

Iridium-Catalysed Reductive Allylic Amination of α, β -Unsaturated Aldehydes

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A. General Methods

¹H and ¹³C NMR spectra were recorded by using a Bruker AVANCE-NEO 400M Hz spectrometer (CDCl_3 , $\delta_{\text{H}}=7.26$ ppm, $\delta_{\text{C}}=77.23$ ppm). The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Chemical shifts (δ) are reported in ppm and quoted to the nearest 0.01 ppm relative to the residual protons in CDCl_3 (7.26 ppm for ¹H) or TMS (0.0 ppm for ¹H) and CDCl_3 (77.0 ppm for ¹³C). The melting point is determined by WRR melting point apparatus. HRMS data were obtained from a high-resolution mass spectrometer (LCMS-IT-TOF). The progress of the reaction is monitored by thin layer chromatography (TLC).

B. Procedure for the Preparation of **3** and **5**

To 25.0 mL Schlenk tube was added aldehydes (0.5 mmol), amine (0.6 mmol), **TC-5** (1.0 mol%, 2.81 mg), PhSiH_3 (4.0 equivalent, 2.0 mmol), as well as toluene (2.0 mL) were added successively. The mixture was stirred for 13 h under sealed conditions at 80 °C. After the reaction was completed, the solution was quenched with 2.0 mL 3M NaOH aqueous solution and stirred. The mixture was extracted with ethyl acetate (5.0 mL*3). The organic layer was dried with anhydrous MgSO_4 , removed in vacuum, and purified by column chromatography on silica gel with dichloromethane/methanol (7:1 ~ 20:1) as eluting solvents to afford the desired products **3** and **5**. The optically pure products was determined with Chiral OD or OJ column.

C. Analysis Data for the Products

1-Cinnamyl-4-methylpiperazine(3aa):^[1] Prepared in 97% yield (105.6mg), yellow oil. ¹H NMR (400 MHz, CDCl_3) δ 7.38 (d, $J = 7.9$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 6.53 (d, $J = 15.8$ Hz, 1H), 6.33-6.23 (m, 1H), 3.17 (d, $J = 6.8$ Hz, 2H), 2.53 (s, 8H), 2.31 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl_3 , ppm) δ 136.9, 133.2, 128.6, 127.5, 126.5, 126.3, 61.1, 55.1, 53.2, 46.1.

(E)-1-methyl-4-(3-(*p*-tolyl)allyl)piperazine(3ba): Prepared in 81% yield (93 mg), yellow oil. ¹H NMR (400 MHz, CDCl_3) δ 7.21-7.16 (m, 2H), 7.03 (d, $J = 8.0$ Hz, 2H), 6.41 (d, $J = 15.8$ Hz, 1H), 6.14 (dt, $J = 15.8, 6.8$ Hz, 1H), 3.07 (d, $J = 6.9$ Hz, 2H),

2.41 (s, 8H), 2.25 (s, 3H), 2.22 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 137.3, 134.1, 133.0, 129.3, 126.2, 125.5, 61.1, 55.1, 53.2, 46.1, 21.2. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2$ 231.1861; Found 231.1862.

(E)-1-(3-(4-methoxyphenyl)allyl)-4-methylpiperazine(3ca): Prepared in 87% yield (107 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 8.5$ Hz, 2H), 6.85 (d, $J = 8.5$ Hz, 2H), 6.46 (d, $J = 15.8$ Hz, 1H), 6.18-6.08 (m, 1H), 3.80 (s, 3H), 3.14 (d, $J = 6.8$ Hz, 2H), 2.54 (s, 8H), 2.30 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 159.1, 132.6, 129.7, 127.5, 124.2, 114.0, 61.2, 55.3, 55.1, 53.1, 46.0. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}$ 247.1810; Found 247.1813.

(E)-1-(3-(4-fluorophenyl)allyl)-4-methylpiperazine(3da): Prepared in 63% yield (73.7 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.33 (dd, $J = 7.8, 5.9$ Hz, 2H), 6.99 (t, $J = 8.5$ Hz, 2H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.23-6.14 (m, 1H), 3.15 (d, $J = 6.8$ Hz, 2H), 2.49 (s, 8H), 2.30 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 162.2 (d, $J = 246.6$ Hz), 133.1 (d, $J = 3.4$ Hz), 131.9, 127.8 (d, $J = 8.0$ Hz), 126.3 (d, $J = 2.3$ Hz), 115.5 (d, $J = 21.5$ Hz), 61.0, 55.1, 53.2, 46.1. ^{19}F NMR (377 MHz, CDCl_3 , ppm) δ -114.62. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{20}\text{FN}_2$ 235.1611; Found 235.1615.

(E)-N, N-dimethyl-4-(3-(4-methylpiperazin-1-yl)prop-1-en-1-yl)anilines(3ea): Prepared in 63% yield (91 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.15 (m, 2H), 6.57 (d, $J = 8.8$ Hz, 2H), 6.33 (d, $J = 15.8$ Hz, 1H), 5.97 (dt, $J = 15.8, 6.9$ Hz, 1H), 3.03 (dd, $J = 7.0, 1.3$ Hz, 2H), 2.84 (s, 6H), 2.39 (s, 8H), 2.20 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 163.5, 161.0, 133.1, 133.1, 131.9, 127.8, 127.8, 126.3, 115.6, 115.4, 61.0, 55.1, 53.2, 46.1. $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{25}\text{N}_3\text{Na}$ 282.1941; Found 282.1940.

(E)-1-(3-(2-bromophenyl)allyl)-4-methylpiperazine(3fa): Prepared in 84% yield (123.5 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.45 (t, $J = 7.0$ Hz, 2H), 7.21-7.14 (m, 2H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 15.7$ Hz, 1H), 6.15 (dt, $J = 15.3, 6.7$ Hz, 1H), 3.14 (d, $J = 6.7$ Hz, 2H), 2.44 (s, 8H), 2.23 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 136.8, 132.9, 131.8, 129.7, 128.8, 127.5, 127.1, 123.4, 60.9, 55.1, 53.2, 46.1. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{20}\text{BrN}_2$ 295.0810; Found

295.0815.

(E)-1-(3-(2-methoxyphenyl)allyl)-4-methylpiperazine(3ga): Prepared in 86% yield (106.3 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 7.6$ Hz, 1H), 7.13 (t, $J = 7.7$ Hz, 1H), 6.83 (t, $J = 7.5$ Hz, 1H), 6.81-6.73 (m, 2H), 6.27-6.16 (m, 1H), 3.76 (d, $J = 2.2$ Hz, 3H), 3.11 (d, $J = 6.7$ Hz, 2H), 2.43 (s, 8H), 2.22 (d, $J = 2.1$ Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 156.5, 128.5, 127.9, 127.1, 126.8, 125.8, 120.6, 110.8, 61.5, 55.4, 55.1, 53.1, 46.0. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}$ 247.1810; Found 247.1812.

(E)-1-methyl-4-(3-(m-tolyl)allyl)piperazine(3ha): Prepared in 94% yield (108.2 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.14 (m, 3H), 7.06-7.00 (m, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.25 (dt, $J = 15.8, 6.8$ Hz, 1H), 3.13 (d, $J = 6.9$ Hz, 2H), 2.48 (s, 8H), 2.32 (s, 3H), 2.28 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 138.0, 136.8, 133.2, 128.5, 128.3, 127.1, 126.3, 123.4, 61.1, 55.1, 53.1, 46.0, 21.4. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2$ 231.1861; Found 231.1865.

(E)-1-methyl-4-(2-methyl-3-phenylallyl)piperazine(3ia): Prepared in 62% yield (71.3 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.18 (m, 5H), 7.15-7.10 (m, 1H), 6.35 (s, 1H), 2.95-2.92 (m, 2H), 2.39 (s, 8H), 2.22 (s, 3H), 1.83 (d, $J = 1.3$ Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 138.0, 135.9, 128.9, 128.1, 127.4, 126.2, 67.8, 55.3, 53.1, 46.1, 16.8. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2$ 231.1861; Found 231.1865.

(E)-1-(2-benzylideneheptyl)-4-methylpiperazine(3ja): Prepared in 65% yield (93.0 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.23 (t, $J = 7.4$ Hz, 2H), 7.19-7.10 (m, 3H), 6.35 (s, 1H), 2.92 (s, 2H), 2.38 (s, 8H), 2.19 (d, $J = 13.0$ Hz, 5H), 1.19 (d, $J = 11.6$ Hz, 6H), 0.80 (t, $J = 6.2$ Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 140.4, 138.1, 128.7, 128.1, 127.2, 126.2, 65.1, 55.3, 53.3, 46.1, 32.0, 29.7, 27.9, 22.5, 14.1. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{31}\text{N}_2$ 287.2487; Found 287.2494.

(E)-1-(3-(anthracen-9-yl)allyl)-4-methylpiperazine(3ka): Prepared in 65% yield (102.7 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.28-8.26 (m, 1H), 8.22 (d, $J = 9.7$ Hz, 2H), 7.92-7.88 (m, 2H), 7.43-7.38 (m, 4H), 7.22 (d, $J = 16.1$ Hz, 1H), 6.07 (dt, $J = 16.1, 6.6$ Hz, 1H), 3.39 (dd, $J = 6.6, 1.5$ Hz, 2H), 2.55 (s, 8H), 2.27 (s, 3H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 135.0, 132.2, 131.2, 129.2, 128.6, 128.4, 126.1, 125.7, 125.2, 124.8, 61.3, 54.9, 53.0, 45.8. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2$ 317.2018; Found 317.2021.

(E)-1-(3-(furan-2-yl)allyl)-4-methylpiperazine(3la): Prepared in 60% yield (61.8 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, $J = 1.3$ Hz, 1H), 6.35-6.22 (m, 2H), 6.17-6.05 (m, 2H), 3.06 (d, $J = 5.9$ Hz, 2H), 2.45 (s, 8H), 2.23 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 152.6, 141.9, 125.3, 121.5, 111.2, 107.4, 60.7, 55.1, 53.1, 46.0. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{19}\text{N}_2\text{O}$ 207.1497; Found 207.1500.

(E)-1-methyl-4-(3-phenylbut-2-en-1-yl)piperazine(3ma): Prepared in 67% yield (77 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.38 (m, 2H), 7.31 (dd, $J = 8.5, 6.6$ Hz, 2H), 7.27-7.23 (m, 1H), 5.89 (m, 1H), 3.21 (d, $J = 6.8$ Hz, 2H), 2.52 (s, 8H), 2.32 (s, 3H), 2.06 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 143.2, 137.8, 128.2, 127.0, 125.6, 124.2, 56.5, 55.0, 53.0, 45.9, 16.2. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2$ 231.1861; Found 231.1861.

1-((2E,4E)-deca-2,4-dien-1-yl)-4-phenylpiperazine(3nb): Prepared in 65% yield (96.8 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 7.3$ Hz, 1H), 7.25 (d, $J = 1.0$ Hz, 1H), 6.93 (d, $J = 7.7$ Hz, 2H), 6.86 (t, $J = 7.3$ Hz, 1H), 6.18 (dd, $J = 14.9, 10.4$ Hz, 1H), 6.05 (dd, $J = 15.0, 10.4$ Hz, 1H), 5.66 (m, 2H), 3.22 (t, $J = 5.0$ Hz, 4H), 3.08 (d, $J = 7.0$ Hz, 2H), 2.63 (t, $J = 5.0$ Hz, 4H), 2.08 (q, $J = 6.9$ Hz, 2H), 1.36-1.23 (m, 6H), 0.91-0.87 (m, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 151.3, 135.2, 129.5, 129.1, 119.8, 116.1, 60.8, 53.1, 49.1, 32.6, 31.5, 29.0, 22.6, 14.1. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{31}\text{N}_2$ 299.2487; Found 299.2488.

(E)-1-(2-methylpent-2-en-1-yl)-4-phenylpiperazine(3ob): Prepared in 72% yield (87.8 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.23 (m, 2H), 6.93 (d, $J = 7.8$ Hz, 2H), 6.84 (t, $J = 7.2$ Hz, 1H), 5.33 (t, $J = 6.7$ Hz, 1H), 3.19 (s, 4H), 2.88 (s, 2H), 2.51 (s, 4H), 2.05 (p, $J = 7.0$ Hz, 2H), 1.66 (s, 3H), 1.02-0.91 (m, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 151.5, 131.4, 130.3, 129.1, 119.5, 116.0, 67.4, 53.0, 49.2, 21.1, 15.0, 14.3. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2$ 245.2018; Found 245.2017.

1-Cinnamyl-4-phenylpiperazine(3ab):^[2] Prepared in 88% yield (122.3 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 7.5$ Hz, 2H), 7.26-7.12 (m, 5H), 6.84

(d, $J = 8.2$ Hz, 2H), 6.77 (t, $J = 7.3$ Hz, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 6.23 (dt, $J = 15.7, 6.8$ Hz, 1H), 3.13 (t, $J = 5.2$ Hz, 6H), 2.61-2.53 (m, 4H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 151.4, 136.9, 133.4, 129.2, 128.7, 127.7, 126.4, 119.8, 116.2, 61.2, 53.3, 49.2.

1-Benzyl-4-cinnamylpiperazine(3ac):^[3] Prepared in 80% yield (116.8 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 4.9$ Hz, 6H), 7.16 (d, $J = 13.8$ Hz, 2H), 6.44 (d, $J = 15.8$ Hz, 1H), 6.20 (dt, $J = 15.8, 6.8$ Hz, 1H), 3.45 (s, 2H), 3.09 (d, $J = 6.8$ Hz, 2H), 2.45 (s, 8H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 138.1, 136.9, 133.1, 129.3, 128.6, 128.2, 127.5, 127.1, 126.6, 126.3, 63.1, 61.1, 53.2, 53.1.

1-Cinnamyl-4-cyclohexylpiperazine(3ad): Prepared in 81% yield (115.3 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 7.4$ Hz, 2H), 7.22 (dd, $J = 14.4, 6.7$ Hz, 2H), 7.15 (t, $J = 7.2$ Hz, 1H), 6.45 (d, $J = 15.8$ Hz, 1H), 6.22 (dt, $J = 15.8, 6.8$ Hz, 1H), 3.08 (d, $J = 6.7$ Hz, 2H), 2.56 (s, 8H), 2.17 (dt, $J = 10.3, 5.2$ Hz, 1H), 1.82 (d, $J = 8.8$ Hz, 2H), 1.76-1.68 (m, 2H), 1.55 (d, $J = 12.2$ Hz, 1H), 1.23-1.00 (m, 5H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 136.9, 133.1, 128.6, 127.5, 126.7, 126.3, 63.5, 61.2, 53.7, 48.9, 29.0, 26.3, 25.9. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{29}\text{N}_2$ 285.2331; Found 285.2333.

(4-Cinnamylpiperazin-1-yl)(phenyl)methanone(3ae): Prepared in 51% yield (78.3 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 15.2$ Hz, 7H), 7.24 (t, $J = 7.6$ Hz, 2H), 7.17 (d, $J = 10.2$ Hz, 1H), 6.46 (d, $J = 15.7$ Hz, 1H), 6.23-6.12 (m, 1H), 3.75 (s, 2H), 3.38 (s, 2H), 3.12 (d, $J = 6.8$ Hz, 2H), 2.44 (d, $J = 60.3$ Hz, 4H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 170.4, 136.7, 135.8, 133.6, 129.7, 128.6, 128.5, 127.7, 127.1, 126.4, 125.8, 61.0. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}$ 307.1810; Found 307.1816.

1-Benzyl-4-cinnamyl-1,4-diazepane(3af): Prepared in 83% yield (127.0 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.21 (m, 8H), 7.19-7.06 (m, 3H), 6.40 (d, $J = 15.9$ Hz, 1H), 6.28-6.15 (m, 1H), 3.55 (s, 2H), 3.19 (d, $J = 6.6$ Hz, 2H), 2.70-2.59 (m, 8H), 1.72 (m, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 139.60, 137.11, 132.4, 128.9, 128.6, 128.2, 127.9, 127.4, 126.9, 126.3, 62.9, 61.1, 55.3, 54.9, 54.5, 27.7.

$[M+H]^+$ Calcd for $C_{21}H_{26}N_2$ 307.2174; Found 307.2179.

(E)-3-phenyl-N,N-dipropylprop-2-en-1-amine(3ag):^[4] Prepared in 82% yield (89.0 mg), yellow oil. 1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 (d, $J = 7.0$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.25-7.19 (m, 1H), 6.50 (d, $J = 15.9$ Hz, 1H), 6.29 (dt, $J = 15.9, 6.6$ Hz, 1H), 3.24 (dd, $J = 6.6, 1.4$ Hz, 2H), 2.46-2.38 (m, 4H), 1.55-1.43 (m, 4H), 0.88 (t, $J = 7.4$ Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm) δ 137.3, 131.9, 128.6, 128.1, 127.3, 126.3, 56.8, 56.0, 20.2, 12.1.

N-butyl-N-cinnamylbutan-1-amine(3ah):^[1] Prepared in 86% yield (105.4 mg), yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, $J = 7.0$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.22 (q, $J = 6.8$ Hz, 1H), 6.50 (d, $J = 15.9$ Hz, 1H), 6.29 (m, 1H), 3.24 (dd, $J = 6.7, 1.4$ Hz, 2H), 2.49-2.41 (m, 4H), 1.51-1.41 (m, 4H), 1.34-1.26 (m, 4H), 0.91 (t, $J = 7.3$ Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm) δ 137.3, 132.0, 128.6, 128.1, 127.3, 126.3, 56.7, 53.6, 29.2, 20.8, 14.2.

(E)-N-methyl-N-(naphthalen-2-ylmethyl)-3-phenylprop-2-en-1-amine(3ai):^[5] Prepared in 93% yield (133.5 mg), yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.65 (d, $J = 8.2$ Hz, 1H), 7.44-7.26 (m, 6H), 7.23-7.16 (m, 2H), 7.11 (dt, $J = 8.8, 4.7$ Hz, 1H), 6.46 (d, $J = 15.8$ Hz, 1H), 6.32-6.22 (m, 1H), 3.82 (s, 2H), 3.15 (d, $J = 6.9$ Hz, 2H), 2.15 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm) δ 137.2, 135.0, 134.0, 132.8, 132.6, 128.7, 128.6, 128.6, 128.1, 127.7, 127.6, 127.5, 126.5, 126.0, 125.7, 125.3, 124.8, 60.6, 60.2, 42.6.

1-Benzhydryl-4-cinnamylpiperazine(3aj):^[1] Prepared in 75% yield (138.1 mg), yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, $J = 8.0$ Hz, 4H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.32-7.27 (m, 3H), 7.23 (d, $J = 10.7$ Hz, 3H), 7.19-7.13 (m, 2H), 6.51 (d, $J = 15.8$ Hz, 1H), 6.27 (m, 1H), 4.23 (s, 1H), 3.18 (d, $J = 6.8$ Hz, 2H), 2.54 (s, 8H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm) δ 142.8, 137.0, 133.1, 128.6, 128.5, 128.0, 127.5, 126.9, 126.6, 126.4, 61.1, 53.5, 51.9.

1-(Bis(4-fluorophenyl)methyl)-4-cinnamylpiperazine(3ak):^[4] Prepared in 79% yield (159.5 mg), yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, $J = 8.0$ Hz, 4H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.33-7.27 (m, 3H), 7.23 (d, $J = 10.2$ Hz, 2H), 7.17 (t, $J = 7.2$ Hz, 2H), 6.51 (m, 1H), 6.27 (m, 1H), 4.23 (s, 1H), 3.18 (d, $J = 6.8$ Hz, 2H), 2.53 (s,

8H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 161.8 (d, $J = 245.6$ Hz), 138.2 (d, $J = 3.2$ Hz), 136.8, 133.4, 129.3 (d, $J = 7.9$ Hz), 128.6, 127.6, 126.3, 126.1, 115.4 (d, $J = 21.2$ Hz), 75.5, 60.9, 53.3, 51.6. ^{19}F NMR (377 MHz, CDCl_3 , ppm) δ -115.69.

(E)-N-(2-(1H-indol-2-yl)ethyl)-N-benzyl-3-phenylprop-2-en-1-amine(3al):^[6]

Prepared in 90% yield (164.5 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (s, 1H), 7.49 (d, $J = 8.3$ Hz, 1H), 7.39- 7.27 (m, 9H), 7.25-7.18 (m, 2H), 7.17-7.12 (m, 1H), 7.02 (ddd, $J = 8.0, 6.9, 1.0$ Hz, 1H), 6.91 (d, $J = 2.3$ Hz, 1H), 6.57-6.50 (m, 1H), 6.31 (dt, $J = 15.9, 6.6$ Hz, 1H), 3.75 (s, 2H), 3.36 (dd, $J = 6.6, 1.4$ Hz, 2H), 3.04-2.94 (m, 2H), 2.91-2.83 (m, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 139.6, 137.3, 136.3, 132.5, 129.1, 128.6, 128.3, 127.8, 127.6, 127.4, 127.0, 126.4, 121.9, 121.6, 119.2, 119.0, 114.6, 111.1, 58.4, 56.3, 54.2, 23.1.

N-Cinnamylaniline(5aa):^[7] Prepared in 96% yield (100.7 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.33 (m, 2H), 7.29 (dd, $J = 8.3, 6.6$ Hz, 2H), 7.24-7.15 (m, 3H), 6.75-6.56 (m, 4H), 6.30 (dt, $J = 15.9, 5.7$ Hz, 1H), 3.90 (dd, $J = 5.8, 1.6$ Hz, 2H), 3.70 (s, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 148.1, 136.9, 131.6, 129.4, 128.7, 127.6, 127.1, 126.4, 117.7, 113.1, 46.3.

N-Cinnamyl-4-methoxyaniline(5ab):^[7] Prepared in 70% yield (84.0 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 9.1$ Hz, 2H), 7.29 (t, $J = 6.6$ Hz, 2H), 7.21 (t, $J = 7.7$ Hz, 1H), 6.82-6.74 (m, 2H), 6.65-6.55 (m, 3H), 6.31 (dt, $J = 15.9, 5.8$ Hz, 1H), 3.86 (d, $J = 5.9$ Hz, 2H), 3.72 (s, 3H), 3.54 (s, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 152.3, 142.3, 137.0, 131.5, 128.7, 127.6, 127.4, 126.4, 114.9, 114.5, 55.8, 47.3.

N-Cinnamyl-4-fluoroaniline(5ac):^[8] Prepared in 86% yield (97.6 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.27 (m, 4H), 7.23 (t, $J = 7.1$ Hz, 1H), 6.89 (t, $J = 8.1$ Hz, 2H), 6.60 (dd, $J = 10.2, 5.0$ Hz, 3H), 6.30 (dt, $J = 15.8, 5.7$ Hz, 1H), 3.88 (d, $J = 5.8$ Hz, 2H), 3.73 (s, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 156.0 (d, $J = 235.0$ Hz), 144.4, 144.4, 136.8, 131.7, 128.7, 127.7, 126.9, 126.4, 115.7 (d, $J = 22.4$ Hz), 113.9 (d, $J = 7.3$ Hz), 46.9. ^{19}F NMR (377 MHz, CDCl_3 , ppm) δ -127.78.

Cinnamyl-4-(trifluoromethyl)aniline(5ad):^[4] Prepared in 93% yield (129.0 mg), white solid; m.p.72-74°C. ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.28 (m, 6H), 7.25 (d, J

= 7.1 Hz, 1H), 6.68-6.56 (m, 3H), 6.28 (dt, J = 15.8, 5.7 Hz, 1H), 4.21 (s, 1H), 3.96 (s, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 150.4, 136.6, 132.0, 128.7, 127.8, 126.7 (q, J = 3.8 Hz), 126.4, 125.9, 123.7, 119.0 (q, J = 32.3 Hz), 112.1, 45.7. ^{19}F NMR (377 MHz, CDCl_3 , ppm) δ -60.98.

Methyl 4-(cinnamylamino)benzoate(5ae):^[8] Prepared in 75% yield (100.3 mg), white solid, m.p.88-90°C. ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 8.5 Hz, 2H), 7.33 (dd, J = 16.0, 7.5 Hz, 4H), 7.23 (s, 1H), 6.62-6.55 (m, 3H), 6.26 (dt, J = 15.9, 5.6 Hz, 1H), 4.38 (s, 1H), 3.96 (s, 2H), 3.84 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 167.4, 151.8, 136.6, 132.0, 131.6, 128.7, 127.8, 126.4, 125.8, 118.5, 111.8, 51.6, 45.5.

2-Chloro-N-cinnamylaniline(5af):^[9] Prepared in 51% yield (62.0 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.29 (m, 4H), 7.26-7.21 (m, 1H), 7.07 (t, J = 8.0 Hz, 1H), 6.67 (d, J = 7.9 Hz, 1H), 6.65- 6.56 (m, 2H), 6.51 (dd, J = 8.3, 2.3 Hz, 1H), 6.28 (dt, J = 15.8, 5.4 Hz, 1H), 3.90 (d, J = 6.0 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 149.1, 136.7, 135.1, 131.9, 130.3, 128.7, 127.7, 126.4, 126.3, 117.5, 112.6, 111.3, 46.0.

N-Cinnamyl-2-iodoaniline(5ag):^[10] Prepared in 93% yield (155.8 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.67 (dd, J = 7.8, 1.5 Hz, 1H), 7.39-7.16 (m, 6H), 6.69-6.57 (m, 2H), 6.50-6.40 (m, 1H), 6.31 (dt, J = 15.9, 5.6 Hz, 1H), 4.39 (s, 1H), 3.97 (t, J = 6.3 Hz, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 147.1, 139.1, 136.7, 131.8, 129.5, 128.7, 127.7, 126.5, 126.3, 118.9, 111.1, 85.5, 46.4.

N-Cinnamylnaphthalen-2-amine(5ah):^[10] Prepared in 65% yield (84.3 mg), white solid; m.p.45-46°C. ^1H NMR (400 MHz, CDCl_3) δ 7.59-7.48 (m, 3H), 7.29-7.18 (m, 5H), 7.11 (dd, J = 16.4, 7.2 Hz, 2H), 6.82- 6.71 (m, 2H), 6.53 (d, J = 15.9 Hz, 1H), 6.24 (dt, J = 15.9, 5.6 Hz, 1H), 3.88 (d, J = 5.8 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 145.7, 136.9, 135.3, 131.8, 129.1, 128.7, 127.8, 127.7, 126.7, 126.5, 126.1, 122.2, 118.1, 104.9, 46.2.

(E)-3-Phenyl-N-(1-phenylethyl)prop-2-en-1-amine(5ai):^[4] Prepared in 73% yield (86.5 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.19 (m, 11H), 6.50-6.42 (m, 1H), 6.28 (dt, J = 15.8, 6.3 Hz, 1H), 3.86 (q, J = 6.6 Hz, 1H), 3.26 (d, J = 6.4 Hz,

2H), 1.39 (d, J = 6.6 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 145.4, 137.2, 131.2, 128.6, 128.5, 127.4, 127.0, 126.7, 126.3, 57.6, 49.7, 24.3.

N-(1-(naphthalen-1-yl)ethyl)-3-phenylprop-2-en-1-amine(5aj): Prepared in 60% yield (86.3 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, J = 7.4 Hz, 1H), 7.87-7.81 (m, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 7.1 Hz, 1H), 7.49-7.41 (m, 3H), 7.33-7.23 (m, 4H), 7.17 (t, J = 7.2 Hz, 1H), 6.42 (d, J = 15.9 Hz, 1H), 6.29 (dt, J = 15.9, 6.2 Hz, 1H), 4.69 (q, J = 6.6 Hz, 1H), 3.31 (qd, J = 14.0, 6.2 Hz, 2H), 1.67 (s, 1H), 1.49 (d, J = 6.6 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 141.2, 137.3, 134.1, 131.5, 131.4, 129.2, 128.7, 128.7, 127.5, 127.4, 126.4, 126.0, 125.9, 125.5, 123.1, 122.8, 52.8, 49.9, 23.8. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{N}$ 288.1752; Found 288.1749.

(E)-N-benzhydryl-3-phenylprop-2-en-1-amine(5ak):^[5] Prepared in 90% yield (135.0 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.38 (m, 4H), 7.37-7.34 (m, 2H), 7.29 (td, J = 7.7, 2.2 Hz, 6H), 7.23-7.18 (m, 3H), 6.53-6.44 (m, 1H), 6.31 (dt, J = 15.9, 6.2 Hz, 1H), 4.91 (s, 1H), 3.36 (dd, J = 6.3, 1.4 Hz, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 144.0, 137.2, 131.4, 128.6, 128.6, 128.5, 128.5, 127.4, 127.1, 126.3, 66.6, 50.0.

(E)-N-(3,3-diphenylpropyl)-3-phenylprop-2-en-1-amine(5al): Prepared in 80% yield (130.5 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (t, J = 7.5 Hz, 5H), 7.26-7.10 (m, 10H), 6.44 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.8, 6.3 Hz, 1H), 4.01 (t, J = 7.8 Hz, 1H), 3.32 (d, J = 6.3 Hz, 2H), 2.61 (t, J = 7.3 Hz, 2H), 2.26 (q, J = 7.5 Hz, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 144.8, 137.2, 131.3, 128.6, 128.6, 128.4, 127.9, 127.4, 126.3, 126.3, 51.8, 49.2, 47.9, 36.0. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{26}\text{N}$ 328.2065; Found 328.2068.

N-Cinnamylloctan-1-amine(5am):^[4] Prepared in 77% yield (94.0 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.17 (m, 5H), 6.56-6.47 (m, 1H), 6.30 (dt, J = 15.9, 6.4 Hz, 1H), 3.41 (dd, J = 6.4, 1.5 Hz, 2H), 2.64 (t, J = 7.3 Hz, 2H), 1.51 (p, J = 7.0 Hz, 2H), 1.35-1.21 (m, 11H), 0.91-0.84 (m, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 137.1, 131.3, 128.6, 128.5, 127.4, 126.3, 52.0, 49.5, 31.9, 30.1, 29.6, 29.3, 27.4, 22.7, 14.2.

N-Cinnamyl-2,3-dihydro-1H-inden-1-amine(5an): Prepared in 67% yield (82.5

mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.16 (m, 9H), 6.62-6.53 (m, 1H), 6.36 (dt, $J = 15.8, 6.3$ Hz, 1H), 4.31 (t, $J = 6.5$ Hz, 1H), 3.59-3.47 (m, 2H), 3.02 (ddd, $J = 15.9, 8.5, 4.9$ Hz, 1H), 2.81 (ddd, $J = 15.7, 8.2, 7.0$ Hz, 1H), 2.48-2.38 (m, 1H), 1.86 (dddd, $J = 12.9, 8.5, 7.0, 6.1$ Hz, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 145.2, 143.7, 137.2, 131.3, 128.7, 128.6, 127.5, 127.4, 126.3, 124.9, 124.2, 62.8, 49.6, 33.8, 30.4. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{N}$ 250.1596; Found 250.1600.

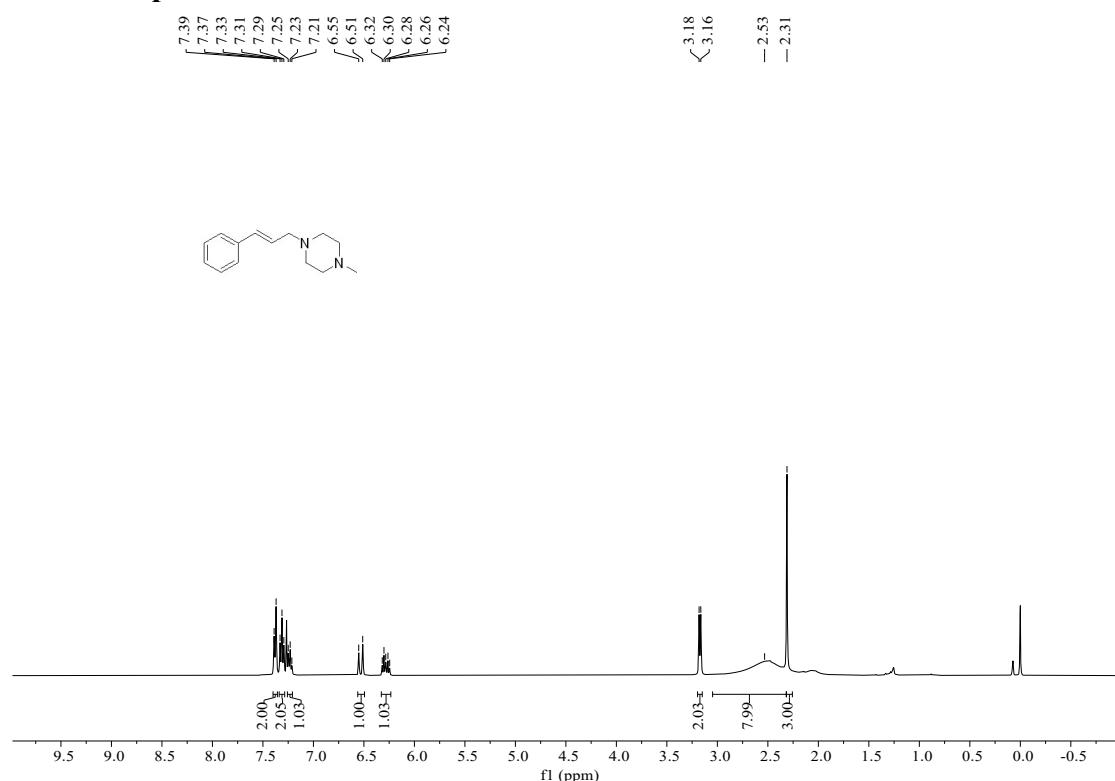
(E)-3-Phenyl-N-(3-phenylpropyl)prop-2-en-1-amine(5ao): Prepared in 71% yield (89.3 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.16 (m, 10H), 6.51 (dt, $J = 15.7, 1.5$ Hz, 1H), 6.29 (dt, $J = 15.8, 6.4$ Hz, 1H), 3.40 (dd, $J = 6.4, 1.5$ Hz, 2H), 2.68 (dt, $J = 11.9, 7.6$ Hz, 4H), 1.85 (dt, $J = 14.3, 7.7$ Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 142.1, 137.1, 131.4, 128.6, 128.4, 128.4, 128.3, 127.4, 126.3, 125.9, 51.9, 48.9, 33.7, 31.7. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{22}\text{N}$ 252.1752; Found 252.1750.

(E)-N-(2-ethylhex-2-en-1-yl)aniline(5pa): Prepared in 69% yield (70.0 mg), yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.15 (dd, $J = 8.5, 7.3$ Hz, 2H), 6.70-6.65 (m, 1H), 6.62-6.58 (m, 2H), 5.37 (t, $J = 7.3$ Hz, 1H), 3.76-3.60 (m, 3H), 2.06 (dq, $J = 33.0, 7.4$ Hz, 4H), 1.39-1.33 (m, 2H), 1.01 (t, $J = 7.6$ Hz, 3H), 0.89 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3 , ppm) δ 148.7, 138.1, 129.2, 126.3, 117.1, 112.9, 49.4, 29.6, 23.0, 22.0, 13.9, 13.4. $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{22}\text{N}$ 204.1752; Found 204.1757.

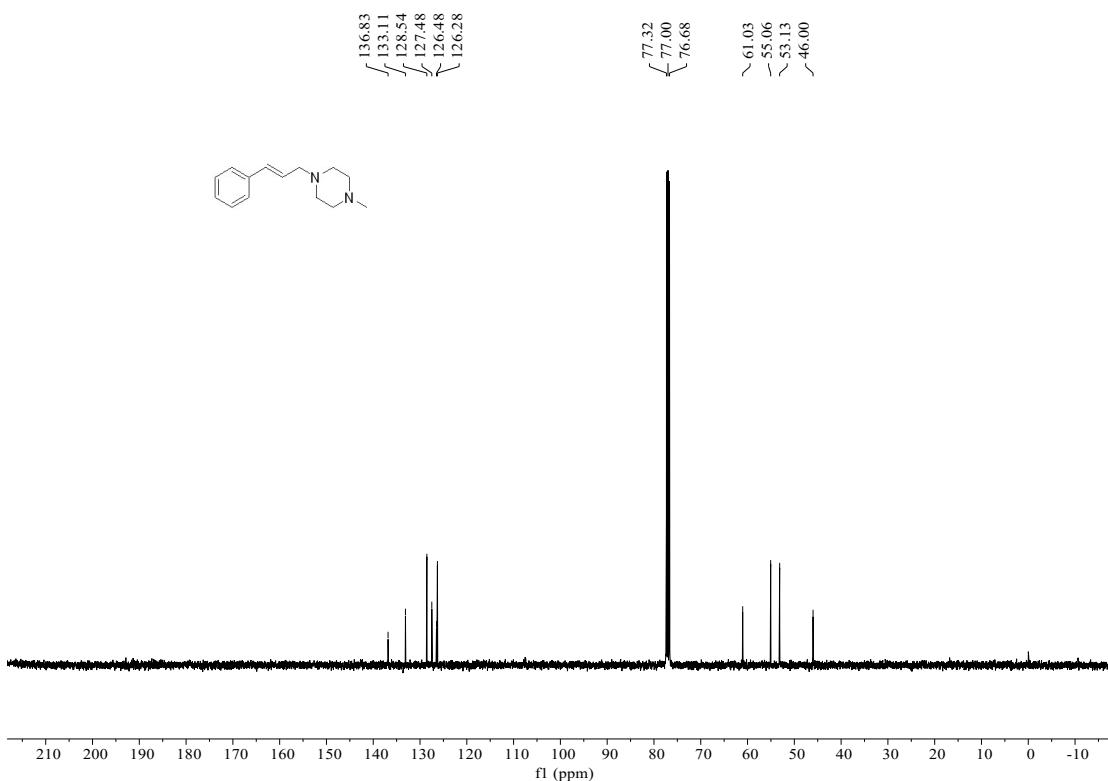
D. References

- [1] Xie, Y.; Hu, J.; Wang, Y.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2012**, *134*, 20613-20616.
- [2] G. Hirata, H. Satomura, H. Kumagae, A. Shimizu, G. Onodera, M. Kimura, *Org. Lett.*, **2017**, *19*, 6148.
- [3] Liang, H.; Bao, L.; Du, Y.; Zhang, Y.; Pang, S.; Sun, C. *Synlett.* **2017**, *28*, 2675-2679.
- [4] D. Banerjee, R. V. Jagadeesh, K. Junge, H. Junge, M. Beller, *ChemSusChem.*, **2012**, *5*, 2039
- [5] (a) J.-Y. Jing, X.-H. Huo, J.-F. Shen, J.-K. Fu, Q.-H. Meng, W.-B. Zhang, *Chem. Commun.*, **2017**, *53*, 5151
- [6] Y. Jin, Y. Jing, C. Li, M. Li, W. Wu, Z. Ke, H. Jiang, *Nat. chem.*, **2022**, *14*, 1118.
- [7] Niu, Z.; Zhang, W.; Lan, P. C.; Aguilal, B.; Ma, S. *Angew. Chem. Int. Ed.* **2019**, *58*, 7420-7424.
- [8] T. Ohshima, Y. Miyamoto, J. Ipposhi, Y. Nakahara, M. Utsunomiya, K. Mashima, *J. Am. Chem. Soc.*, **2009**, *131*, 14317.
- [9] Voronov, A. A.; Alekseeva, K. A.; Ryzhkova, E. A.; Zarubaev, V. V.; Galochkina, A. V.; Zaytsev, V. P.; Majik, M. S.; Tilve, S. G.; Gurbanov, A. V.; Zubkov, F. I. *Tetrahedron Lett.* **2018**, *59*, 1108-1111.
- [10] Takale, B. S.; Tao, S. M.; Yu, X. Q.; Feng, X. J.; Jin, T.; Bao, M.; Yamamoto, Y. *Org. Lett.* **2014**, *16*, 2558-2561.

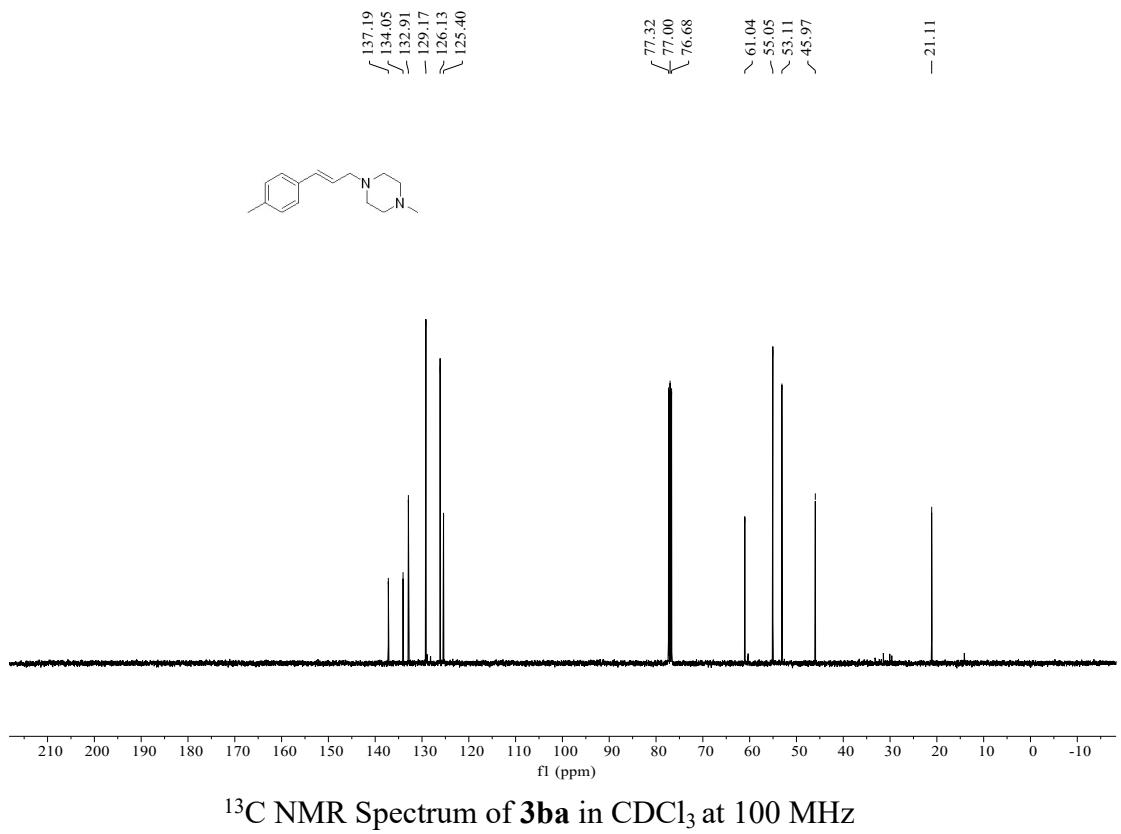
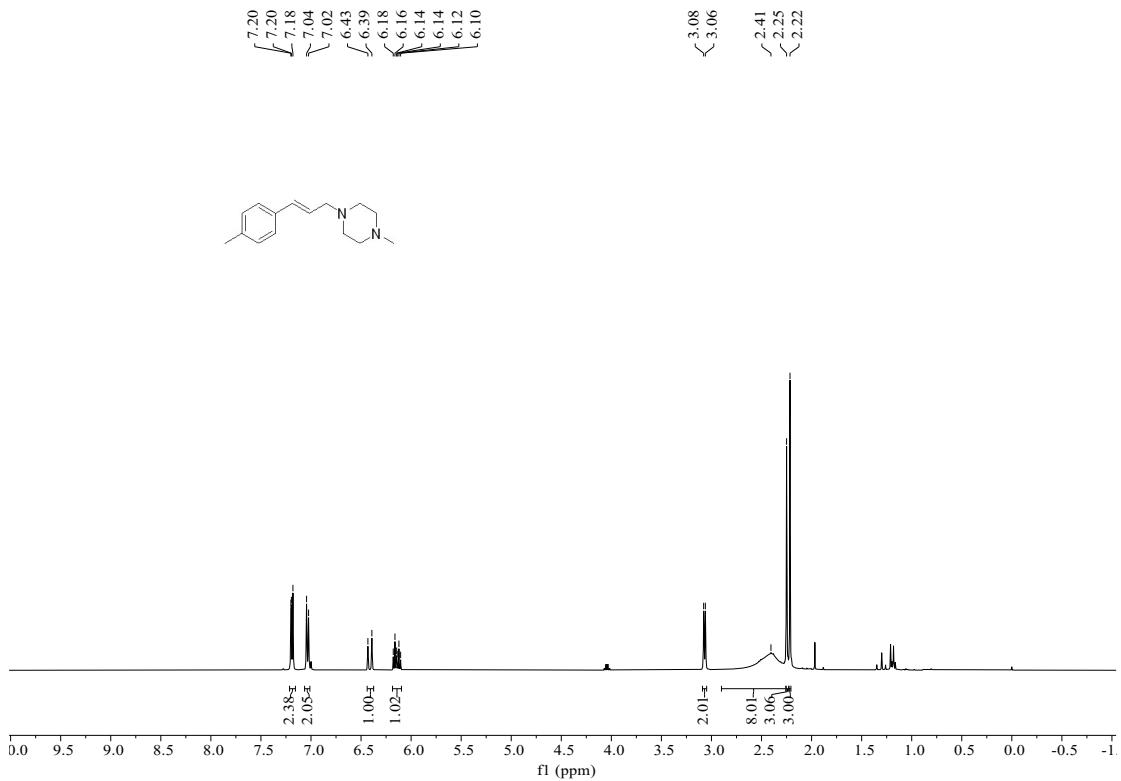
E. NMR Spectra

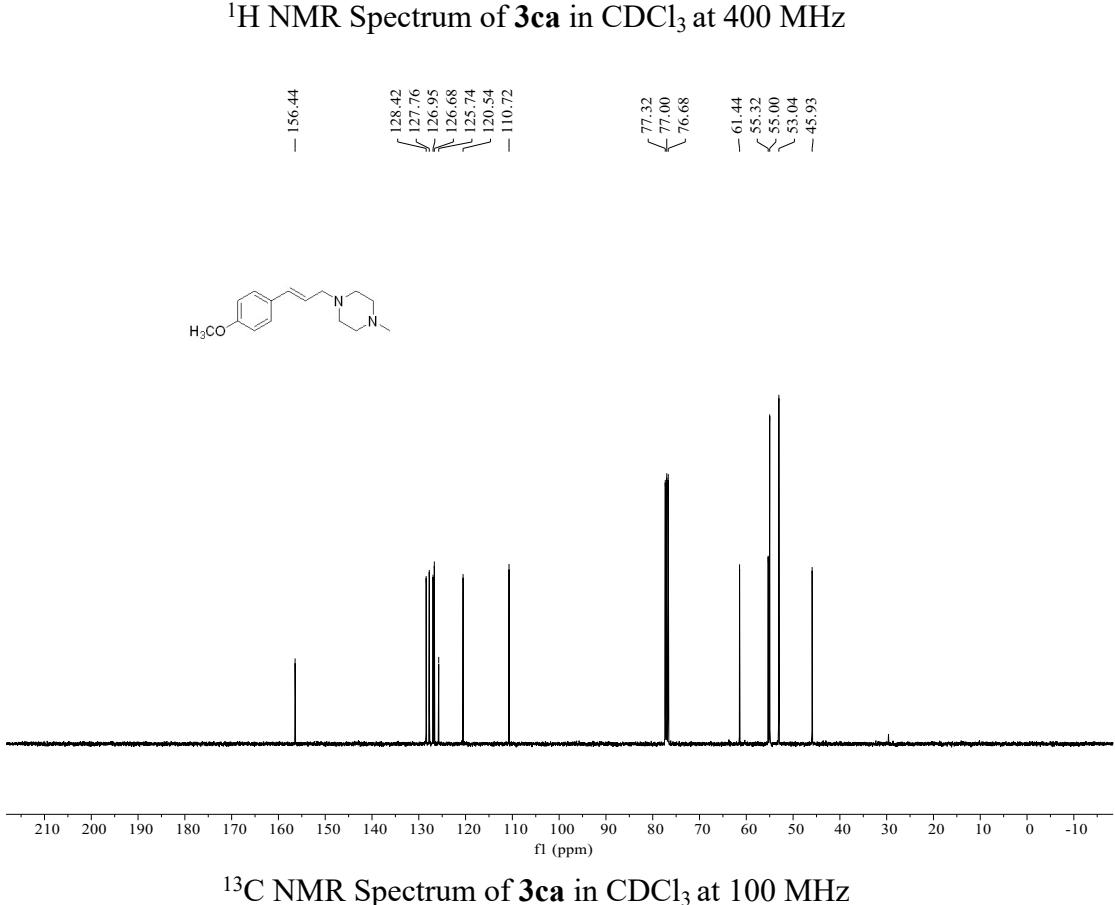
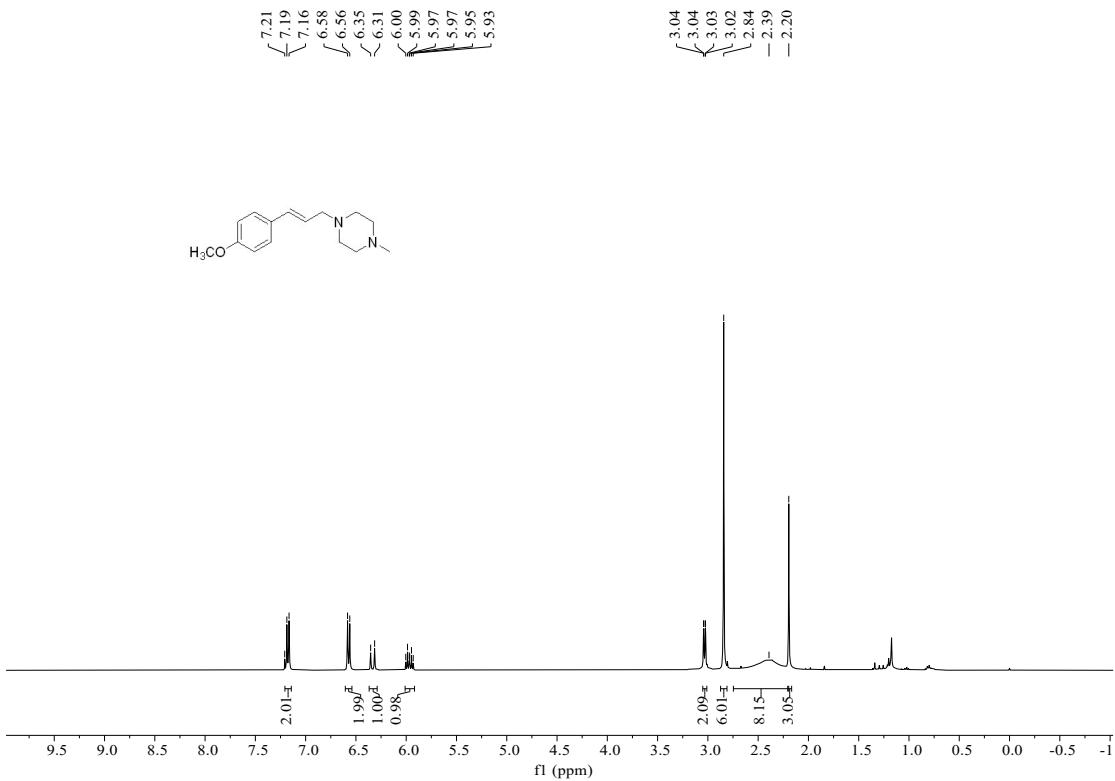


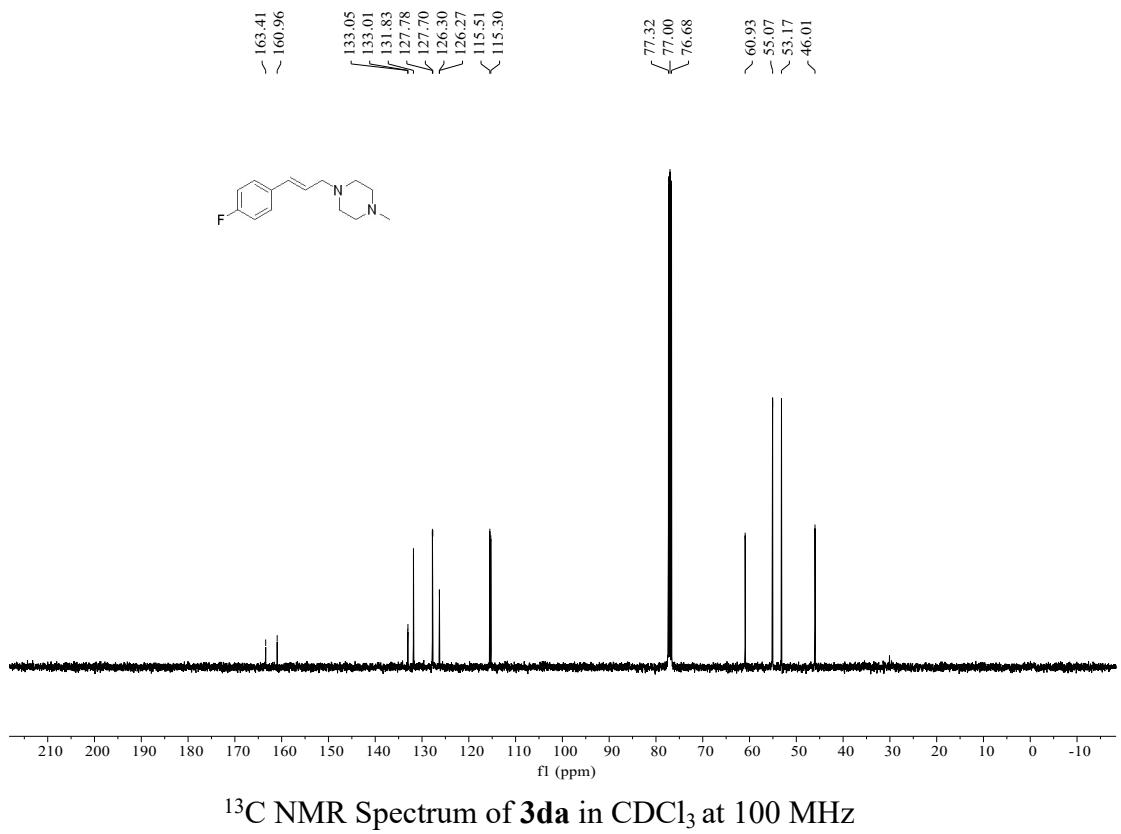
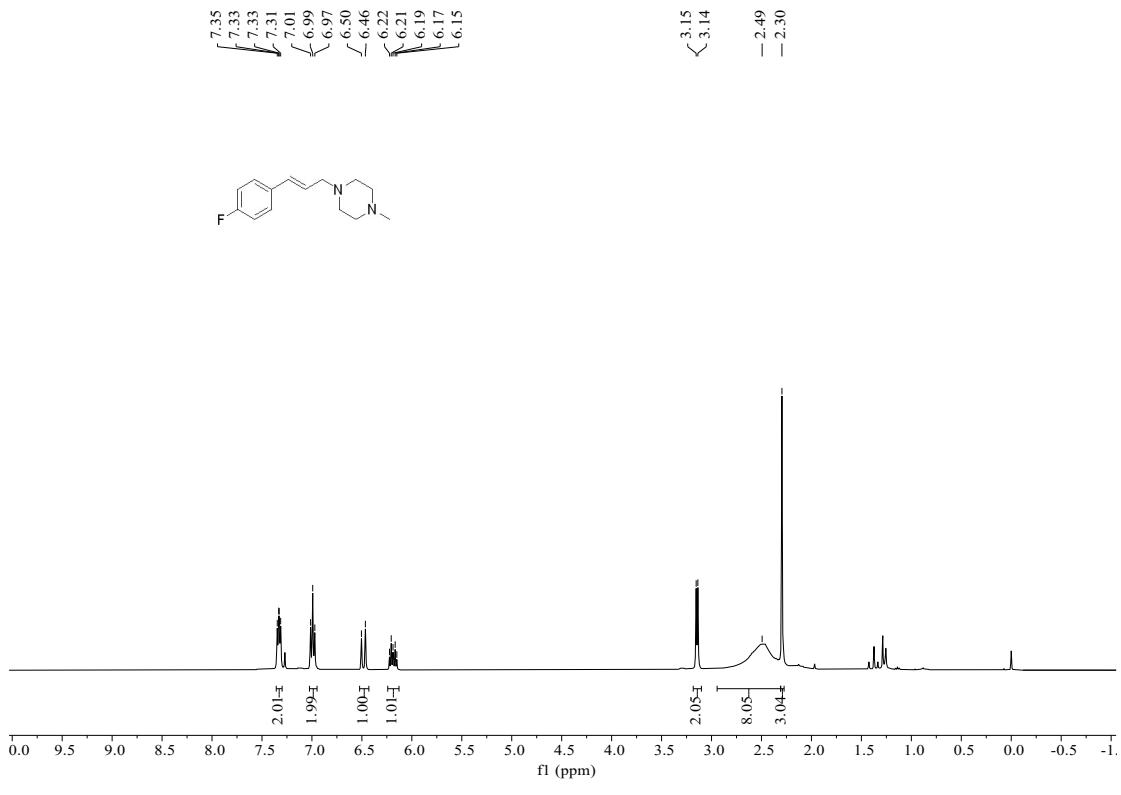
¹H NMR Spectrum of 3aa in CDCl_3 at 400 MHz

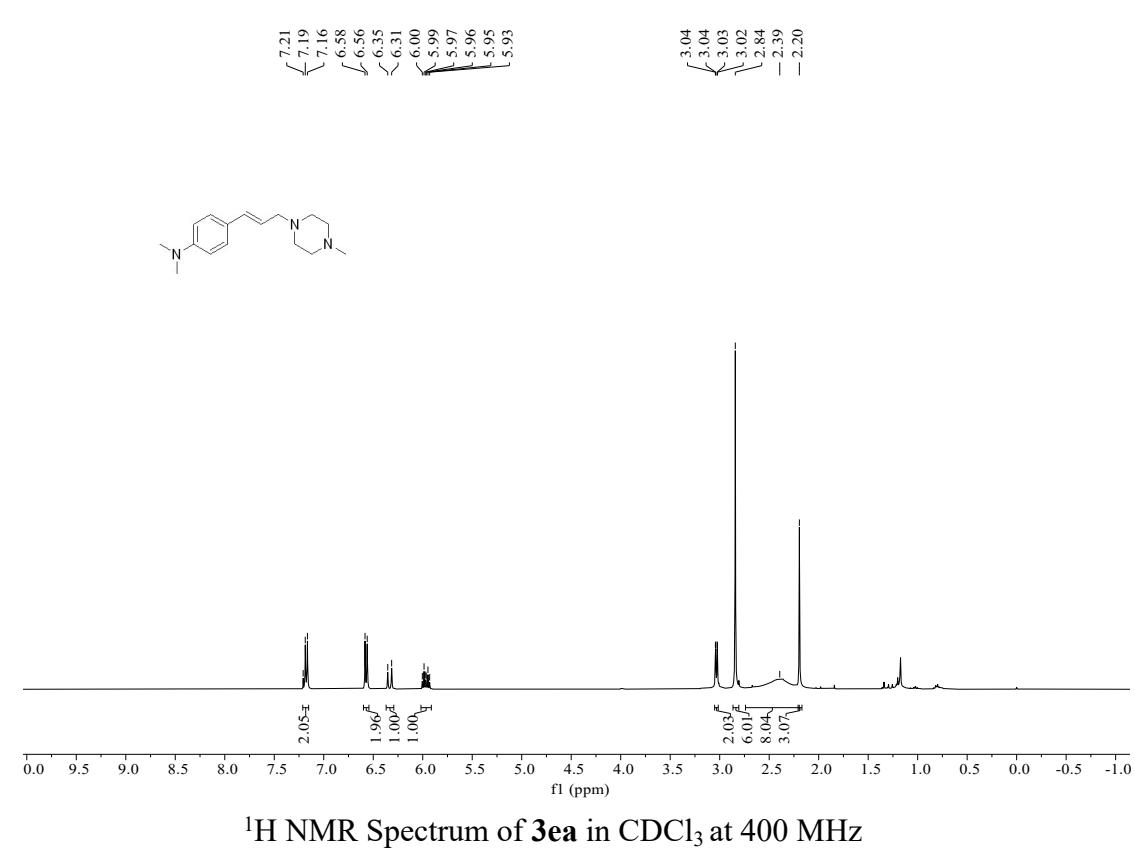
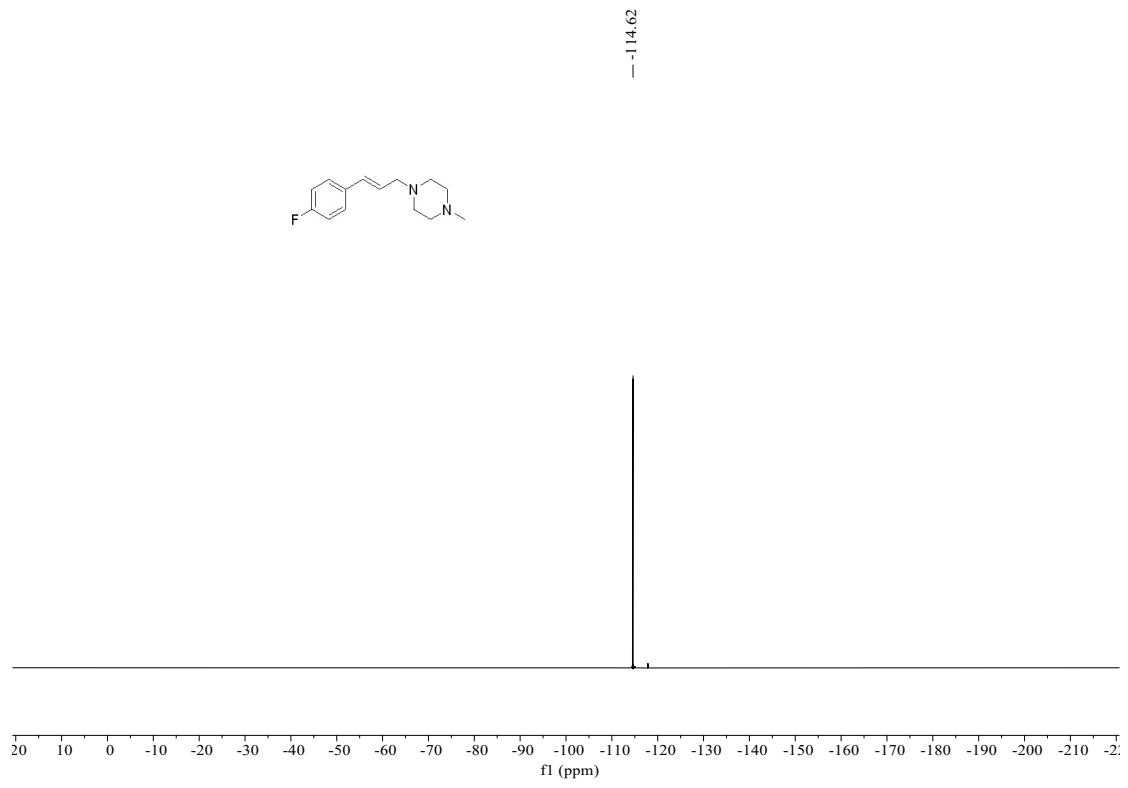


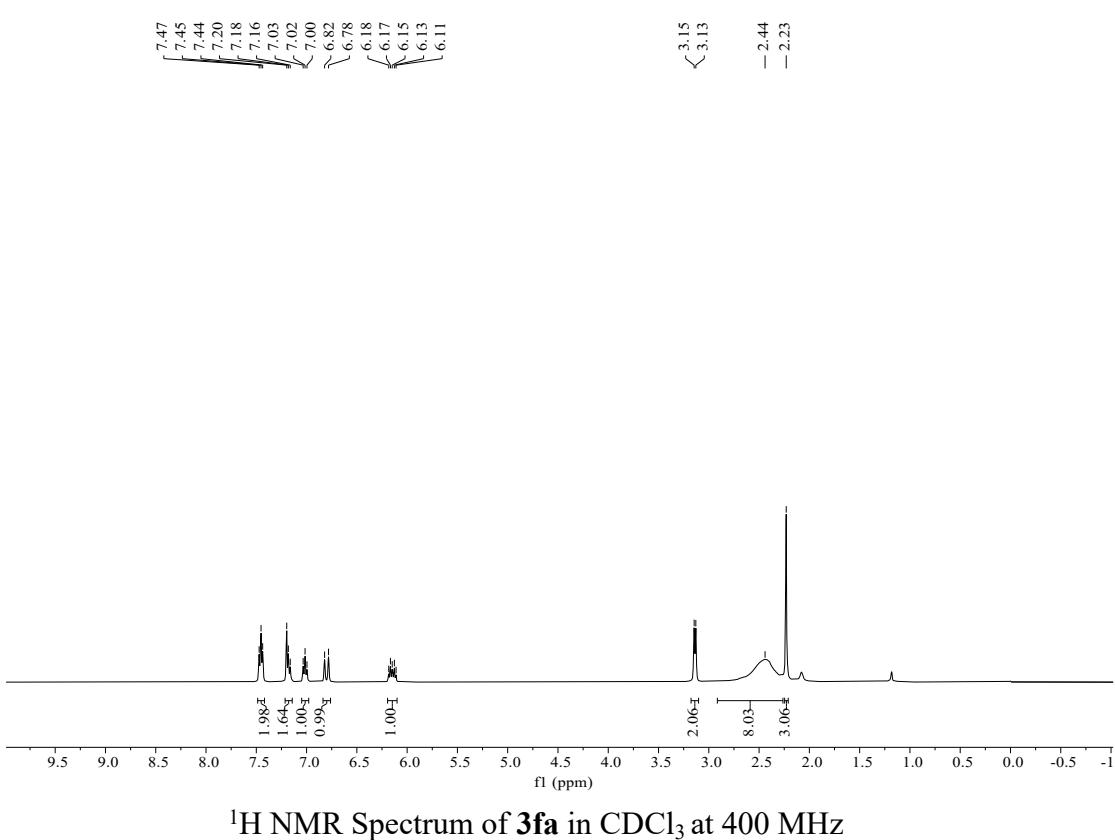
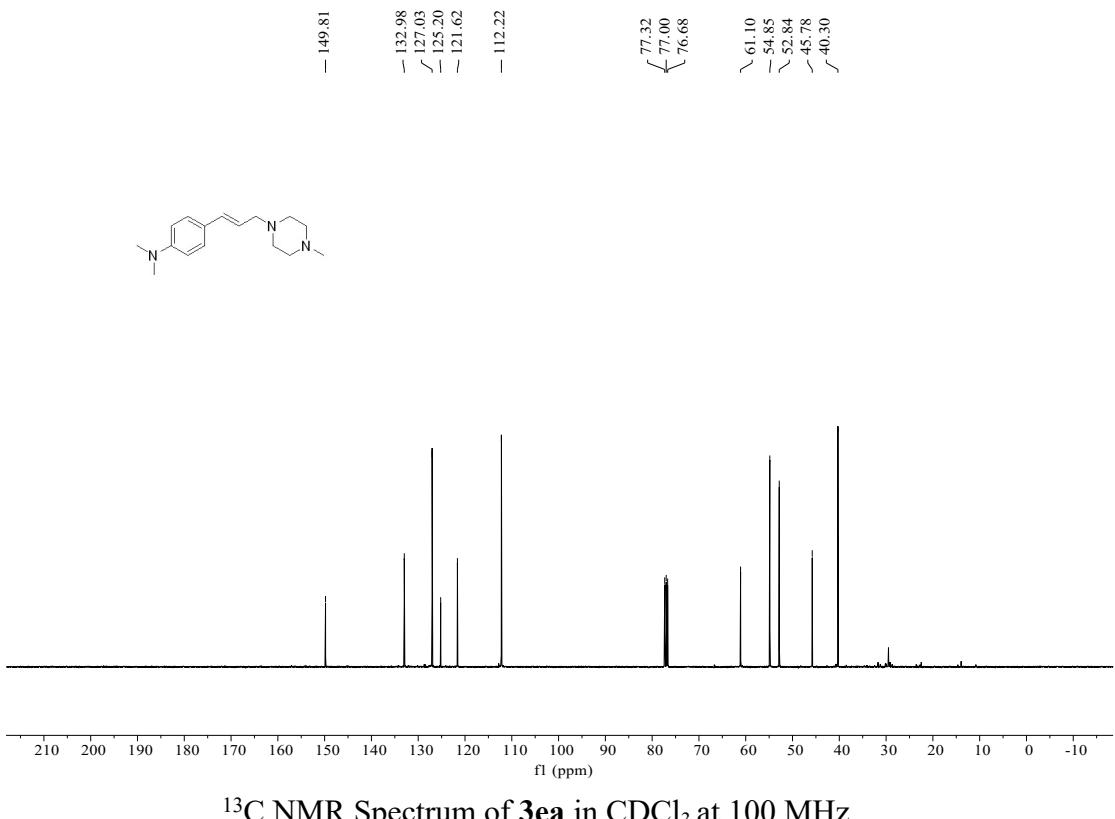
¹³C NMR Spectrum of 3aa in CDCl_3 at 100 MHz

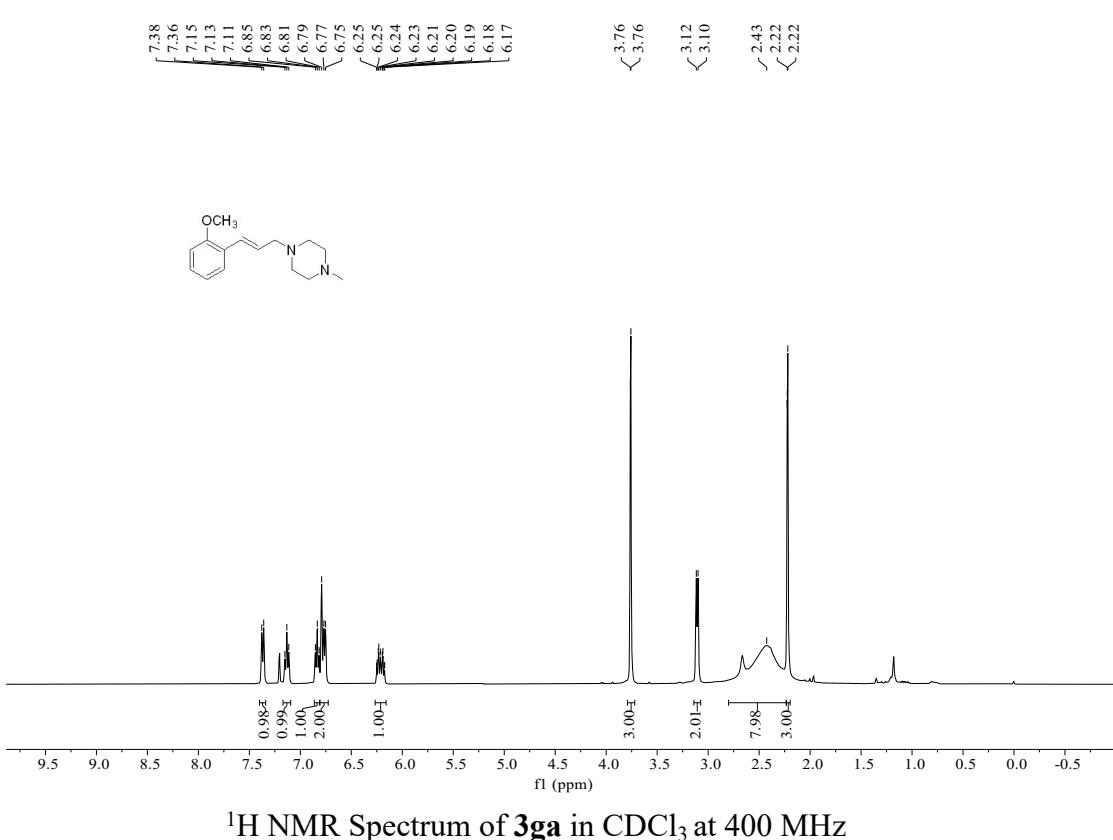
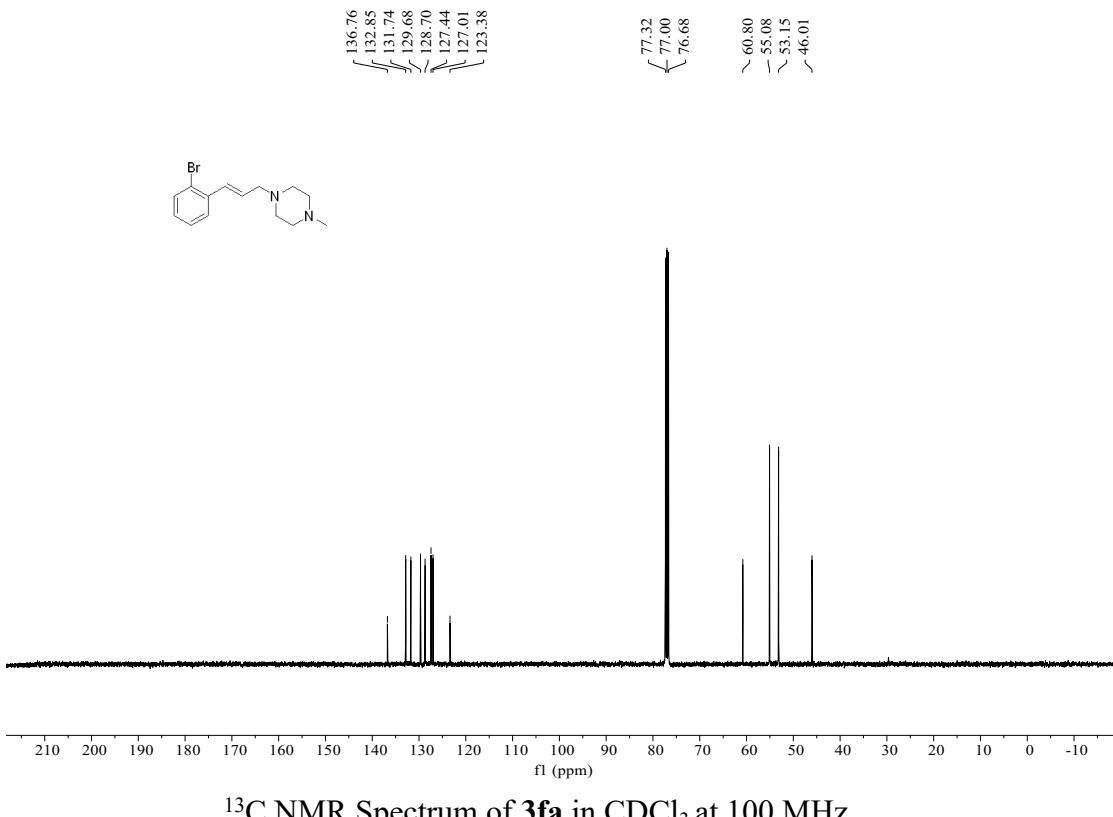


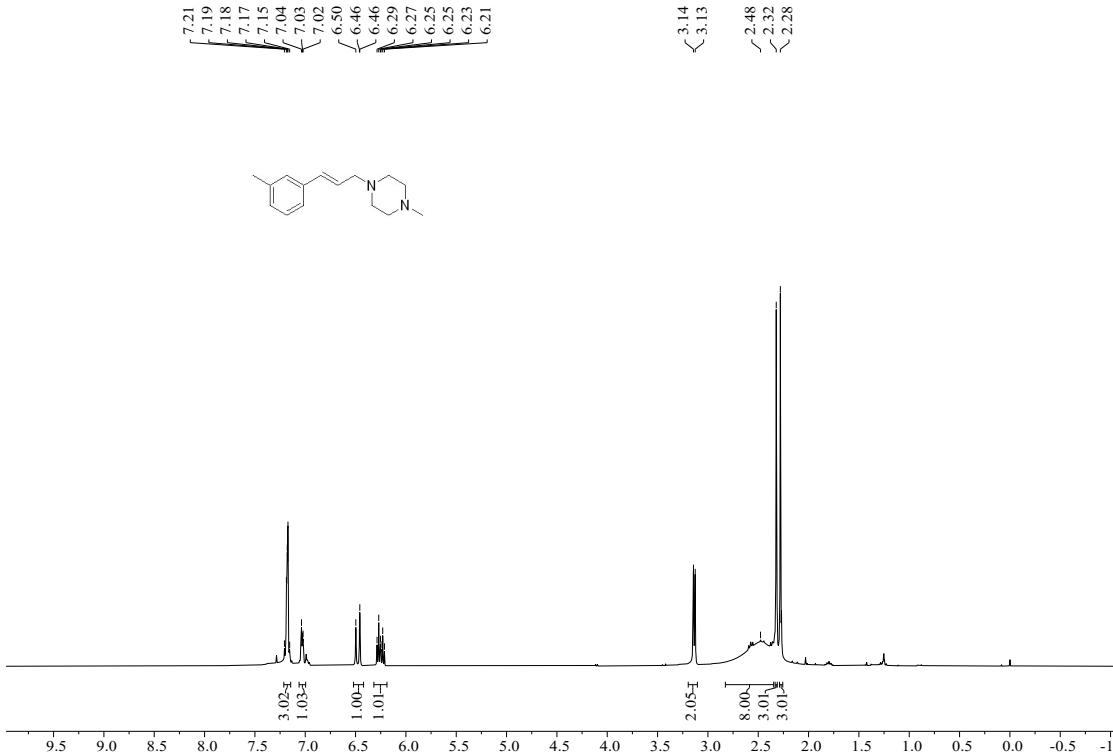
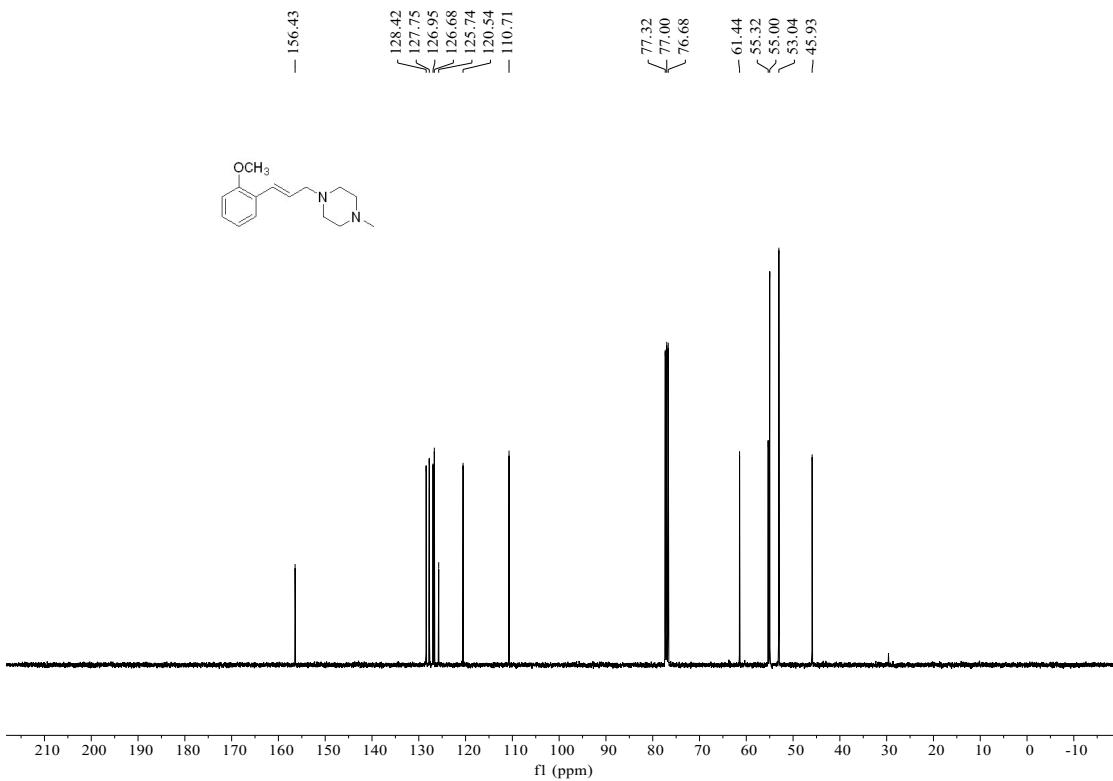


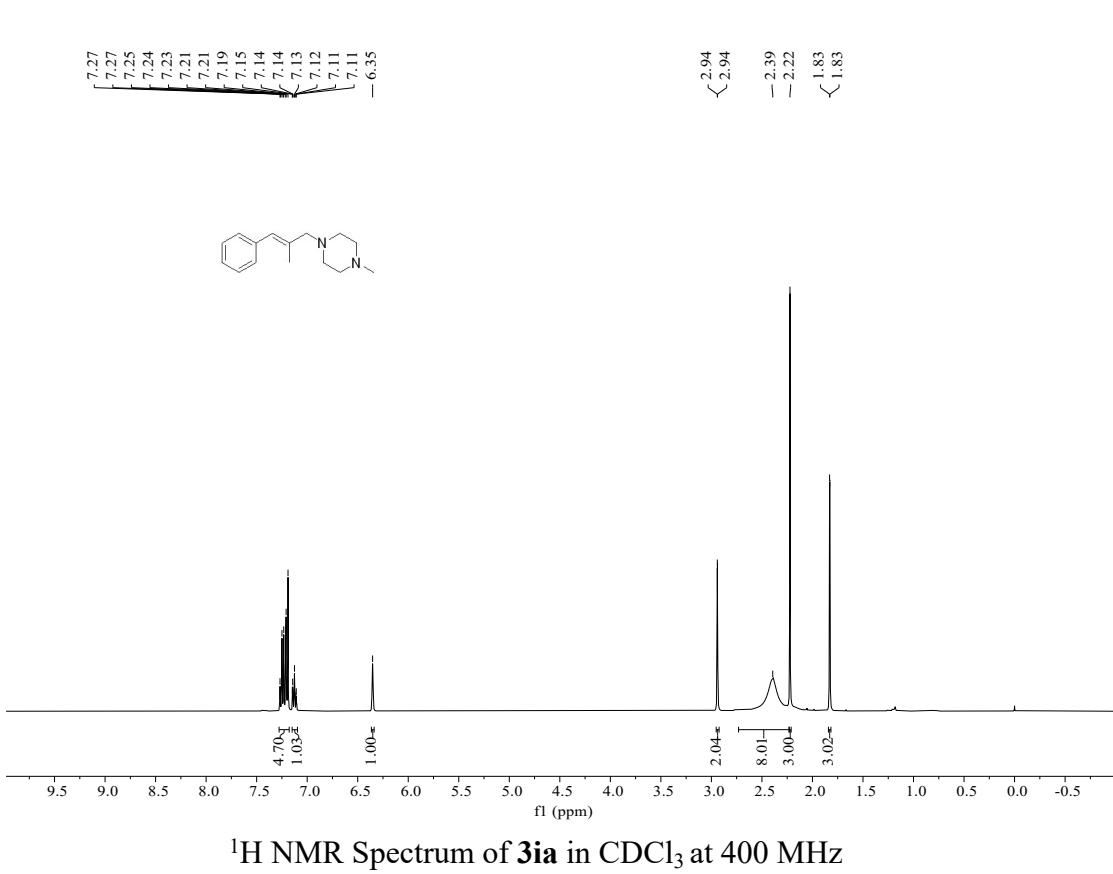
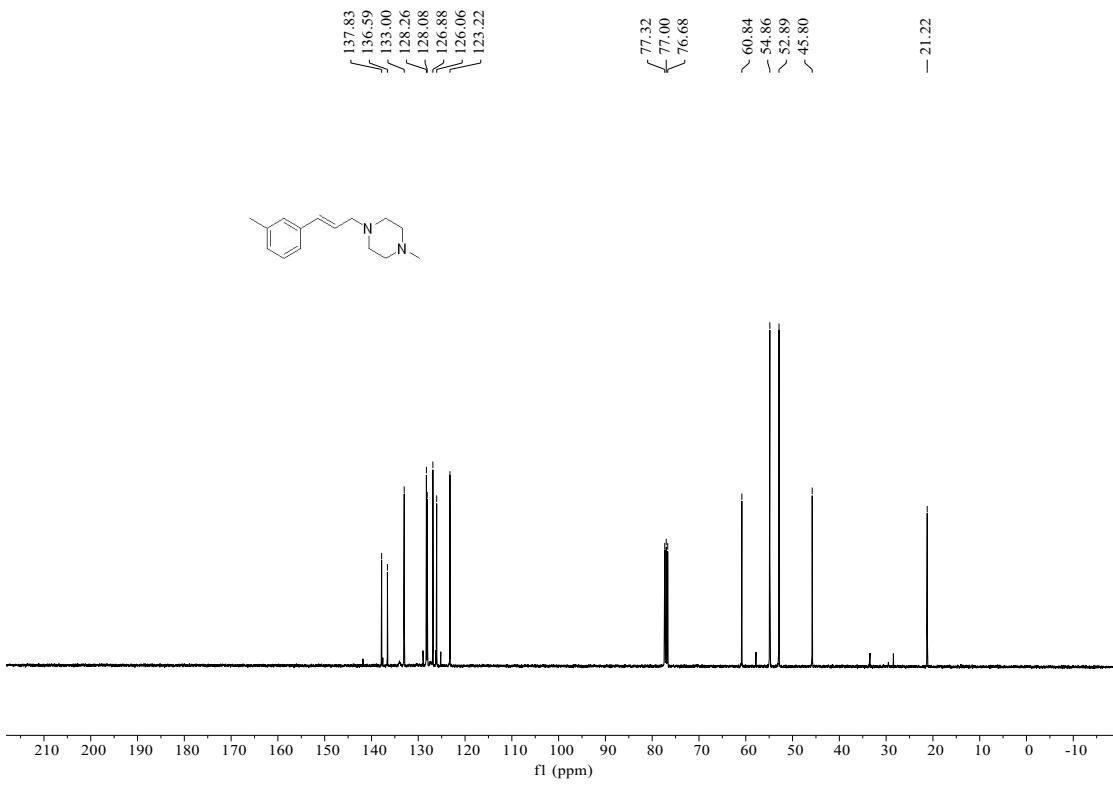


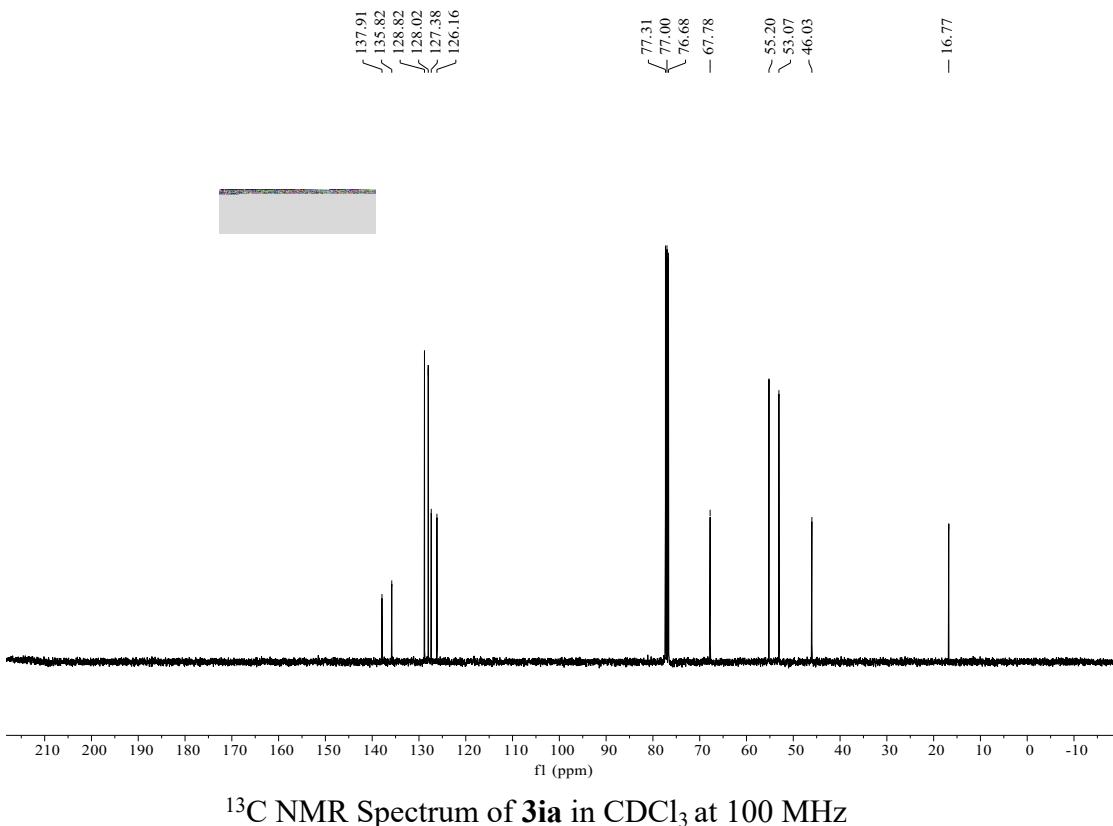




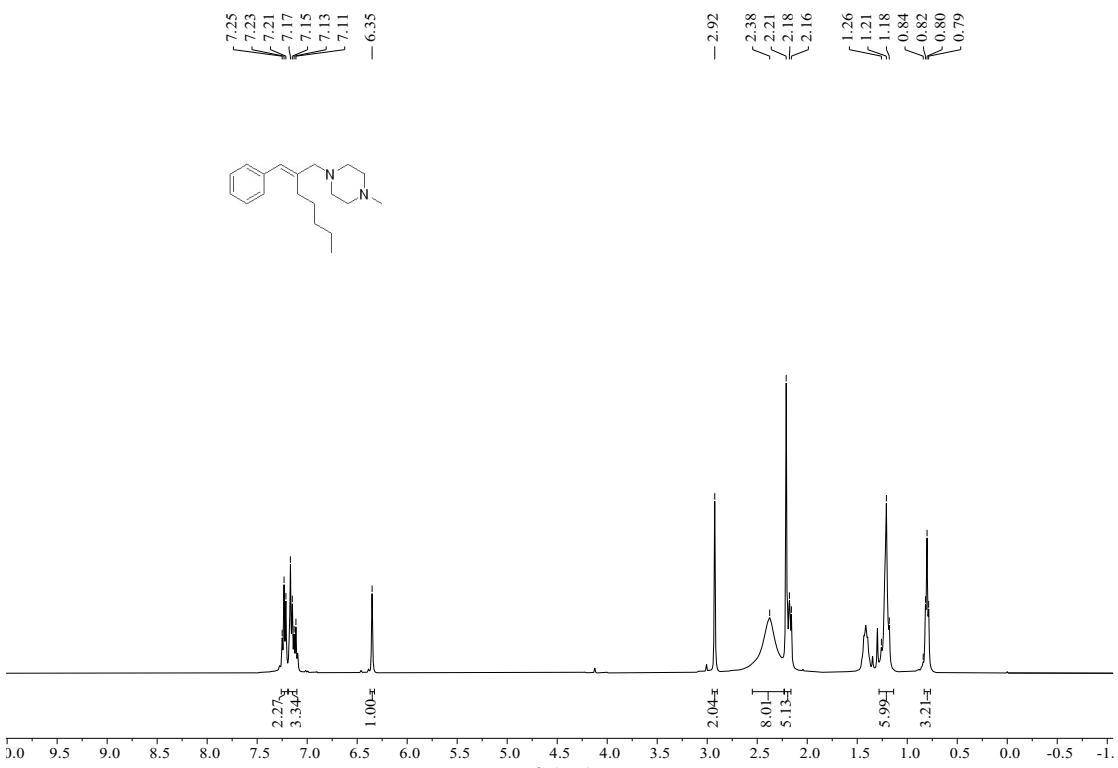




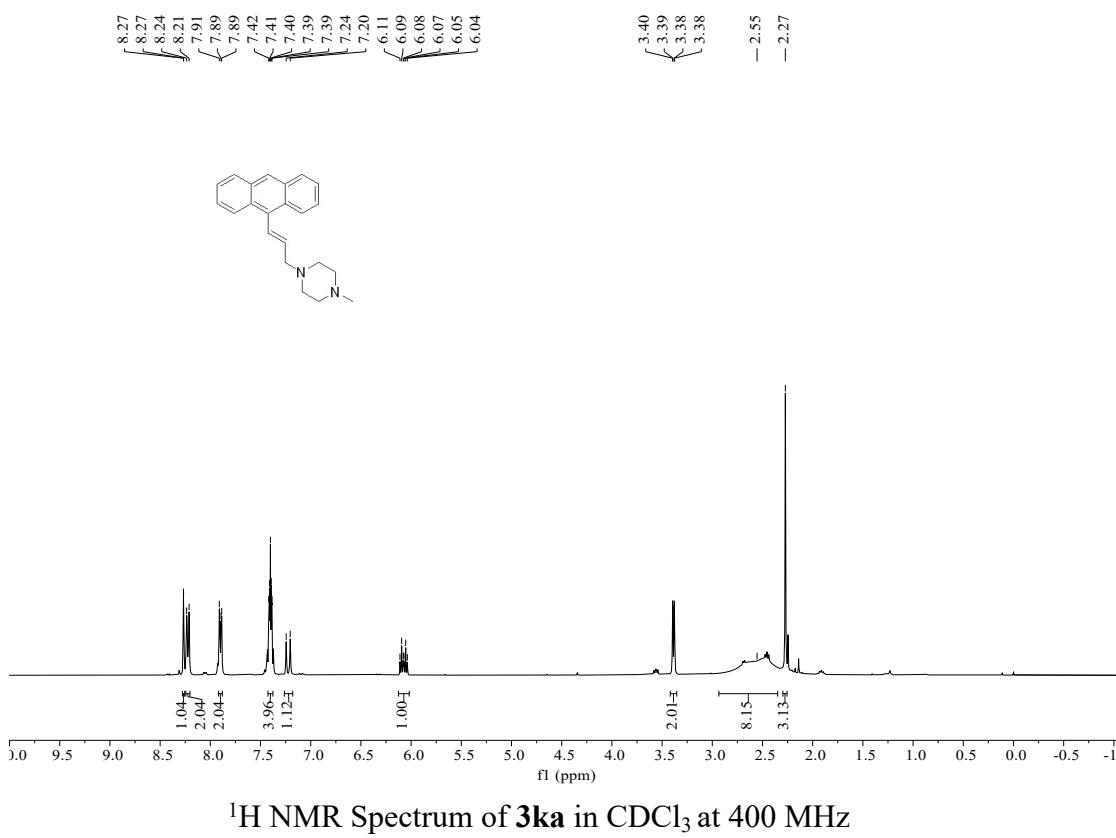
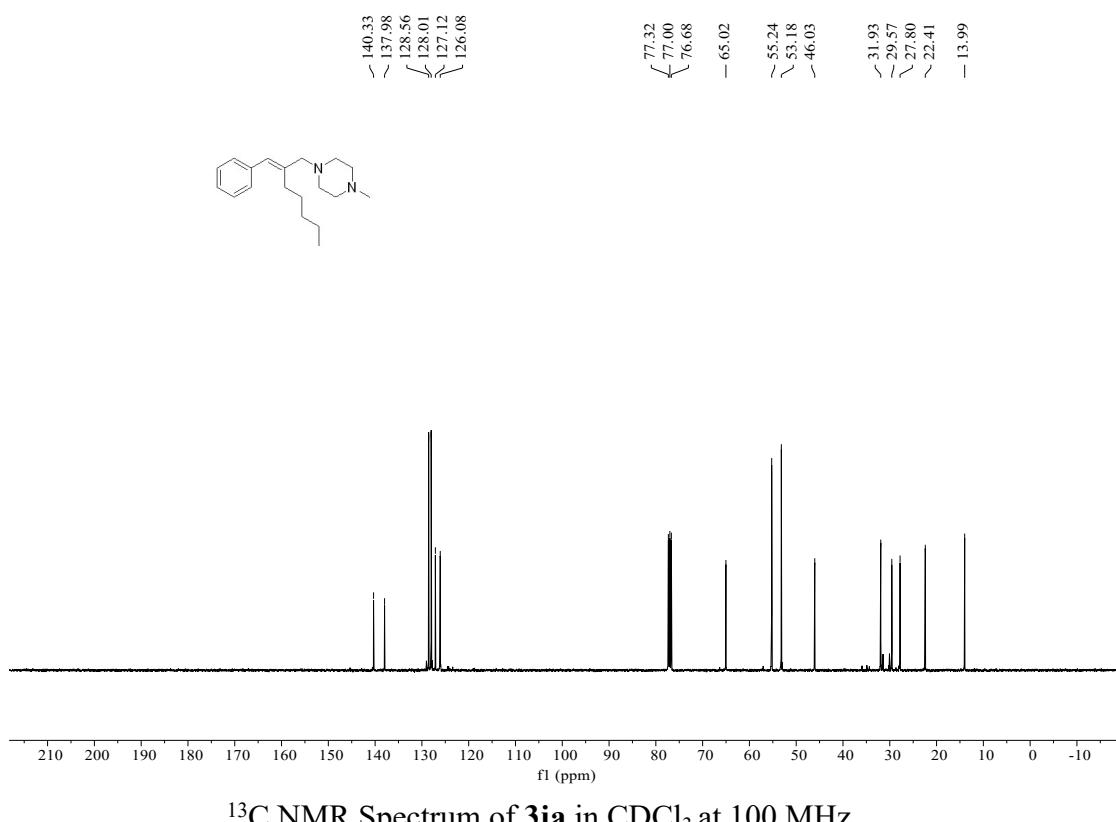


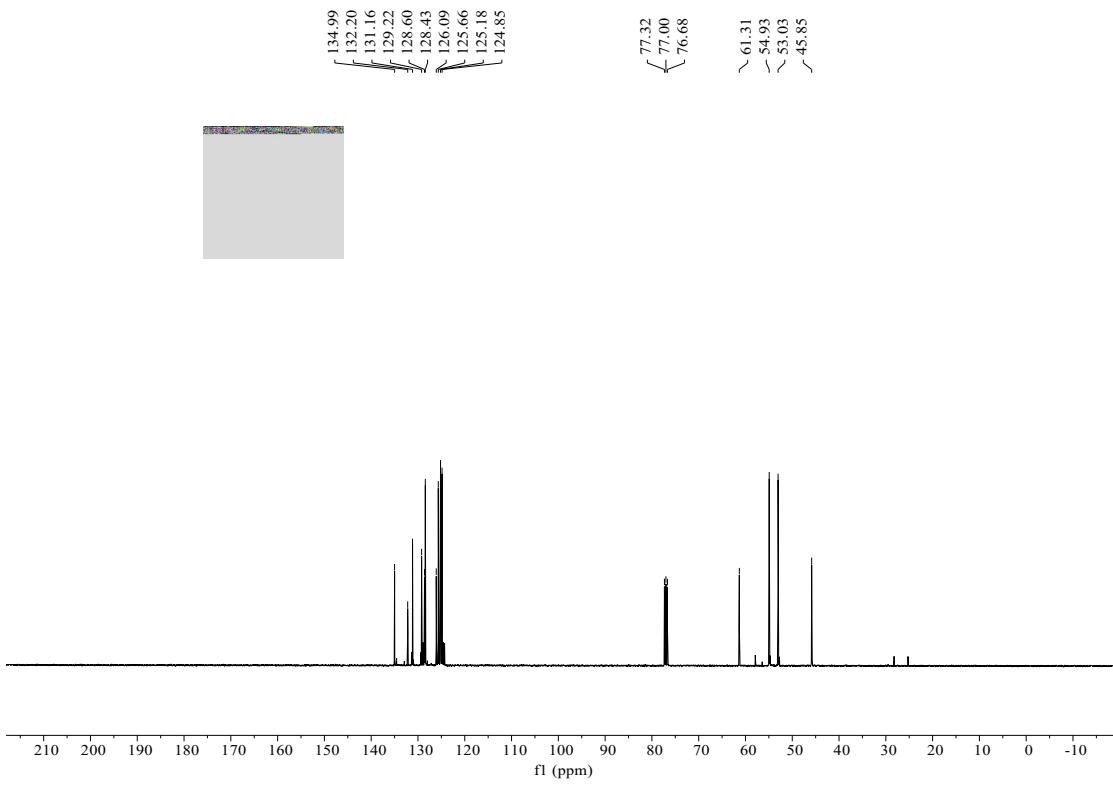


¹³C NMR Spectrum of **3ia** in CDCl_3 at 100 MHz

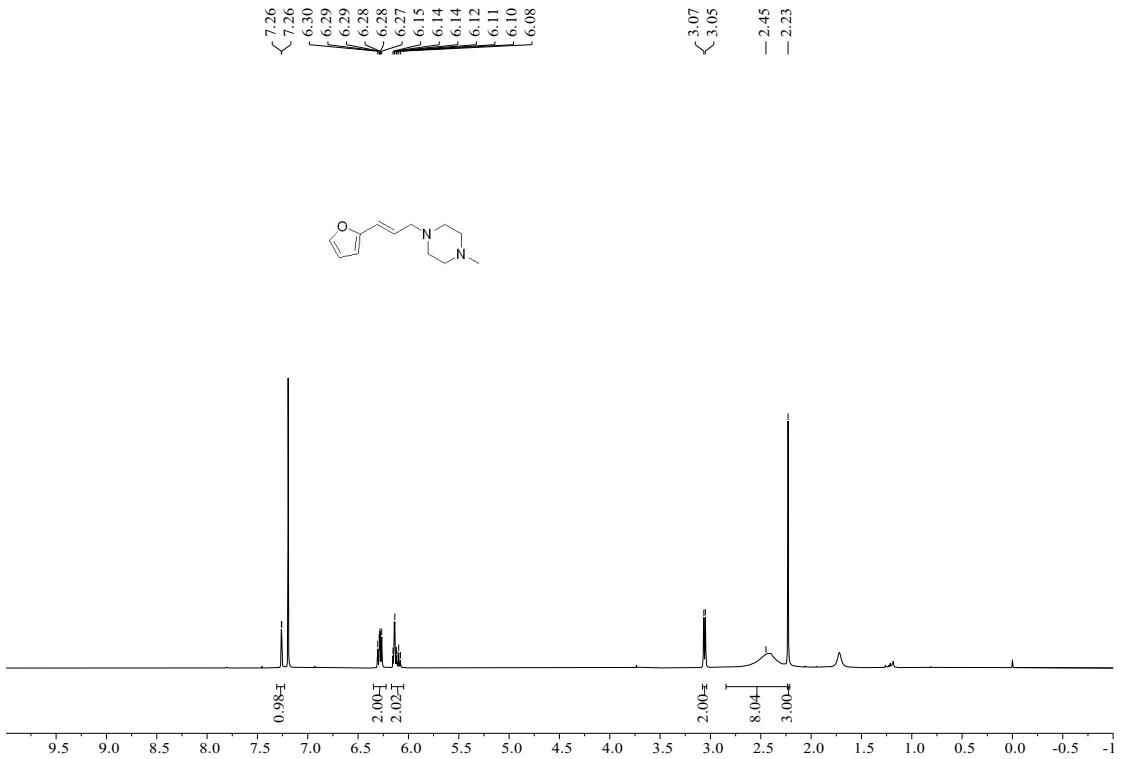


¹H NMR Spectrum of **3ja** in CDCl_3 at 400 MHz

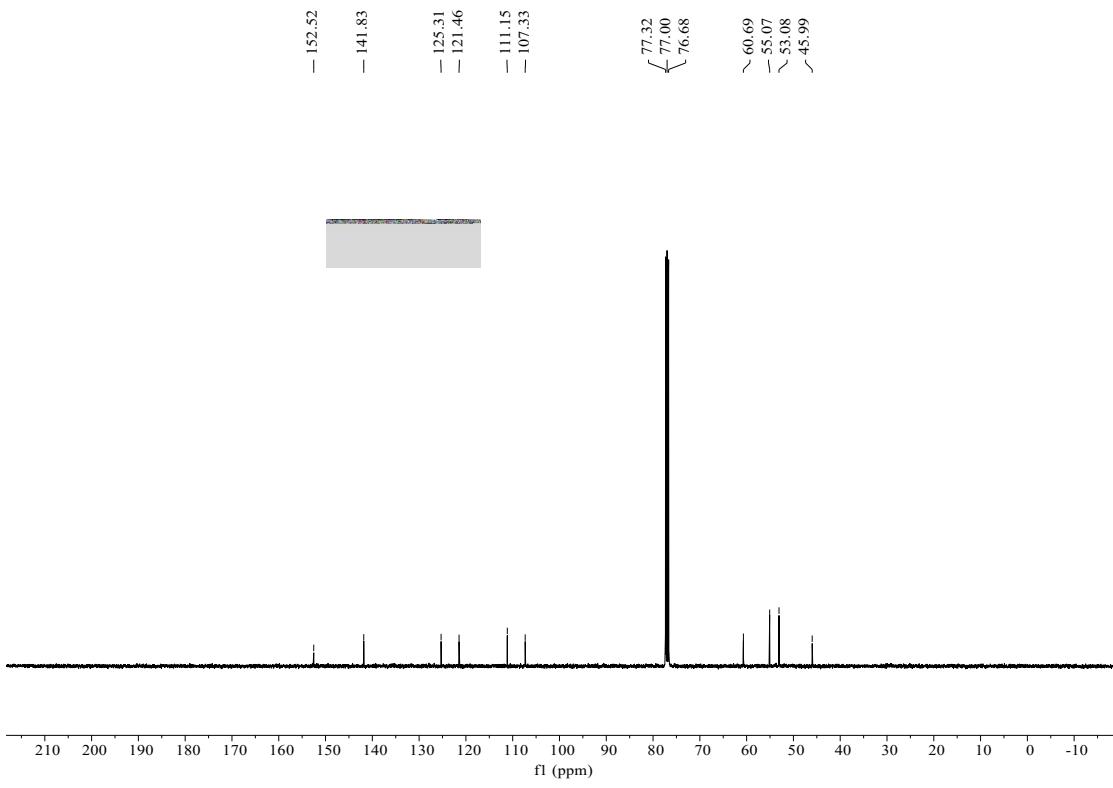




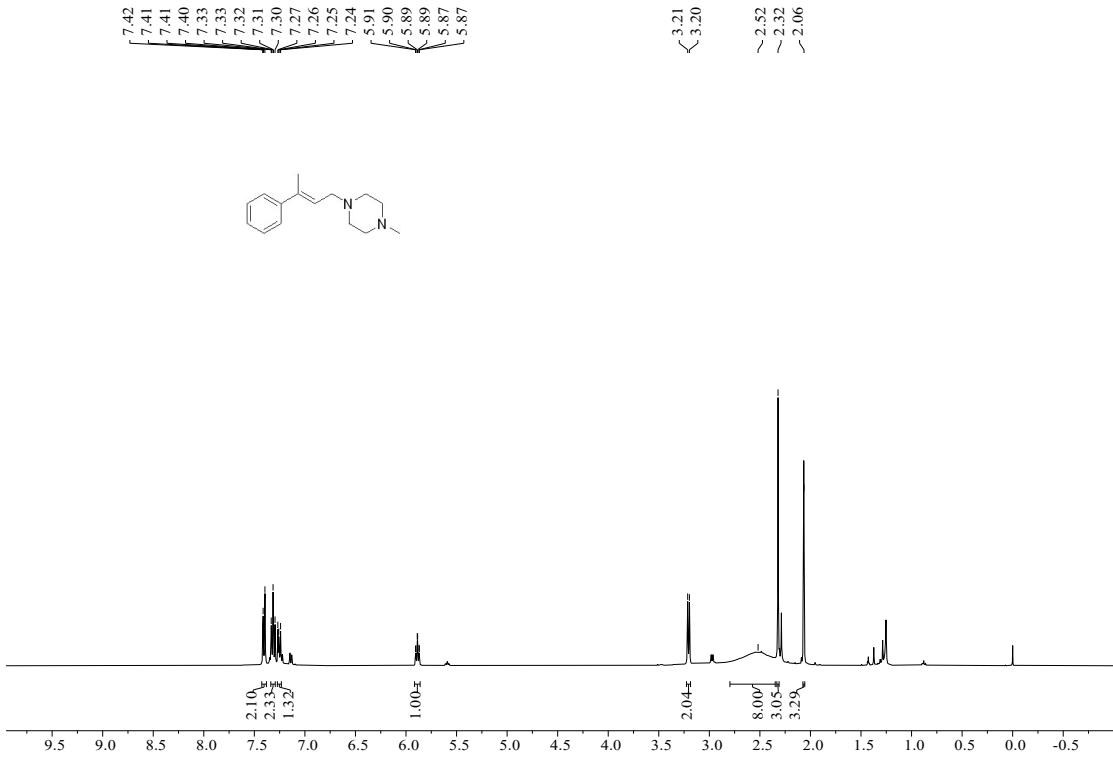
¹³C NMR Spectrum of **3ka** in CDCl_3 at 100 MHz



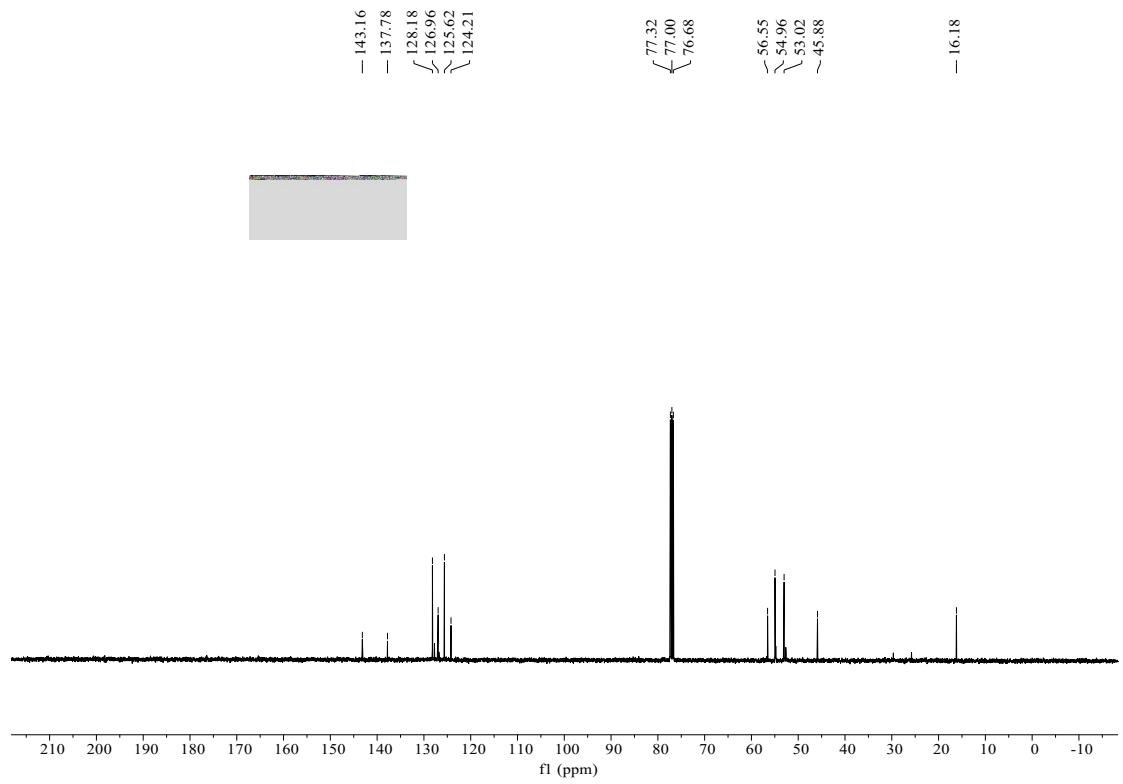
¹H NMR Spectrum of **3la** in CDCl_3 at 400 MHz



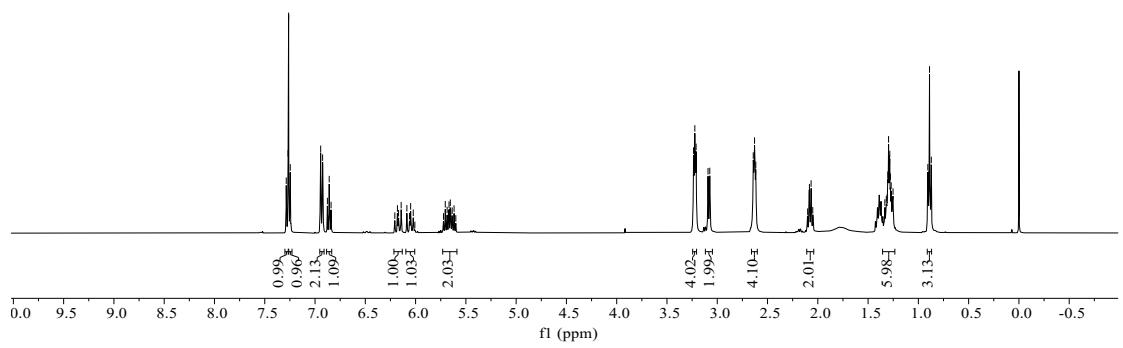
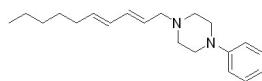
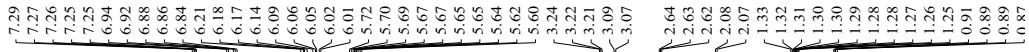
¹³C NMR Spectrum of **3la** in CDCl_3 at 100 MHz



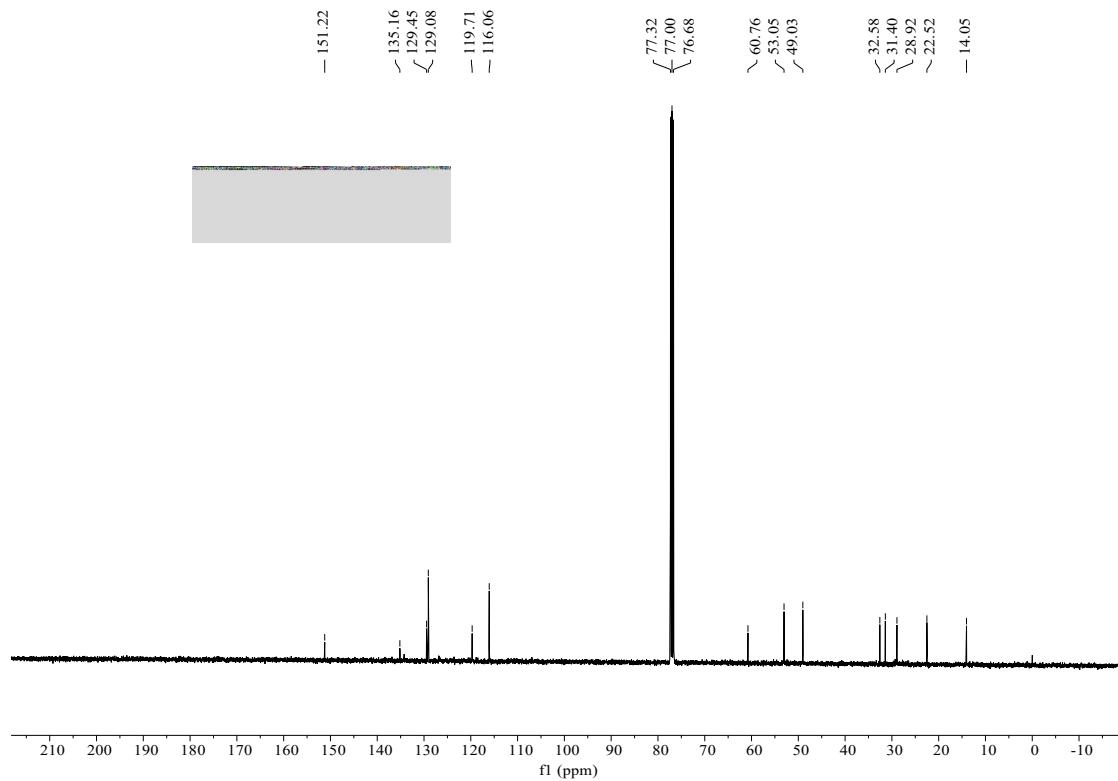
¹H NMR Spectrum of **3ma** in CDCl_3 at 400 MHz



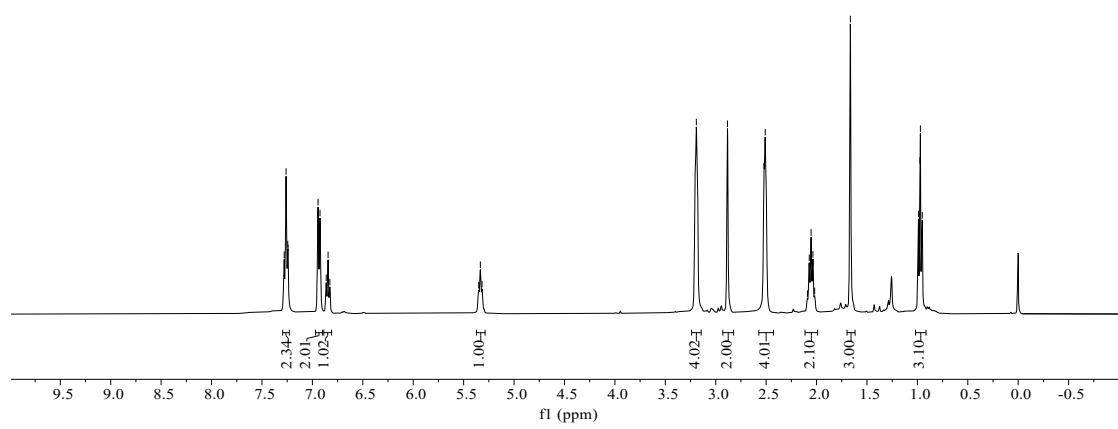
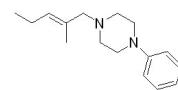
¹³C NMR Spectrum of **3ma** in CDCl₃ at 100 MHz



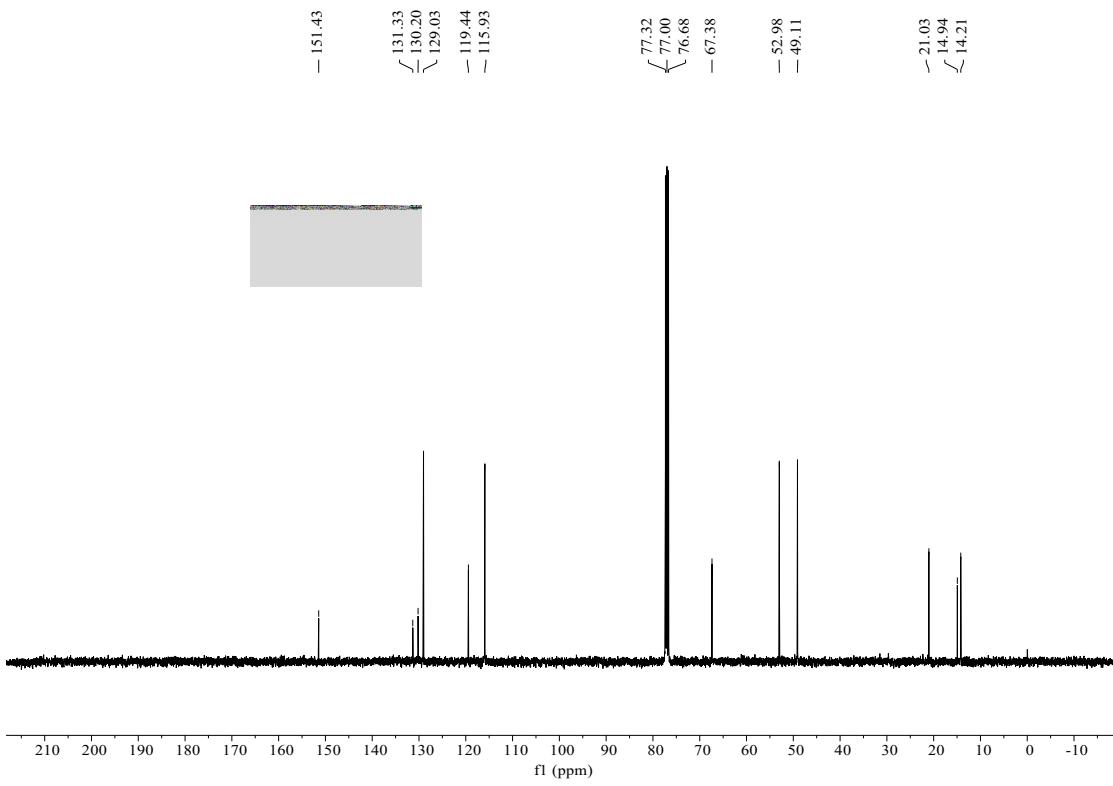
¹H NMR Spectrum of **3nb** in CDCl₃ at 400 MHz



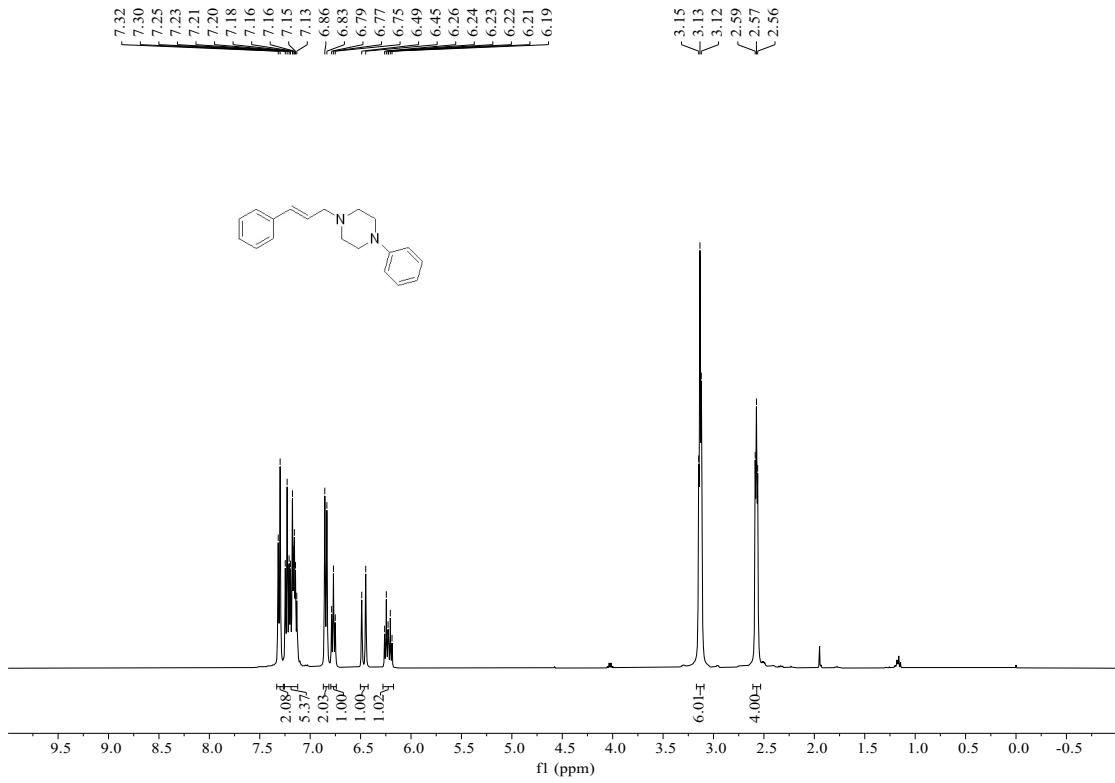
¹³C NMR Spectrum of **3nb** in CDCl₃ at 100 MHz



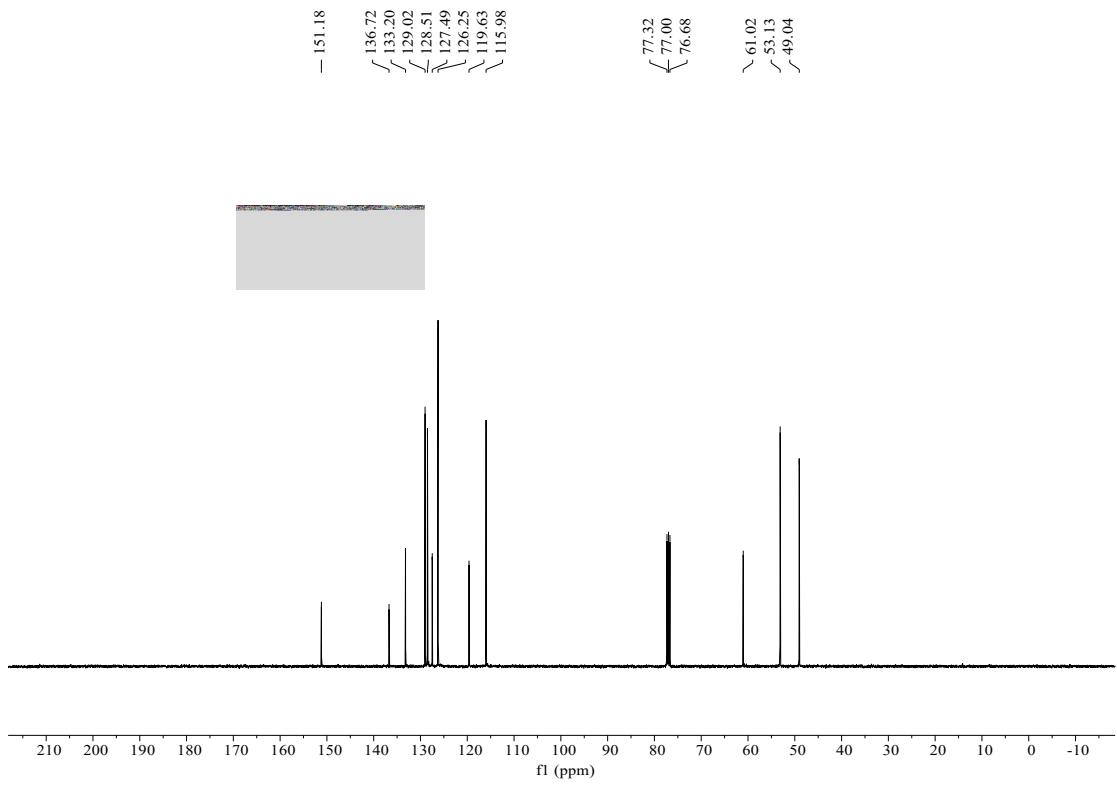
¹H NMR Spectrum of **3ob** in CDCl₃ at 400 MHz



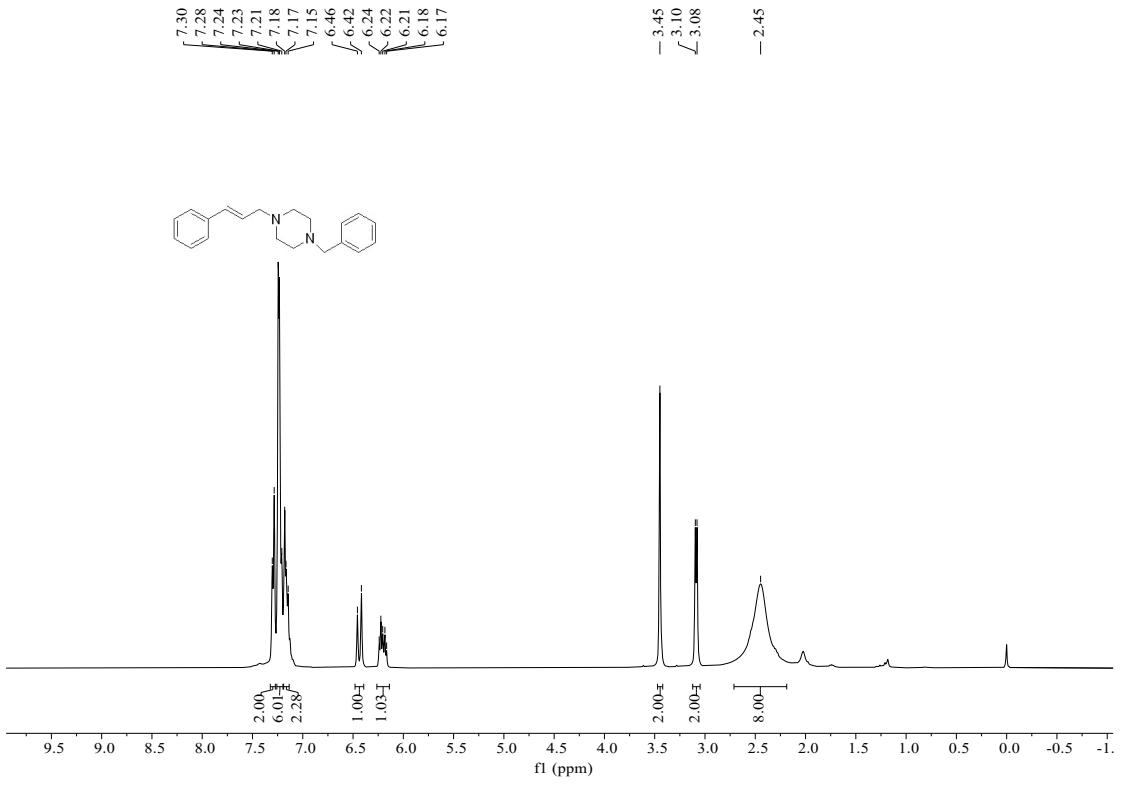
¹³C NMR Spectrum of **3ob** in CDCl_3 at 100 MHz



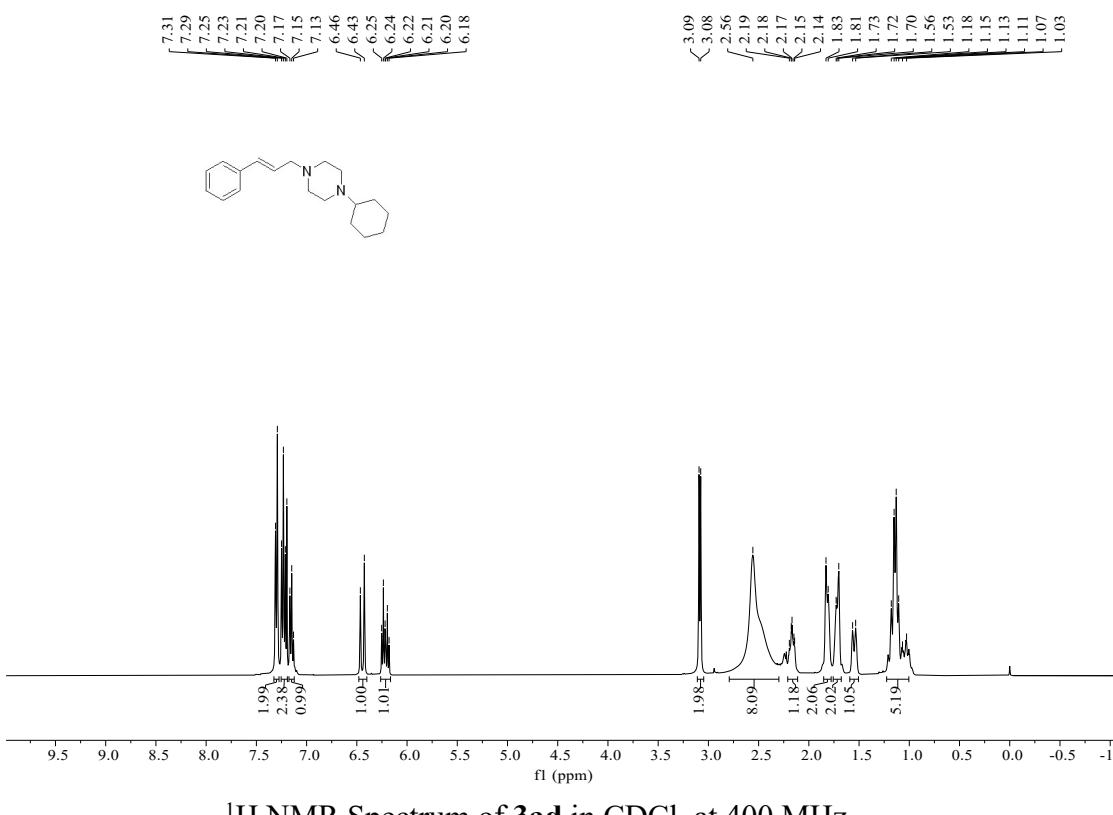
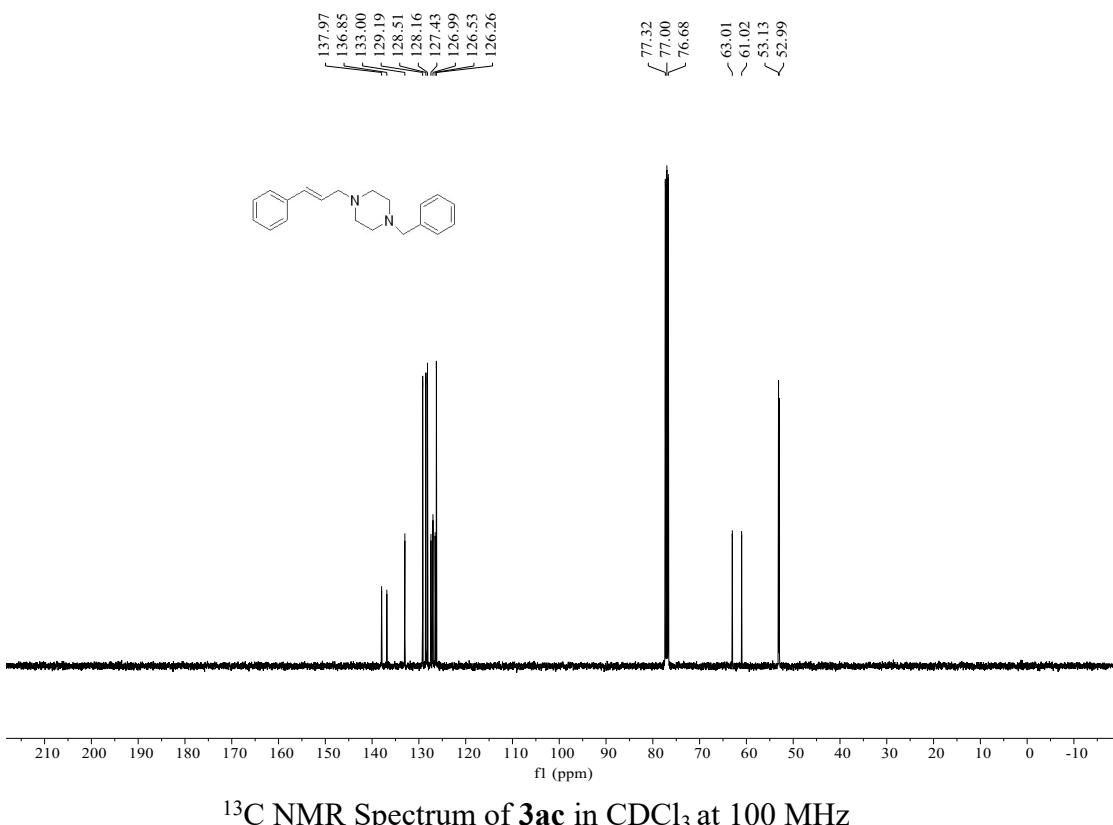
¹H NMR Spectrum of **3ab** in CDCl_3 at 400 MHz

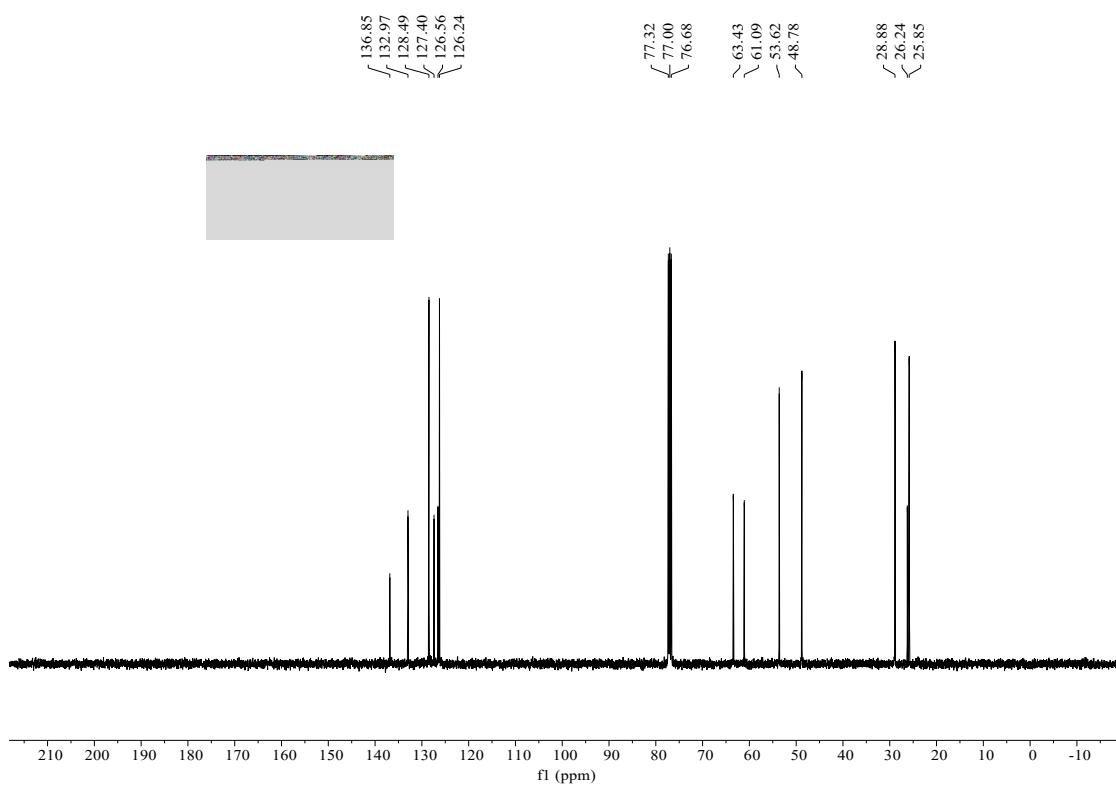


¹³C NMR Spectrum of **3ab** in CDCl_3 at 100 MHz

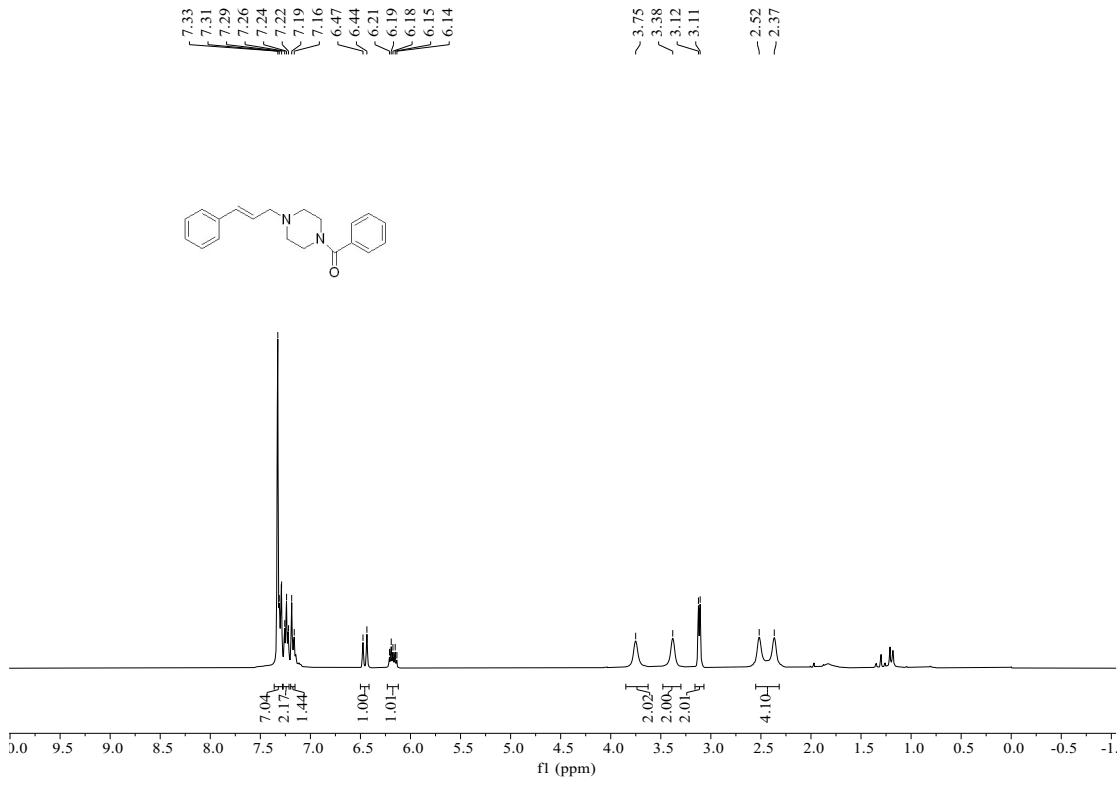


¹H NMR Spectrum of **3ac** in CDCl_3 at 400 MHz

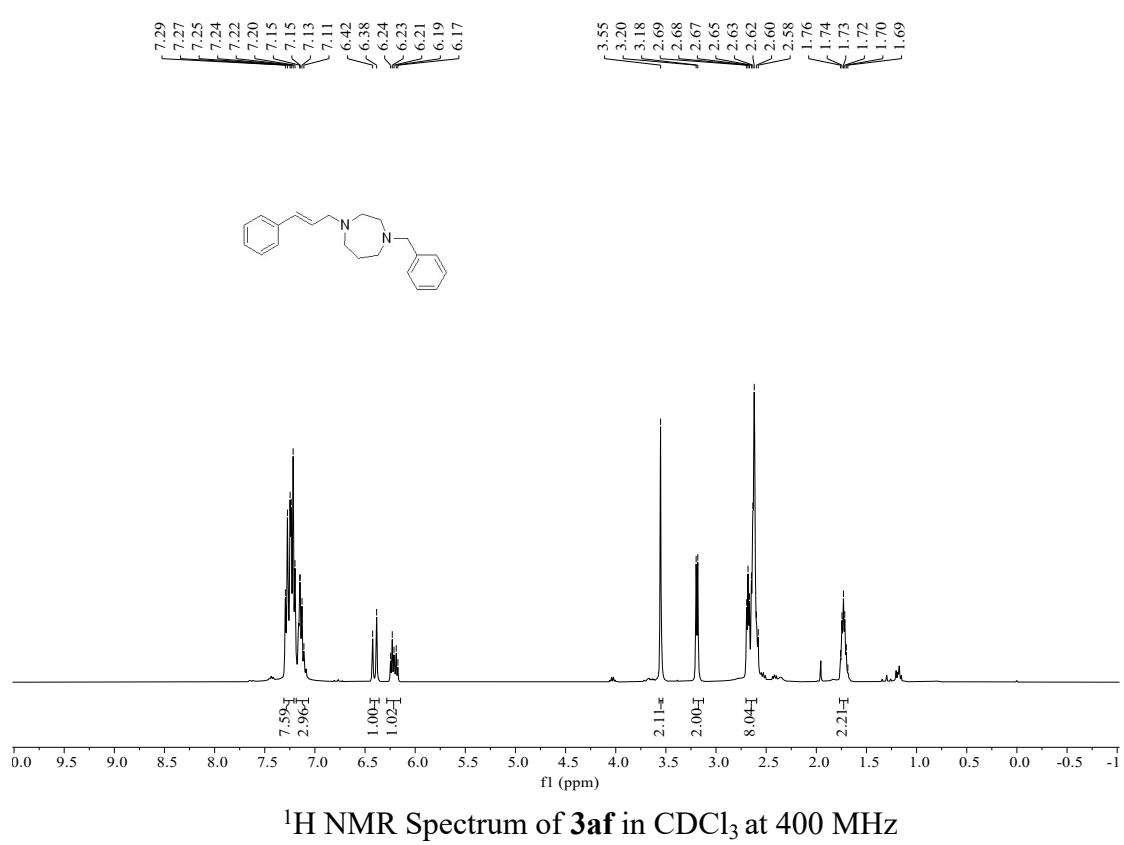
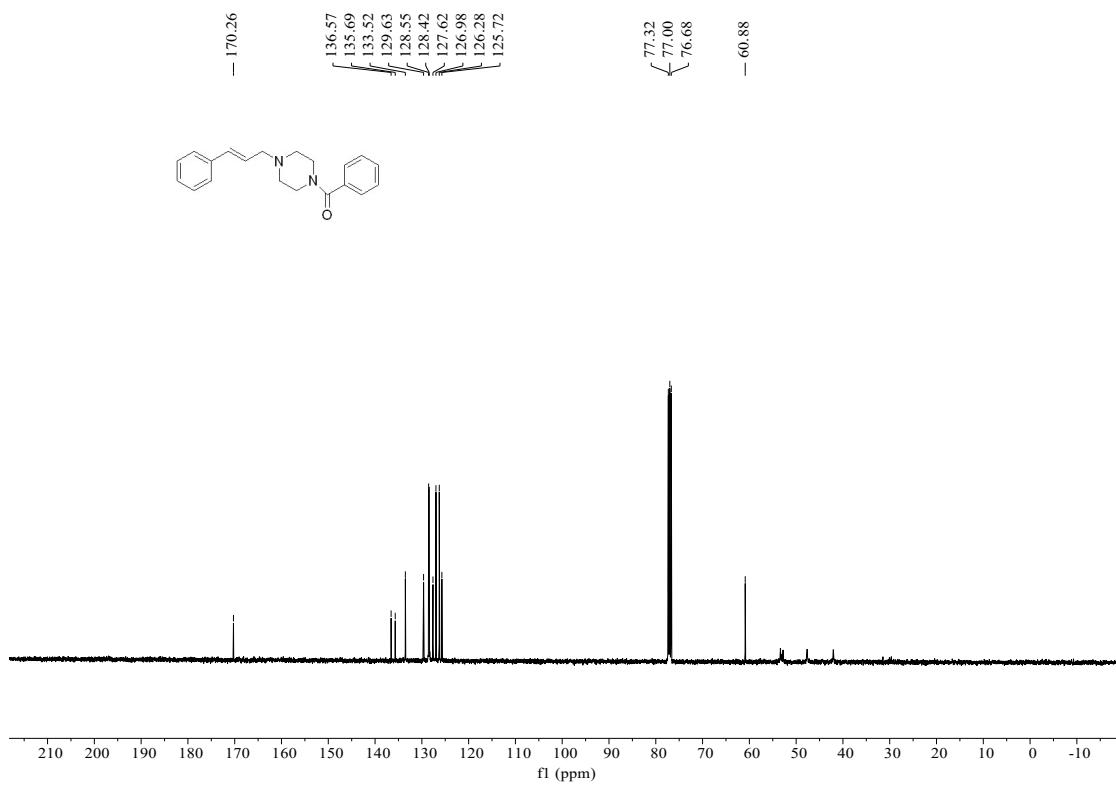


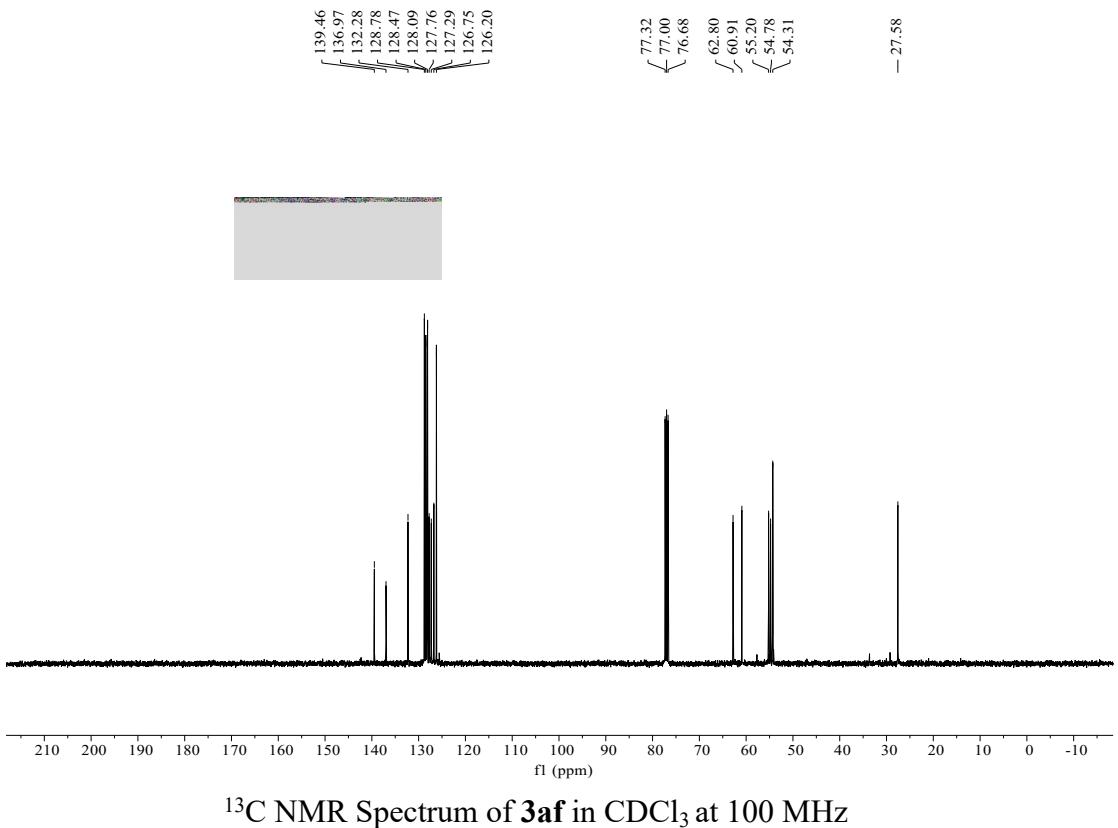


¹³C NMR Spectrum of **3ad** in CDCl_3 at 100 MHz

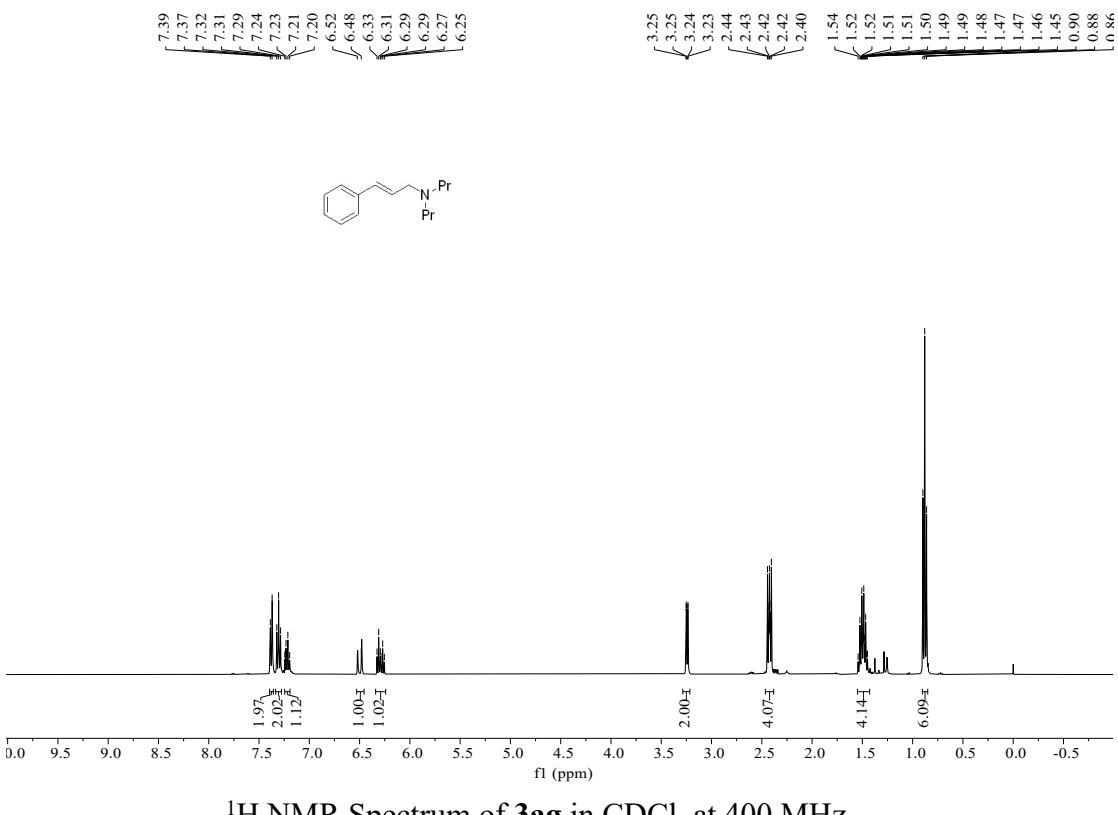


¹H NMR Spectrum of **3ae** in CDCl_3 at 400 MHz

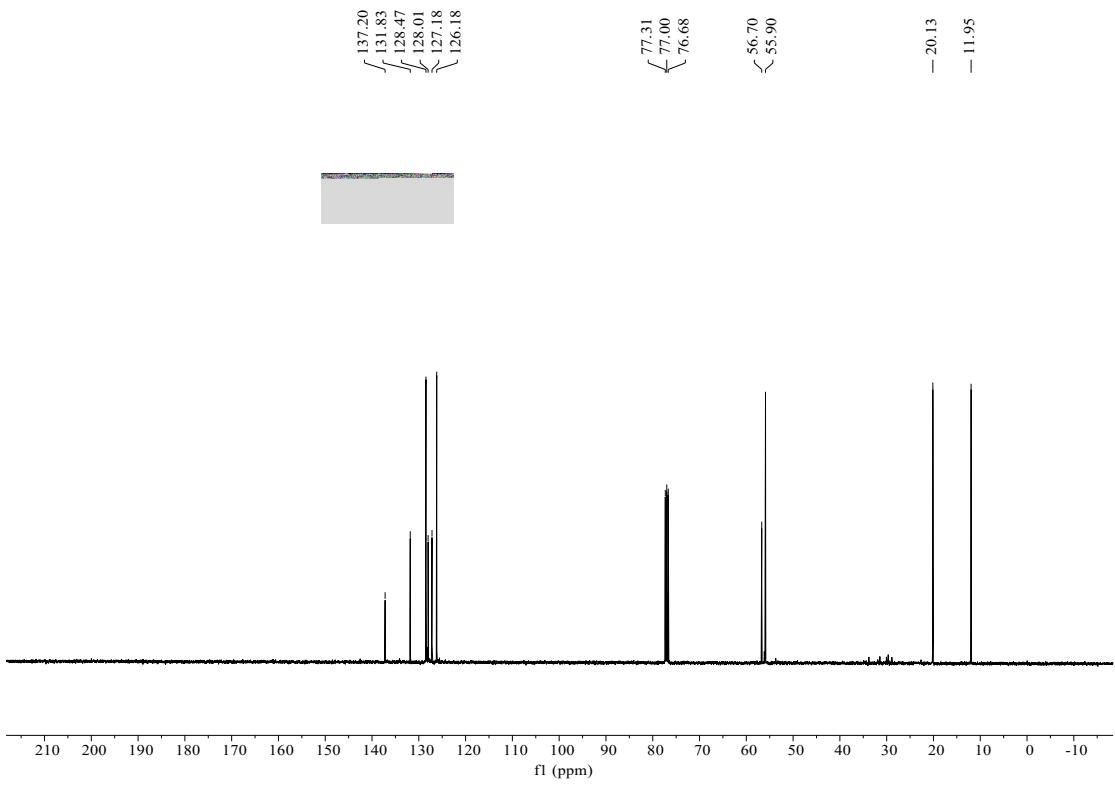




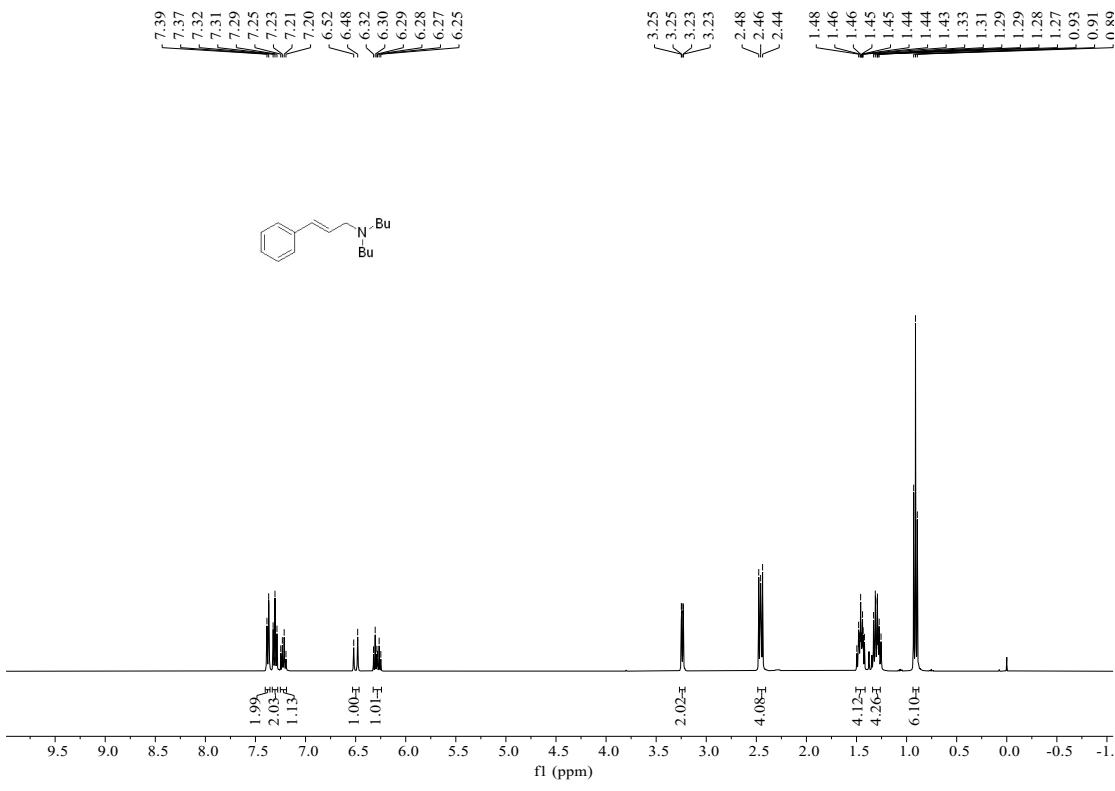
¹³C NMR Spectrum of **3af** in CDCl_3 at 100 MHz



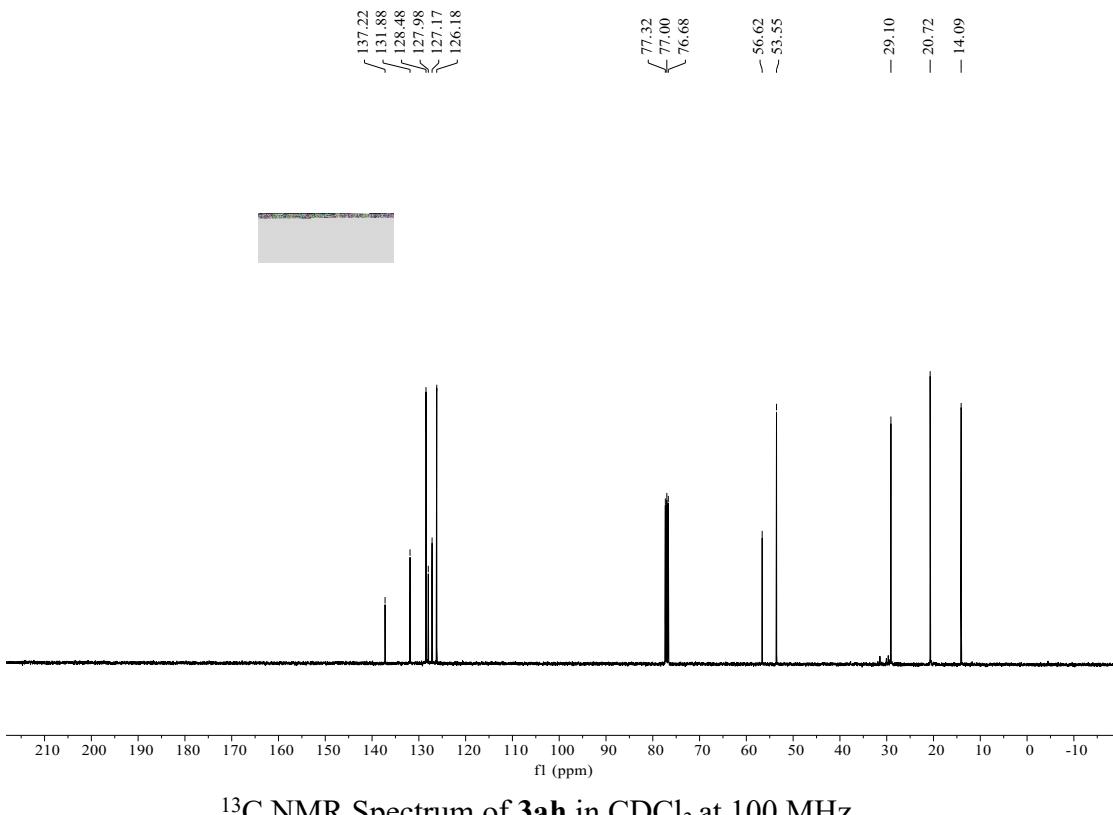
¹H NMR Spectrum of **3ag** in CDCl_3 at 400 MHz



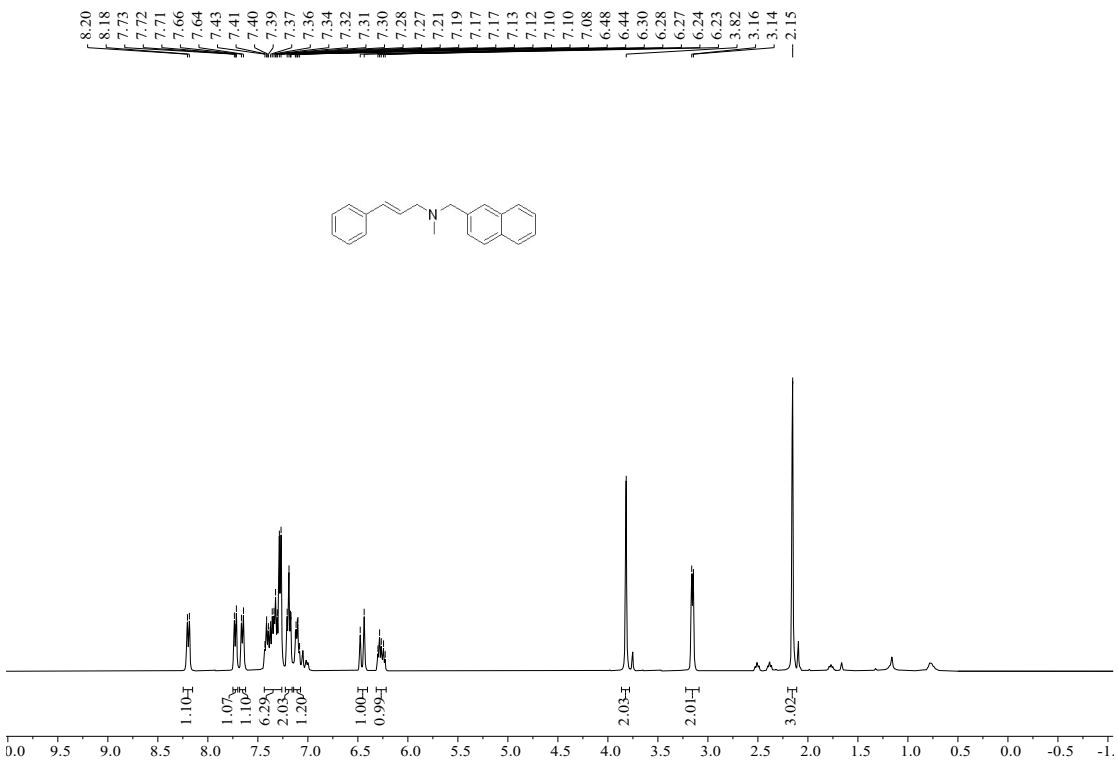
¹³C NMR Spectrum of **3ag** in CDCl_3 at 100 MHz



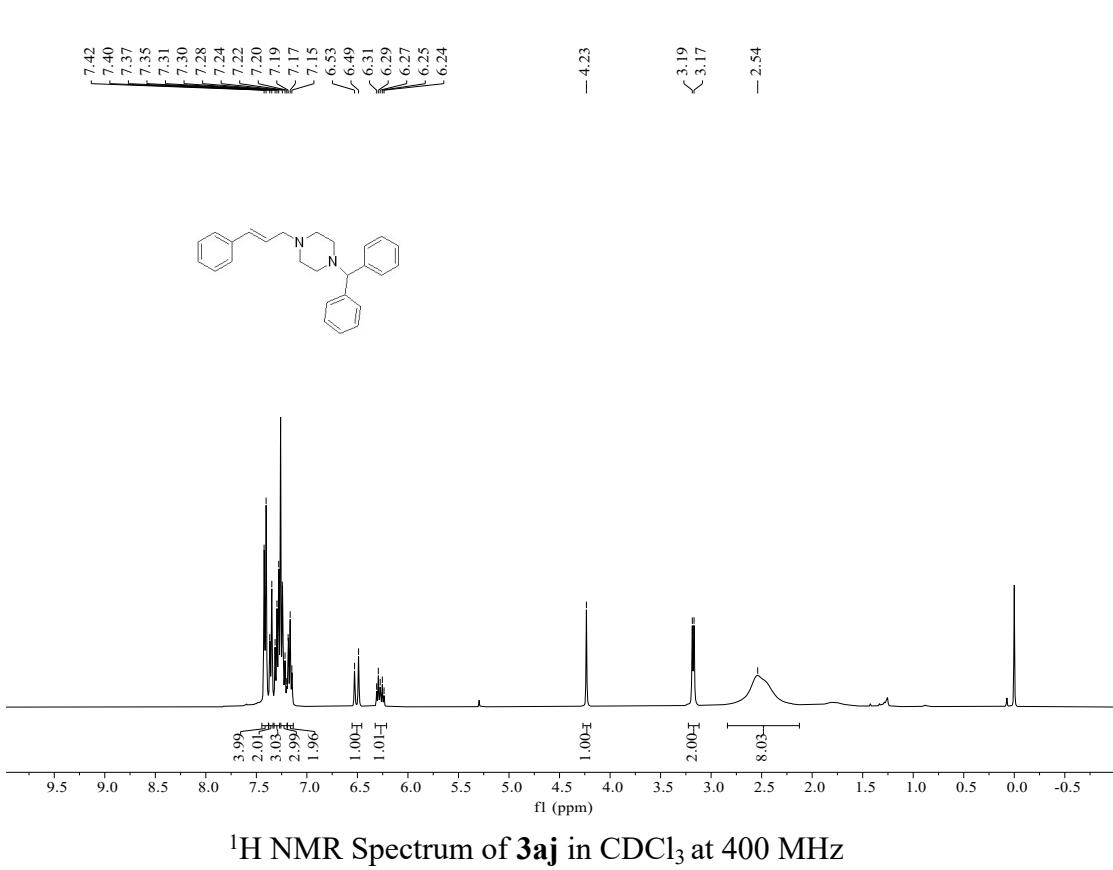
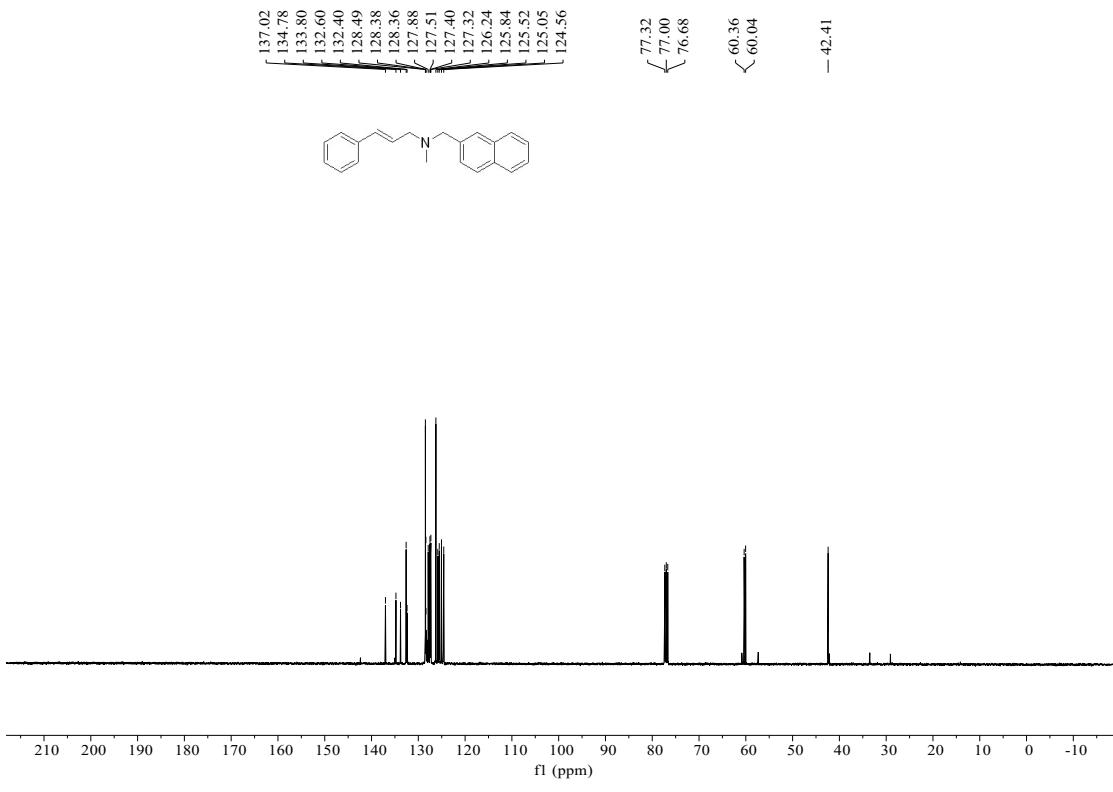
¹H NMR Spectrum of **3ah** in CDCl_3 at 400 MHz

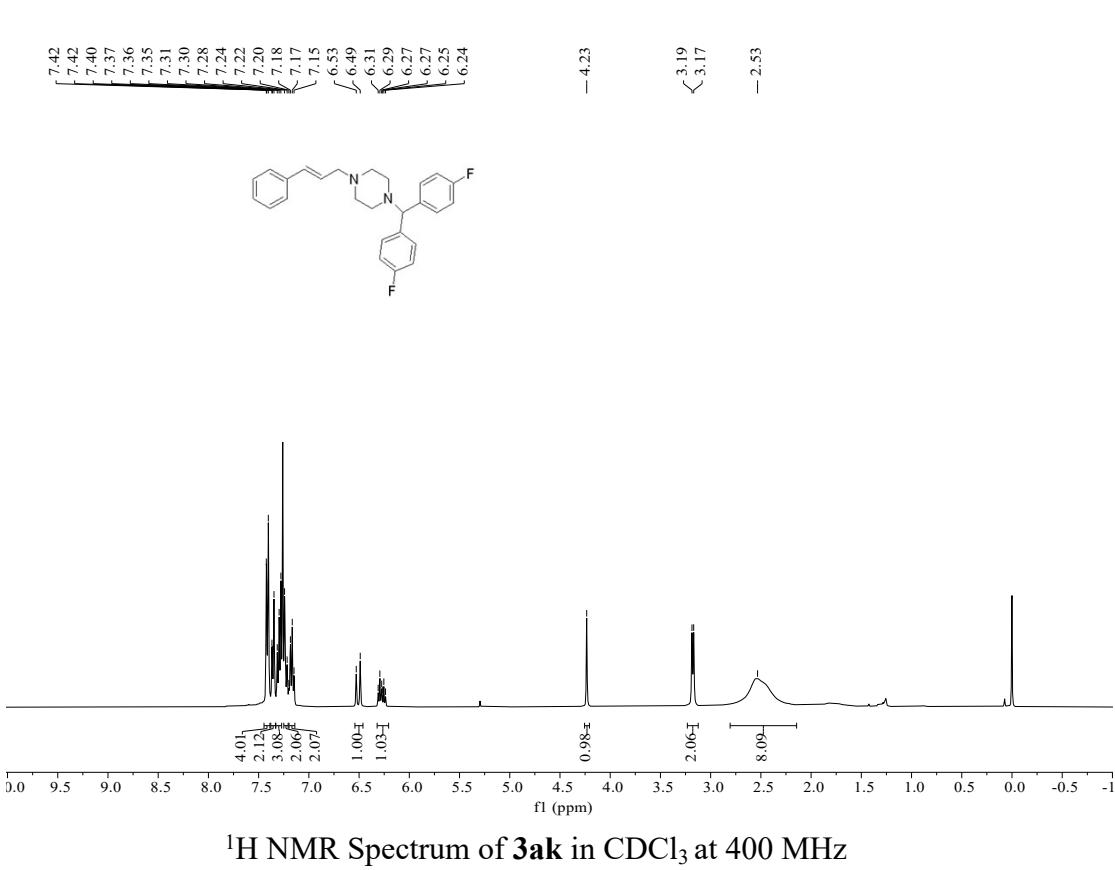
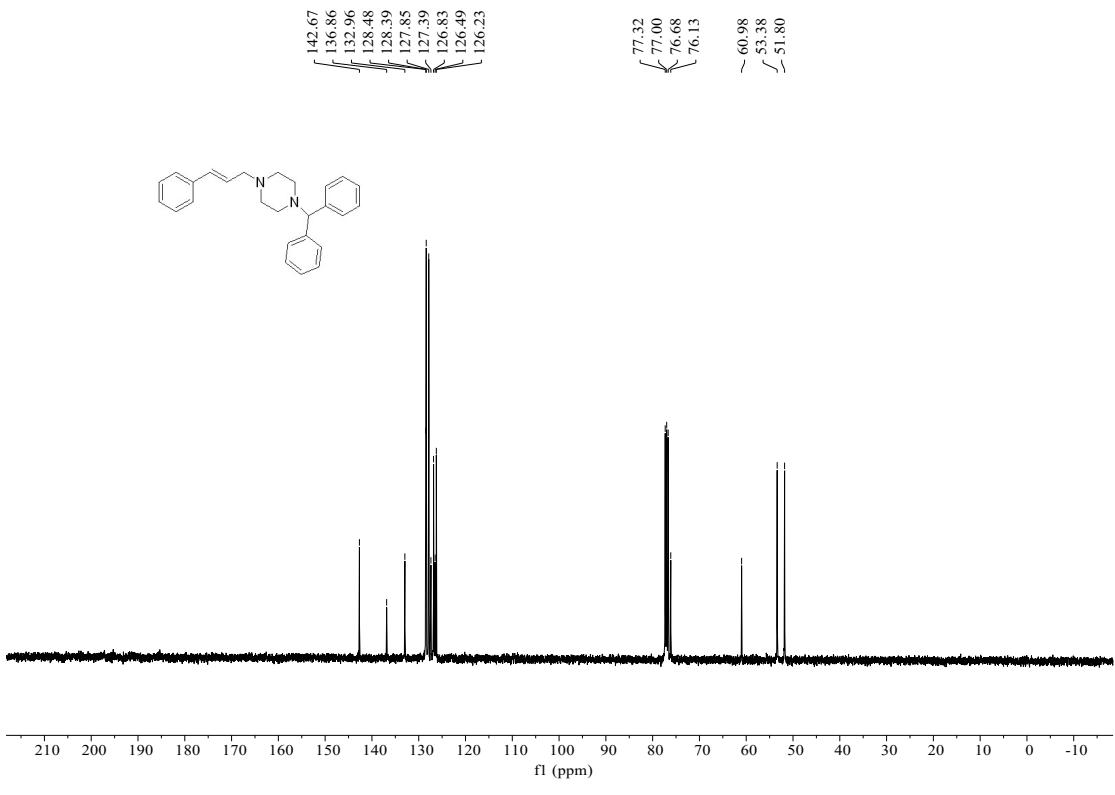


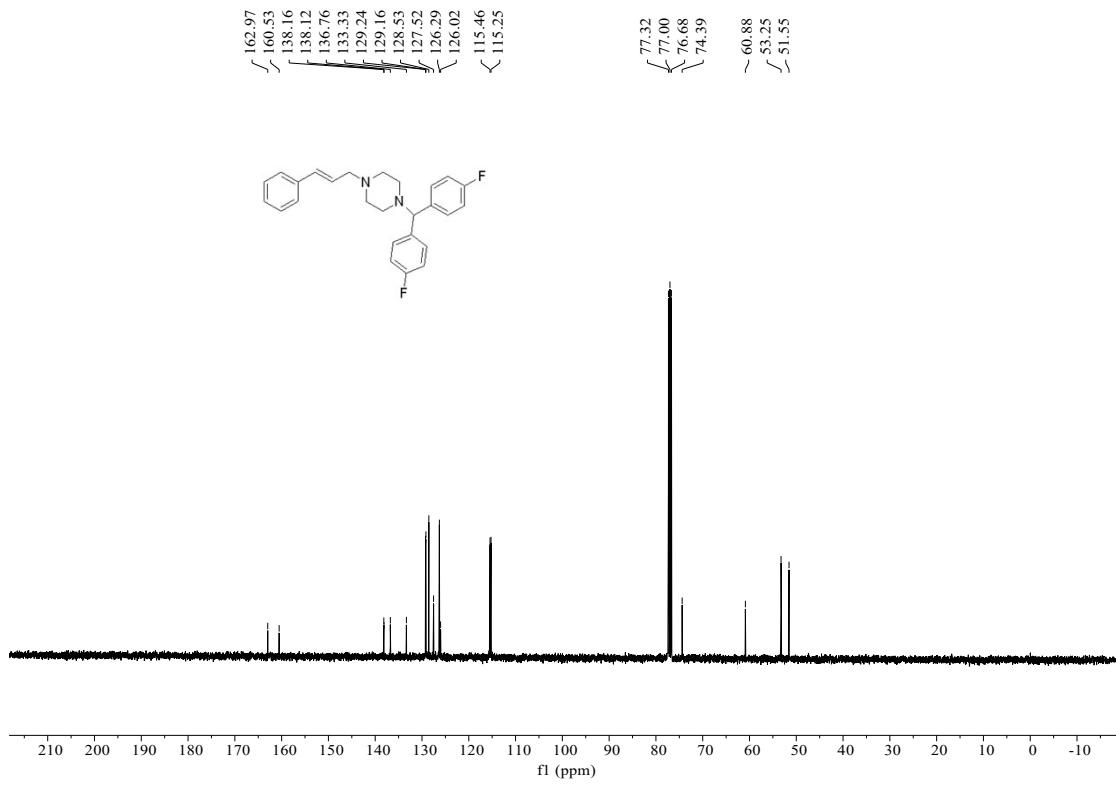
¹³C NMR Spectrum of **3ah** in CDCl_3 at 100 MHz



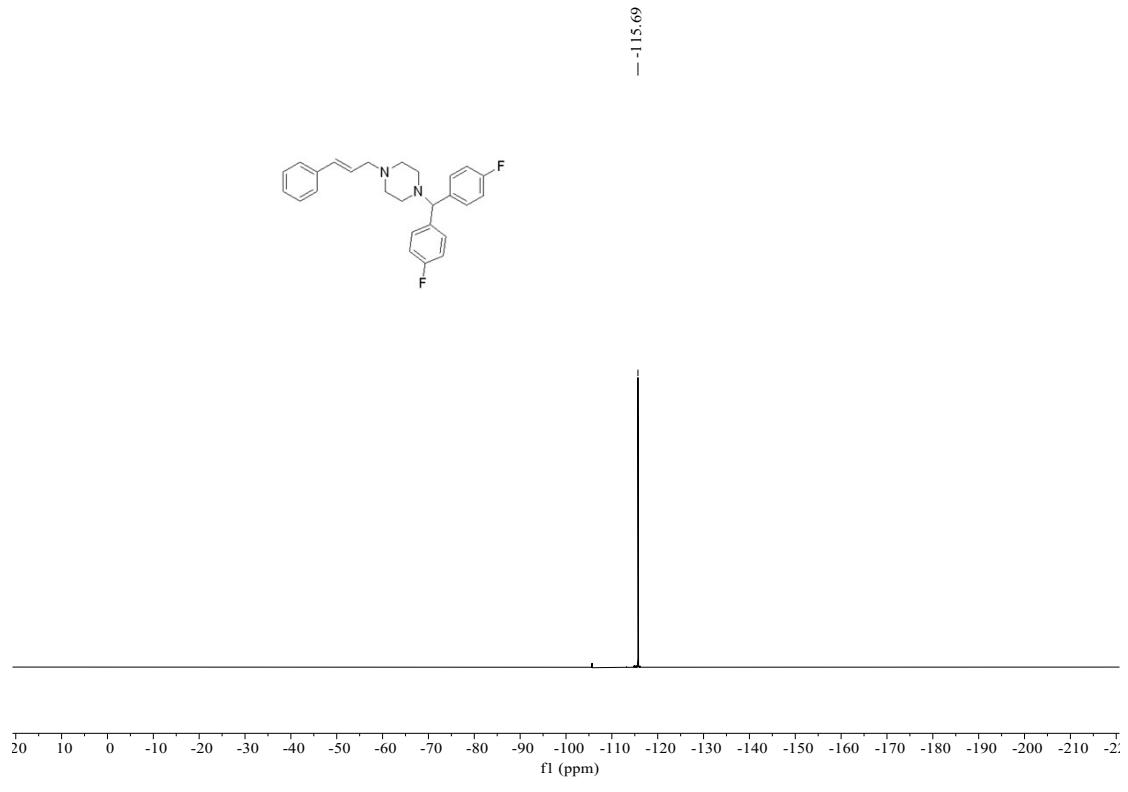
¹H NMR Spectrum of **3ai** in CDCl_3 at 400 MHz



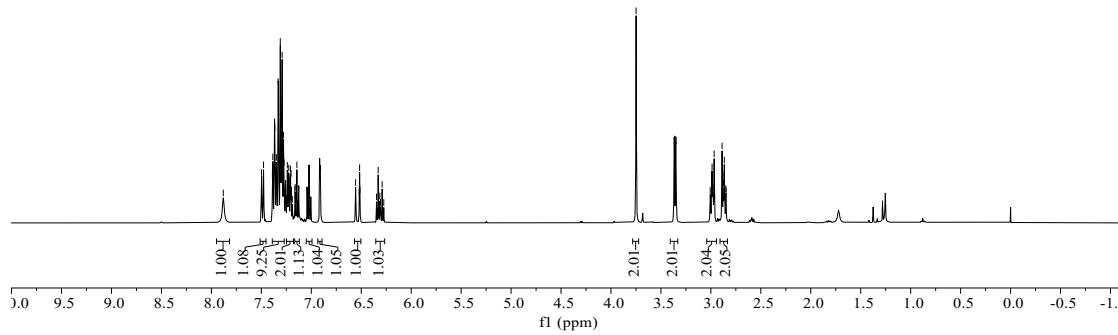
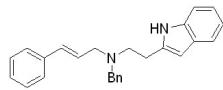
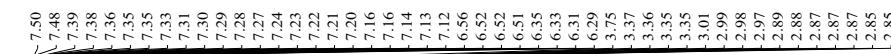




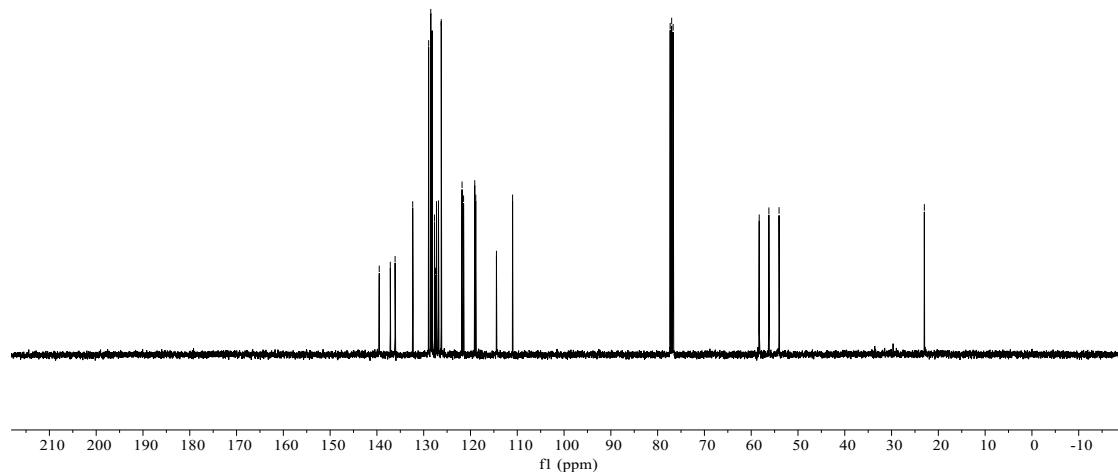
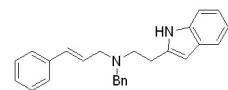
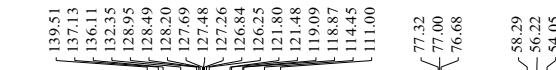
^{13}C NMR Spectrum of **3ak** in CDCl_3 at 100 MHz



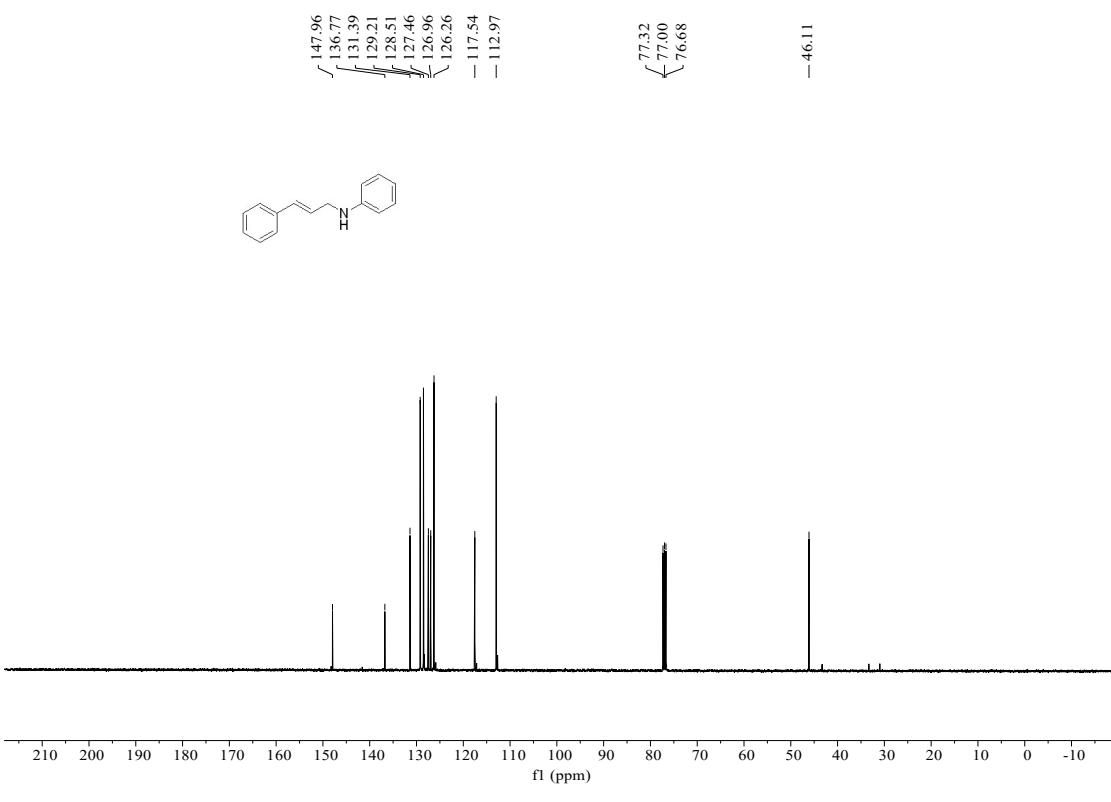
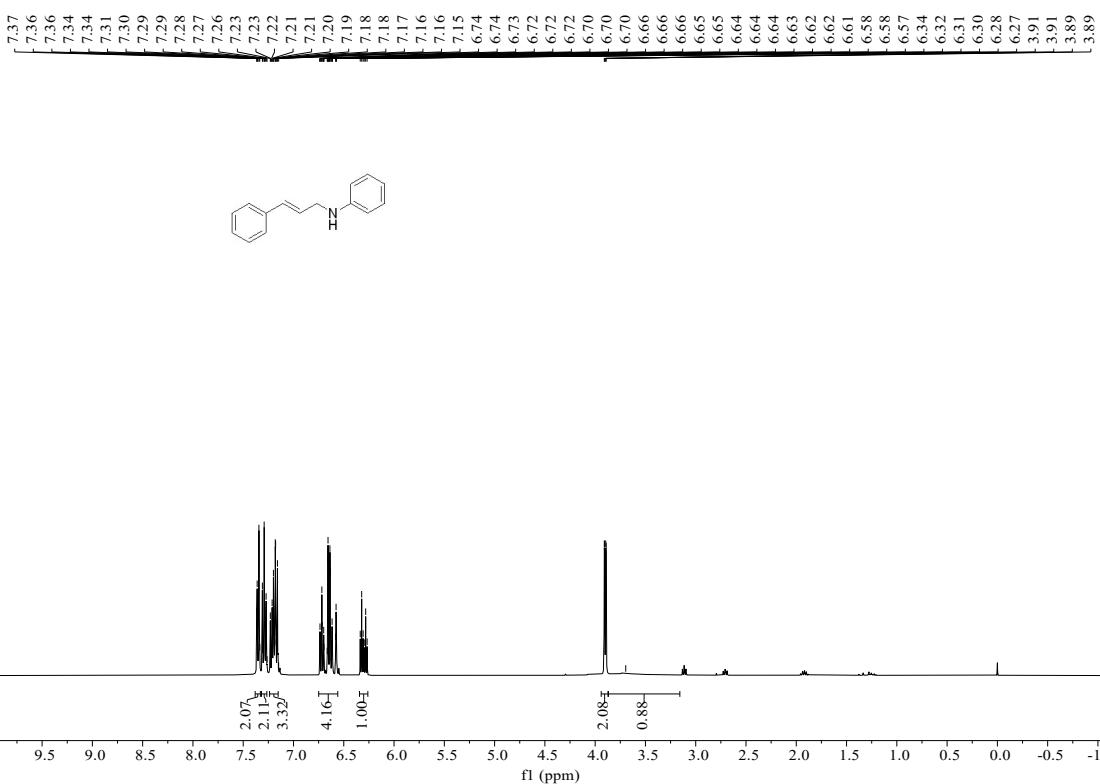
^{19}F NMR Spectrum of **3ak** in CDCl_3 at 377 MHz

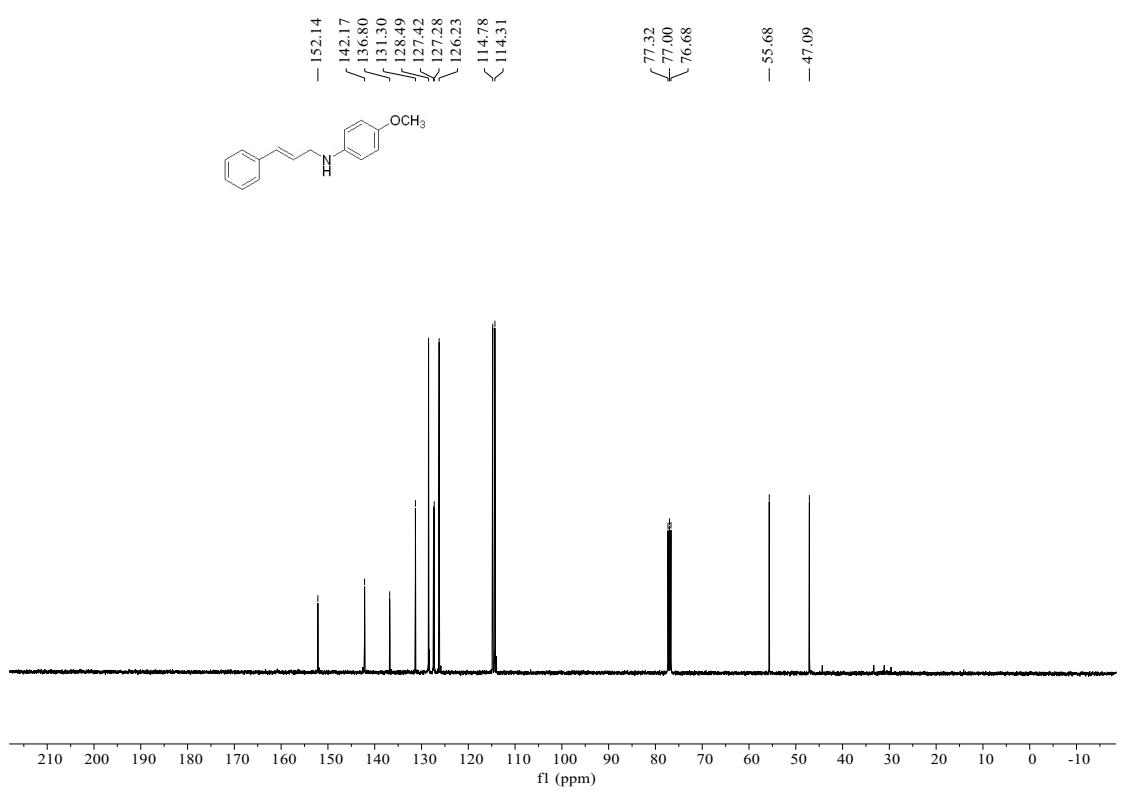
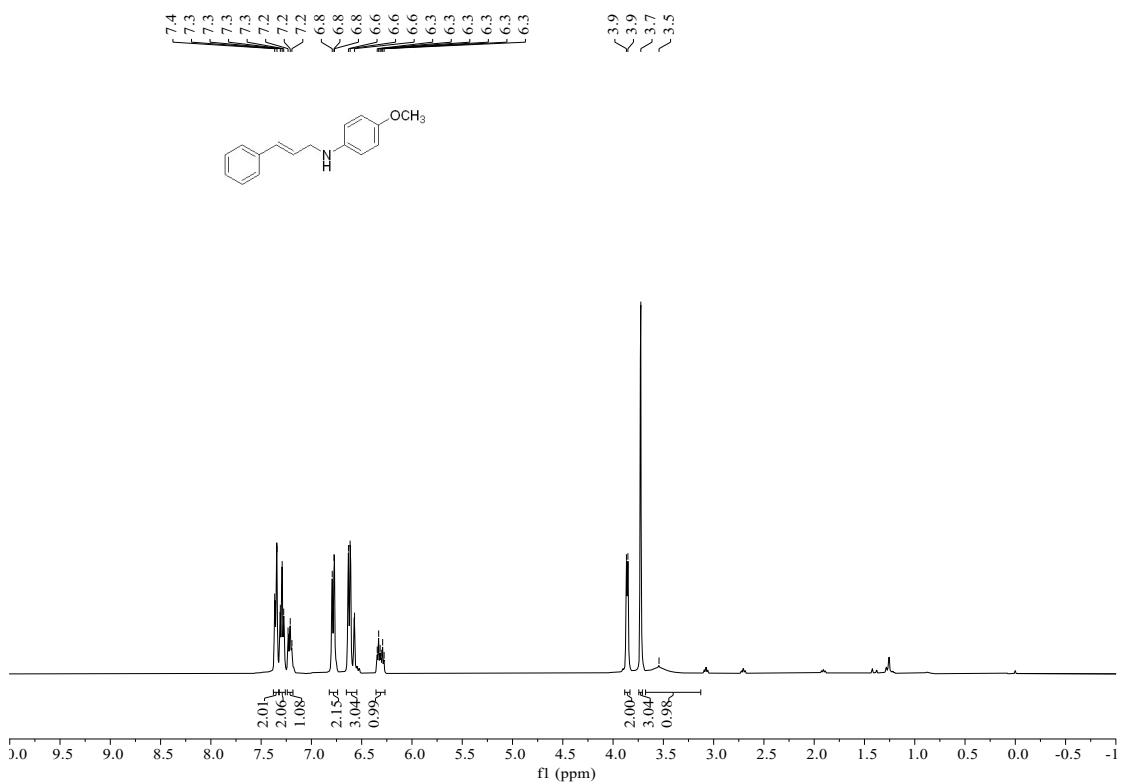


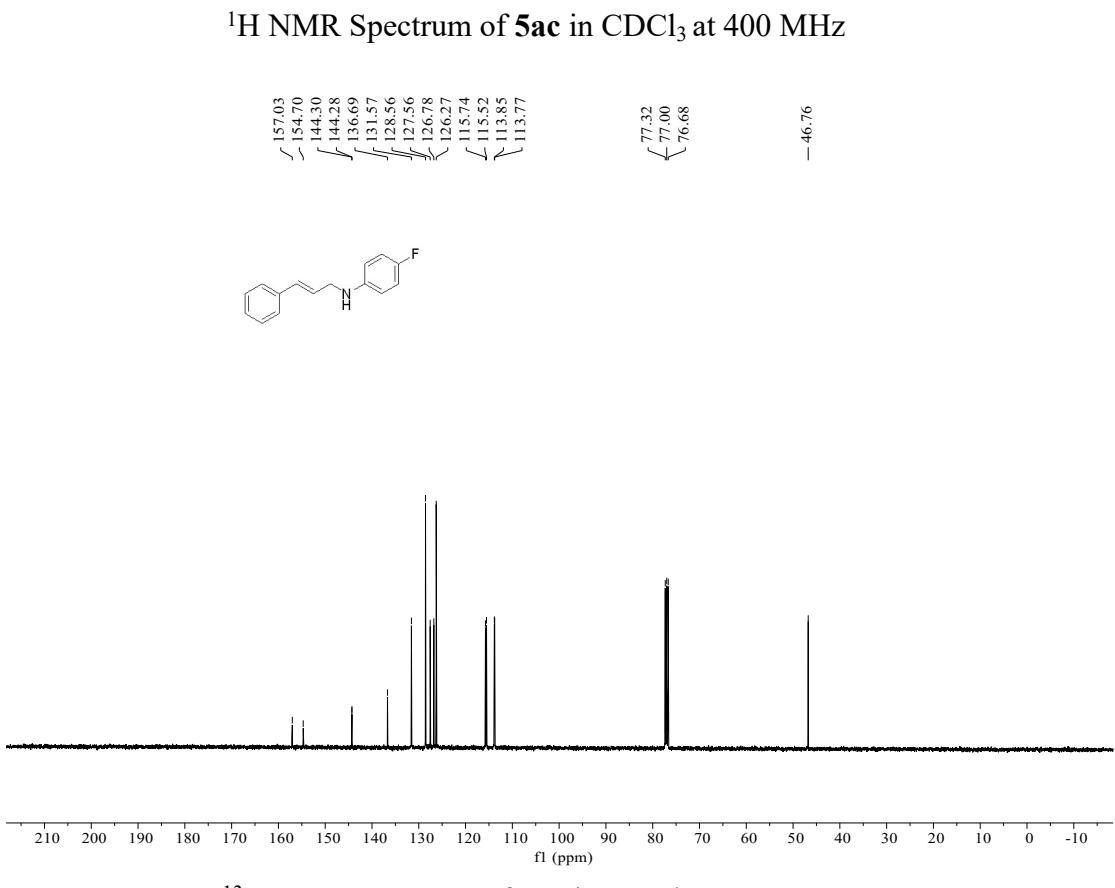
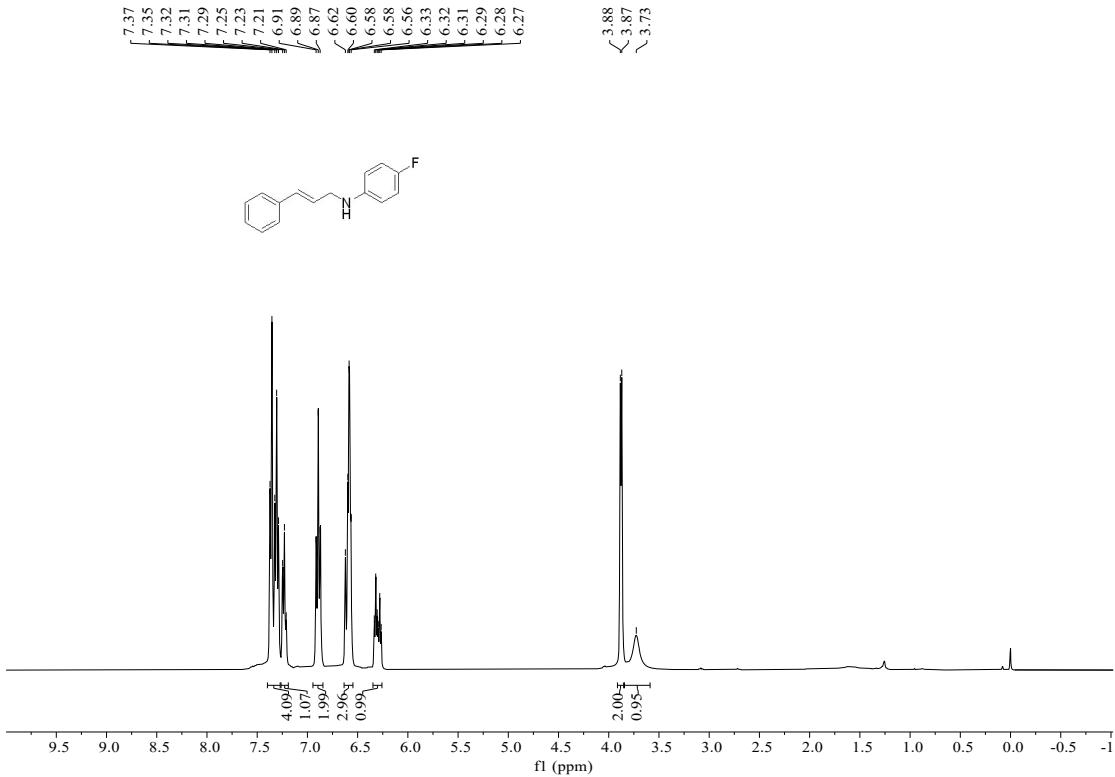
¹H NMR Spectrum of **3al** in CDCl₃ at 400 MHz

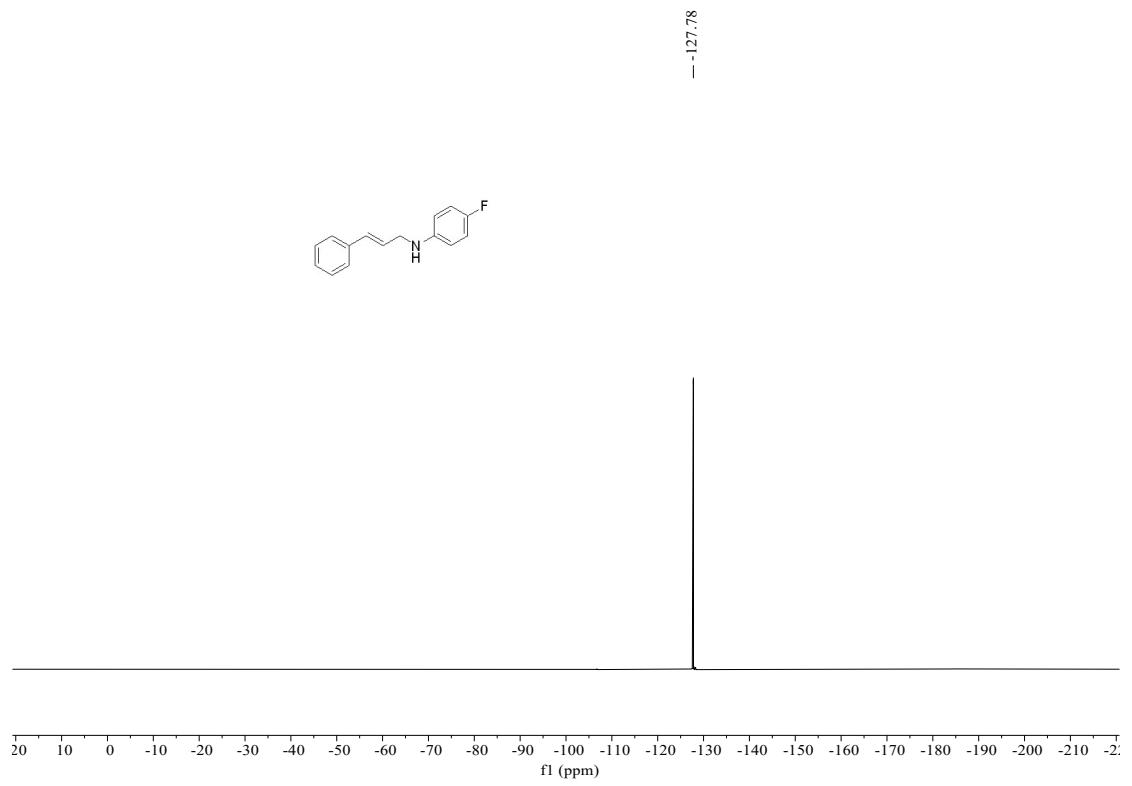


¹³C NMR Spectrum of **3al** in CDCl₃ at 100 MHz

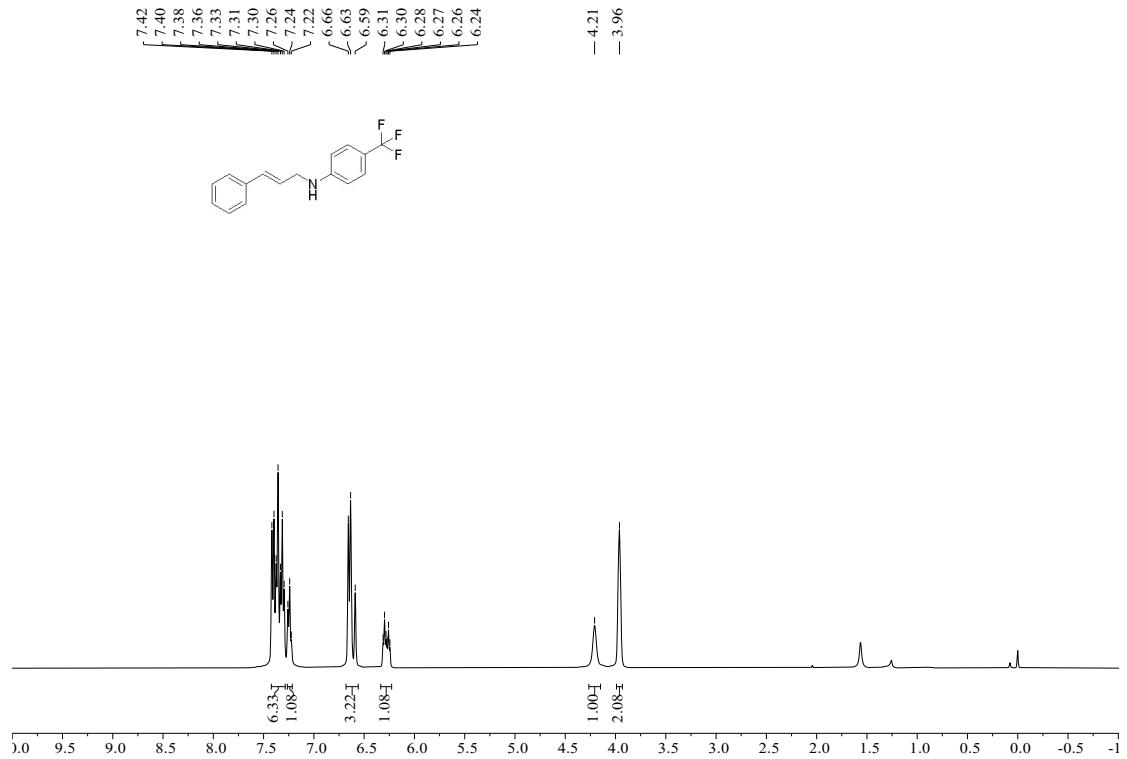




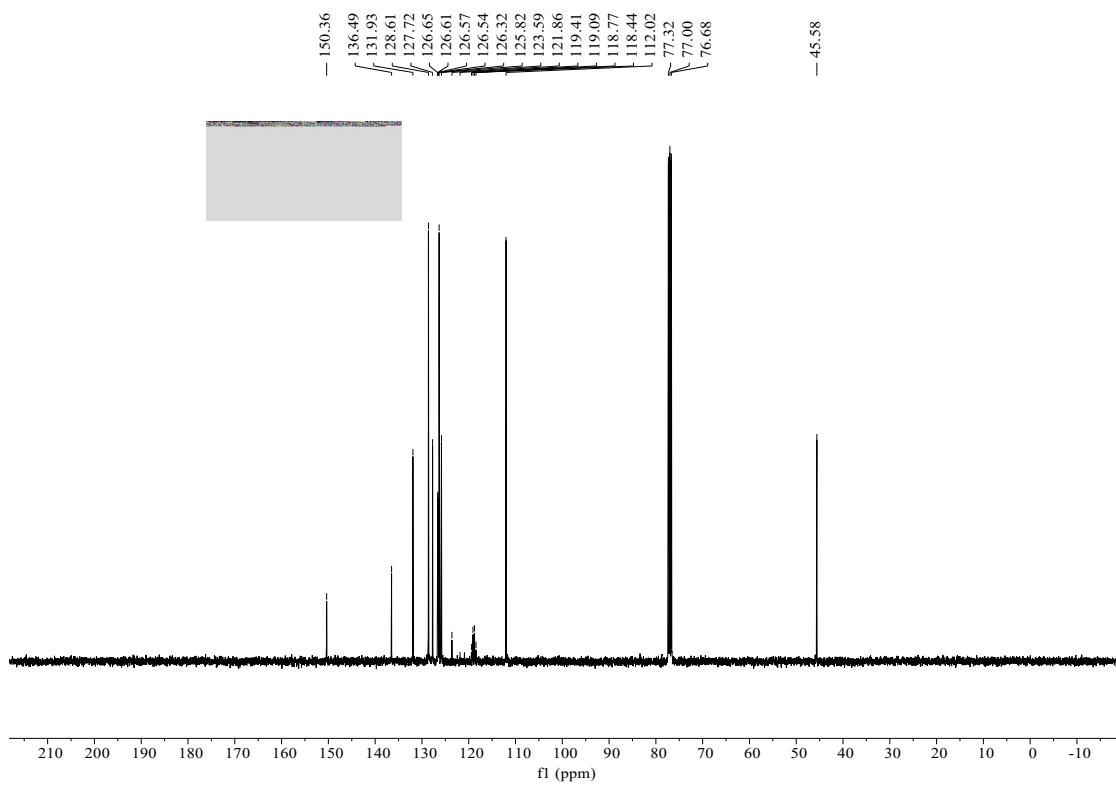




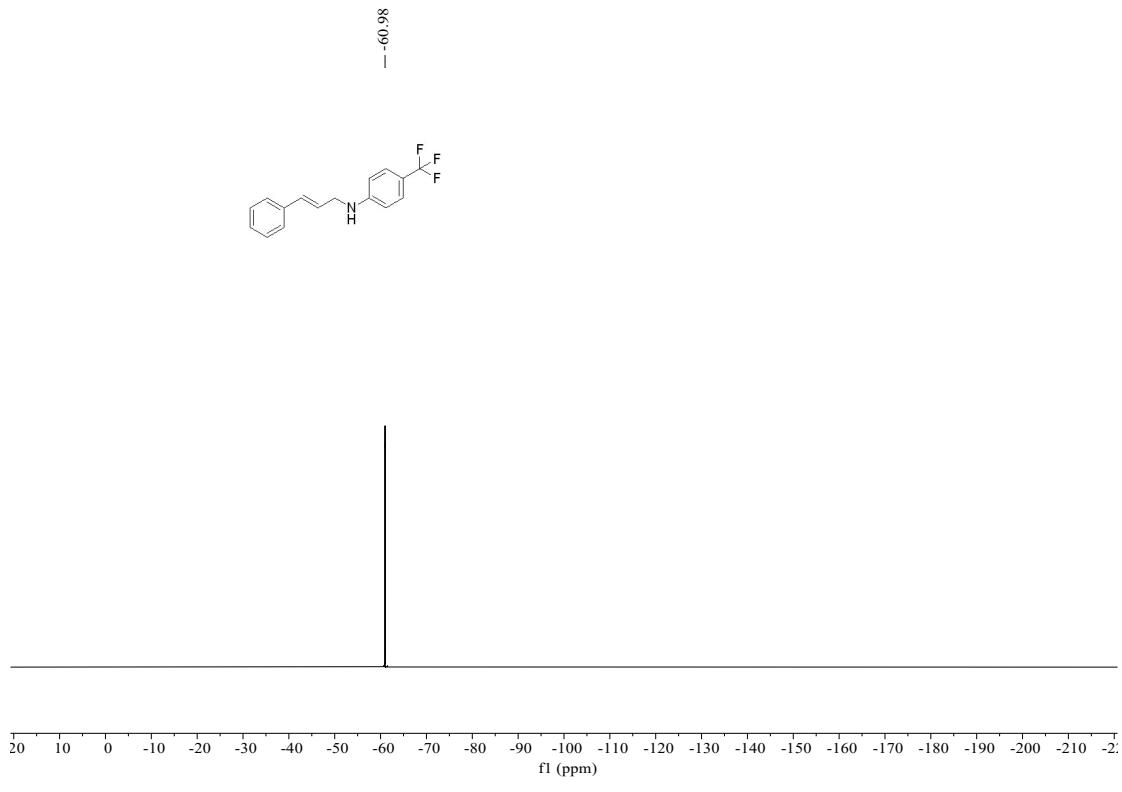
¹⁹F NMR Spectrum of **3ac** in CDCl₃ at 377 MHz



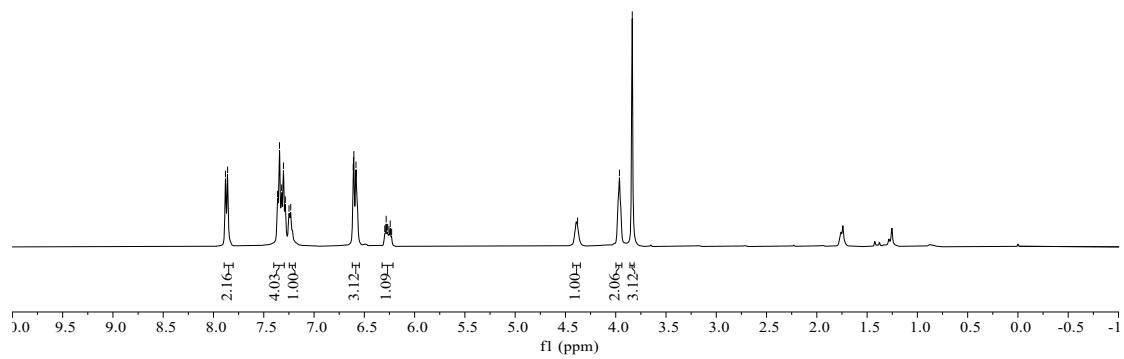
¹H NMR Spectrum of **5ad** in CDCl₃ at 400 MHz



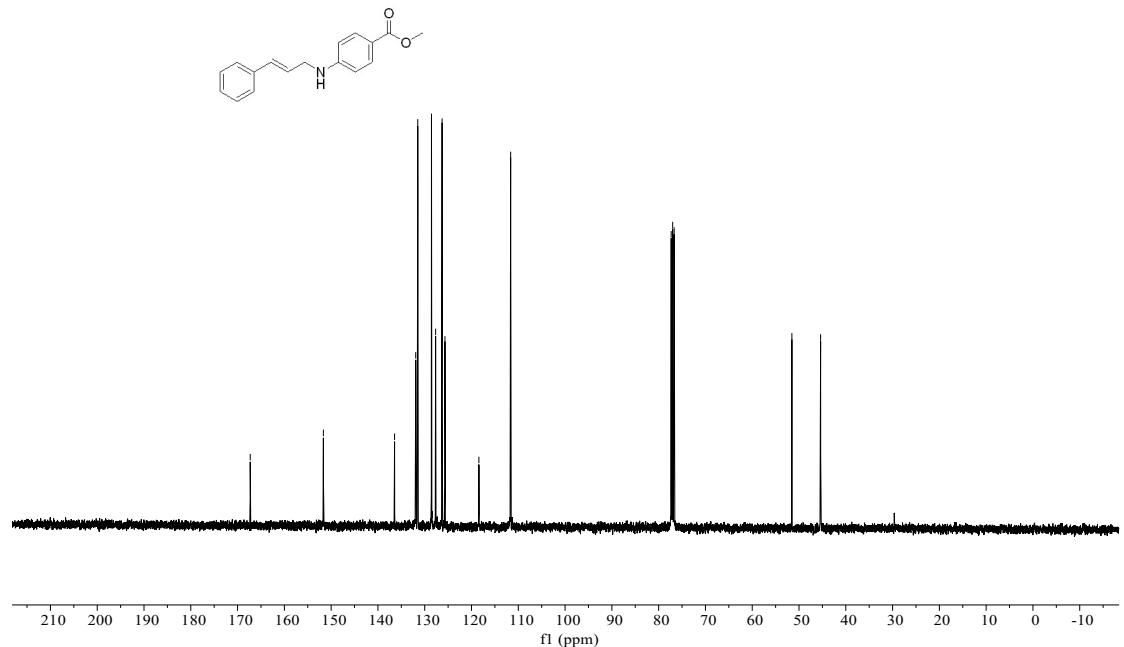
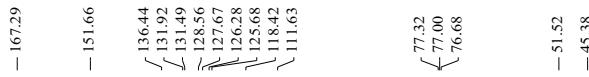
¹³C NMR Spectrum of **5ad** in CDCl_3 at 100 MHz



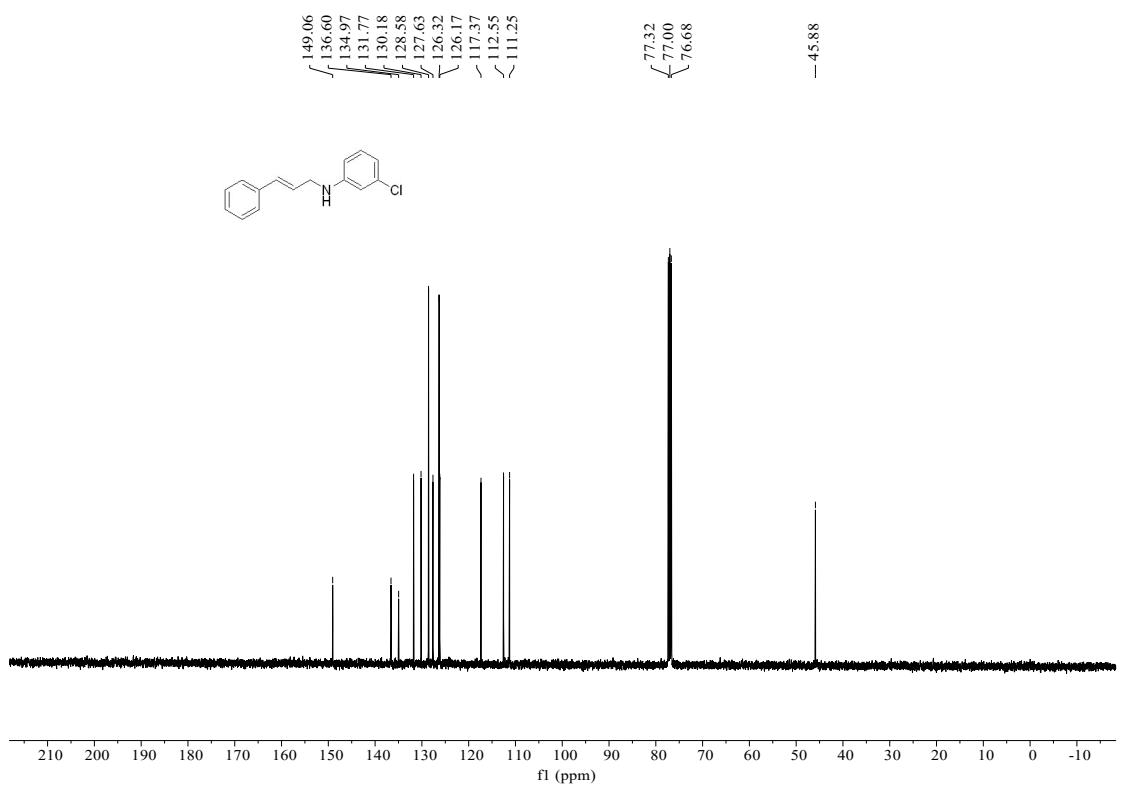
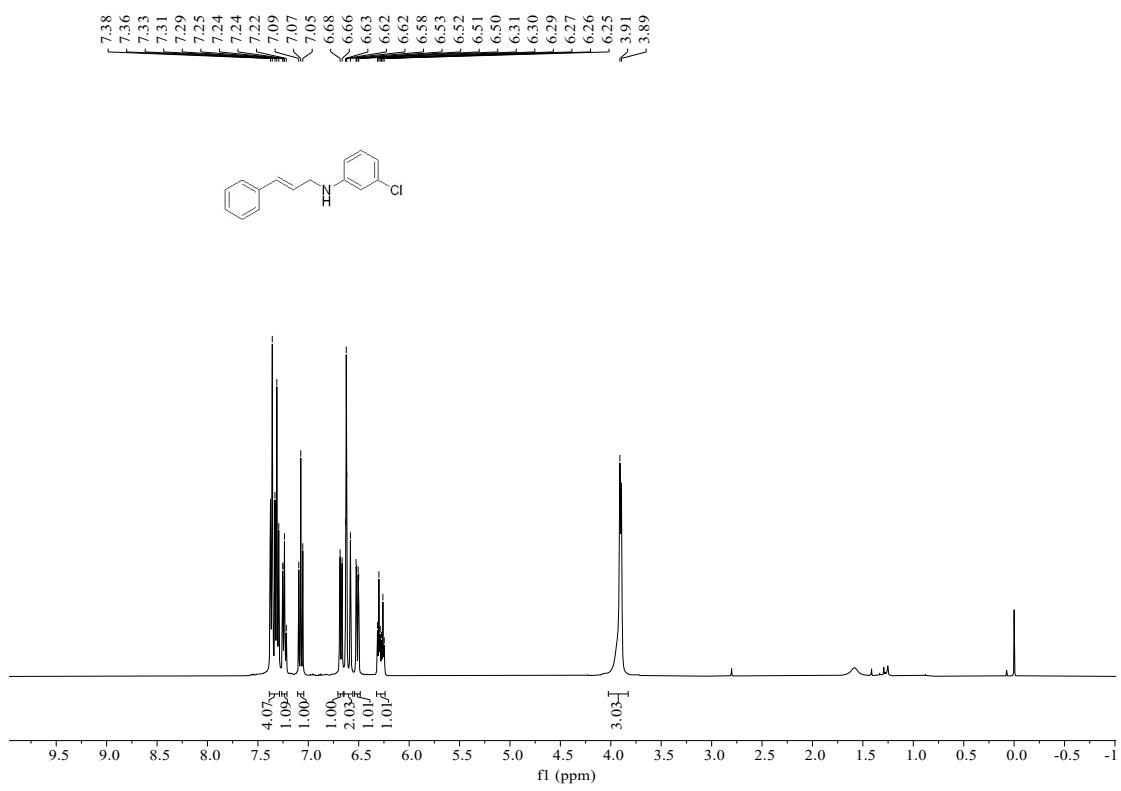
¹⁹F NMR Spectrum of **5ad** in CDCl_3 at 377 MHz

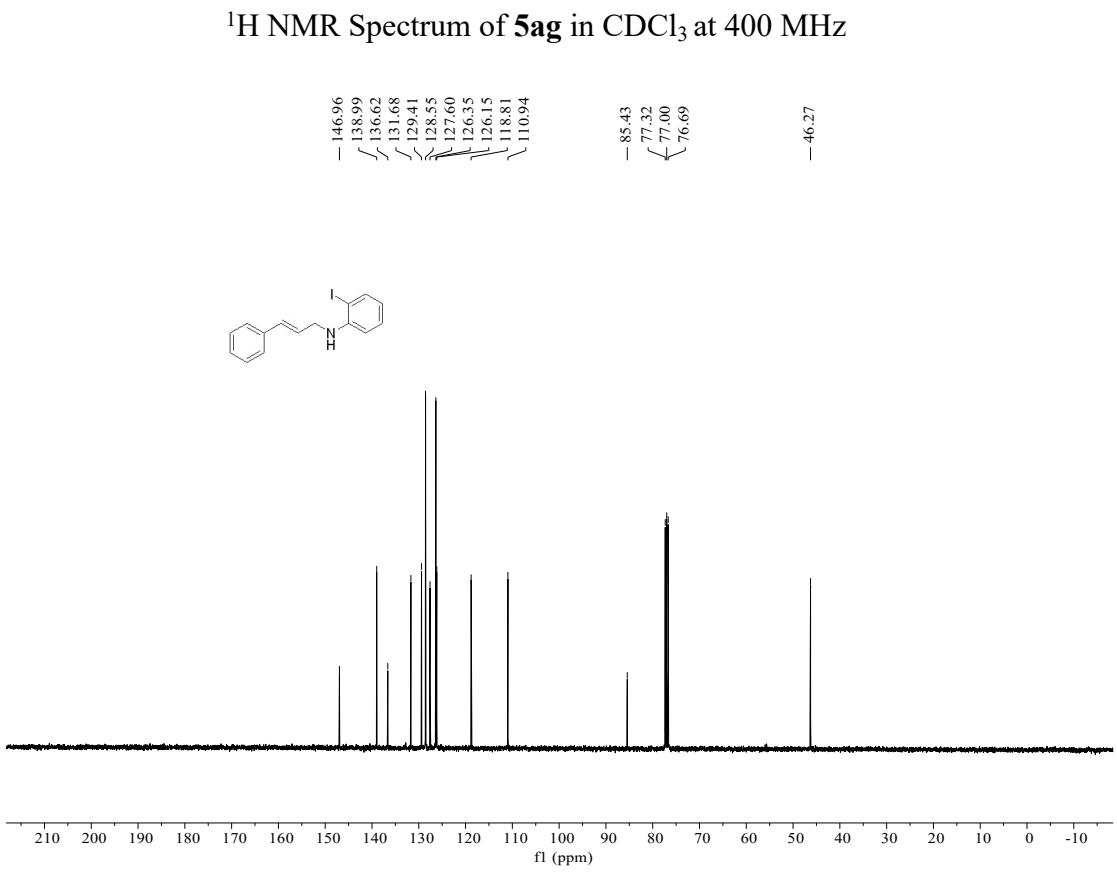
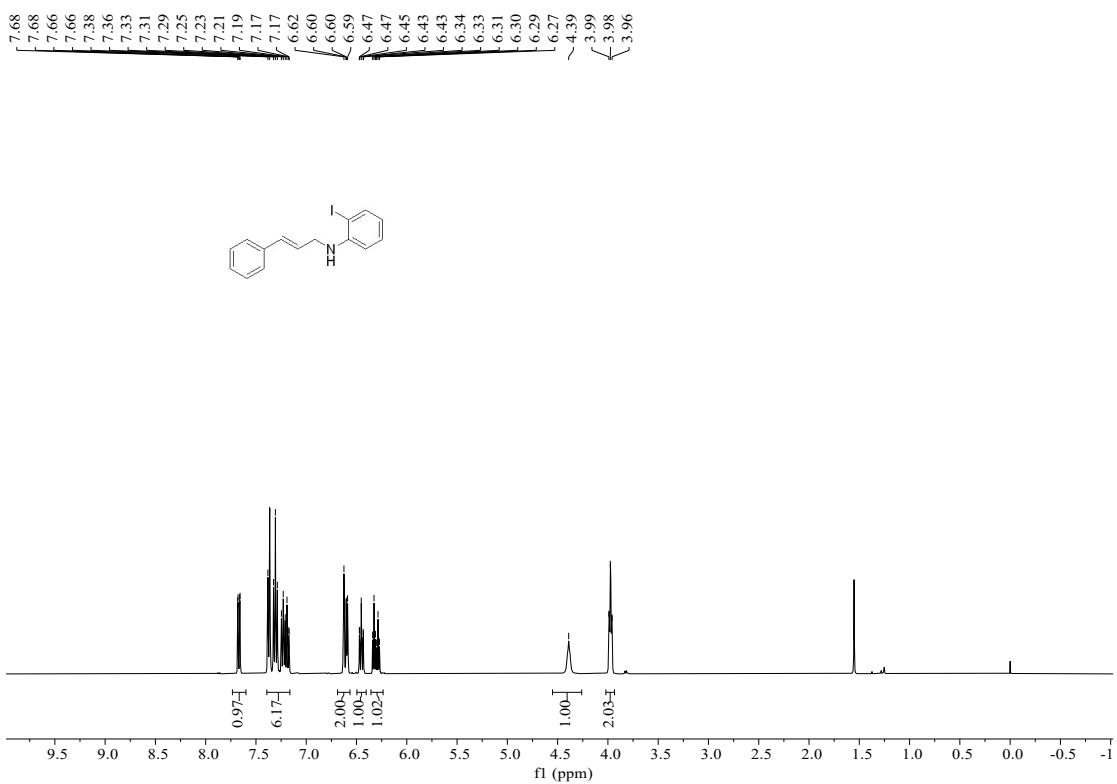


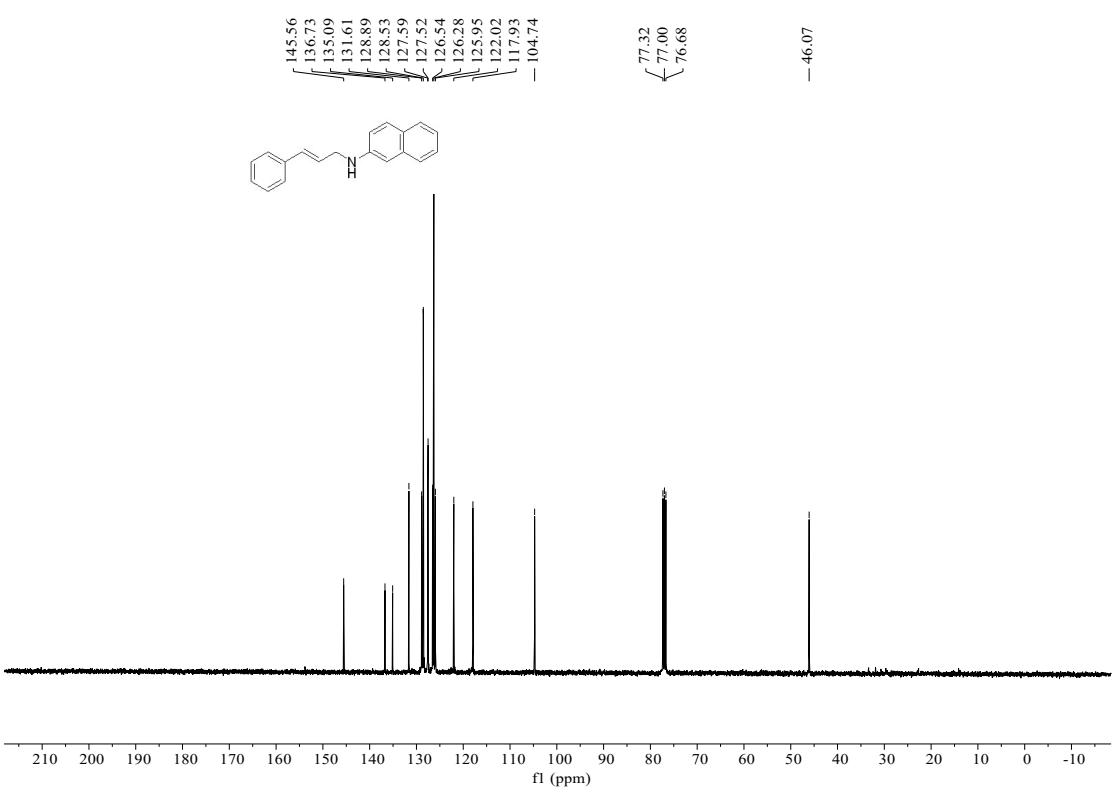
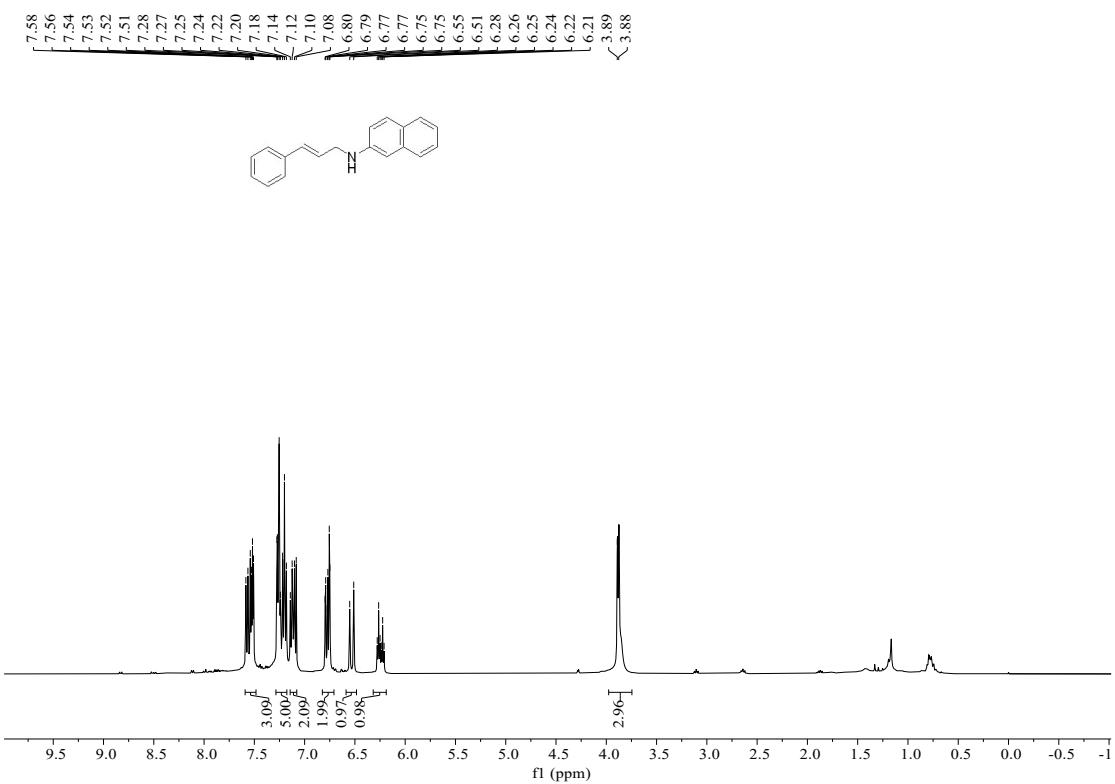
¹H NMR Spectrum of **5ae** in CDCl_3 at 400 MHz

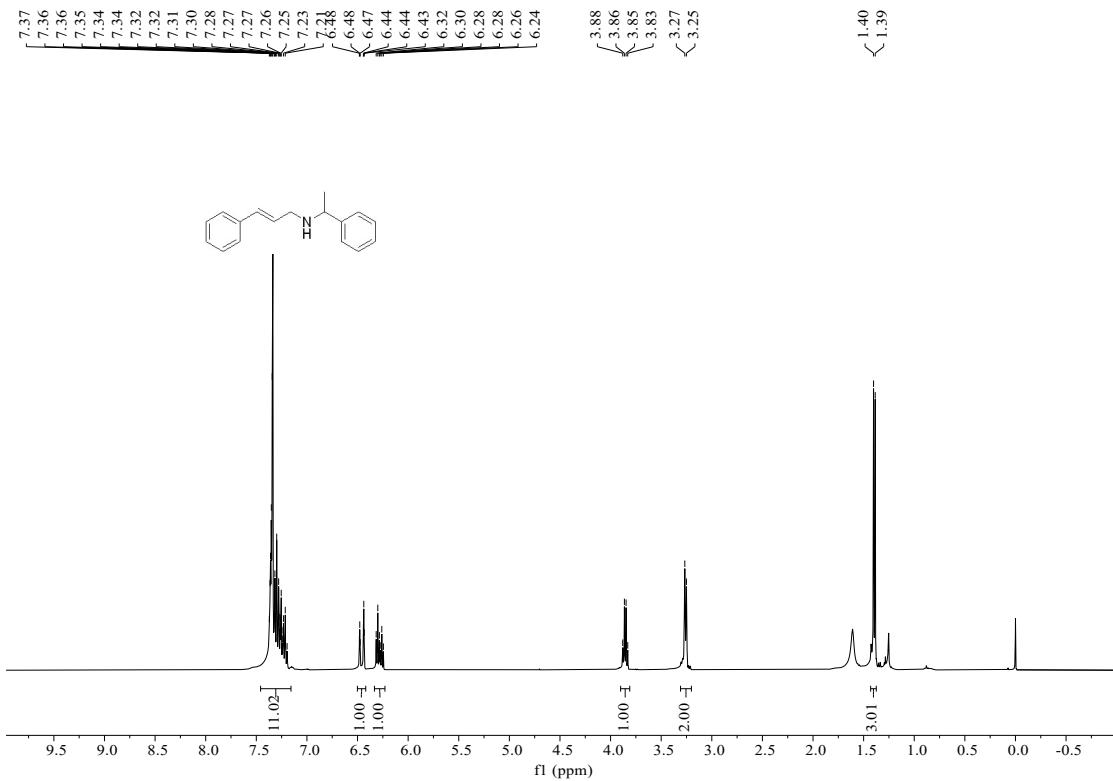


¹³C NMR Spectrum of **5ae** in CDCl_3 at 100 MHz

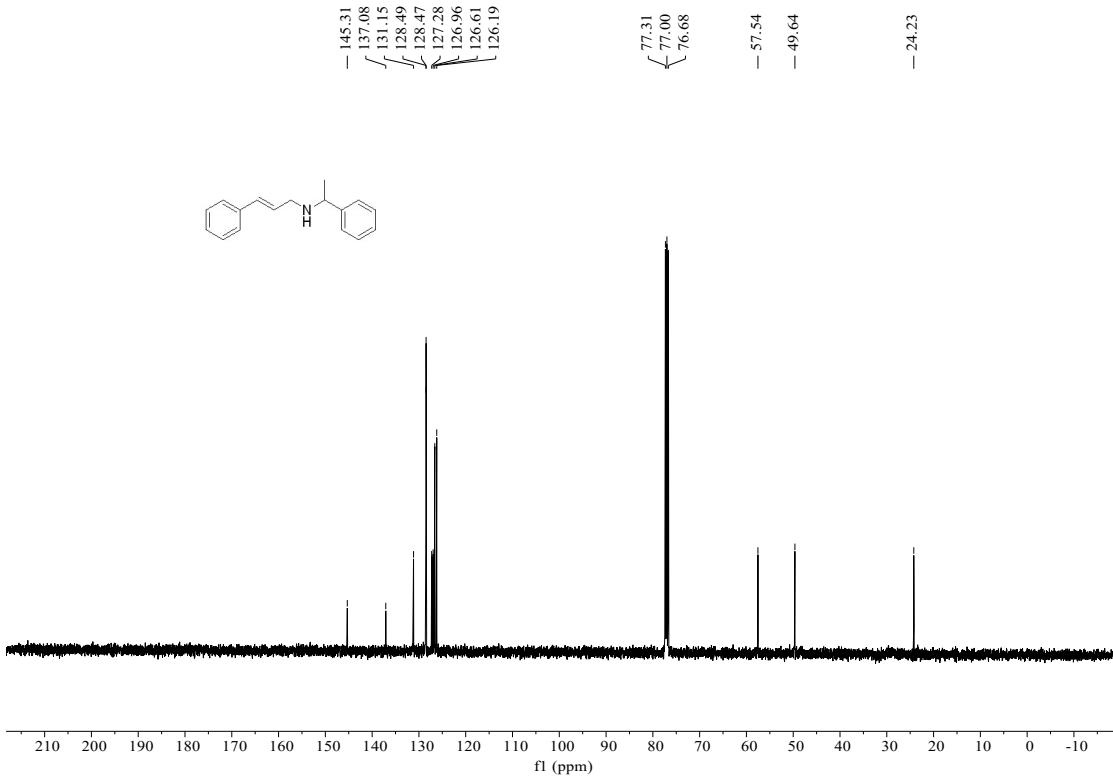




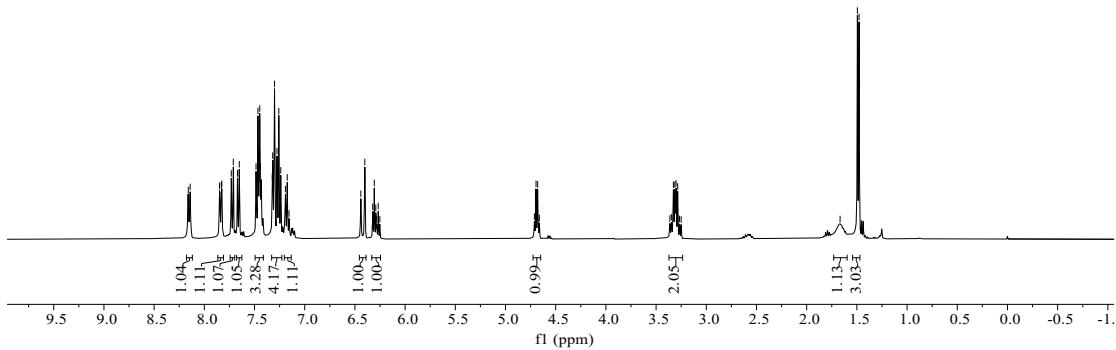
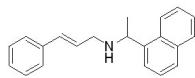
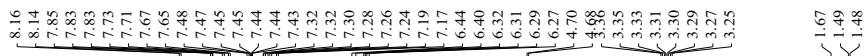




¹H NMR Spectrum of **5ai** in CDCl₃ at 400 MHz

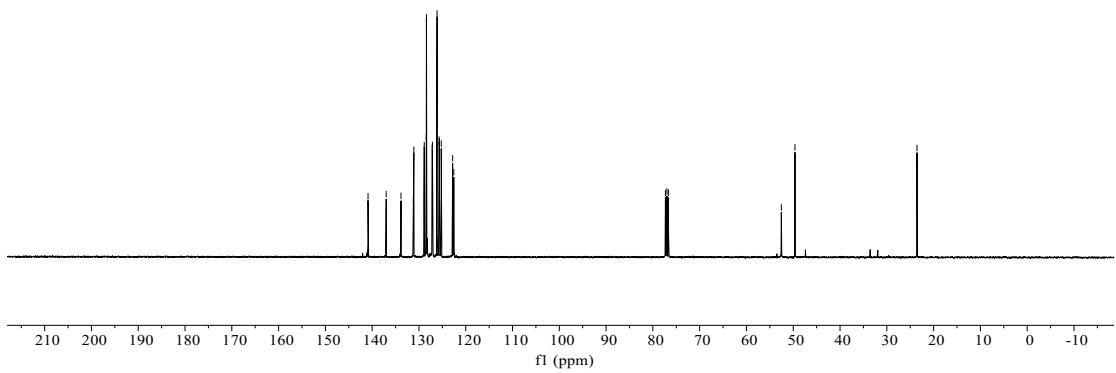
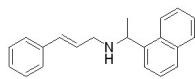


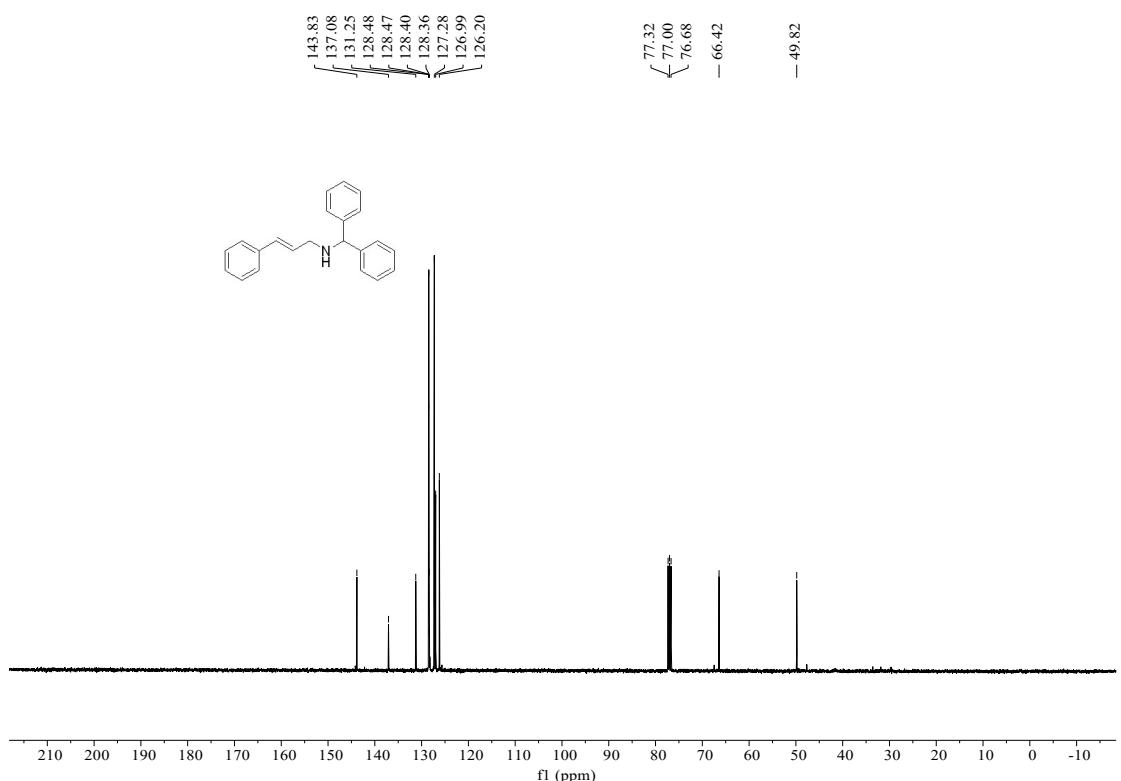
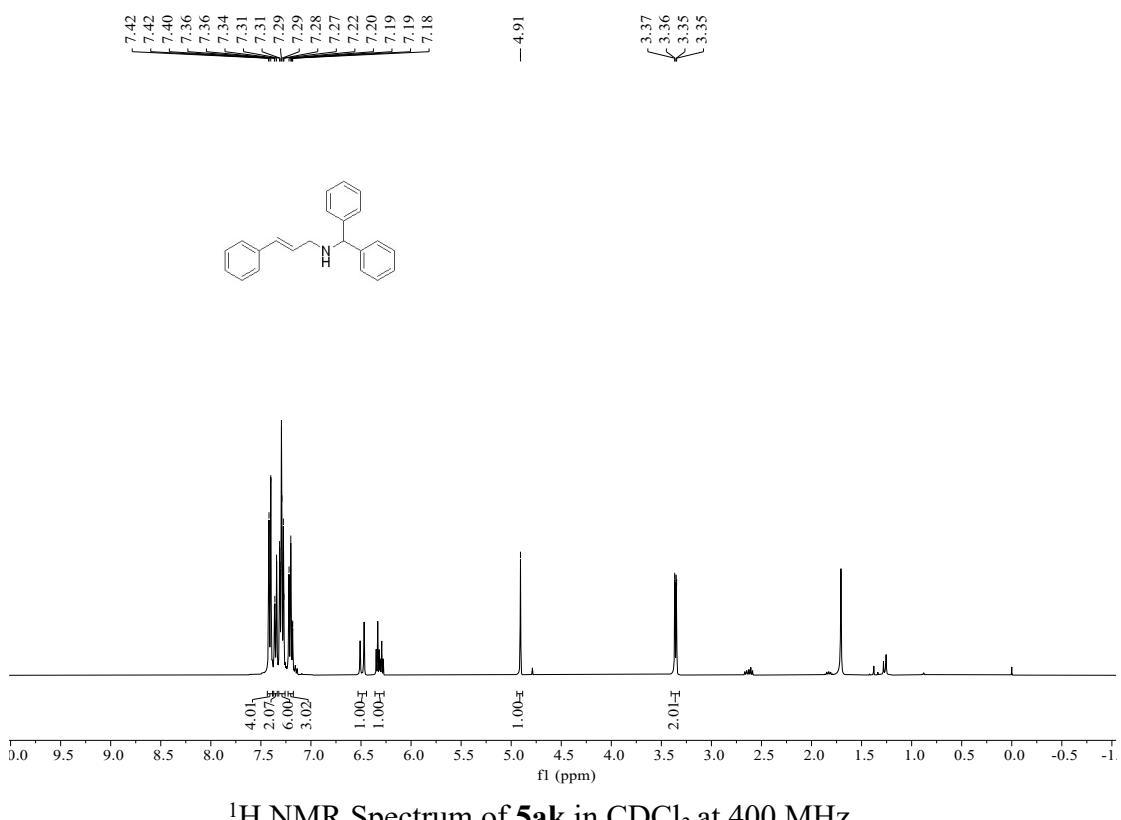
¹³C NMR Spectrum of **5ai** in CDCl₃ at 100 MHz

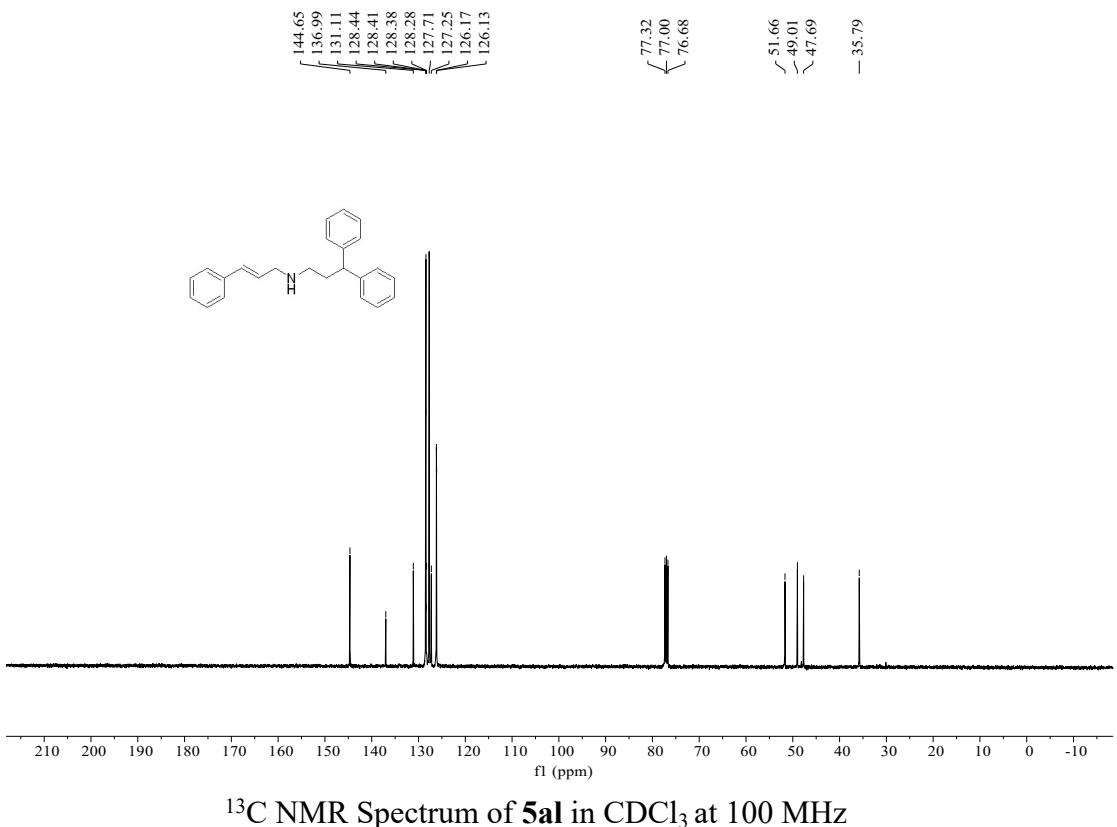
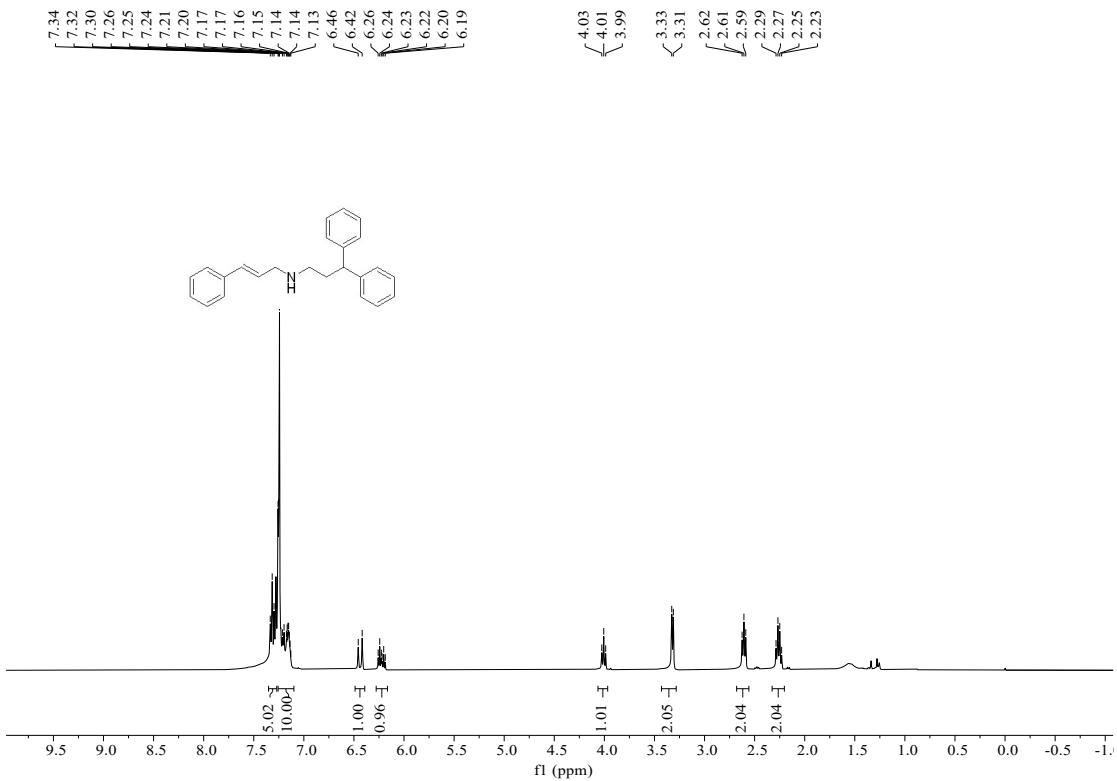


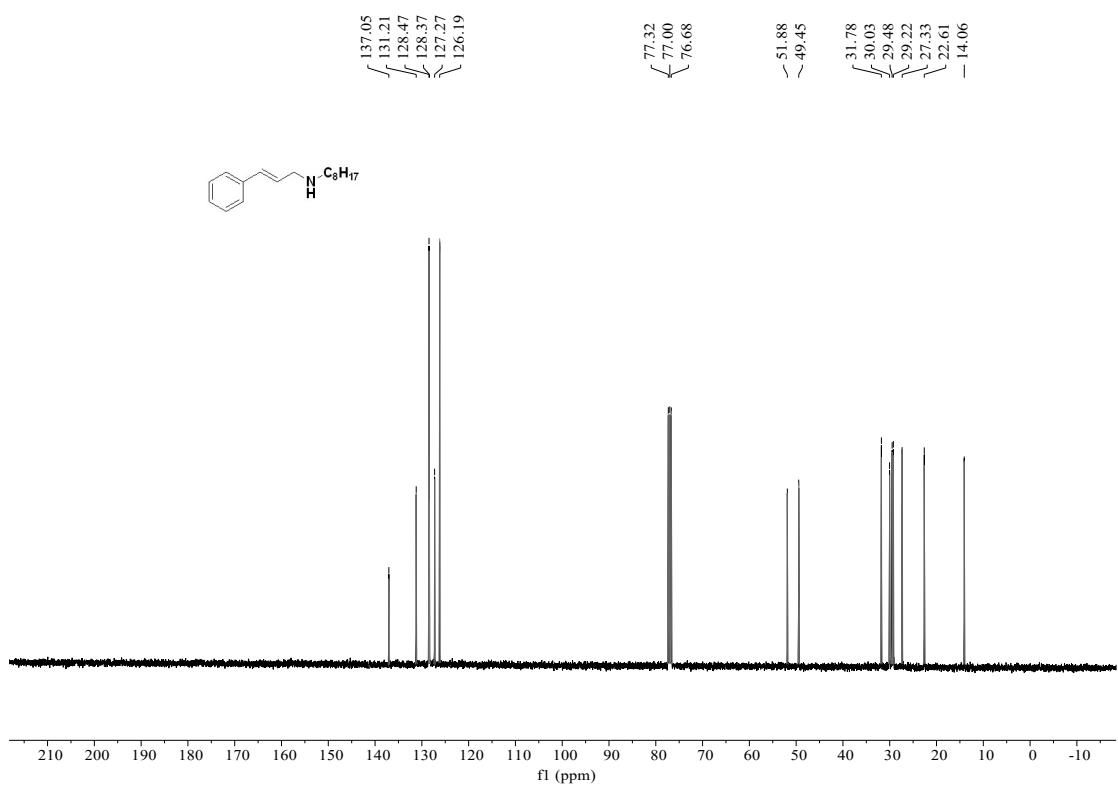
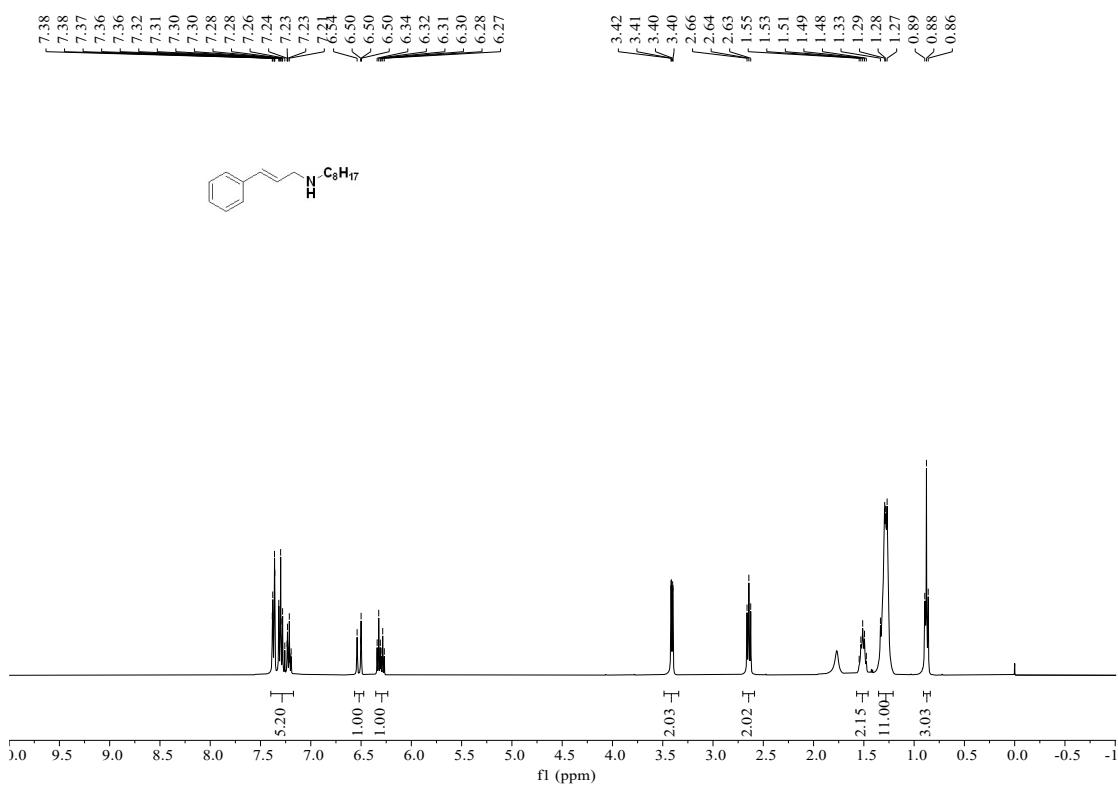
140.89
 137.00
 133.84
 131.20
 131.09
 128.87
 128.43
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 127.12
 126.13
 125.69
 125.64
 125.23
 122.80
 122.56

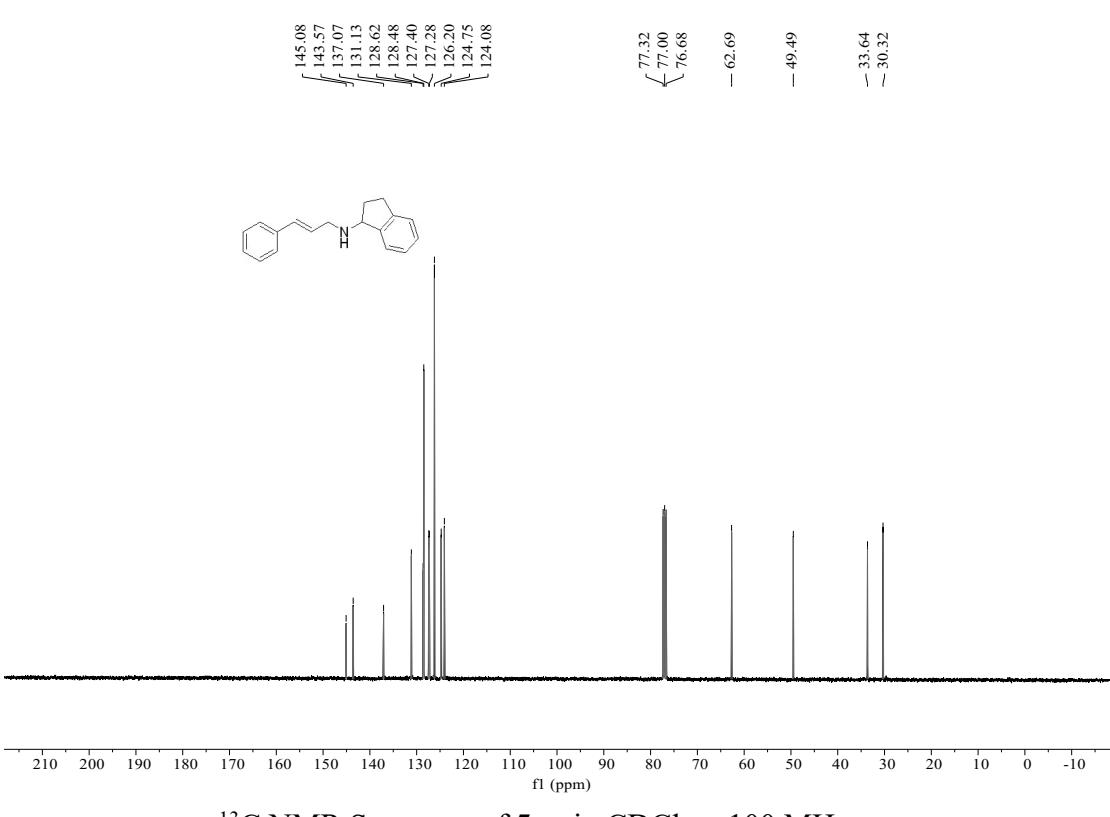
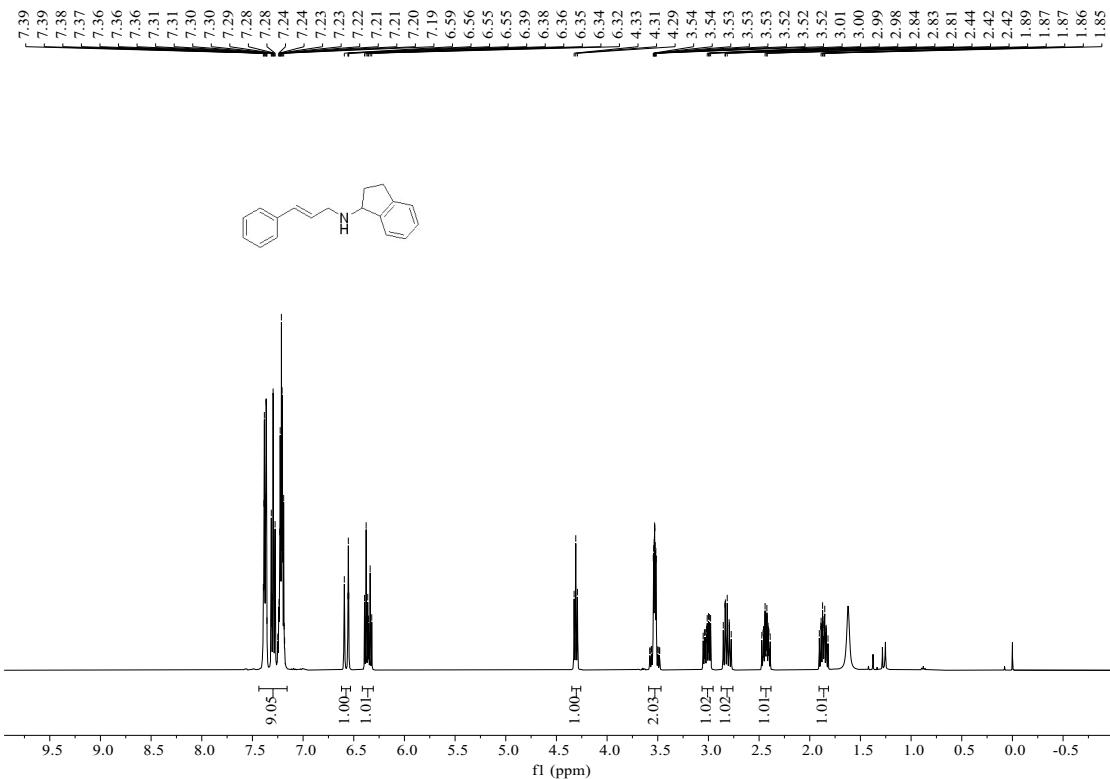
77.32
 77.00
 76.68
 52.55
 49.63
 -23.55

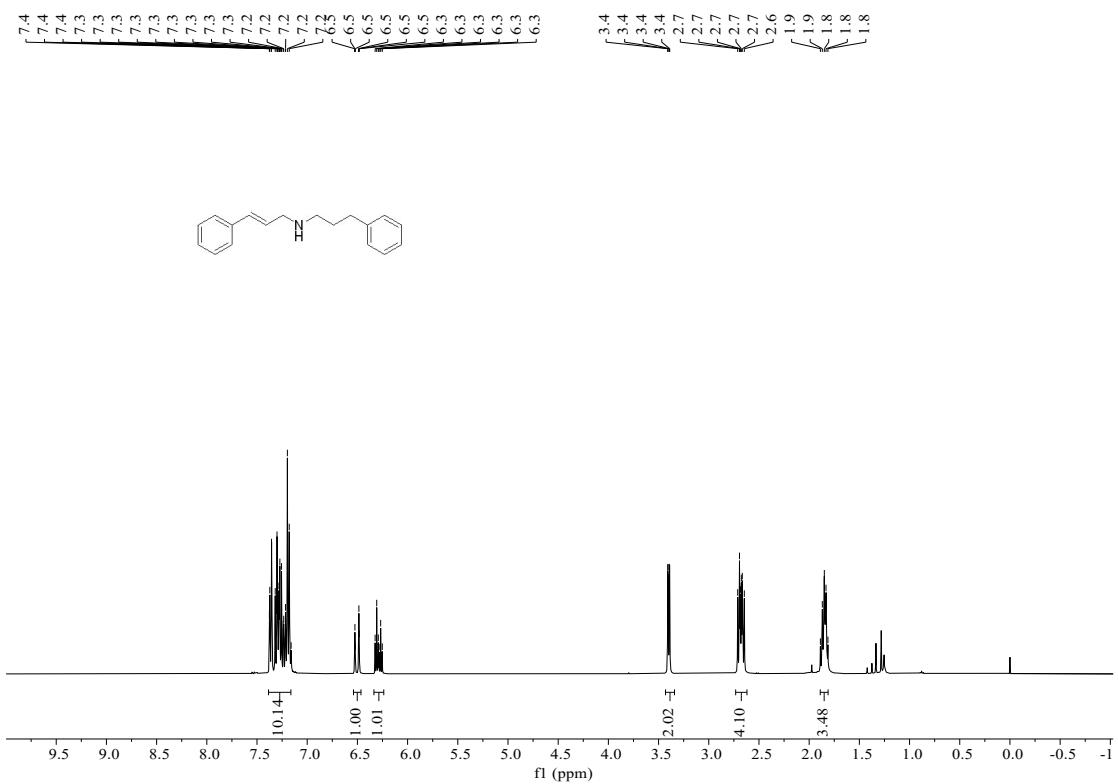




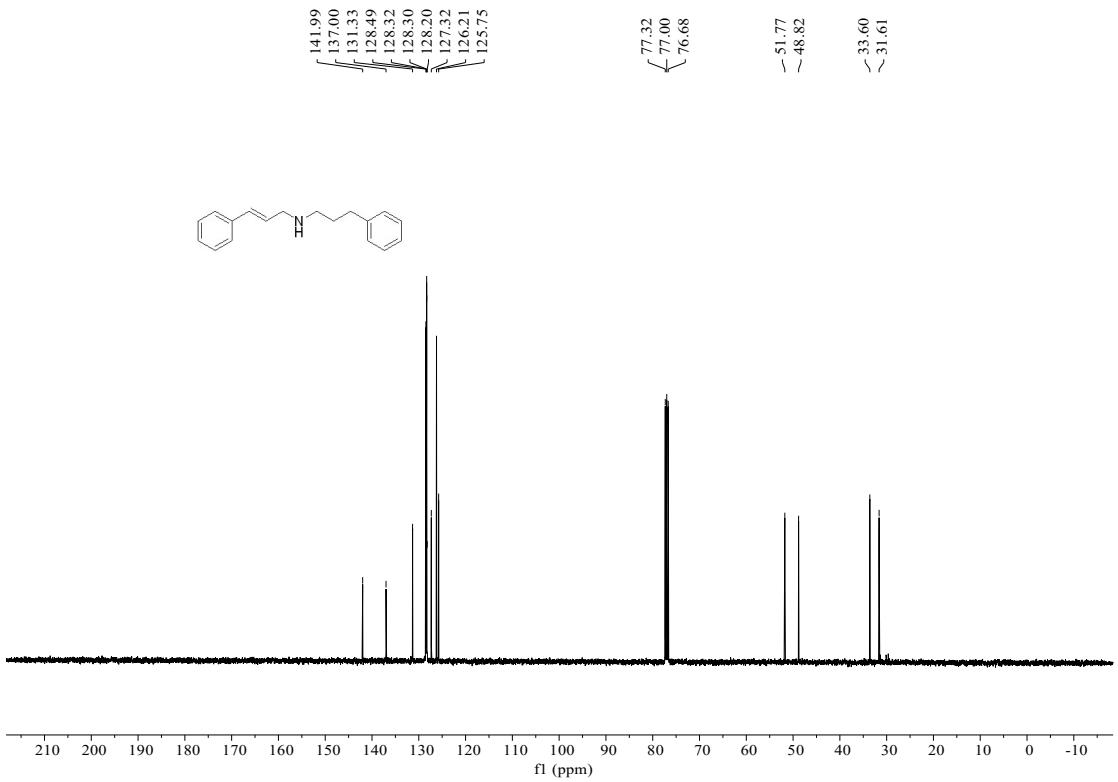




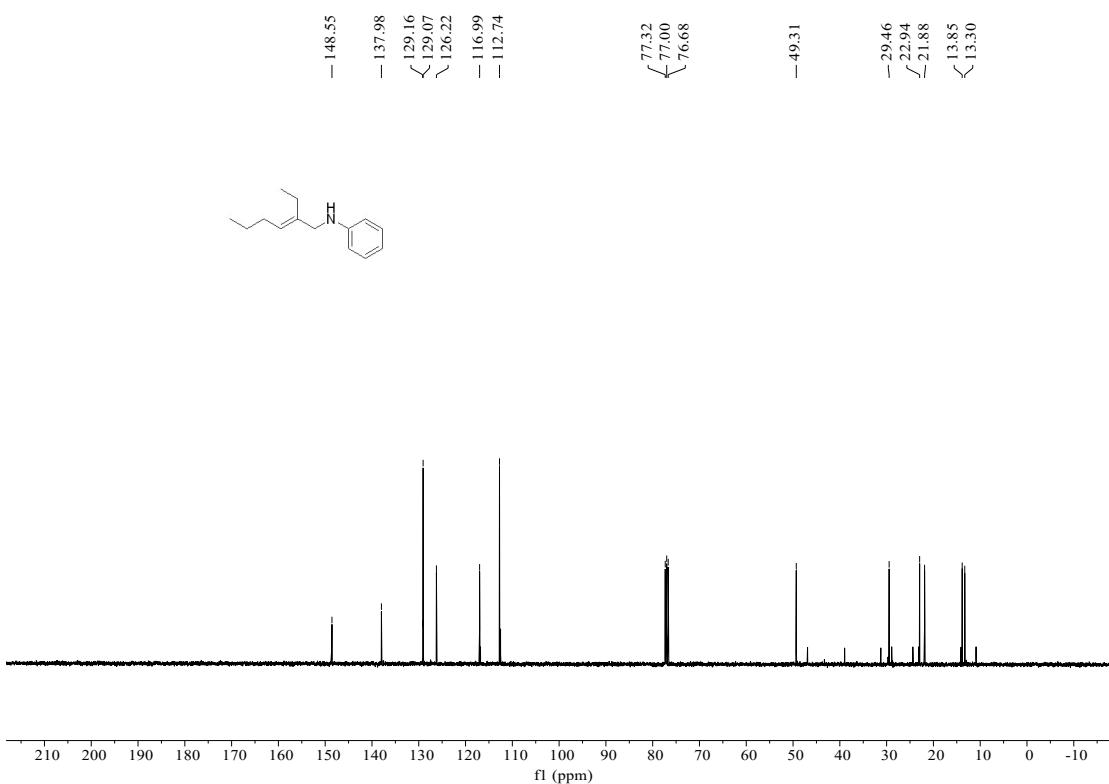
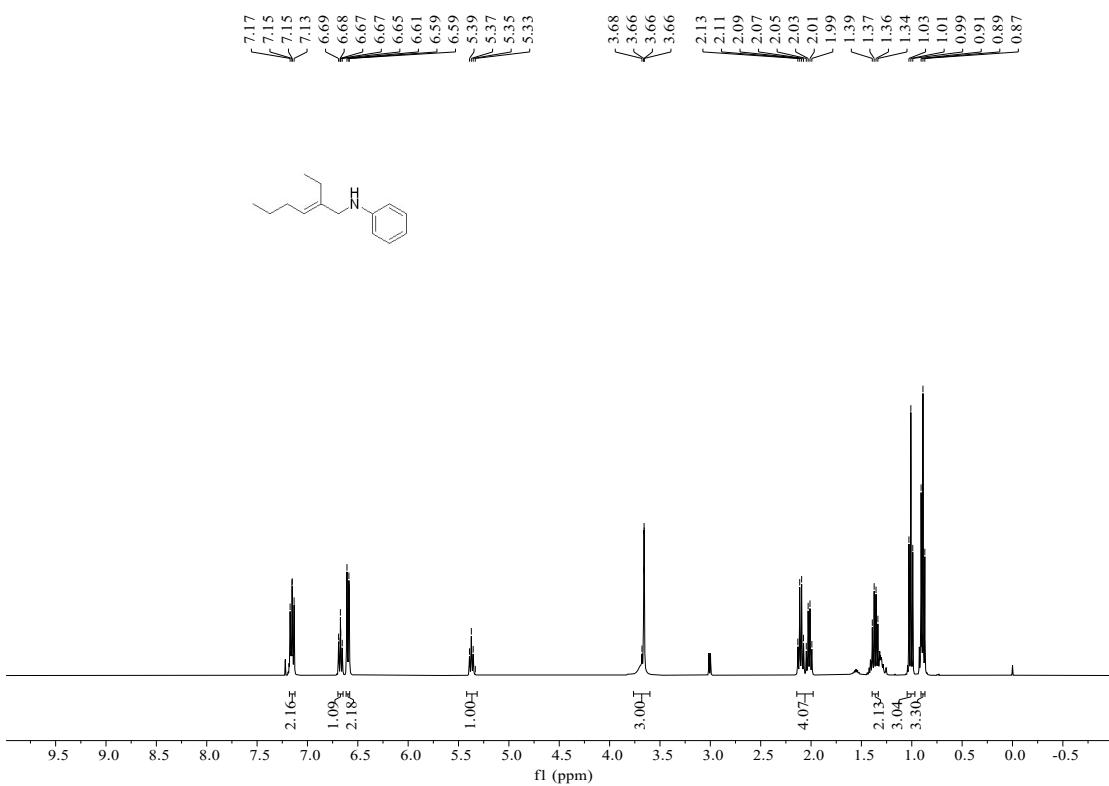




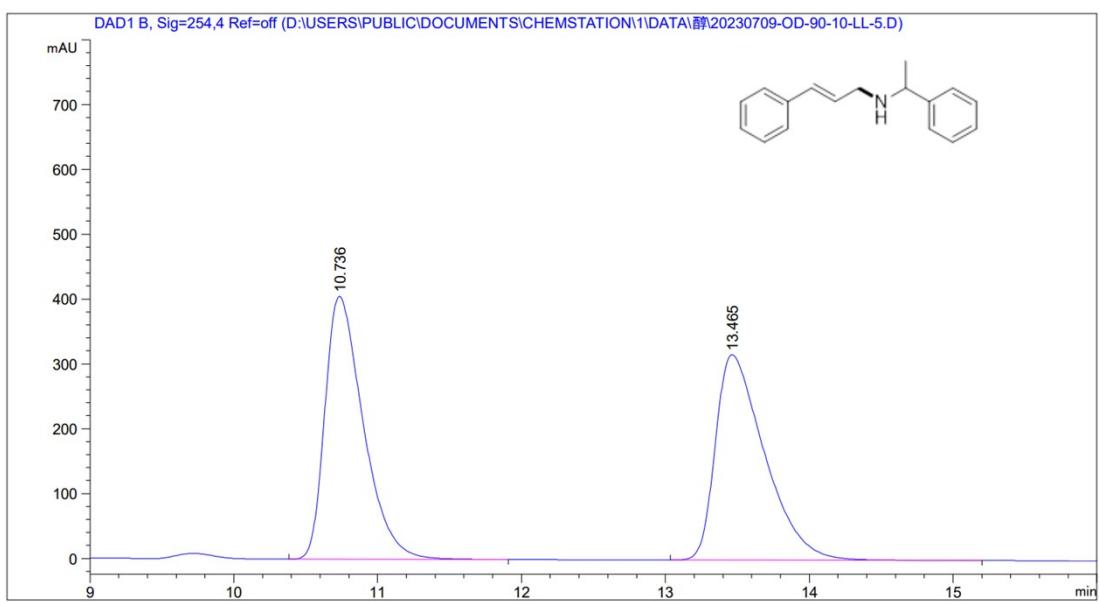
¹H NMR Spectrum of **5ao** in CDCl₃ at 400 MHz



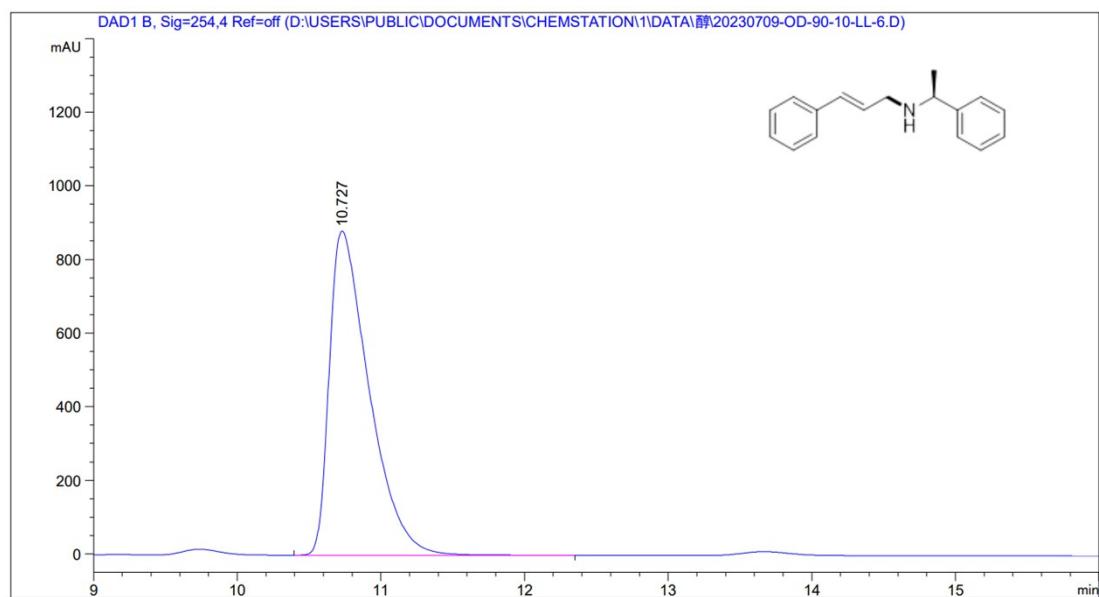
¹³C NMR Spectrum of **5ao** in CDCl₃ at 100 MHz



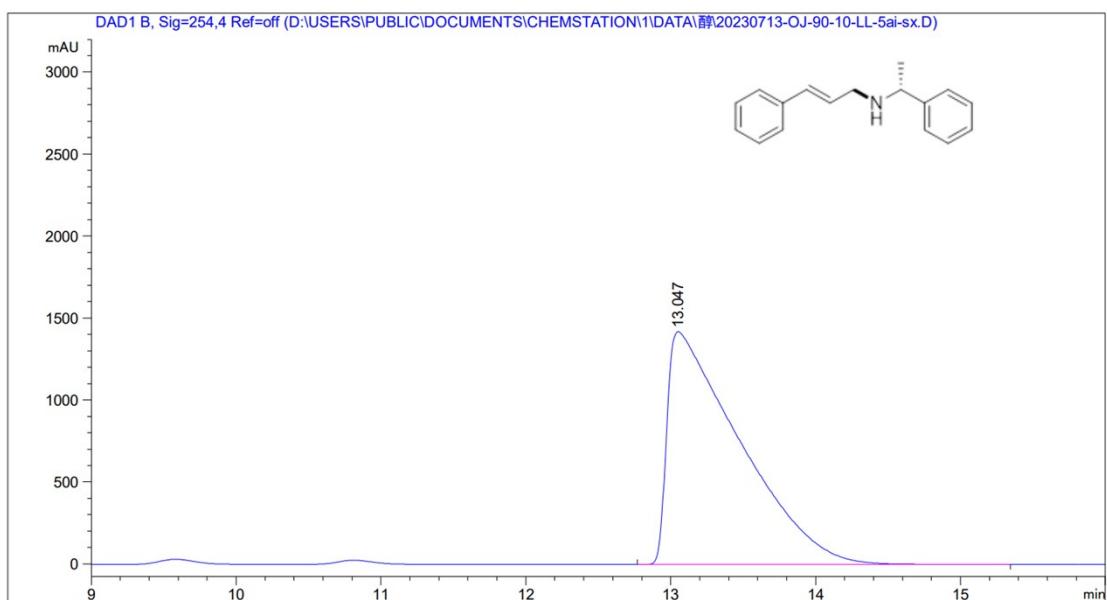
F. HPLC spectra



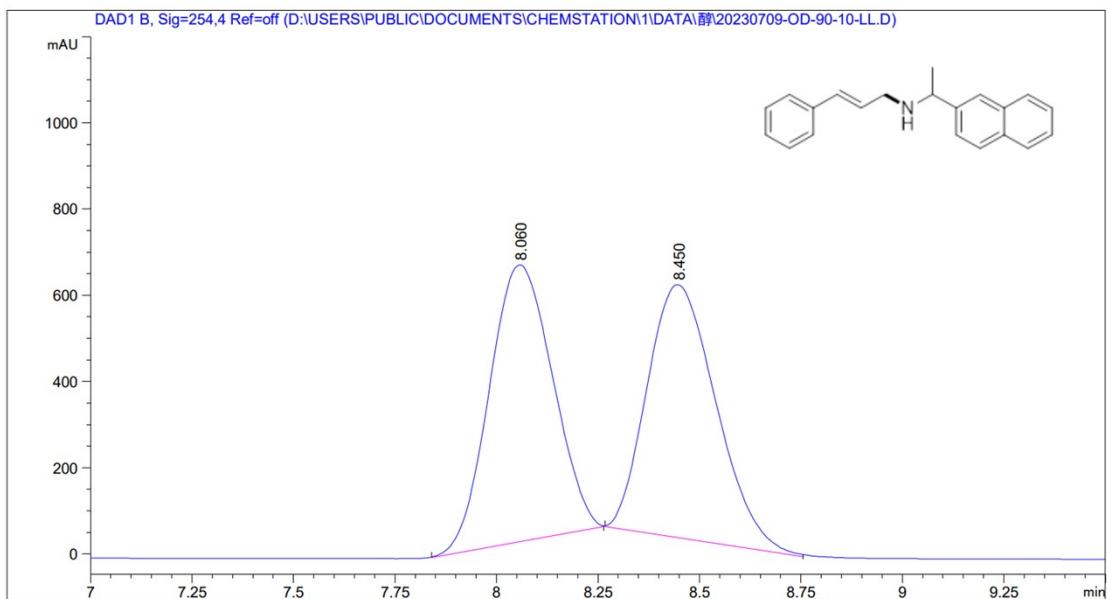
Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Arer %
1	10.736	BB	0.2819	7507.10986	405.62988	50.0104
2	13.465	BB	0.3587	7503.97949	316.43756	49.9896



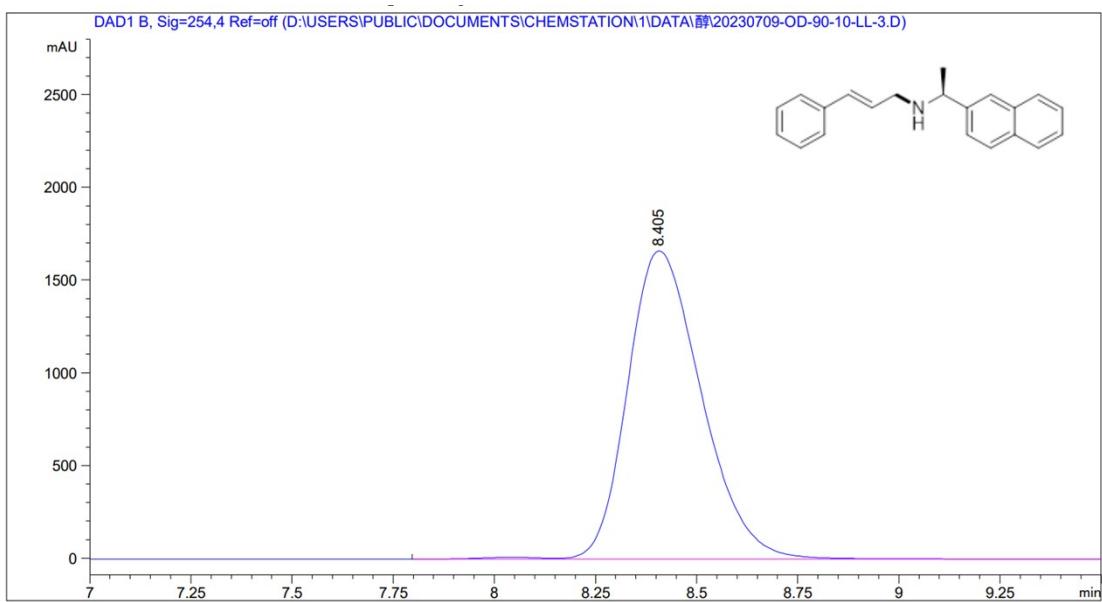
Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Arer %
1	10.727	BB	0.2881	1.6924e4	880.89807	100.0000



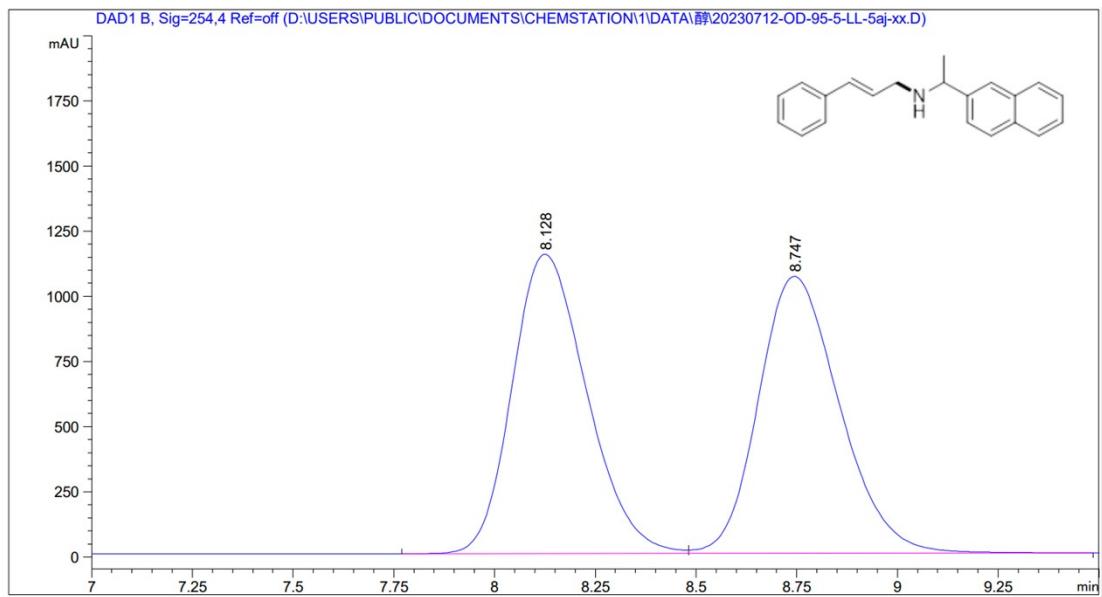
Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Arer %
1	13.047	BB	0.4708	4.95305e4	1420.49255	100.0000



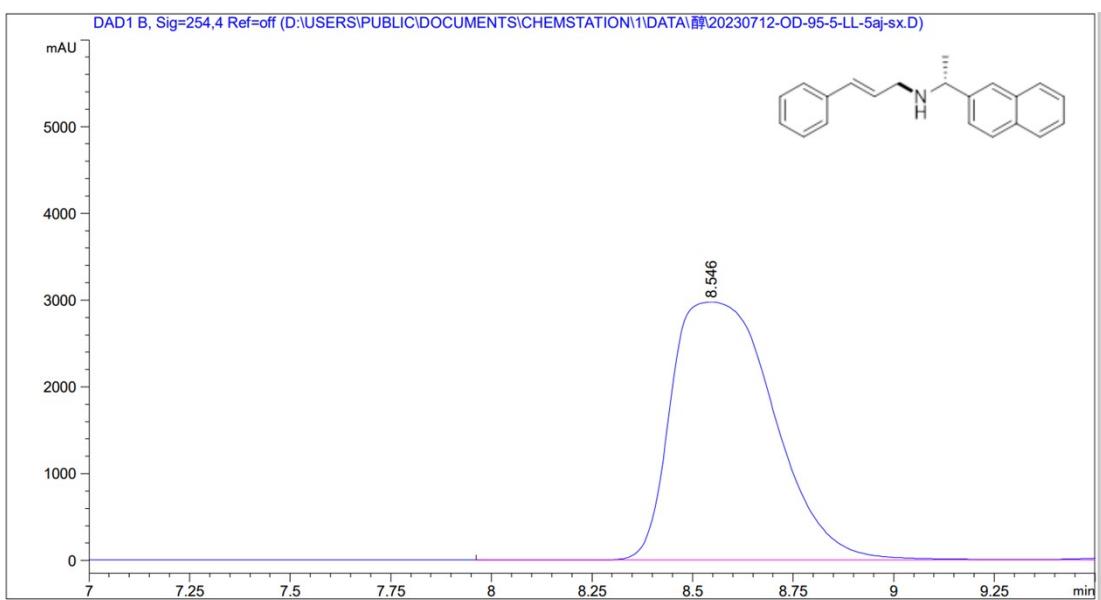
Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Arer %
1	8.060	MM R	0.1797	6931.49561	642.76056	49.9672
2	8.450	MM R	0.1971	6940.59229	587.04022	50.0328



Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Arer %
1	8.405	VB R	0.1985	2.12833e4	1663.42688	100.0000

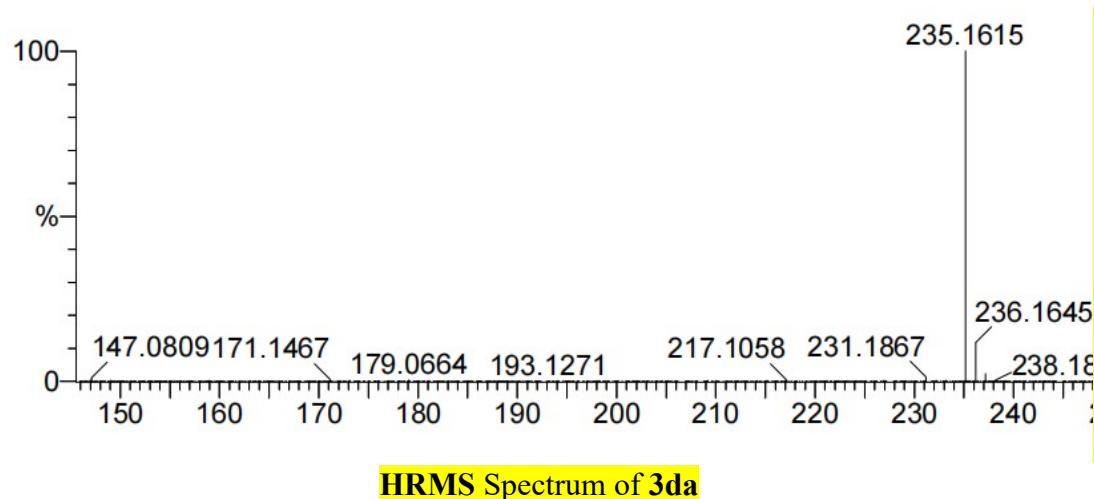
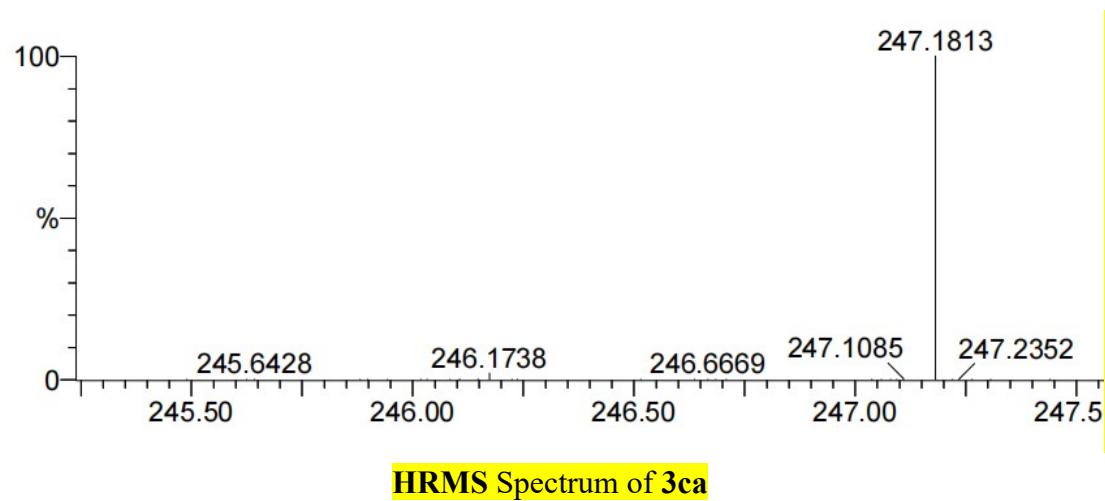
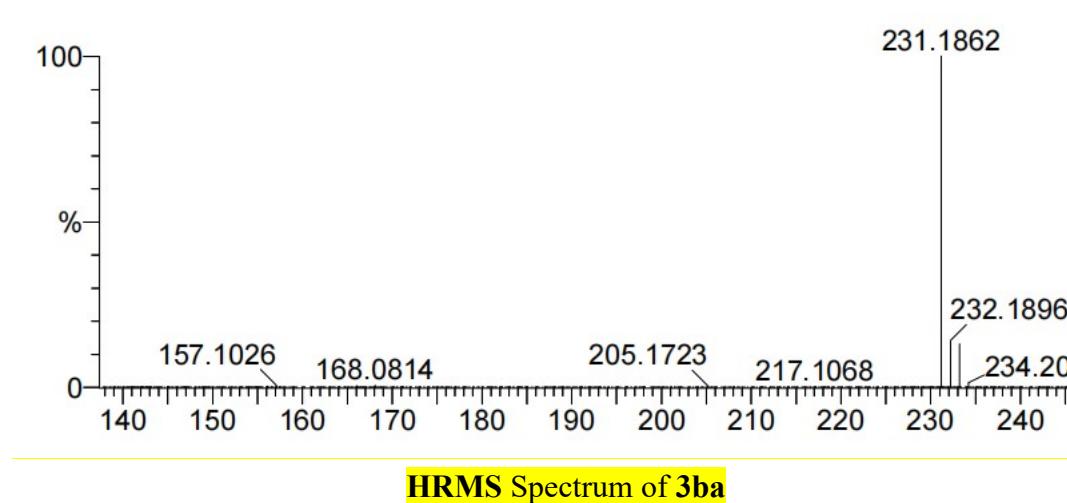


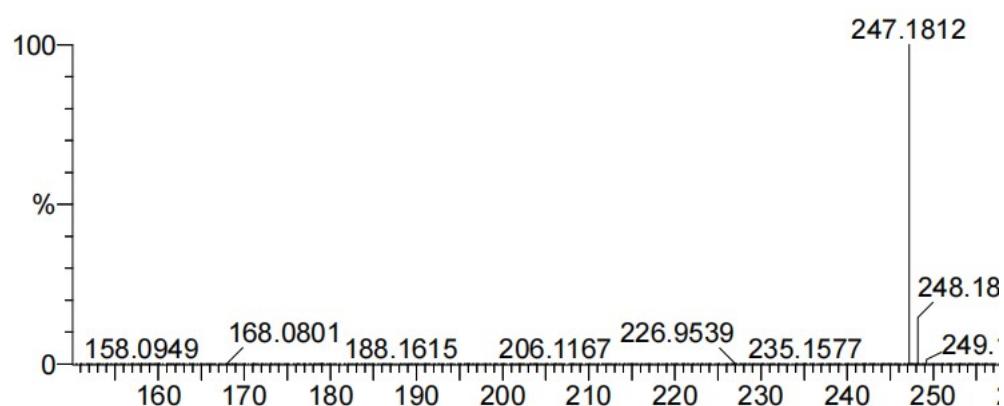
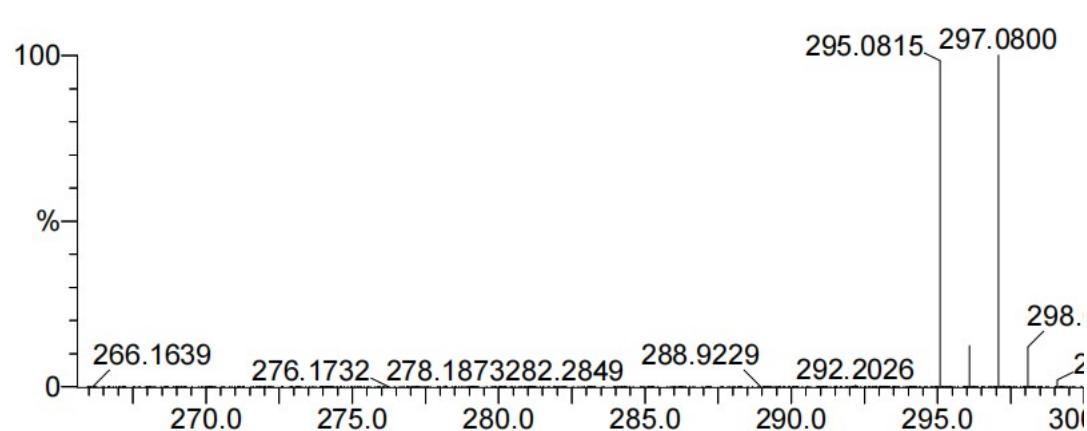
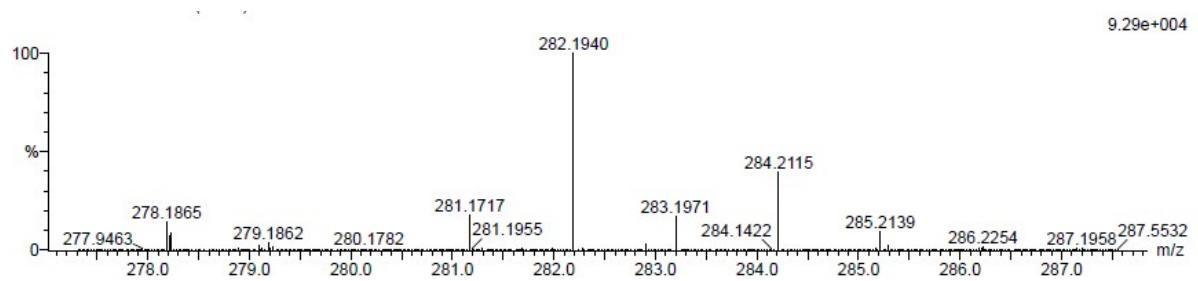
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1	8.128	BV	0.2000	1.47689e4	1148.91370	49.8949
2	8.747	VB	0.2169	1.48312e4	1062.42920	50.1051

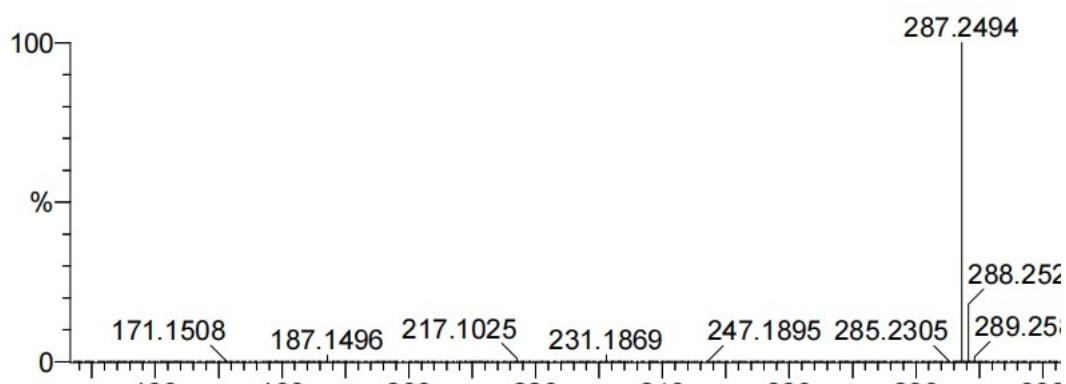
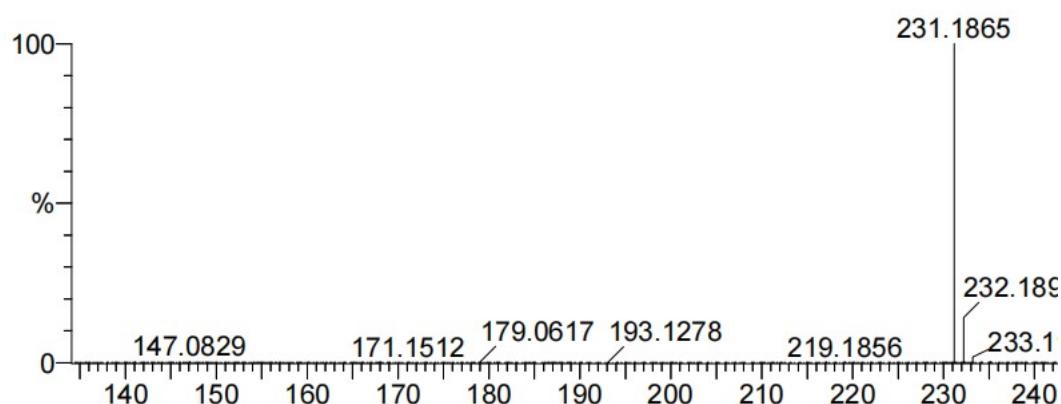
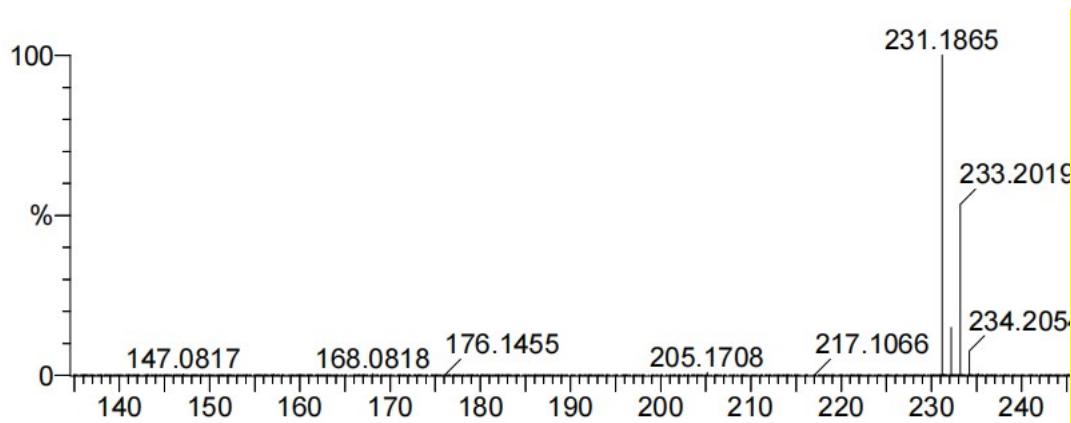


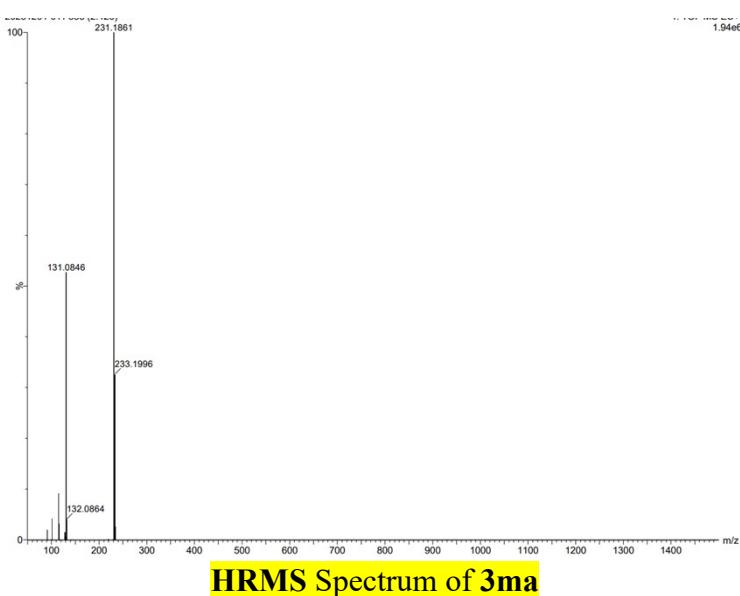
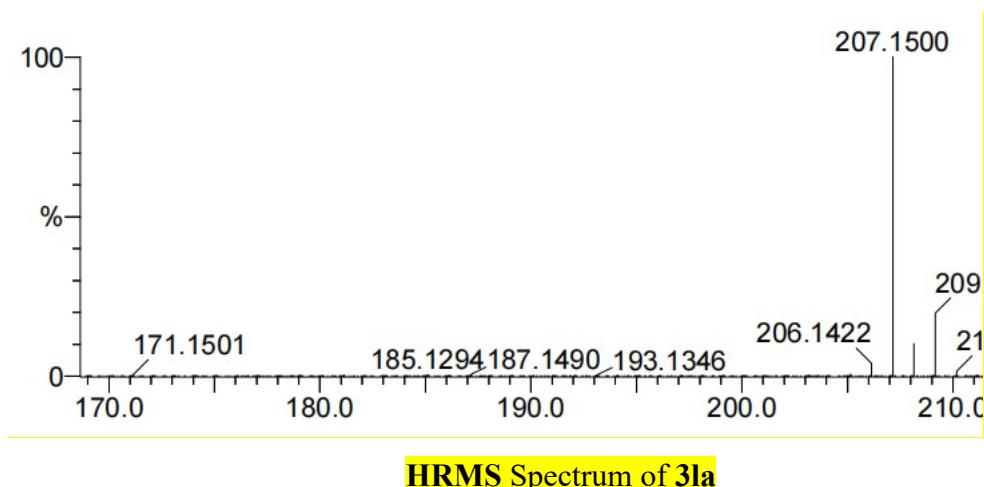
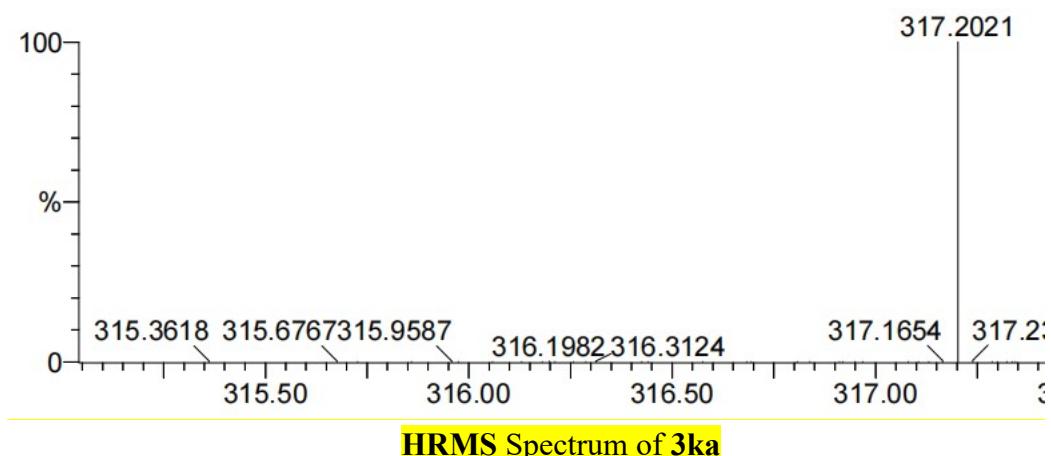
Peak #	RetTime [min]	Type	Width [min]	Area [mAu*s]	Height [mAu]	Arer %
1	8.546	BV R	0.2799	5.31265e4	2974.11206	100.0000

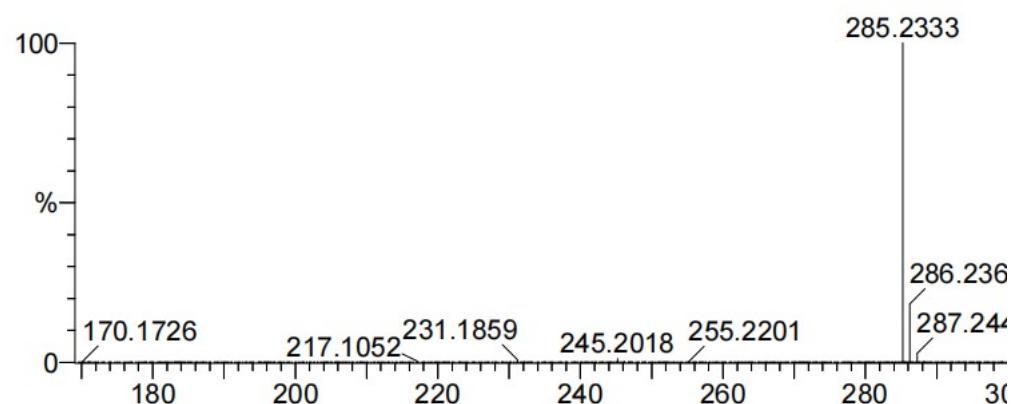
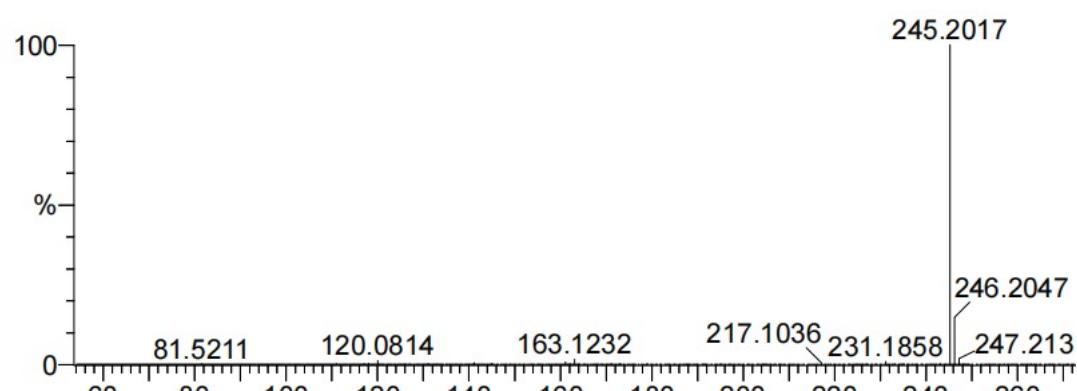
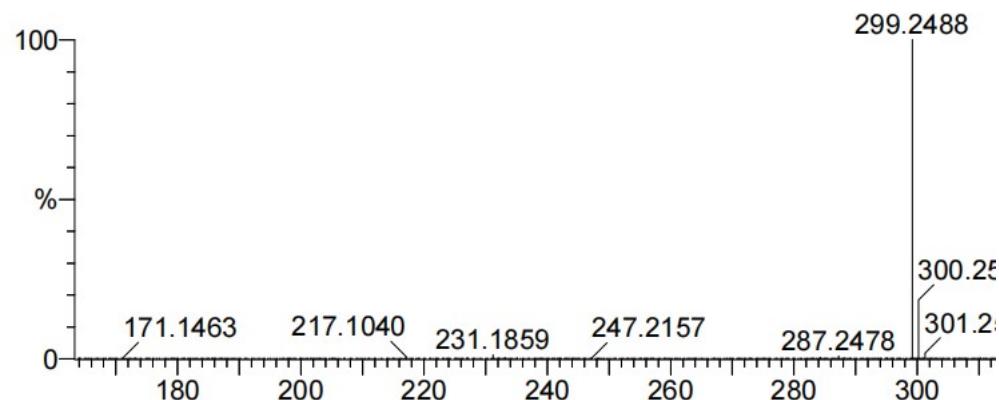
G. HRMS Spectra

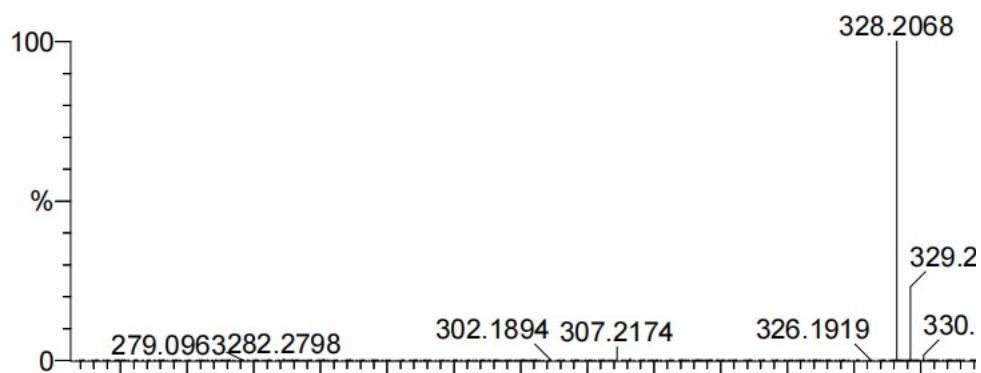
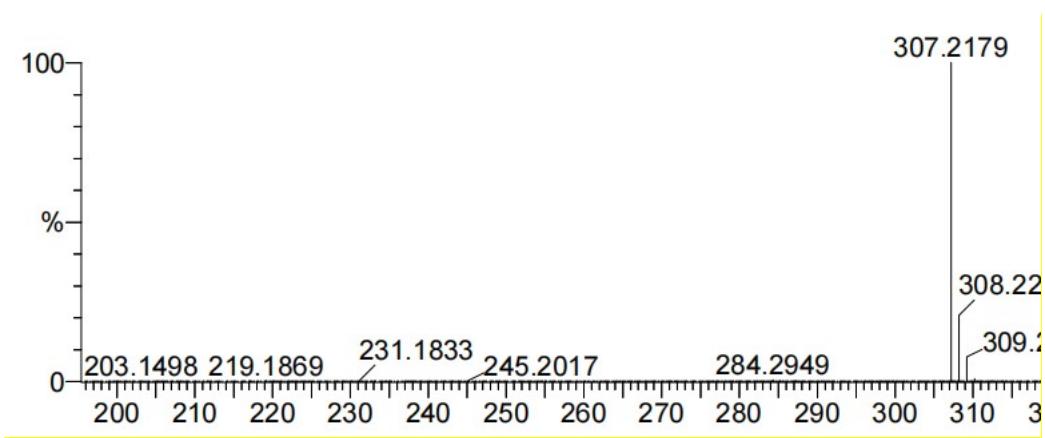
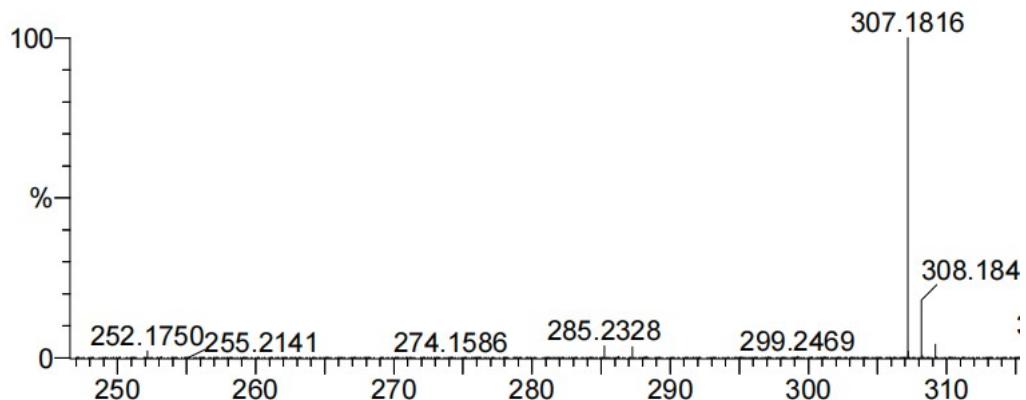


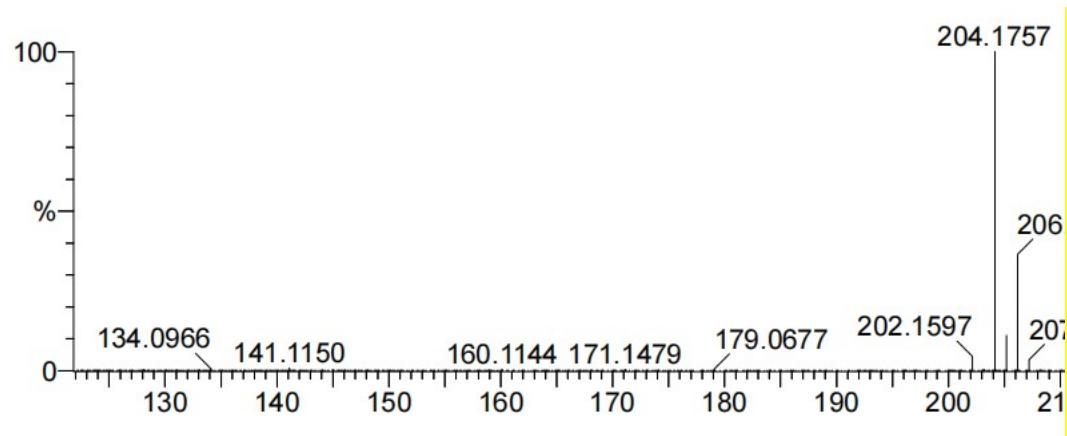
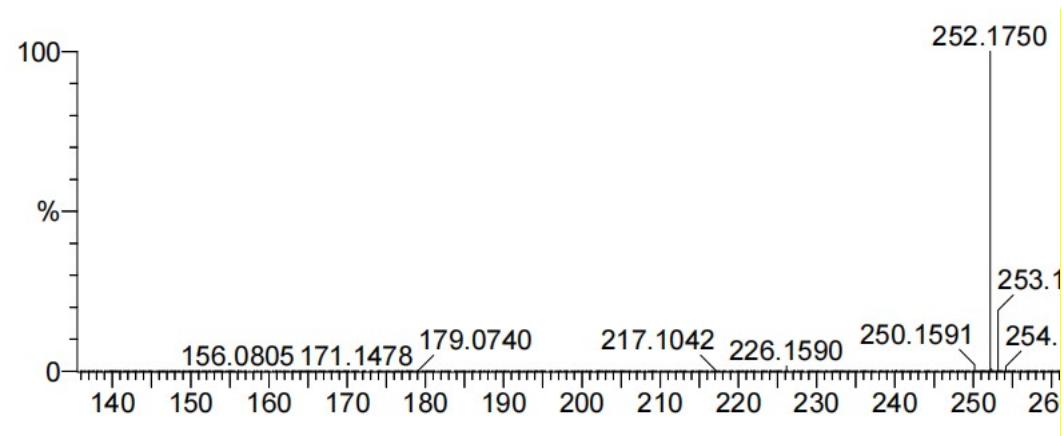
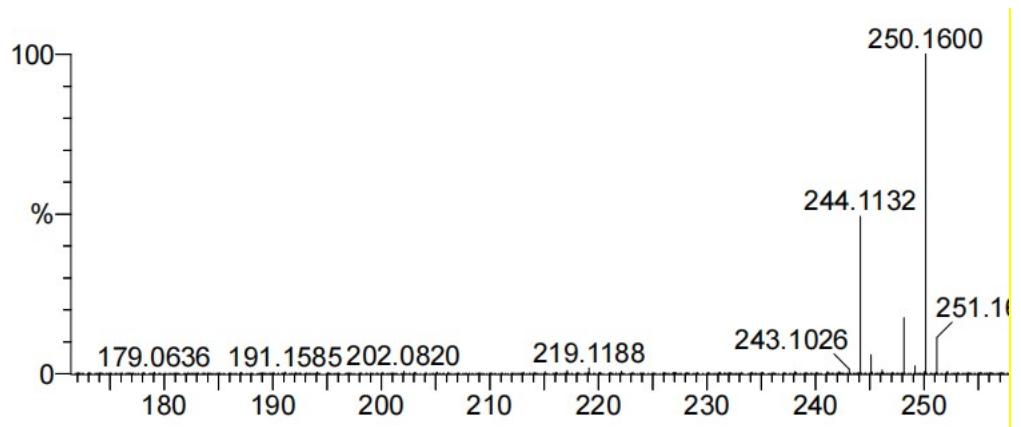


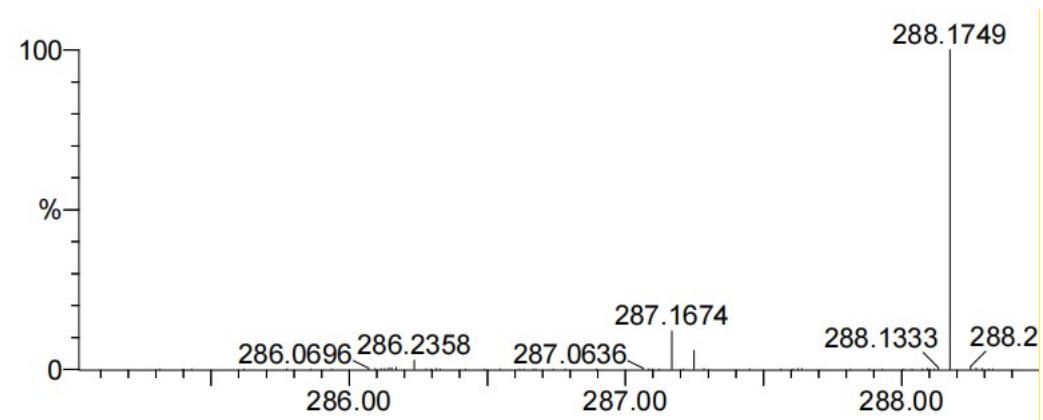












HRMS Spectrum of **5aj**