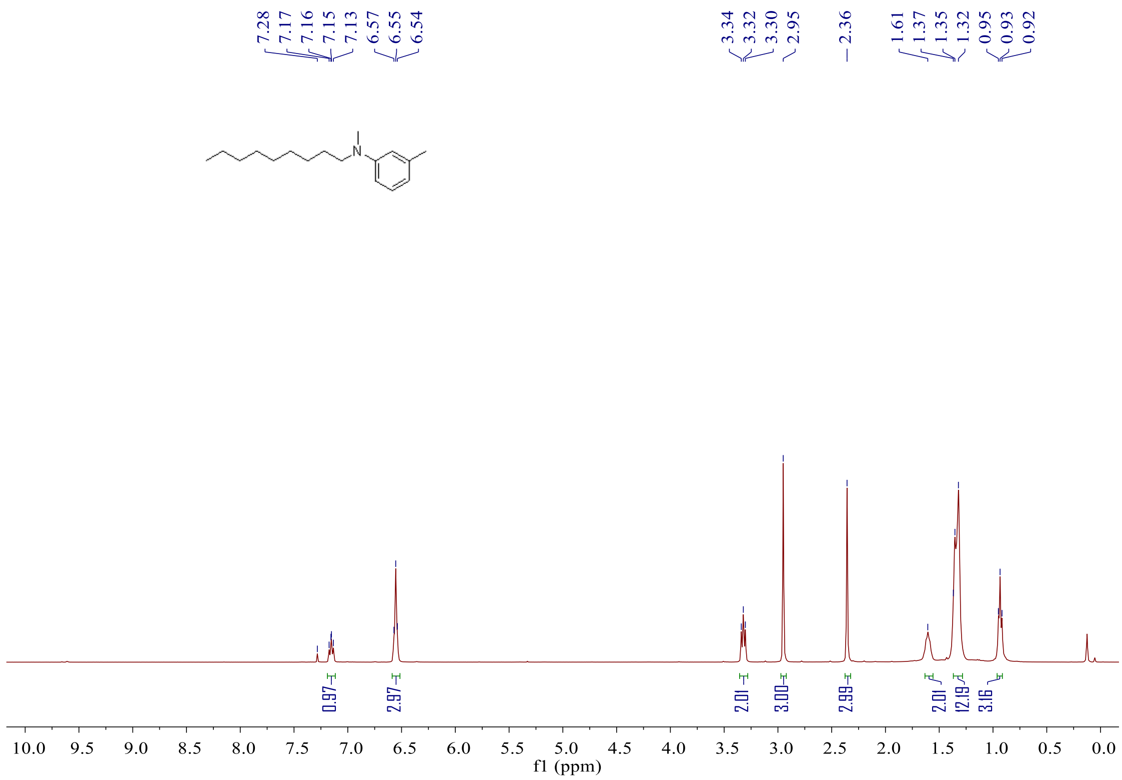

Fig. S150. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9mc.**

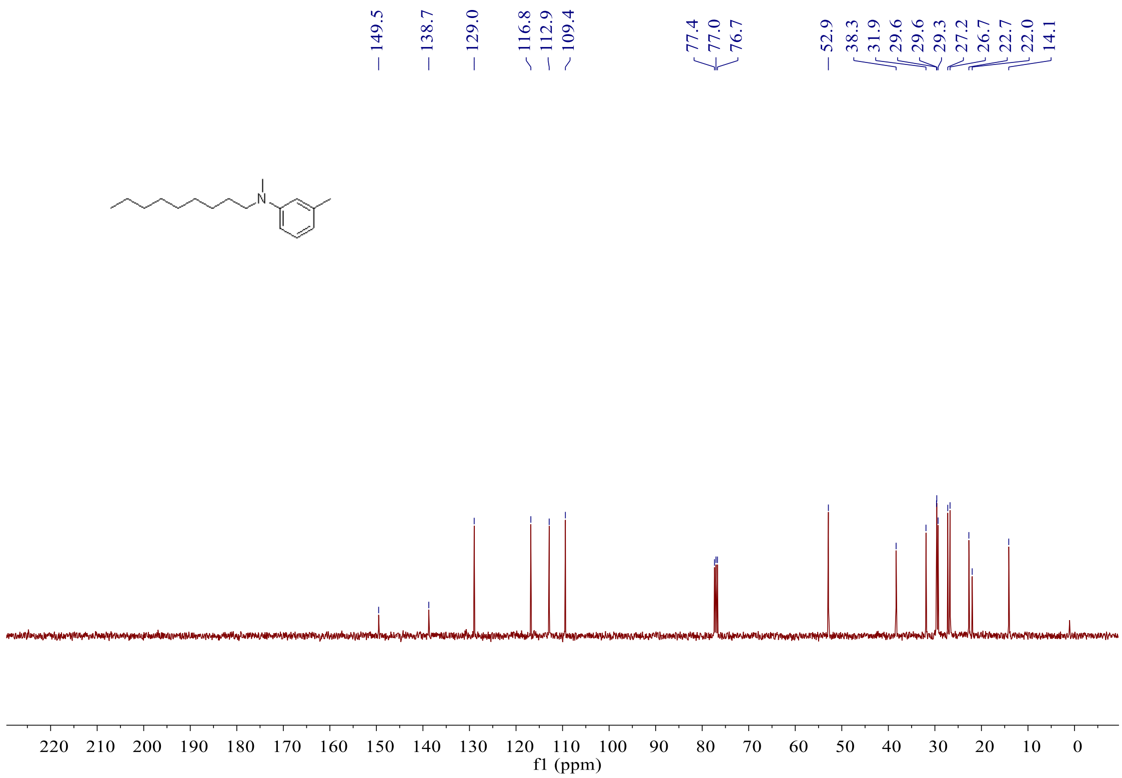

Fig. S151. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9mc**.

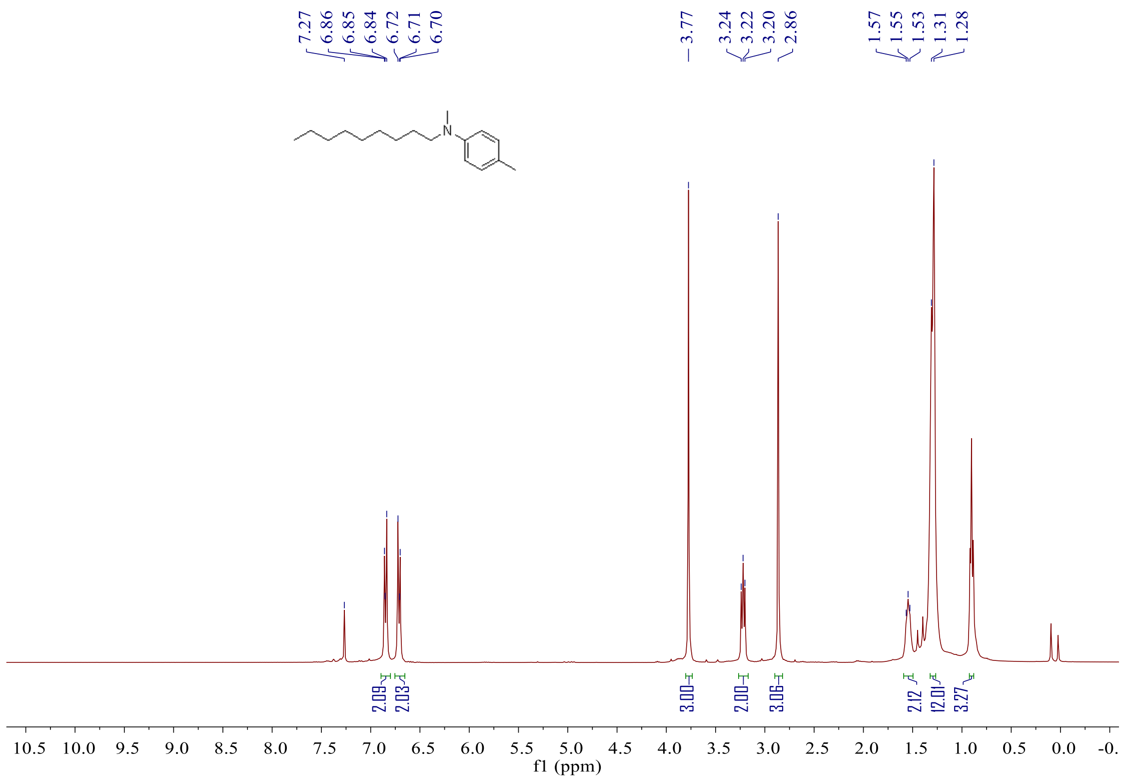

Fig. S152. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9md**.

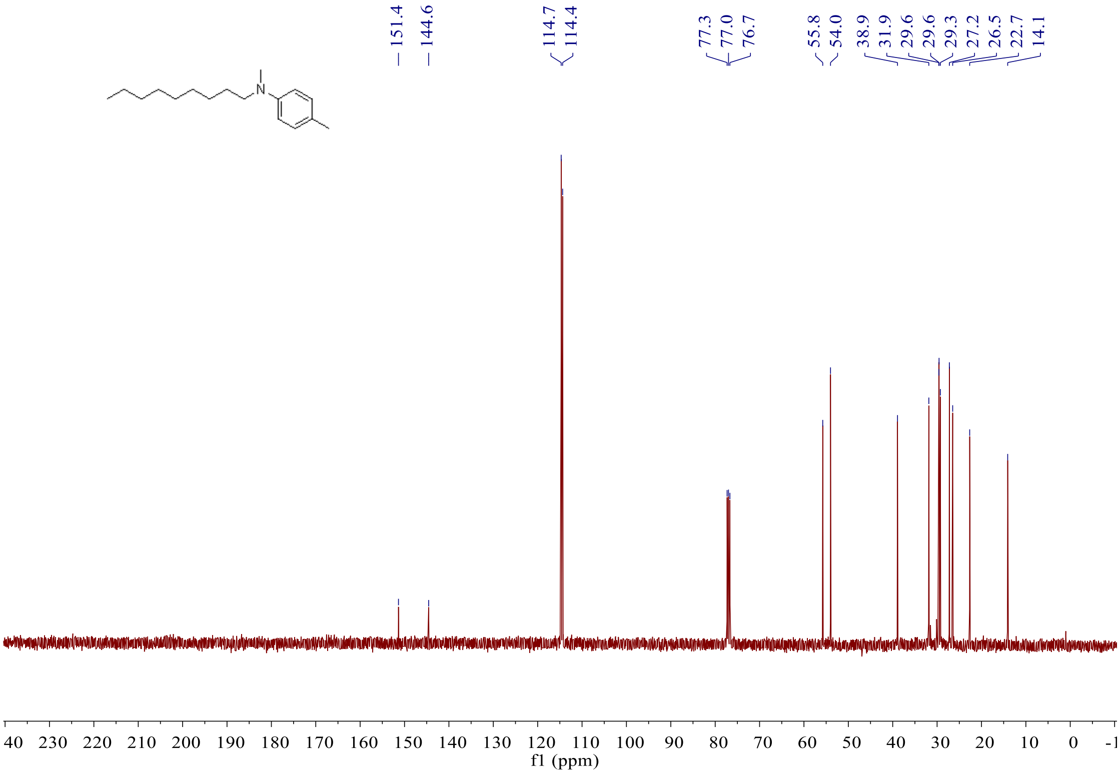

Fig. S153. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9md.**

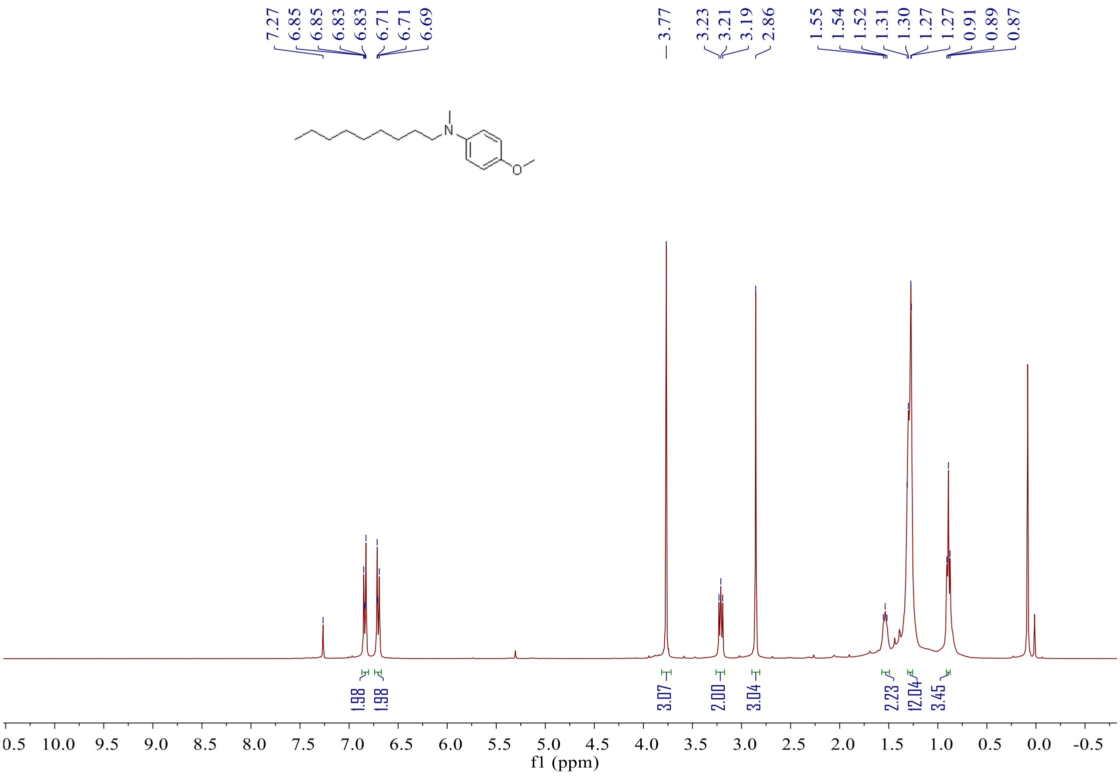

Fig. S154. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9me**.

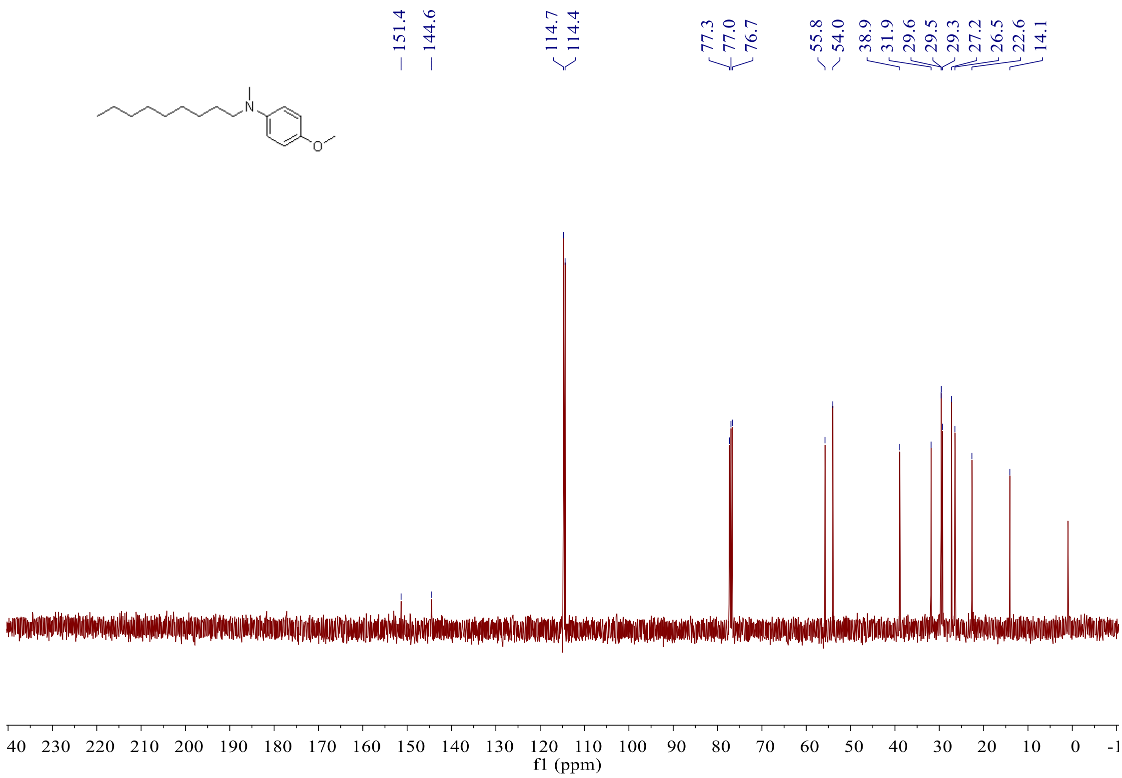

Fig. S155. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9me**.

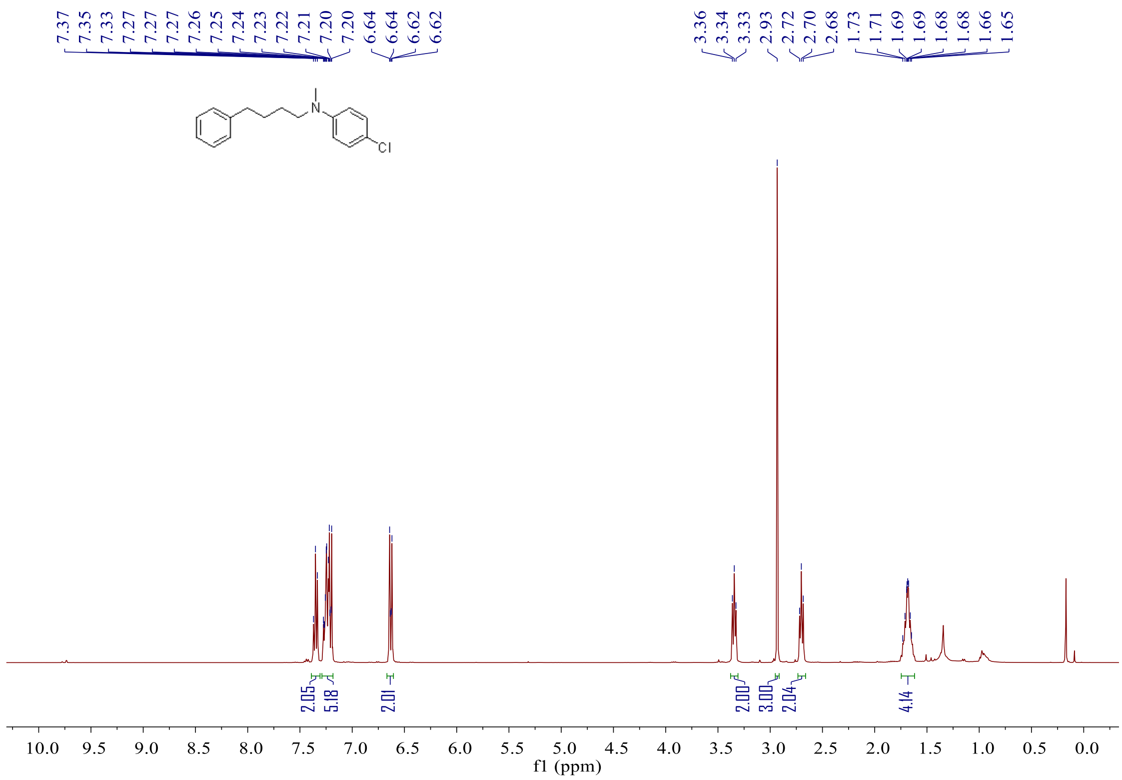

Fig. S156. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9af**.

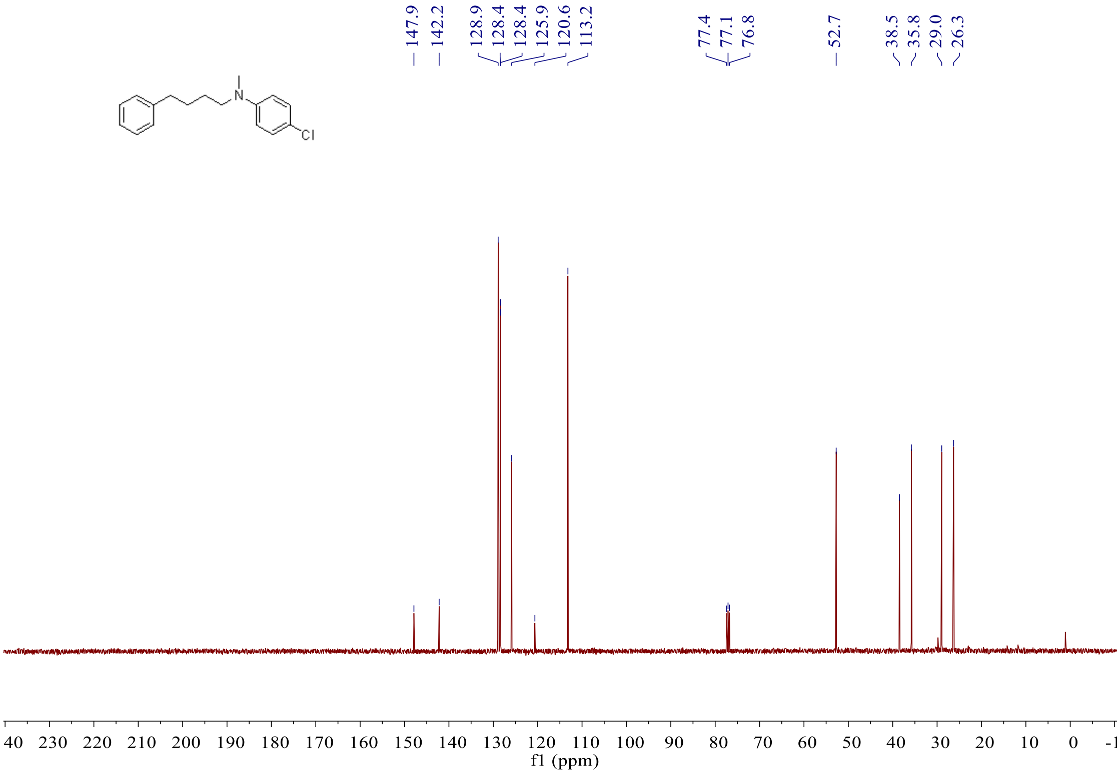

Fig. S157. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9af**.

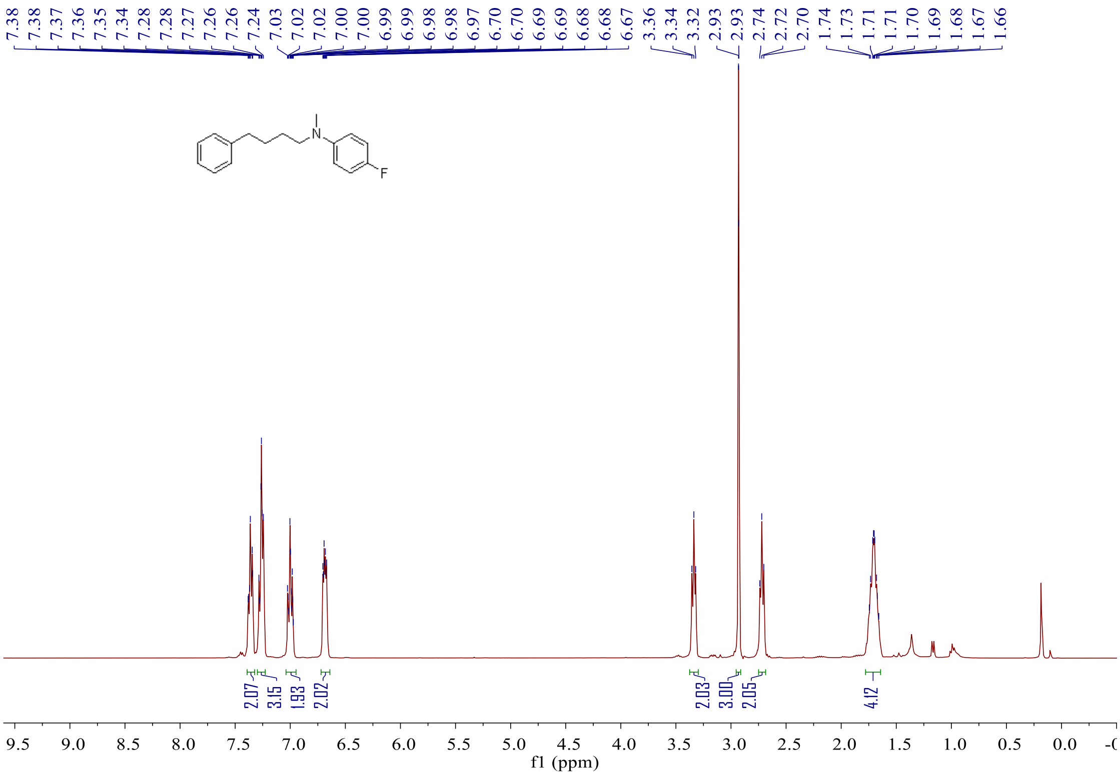

Fig. S158. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ag**.

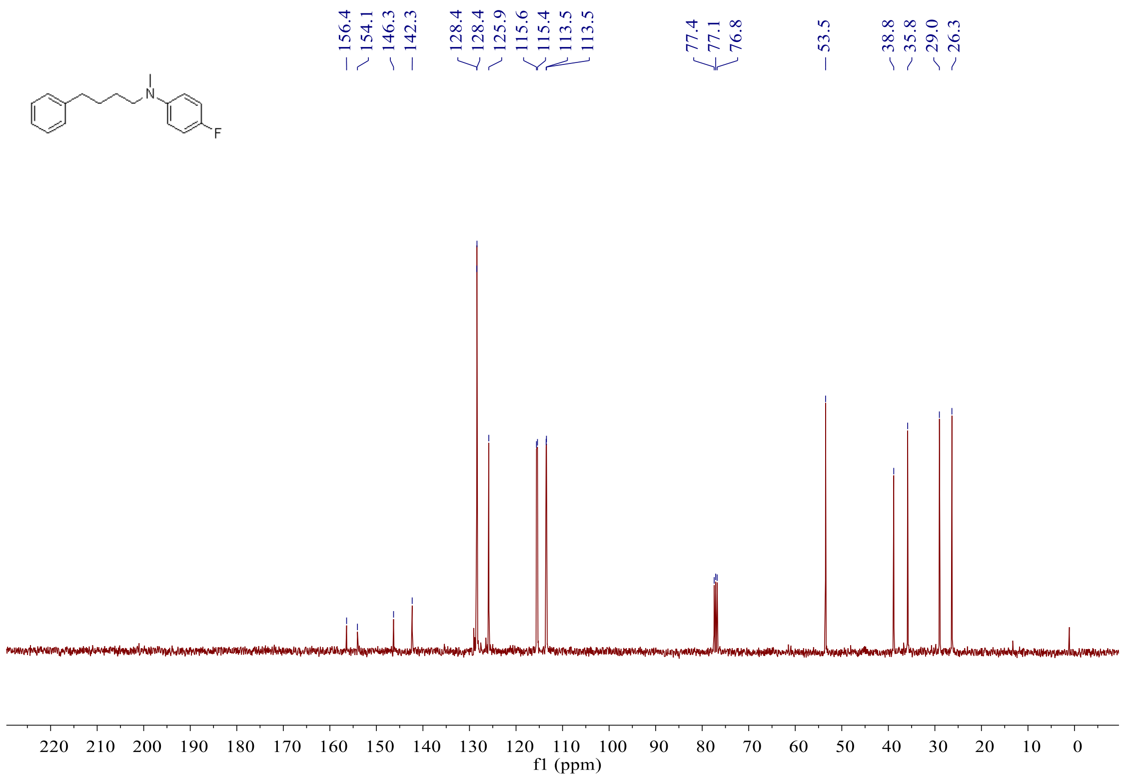

Fig. S159. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ag**.

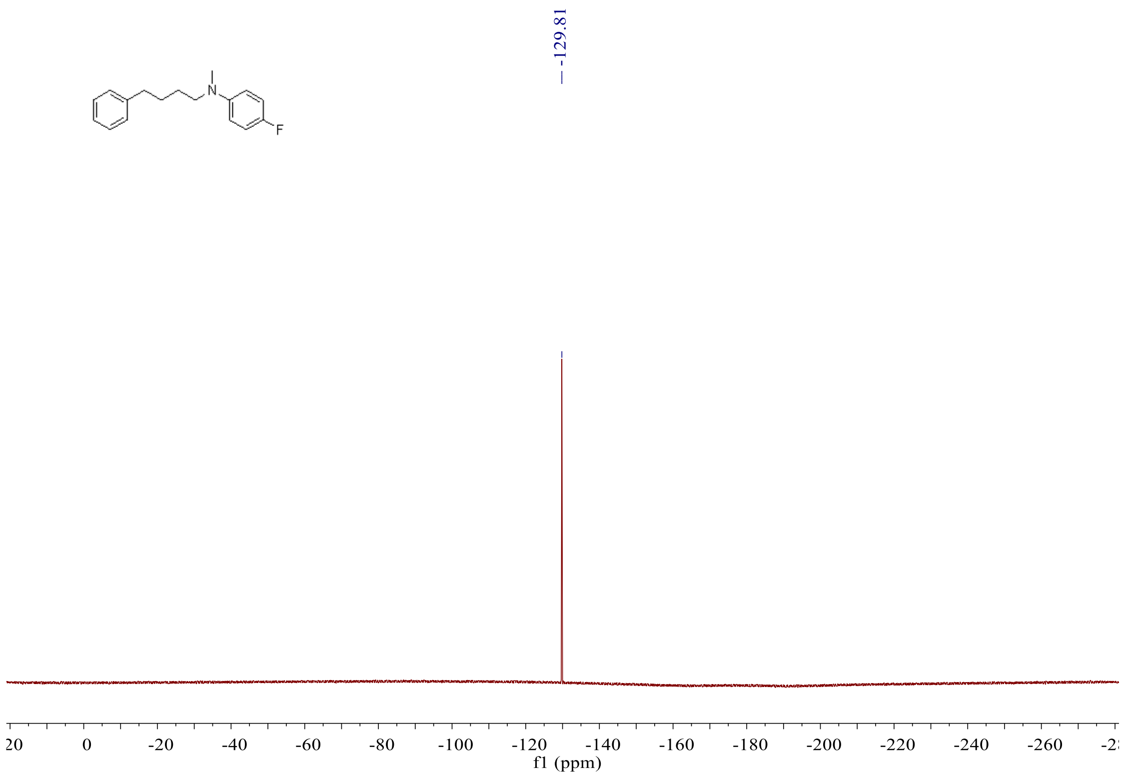

Fig. S160. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) spectrum of compound **9ag.**

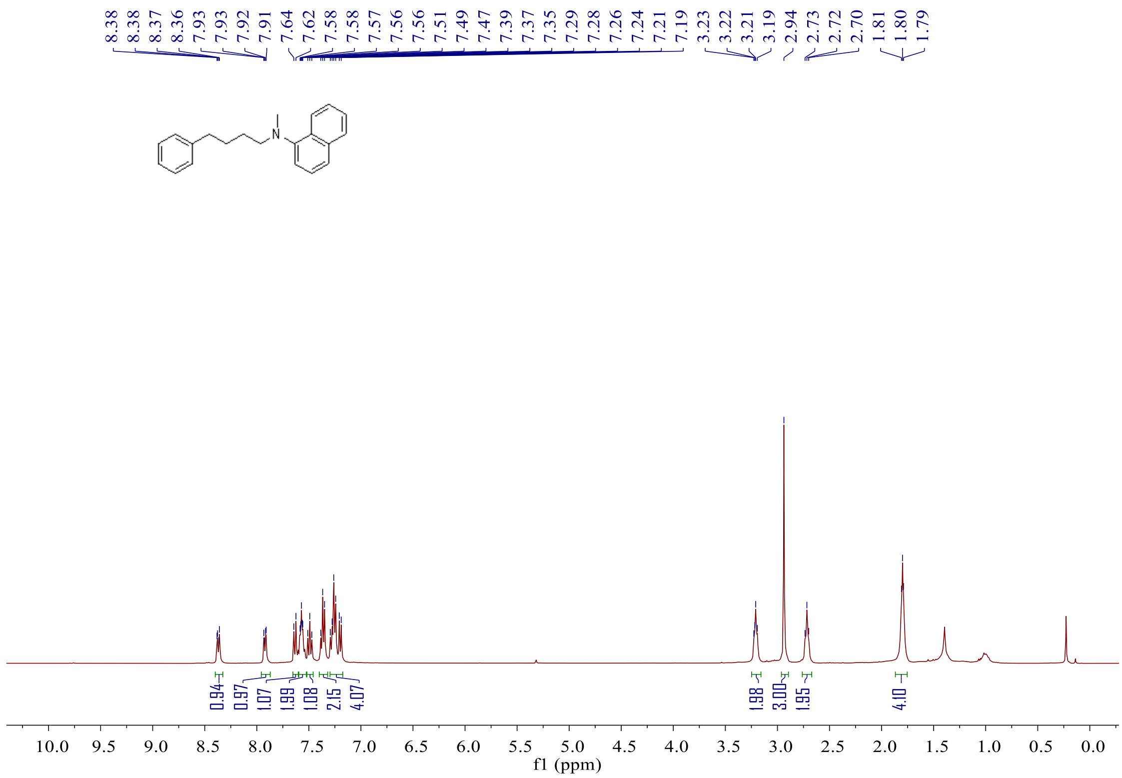

Fig. S161. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ah**.

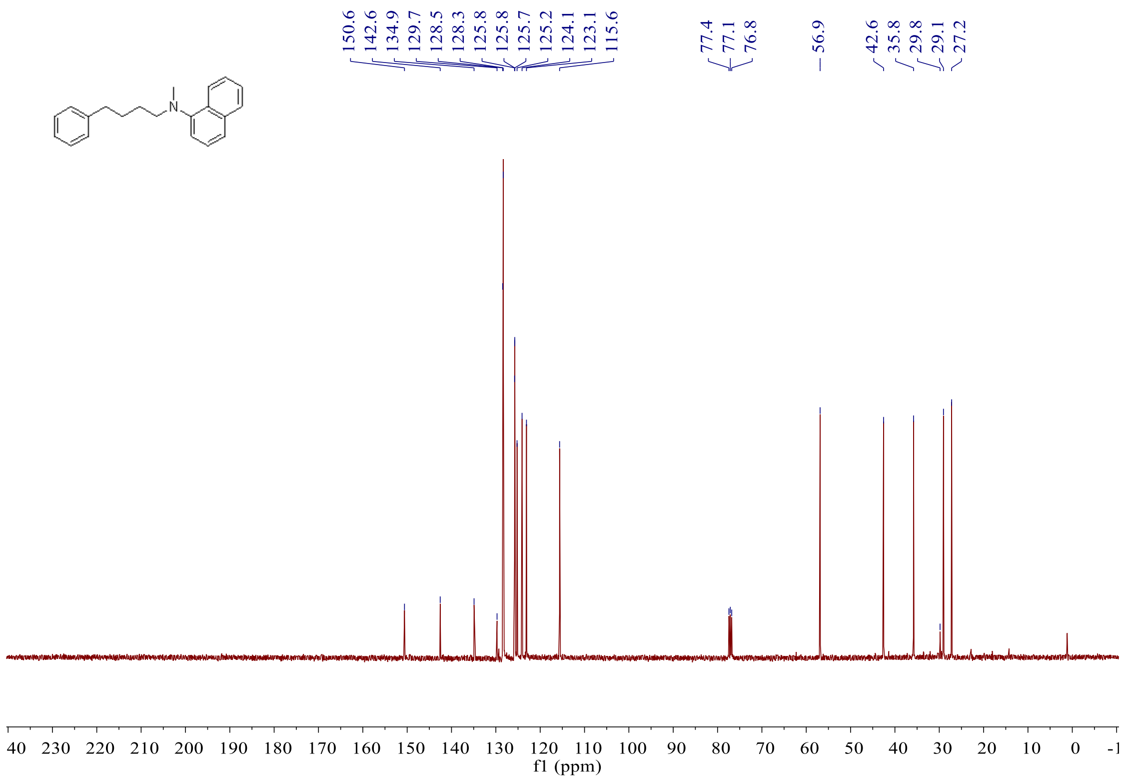

Fig. S162. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ah**.

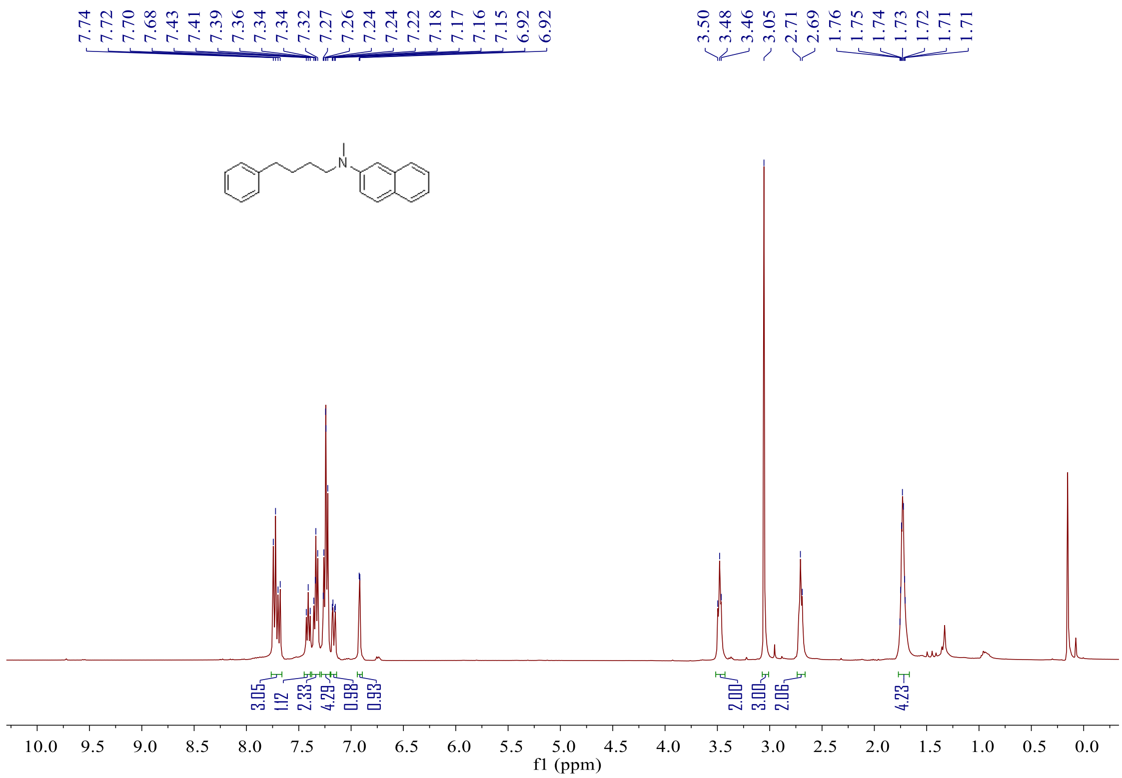

Fig. S163. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ai**.

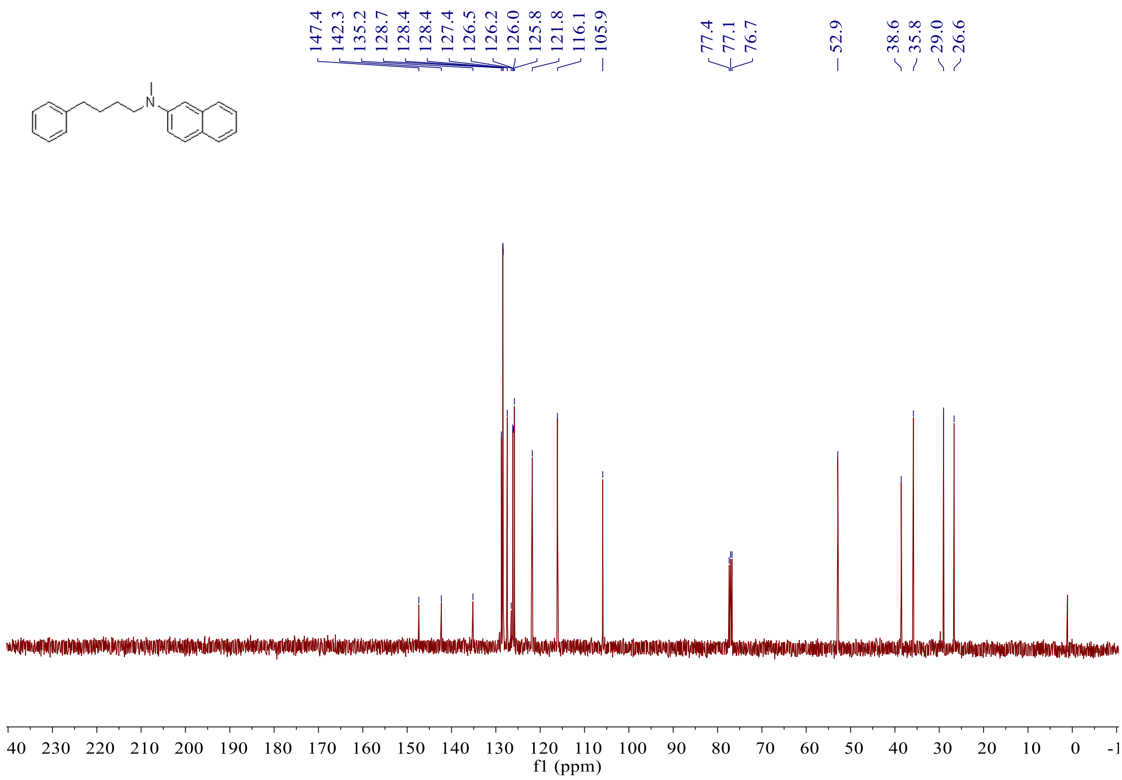

Fig. S164. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ai.**

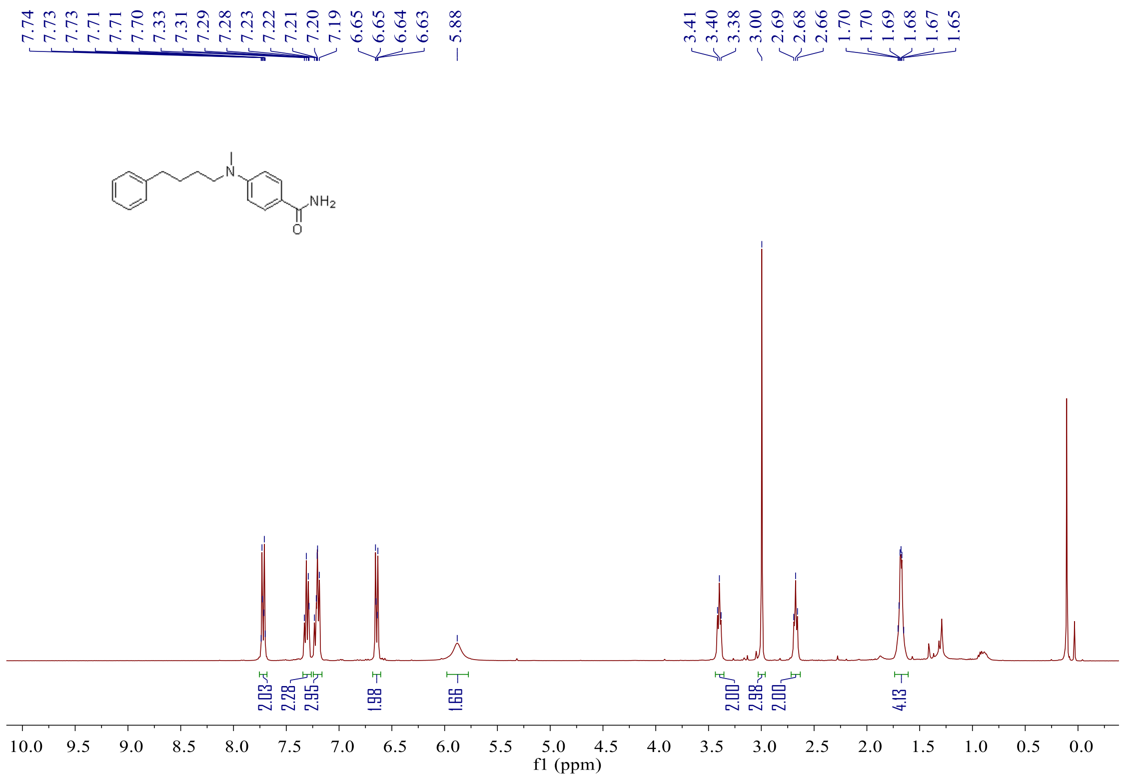

Fig. S165. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9aj**.

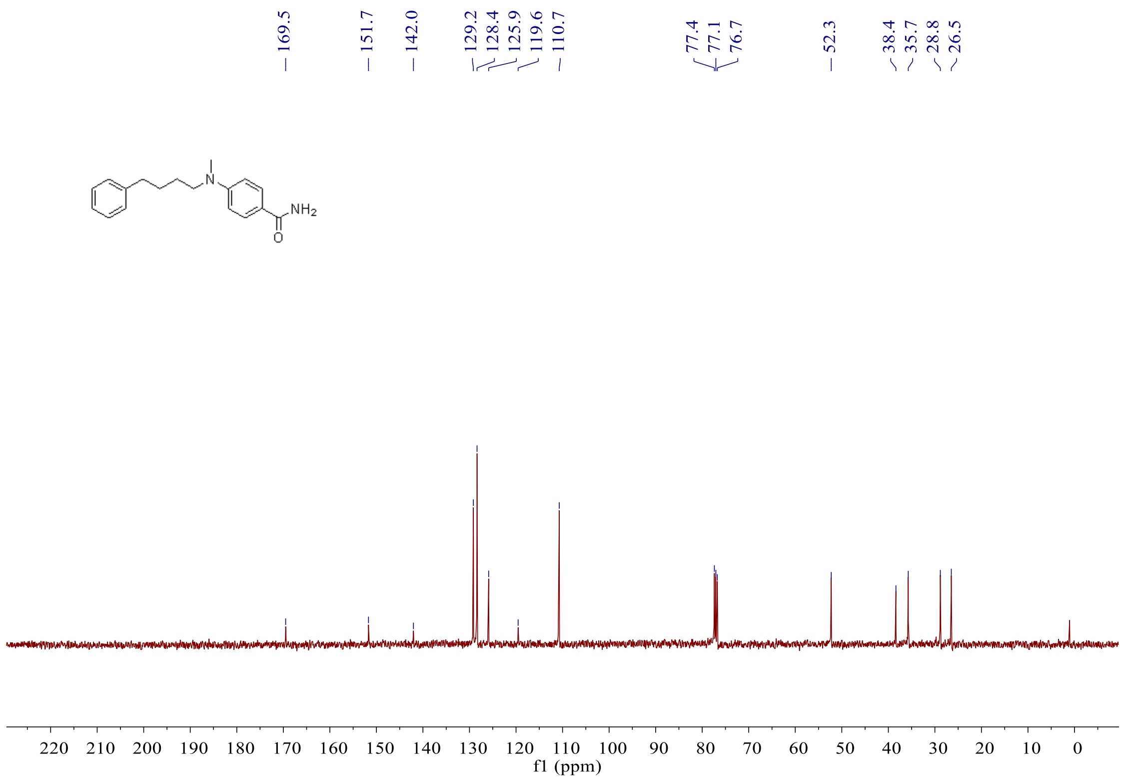

Fig. S166. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9aj**.

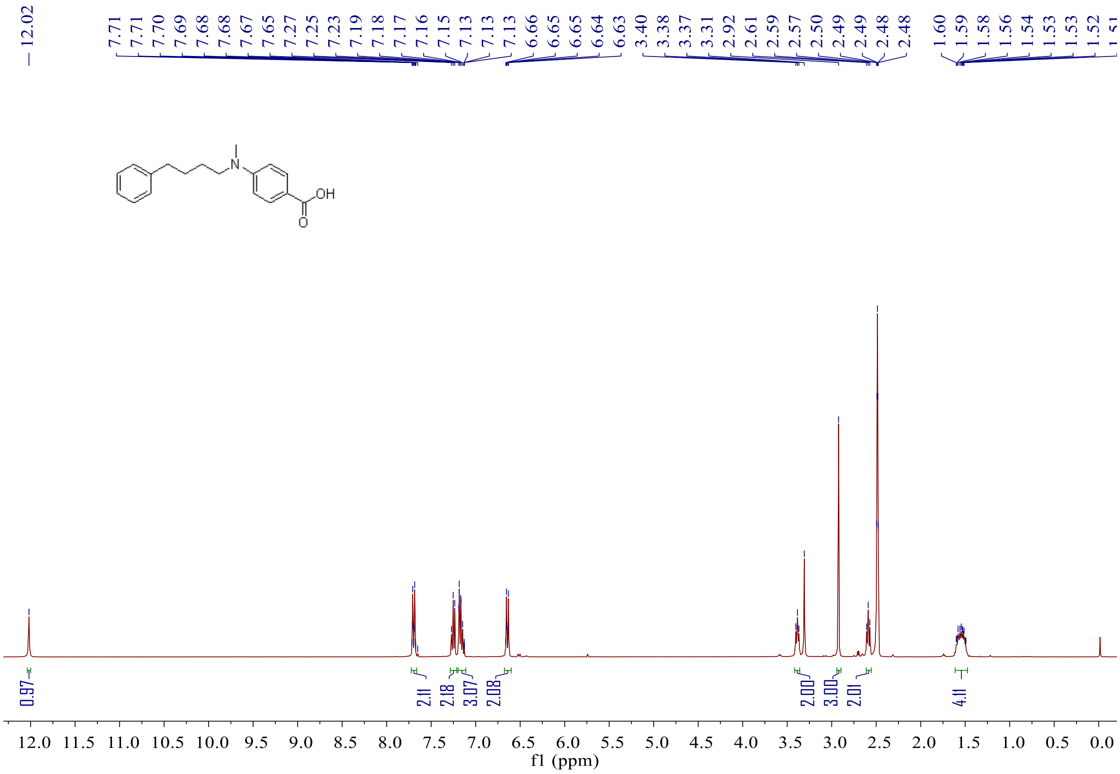

Fig. S167. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of compound **9ak.**

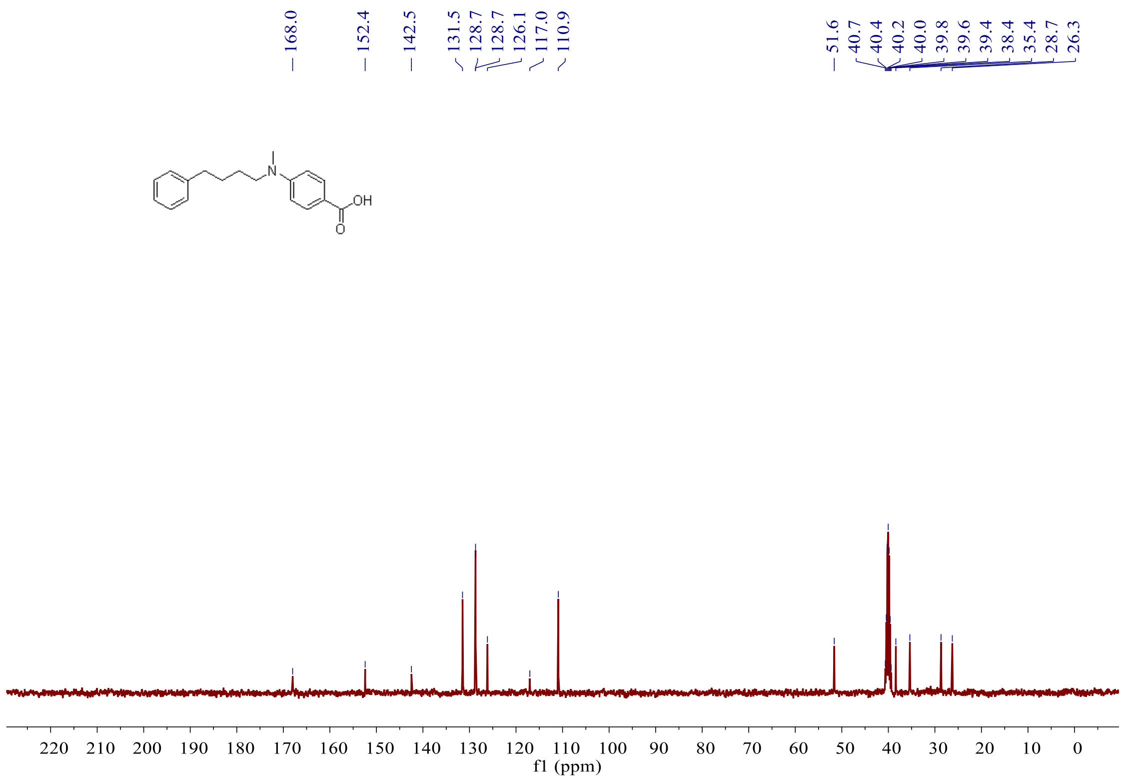

Fig. S168. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) spectrum of compound **9ak**.

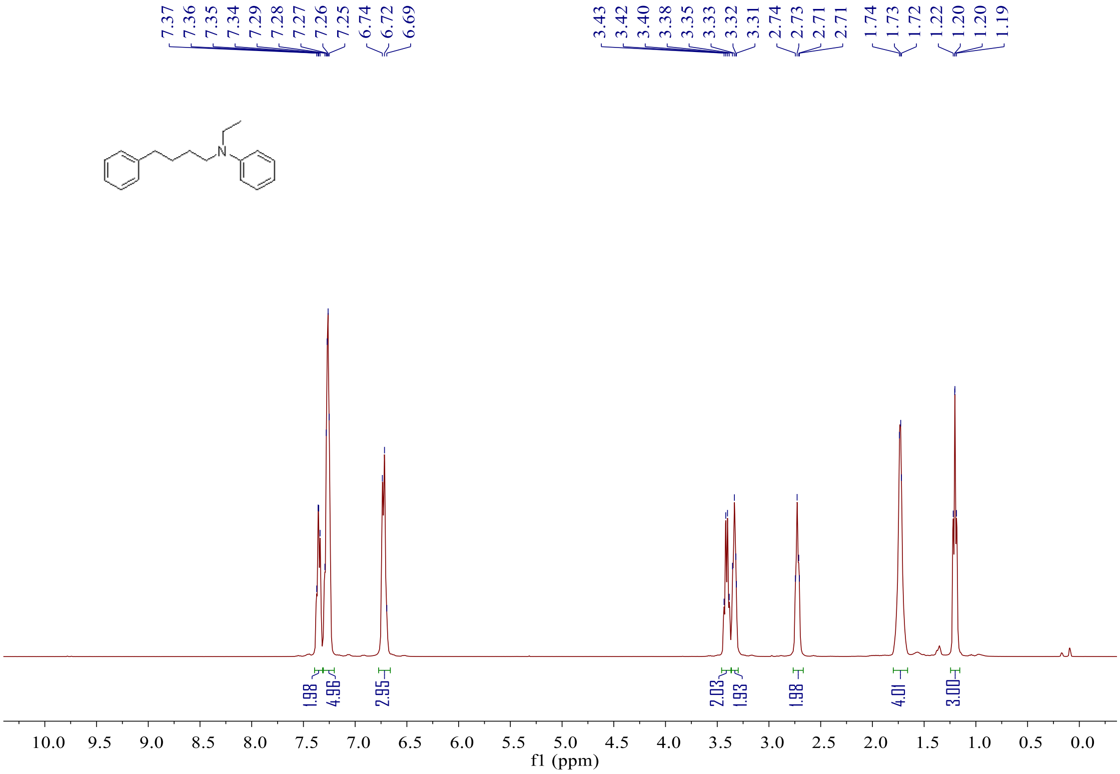

Fig. S169. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9al**.

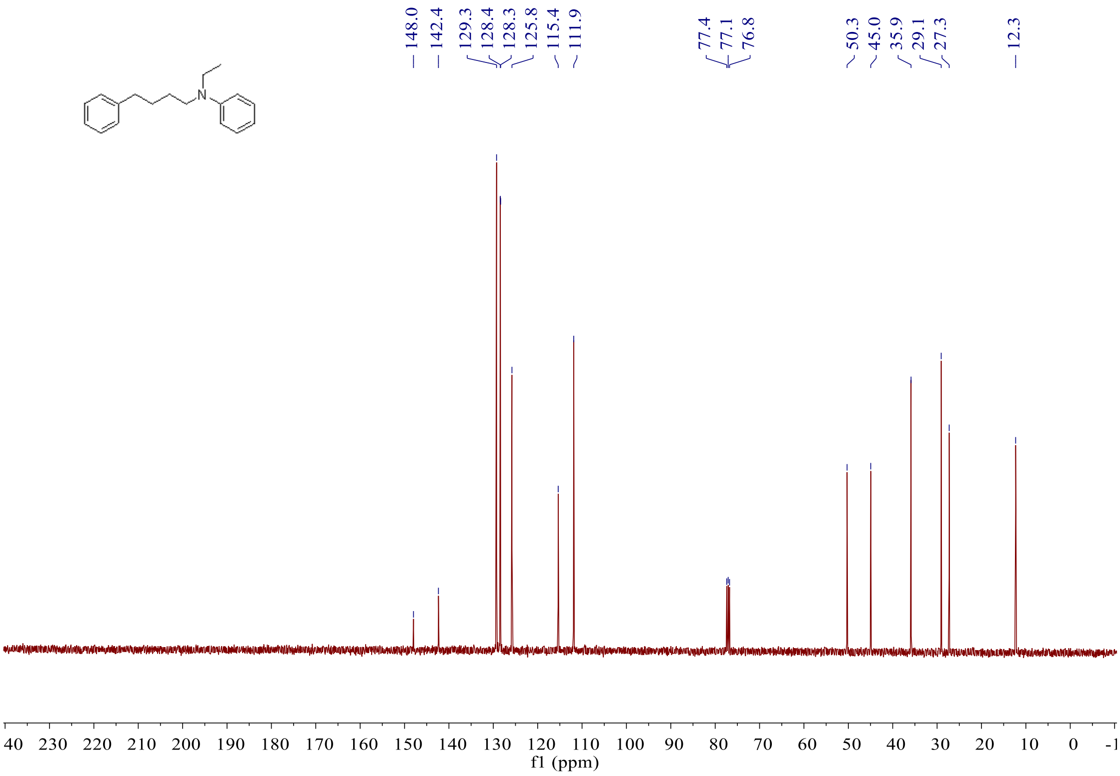

Fig. S170. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9al.**

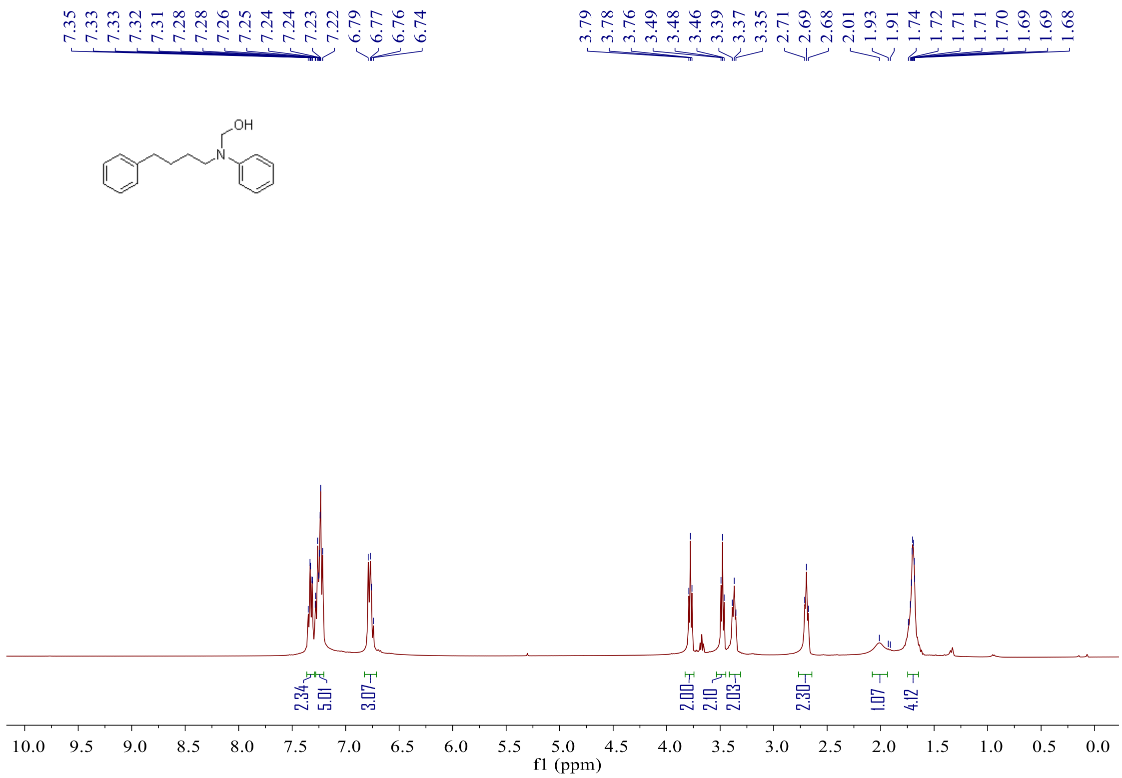

Fig. S171. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9am**.

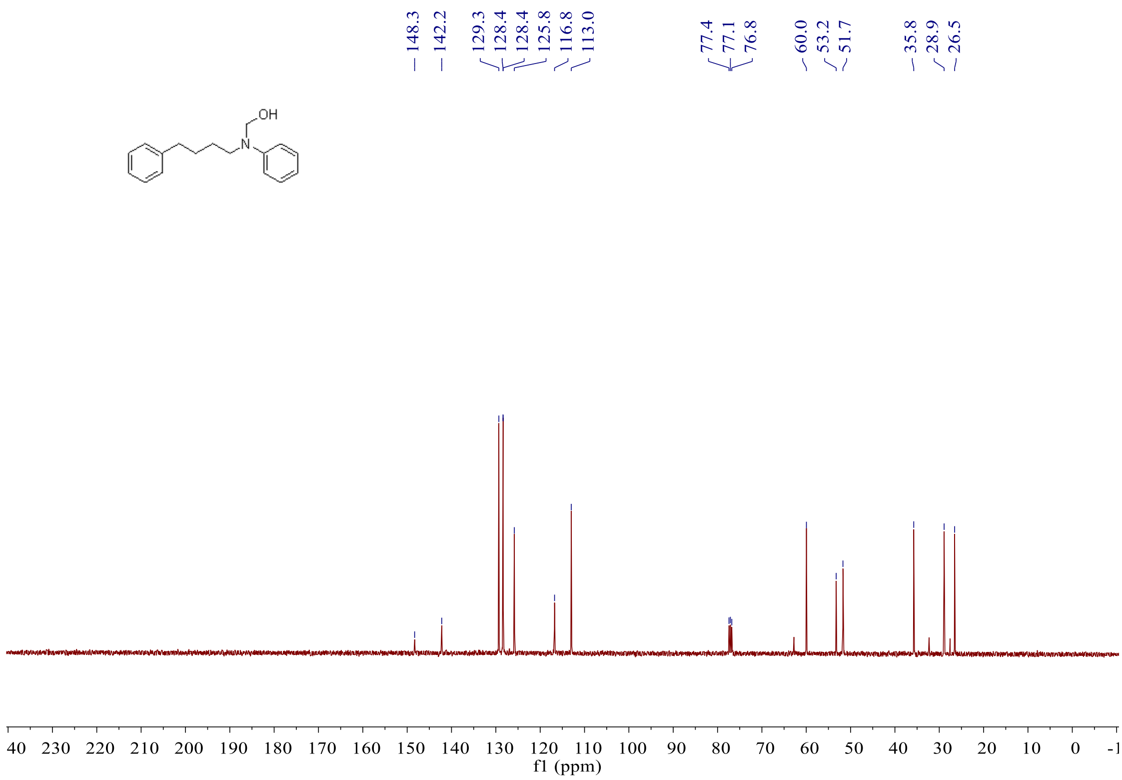

Fig. S172. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9am.**

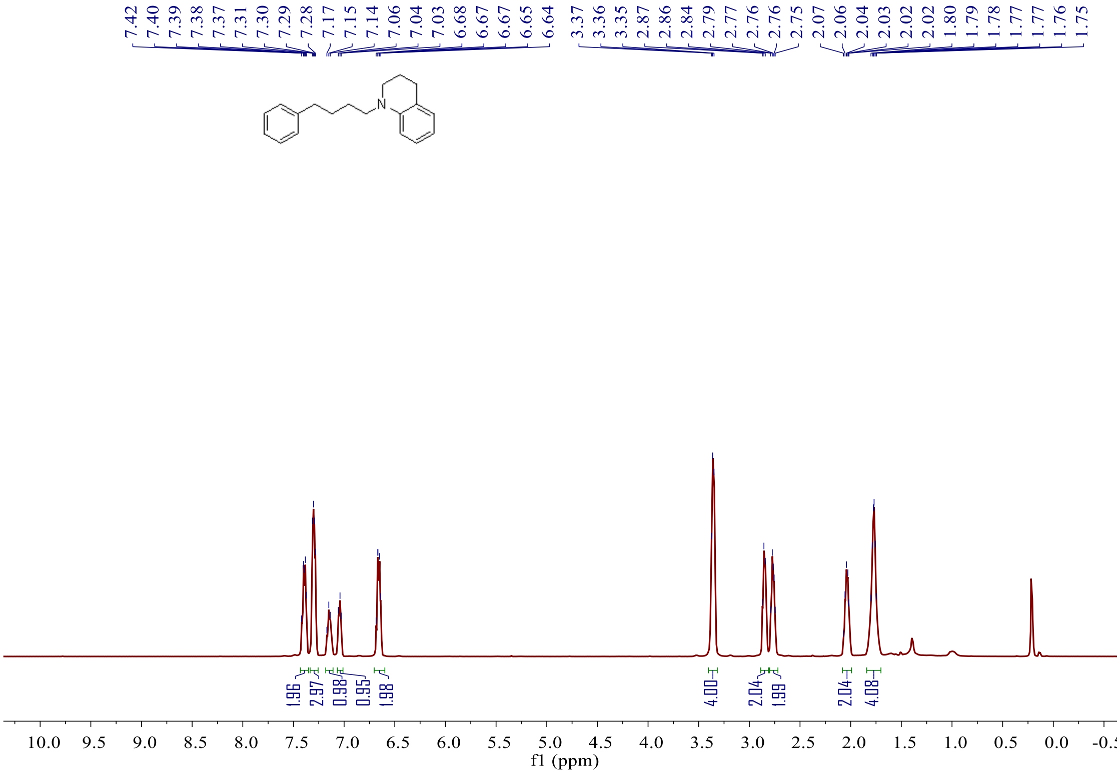

Fig. S173. [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9an**.

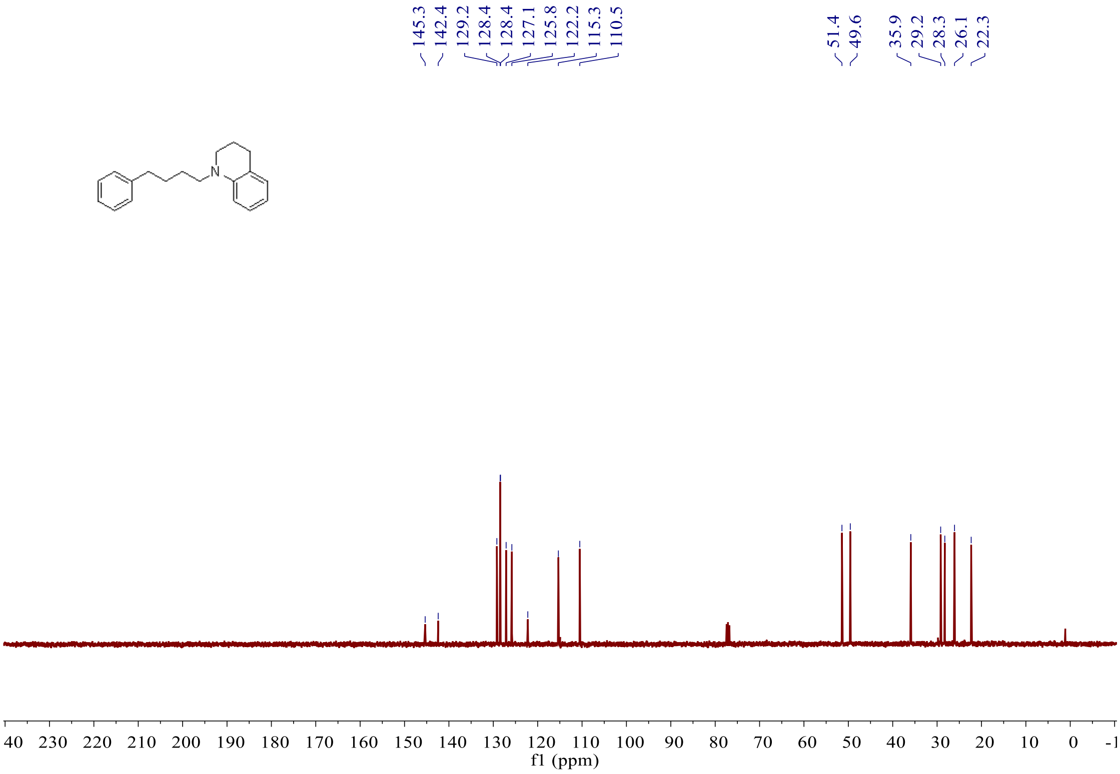

Fig. S174. [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9an**.

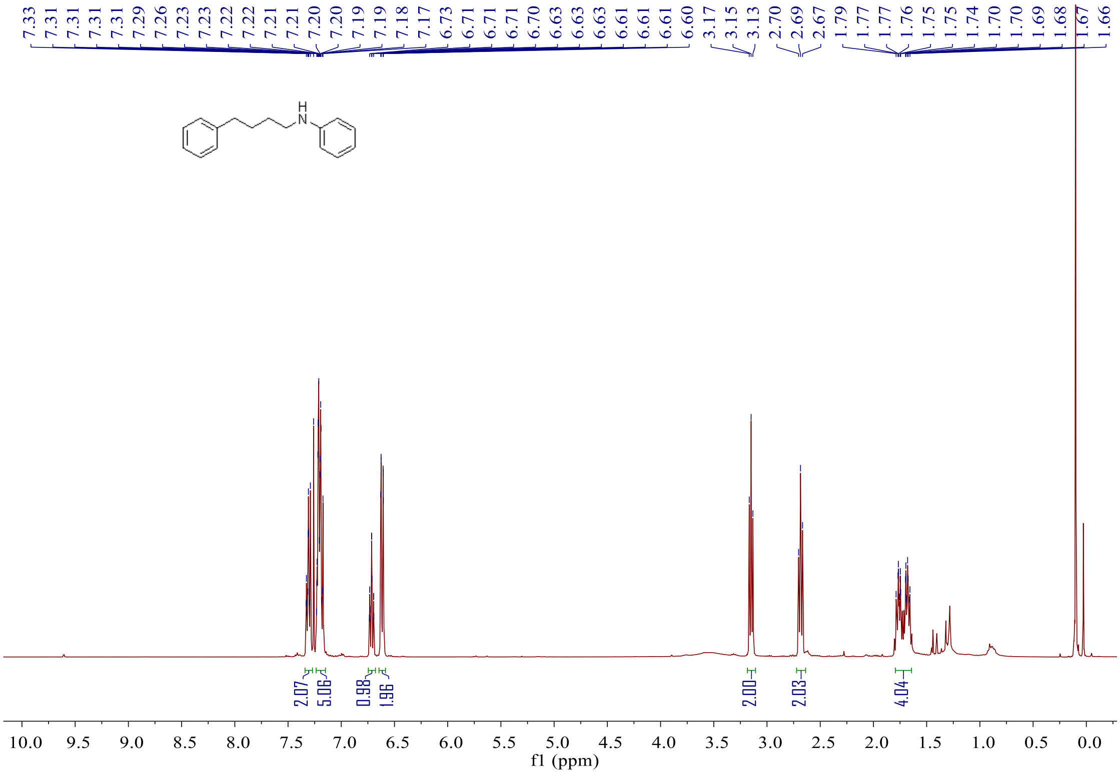

Fig. S175. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ao**.

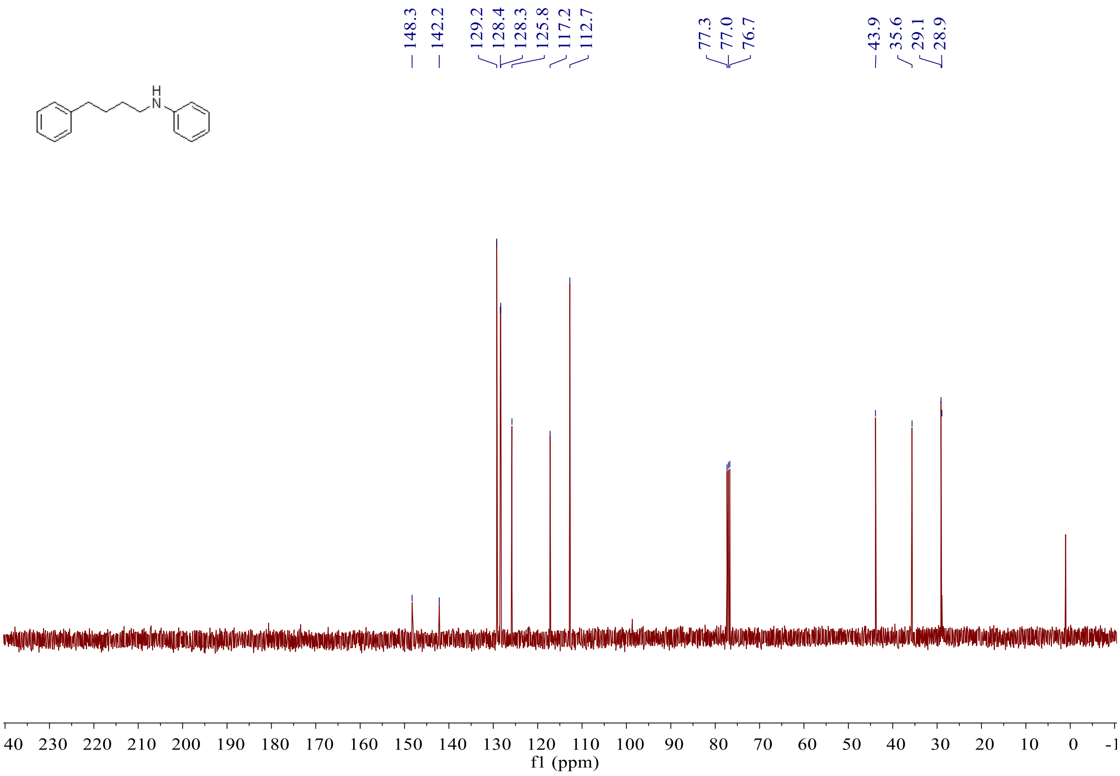

Fig. S176. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ao.**

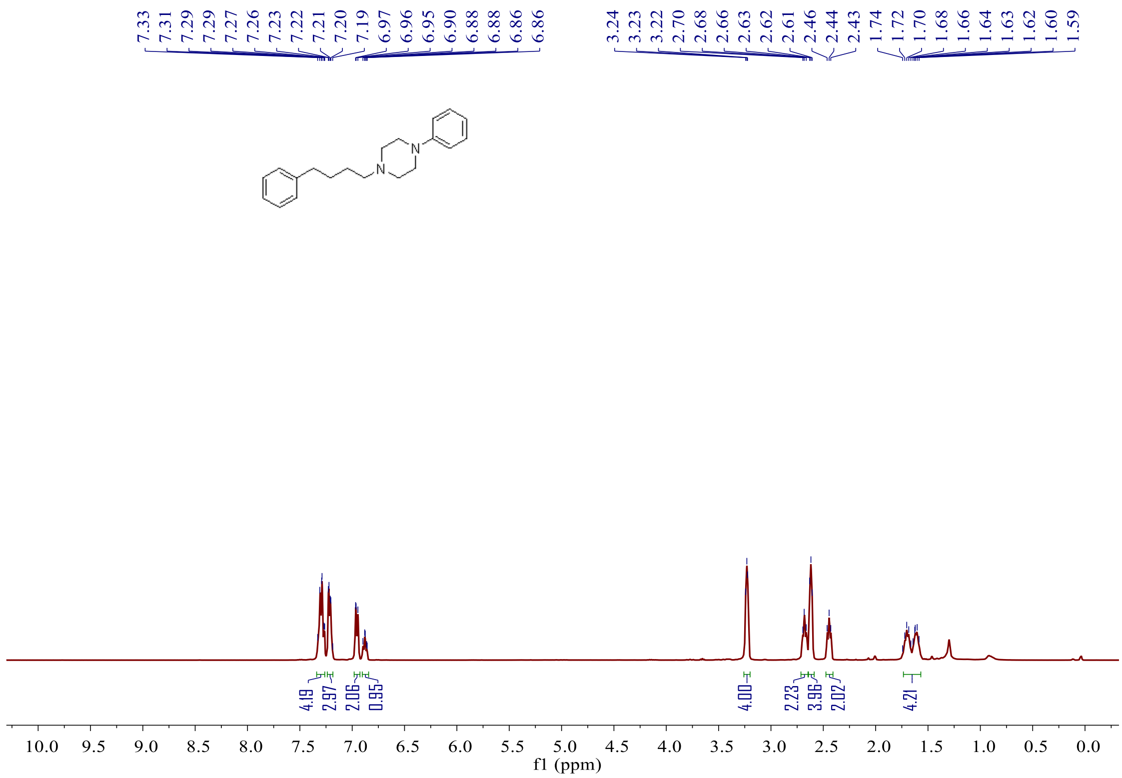

Fig. S177. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **9ap**.

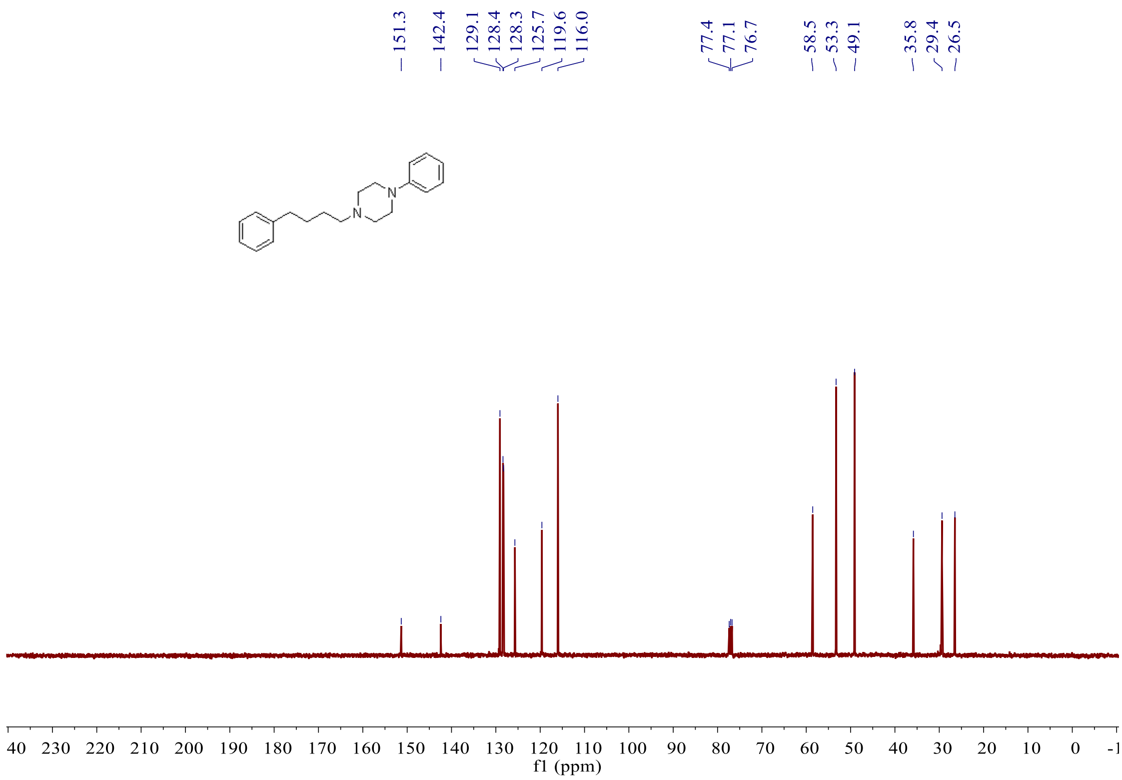

Fig. S178. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9ap.**

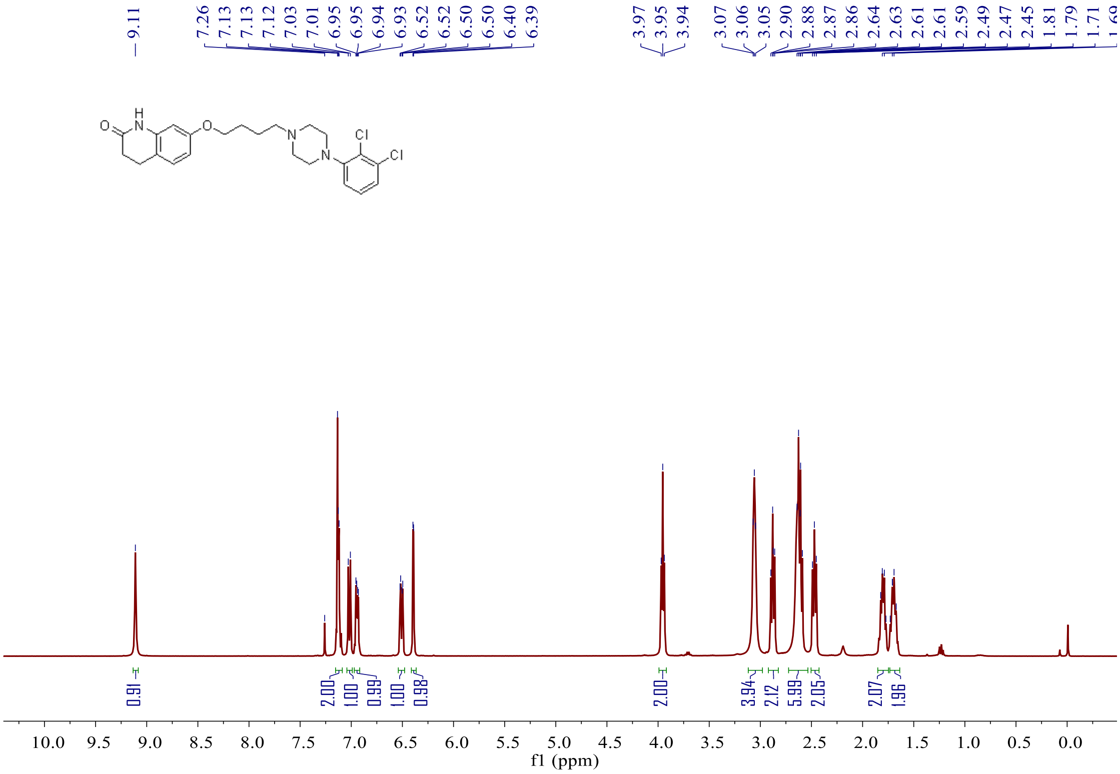

Fig. S179. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **13a**.

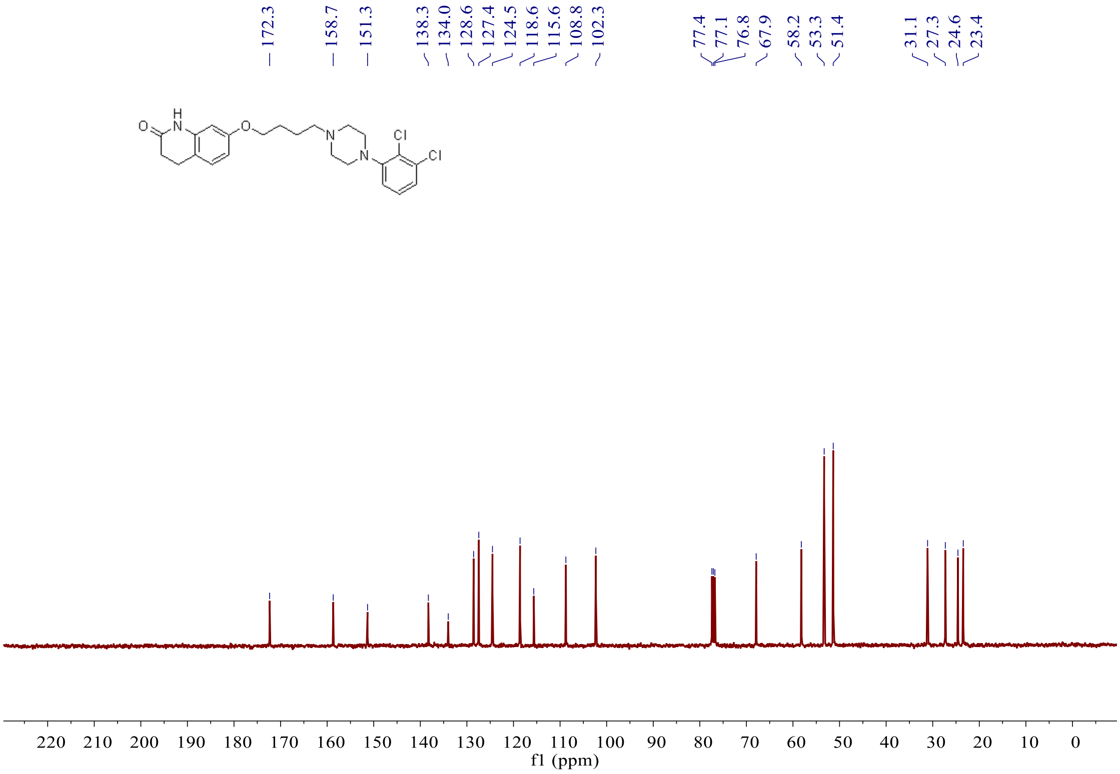

Fig. S180. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **13a.**

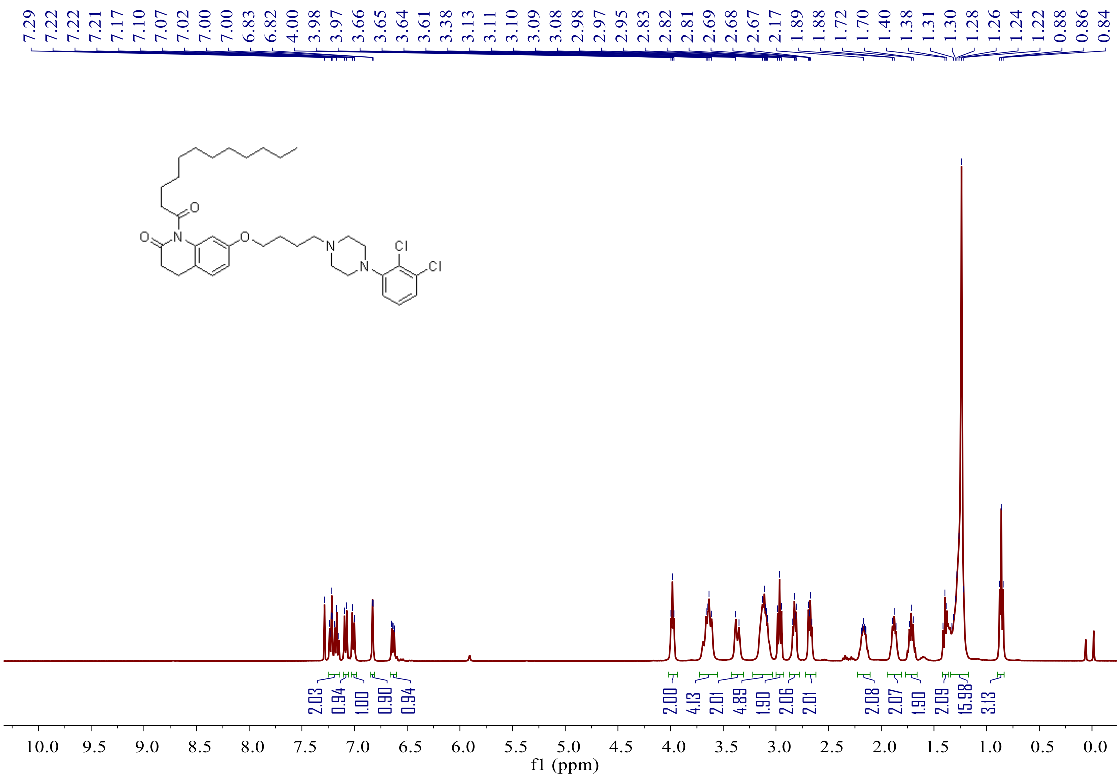

Fig. S181. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **13b**.

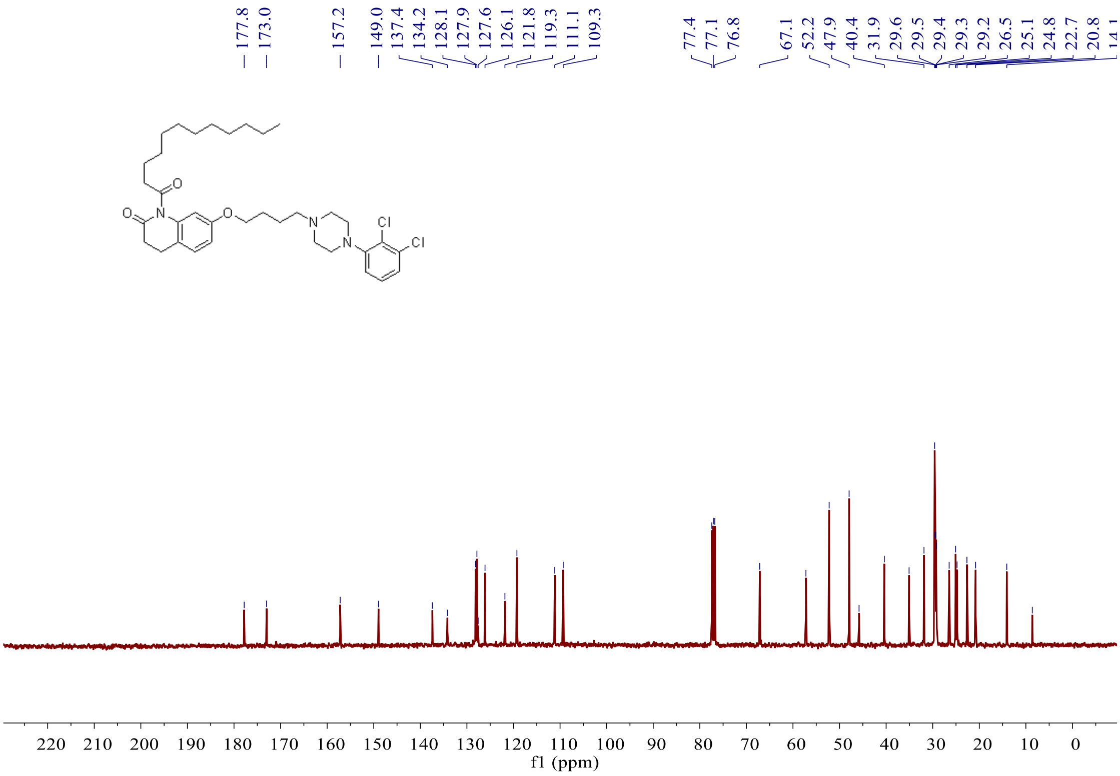

Fig. S182. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **13b.**

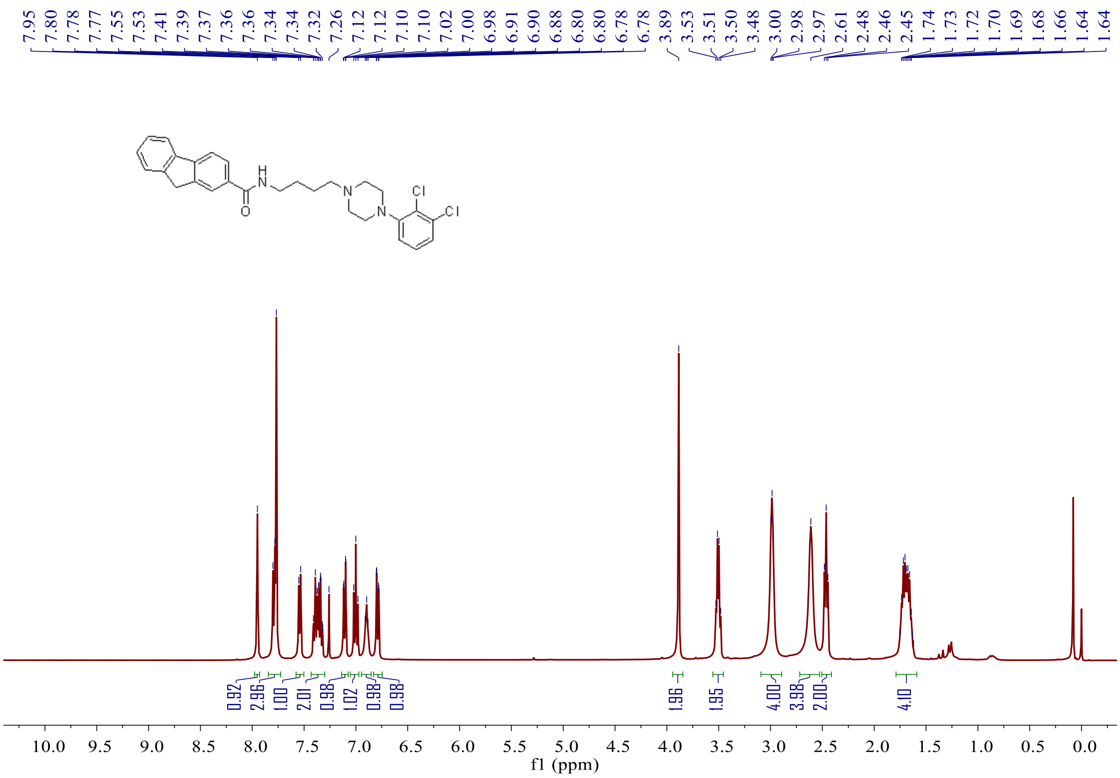

Fig. S183. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **14**.

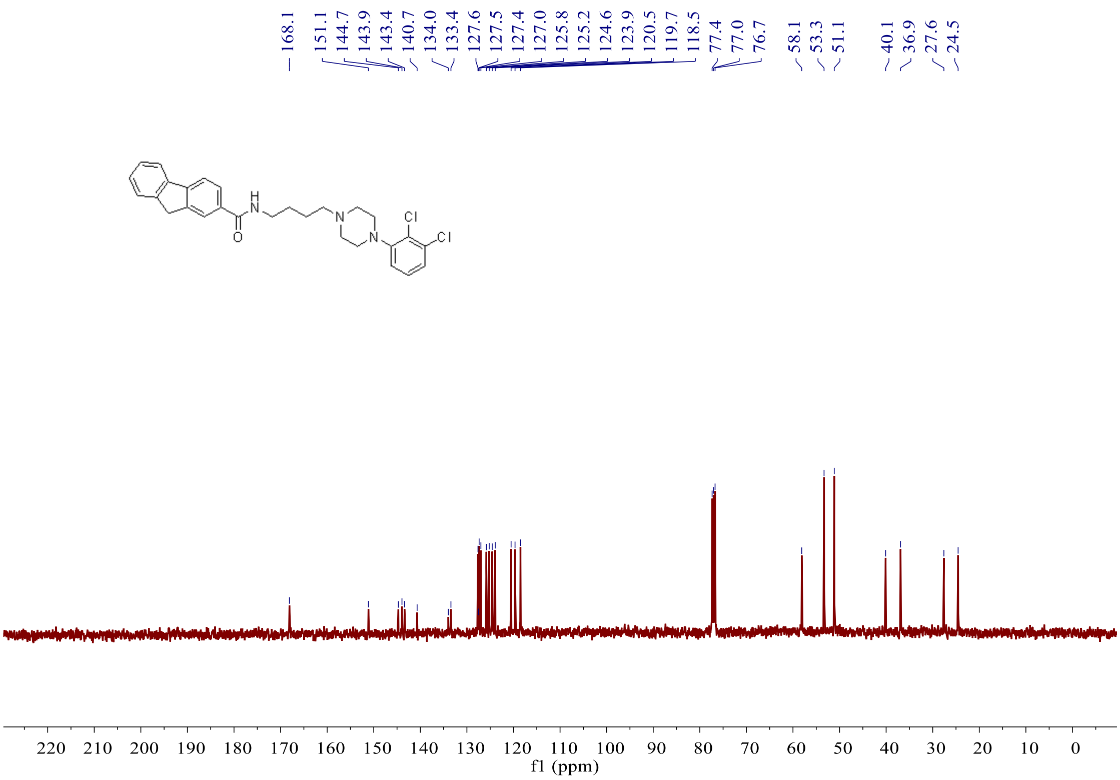

Fig. S184. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **14.**

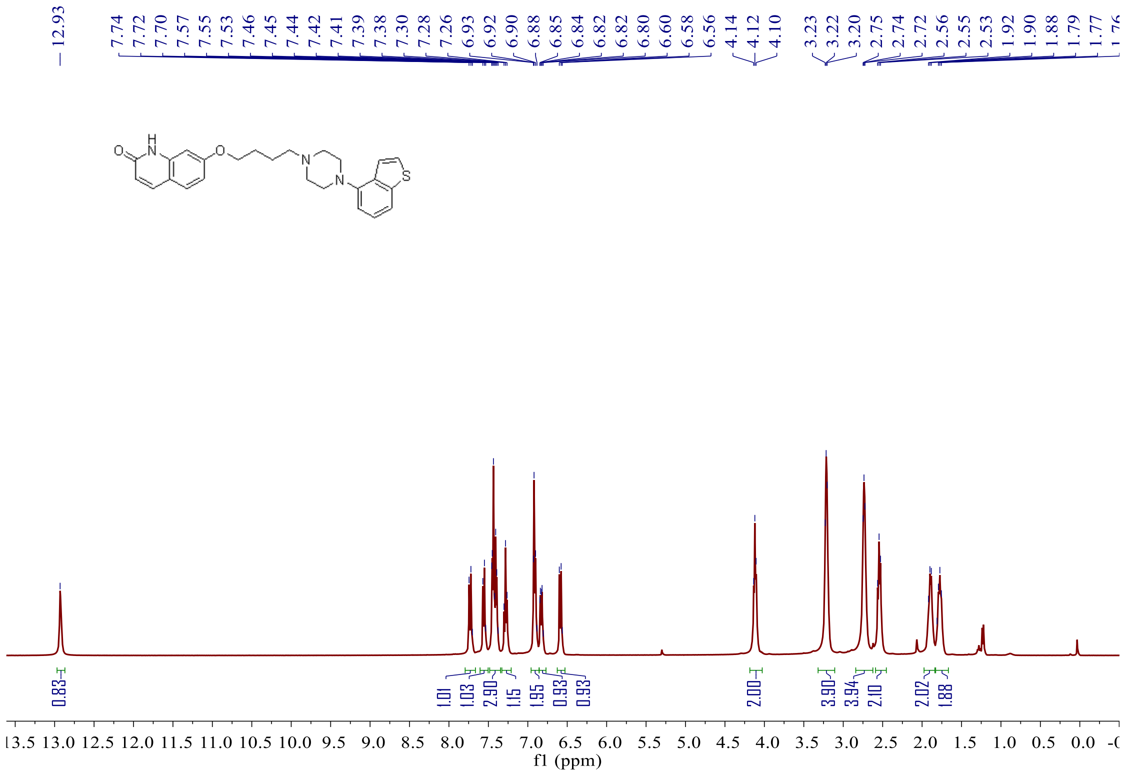

Fig. S185. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **15**.

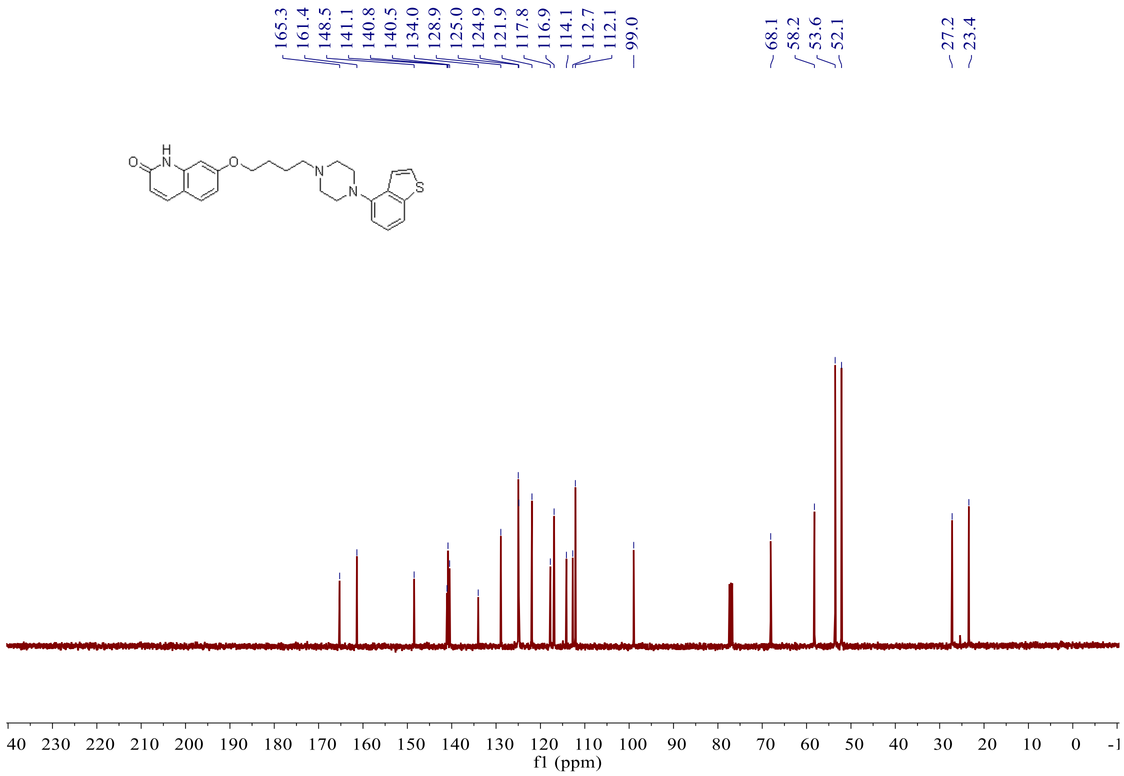

Fig. S186. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **15.**

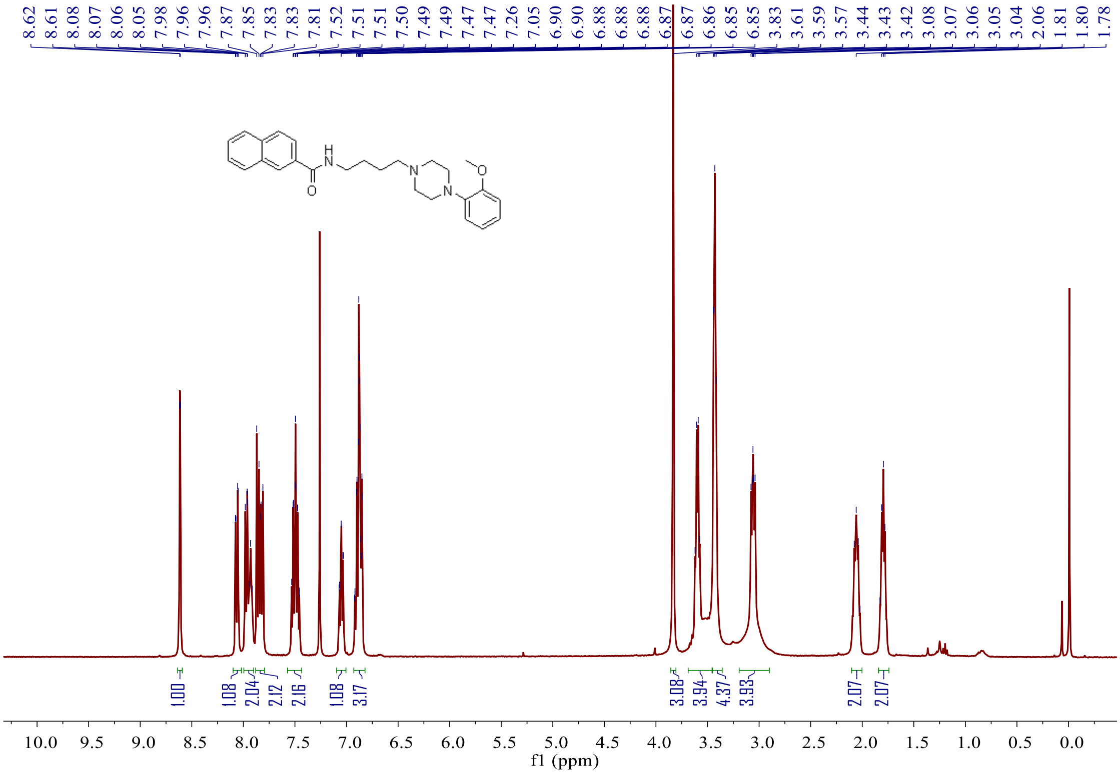

Fig. S187. [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **16**.

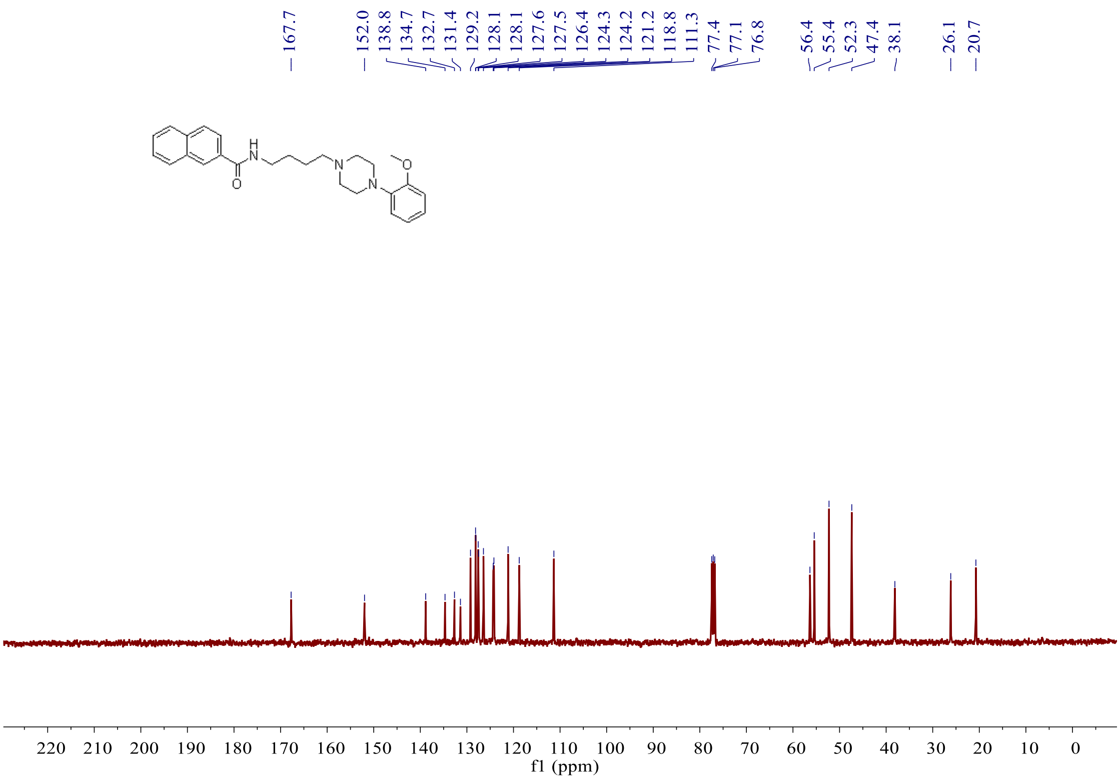

Fig. S188. [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **16.**

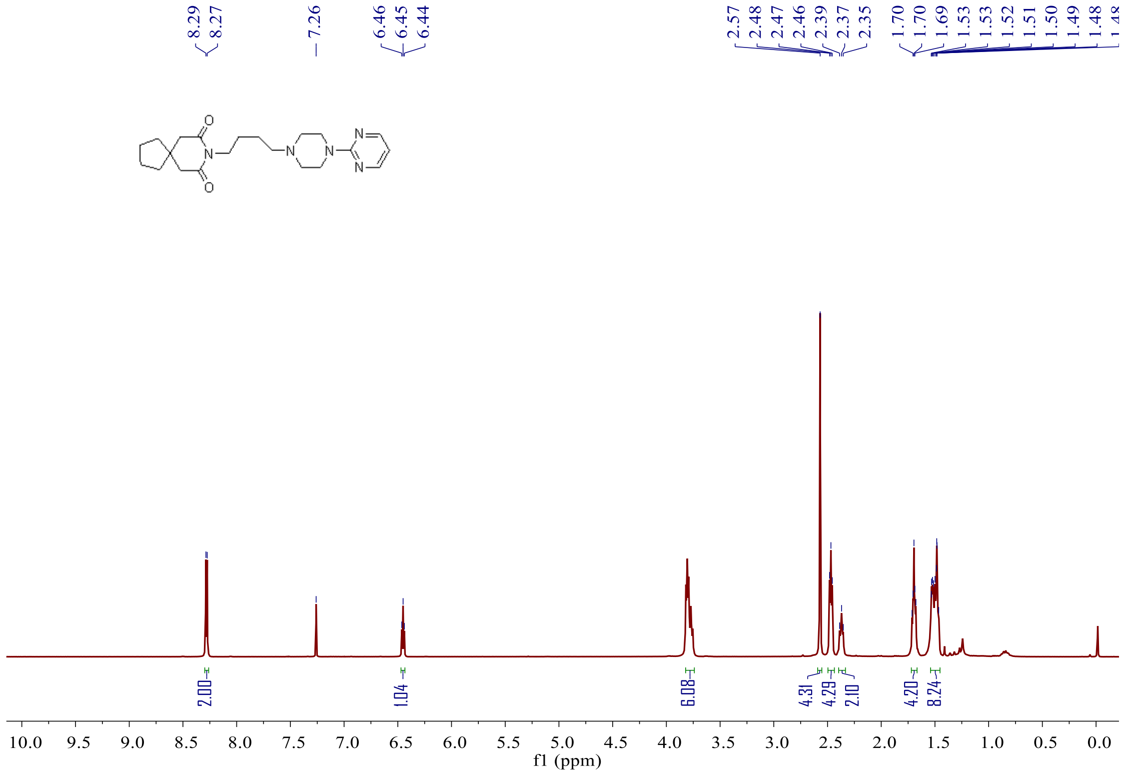

Fig. S189. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **18**.

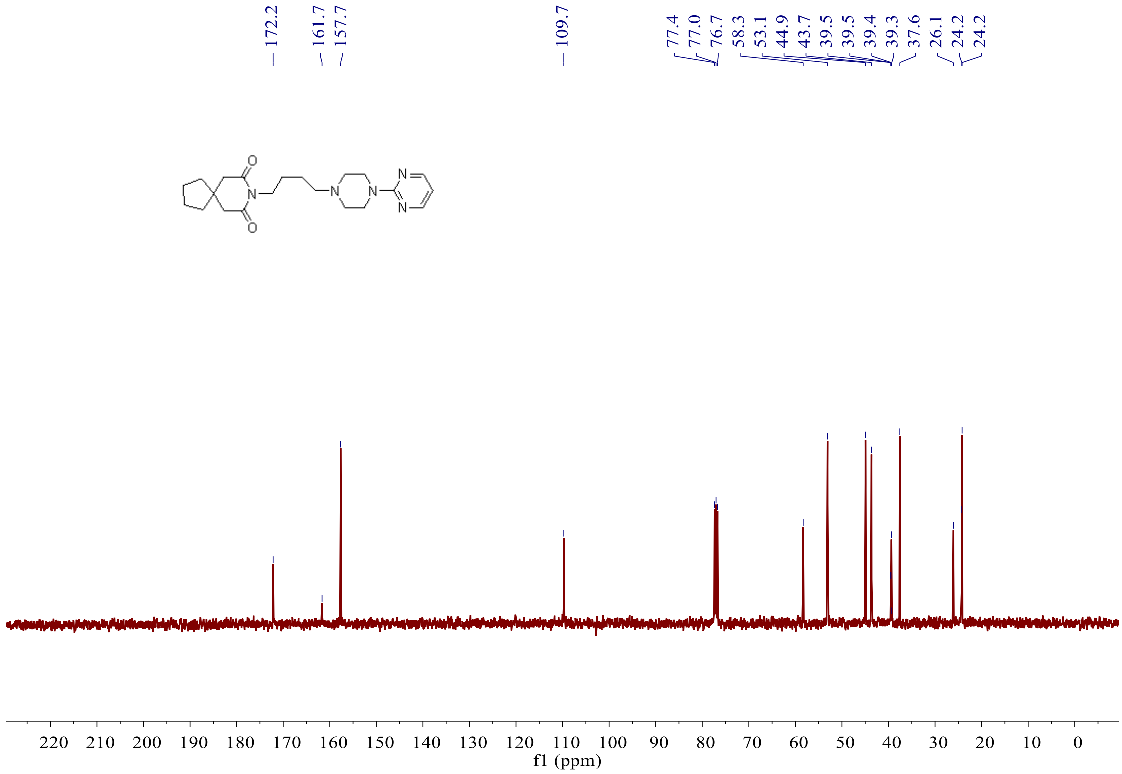

Fig. S190. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **18.**

11. High-resolution mass spectra

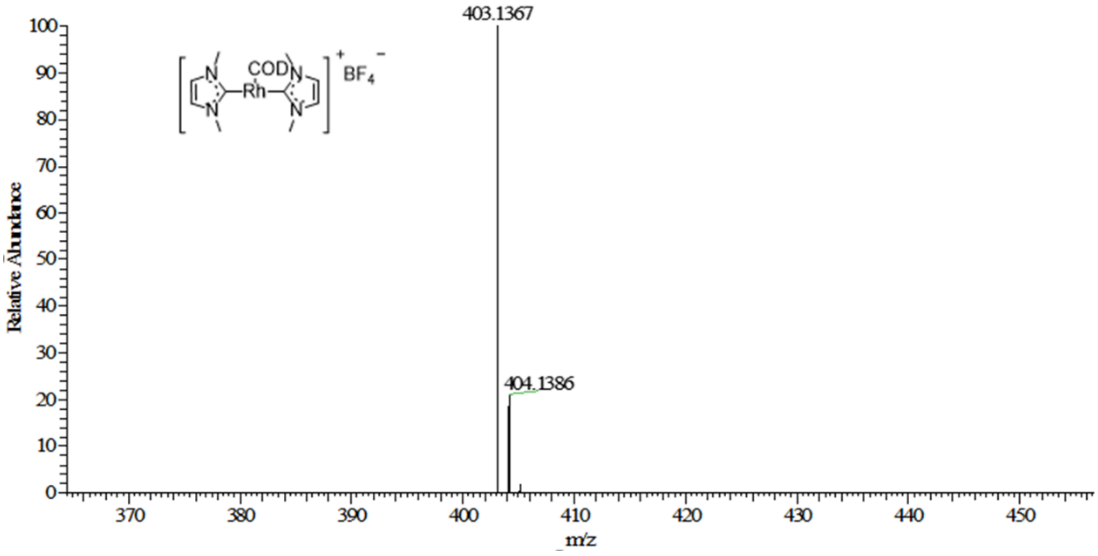

Fig. S191. HR-MS spectrum of compound **2**.

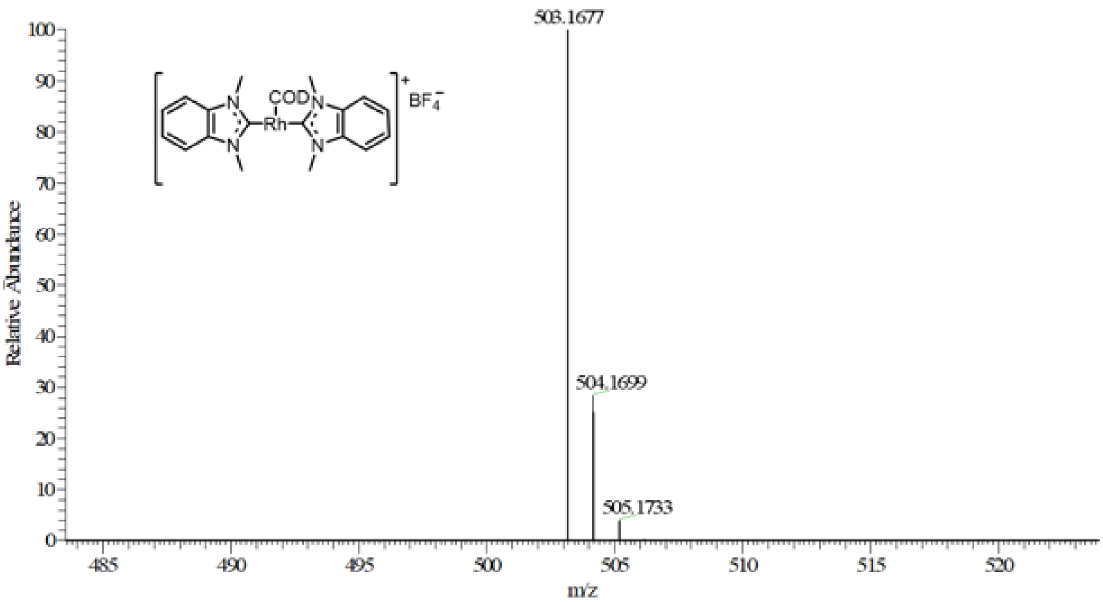

Fig. S192. HR-MS spectrum of compound **3**.

Analysis Info

Analysis Name	D:\Data\2021MS\TT\0311\QC210308_RC5_01_832.d	Acquisition Date	3/11/2021 3:16:57 PM
Method	tune_wide_500-3000_pos-3min.m	Operator	gftang
Sample Name	QC210308	Instrument / Ser#	micrOTOF 10257
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Not active			Set Dry Heater	100 ℃
Scan Begin	500 m/z	Set Capillary	4000 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

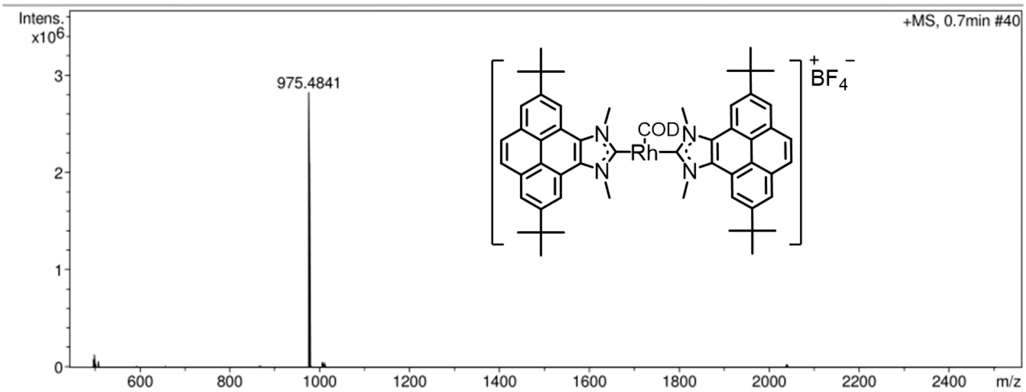

Fig. S193. HR-MS spectrum of compound **4b.**

12. Crystallography

Table S5. Crystal data and structure refinement for compound **2**

Identification code	compound **2**	
Empirical formula	$C_{18}H_{28}BF_4N_4Rh$	
Formula weight	490.14	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Tetragonal	
Space group	$I4_1/acd$	
Unit cell dimensions	a = 15.9403(10) Å	α= 90 °.
	b = 15.9403(10) Å	β= 90 °.
	c = 31.662(2) Å	γ = 90 °.
Volume	8045.0(12) $Å^3$	
Z	72	
Density (calculated)	1.619 mg/m^3	
Absorption coefficient	4.919 mm^{-1}	
F(000)	4000	
Crystal size	0.160 x 0.120 x 0.050 mm^3	
Theta range for data collection	4.189 to 56.993 °.	
Index ranges	-19<=h<=19, -19<=k<=19, -39<=l<=35	
Reflections collected	54960	
Independent reflections	2064 [R(int) = 0.0543]	
Completeness to theta = 53.594 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.554	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2064 / 42 / 149	
Goodness-of-fit on F^2	1.121	
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.1083	
R indices (all data)	R1 = 0.0427, wR2 = 0.1118	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.342 and -1.185 e.$Å^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for Rh complex **2**.

Rh(1)-C(1)#1	2.045(4)
Rh(1)-C(1)	2.045(4)
Rh(1)-C(6)#1	2.203(3)
Rh(1)-C(6)	2.203(3)
Rh(1)-C(6')	2.203(3)
Rh(1)-C(9)#1	2.205(3)
Rh(1)-C(9')	2.205(3)
Rh(1)-C(9)	2.205(3)
B(1)-F(1)	1.342(3)
B(1)-F(1)#2	1.342(3)
B(1)-F(1)#3	1.342(3)
B(1)-F(1)#4	1.342(3)
B(2)-F(2)#5	1.308(4)
B(2)-F(2)#6	1.308(4)
B(2)-F(2)#7	1.308(4)
B(2)-F(2)	1.308(4)
N(1)-C(1)	1.358(5)
N(1)-C(3)	1.383(5)
N(1)-C(4)	1.447(5)
N(2)-C(1)	1.358(5)
N(2)-C(2)	1.381(5)
N(2)-C(5)	1.458(6)
C(2)-C(3)	1.337(7)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(9)#1	1.380(6)
C(6)-C(7)	1.544(11)
C(6)-H(6)	0.9500
C(7)-C(8)	1.513(16)
C(7)-H(7A)	0.9900

C(7)-H(7B)	0.9900
C(8)-C(9)	1.501(11)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9)	0.9500
C(6')-C(7')	1.504(14)
C(6')-H(6')	0.9500
C(7')-C(8')	1.544(19)
C(7')-H(7'1)	0.9900
C(7')-H(7'2)	0.9900
C(8')-C(9')	1.571(12)
C(8')-H(8'1)	0.9900
C(8')-H(8'2)	0.9900
C(9')-H(9')	0.9500
C(1)#1-Rh(1)-C(1)	91.20(18)
C(1)#1-Rh(1)-C(6)#1	160.08(15)
C(1)-Rh(1)-C(6)#1	91.80(13)
C(1)#1-Rh(1)-C(6)	91.80(13)
C(1)-Rh(1)-C(6)	160.08(15)
C(6)#1-Rh(1)-C(6)	92.0(2)
C(1)#1-Rh(1)-C(6')	91.80(13)
C(1)-Rh(1)-C(6')	160.08(15)
C(1)#1-Rh(1)-C(9)#1	90.69(13)
C(1)-Rh(1)-C(9)#1	163.12(15)
C(6)#1-Rh(1)-C(9)#1	80.94(13)
C(6)-Rh(1)-C(9)#1	36.48(15)
C(6')-Rh(1)-C(9)#1	36.48(15)
C(1)#1-Rh(1)-C(9')	163.12(15)
C(1)-Rh(1)-C(9')	90.69(13)
C(6')-Rh(1)-C(9')	80.94(13)
C(1)#1-Rh(1)-C(9)	163.12(15)
C(1)-Rh(1)-C(9)	90.69(13)
C(6)#1-Rh(1)-C(9)	36.47(15)
C(6)-Rh(1)-C(9)	80.94(13)
C(9)#1-Rh(1)-C(9)	92.4(2)
F(1)-B(1)-F(1)#2	108.7(5)
F(1)-B(1)-F(1)#3	108.8(4)

F(1)#2-B(1)-F(1)#3	111.0(5)
F(1)-B(1)-F(1)#4	111.0(5)
F(1)#2-B(1)-F(1)#4	108.8(4)
F(1)#3-B(1)-F(1)#4	108.7(5)
F(2)#5-B(2)-F(2)#6	111.9(6)
F(2)#5-B(2)-F(2)#7	108.3(3)
F(2)#6-B(2)-F(2)#7	108.3(3)
F(2)#5-B(2)-F(2)	108.3(3)
F(2)#6-B(2)-F(2)	108.3(3)
F(2)#7-B(2)-F(2)	111.9(6)
C(1)-N(1)-C(3)	111.9(3)
C(1)-N(1)-C(4)	124.7(3)
C(3)-N(1)-C(4)	123.4(3)
C(1)-N(2)-C(2)	111.7(3)
C(1)-N(2)-C(5)	124.8(3)
C(2)-N(2)-C(5)	123.4(3)
N(2)-C(1)-N(1)	103.1(3)
N(2)-C(1)-Rh(1)	128.3(3)
N(1)-C(1)-Rh(1)	128.5(3)
C(3)-C(2)-N(2)	106.9(3)
C(3)-C(2)-H(2)	126.6
N(2)-C(2)-H(2)	126.6
C(2)-C(3)-N(1)	106.3(3)
C(2)-C(3)-H(3)	126.8
N(1)-C(3)-H(3)	126.8
N(1)-C(4)-H(4A)	109.5
N(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
N(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
N(2)-C(5)-H(5A)	109.5
N(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
N(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(9)#1-C(6)-C(7)	117.4(6)

C(9)#1-C(6)-Rh(1)	71.9(2)
C(7)-C(6)-Rh(1)	110.0(4)
C(9)#1-C(6)-H(6)	121.3
C(7)-C(6)-H(6)	121.3
Rh(1)-C(6)-H(6)	88.3
C(8)-C(7)-C(6)	113.4(8)
C(8)-C(7)-H(7A)	108.9
C(6)-C(7)-H(7A)	108.9
C(8)-C(7)-H(7B)	108.9
C(6)-C(7)-H(7B)	108.9
H(7A)-C(7)-H(7B)	107.7
C(9)-C(8)-C(7)	112.1(8)
C(9)-C(8)-H(8A)	109.2
C(7)-C(8)-H(8A)	109.2
C(9)-C(8)-H(8B)	109.2
C(7)-C(8)-H(8B)	109.2
H(8A)-C(8)-H(8B)	107.9
C(6)#1-C(9)-C(8)	135.6(6)
C(6)#1-C(9)-Rh(1)	71.7(2)
C(8)-C(9)-Rh(1)	107.1(4)
C(6)#1-C(9)-H(9)	112.2
C(8)-C(9)-H(9)	112.2
Rh(1)-C(9)-H(9)	91.6
C(7')-C(6')-Rh(1)	106.5(5)
C(7')-C(6')-H(6')	126.8
Rh(1)-C(6')-H(6')	126.8
C(6')-C(7')-C(8')	109.7(9)
C(6')-C(7')-H(7'1)	109.7
C(8')-C(7')-H(7'1)	109.7
C(6')-C(7')-H(7'2)	109.7
C(8')-C(7')-H(7'2)	109.7
H(7'1)-C(7')-H(7'2)	108.2
C(7')-C(8')-C(9')	110.6(10)
C(7')-C(8')-H(8'1)	109.5
C(9')-C(8')-H(8'1)	109.5
C(7')-C(8')-H(8'2)	109.5
C(9')-C(8')-H(8'2)	109.5
H(8'1)-C(8')-H(8'2)	108.1

C(8')-C(9')-Rh(1)	109.8(5)
C(8')-C(9')-H(9')	125.1
Rh(1)-C(9')-H(9')	125.1

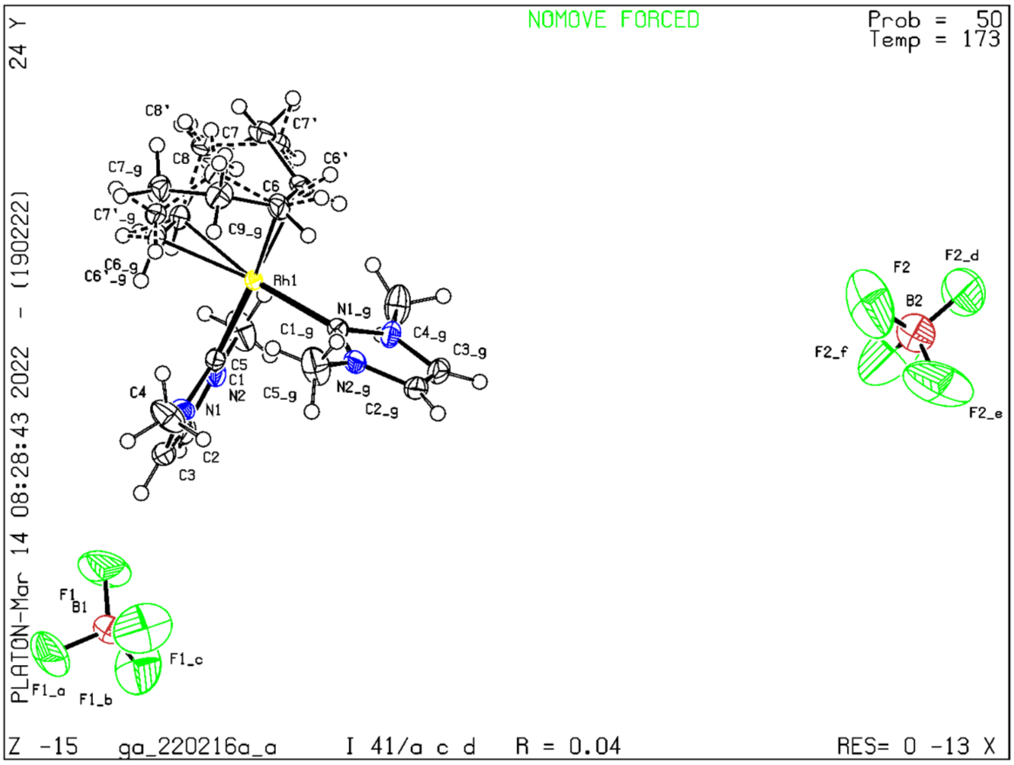

Fig. S194. Crystal structure of rhodium complex **2**.

Table S7. Crystal data and structure refinement for compound **3**

Identification code	compound **3**	
Empirical formula	$C_{13.50}H_{17}B_{0.50}ClF_2N_2Rh_{0.50}$	
Formula weight	337.60	
Temperature	181(2) K	
Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.6170(10) Å	α= 90°.
	b = 17.2920(12) Å	β= 116.871(2)°.
	c = 13.8897(10) Å	γ = 90°.
Volume	2917.4(4) $Å^3$	
Z	8	
Density (calculated)	1.537 Mg/m^3	
Absorption coefficient	4.603 mm^{-1}	
F(000)	1376	
Crystal size	0.160 x 0.120 x 0.090 mm^3	
Theta range for data collection	5.346 to 59.478°.	
Index ranges	-16<=h<=17, -22<=k<=22, -17<=l<=17	
Reflections collected	34511	
Independent reflections	6455 [R(int) = 0.0634]	
Completeness to theta = 53.594°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.752 and 0.435	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6455 / 37 / 391	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0895	
R indices (all data)	R1 = 0.0428, wR2 = 0.0941	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.957 and -1.120 e.$Å^{-3}$	

Table S8. Bond lengths [Å] and angles [°] for Rh complex **3**.

Rh(1)-C(1)	2.036(3)
Rh(1)-C(10)	2.045(3)
Rh(1)-C(23)	2.200(3)
Rh(1)-C(20)	2.203(3)
Rh(1)-C(19)	2.206(3)
Rh(1)-C(24)	2.208(3)
B(1)-F(3)	1.358(4)
B(1)-F(4)	1.365(4)
B(1)-F(1)	1.371(4)
B(1)-F(2)	1.379(4)
N(1)-C(1)	1.359(3)
N(1)-C(7)	1.391(3)
N(1)-C(8)	1.457(4)
N(2)-C(1)	1.356(3)
N(2)-C(2)	1.389(3)
N(2)-C(9)	1.451(3)
N(3)-C(10)	1.357(3)
N(3)-C(16)	1.388(3)
N(3)-C(17)	1.459(4)
N(4)-C(10)	1.360(3)
N(4)-C(11)	1.393(3)
N(4)-C(18)	1.458(3)
C(2)-C(7)	1.382(4)
C(2)-C(3)	1.390(4)
C(3)-C(4)	1.384(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.385(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.388(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.391(4)
C(6)-H(6)	0.9500
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800

C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(11)-C(16)	1.387(4)
C(11)-C(12)	1.390(4)
C(12)-C(13)	1.392(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.386(5)
C(13)-H(13)	0.9500
C(14)-C(15)	1.387(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.392(4)
C(15)-H(15)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(20)	1.377(4)
C(19)-C(26)	1.506(4)
C(19)-H(19)	0.95(3)
C(20)-C(21)	1.490(6)
C(20)-C(21')	1.591(13)
C(20)-H(20)	1.02(3)
C(21)-C(22)	1.529(10)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.517(8)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(21')-C(22')	1.509(16)
C(21')-H(21C)	0.9900
C(21')-H(21D)	0.9900
C(22')-C(23)	1.527(16)
C(22')-H(22C)	0.9900
C(22')-H(22D)	0.9900
C(23)-C(24)	1.375(4)
C(23)-H(23)	0.98(3)

C(24)-C(25)	1.506(4)
C(24)-H(24)	0.97(3)
C(25)-C(26)	1.467(5)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-Cl(2)	1.740(4)
C(27)-Cl(1)	1.748(4)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(1)-Rh(1)-C(10)	92.42(10)
C(1)-Rh(1)-C(23)	158.36(11)
C(10)-Rh(1)-C(23)	93.15(10)
C(1)-Rh(1)-C(20)	87.94(11)
C(10)-Rh(1)-C(20)	163.28(11)
C(23)-Rh(1)-C(20)	80.84(11)
C(1)-Rh(1)-C(19)	91.94(10)
C(10)-Rh(1)-C(19)	160.07(11)
C(23)-Rh(1)-C(19)	89.90(11)
C(20)-Rh(1)-C(19)	36.39(11)
C(1)-Rh(1)-C(24)	164.56(11)
C(10)-Rh(1)-C(24)	89.71(10)
C(23)-Rh(1)-C(24)	36.36(11)
C(20)-Rh(1)-C(24)	94.38(12)
C(19)-Rh(1)-C(24)	81.13(11)
F(3)-B(1)-F(4)	108.9(3)
F(3)-B(1)-F(1)	108.7(3)
F(4)-B(1)-F(1)	110.6(3)
F(3)-B(1)-F(2)	110.1(3)
F(4)-B(1)-F(2)	110.6(3)
F(1)-B(1)-F(2)	107.9(3)
C(1)-N(1)-C(7)	110.7(2)
C(1)-N(1)-C(8)	126.0(2)
C(7)-N(1)-C(8)	123.0(2)
C(1)-N(2)-C(2)	111.2(2)
C(1)-N(2)-C(9)	125.7(2)

C(2)-N(2)-C(9)	123.0(2)
C(10)-N(3)-C(16)	111.1(2)
C(10)-N(3)-C(17)	125.7(2)
C(16)-N(3)-C(17)	123.3(2)
C(10)-N(4)-C(11)	111.0(2)
C(10)-N(4)-C(18)	125.8(2)
C(11)-N(4)-C(18)	123.2(2)
N(2)-C(1)-N(1)	105.5(2)
N(2)-C(1)-Rh(1)	127.39(19)
N(1)-C(1)-Rh(1)	126.87(19)
C(7)-C(2)-N(2)	106.0(2)
C(7)-C(2)-C(3)	122.2(3)
N(2)-C(2)-C(3)	131.8(3)
C(4)-C(3)-C(2)	115.8(3)
C(4)-C(3)-H(3)	122.1
C(2)-C(3)-H(3)	122.1
C(3)-C(4)-C(5)	122.4(3)
C(3)-C(4)-H(4)	118.8
C(5)-C(4)-H(4)	118.8
C(4)-C(5)-C(6)	121.8(3)
C(4)-C(5)-H(5)	119.1
C(6)-C(5)-H(5)	119.1
C(5)-C(6)-C(7)	116.1(3)
C(5)-C(6)-H(6)	122.0
C(7)-C(6)-H(6)	122.0
C(2)-C(7)-N(1)	106.5(2)
C(2)-C(7)-C(6)	121.8(3)
N(1)-C(7)-C(6)	131.6(3)
N(1)-C(8)-H(8A)	109.5
N(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
N(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
N(2)-C(9)-H(9A)	109.5
N(2)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(2)-C(9)-H(9C)	109.5

H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
N(3)-C(10)-N(4)	105.5(2)
N(3)-C(10)-Rh(1)	127.9(2)
N(4)-C(10)-Rh(1)	126.53(19)
C(16)-C(11)-C(12)	121.7(3)
C(16)-C(11)-N(4)	106.0(2)
C(12)-C(11)-N(4)	132.2(3)
C(11)-C(12)-C(13)	116.0(3)
C(11)-C(12)-H(12)	122.0
C(13)-C(12)-H(12)	122.0
C(14)-C(13)-C(12)	122.3(3)
C(14)-C(13)-H(13)	118.9
C(12)-C(13)-H(13)	118.9
C(13)-C(14)-C(15)	121.8(3)
C(13)-C(14)-H(14)	119.1
C(15)-C(14)-H(14)	119.1
C(14)-C(15)-C(16)	116.1(3)
C(14)-C(15)-H(15)	122.0
C(16)-C(15)-H(15)	122.0
C(11)-C(16)-N(3)	106.4(2)
C(11)-C(16)-C(15)	122.2(3)
N(3)-C(16)-C(15)	131.4(3)
N(3)-C(17)-H(17A)	109.5
N(3)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
N(3)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(4)-C(18)-H(18A)	109.5
N(4)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(4)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(20)-C(19)-C(26)	124.0(3)
C(20)-C(19)-Rh(1)	71.68(16)
C(26)-C(19)-Rh(1)	109.9(2)

C(20)-C(19)-H(19)	117.8(19)
C(26)-C(19)-H(19)	115.0(19)
Rh(1)-C(19)-H(19)	106.3(19)
C(19)-C(20)-C(21)	132.6(4)
C(19)-C(20)-C(21')	110.4(7)
C(19)-C(20)-Rh(1)	71.93(16)
C(21)-C(20)-Rh(1)	105.4(3)
C(21')-C(20)-Rh(1)	111.0(4)
C(19)-C(20)-H(20)	115(2)
C(21)-C(20)-H(20)	110(2)
C(21')-C(20)-H(20)	127(2)
Rh(1)-C(20)-H(20)	107(2)
C(20)-C(21)-C(22)	113.1(5)
C(20)-C(21)-H(21A)	109.0
C(22)-C(21)-H(21A)	109.0
C(20)-C(21)-H(21B)	109.0
C(22)-C(21)-H(21B)	109.0
H(21A)-C(21)-H(21B)	107.8
C(23)-C(22)-C(21)	111.4(6)
C(23)-C(22)-H(22A)	109.3
C(21)-C(22)-H(22A)	109.3
C(23)-C(22)-H(22B)	109.3
C(21)-C(22)-H(22B)	109.3
H(22A)-C(22)-H(22B)	108.0
C(22')-C(21')-C(20)	110.4(12)
C(22')-C(21')-H(21C)	109.6
C(20)-C(21')-H(21C)	109.6
C(22')-C(21')-H(21D)	109.6
C(20)-C(21')-H(21D)	109.6
H(21C)-C(21')-H(21D)	108.1
C(21')-C(22')-C(23)	112.2(13)
C(21')-C(22')-H(22C)	109.2
C(23)-C(22')-H(22C)	109.2
C(21')-C(22')-H(22D)	109.2
C(23)-C(22')-H(22D)	109.2
H(22C)-C(22')-H(22D)	107.9
C(24)-C(23)-C(22)	121.0(4)
C(24)-C(23)-C(22')	138.0(7)

C(24)-C(23)-Rh(1)	72.11(16)
C(22)-C(23)-Rh(1)	111.0(4)
C(22')-C(23)-Rh(1)	107.7(8)
C(24)-C(23)-H(23)	116(2)
C(22)-C(23)-H(23)	120(2)
C(22')-C(23)-H(23)	105(2)
Rh(1)-C(23)-H(23)	101.7(19)
C(23)-C(24)-C(25)	126.8(3)
C(23)-C(24)-Rh(1)	71.52(15)
C(25)-C(24)-Rh(1)	108.0(2)
C(23)-C(24)-H(24)	116.4(19)
C(25)-C(24)-H(24)	114.3(19)
Rh(1)-C(24)-H(24)	106.6(19)
C(26)-C(25)-C(24)	115.9(3)
C(26)-C(25)-H(25A)	108.3
C(24)-C(25)-H(25A)	108.3
C(26)-C(25)-H(25B)	108.3
C(24)-C(25)-H(25B)	108.3
H(25A)-C(25)-H(25B)	107.4
C(25)-C(26)-C(19)	117.4(3)
C(25)-C(26)-H(26A)	108.0
C(19)-C(26)-H(26A)	108.0
C(25)-C(26)-H(26B)	108.0
C(19)-C(26)-H(26B)	108.0
H(26A)-C(26)-H(26B)	107.2
Cl(2)-C(27)-Cl(1)	112.7(2)
Cl(2)-C(27)-H(27A)	109.0
Cl(1)-C(27)-H(27A)	109.0
Cl(2)-C(27)-H(27B)	109.0
Cl(1)-C(27)-H(27B)	109.0
H(27A)-C(27)-H(27B)	107.8

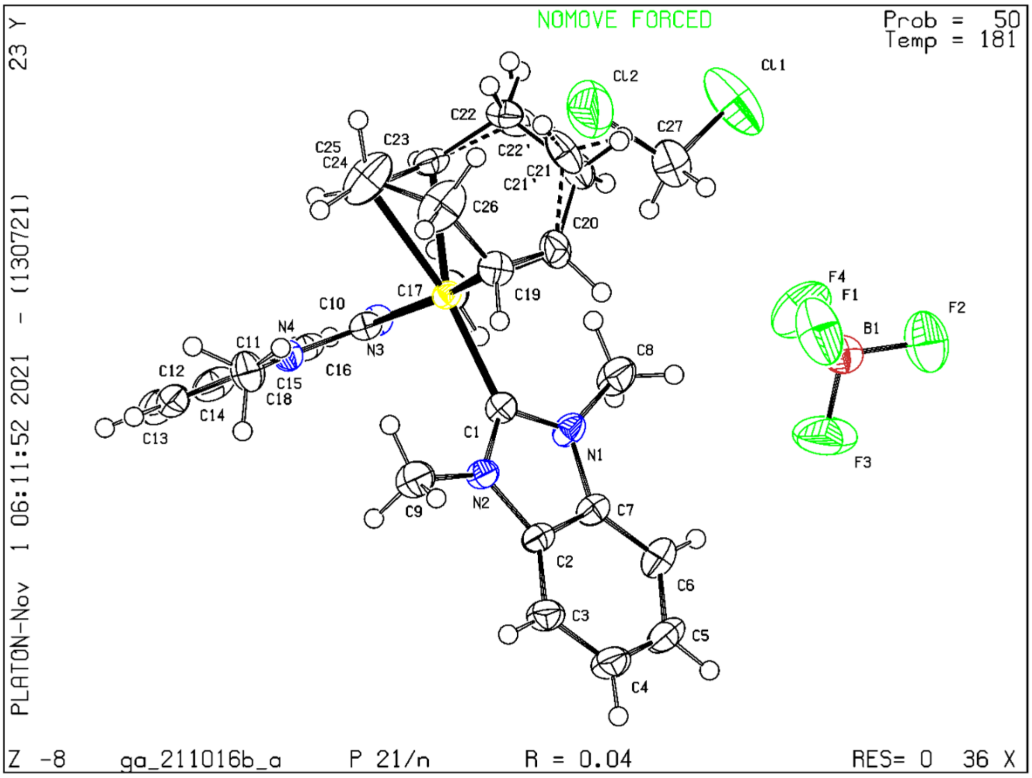

Fig. S195. Crystal structure of rhodium complex **3**.

Table S9. Crystal data and structure refinement for compound **4b**

Identification code	compound **4b**	
Empirical formula	$C_{127}H_{147}B_2Cl_9F_8N_8Rh_2$	
Formula weight	2484.01	
Temperature	175(2) K	
Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 15.1914(9) Å	α= 90 °.
	b = 15.8408(9) Å	β= 93.157(2) °.
	c = 55.703(3) Å	γ = 90 °.
Volume	13384.2(13) Å^3	
Z	4	
Density (calculated)	1.233 Mg/m^3	
Absorption coefficient	2.755 mm^{-1}	
F(000)	5160	
Crystal size	0.250 x 0.220 x 0.180 mm^3	
Theta range for data collection	3.510 to 56.500 °.	
Index ranges	-18<=h<=18, -19<=k<=18, -69<=l<=69	
Reflections collected	148292	
Independent reflections	26519 [R(int) = 0.0653]	
Completeness to theta = 53.594 °	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.454	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	26519 / 308 / 1482	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.1248, wR2 = 0.3036	
R indices (all data)	R1 = 0.1326, wR2 = 0.3069	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.428 and -2.474 e.Å^{-3}	

Table S10. Bond lengths [Å] and angles [°] for Rh complex **4**.

Rh(1)-C(28)	2.057(8)
Rh(1)-C(1)	2.061(8)
Rh(1)-C(77)	2.187(9)
Rh(1)-C(73)	2.188(8)
Rh(1)-C(72)	2.202(9)
Rh(1)-C(76)	2.214(9)
Rh(2)-C(90)	2.062(9)
Rh(2)-C(55)	2.072(9)
Rh(2)-C(117)	2.168(9)
Rh(2)-C(118)	2.203(9)
Rh(2)-C(121)	2.214(9)
Rh(2)-C(122)	2.226(10)
B(1)-F(4)	1.21(2)
B(1)-F(3)	1.358(17)
B(1)-F(1)	1.374(16)
B(1)-F(2)	1.378(16)
B(2)-F(8)	1.313(17)
B(2)-F(7)	1.32(3)
B(2)-F(5)	1.33(3)
B(2)-F(6)	1.400(18)
B(2')-F(6')	1.325(16)
B(2')-F(8')	1.328(17)
B(2')-F(7')	1.330(17)
B(2')-F(5')	1.358(13)
N(1)-C(1)	1.345(11)
N(1)-C(15)	1.399(10)
N(1)-C(26)	1.472(11)
N(2)-C(1)	1.366(11)
N(2)-C(2)	1.402(10)
N(2)-C(27)	1.447(10)
N(3)-C(28)	1.354(10)
N(3)-C(42)	1.410(9)
N(3)-C(53)	1.433(11)
N(4)-C(28)	1.373(10)
N(4)-C(29)	1.396(10)
N(4)-C(54)	1.456(11)

N(5)-C(55)	1.342(11)
N(5)-C(69)	1.397(10)
N(5)-C(88)	1.457(10)
N(6)-C(55)	1.349(11)
N(6)-C(56)	1.398(12)
N(6)-C(89)	1.446(11)
N(7)-C(90)	1.375(11)
N(7)-C(104)	1.382(12)
N(7)-C(115)	1.460(13)
N(8)-C(90)	1.341(11)
N(8)-C(91)	1.399(13)
N(8)-C(116)	1.438(14)
C(2)-C(15)	1.371(11)
C(2)-C(3)	1.445(11)
C(3)-C(4)	1.407(12)
C(3)-C(16)	1.430(11)
C(4)-C(5)	1.401(12)
C(4)-H(4)	0.9500
C(5)-C(6)	1.390(12)
C(5)-C(18)	1.501(12)
C(6)-C(7)	1.392(12)
C(6)-H(6)	0.9500
C(7)-C(16)	1.400(11)
C(7)-C(8)	1.442(11)
C(8)-C(9)	1.326(12)
C(8)-H(8)	0.9500
C(9)-C(10)	1.441(12)
C(9)-H(9)	0.9500
C(10)-C(11)	1.395(12)
C(10)-C(17)	1.415(11)
C(11)-C(12)	1.386(12)
C(11)-H(11)	0.9500
C(12)-C(13)	1.396(11)
C(12)-C(22)	1.533(12)
C(13)-C(14)	1.373(11)
C(13)-H(13)	0.9500
C(14)-C(17)	1.423(11)
C(14)-C(15)	1.457(11)

C(16)-C(17)	1.435(11)
C(18)-C(20)	1.479(18)
C(18)-C(21)	1.532(16)
C(18)-C(19)	1.578(17)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(24)	1.507(15)
C(22)-C(23)	1.533(14)
C(22)-C(25)	1.536(15)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(29)-C(42)	1.341(12)
C(29)-C(30)	1.458(11)
C(30)-C(31)	1.383(11)
C(30)-C(43)	1.415(12)
C(31)-C(32)	1.388(12)
C(31)-H(31)	0.9500
C(32)-C(33)	1.343(13)

C(32)-C(45)	1.552(13)
C(33)-C(34)	1.393(13)
C(33)-H(33)	0.9500
C(34)-C(43)	1.446(11)
C(34)-C(35)	1.449(12)
C(35)-C(36)	1.358(11)
C(35)-H(35)	0.9500
C(36)-C(37)	1.436(12)
C(36)-H(36)	0.9500
C(37)-C(38)	1.378(13)
C(37)-C(44)	1.437(12)
C(38)-C(39)	1.388(14)
C(38)-H(38)	0.9500
C(39)-C(40)	1.418(13)
C(39)-C(49)	1.521(14)
C(40)-C(41)	1.392(12)
C(40)-H(40)	0.9500
C(41)-C(44)	1.413(11)
C(41)-C(42)	1.442(11)
C(43)-C(44)	1.420(12)
C(45)-C(47)	1.528(15)
C(45)-C(46)	1.559(15)
C(45)-C(48)	1.561(16)
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-C(51)	1.512(17)
C(49)-C(52)	1.523(17)
C(49)-C(50)	1.556(16)
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800

C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
C(56)-C(69)	1.375(12)
C(56)-C(57)	1.441(12)
C(57)-C(70)	1.405(14)
C(57)-C(58)	1.421(14)
C(58)-C(59)	1.394(15)
C(58)-H(58)	0.9500
C(59)-C(60)	1.376(18)
C(59)-C(80)	1.515(16)
C(60)-C(61)	1.412(16)
C(60)-H(60)	0.9500
C(61)-C(62)	1.404(16)
C(61)-C(70)	1.415(13)
C(62)-C(63)	1.355(13)
C(62)-H(62)	0.9500
C(63)-C(64)	1.420(13)
C(63)-H(63)	0.9500
C(64)-C(65)	1.412(13)
C(64)-C(71)	1.438(13)
C(65)-C(66)	1.405(13)
C(65)-H(65)	0.9500
C(66)-C(67)	1.386(12)
C(66)-C(84)	1.491(13)
C(67)-C(68)	1.418(12)
C(67)-H(67)	0.9500
C(68)-C(69)	1.419(11)
C(68)-C(71)	1.427(12)

C(70)-C(71)	1.419(13)
C(72)-C(73)	1.360(15)
C(72)-C(79)	1.536(16)
C(72)-H(72)	1.0000
C(73)-C(74)	1.496(15)
C(73)-H(73)	1.0000
C(74)-C(75)	1.504(16)
C(74)-H(74A)	0.9900
C(74)-H(74B)	0.9900
C(75)-C(76)	1.483(14)
C(75)-H(75A)	0.9900
C(75)-H(75B)	0.9900
C(76)-C(77)	1.367(16)
C(76)-H(76)	1.0000
C(77)-C(78)	1.547(18)
C(77)-H(77)	1.0000
C(78)-C(79)	1.487(19)
C(78)-H(78A)	0.9900
C(78)-H(78B)	0.9900
C(79)-H(79A)	0.9900
C(79)-H(79B)	0.9900
C(80)-C(82)	1.510(19)
C(80)-C(83)	1.518(15)
C(80)-C(81)	1.530(19)
C(81)-H(81A)	0.9800
C(81)-H(81B)	0.9800
C(81)-H(81C)	0.9800
C(82)-H(82A)	0.9800
C(82)-H(82B)	0.9800
C(82)-H(82C)	0.9800
C(83)-H(83A)	0.9800
C(83)-H(83B)	0.9800
C(83)-H(83C)	0.9800
C(84)-C(85)	1.514(15)
C(84)-C(87)	1.537(13)
C(84)-C(86)	1.552(13)
C(85)-H(85A)	0.9800
C(85)-H(85B)	0.9800

C(85)-H(85C)	0.9800
C(86)-H(86A)	0.9800
C(86)-H(86B)	0.9800
C(86)-H(86C)	0.9800
C(87)-H(87A)	0.9800
C(87)-H(87B)	0.9800
C(87)-H(87C)	0.9800
C(88)-H(88A)	0.9800
C(88)-H(88B)	0.9800
C(88)-H(88C)	0.9800
C(89)-H(89A)	0.9800
C(89)-H(89B)	0.9800
C(89)-H(89C)	0.9800
C(91)-C(104)	1.359(16)
C(91)-C(92)	1.448(14)
C(92)-C(93)	1.391(14)
C(92)-C(105)	1.452(17)
C(93)-C(94)	1.431(14)
C(93)-H(93)	0.9500
C(94)-C(95)	1.36(3)
C(94)-C(107)	1.53(3)
C(95)-C(96)	1.34(2)
C(95)-H(95)	0.9500
C(96)-C(105)	1.462(16)
C(96)-C(97)	1.46(2)
C(97)-C(98)	1.337(19)
C(97)-H(97)	0.9500
C(98)-C(99)	1.415(17)
C(98)-H(98)	0.9500
C(99)-C(100)	1.378(14)
C(99)-C(106)	1.416(13)
C(100)-C(101)	1.37(2)
C(100)-H(100)	0.9500
C(101)-C(102)	1.390(16)
C(101)-C(111)	1.46(2)
C(102)-C(103)	1.406(18)
C(102)-H(102)	0.9500
C(103)-C(106)	1.391(12)

C(103)-C(104)	1.456(16)
C(105)-C(106)	1.415(14)
C(107)-C(109)	1.41(3)
C(107)-C(108)	1.512(18)
C(107)-C(110)	1.60(4)
C(108)-H(10A)	0.9800
C(108)-H(10B)	0.9800
C(108)-H(10C)	0.9800
C(109)-H(10D)	0.9800
C(109)-H(10E)	0.9800
C(109)-H(10F)	0.9800
C(110)-H(11A)	0.9800
C(110)-H(11B)	0.9800
C(110)-H(11C)	0.9800
C(111)-C(114)	1.524(16)
C(111)-C(112)	1.551(13)
C(111)-C(113)	1.571(17)
C(112)-H(11D)	0.9800
C(112)-H(11E)	0.9800
C(112)-H(11F)	0.9800
C(113)-H(11G)	0.9800
C(113)-H(11H)	0.9800
C(113)-H(11I)	0.9800
C(114)-H(11J)	0.9800
C(114)-H(11K)	0.9800
C(114)-H(11L)	0.9800
C(115)-H(11M)	0.9800
C(115)-H(11N)	0.9800
C(115)-H(11O)	0.9800
C(116)-H(11P)	0.9800
C(116)-H(11Q)	0.9800
C(116)-H(11R)	0.9800
C(117)-C(118)	1.373(15)
C(117)-C(124)	1.490(17)
C(117)-H(117)	1.0000
C(118)-C(119)	1.534(15)
C(118)-H(118)	1.0000
C(119)-C(120)	1.515(15)

C(119)-H(11S)	0.9900
C(119)-H(11T)	0.9900
C(120)-C(121)	1.507(14)
C(120)-H(12A)	0.9900
C(120)-H(12B)	0.9900
C(121)-C(122)	1.371(15)
C(121)-H(121)	1.0000
C(122)-C(123)	1.503(15)
C(122)-H(122)	1.0000
C(123)-C(124)	1.550(17)
C(123)-H(12C)	0.9900
C(123)-H(12D)	0.9900
C(124)-H(12E)	0.9900
C(124)-H(12F)	0.9900
C(125)-Cl(1)	1.683(16)
C(125)-Cl(3)	1.72(2)
C(125)-Cl(2)	1.770(17)
C(125)-H(125)	1.0000
C(126)-Cl(5)	1.698(18)
C(126)-Cl(4)	1.718(18)
C(126)-Cl(6)	1.795(17)
C(126)-H(126)	1.0000
C(127)-Cl(7)	1.66(2)
C(127)-Cl(9)	1.72(3)
C(127)-Cl(8)	1.73(2)
C(127)-H(127)	1.0000

C(28)-Rh(1)-C(1)	91.9(3)
C(28)-Rh(1)-C(77)	154.4(4)
C(1)-Rh(1)-C(77)	91.6(4)
C(28)-Rh(1)-C(73)	92.5(3)
C(1)-Rh(1)-C(73)	153.7(4)
C(77)-Rh(1)-C(73)	95.5(4)
C(28)-Rh(1)-C(72)	90.4(3)
C(1)-Rh(1)-C(72)	169.6(4)
C(77)-Rh(1)-C(72)	82.0(4)
C(73)-Rh(1)-C(72)	36.1(4)
C(28)-Rh(1)-C(76)	168.9(4)

C(1)-Rh(1)-C(76)	90.6(4)
C(77)-Rh(1)-C(76)	36.2(4)
C(73)-Rh(1)-C(76)	80.5(4)
C(72)-Rh(1)-C(76)	89.0(4)
C(90)-Rh(2)-C(55)	91.1(3)
C(90)-Rh(2)-C(117)	161.0(4)
C(55)-Rh(2)-C(117)	89.1(4)
C(90)-Rh(2)-C(118)	162.2(4)
C(55)-Rh(2)-C(118)	92.7(4)
C(117)-Rh(2)-C(118)	36.6(4)
C(90)-Rh(2)-C(121)	89.6(3)
C(55)-Rh(2)-C(121)	162.1(4)
C(117)-Rh(2)-C(121)	96.0(4)
C(118)-Rh(2)-C(121)	81.6(4)
C(90)-Rh(2)-C(122)	93.6(4)
C(55)-Rh(2)-C(122)	161.5(4)
C(117)-Rh(2)-C(122)	80.7(4)
C(118)-Rh(2)-C(122)	88.3(4)
C(121)-Rh(2)-C(122)	36.0(4)
F(4)-B(1)-F(3)	116(2)
F(4)-B(1)-F(1)	111.0(17)
F(3)-B(1)-F(1)	109.3(19)
F(4)-B(1)-F(2)	119.8(19)
F(3)-B(1)-F(2)	96.1(16)
F(1)-B(1)-F(2)	102.6(17)
F(8)-B(2)-F(7)	115(3)
F(8)-B(2)-F(5)	113(3)
F(7)-B(2)-F(5)	112(3)
F(8)-B(2)-F(6)	108(2)
F(7)-B(2)-F(6)	108(2)
F(5)-B(2)-F(6)	101(3)
F(6')-B(2')-F(8')	110(3)
F(6')-B(2')-F(7')	122(3)
F(8')-B(2')-F(7')	107(3)
F(6')-B(2')-F(5')	109(3)
F(8')-B(2')-F(5')	100(3)
F(7')-B(2')-F(5')	106(2)
C(1)-N(1)-C(15)	110.7(7)

C(1)-N(1)-C(26)	123.1(7)
C(15)-N(1)-C(26)	126.2(7)
C(1)-N(2)-C(2)	110.0(7)
C(1)-N(2)-C(27)	121.5(7)
C(2)-N(2)-C(27)	127.5(7)
C(28)-N(3)-C(42)	109.4(7)
C(28)-N(3)-C(53)	121.8(7)
C(42)-N(3)-C(53)	128.8(7)
C(28)-N(4)-C(29)	108.5(7)
C(28)-N(4)-C(54)	123.4(7)
C(29)-N(4)-C(54)	128.0(7)
C(55)-N(5)-C(69)	110.7(7)
C(55)-N(5)-C(88)	123.3(7)
C(69)-N(5)-C(88)	126.0(7)
C(55)-N(6)-C(56)	110.0(7)
C(55)-N(6)-C(89)	122.2(8)
C(56)-N(6)-C(89)	127.9(8)
C(90)-N(7)-C(104)	108.4(9)
C(90)-N(7)-C(115)	123.5(8)
C(104)-N(7)-C(115)	128.1(9)
C(90)-N(8)-C(91)	109.6(9)
C(90)-N(8)-C(116)	123.0(8)
C(91)-N(8)-C(116)	127.4(9)
N(1)-C(1)-N(2)	106.2(7)
N(1)-C(1)-Rh(1)	127.5(6)
N(2)-C(1)-Rh(1)	126.3(6)
C(15)-C(2)-N(2)	106.4(7)
C(15)-C(2)-C(3)	123.6(7)
N(2)-C(2)-C(3)	130.0(7)
C(4)-C(3)-C(16)	119.3(8)
C(4)-C(3)-C(2)	125.8(7)
C(16)-C(3)-C(2)	114.8(7)
C(5)-C(4)-C(3)	122.6(8)
C(5)-C(4)-H(4)	118.7
C(3)-C(4)-H(4)	118.7
C(6)-C(5)-C(4)	116.8(8)
C(6)-C(5)-C(18)	120.7(8)
C(4)-C(5)-C(18)	122.4(8)

C(5)-C(6)-C(7)	122.3(8)
C(5)-C(6)-H(6)	118.8
C(7)-C(6)-H(6)	118.8
C(6)-C(7)-C(16)	121.3(8)
C(6)-C(7)-C(8)	120.3(8)
C(16)-C(7)-C(8)	118.4(8)
C(9)-C(8)-C(7)	121.4(8)
C(9)-C(8)-H(8)	119.3
C(7)-C(8)-H(8)	119.3
C(8)-C(9)-C(10)	121.3(8)
C(8)-C(9)-H(9)	119.4
C(10)-C(9)-H(9)	119.4
C(11)-C(10)-C(17)	118.5(8)
C(11)-C(10)-C(9)	121.8(8)
C(17)-C(10)-C(9)	119.7(8)
C(12)-C(11)-C(10)	123.5(8)
C(12)-C(11)-H(11)	118.2
C(10)-C(11)-H(11)	118.2
C(11)-C(12)-C(13)	116.8(8)
C(11)-C(12)-C(22)	123.5(8)
C(13)-C(12)-C(22)	119.7(8)
C(14)-C(13)-C(12)	122.5(8)
C(14)-C(13)-H(13)	118.7
C(12)-C(13)-H(13)	118.7
C(13)-C(14)-C(17)	120.1(7)
C(13)-C(14)-C(15)	126.0(8)
C(17)-C(14)-C(15)	113.9(7)
C(2)-C(15)-N(1)	106.7(7)
C(2)-C(15)-C(14)	122.8(7)
N(1)-C(15)-C(14)	130.5(7)
C(7)-C(16)-C(3)	117.6(8)
C(7)-C(16)-C(17)	121.2(7)
C(3)-C(16)-C(17)	121.1(7)
C(10)-C(17)-C(14)	118.5(7)
C(10)-C(17)-C(16)	118.0(7)
C(14)-C(17)-C(16)	123.6(7)
C(20)-C(18)-C(5)	112.7(9)
C(20)-C(18)-C(21)	109.4(12)

C(5)-C(18)-C(21)	115.2(9)
C(20)-C(18)-C(19)	105.6(12)
C(5)-C(18)-C(19)	109.6(9)
C(21)-C(18)-C(19)	103.6(11)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(24)-C(22)-C(12)	110.8(9)
C(24)-C(22)-C(23)	108.3(9)
C(12)-C(22)-C(23)	112.4(8)
C(24)-C(22)-C(25)	108.1(10)
C(12)-C(22)-C(25)	108.7(8)
C(23)-C(22)-C(25)	108.5(10)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5

H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
N(1)-C(26)-H(26A)	109.5
N(1)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
N(1)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
N(2)-C(27)-H(27A)	109.5
N(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
N(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(3)-C(28)-N(4)	106.8(7)
N(3)-C(28)-Rh(1)	128.7(6)
N(4)-C(28)-Rh(1)	124.4(6)
C(42)-C(29)-N(4)	108.4(7)
C(42)-C(29)-C(30)	122.6(8)
N(4)-C(29)-C(30)	128.9(8)
C(31)-C(30)-C(43)	119.6(8)
C(31)-C(30)-C(29)	125.6(8)
C(43)-C(30)-C(29)	114.7(7)
C(30)-C(31)-C(32)	122.0(8)
C(30)-C(31)-H(31)	119.0
C(32)-C(31)-H(31)	119.0
C(33)-C(32)-C(31)	120.4(9)
C(33)-C(32)-C(45)	119.7(8)
C(31)-C(32)-C(45)	119.8(9)
C(32)-C(33)-C(34)	120.3(8)
C(32)-C(33)-H(33)	119.9
C(34)-C(33)-H(33)	119.9

C(33)-C(34)-C(43)	121.1(8)
C(33)-C(34)-C(35)	122.1(8)
C(43)-C(34)-C(35)	116.8(8)
C(36)-C(35)-C(34)	122.4(8)
C(36)-C(35)-H(35)	118.8
C(34)-C(35)-H(35)	118.8
C(35)-C(36)-C(37)	121.2(8)
C(35)-C(36)-H(36)	119.4
C(37)-C(36)-H(36)	119.4
C(38)-C(37)-C(36)	121.3(9)
C(38)-C(37)-C(44)	119.9(8)
C(36)-C(37)-C(44)	118.8(8)
C(37)-C(38)-C(39)	122.9(9)
C(37)-C(38)-H(38)	118.5
C(39)-C(38)-H(38)	118.5
C(38)-C(39)-C(40)	116.8(9)
C(38)-C(39)-C(49)	124.1(9)
C(40)-C(39)-C(49)	119.1(9)
C(41)-C(40)-C(39)	122.6(8)
C(41)-C(40)-H(40)	118.7
C(39)-C(40)-H(40)	118.7
C(40)-C(41)-C(44)	119.4(8)
C(40)-C(41)-C(42)	125.6(8)
C(44)-C(41)-C(42)	115.0(7)
C(29)-C(42)-N(3)	106.8(7)
C(29)-C(42)-C(41)	123.5(7)
N(3)-C(42)-C(41)	129.7(8)
C(30)-C(43)-C(44)	122.2(7)
C(30)-C(43)-C(34)	116.7(8)
C(44)-C(43)-C(34)	121.0(8)
C(41)-C(44)-C(43)	121.9(7)
C(41)-C(44)-C(37)	118.3(8)
C(43)-C(44)-C(37)	119.7(8)
C(47)-C(45)-C(32)	109.0(8)
C(47)-C(45)-C(46)	111.7(10)
C(32)-C(45)-C(46)	110.3(9)
C(47)-C(45)-C(48)	106.3(10)
C(32)-C(45)-C(48)	114.2(8)

C(46)-C(45)-C(48)	105.3(9)
C(45)-C(46)-H(46A)	109.5
C(45)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(45)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(45)-C(47)-H(47A)	109.5
C(45)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(45)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(45)-C(48)-H(48A)	109.5
C(45)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(45)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(51)-C(49)-C(39)	110.3(10)
C(51)-C(49)-C(52)	108.8(13)
C(39)-C(49)-C(52)	112.8(10)
C(51)-C(49)-C(50)	104.6(10)
C(39)-C(49)-C(50)	113.3(9)
C(52)-C(49)-C(50)	106.7(12)
C(49)-C(50)-H(50A)	109.5
C(49)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(49)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
C(49)-C(51)-H(51A)	109.5
C(49)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5
C(49)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
C(49)-C(52)-H(52A)	109.5

C(49)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
C(49)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
N(3)-C(53)-H(53A)	109.5
N(3)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53B)	109.5
N(3)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
N(4)-C(54)-H(54A)	109.5
N(4)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
N(4)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
N(5)-C(55)-N(6)	106.7(8)
N(5)-C(55)-Rh(2)	126.5(6)
N(6)-C(55)-Rh(2)	126.8(6)
C(69)-C(56)-N(6)	106.7(7)
C(69)-C(56)-C(57)	122.2(9)
N(6)-C(56)-C(57)	131.1(8)
C(70)-C(57)-C(58)	118.9(9)
C(70)-C(57)-C(56)	116.5(8)
C(58)-C(57)-C(56)	124.6(10)
C(59)-C(58)-C(57)	122.2(12)
C(59)-C(58)-H(58)	118.9
C(57)-C(58)-H(58)	118.9
C(60)-C(59)-C(58)	117.5(11)
C(60)-C(59)-C(80)	122.3(11)
C(58)-C(59)-C(80)	120.3(13)
C(59)-C(60)-C(61)	123.1(11)
C(59)-C(60)-H(60)	118.4
C(61)-C(60)-H(60)	118.4
C(62)-C(61)-C(60)	121.3(10)
C(62)-C(61)-C(70)	120.2(10)
C(60)-C(61)-C(70)	118.6(11)

C(63)-C(62)-C(61)	120.9(10)
C(63)-C(62)-H(62)	119.5
C(61)-C(62)-H(62)	119.5
C(62)-C(63)-C(64)	122.0(10)
C(62)-C(63)-H(63)	119.0
C(64)-C(63)-H(63)	119.0
C(65)-C(64)-C(63)	121.9(9)
C(65)-C(64)-C(71)	120.4(8)
C(63)-C(64)-C(71)	117.7(10)
C(66)-C(65)-C(64)	121.8(8)
C(66)-C(65)-H(65)	119.1
C(64)-C(65)-H(65)	119.1
C(67)-C(66)-C(65)	116.9(9)
C(67)-C(66)-C(84)	123.3(9)
C(65)-C(66)-C(84)	119.8(9)
C(66)-C(67)-C(68)	124.5(8)
C(66)-C(67)-H(67)	117.7
C(68)-C(67)-H(67)	117.7
C(67)-C(68)-C(69)	125.3(8)
C(67)-C(68)-C(71)	118.2(8)
C(69)-C(68)-C(71)	116.4(8)
C(56)-C(69)-N(5)	105.9(7)
C(56)-C(69)-C(68)	122.1(8)
N(5)-C(69)-C(68)	132.0(8)
C(57)-C(70)-C(61)	119.7(9)
C(57)-C(70)-C(71)	121.3(8)
C(61)-C(70)-C(71)	119.0(10)
C(70)-C(71)-C(68)	121.6(8)
C(70)-C(71)-C(64)	120.3(8)
C(68)-C(71)-C(64)	118.1(8)
C(73)-C(72)-C(79)	125.1(11)
C(73)-C(72)-Rh(1)	71.4(6)
C(79)-C(72)-Rh(1)	109.7(7)
C(73)-C(72)-H(72)	114.2
C(79)-C(72)-H(72)	114.2
Rh(1)-C(72)-H(72)	114.2
C(72)-C(73)-C(74)	127.0(10)
C(72)-C(73)-Rh(1)	72.5(5)

C(74)-C(73)-Rh(1)	108.8(6)
C(72)-C(73)-H(73)	113.5
C(74)-C(73)-H(73)	113.5
Rh(1)-C(73)-H(73)	113.5
C(73)-C(74)-C(75)	113.9(10)
C(73)-C(74)-H(74A)	108.8
C(75)-C(74)-H(74A)	108.8
C(73)-C(74)-H(74B)	108.8
C(75)-C(74)-H(74B)	108.8
H(74A)-C(74)-H(74B)	107.7
C(76)-C(75)-C(74)	115.5(9)
C(76)-C(75)-H(75A)	108.4
C(74)-C(75)-H(75A)	108.4
C(76)-C(75)-H(75B)	108.4
C(74)-C(75)-H(75B)	108.4
H(75A)-C(75)-H(75B)	107.5
C(77)-C(76)-C(75)	123.8(12)
C(77)-C(76)-Rh(1)	70.8(6)
C(75)-C(76)-Rh(1)	110.9(7)
C(77)-C(76)-H(76)	114.4
C(75)-C(76)-H(76)	114.4
Rh(1)-C(76)-H(76)	114.4
C(76)-C(77)-C(78)	128.1(12)
C(76)-C(77)-Rh(1)	73.0(6)
C(78)-C(77)-Rh(1)	106.3(7)
C(76)-C(77)-H(77)	113.5
C(78)-C(77)-H(77)	113.5
Rh(1)-C(77)-H(77)	113.5
C(79)-C(78)-C(77)	113.8(12)
C(79)-C(78)-H(78A)	108.8
C(77)-C(78)-H(78A)	108.8
C(79)-C(78)-H(78B)	108.8
C(77)-C(78)-H(78B)	108.8
H(78A)-C(78)-H(78B)	107.7
C(78)-C(79)-C(72)	115.3(9)
C(78)-C(79)-H(79A)	108.5
C(72)-C(79)-H(79A)	108.4
C(78)-C(79)-H(79B)	108.5

C(72)-C(79)-H(79B)	108.5
H(79A)-C(79)-H(79B)	107.5
C(82)-C(80)-C(59)	111.8(10)
C(82)-C(80)-C(83)	107.1(12)
C(59)-C(80)-C(83)	112.3(13)
C(82)-C(80)-C(81)	106.9(14)
C(59)-C(80)-C(81)	110.5(10)
C(83)-C(80)-C(81)	108.0(11)
C(80)-C(81)-H(81A)	109.5
C(80)-C(81)-H(81B)	109.5
H(81A)-C(81)-H(81B)	109.5
C(80)-C(81)-H(81C)	109.5
H(81A)-C(81)-H(81C)	109.5
H(81B)-C(81)-H(81C)	109.5
C(80)-C(82)-H(82A)	109.5
C(80)-C(82)-H(82B)	109.5
H(82A)-C(82)-H(82B)	109.5
C(80)-C(82)-H(82C)	109.5
H(82A)-C(82)-H(82C)	109.5
H(82B)-C(82)-H(82C)	109.5
C(80)-C(83)-H(83A)	109.5
C(80)-C(83)-H(83B)	109.5
H(83A)-C(83)-H(83B)	109.5
C(80)-C(83)-H(83C)	109.5
H(83A)-C(83)-H(83C)	109.5
H(83B)-C(83)-H(83C)	109.5
C(66)-C(84)-C(85)	113.0(8)
C(66)-C(84)-C(87)	109.5(8)
C(85)-C(84)-C(87)	107.7(9)
C(66)-C(84)-C(86)	109.0(8)
C(85)-C(84)-C(86)	108.2(9)
C(87)-C(84)-C(86)	109.5(9)
C(84)-C(85)-H(85A)	109.5
C(84)-C(85)-H(85B)	109.5
H(85A)-C(85)-H(85B)	109.5
C(84)-C(85)-H(85C)	109.5
H(85A)-C(85)-H(85C)	109.5
H(85B)-C(85)-H(85C)	109.5

C(84)-C(86)-H(86A)	109.5
C(84)-C(86)-H(86B)	109.5
H(86A)-C(86)-H(86B)	109.5
C(84)-C(86)-H(86C)	109.5
H(86A)-C(86)-H(86C)	109.5
H(86B)-C(86)-H(86C)	109.5
C(84)-C(87)-H(87A)	109.5
C(84)-C(87)-H(87B)	109.5
H(87A)-C(87)-H(87B)	109.5
C(84)-C(87)-H(87C)	109.5
H(87A)-C(87)-H(87C)	109.5
H(87B)-C(87)-H(87C)	109.5
N(5)-C(88)-H(88A)	109.5
N(5)-C(88)-H(88B)	109.5
H(88A)-C(88)-H(88B)	109.5
N(5)-C(88)-H(88C)	109.5
H(88A)-C(88)-H(88C)	109.5
H(88B)-C(88)-H(88C)	109.5
N(6)-C(89)-H(89A)	109.5
N(6)-C(89)-H(89B)	109.5
H(89A)-C(89)-H(89B)	109.5
N(6)-C(89)-H(89C)	109.5
H(89A)-C(89)-H(89C)	109.5
H(89B)-C(89)-H(89C)	109.5
N(8)-C(90)-N(7)	107.3(8)
N(8)-C(90)-Rh(2)	127.6(7)
N(7)-C(90)-Rh(2)	125.1(6)
C(104)-C(91)-N(8)	106.5(8)
C(104)-C(91)-C(92)	122.8(11)
N(8)-C(91)-C(92)	130.7(12)
C(93)-C(92)-C(91)	123.5(12)
C(93)-C(92)-C(105)	122.3(11)
C(91)-C(92)-C(105)	114.2(12)
C(92)-C(93)-C(94)	119.5(15)
C(92)-C(93)-H(93)	120.2
C(94)-C(93)-H(93)	120.2
C(95)-C(94)-C(93)	118.7(17)
C(95)-C(94)-C(107)	125.5(17)

C(93)-C(94)-C(107)	115.5(19)
C(96)-C(95)-C(94)	123.4(14)
C(96)-C(95)-H(95)	118.3
C(94)-C(95)-H(95)	118.3
C(95)-C(96)-C(105)	122.1(15)
C(95)-C(96)-C(97)	124.8(14)
C(105)-C(96)-C(97)	113.0(15)
C(98)-C(97)-C(96)	123.4(12)
C(98)-C(97)-H(97)	118.3
C(96)-C(97)-H(97)	118.3
C(97)-C(98)-C(99)	121.8(13)
C(97)-C(98)-H(98)	119.1
C(99)-C(98)-H(98)	119.1
C(100)-C(99)-C(98)	123.1(12)
C(100)-C(99)-C(106)	116.6(12)
C(98)-C(99)-C(106)	120.2(13)
C(101)-C(100)-C(99)	124.8(12)
C(101)-C(100)-H(100)	117.6
C(99)-C(100)-H(100)	117.6
C(100)-C(101)-C(102)	118.2(16)
C(100)-C(101)-C(111)	121.7(12)
C(102)-C(101)-C(111)	120.1(15)
C(101)-C(102)-C(103)	119.9(14)
C(101)-C(102)-H(102)	120.0
C(103)-C(102)-H(102)	120.0
C(106)-C(103)-C(102)	120.0(12)
C(106)-C(103)-C(104)	116.2(12)
C(102)-C(103)-C(104)	123.7(10)
C(91)-C(104)-N(7)	108.1(9)
C(91)-C(104)-C(103)	122.5(10)
N(7)-C(104)-C(103)	129.4(12)
C(106)-C(105)-C(92)	122.2(10)
C(106)-C(105)-C(96)	123.9(13)
C(92)-C(105)-C(96)	113.9(13)
C(103)-C(106)-C(105)	122.0(11)
C(103)-C(106)-C(99)	120.4(13)
C(105)-C(106)-C(99)	117.6(11)
C(109)-C(107)-C(108)	108(2)

C(109)-C(107)-C(94)	115(3)
C(108)-C(107)-C(94)	117(2)
C(109)-C(107)-C(110)	98(3)
C(108)-C(107)-C(110)	105(3)
C(94)-C(107)-C(110)	112(2)
C(107)-C(108)-H(10A)	109.5
C(107)-C(108)-H(10B)	109.5
H(10A)-C(108)-H(10B)	109.5
C(107)-C(108)-H(10C)	109.5
H(10A)-C(108)-H(10C)	109.5
H(10B)-C(108)-H(10C)	109.5
C(107)-C(109)-H(10D)	109.5
C(107)-C(109)-H(10E)	109.5
H(10D)-C(109)-H(10E)	109.5
C(107)-C(109)-H(10F)	109.5
H(10D)-C(109)-H(10F)	109.5
H(10E)-C(109)-H(10F)	109.5
C(107)-C(110)-H(11A)	109.5
C(107)-C(110)-H(11B)	109.5
H(11A)-C(110)-H(11B)	109.5
C(107)-C(110)-H(11C)	109.5
H(11A)-C(110)-H(11C)	109.5
H(11B)-C(110)-H(11C)	109.5
C(101)-C(111)-C(114)	113.8(15)
C(101)-C(111)-C(112)	116.0(13)
C(114)-C(111)-C(112)	105.4(19)
C(101)-C(111)-C(113)	107.6(17)
C(114)-C(111)-C(113)	105.3(18)
C(112)-C(111)-C(113)	108.1(18)
C(111)-C(112)-H(11D)	109.5
C(111)-C(112)-H(11E)	109.5
H(11D)-C(112)-H(11E)	109.5
C(111)-C(112)-H(11F)	109.5
H(11D)-C(112)-H(11F)	109.5
H(11E)-C(112)-H(11F)	109.5
C(111)-C(113)-H(11G)	109.5
C(111)-C(113)-H(11H)	109.5
H(11G)-C(113)-H(11H)	109.5

C(111)-C(113)-H(11I)	109.5
H(11G)-C(113)-H(11I)	109.5
H(11H)-C(113)-H(11I)	109.5
C(111)-C(114)-H(11J)	109.5
C(111)-C(114)-H(11K)	109.5
H(11J)-C(114)-H(11K)	109.5
C(111)-C(114)-H(11L)	109.5
H(11J)-C(114)-H(11L)	109.5
H(11K)-C(114)-H(11L)	109.5
N(7)-C(115)-H(11M)	109.5
N(7)-C(115)-H(11N)	109.5
H(11M)-C(115)-H(11N)	109.5
N(7)-C(115)-H(11O)	109.5
H(11M)-C(115)-H(11O)	109.5
H(11N)-C(115)-H(11O)	109.5
N(8)-C(116)-H(11P)	109.5
N(8)-C(116)-H(11Q)	109.5
H(11P)-C(116)-H(11Q)	109.5
N(8)-C(116)-H(11R)	109.5
H(11P)-C(116)-H(11R)	109.5
H(11Q)-C(116)-H(11R)	109.5
C(118)-C(117)-C(124)	129.1(11)
C(118)-C(117)-Rh(2)	73.1(6)
C(124)-C(117)-Rh(2)	108.1(7)
C(118)-C(117)-H(117)	112.8
C(124)-C(117)-H(117)	112.8
Rh(2)-C(117)-H(117)	112.8
C(117)-C(118)-C(119)	123.2(12)
C(117)-C(118)-Rh(2)	70.3(5)
C(119)-C(118)-Rh(2)	110.1(7)
C(117)-C(118)-H(118)	114.9
C(119)-C(118)-H(118)	114.9
Rh(2)-C(118)-H(118)	114.9
C(120)-C(119)-C(118)	113.5(9)
C(120)-C(119)-H(11S)	108.9
C(118)-C(119)-H(11S)	108.9
C(120)-C(119)-H(11T)	108.9
C(118)-C(119)-H(11T)	108.9

H(11S)-C(119)-H(11T)	107.7
C(121)-C(120)-C(119)	113.5(9)
C(121)-C(120)-H(12A)	108.9
C(119)-C(120)-H(12A)	108.9
C(121)-C(120)-H(12B)	108.9
C(119)-C(120)-H(12B)	108.9
H(12A)-C(120)-H(12B)	107.7
C(122)-C(121)-C(120)	127.6(10)
C(122)-C(121)-Rh(2)	72.5(6)
C(120)-C(121)-Rh(2)	105.9(7)
C(122)-C(121)-H(121)	113.9
C(120)-C(121)-H(121)	113.9
Rh(2)-C(121)-H(121)	113.9
C(121)-C(122)-C(123)	125.0(10)
C(121)-C(122)-Rh(2)	71.5(6)
C(123)-C(122)-Rh(2)	111.0(7)
C(121)-C(122)-H(122)	113.9
C(123)-C(122)-H(122)	113.9
Rh(2)-C(122)-H(122)	113.9
C(122)-C(123)-C(124)	112.4(9)
C(122)-C(123)-H(12C)	109.1
C(124)-C(123)-H(12C)	109.1
C(122)-C(123)-H(12D)	109.1
C(124)-C(123)-H(12D)	109.1
H(12C)-C(123)-H(12D)	107.9
C(117)-C(124)-C(123)	113.0(9)
C(117)-C(124)-H(12E)	109.0
C(123)-C(124)-H(12E)	109.0
C(117)-C(124)-H(12F)	109.0
C(123)-C(124)-H(12F)	109.0
H(12E)-C(124)-H(12F)	107.8
Cl(1)-C(125)-Cl(3)	112.6(13)
Cl(1)-C(125)-Cl(2)	108.2(9)
Cl(3)-C(125)-Cl(2)	107.9(9)
Cl(1)-C(125)-H(125)	109.4
Cl(3)-C(125)-H(125)	109.4
Cl(2)-C(125)-H(125)	109.4
Cl(5)-C(126)-Cl(4)	112.1(12)

Cl(5)-C(126)-Cl(6)	103.5(9)
Cl(4)-C(126)-Cl(6)	109.3(10)
Cl(5)-C(126)-H(126)	110.6
Cl(4)-C(126)-H(126)	110.6
Cl(6)-C(126)-H(126)	110.6
Cl(7)-C(127)-Cl(9)	103.4(16)
Cl(7)-C(127)-Cl(8)	112.8(14)
Cl(9)-C(127)-Cl(8)	121.3(16)
Cl(7)-C(127)-H(127)	106.1
Cl(9)-C(127)-H(127)	106.1
Cl(8)-C(127)-H(127)	106.1

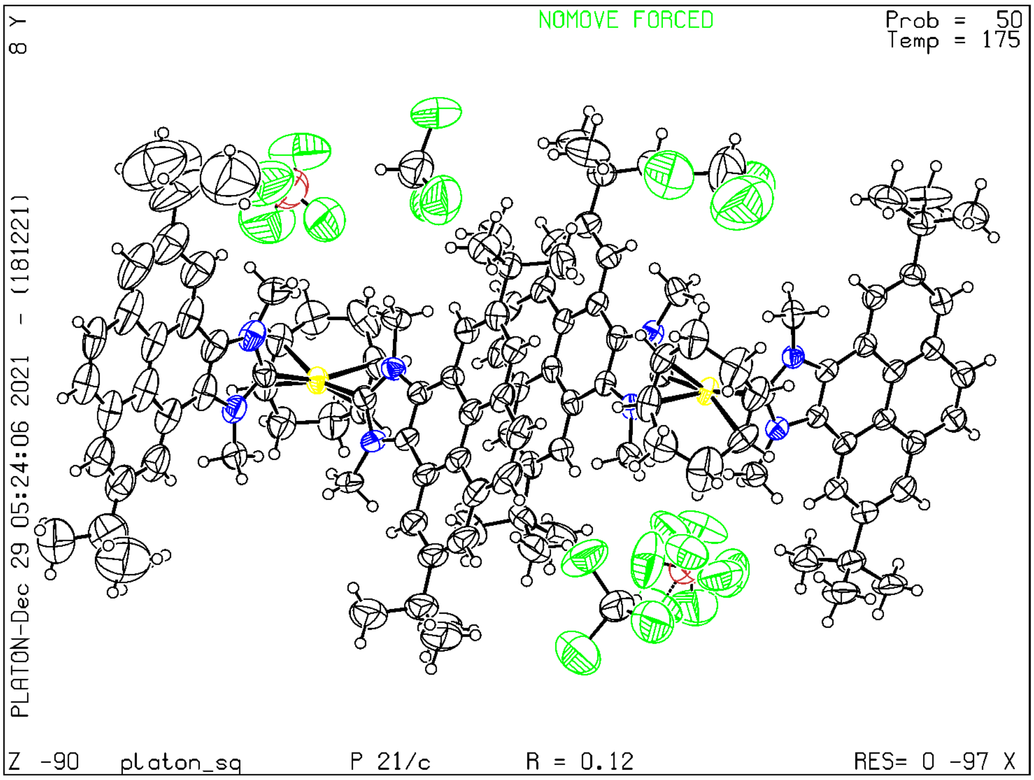

Fig. S196. Crystal structure of rhodium complex **4b**.

13. The calculated steric bulkiness of oligomer analogues.

The percent buried volumes (%V_{bur}) and steric maps of complexes **3**, **4b** were calculated by SambVca 2.1. With this hint in our mind, the steric bulkiness around Rh center in the possible oligomer analogues with unit number (n = 3, 5, and 7) was calculated using PBE /LANL2DZ with D3BJ dispersion correction.

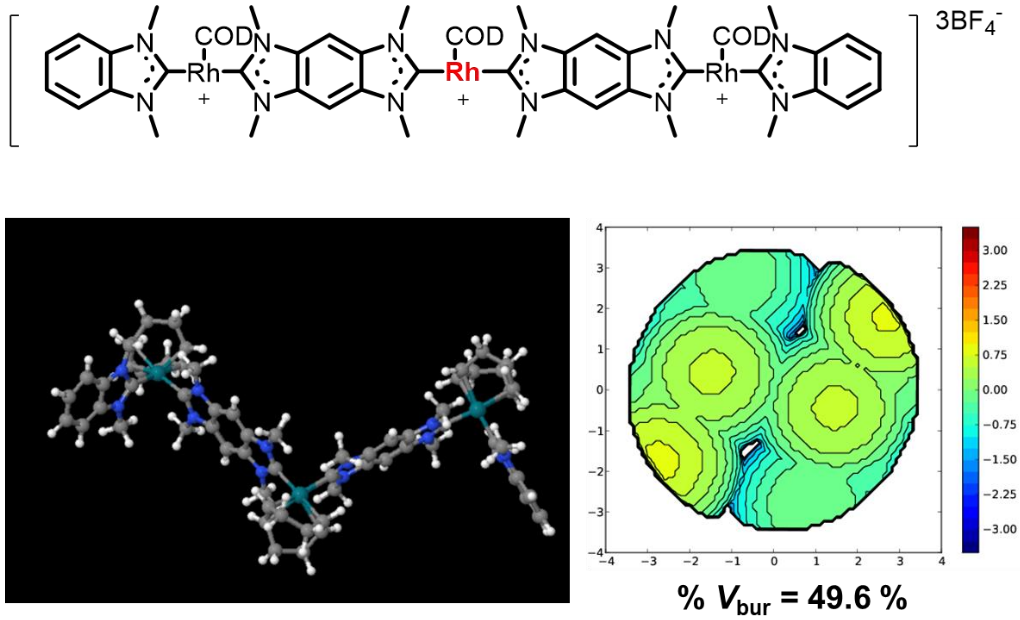

Fig. S197. Percent buried volumes and steric maps of oligomer-3Rh analogue.

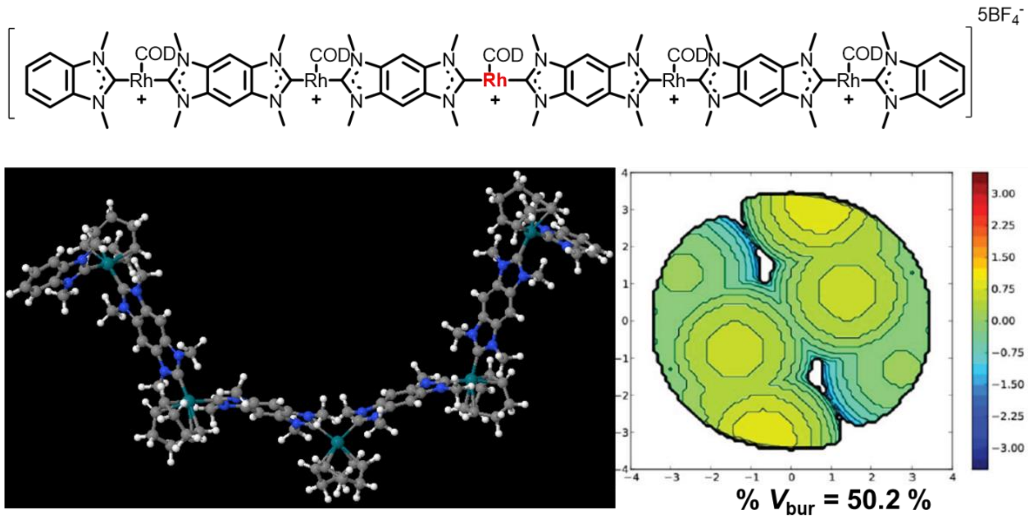

Fig. S198. Percent buried volumes and steric maps of oligomer-5Rh analogue.

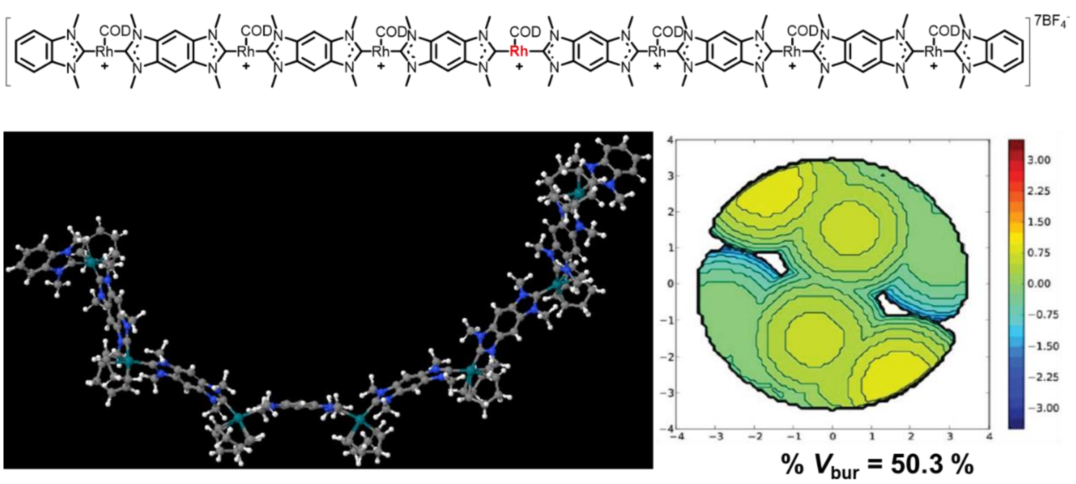

Fig. S199. Percent buried volumes and steric maps of oligomer-7Rh analogue.

14. References

[1]. S. Gonell and E. Peris, *ACS Catal*., 2014, **4***,* 2811-2817.

[2]. S. Ibanez, A. Guerrero, M. Poyatos and E. Peris, *Chem. Eur. J.*, 2015, **21**, 10566-10575.

[3]. J. Chen, J. Lin and J. Xiao. *Chem. Commun.,* 2018*,* **54***,* 7034-7037.

[4]. M. T. Peruzzi, Q. Mei, S. J. Lee and M. R. Gagne, *Chem. Commun*., 2018, **54**, 5855-5858.

[5]. N. A. Larionova, J. M. Ondozabal, E. G. Smith and X. C. Cambeiro, *Org. Lett.,* 2021, **23**, 5383-5388.

[6]. Z. Lu, Q. Zheng, S. Yang, C. Qian, Y. Shen and T. Tu, *ACS Catal.,* 2021, **11**, 10796-10801.

[7]. T. Satoh, A. Osawa, T. Ohbayashi and A. Kondo, *Tetrahedron.,* 2006, **62**, 7892-7901.

[8]. H. Liu, D. Yang, D.-L.Wang, P. Wang, Y. Lu, V.-T. Giang and Y. Liu, *Chem. Commun*., 2018, **54**, 7979-7982.

[9]. Z.-C. Wang, D. Shen, J. Gao, X. Jia, Y. Xu and S.-L. Shi, *Chem. Commun.,* 2019, **55**, 8848-8851.

[10] H. Reed, T. R. Paul and William J. Chain, *J. Org. Chem.,* 2018, **83**, 11359−11368.

[11]. A. Wetzel, S. Wöckel, M. Schelwies, M. K. Brinks, F. Rominger, P. Hofmann and M. Limbach, *Org. Lett.,* 2013, **15**, 2-5.

[12]. H. Chung and Y. K. Chung, *J. Org. Chem.*, 2018, **83**, 8533−8542.

[13]. S. M. Bronner and R. H. Grubbs, *Chem. Sci.*, 2014, **5**, 101-106.

[14]. J. Yang, F. G. Delolo, A. Spannenberg, R. Jackstell and M. Beller. *Angew. Chem., Int. Ed.,* 2022*,* **61***,* e202112597.

[15]. I. Sorribes, J. R. Cabrero-Antonino, C. Vicent, K. Junge and M. Beller, *J. Am. Chem. Soc.*, 2015, **137**, 13580-13587.

[16]. Y. Ogiwara, W. Shimoda, K. Ide, T. Nakajima and N. Sakai, *Eur. J. Org. Chem.,* 2017, **20***,* 2866-2870.

[17]. T. J. Brown, M. Cumbes, L. J. Diorazio, G. J. Clarkson and M. Wills, *J. Org. Chem.,* 2017, **82***,* 10489-10503.

[18]. S. K. Pedersen, H. G. Gudmundsson, D. U. Nielsen, B. S. Donslund, H. C. D. Hammershøj, K. Daasbjerg and T. Skrydstrup, *Nat. Catal.*, 2020, **3**, 843-850.