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Supporting Information

One-pot synthesis of benzo[b][1,4]diazepines via carbonylative Sonogashira reaction and *aza*-Michael addition cyclocondensation

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S-1 General Experimental

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin layer chromatography using silica gel. The thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point was between 60-90 ^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they were listed as volume/volume ratios. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker-600 MHz Spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz), using $CDCl_3$ as the solvent at room temperature. The chemical shifts (δ) were expressed in ppm and the coupling constants (*J*) were expressed in Hz. High-resolution mass spectra (HRMS) were recorded on a Bruker MAXIS spectrometer.

S-2. General procedure for the synthesis of 3H-benzo[b][1,4]diazepines

A representative example for preparation of 4aaa is as following: In 10 mL reaction tube, iodobenzene **1a** (1.0 mmol), phenylacetylene **2a** (1.2 mmol) and Et_3N (1.4 mmol) were added. Then, 1 mL stock solution containing 10 ppm T-NHC-Pd was added. The reaction tube was loaded in autoclave. After being charged, released and refilled CO (5 atm) for three times, the reaction was stirred at 100 ^oC for 8 h. The reaction was cool down to room temperature. The solvents and Et_3N were evaporated completely. Then add *o*-phenylenediamine **3a** (1.2 mmol), Cp_2TiCl_2 (10 mol%) and *m*-phthalic acid (10 mol%), add 1 mL C_2H_5OH, react at room temperature for 12 h and then end the reaction. The solvent was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether as an eluent to give the desired product **4aaa** 266 mg as yellow solid. Yield: 90%.

The Pd catalysed carbonylation was carried out using a high-pressure steel autoclave with heating jacket (from WATTCAS). For each carbonylation procedure, seven reactions were carried out in a parallel reaction modulor, a spare vial was used to monitor the reaction temperature. The pressure of CO can be adjusted (1-20 atm).

Figure S1. High-pressure steel autoclave and parallel reaction modulor.

The stock solutions prepared by the step-wise diluting Pd precatalyst with toluene. For instance, T-NHC-Pd (6.0 mg, 0.01 mmol) was dissolved in 100 mL of toluene solution, and 100 ppm of T-NHC-Pd in toluene was prepared. Then, 1 mL of 100 ppm T-NHC-Pd solution was diluted with 9 mL toluene, and 10 ppm T-NHC-Pd solution was prepared. In the reaction, 1 mL of 10 ppm stock solution was added to the mixture of 1 mmol of aryl iodides, 1.2 mmol of alkynes and 1.4 mmol of triethylamine in reaction vials. No special precautions for the preparation of the catalyst stock solutions were not taken, and the catalysts were handled in air. In order to avoid the contamination of residue Pd in each experiment, the following general procedure was used: A test glass tube and a stirrer bar coated with PTFE were treated with aqua regia (1:3 concd aq HCl–concd aq HNO_3) for 30 min and then washed sequentially with pure water and acetone, and dried with heating.

S-3 Optimization of Sonogashira carbonylation coupling reaction and *aza*-Michael addition cyclocondensation between1a, 2a and 3a

S-3.1 Optimization of solvents in the titled reaction between 1a, 2a and 3a

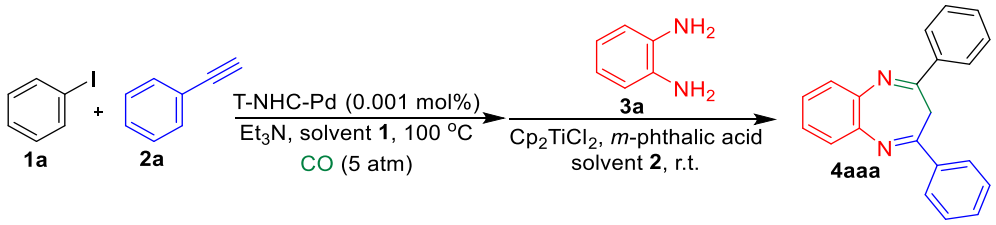


Table S1. Optimization of solvents in the titled reaction between **1a**, **2a** and **3a**.

Entry	Solvent **1**	Base	Solvent **2**	Cp_2TiCl_2 (mol%)	*m*-phthalic acid (mol%)	Yield (%)
1	Toluene	Et_3N	Toluene	10	10	5
2	Dioxane	Et_3N	Dioxane	10	10	15
3	CH_3CN	Et_3N	CH_3CN	10	10	13
4	THF	Et_3N	THF	10	10	12
5	EtOH	Et_3N	EtOH	10	10	46
6	DMSO	Et_3N	DMSO	10	10	18

[a] Reaction conditions: **1a** iodobenzene (1mmol), **2a** phenylacetylene (1.2 mmol), solvent **1** (1 mL), Et_3N (1.4 mmol, 1.4 equiv.), T-NHC-Pd (0.001 mol%), CO (5 atm), 100 °C, 8 h; [b] **3a** *o*-phenylenediamine (1.2 mmol), Cp_2TiCl_2 (10 mol%), *m*-phthalic acid (10 mol%), solvent **2** (1 mL), r.t., 12 h; [c] Determined by GC analysis of the reaction mixture using biphenyl as an internal standard.

S-3-2 Solvent effect and the amount of Et_3N effect in Sonogashira carbonylation coupling reaction between1a and 2a

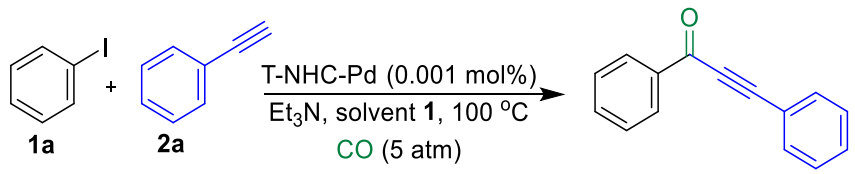


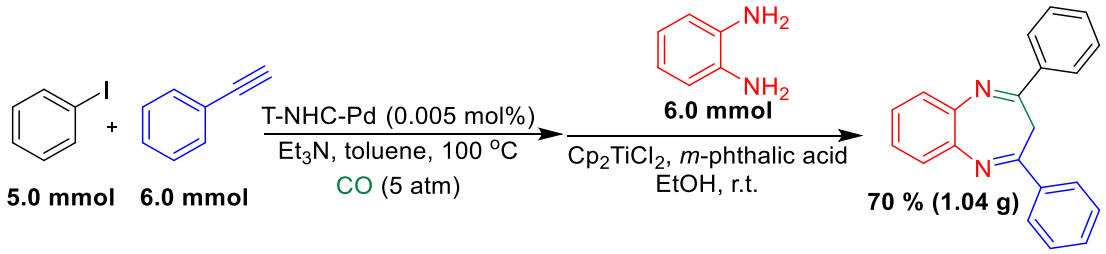
Table S2. Solvent effect and the amount of Et_3N effect in Sonogashira carbonylation coupling reaction between**1a** and **2a**.

Entry	Solvent **1**	Base	Yield (%)	Entry	Solvent **1**	Et_3N (mmol)	Yield (%)
1	Toluene	Et_3N	90	8	Toluene	1.0	82
2	THF	Et_3N	54	9	Toluene	1.2	87
3	Dioxane	Et_3N	39	10	Toluene	1.4	95
4	CH_3CN	Et_3N	47	11	Toluene	1.6	93
5	DMF	Et_3N	47	12	Toluene	1.8	89
6	DMSO	Et_3N	67	13	Toluene	2.0	90
7	EtOH	Et_3N	43	14	Toluene	2.2	89

[a] Reaction conditions: **1a** ¡odobenzene (1 mmol), **2a** phenylacetylene (1.2 mmol), solvent 1 (1 mL), Et_3N (1.0 - 2.2 mmol, 1.0 - 2.2 equiv.), T-NHC-Pd (0.001 mol%), CO (5 atm), 100 °C, 8 h; [b] Determined by GC analysis of the reaction mixture using biphenyl as an internal standard.

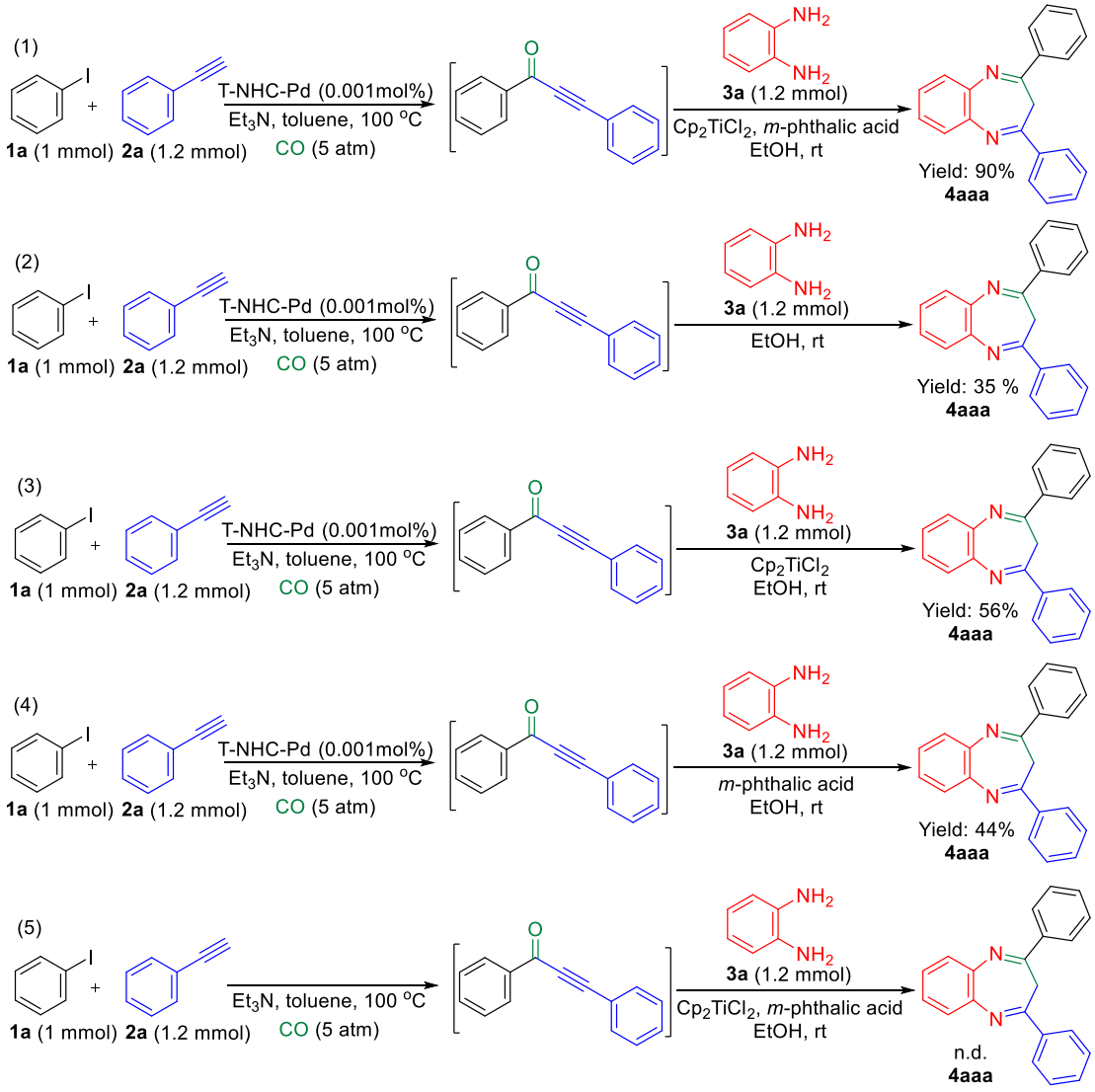
S-4 The scale-up reaction

The large-scale reaction was performed using 5.0 mmol of starting materials, affording 1.04 g of **4aaa** with 70% yield. The gram-scale experimental procedure was as follows: In 25 mL reaction tube, iodobenzene **1a** (5.0 mmol), phenylacetylene **2a** (6.0 mmol) and Et_3N (7.0 mmol) were added. Then, 5 mL stock solution containing 10 ppm T-NHC-Pd was added. The reaction tube was loaded in autoclave. After being charged, released and refilled CO (5 atm) for three times, the reaction was stirred at 100 °C for 12 h. The reaction was cool down to room temperature. The solvents and Et_3N were evaporated completely. Then add *o*-phenylenediamine **3a** (6 mmol), Cp_2TiCl_2 (50 mol%) and *m*-phthalic acid (50 mol%), add 5 mL C_2H_5OH, react at room temperature for 12 h and then end the reaction. The solvent was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel with Ethyl acetate/Petroleum ether as an eluent to give the desired product **4aaa** 1.04 g as yellow solid. Yield: 70%.



Scheme S1. The scale-up reaction.

S-5 Proposed mechanism.



Scheme S2. The control experiments.

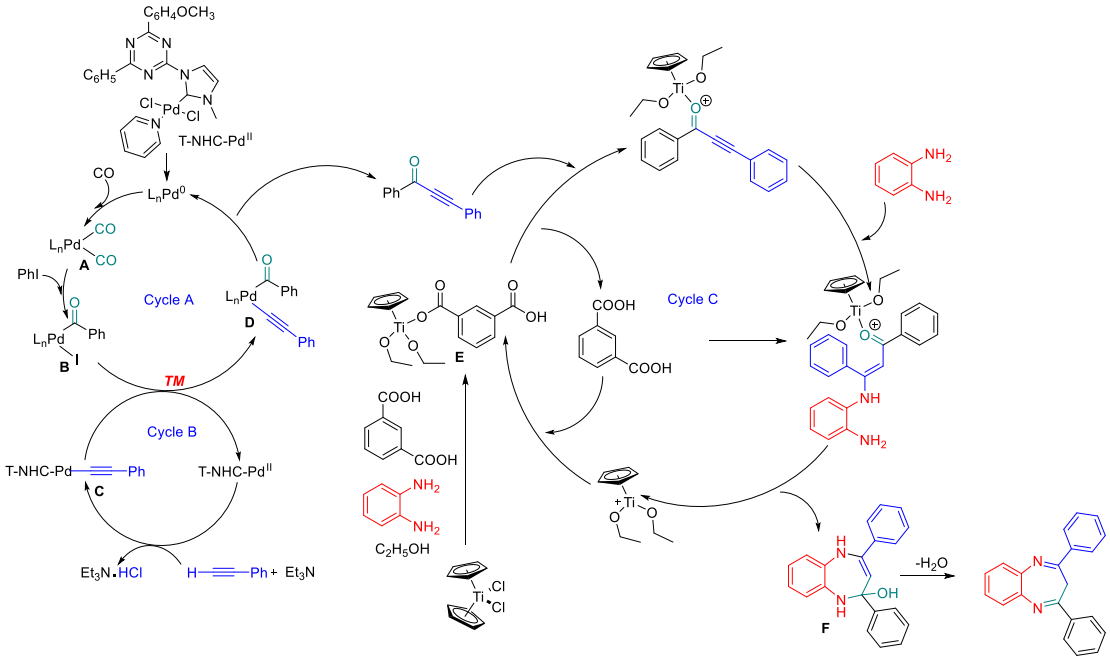
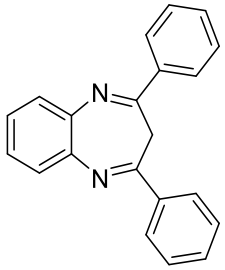
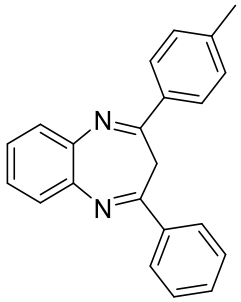


Figure S2. Proposed mechanism of T-NHC-Pd catalysed carbonylative Sonogashira reaction and Cp_2TiCl_2 catalysed *aza*-Michael addition cyclocondensation.

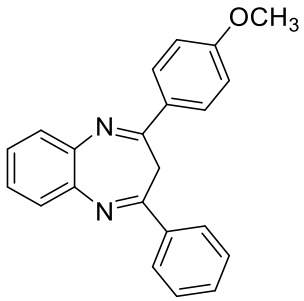
S-6 NMR-Data of 2,4-disubstituted-3H- benzo[b]-[1,4]diazepine products



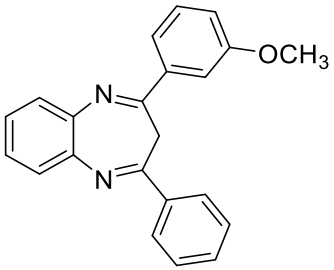
2,4-diphenyl-3H-benzo[b][1,4]diazepine (4aaa).[1] (Yellow solid was obtained in 90% isolated yield, 266 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 - 7.97 (m, 4H), 7.62 (dd, *J* = 6.0, 3.5 Hz, 2H), 7.45 - 7.40 (m, 6H), 7.35 (dd, *J* = 6.0, 3.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 140.9, 137.5, 130.8, 128.88, 128.85, 128.3, 125.6, 35.2.



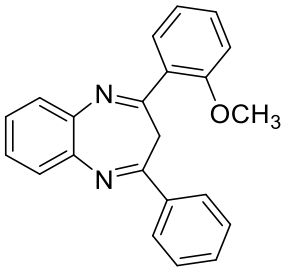
2-phenyl-4-(*p*-tolyl)-3H-benzo[b][1,4]diazepine (4baa).[1] (White solid was obtained in 84% isolated yield, 260 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 - 7.97 (m, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.62 - 7.60 (m, 2H), 7.43 - 7.41 (m, 3H), 7.35 - 7.33 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 154.2, 141.2, 141.0, 140.1, 137.5, 134.7, 130.7, 129.6, 128.9, 128.8, 128.8, 128.3, 128.2, 125.5, 125.4, 35.0, 21.5.



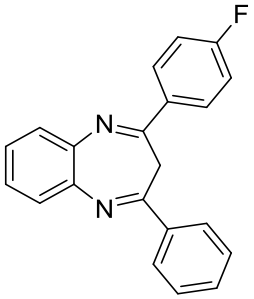
2-(4-methoxyphenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4caa).[1] (White solid was obtained in 70% isolated yield, 228 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 - 7.95 (m, 4H), 7.62 - 7.59 (m, 2H), 7.43 -7.41 (m, 3H), 7.34 - 7.32 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8, 154.4, 153.7, 141.1, 140.8, 137.5, 130.6, 130.07, 130.05, 128.9, 128.8, 128.2, 125.5, 125.2, 114.2, 55.5, 34.9.



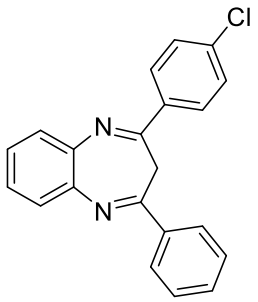
2-(3-methoxyphenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4daa).[1] (White solid was obtained in 75% isolated yield, 230 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 - 7.99 (m, 2H), 7.64 - 7.63 (m, 2H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.50 - 7.49 (m, 1H), 7.44 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.37 - 7.32 (m, 3H), 6.99 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 154.3, 154.1, 140.9, 140.7, 138.9, 137.4, 130.7, 129.7, 128.83, 128.80, 128.3, 125.6, 125.5, 120.5, 117.3, 112.9, 55.4, 35.3.



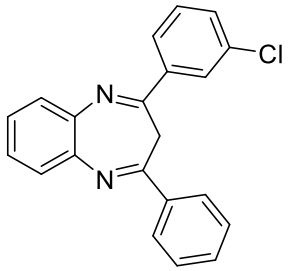
2-(2-methoxyphenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4eaa).[1] (White solid was obtained in 35% isolated yield, 105 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.62 - 7.60 (m, 2H), 7.40 - 7.37 (m, 3H), 7.35 - 7.32 (m, 4H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.94 - 6.91 (m, 1H), 3.71 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 157.1, 155.9, 140.9, 140.6, 138.5, 131.6, 131.6, 130.2, 128.9, 128.7, 128.5, 128.1, 125.5, 125.3, 121.1, 111.1, 55.4, 38.6.



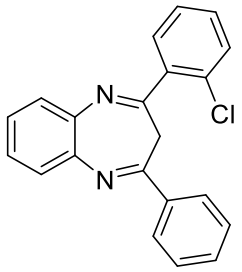
2-(4-fluorophenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4faa).[1] (White solid was obtained in 81% isolated yield, 255 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 - 7.95 (m, 4H), 7.66 - 7.59 (m, 2H), 7.47 - 7.41 (m, 3H), 7.39 - 7.34 (m, 2H), 7.13 - 7.07 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.19 (d, ^{1}J = 253.68 Hz), 154.0, 152.8, 140.8, 140.6, 137.3, 133.6 (d, ^{4}J = 1.51 Hz),130.8, 130.4 (d, ^{3}J = 9.06Hz), 128.8, 128.7, 128.2, 125.6, 115.9 (d, ^{2}J = 22.65Hz), 34.9.



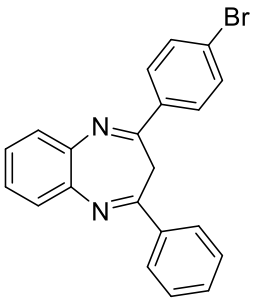
2-(4-chlorophenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4gaa).[1] (White solid was obtained in 65% isolated yield, 215 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.94 - 7.89 (m, 2H), 7.65 - 7.58 (m, 2H), 7.47 - 7.41 (m, 3H), 7.40 - 7.33 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.7, 140.8, 140.6, 136.9, 135.8, 130.9, 129.5, 129.0, 128.9, 128.8, 128.2, 125.8, 125.7, 34.9.



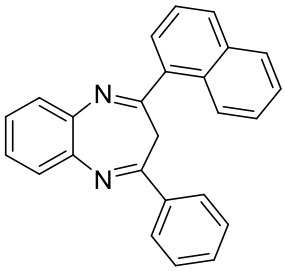
2-(3-chlorophenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4haa).[1] (White solid was obtained in 55% isolated yield, 181 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (t, *J* = 1.9 Hz, 1H), 8.00 - 7.96 (m, 2H), 7.84 - 7.80 (m, 1H), 7.66 - 7.61 (m, 2H), 7.47 - 7.42 (m, 3H), 7.41 - 7.35 (m, 3H), 7.33 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 152.5, 140.9, 140.4, 139.1, 137.1, 135.0, 130.9, 130.7, 130.0, 128.9, 128.86, 128.84, 128.4, 128.3, 126.1, 125.9, 125.7, 34.9.



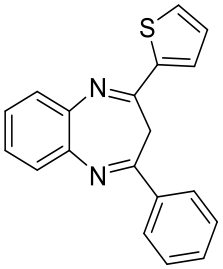
2-(2-chlorophenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4iaa). (White solid was obtained in 35% isolated yield, 115 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 - 7.77 (m, 2H), 7.65 - 7.60 (m, 2H), 7.51 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.41 - 7.36 (m, 3H), 7.36 - 7.31 (m, 3H), 7.20 (td, *J* = 7.5, 1.1 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 154.3, 140.3, 140.2, 138.3, 137.5, 132.6, 131.1, 131.0, 130.6, 130.1, 128.7, 128.6, 128.5, 128.1, 127.3, 126.0, 125.5, 39.2. HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}ClN_2$: 331.0997. Found: 331.0993.



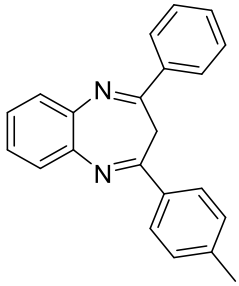
2-(4-bromophenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4jaa).[1] (White solid was obtained in 68% isolated yield, 254 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.86 - 7.82 (m, 2H), 7.63 - 7.58 (m, 2H), 7.56 - 7.52 (m, 2H), 7.46 - 7.41 (m, 3H), 7.38 - 7.33 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.0, 152.9, 140.9, 137.3, 136.3, 132.0, 130.9, 129.8, 128.92, 128.91, 128.8, 128.3, 125.8, 125.7, 34.9.



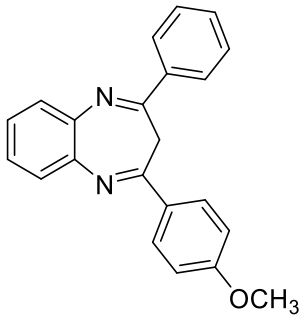
2-(naphthalen-1-yl)-4-phenyl-3H-benzo[b][1,4]diazepine (4kaa).[1] (Yellow solid was obtained in 65% isolated yield, 224 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.70 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.67 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.53 - 7.44 (m, 3H), 7.40 (m, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.25 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 153.9, 140.6, 137.5, 136.8, 130.8, 130.6, 130.5, 128.8, 128.68, 128.66, 128.6, 128.1, 127.2, 127.0, 126.4, 125.8, 125.6, 125.5, 125.1, 40.3.



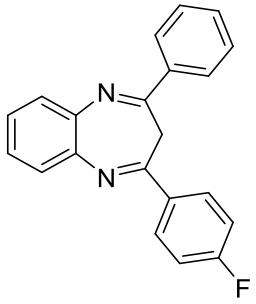
2-phenyl-4-(thiophen-2-yl)-3H-benzo[b][1,4]diazepine (4laa).[1] (Yellow solid was obtained in 45% isolated yield, 136 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.62 (d, *J* = 3.7 Hz, 1H), 7.58 (m, 2H), 7.49-7.42 (m, 4H), 7.33 (m, 2H), 7.06 (dd, *J* = 5.0, 3.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 148.8, 144.2, 141.2, 140.3, 137.3, 131.4, 130.9, 129.0, 128.9, 128.84, 128.82, 128.3, 127.9, 125.7, 125.6, 35.5.



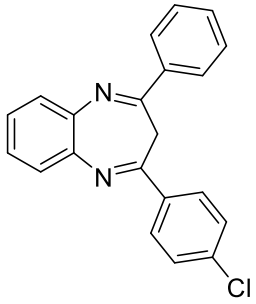
2-phenyl-4-(p-tolyl)-3H-benzo[b][1,4]diazepine (4aba).[1] (White solid was obtained in 82% isolated yield, 254 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.67 - 7.61 (m, 2H), 7.43 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.39 - 7.33 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 154.2, 141.1, 140.9, 140.8, 137.5, 134.62, 130.6, 129.5, 128.82, 128.79, 128.75, 128.3, 128.2, 125.5, 125.3, 34.9, 21.5.



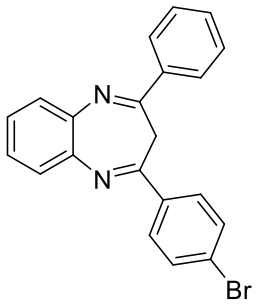
2-(4-methoxyphenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4aca).[1] (White solid was obtained in 85% isolated yield, 276 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 - 7.93 (m, 4H), 7.60 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.42 (m, 3H), 7.37 - 7.29 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8, 154.4, 153.6, 141.1, 140.8, 137.5, 130.6, 130.1, 130.0, 128.9, 128.8, 128.2, 125.5, 125.2, 114.1, 55.5, 34.9.



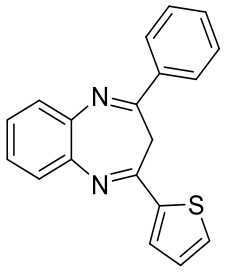
2-(4-fluorophenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4ada).[1] (White solid was obtained in 86% isolated yield, 269 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 - 7.95 (m, 4H), 7.64 (m, 2H), 7.47 - 7.41 (m, 3H), 7.39 - 7.34 (m, 2H), 7.10 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.14 (d, ^{1} *J* = 253.68 Hz), 153.9, 152.8, 140.7, 140.6, 137.2, 133.6 (d, ^{4} *J* = 1.51 Hz), 130.8, 130.4 (d, ^{3} *J* = 9.06Hz), 128.8, 128.7, 128.2, 125.6, 115.9 (d, ^{2} *J* = 22.65Hz), 34.9.



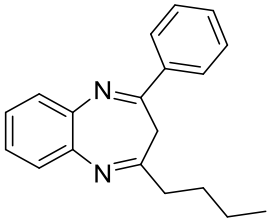
2-(4-chlorophenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4aea).[1] (White solid was obtained in 55% isolated yield, 181 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.64 - 7.58 (m, 2H), 7.46 - 7.41 (m, 3H), 7.40 - 7.33 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 152.8, 140.8, 140.6, 137.3, 135.8, 130.9, 129.5, 129.0, 128.89, 128.88, 128.8, 128.2, 125.8, 125.7, 34.9.



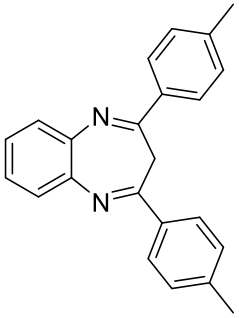
2-(4-bromophenyl)-4-phenyl-3H-benzo[b][1,4]diazepine (4afa).[1] (White solid was obtained in 65% isolated yield, 243 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.77 - 7.73 (m, 2H), 7.51 (dtd, *J* = 9.7, 4.5, 2.8 Hz, 2H), 7.47 - 7.44 (m, 2H), 7.38 - 7.32 (m, 3H), 7.28 - 7.24 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.0, 152.9, 140.9, 140.6, 137.3, 132.0, 130.9, 129.8, 128.92, 128.90, 128.8, 128.3, 125.8, 125.7, 125.5, 34.9.



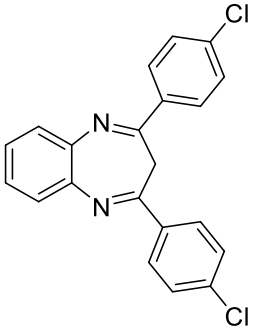
2-phenyl-4-(thiophen-2-yl)-3H-benzo[b][1,4]diazepine (4aga).[1] (Yellow solid was obtained in 50% isolated yield, 151 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.62 (dd, *J* = 3.7, 0.9 Hz, 1H), 7.59 (ddd, *J* = 9.4, 6.0, 3.5 Hz, 2H), 7.47 (m, 3H), 7.44 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.35 - 7.30 (m, 2H), 7.06 (dd, *J* = 5.0, 3.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 148.8, 141.2, 140.3, 137.3, 131.4, 130.9, 129.0, 128.9, 128.8, 128.8, 128.3, 127.9, 125.7, 125.6, 35.5.



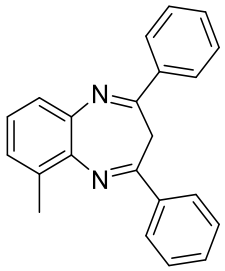
2-butyl-4-phenyl-3H-benzo[b][1,4]diazepine (4aha).[1] (Yellow liquid was obtained in 40% isolated yield, 110 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.1 Hz, 2H), 7.49 - 7.41 (m, 1H), 7.37 (m, 4H), 7.17 (dd, *J* = 9.5, 5.8 Hz, 2H), 2.42 (t, *J* = 7.7 Hz, 2H), 1.51 (t, *J* = 7.8 Hz, 2H), 1.25 - 1.12 (m, 2H), 0.73 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 153.8, 140.7, 140.5, 137.2, 130.7, 128.8, 128.6, 128.3, 127.8, 125.2, 124.9, 40.2, 37.6, 28.4, 22.4, 13.9.



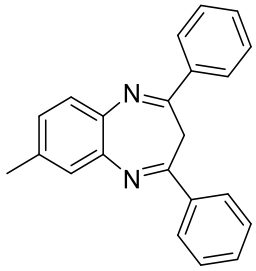
2,4-di-*p*-tolyl-3H-benzo[b][1,4]diazepine (4bba). (White solid was obtained in 87% isolated yield, 282 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (m, 4H), 7.61 (dd, *J* = 6.1, 3.5 Hz, 2H), 7.33 (dd, *J* = 6.1, 3.5 Hz, 2H), 7.22 (m, 4H), 2.37 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.3, 141.0, 140.9, 134.7, 129.5, 128.8, 128.3, 125.3, 34.9, 21.5. HRMS(ESI) m/z：[M+H]$^{+}$calcd for $C_{23}H_{21}N_2$: 325.1699. Found: 325.1694.



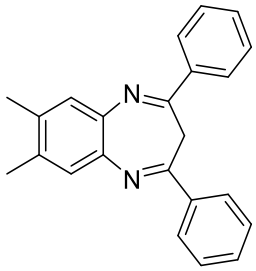
2,4-bis(4-chlorophenyl)-3H-benzo[b][1,4]diazepine (4gea). (White solid was obtained in 45% isolated yield, 163 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 - 7.87 (m, 4H), 7.61 - 7.57 (m, 2H), 7.42 -7.38 (m, 4H), 7.38 - 7.34 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 140.6, 137.2, 135.6, 129.5, 129.2, 128.9, 125.9, 34.7. HRMS(ESI) m/z：[M+H]$^{+}$calcd for $C_{21}H_{15}Cl_2N_2$: 365.0607. Found: 365.0600.



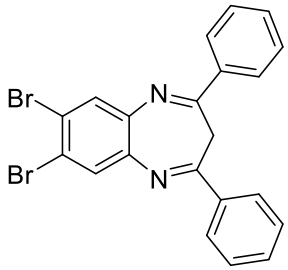
6-methyl-2,4-diphenyl-3H-benzo[b][1,4]diazepine (4aab).[1] (Yellow solid was obtained in 72% isolated yield, 223 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 - 8.06 (m, 2H), 8.04 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.57 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.49 - 7.42 (m, 6H), 7.34 - 7.27 (m, 2H), 2.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 140.5, 137.4, 136.3, 130.5, 130.4, 128.7, 128.6, 128.3, 128.1, 126.6, 125.1, 34.9, 18.7.



7-methyl-2,4-diphenyl-3H-benzo[b][1,4]diazepine (4aac).[1] (White solid was obtained in 85% isolated yield, 263 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (m, 4H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.48 - 7.46 (m, 1H), 7.43 (m, 6H), 7.20 (dd, *J* = 8.2, 2.0 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 153.4, 140.6, 138.6, 137.5, 137.4, 135.4, 130.6, 130.5, 128.7, 128.6, 128.2, 128.1, 126.9, 35.0, 21.2.



7,8-dimethyl-2,4-diphenyl-3H-benzo[b][1,4]diazepine (4aad).[1] (White solid was obtained in 89% isolated yield, 288 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 - 7.94 (m, 4H), 7.44 - 7.39 (m, 8H), 2.39 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.1, 138.9, 137.6, 134.7, 130.5, 129.3, 128.8, 128.2, 35.1, 19.62, 19.61.

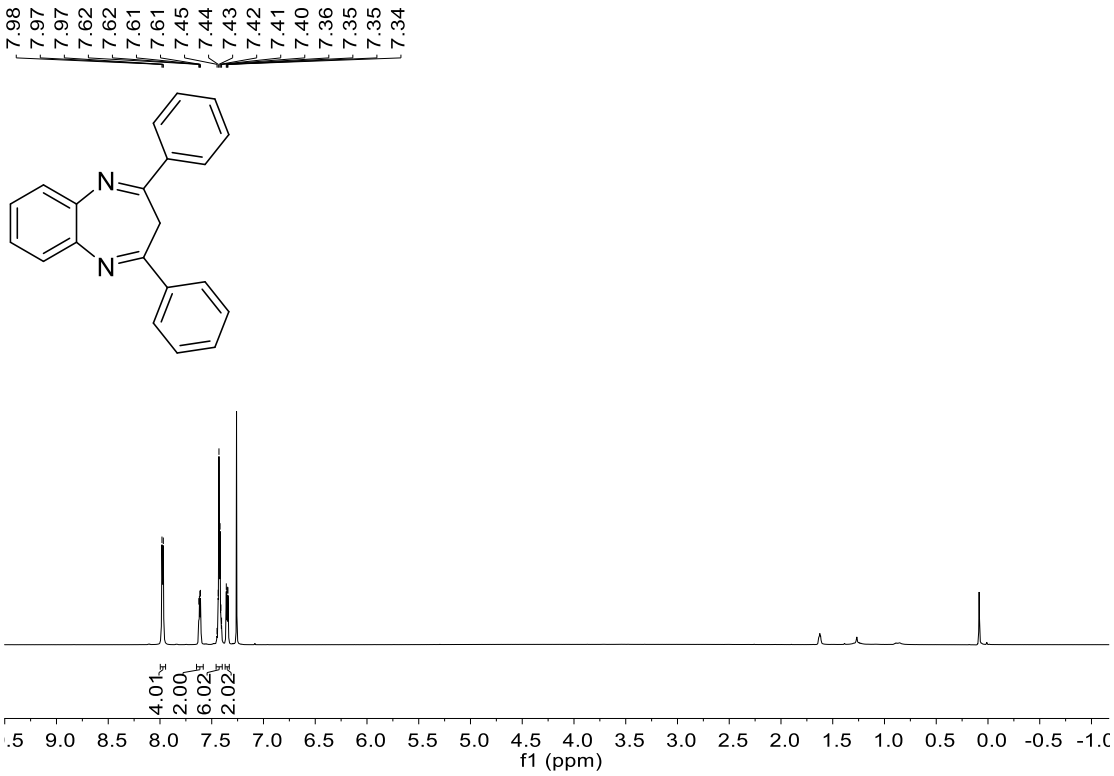


7,8-dibromo-2,4-diphenyl-3H-benzo[b][1,4]diazepine (4aae).[1] (Yellow solid was obtained in 85% isolated yield, 383 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 4H), 7.88 (s, 2H),

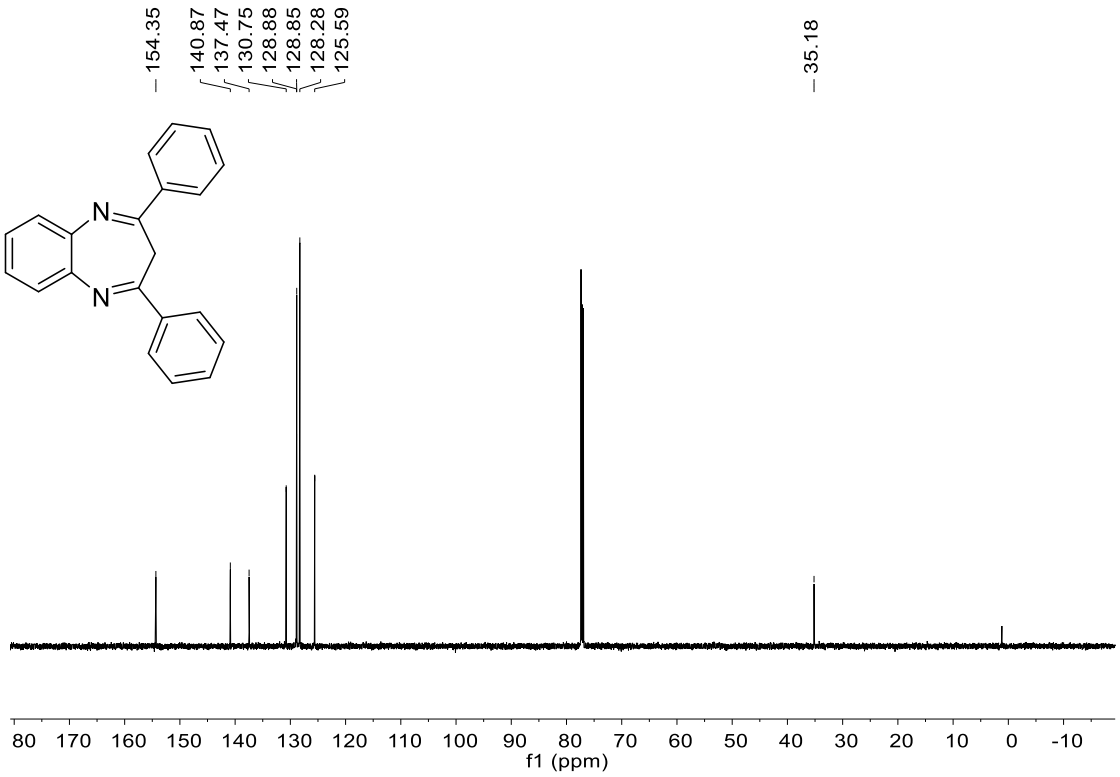
7.44 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 140.8, 136.8, 133.2, 131.3, 128.9, 128.4, 120.7, 35.3.

S-7. NMR Spectrum of products

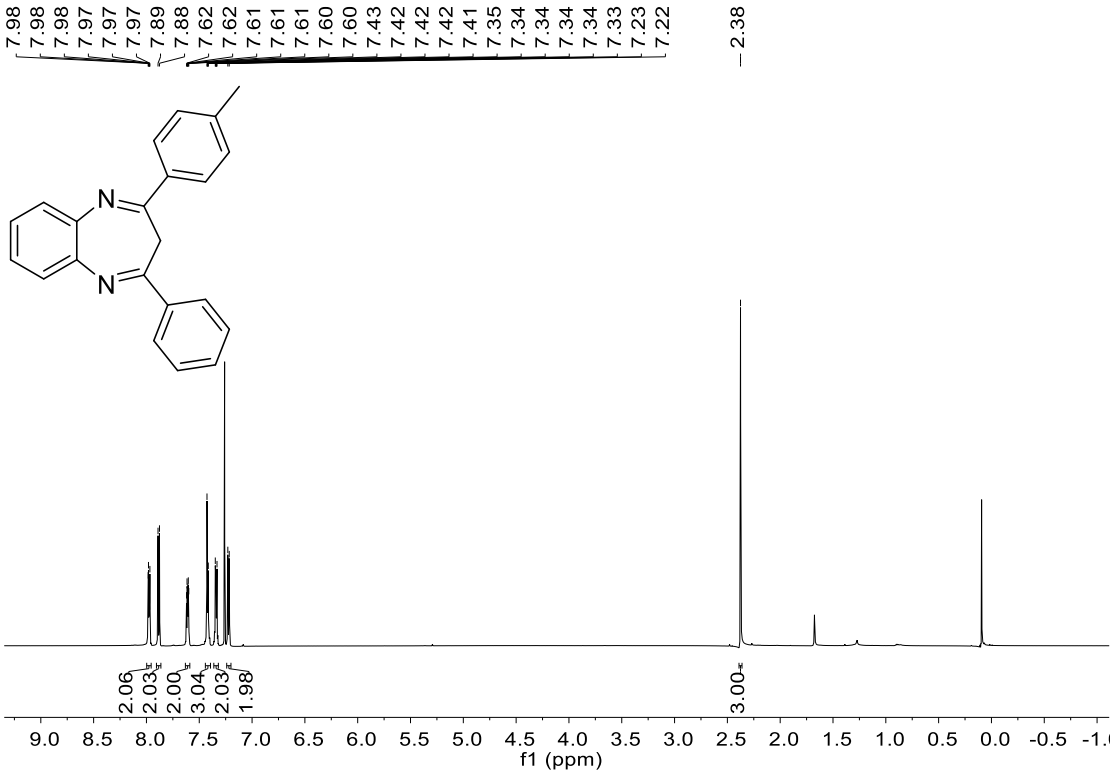
^{1}H NMR of compound **4aaa**



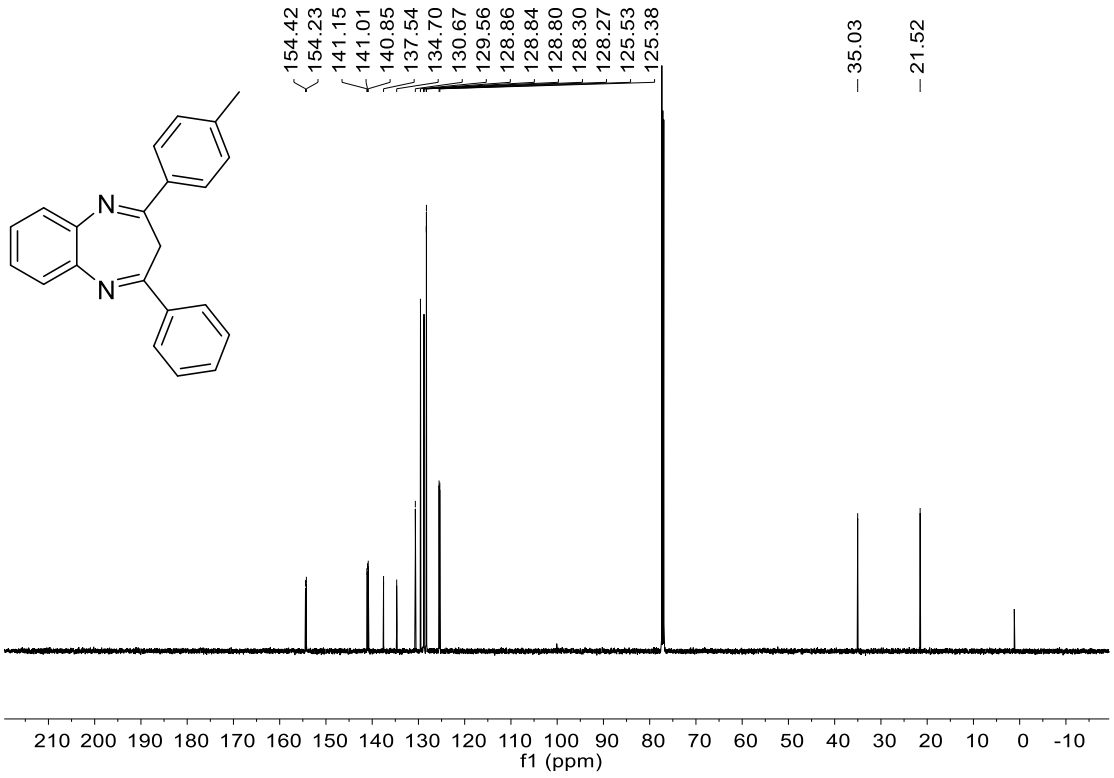
^{13}C NMR of compound **4aaa**



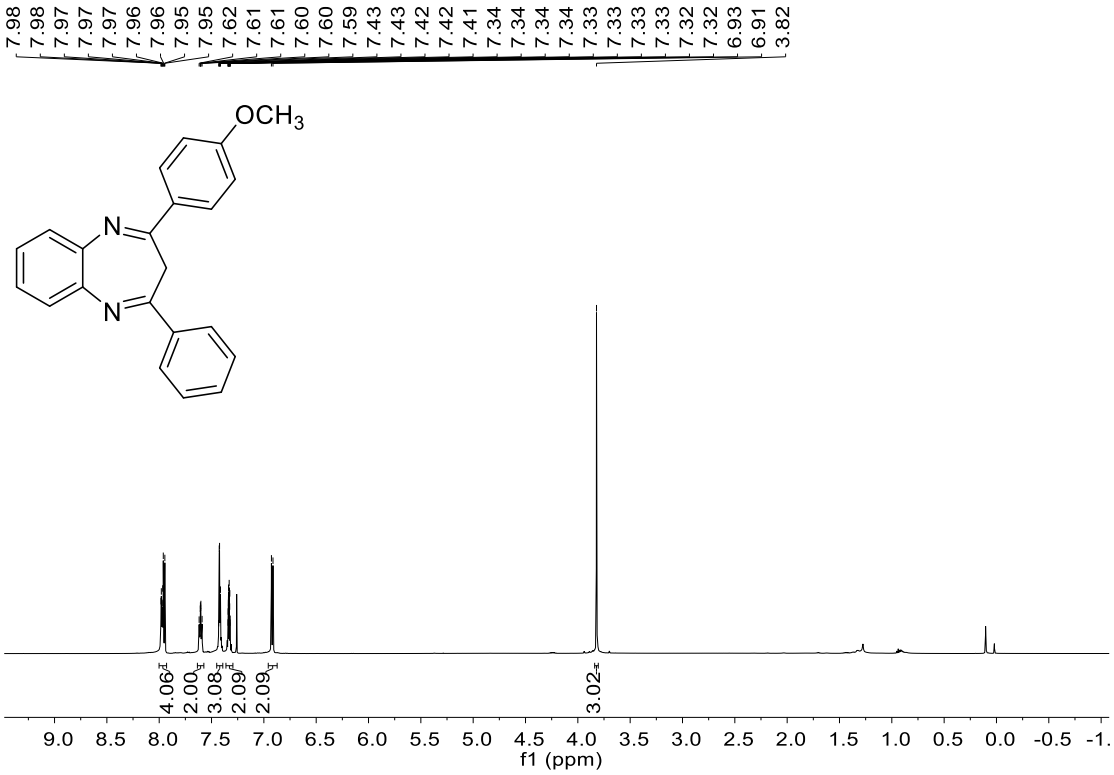
^{1}H NMR of compound **4baa**



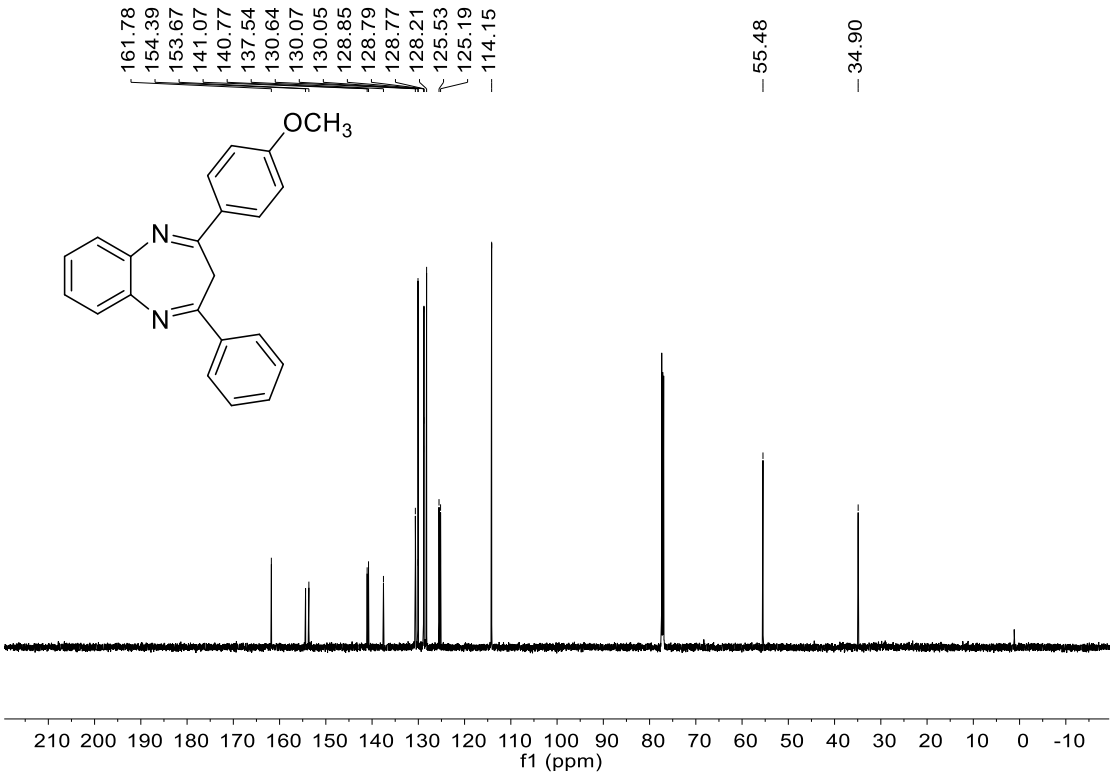
^{13}C NMR of compound **4baa**



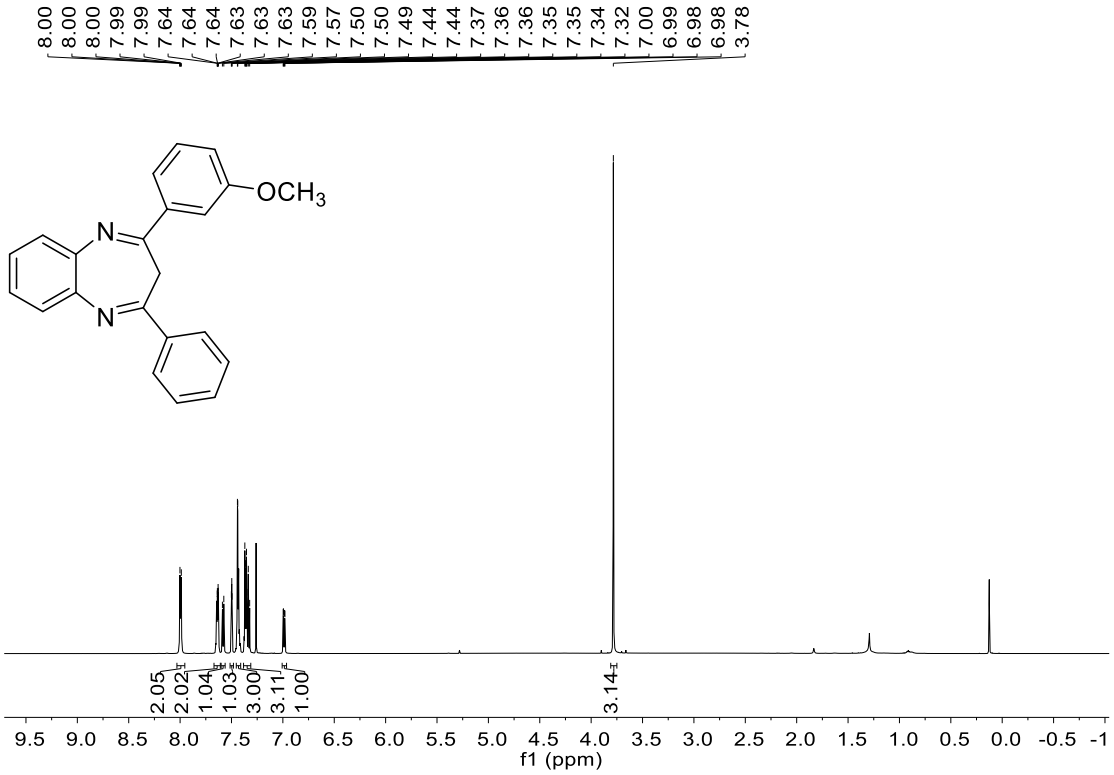
^{1}H NMR of compound **4caa**



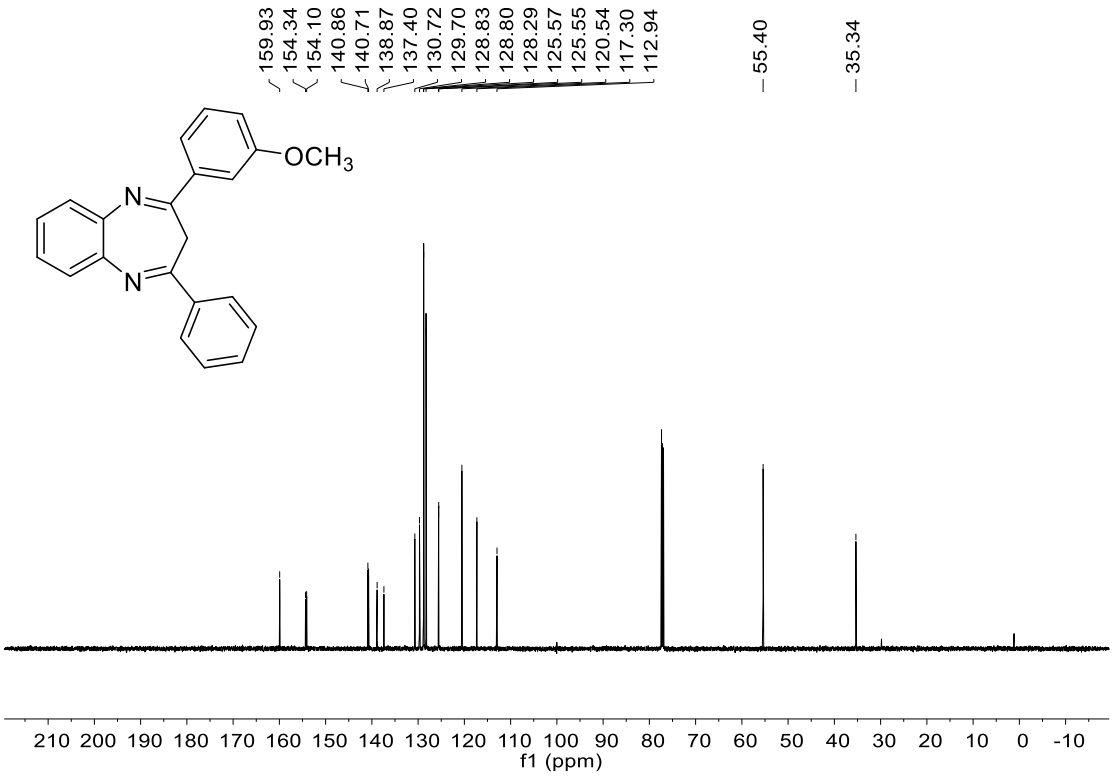
^{13}C NMR of compound **4caa**



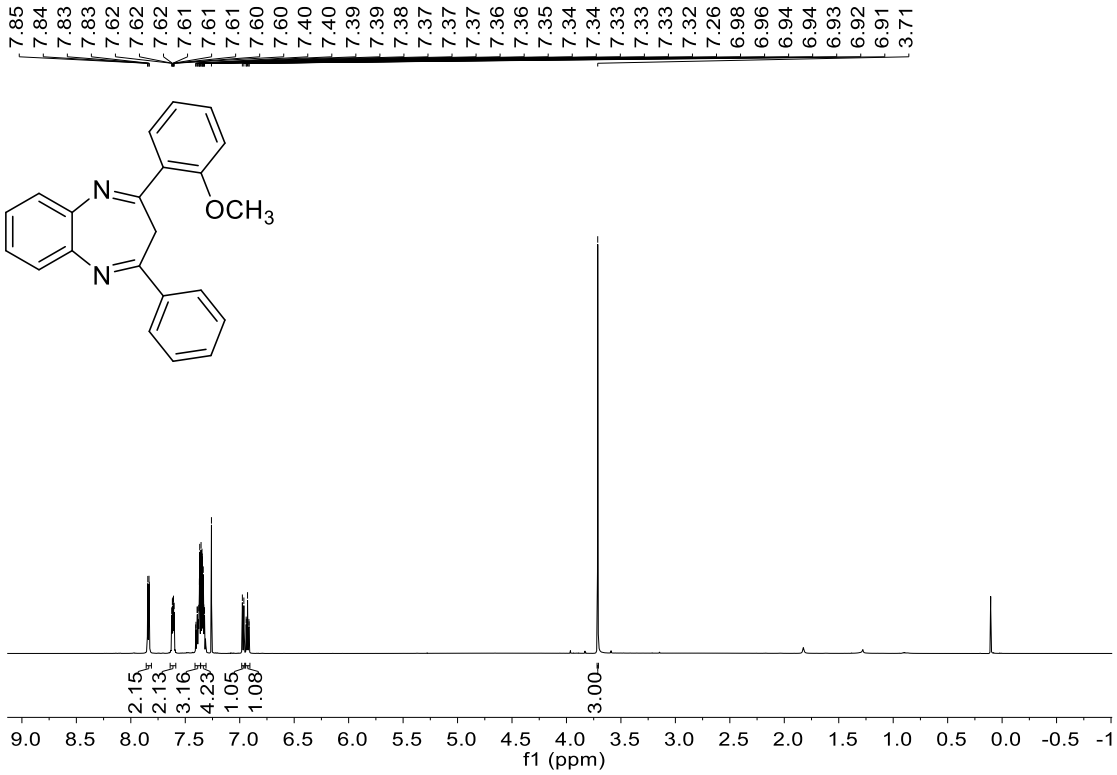
^{1}H NMR of compound **4daa**



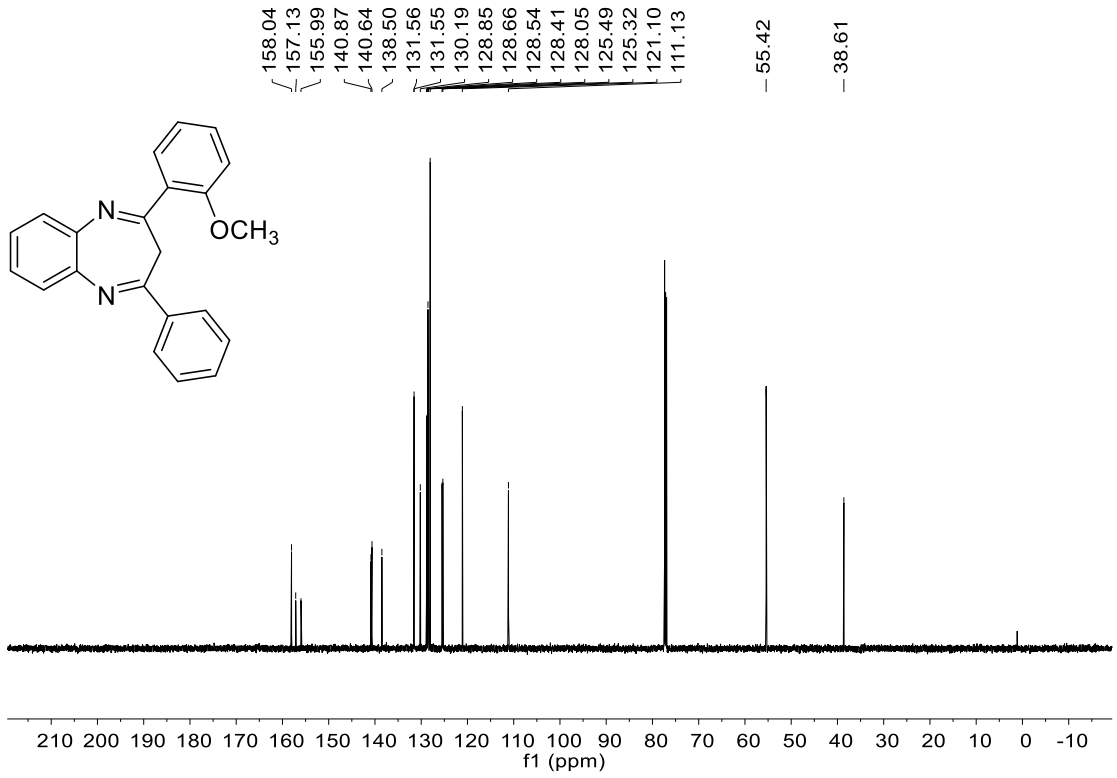
^{13}C NMR of compound **4daa**



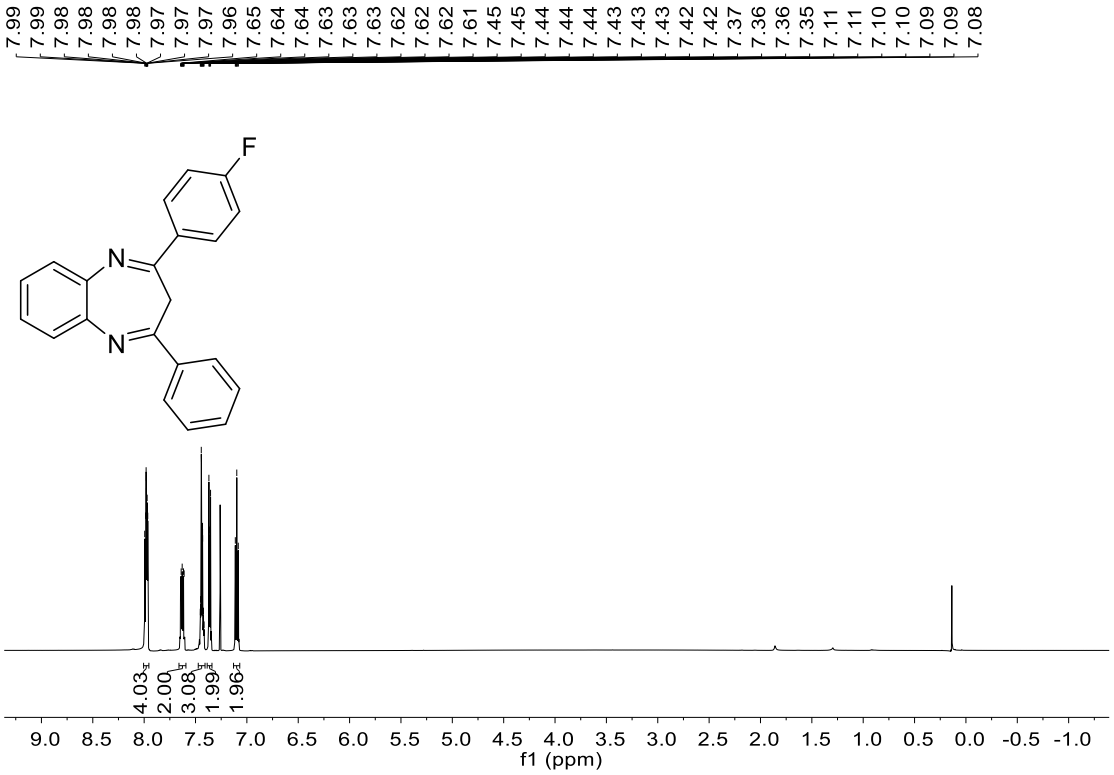
^{1}H NMR of compound **4eaa**



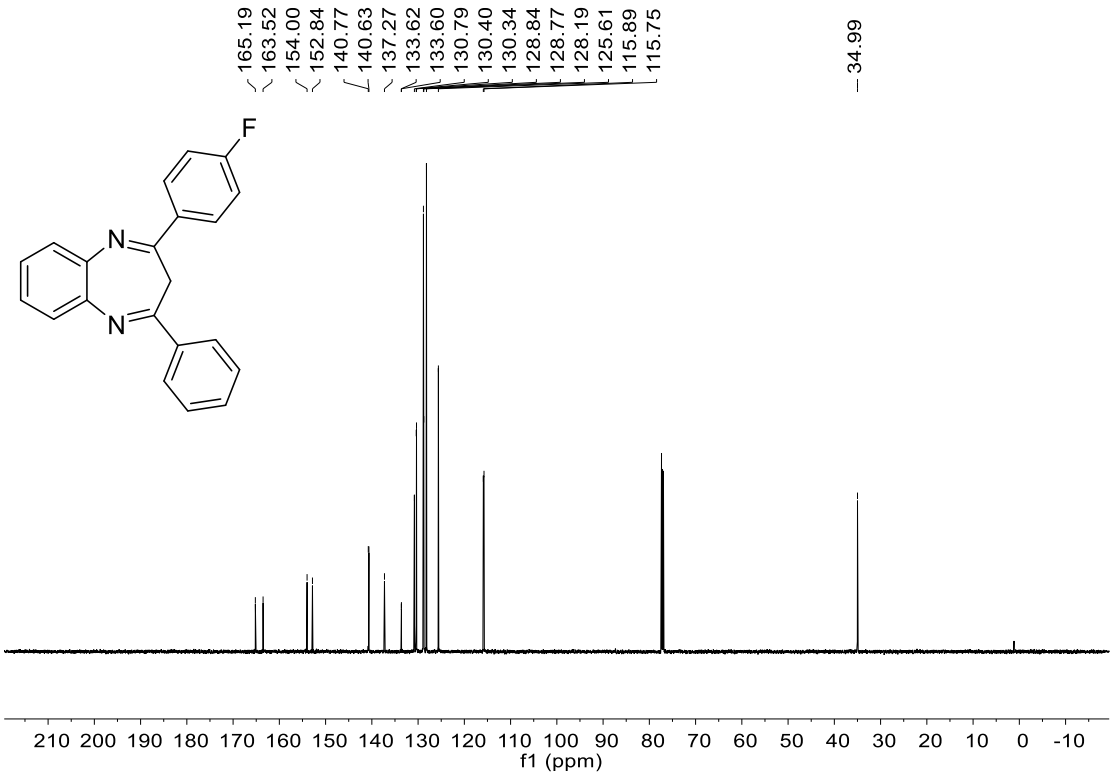
^{13}C NMR of compound **4eaa**



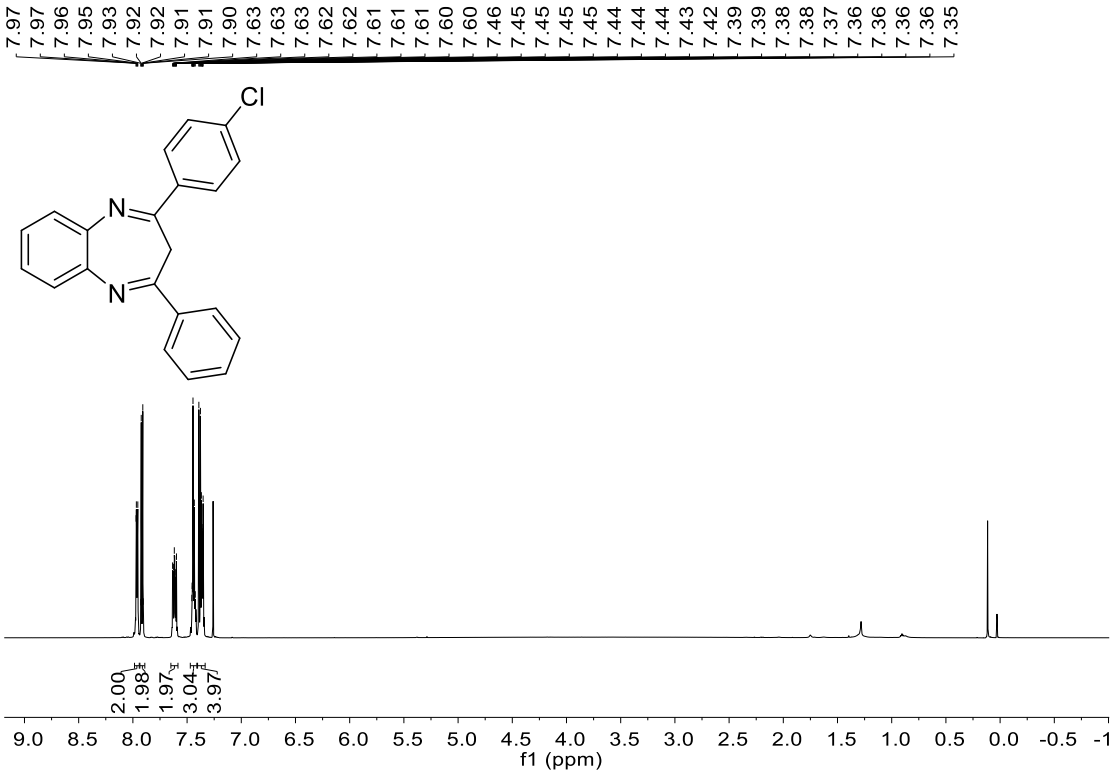
^{1}H NMR of compound **4faa**



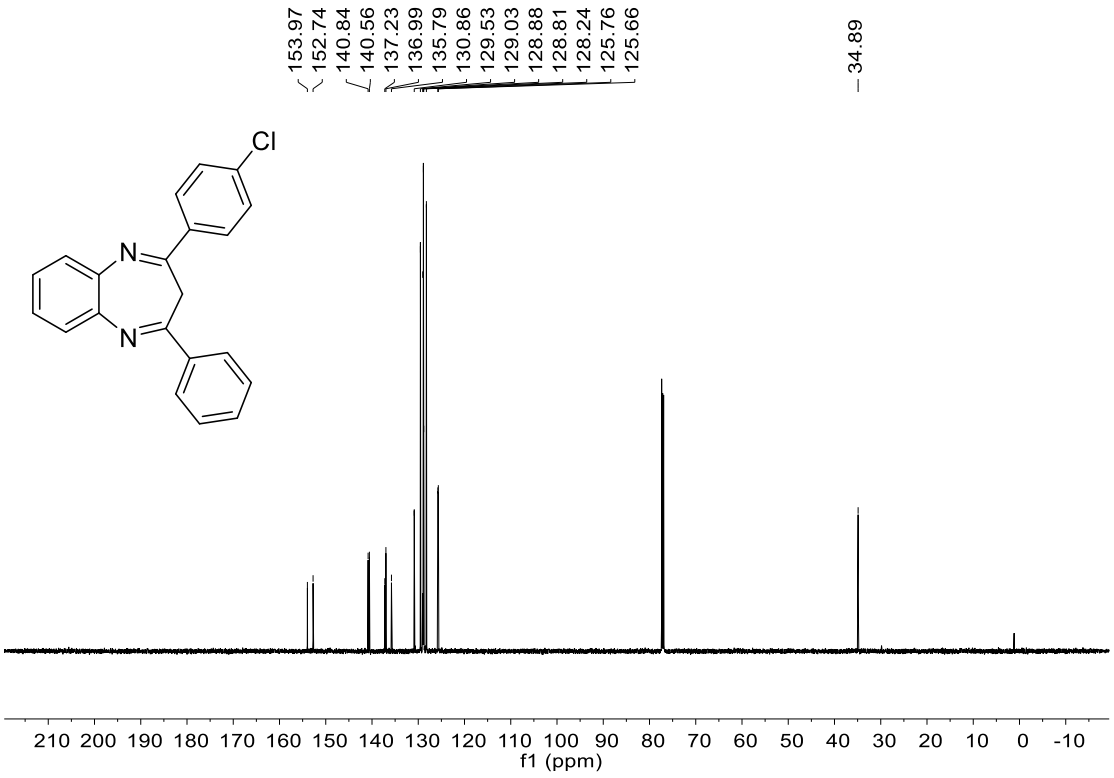
^{13}C NMR of compound **4faa**



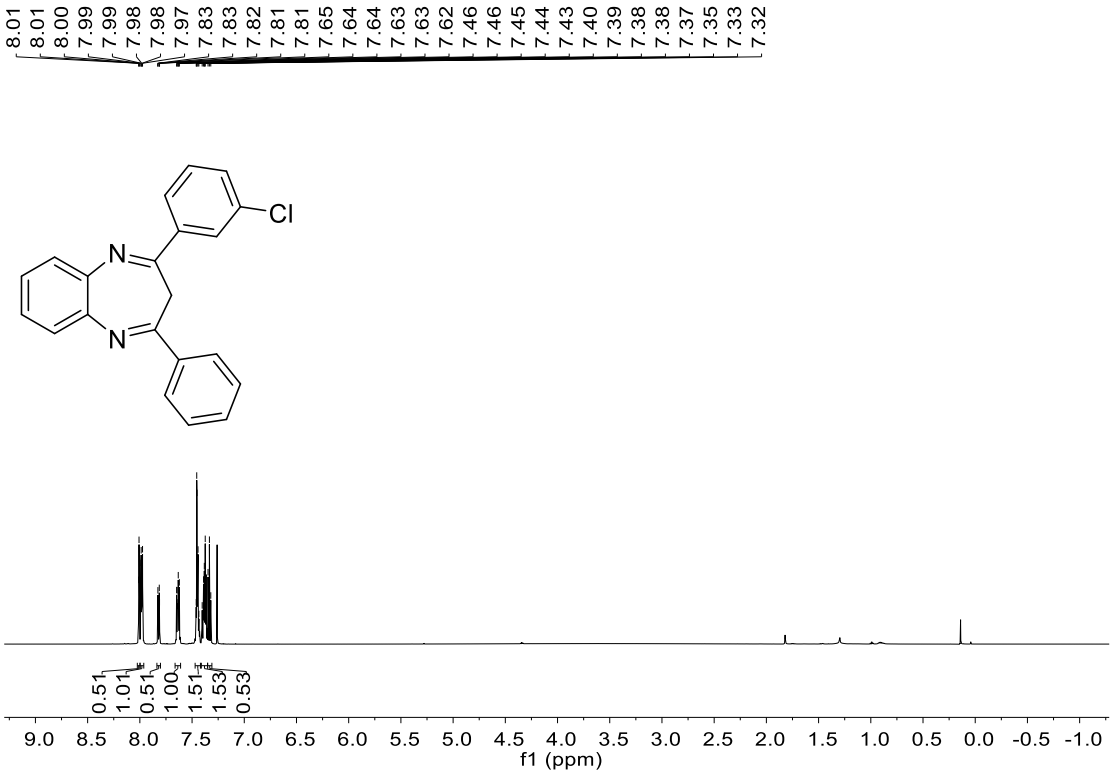
^{1}H NMR of compound **4gaa**



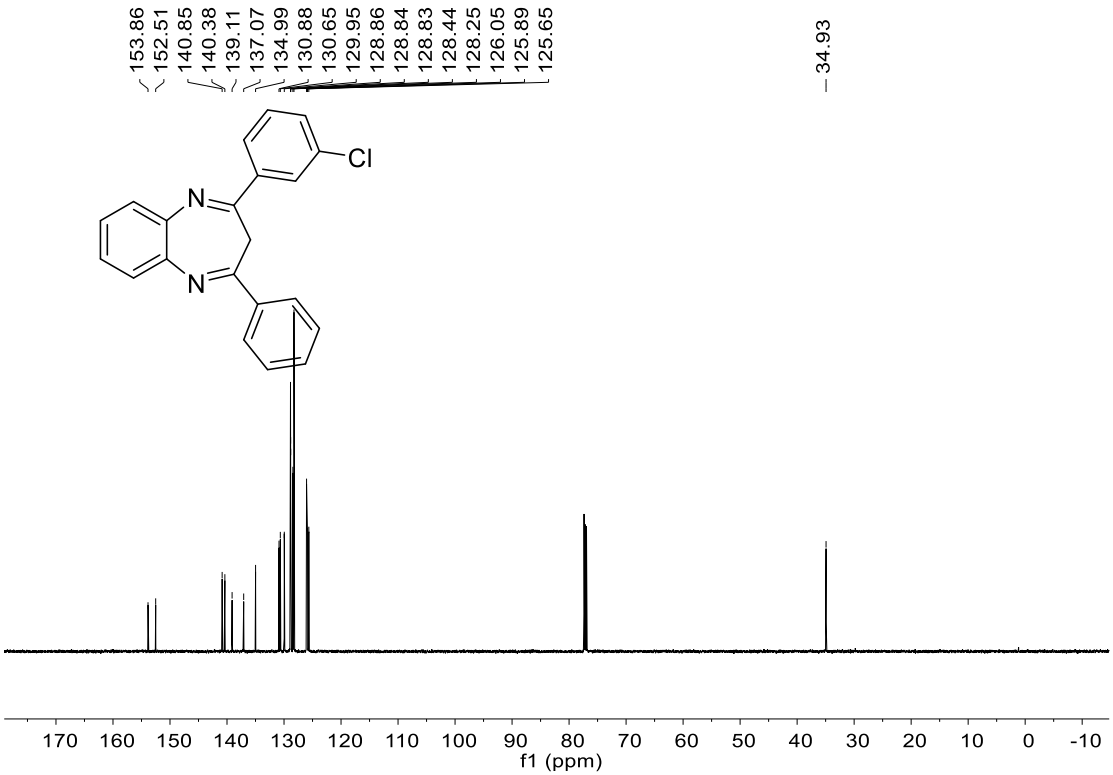
^{13}C NMR of compound **4gaa**



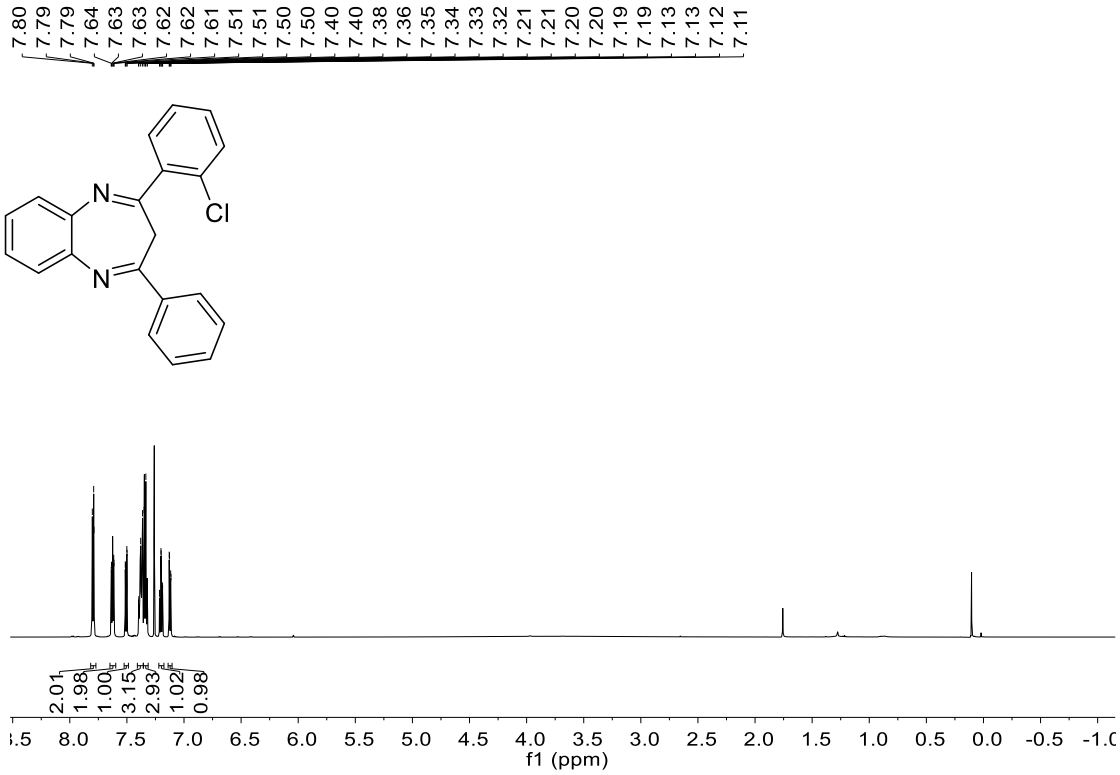
^{1}H NMR of compound **4haa**



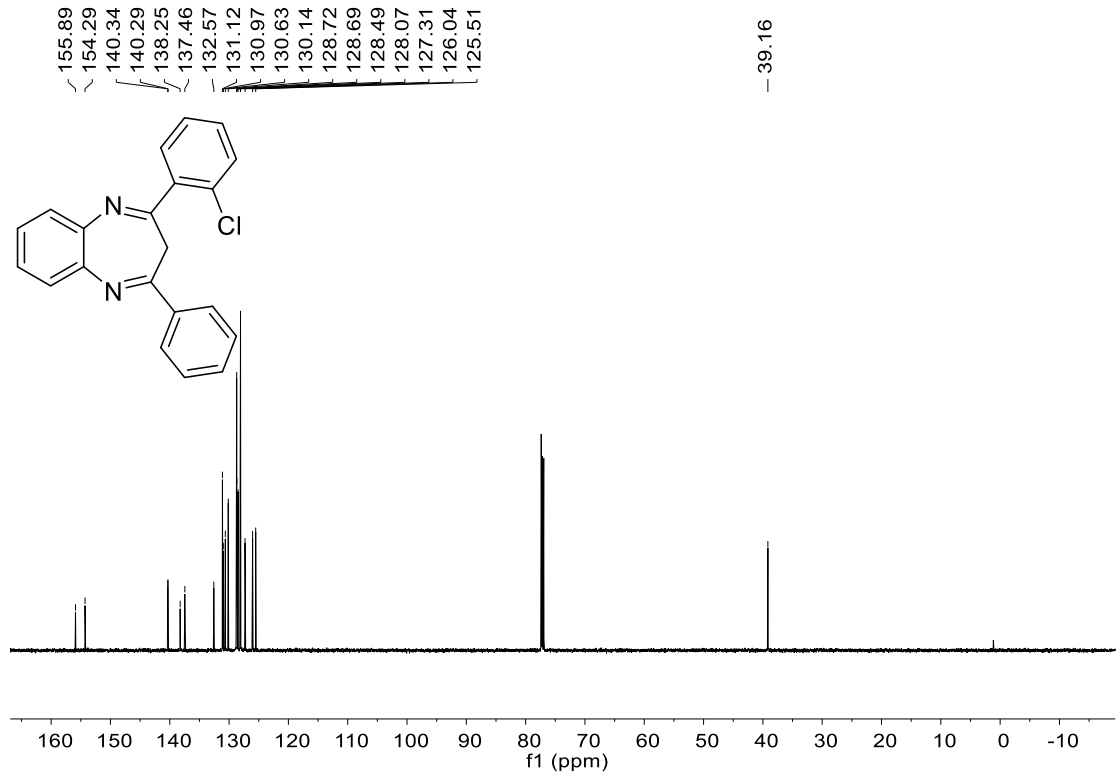
^{13}C NMR of compound **4haa**



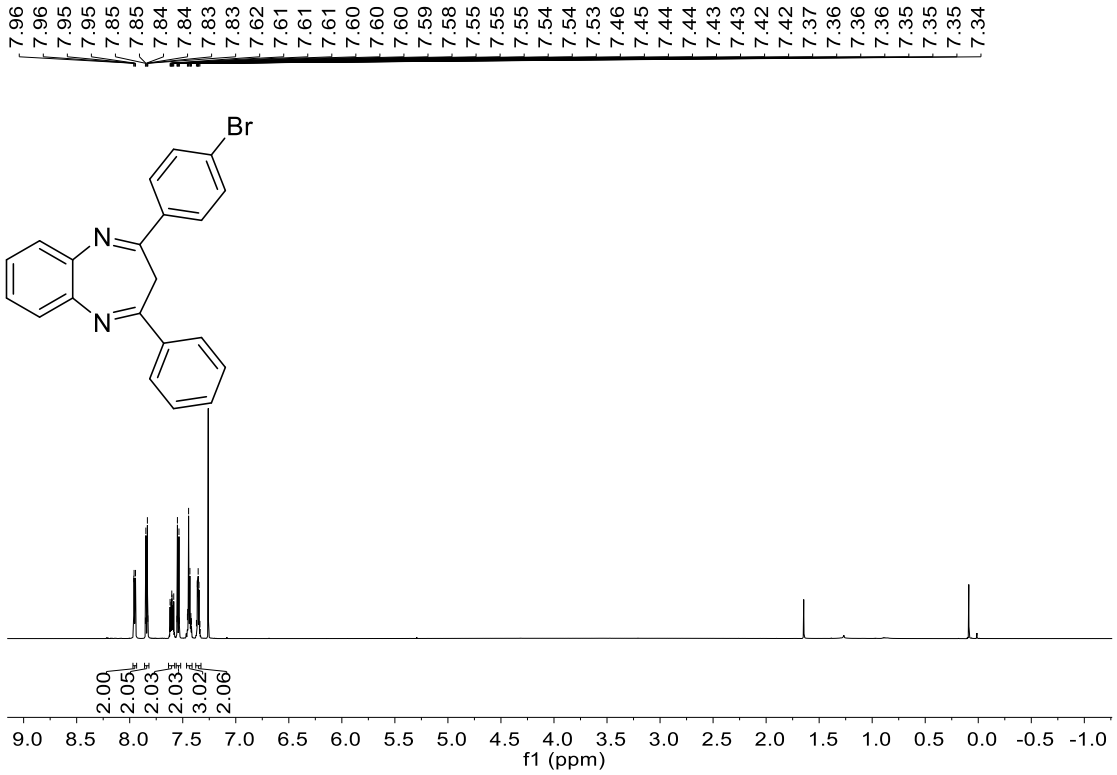
^{1}H NMR of compound **4laa**



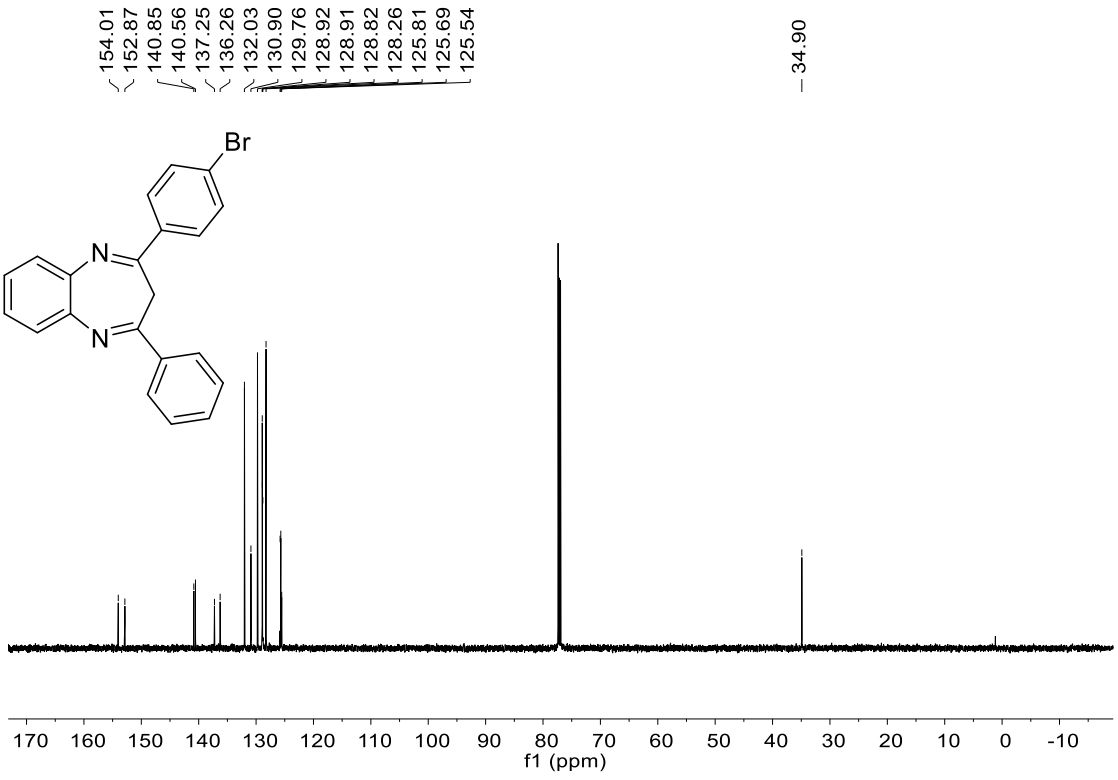
^{13}C NMR of compound **4laa**



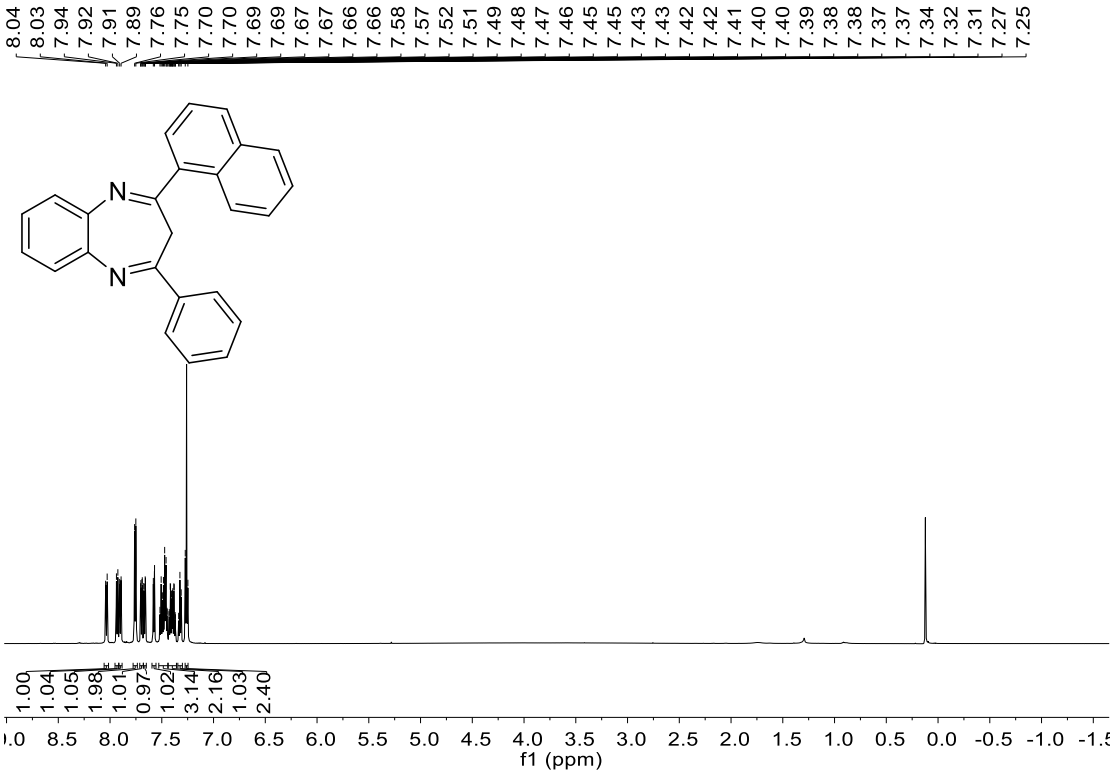
^{1}H NMR of compound **4jaa**



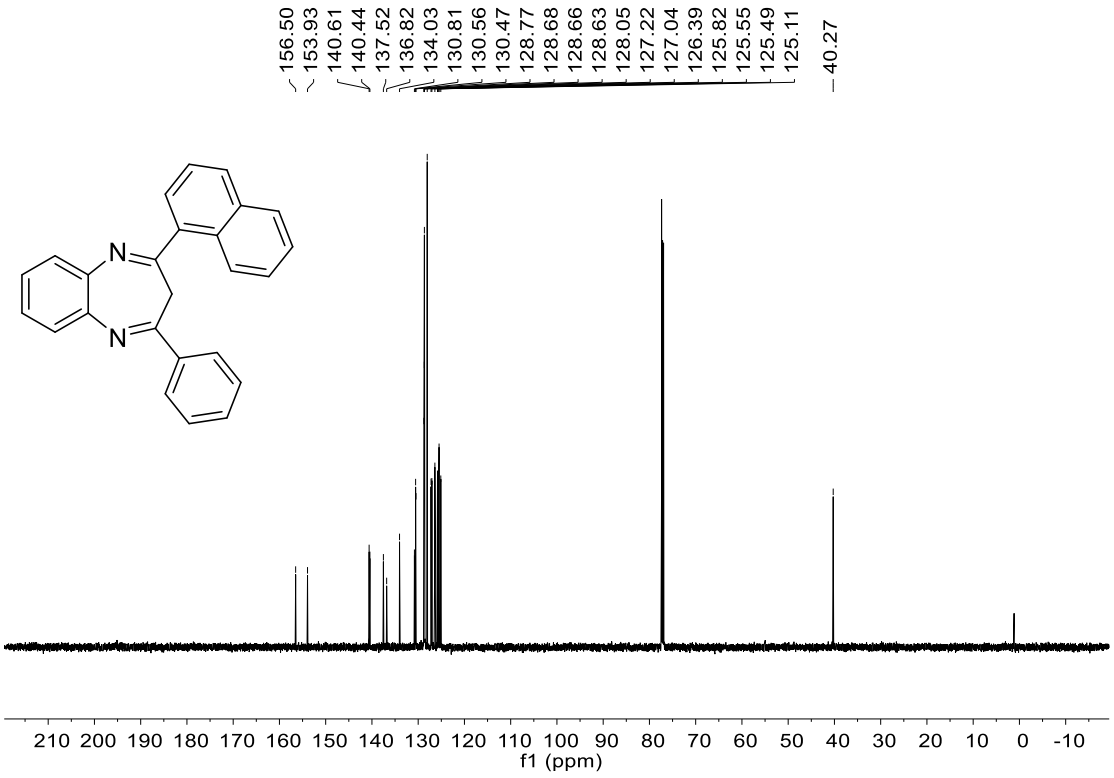
^{13}C NMR of compound **4jaa**



^{1}H NMR of compound **4kaa**



^{13}C NMR of compound **4kaa**



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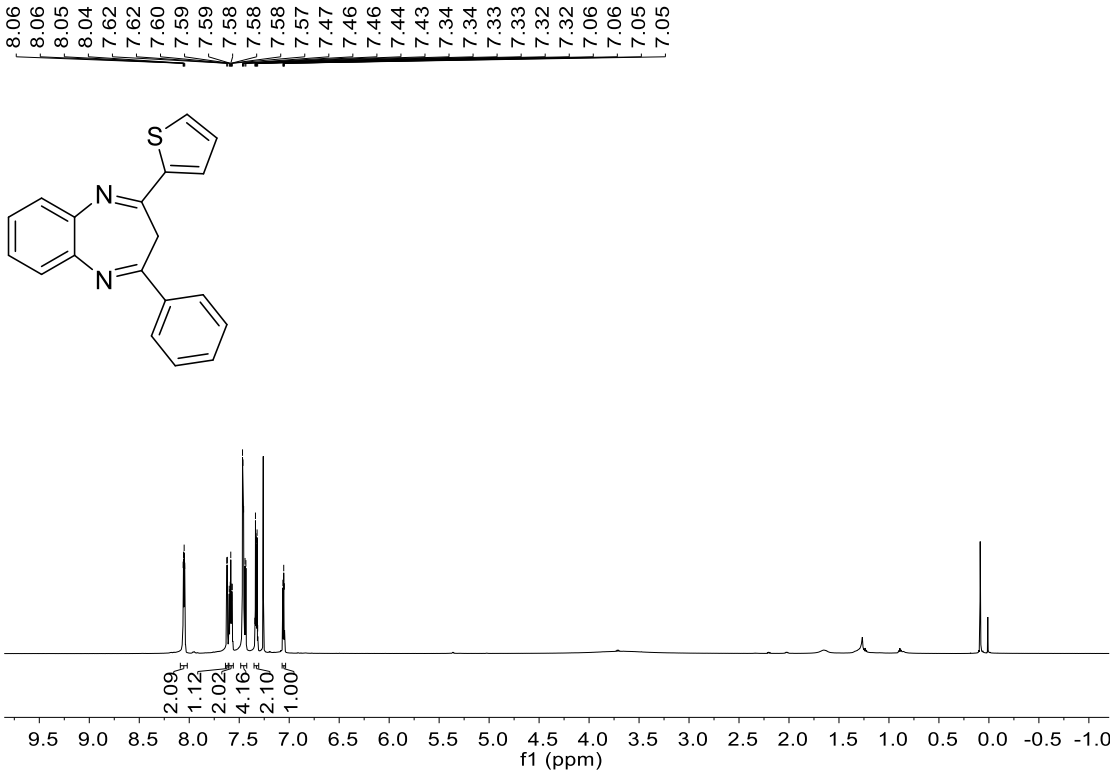

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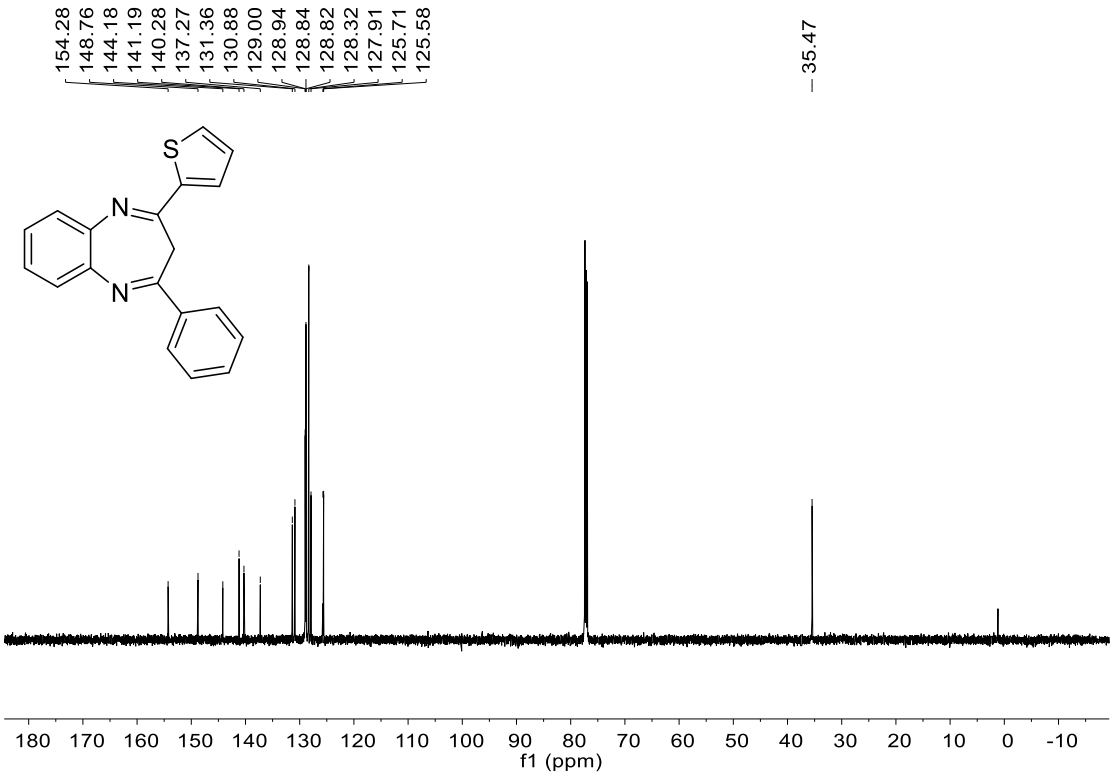
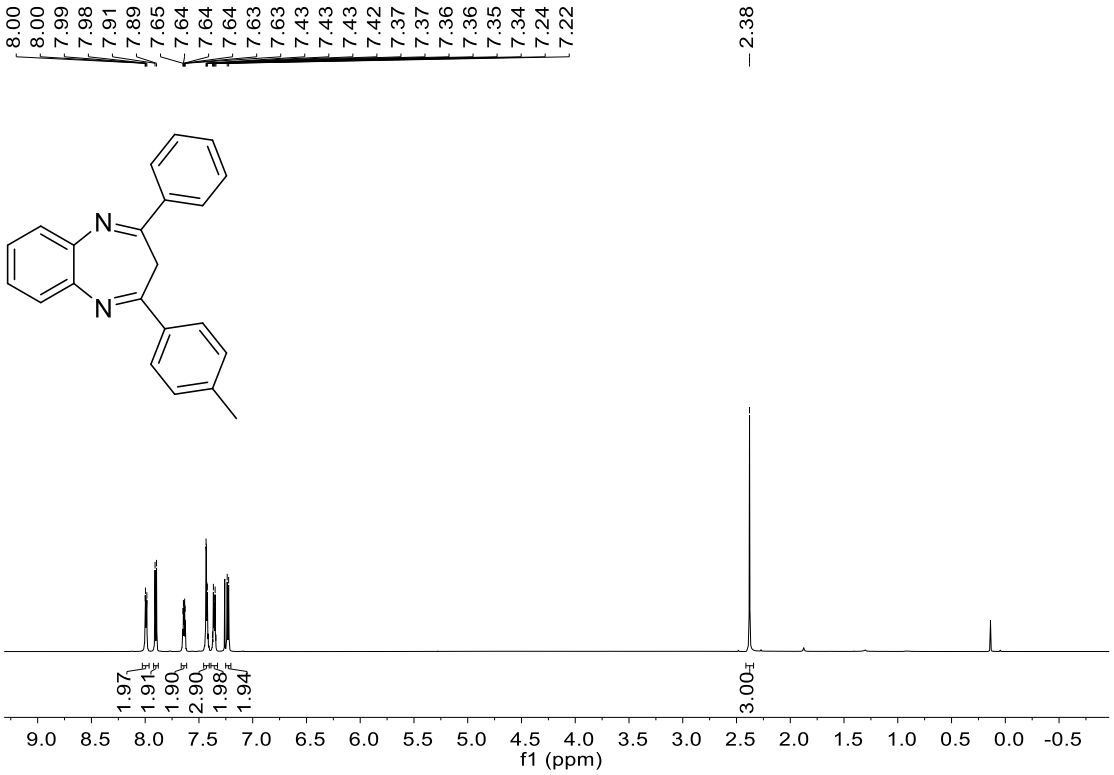


^{1}H NMR of compound **4aba**



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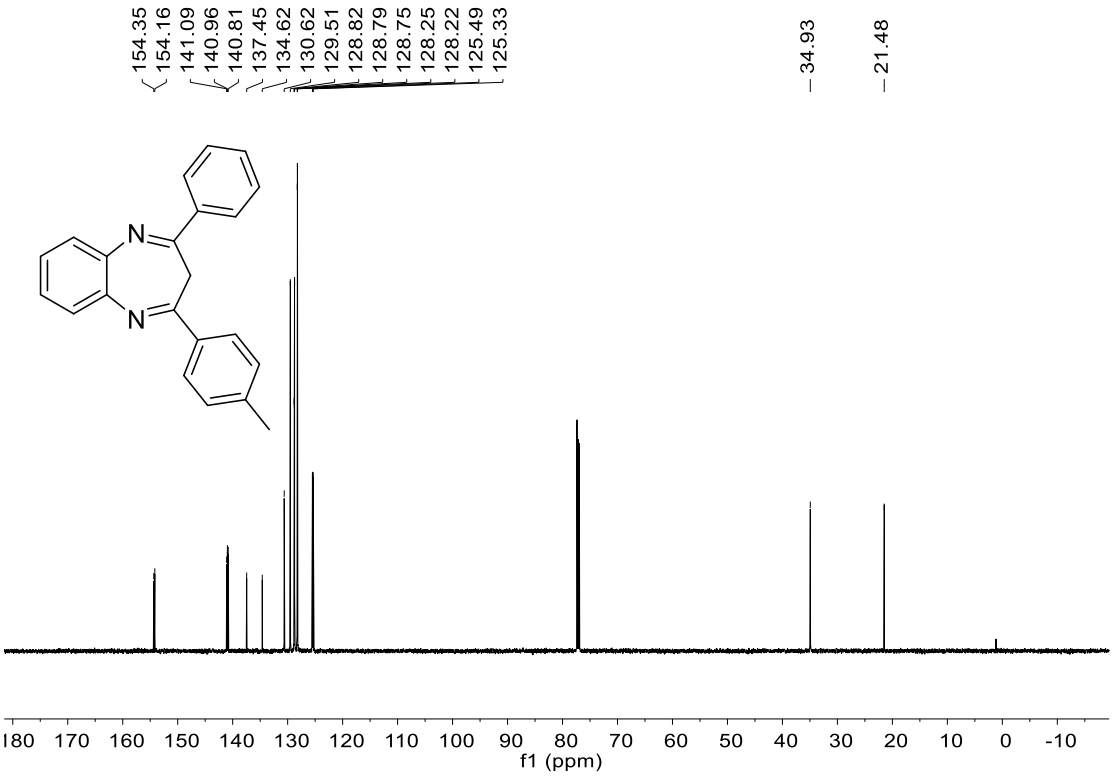

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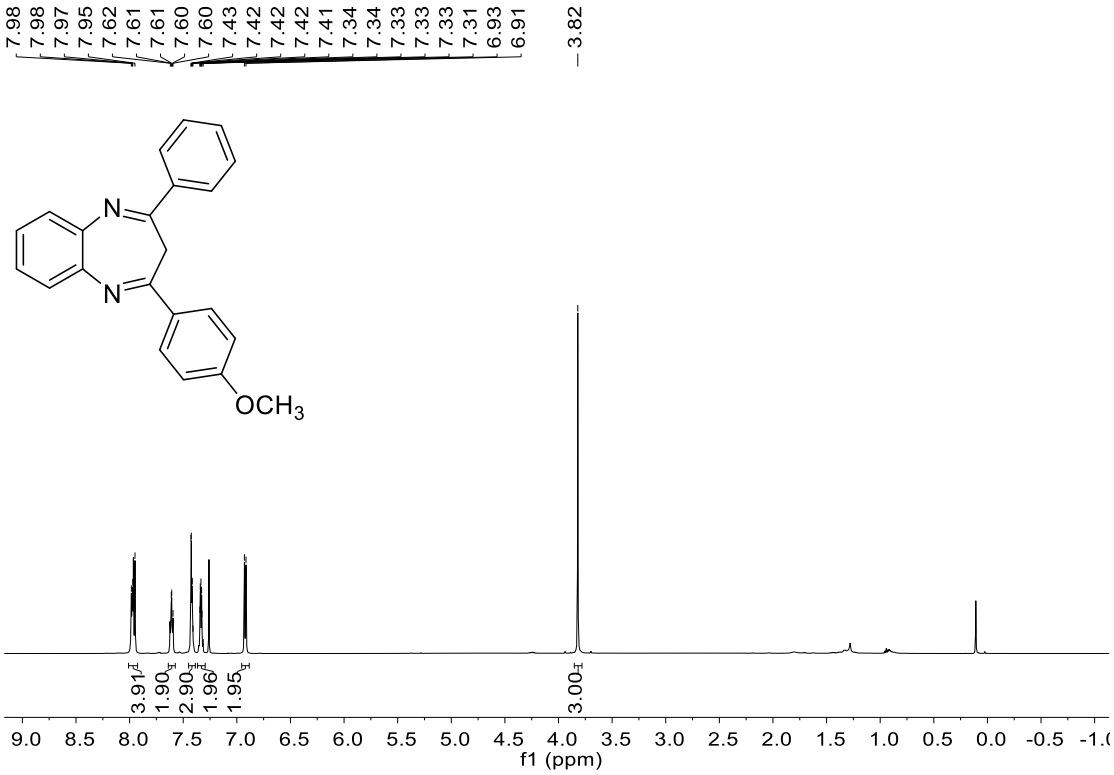

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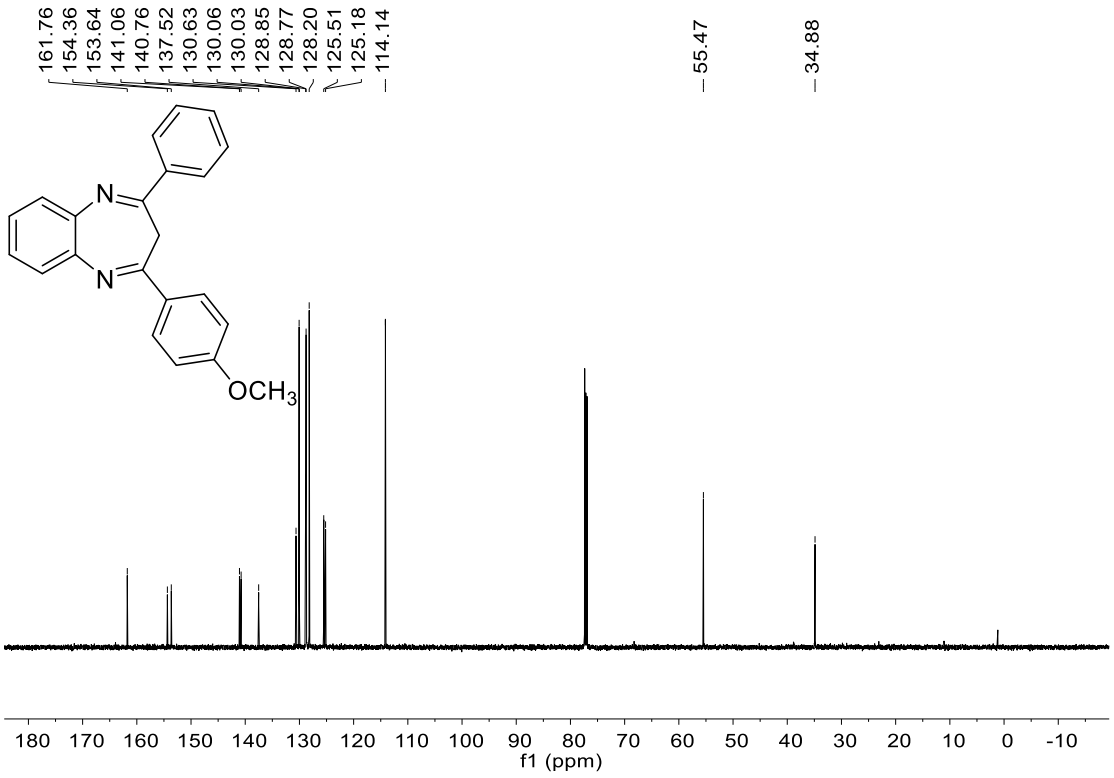

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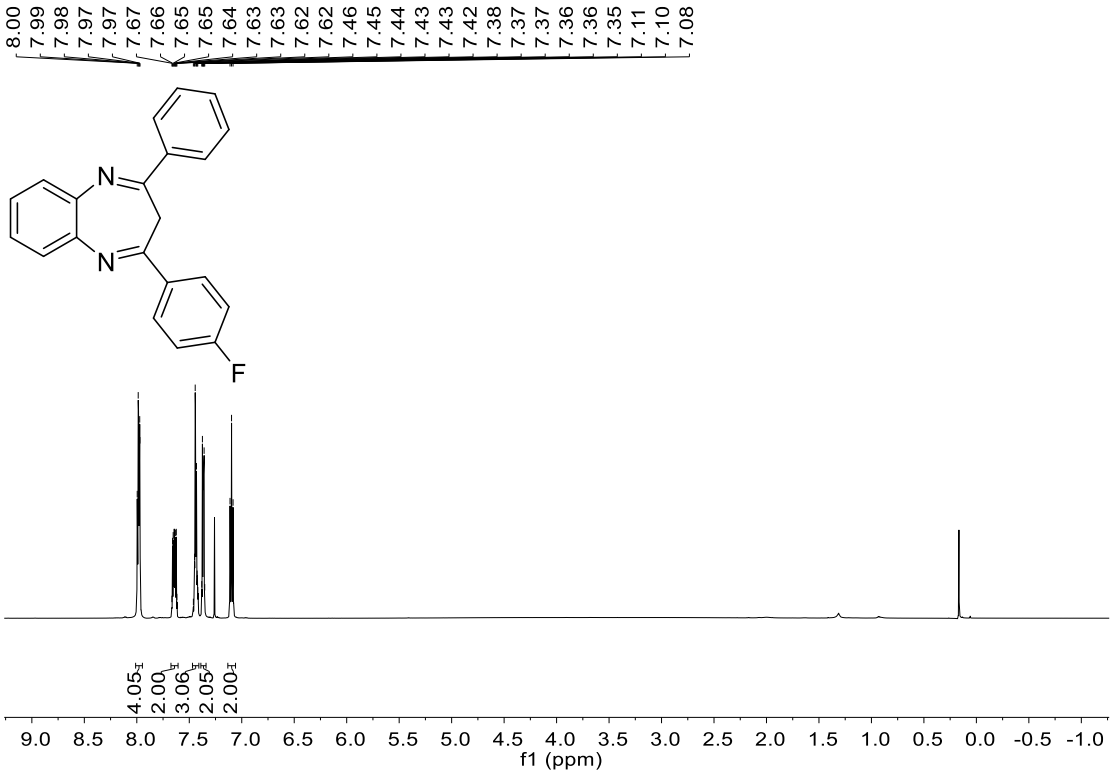

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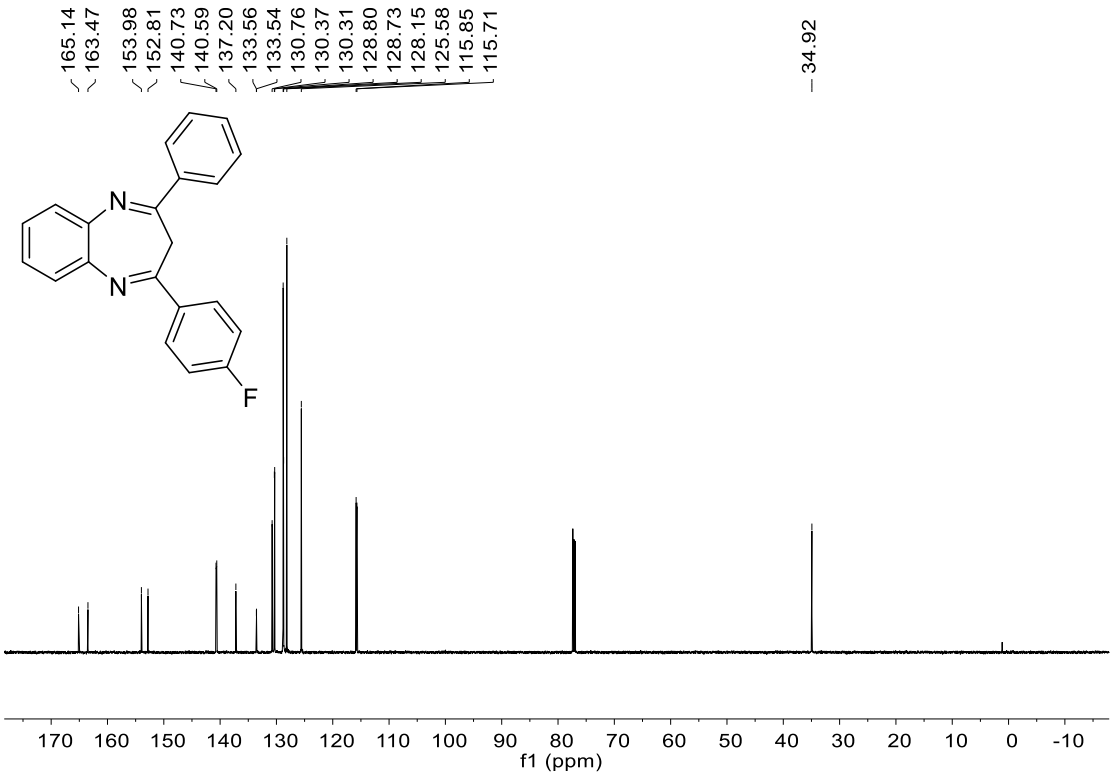

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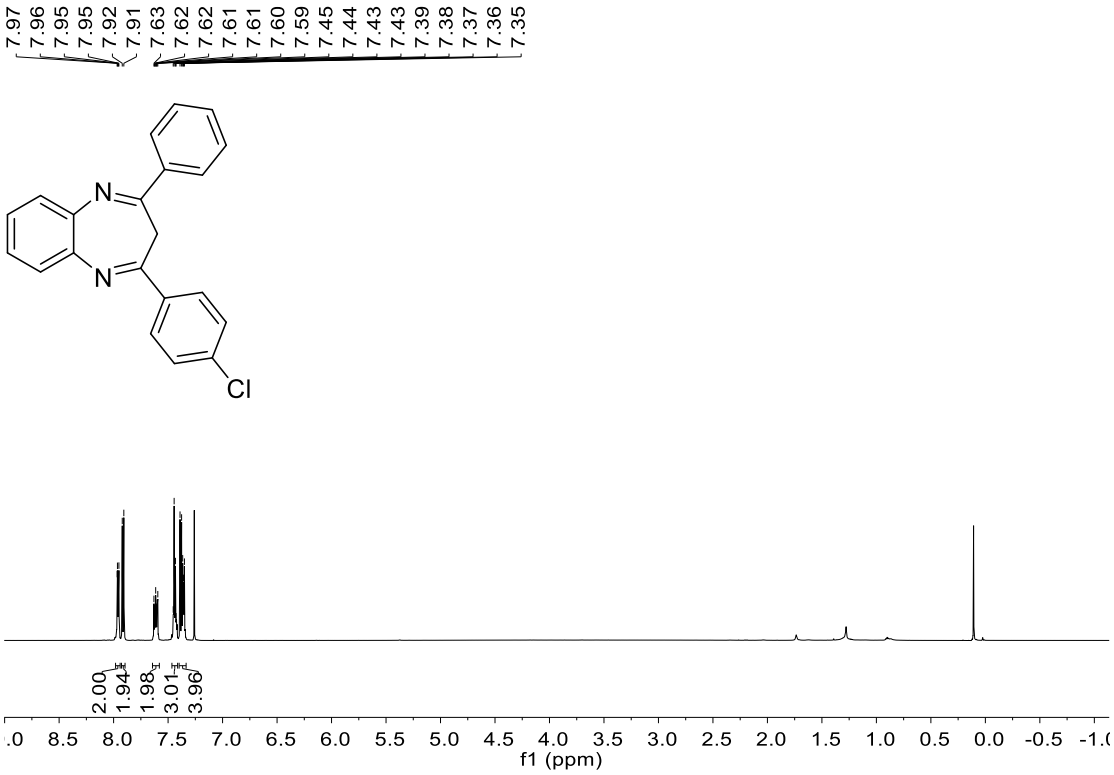

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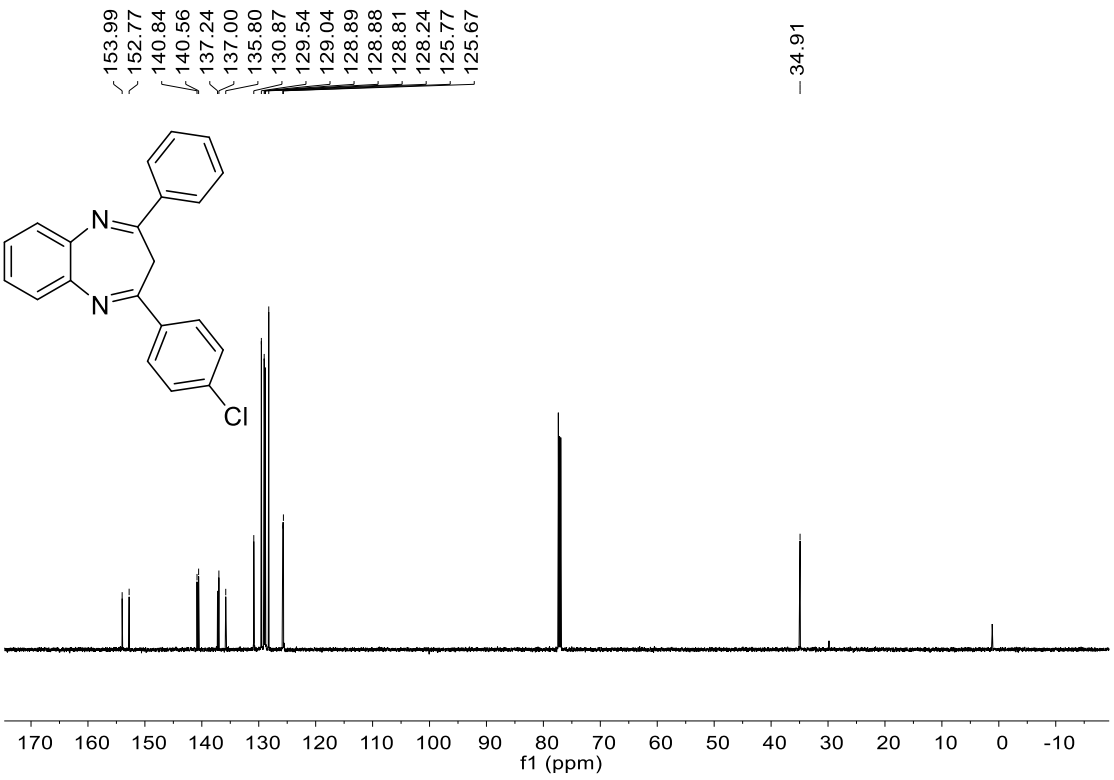

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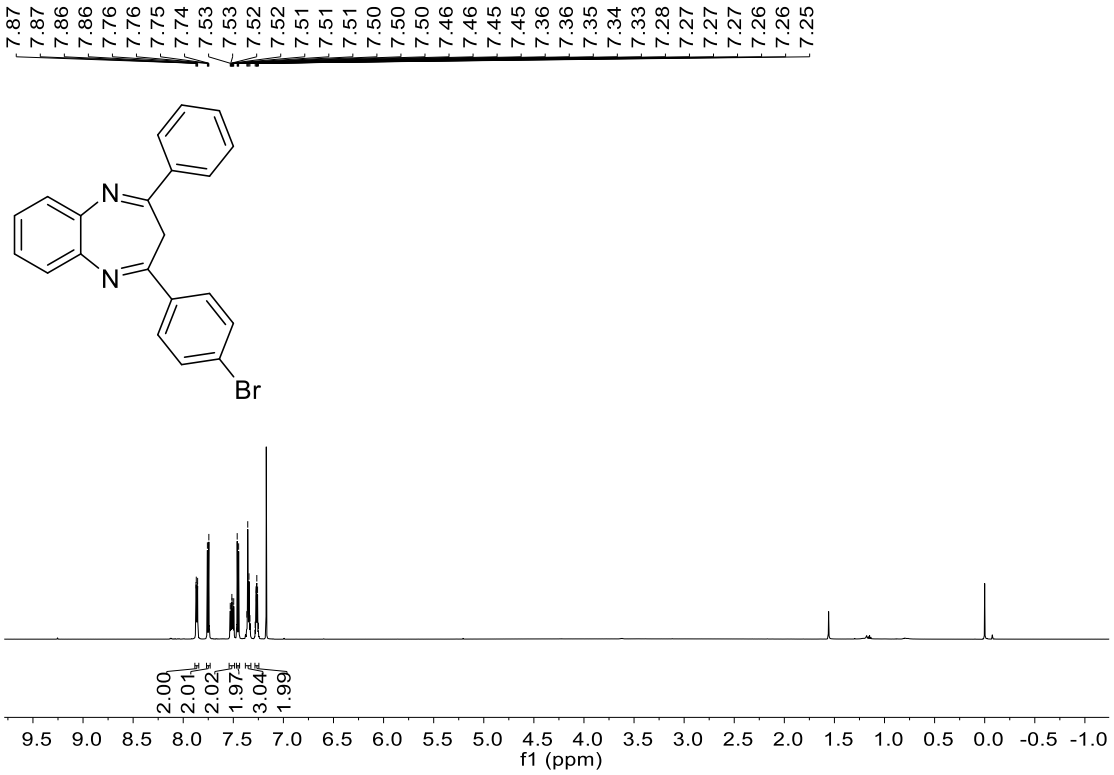

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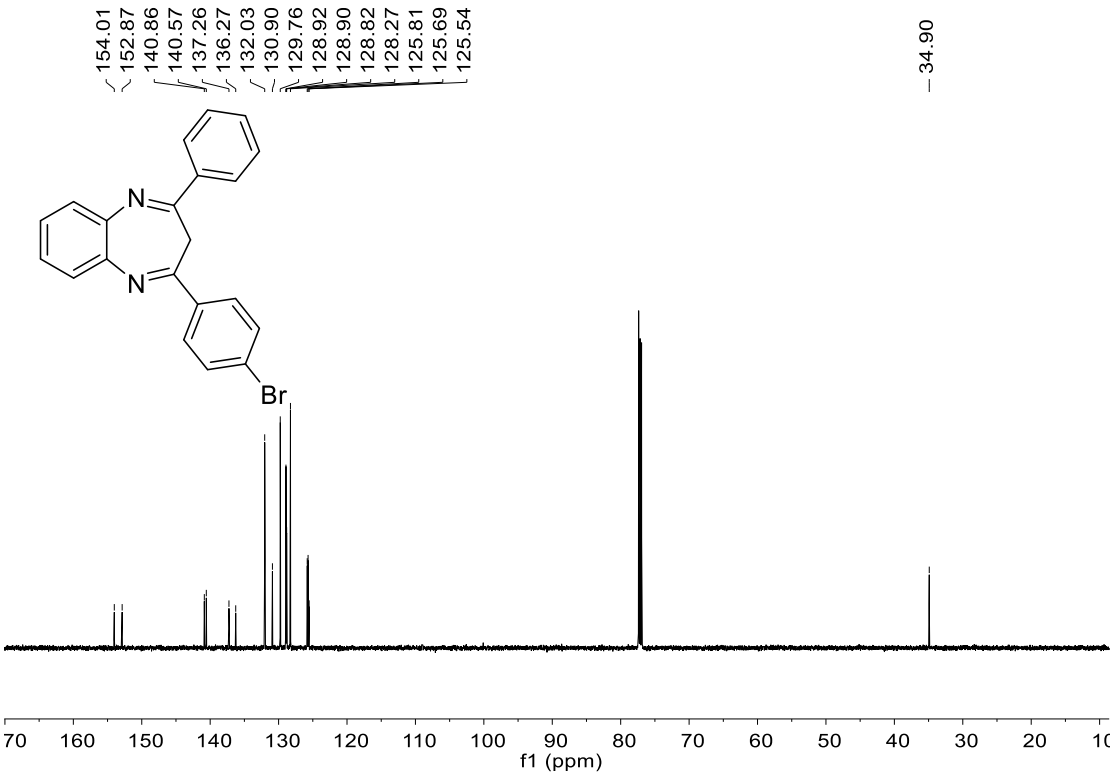

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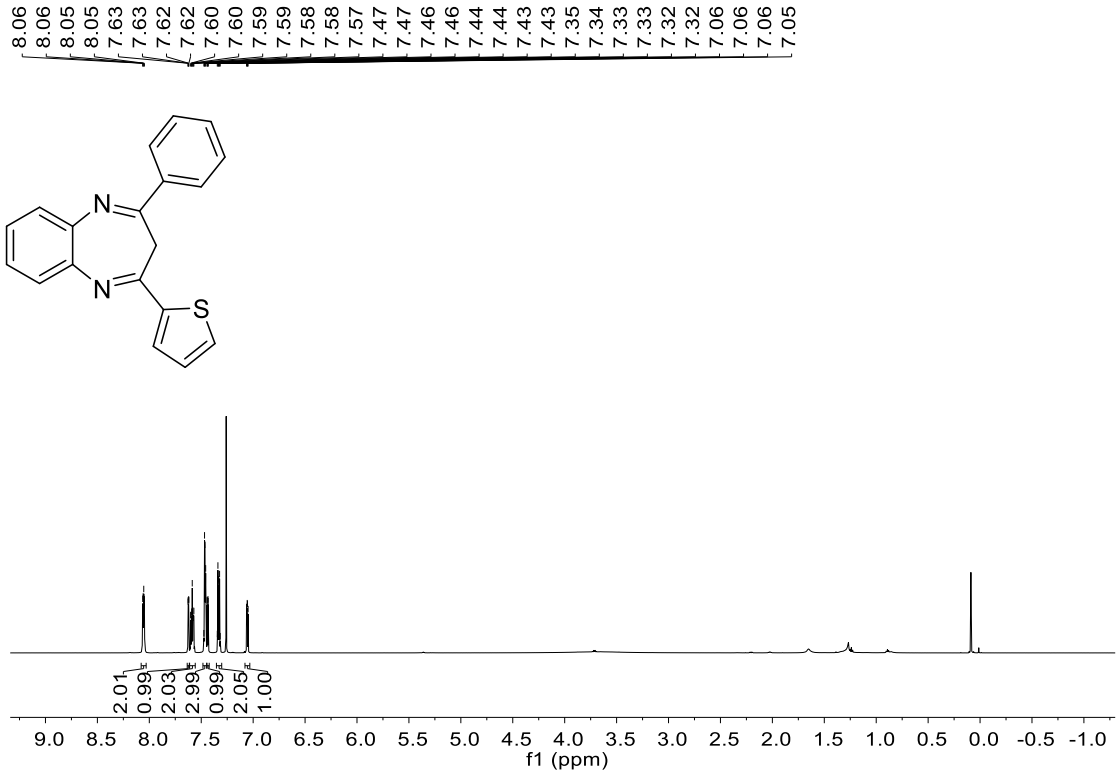

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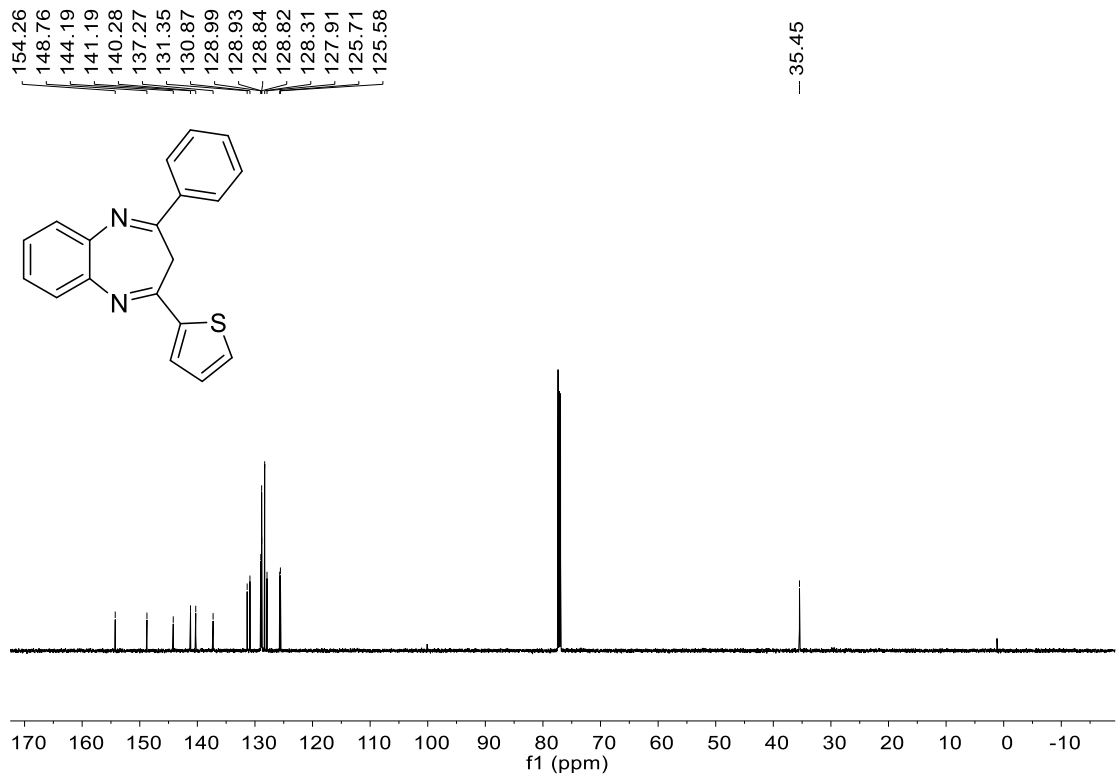

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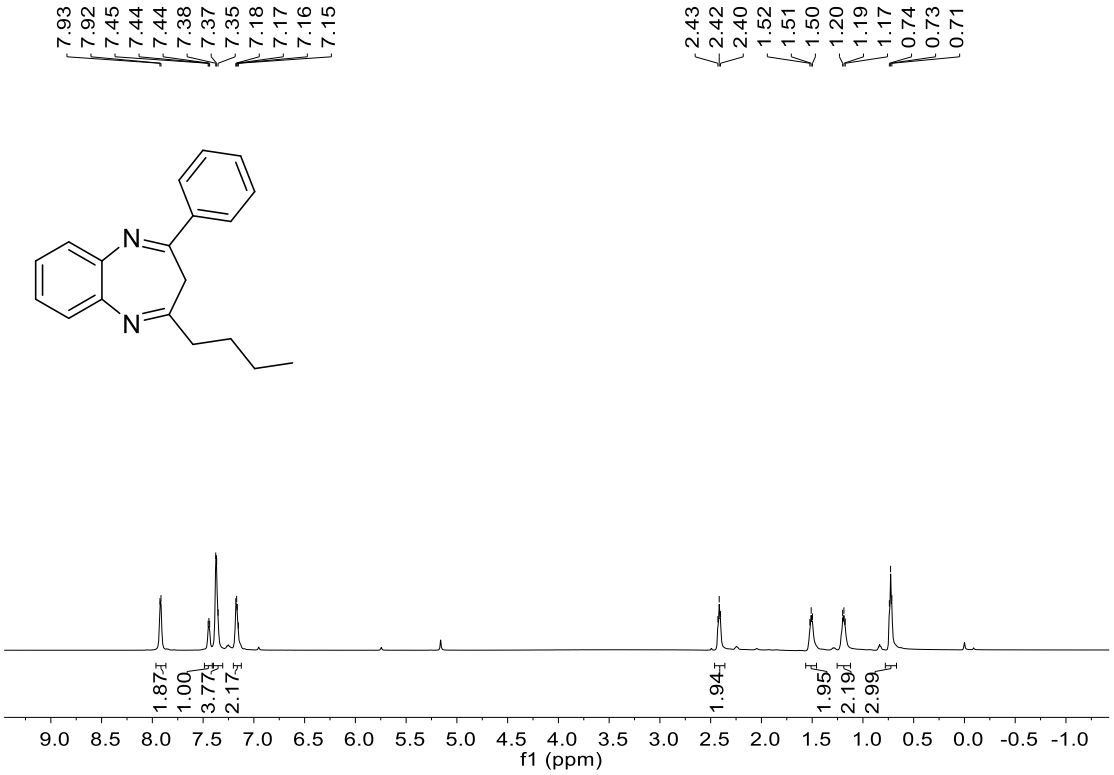

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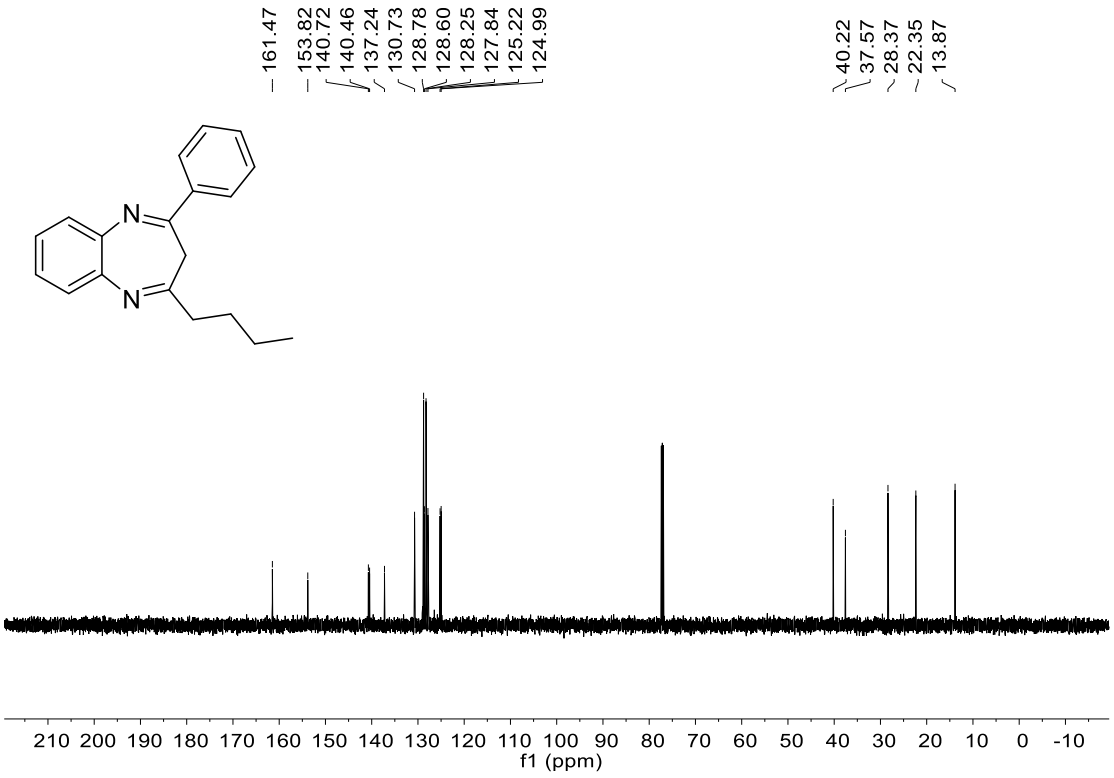
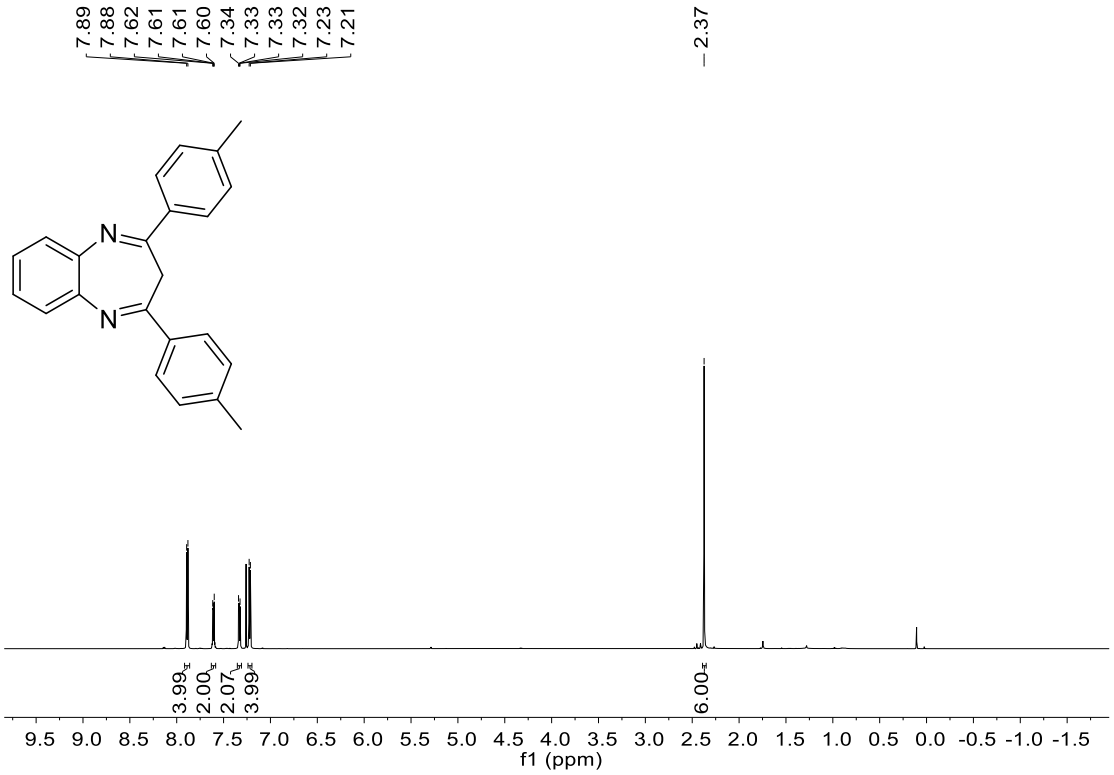


^{1}H NMR of compound **4bba**



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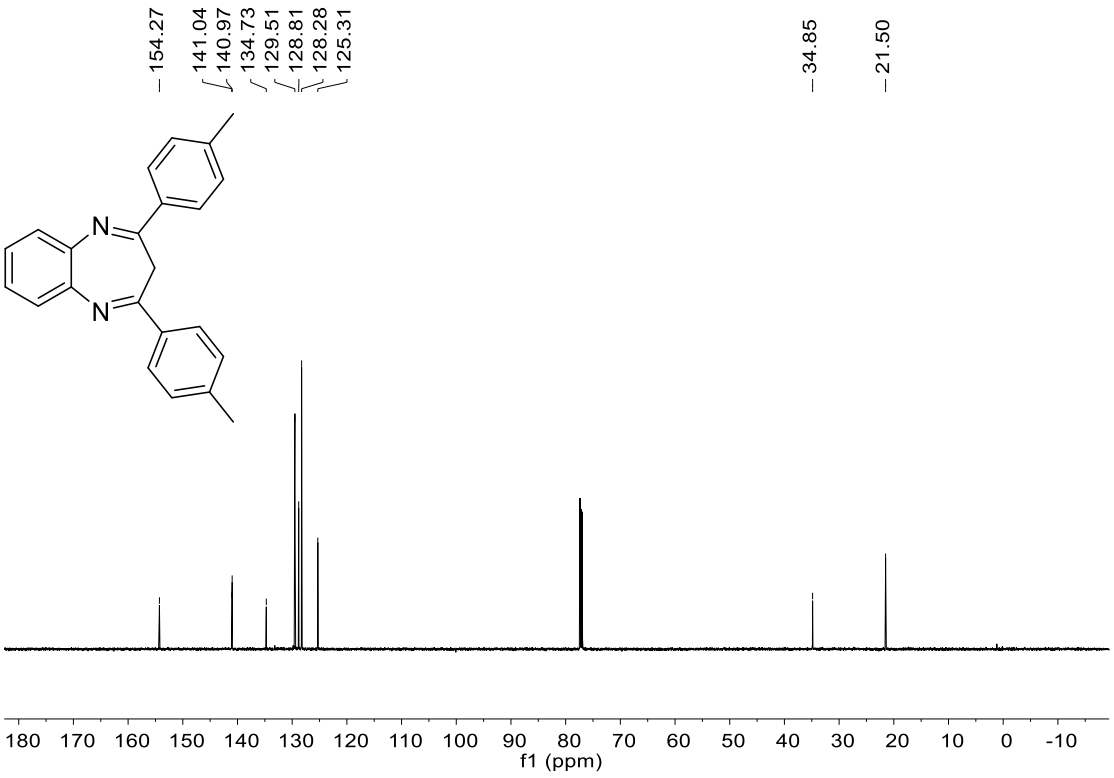

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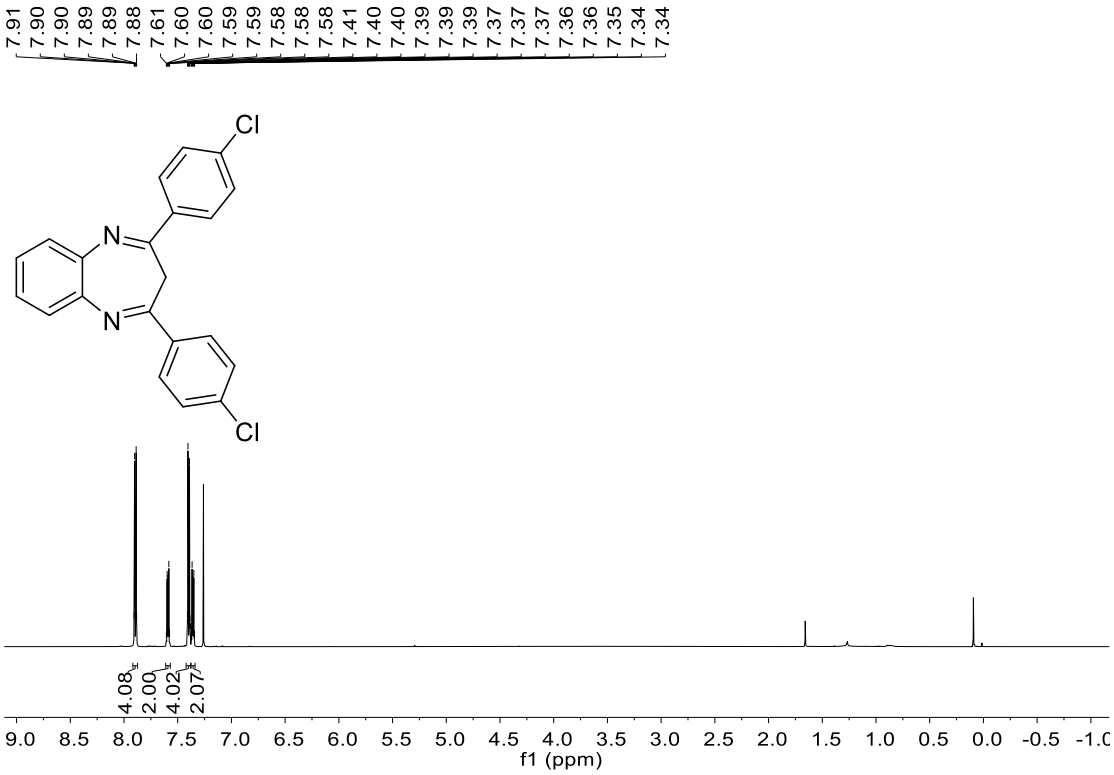

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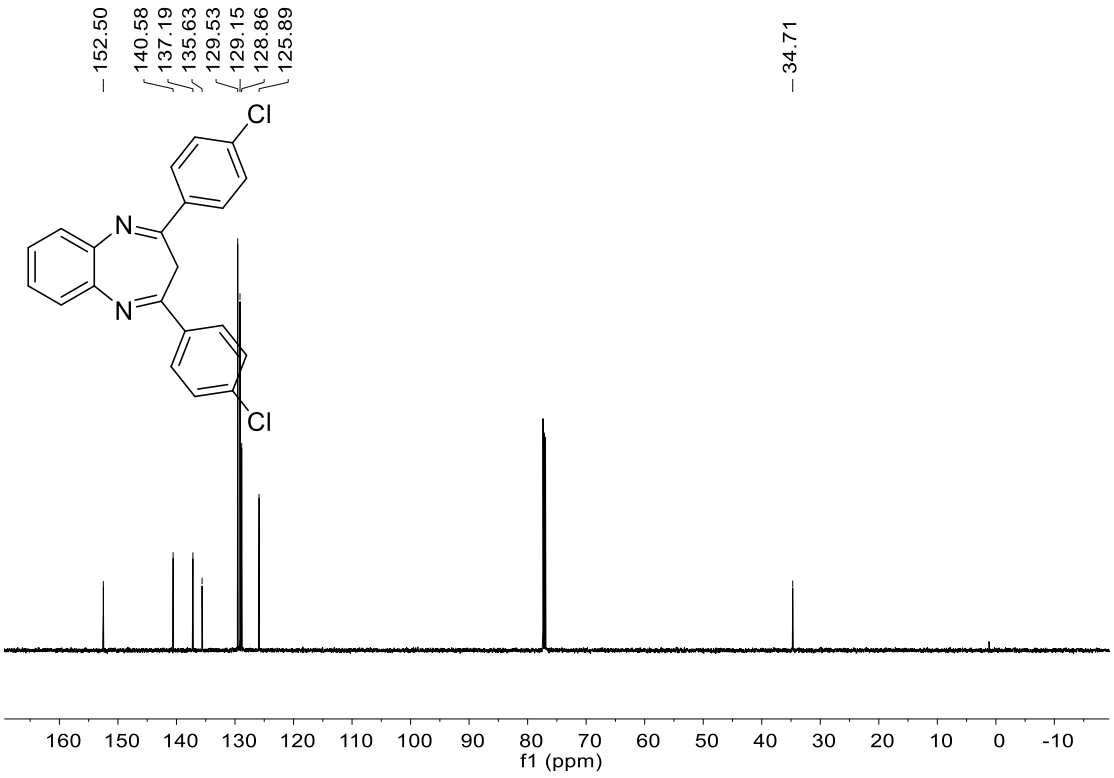

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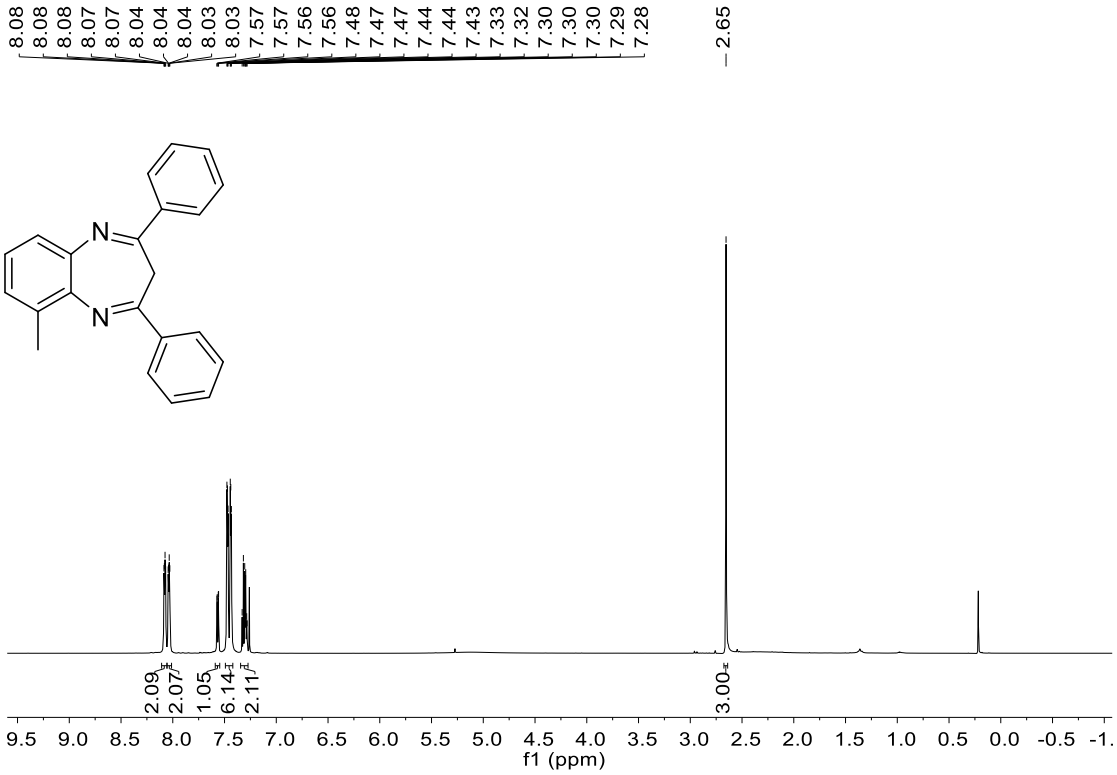

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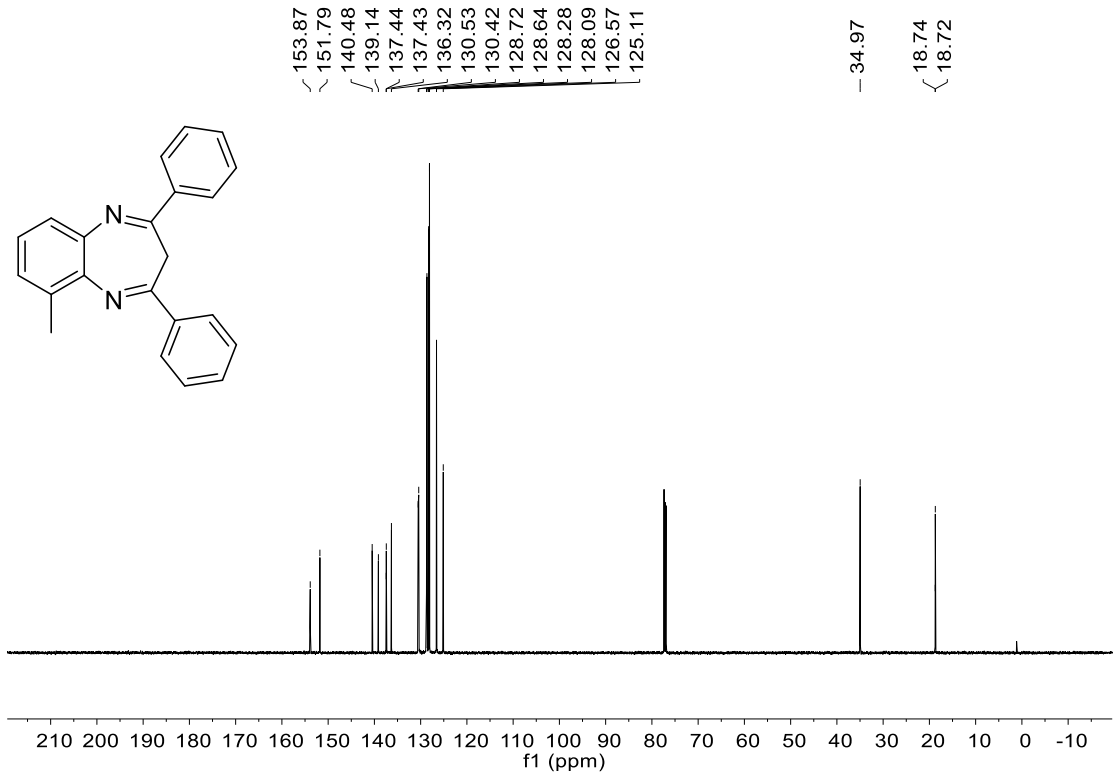

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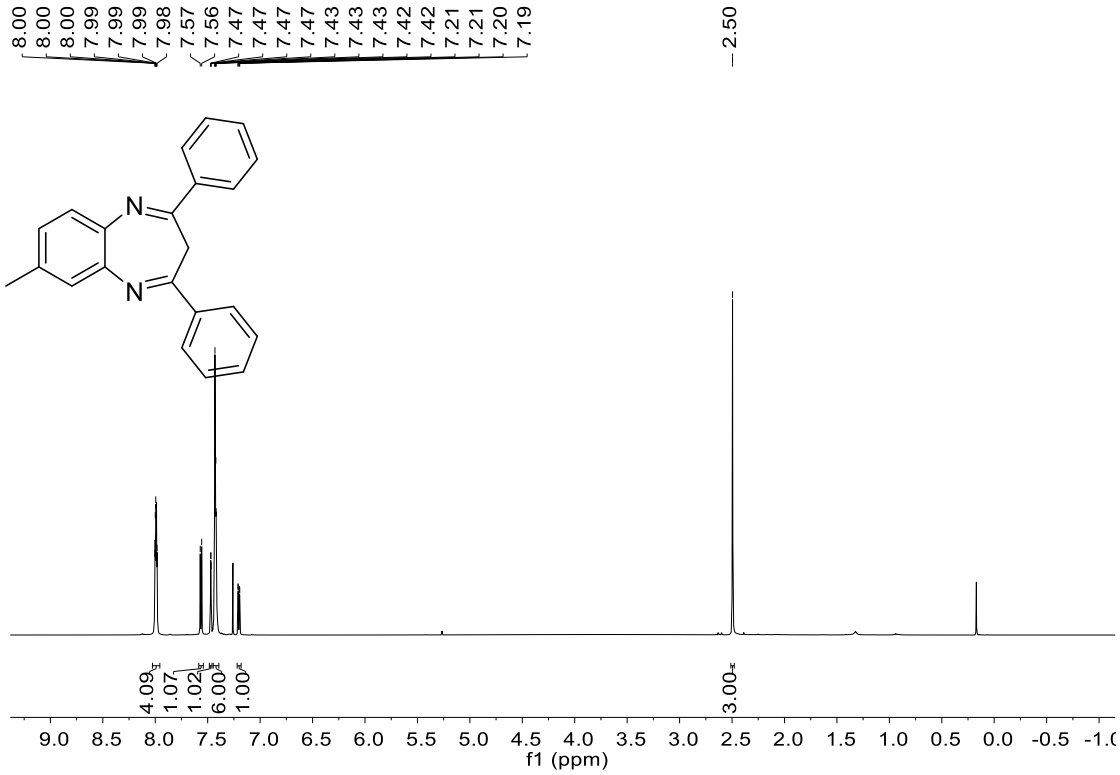

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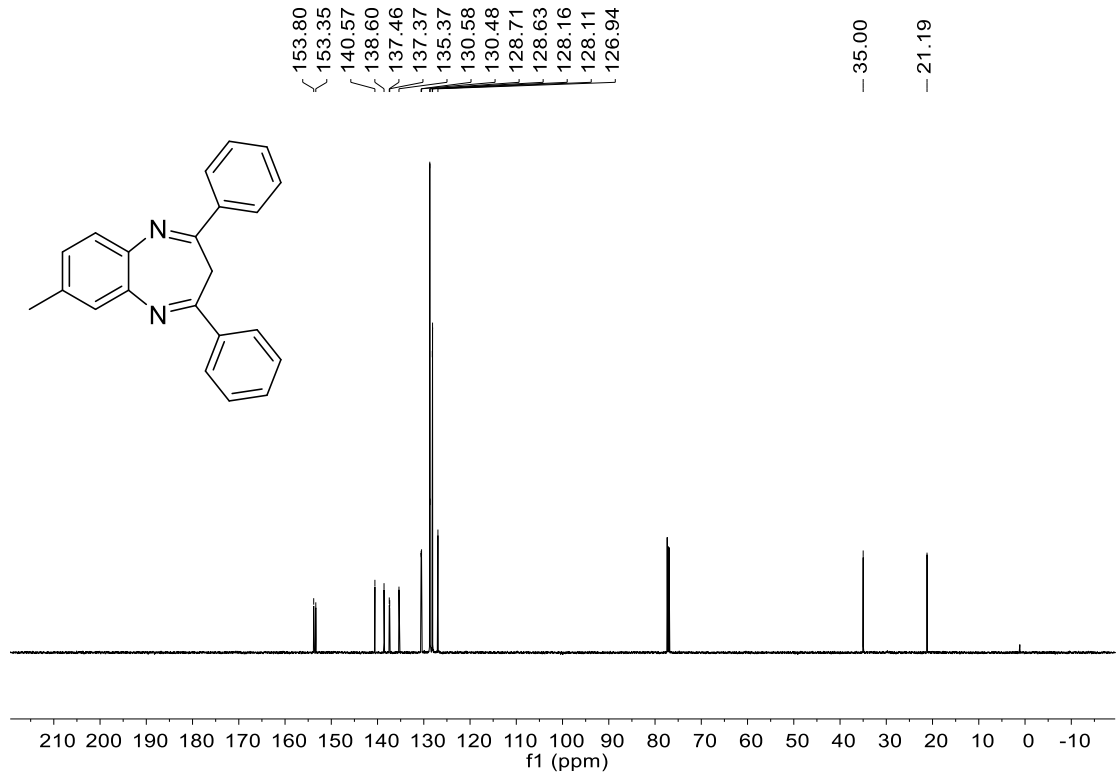

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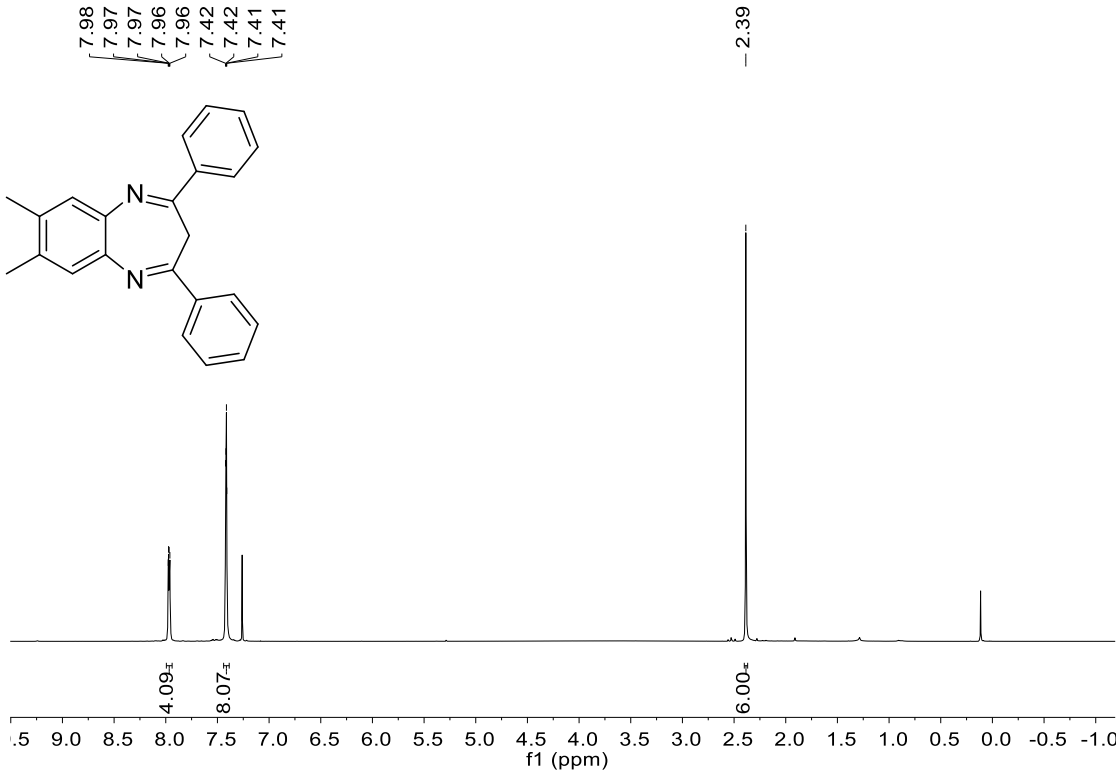

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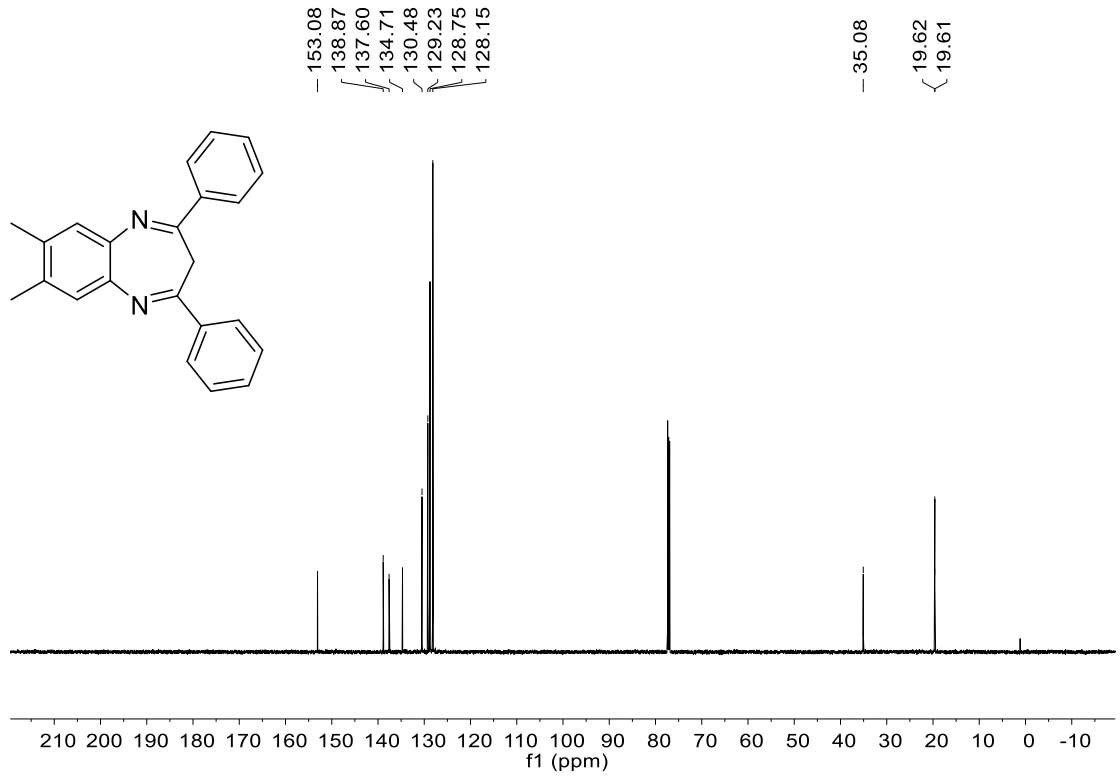

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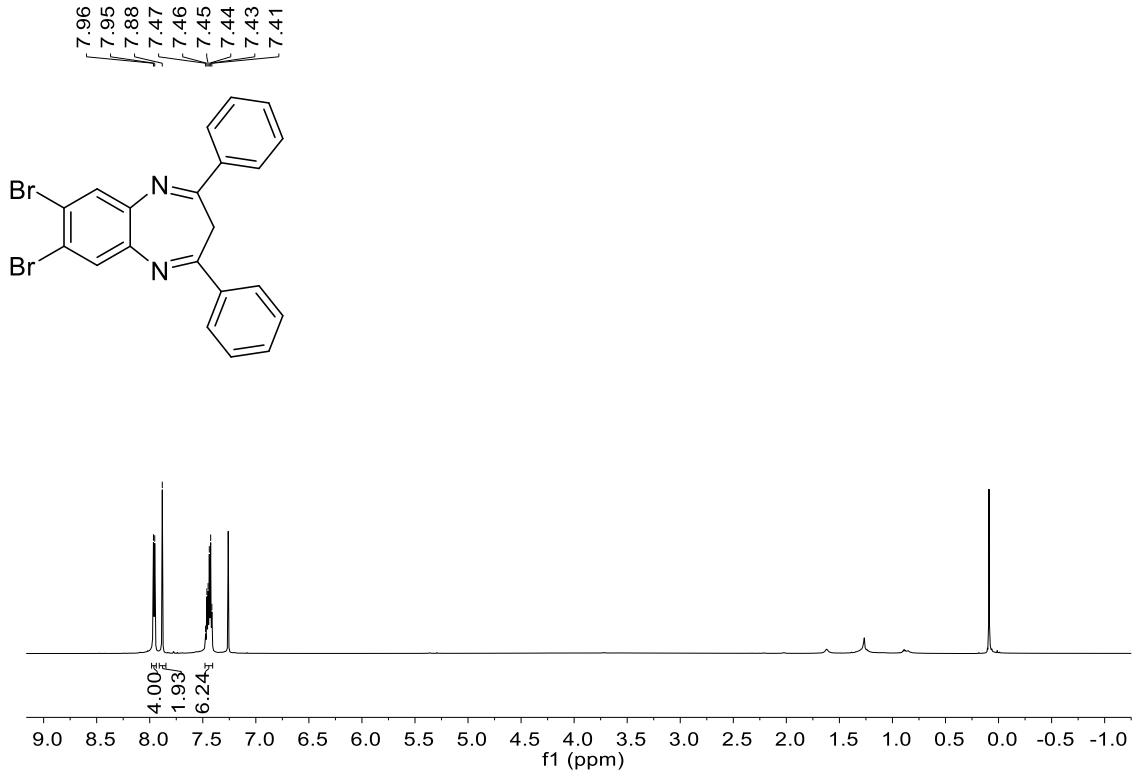

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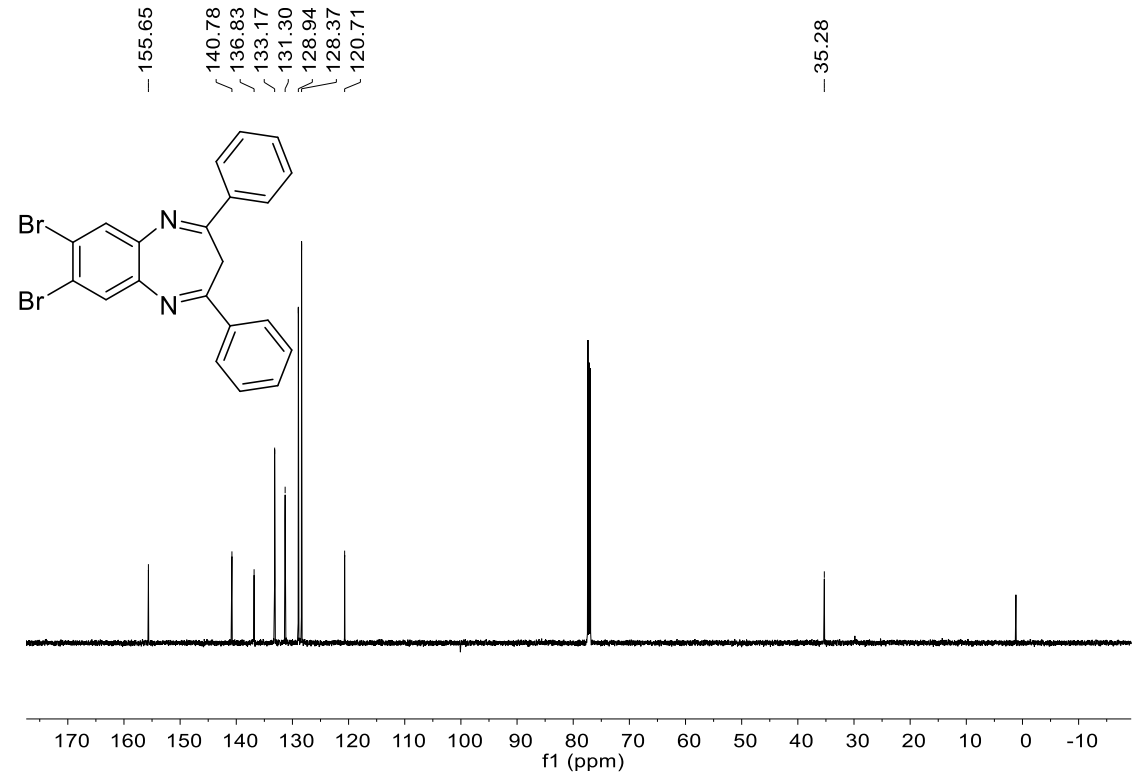

S-7. References

1. M. Yang, Y. Wang, Y. Jian, D. Leng, W. Zhang, G. Zhang, H. Sun and Z. Gao, *Mol. Catal.*, 2020, **498**, 111247.