Preparation, Isolation and Characterization of in-situ formed Lewis Base Adducts (LBAs) of DBU. Their Application as Green Reagents

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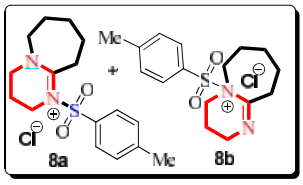
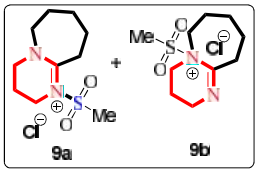
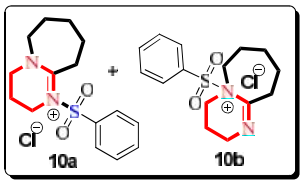
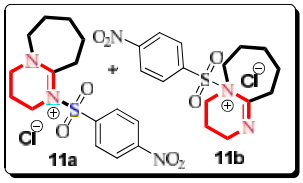
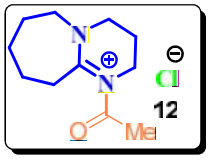
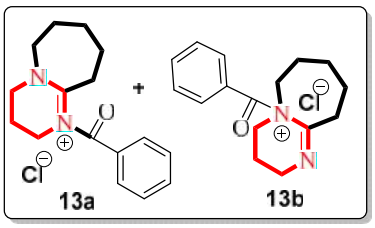
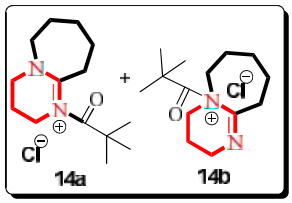
General Considerations. All solvents were treated according to standard methods. Commercial reagents were purchased from AVRA, Merck and TCCI and used without further purification unless otherwise stated. Solvents, unless otherwise specified, were reagent grade and distilled once prior to use. ^{1}H-NMR spectra were recorded at 400 MHz (Varian); ^{13}C NMR spectra were recorded at 100 MHz (Varian). ^{1}H-NMR chemical shifts are calibrated using residual undeuterated solvents $CHCl_3$ (δ = 7.26 ppm), DMSO (δ = 2.50 ppm) ^{13}C-NMR chemical shifts for ^{13}C-NMR are reported relative to the central $CHCl_3$ (δ = 77.16 ppm) or DMSO (δ = 39.52 ppm). Coupling constants are given in Hz. Elemental analyses was done using Elementar Vario EL Cube.

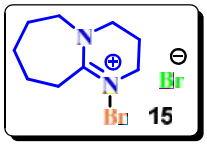
General Procedure for the preparation of LBAs of DBU

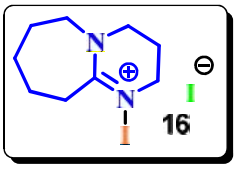
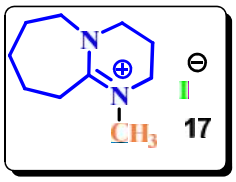
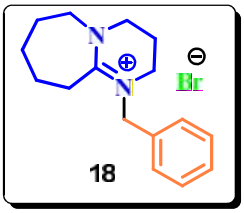
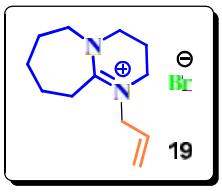
To an ice cold solution of DBU (1.0 equiv) in ethyl acetate (10 mL) was added a solution of reagent (1.1 equiv) in ethyl acetate (5 mL) slowly drop by drop through addition funnel. After addition the reaction mass was warmed to rt and stirred for 30 min. The resultant solid was filtered through Buchner funnel and washed successively with ethyl acetate (10 mL) and ether (10 mL). The solid thus obtained was thoroughly dried under vacuum to furnish different LBAs.

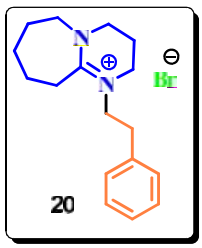
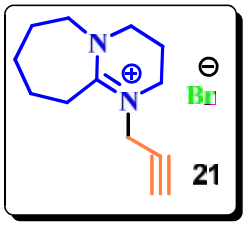
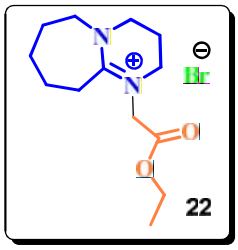
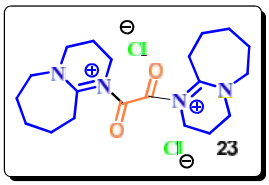
Procedure for recovery of DBU:
The aqueous layer was basified with aq. NaOH and extracted into ethyl acetate. The organic layers were evaporated under vacuum to obtain DBU which was reused again for preparation of LBAs.

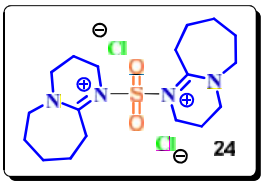
	**Brown color gel; ^{1}H NMR (400 MHz, in $CDCl_3$):** δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 3.53-3.45 (m, 6H), 3.31 – 3.19 (m, 6H), 2.95 (m, 2H), 2.44 (s, 3H), 2.36 (s, 1H), 2.09 – 2.00 (m, 4H), 1.82-1.69 (m, 5H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 166.0, 156.5, 146.1, 143.0, 139.6, 133.7, 130.1, 129.2, 128.6, 125.7, 54.4, 52.34, 50.1, 48.6, 38.8, 37.9, 32.2, 28.8, 26.6, 25.4, 23.9, 23.2, 21.7, 21.1, 19.3, 19.0. **IR (film) ν_{max} :** 1325, 1649, 2939, 3448 cm^{-1} . Mass (ESI-MS): 342.88[M+]. **CHN:** Expected for $C_{16}H_{23}ClN_2O_2S$; C, 56.05; H, 6.76; N, 8.17; Cl, 10.34; S, 9.35; Found: C, 56.07; H, 6.76; N, 8.15; Cl, 10.30; S, 9.34.
	**Light orange gel; ^{1}H NMR (400 MHz, in $CDCl_3$):** δ 3.69 – 3.52 (m, 5H), 3.49 – 3.40 (m, 3H), 3.31 (m, 1H), 3.12 (dd, *J* = 14.9, 8.7 Hz, 1H), 2.98 (m, 1H), 2.94 (d, *J* = 5.7 Hz, 2H), 2.79 (s, 3H), 2.38 – 2.27 (m, 1H), 2.11 – 2.01 (m, 3H), 1.80 – 1.69 (m, 7H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 172.7, 165.9, 57.4, 54.3, 51.5, 48.5, 39.3, 39.0, 37.8, 32.2, 28.7, 27.7, 26.5, 24.5, 23.8, 21.7, 19.3, 18.1. **IR (film) ν_{max} :** 1323, 1529, 1651, 2939, 3417 cm^{-1} . Mass (ESI-MS): 266.09[M+]. **CHN:** Expected for $C_{10}H_{19}ClN_2O_2S$; C, 45.02; H, 7.18; N, 10.50; Cl, 13.29; S, 12.02; Found: C, 45.06; H, 7.21; N, 10.52; Cl, 13.26; S, 12.03.
	**Brown color gel; ^{1}H NMR (400 MHz, in $CDCl_3$):** δ 8.18 (d, *J* = 7.4 Hz, 2H), 7.88 – 7.85 (m, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.37 (m, 1H), 3.57 – 3.49 (m, 6H), 3.45 – 3.27 (m, 5H), 2.94 – 2.89 (m, 2H), 2.05 – 1.99 (m, 4H), 1.69-1.72 (m, 8H).**^{13}C NMR (400 MHz, in $CDCl_3$):** δ 166.2, 156.7, 145.4, 136.8, 134.9, 129.8, 129.6, 129.3, 128.2, 125.9, 54.5, 52.6, 50.2, 48.8, 38.8, 38.1, 32.4, 29.0, 26.8, 25.5, 24.0, 23.3, 21.3, 19.5, 19.3. **IR (film) ν_{max} :** 1325, 1504, 1649, 2939, 3448 cm^{-1} . **Mass (ESI-MS):** 328.86 [M+]. **CHN:** Expected for $C_{15}H_{21}ClN_2O_2S$; C, 54.78; H, 6.44; N, 8.52; Cl, 10.78; S, 9.75; Found: C, 54.80; H, 6.40; N, 8.48; Cl, 10.79; S, 9.75.
	**Orange gel; ^{1}H NMR (400 MHz, in $CDCl_3$):** δ 8.21 (t, *J* = 6.7 Hz, 2H), 8.12 (d, *J* = 8.9 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 8.9 Hz, 1H), 3.58 – 3.51 (m, 5H), 3.41-3.38 (m, 3H), 2.91-2.89 (m, 2H), 2.05-2.01 (m, 2H), 1.78 – 1.71 (m, 7H).**^{13}C NMR (400 MHz, in $CDCl_3$):** δ 166.2, 165.2, 131.4, 130.3, 128.4, 127.3, 124.8, 124.5, 123.5, 123.4, 54.5, 54.0, 49.9, 48.8, 46.5, 38.6, 38.0, 32.4, 29.0, 27.9, 26.7, 26.1, 24.0, 23.7, 19.5. **IR (film) ν_{max} :** 1147, 1369, 1649, 2939, 3448 cm^{-1} . **Mass (ESI-MS):**373.86[M+]. **CHN:** Expected for $C_{15}H_{20}ClN_3O_4S$; C, 48.19; H, 5.39; N, 11.24; Cl, 9.48; S, 8.58; Found: C, 48.21; H, 5.40; N, 11.22; Cl, 9.41; S, 8.53.

	**Colorless gel; ^{1}H NMR (400 MHz, in $CDCl_3$):** δ 3.58 – 3.50 (m, 4H), 3.45 (dd, *J* = 7.7, 5.9 Hz, 2H), 2.99-2.97 (m, 2H), 2.10 – 2.03 (m, 5H), 1.79-1.71 (m, 6H). **^{13}C NMR (400 MHz, in $CDCl_3$):** δ 173.0, 165.8, 54.3, 48.6, 37.8, 32.1, 28.7, 26.52, 23.8, 21.3, 19.3. **IR (film) ν_{max} :** 1325, 1529, 1647, 2935, 3449 cm^{-1}. **Mass (ESI-MS):**230.12[M+]. **CHN:** Expected for $C_{11}H_{19}ClN_2O$; C, 57.26; H, 8.30; N, 12.14; Cl, 15.37; Found: 57.28; H, 8.32; N, 12.10; Cl, 15.34.
	**Colorless gel; ^{1}H NMR (400 MHz, in $CDCl_3$):** δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.73 – 7.62 (m, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.41 (dd, *J* = 13.6, 6.2 Hz, 1H), 7.34 (dd, *J* = 15.6, 8.1 Hz, 1H), 7.11 – 7.07 (m, 1H), 4.29 – 3.67 (m, 5H), 3.67 – 3.49 (m, 2H), 3.44 (s, 1H), 2.97 (t, *J* = 31.3 Hz, 2H), 2.26 (dd, *J* = 19.7, 14.6 Hz, 1H), 2.13 – 2.00 (m, 2H), 1.97 – 1.63 (m, 7H). **^{13}C NMR (400 MHz, in $CDCl_3$):** δ 172.9, 171.6, 166.2, 156.7, 138.9, 136.8, 134.9, 129.8, 129.6, 129.3, 128.2, 125.9,56.2, 54.5, 52.6, 50.2, 48.8, 38.8, 38.1, 32.4, 29.0, 26.8, 25.6, 24.0, 23.3, 21.3, 19.5,19.3. **IR (film) ν_{max} :** 1325, 1529, 1627, 2935, 3446 cm^{-1} . Mass (ESI-MS): 292.13[M+]. **CHN:** Expected for $C_{16}H_{21}ClN_2O$; C, 65.63; H, 7.23; N, 19.57; Cl, 12.11; Found: C, 65.61; H, 7.20; N, 19.58; Cl, 12.13.
	**Brown gel; ^{1}H NMR (400 MHz, in $CDCl_3$):** δ 3.64 – 3.53 (m, 4H), 3.45 (dd, *J* = 7.7, 5.9 Hz, 2H), 3.26-3.24 (m, 2H), 2.98 (d, *J* = 5.9 Hz, 2H), 2.81-2.79 (m, 1H), 2.28 – 2.12 (m, 1H), 2.11 – 2.02 (m, 2H), 1.89 – 1.66 (m, 5H), 1.41 (s, 9H), 1.19-1.16 (m, 2H). **^{13}C NMR (400 MHz, in $CDCl_3$):** δ 184.0, 181.2, 168.7, 166.0, 56.2, 54.4, 50.2, 48.7, 38.2, 37.9, 33.5, 32.2, 28.7, 28.1, 27.0, 26.7, 23.9, 23.0, 20.4, 19.4. **IR (film) ν_{max} :** 1325, 1560, 1620, 2935, 3415 cm^{-1} . Mass (ESI-MS): 272.17[M+]. **CHN:** Expected for $C_{14}H_{25}ClN_2O$; C, 61.64; H, 9.24; N, 10.27; Cl, 13.00; Found: C, 61.66; H, 9.22; N, 10.25; Cl, 13.02.

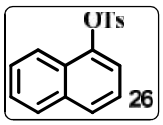
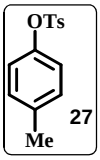
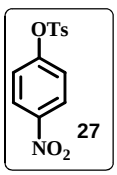
	**Yellow powder; MP** = 140-143 °C. **^{1}H NMR (400 MHz, in $CDCl_3$):** δ 3.73 – 3.43 (m, 6H), 3.02-2.93 (m, 2H), 2.16 (s, 2H), 1.90–1.66 (m, 6H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 168.0, 167.8, 62.3, 55.6, 55.2, 49.6, 48.9, 29.3, 28.2, 25.7, 22.4, 20.0, 14.0. **IR (film) ν_{max} :** 1193, 1253, 1325, 1627,1724, 2935, 3446 cm^{-1} . **Mass (ESI-MS):** 318.09 [M+]. **CHN:** Expected for $C_{13}H_{23}BrN_2O_2$; C, 48.91; H, 7.26; N, 8.78; Br, 25.03; Found: C, 48.89; H, 7.24; N, 8.72; Br, 25.05.

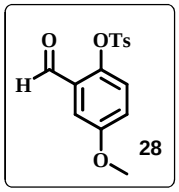
	**Black powder; MP** = 161-164 °C. **^{1}H NMR (400 MHz, in $CDCl_3$):**δ 3.64 (dd, *J* = 12.7, 7.2 Hz, 4H), 3.54 (s, 2H), 2.98 (s, 2H), 2.23 – 2.11 (m, 2H), 1.82 (d, *J* = 23.4 Hz, 6H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 166.2, 55.3, 49.2, 38.4, 33.6, 28.9, 26.7, 24.0, 19.6. **IR (film) ν_{max} :** 1319, 1481, 1643, 2935, 3118 cm^{-1} . **Mass (ESI-MS):** 405.94[M+]. **CHN:** Expected for $C_9H_{16}I_2N_2$; C, 26.62; H, 3.97; N, 8.78; I, 62.97; Found: C, 26.58; H, 3.92; N, 8.75; I, 62.96.
	**White Solid; MP** = 175-177 °C . **^{1}H NMR (400 MHz, in $CDCl_3$):** 3.79 – 3.62 (m, 6H), 3.38 (s, 3H), 2.99 – 2.90 (m, 2H), 2.29 – 2.20 (m, 2H), 1.85 (m, 6H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 166.5, 55.5, 48.9, 42.8, 29.3, 28.3, 26.0, 22.2, 20.0. **IR (film) ν_{max} :** 1325, 1627, 2935, 3070, 3446 cm^{-1} . **Mass (ESI-MS):** 294.06[M+]. **CHN:** Expected for $C_{10}H_{19}IN_2$; C, 40.83; H, 6.51; N, 9.52; I, 43.14; Found: C, 40.81; H, 6.50; N, 9.54; I, 43.12.
	**White Solid; MP** = 170-173 °C . **^{1}H NMR (400 MHz, in $CDCl_3$):**δ 7.40 (t, *J* = 7.3 Hz, 2H), 7.33 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 2H), 4.89 (s, 2H), 3.88 – 3.77 (m, 4H), 3.74 (t, *J* = 5.7 Hz, 2H), 2.98 – 2.89 (m, 2H), 2.29 – 2.17 (m, 2H), 1.80 (dd, *J* = 24.4, 15.1 Hz, 4H), 1.70 (dd, *J* = 9.7, 4.7 Hz, 2H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 167.3, 134.2, 129.3, 128.3, 126.3, 57.0, 55.7, 49.6, 47.8, 29.3, 28.3, 26.0, 22.5, 20.2. **IR (film) ν_{max} :** 1325, 1627, 2935, 3065, 3446cm^{-1} . **Mass (ESI-MS):** 322.10[M+]. **CHN:** Expected for $C_{16}H_{23}BrN_2$; C, 59.45; H, 7.17; N, 8.67; Br, 24.72; Found: C, 59.44; H, 7.14; N, 8.66; Br, 24.74.
	**White Solid; MP** = 113-116 °C. **^{1}H NMR (400 MHz, in $CDCl_3$):**δ 5.88 (ddt, *J* = 15.3, 9.9, 4.8 Hz, 1H), 5.30 (dd, *J* = 22.9, 13.8 Hz, 2H), 4.30 – 4.23 (m, 2H), 3.87 – 3.71 (m, 4H), 3.71 – 3.62 (m, 2H), 2.91 (m, 2H), 2.31 – 2.15 (m, 2H), 1.82 (m, 6H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 166.9, 130.3, 118.1, 55.8, 55.6, 49.4, 47.2, 28.8, 28.3, 26.0, 22.8, 20.1. **IR (film) ν_{max} :** 1327, 1620, 2065, 2937, 3419 cm^{-1} . **Mass (ESI-MS):** 272.09[M+]. **CHN:** Expected for $C_{12}H_{21}BrN_2$; C, 52.72; H, 7.75; N, 10.25; Br, 29.25; Found: C, 52.71; H, 7.70; N,10.23; Br, 29.22.

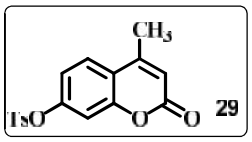
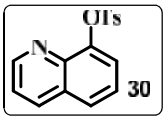
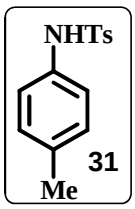
	**White Solid; MP** = 85-87 °C. **^{1}H NMR (400 MHz, in $CDCl_3$):** δ 7.34 (t, *J* = 7.2 Hz, 2H), 7.29 (dd, *J* = 7.8, 6.0 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 2H), 3.88 (t, *J* = 6.9 Hz, 2H), 3.59 (dd, *J* = 12.4, 7.1 Hz, 4H), 3.46 (t, *J* = 5.7 Hz, 2H), 3.02 (t, *J* = 6.4 Hz, 2H), 2.77 – 2.74 (m, 2H), 2.11 – 2.04 (m, 2H), 1.80 – 1.71 (m, 6H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 167.3, 139.8, 129.3, 128.3, 126.3, 55.8, 53.9, 49.6, 45.4, 32.3, 29.3, 28.0, 23.9, 22.3, 20.2. **IR (film) ν_{max} :** 1325, 1620, 2935, 3103, 3421 cm^{-1} . **Mass (ESI-MS):** 337.30 [M+]. **CHN:** Expected for $C_{17}H_{25}BrN_2$; C, 60.53; H, 7.47; N, 8.31; Br, 23.69; Found: C, 60.55; H, 7.45; N, 8.31; Br, 23.65.
	**White Solid; MP** = 200-202 °C. **^{1}H NMR (400 MHz, in $CDCl_3$):** δ 4.48 (d, *J* = 2.4 Hz, 2H), 3.79 (t, *J* = 5.8 Hz, 2H), 3.74 (t, *J* = 5.9 Hz, 1H)3.65 – 3.39 (m, 1H), 3.11 – 2.98 (m, 2H), 2.50 (t, *J* = 2.4 Hz, 1H), 2.31 – 2.16 (m, 2H), 1.91 (m, 2H), 1.84 (m, 3H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 166.2, 83.6, 81.0, 52.4, 46.6, 42.4, 38.0, 29.4, 29.0, 26.8, 23.8, 19.5. **IR (film) ν_{max} :** 1325, 1627, 2935, 3070, 3446 cm^{-1} . **Mass (ESI-MS):** 271.20 [M+]. **CHN:** Expected for $C_{12}H_{19}BrN_2$; C, 53.15; H, 7.06; N, 10.33; Br, 29.34; Found: C, 53.13; H, 7.08; N, 10.31; Br, 29.36.
	**Grey Solid; MP** = 57-60 °C. **^{1}H NMR (400 MHz, in $CDCl_3$):** δ 4.62 (s, 2H), 4.25 (qd, *J* = 7.1, 3.1 Hz, 2H), 3.86 – 3.66 (m, 6H), 2.92 – 2.80 (m, 2H), 2.31 – 2.15 (m, 2H), 1.82 (s, 6H), 1.31 (td, *J* = 7.1, 3.2 Hz, 3H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 168.0, 167.8, 62.3, 55.6, 55.2, 49.6, 48.9, 29.3, 28.2, 25.7, 22.4, 20.0, 14.0. **IR (film) ν_{max} :** 1193, 1253, 1325, 1627,1724, 2935, 3446 cm^{-1} . **Mass (ESI-MS):** 318.09 [M+]. **CHN:** Expected for $C_{13}H_{23}BrN_2O_2$; C, 48.91; H, 7.26; N, 8.78; Br, 25.03; Found: C, 48.89; H, 7.24; N, 8.72; Br, 25.05.
	**Lemon yellow gel; ^{1}H NMR (400 MHz, in $CDCl_3$):** δ 3.65 – 3.50 (m, 8H), 3.45 (s, 4H), 2.97 (d, *J* = 6.0 Hz, 4H), 2.10 – 2.03 (m, 4H), 1.75 (d, *J* = 31.2 Hz, 12H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 168.4, 166.2, 54.5, 48.8, 38.0, 32.3, 29.0, 26.8, 24.0, 19.5. **IR (film) ν_{max} :** 1107, 1325, 1647, 2935, 3419 cm^{-1} . Mass (ESI-MS): 431.19[M+]. **CHN:** Expected for $C_{20}H_{32}Cl_2N_4O_2$; C, 55.68; H, 7.48; N, 12.99; Cl, 16.44; Found: C, 55.66; H, 7.49; N, 12.99; Cl, 16.40.

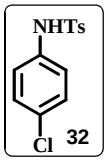
	**Dark red gel; ^{1}H NMR (400 MHz, in $CDCl_3$):** δ 4.11 (dd, *J* = 12.4, 5.3 Hz, 4H), 3.56 – 3.46 (m, 12H), 3.00 (s, 4H), 2.05 (d, *J* = 4.6 Hz, 4H), 1.79 (s, 8H), 1.36–1.15 (m, 2H). **^{13}C NMR (100 MHz, in $CDCl_3$):** δ 160.5, 52.3, 46.6, 38.0, 32.9, 28.9, 26.8, 24.0, 19.5. **IR (film) ν_{max} :** 1323, 1529, 1651, 2939, 3417 cm^{-1} . **Mass (ESI-MS):** 439.4[M+]. **CHN:** Expected for $C_{18}H_{32}Cl_2N_4O_2S$; C, 49.20; H, 7.34; N, 12.75; Cl, 16.14; S, 7.30 Found: C, 49.22; H, 7.35; N, 12.72; Cl, 16.13; S, 7.32.

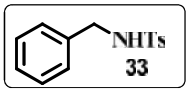
General Experimental procedure for tosylation using 31:
To a stirred solution of compound (5 mmol) in H_2O (5 ml) was added $[DBUTs]^+Cl^-$, **8a+b** (5.5 mmol) at rt and the reaction mixture was stirred until TLC indicates completion. The solid thus obtained was filtered through syntered disc, washed with water (5 mL) and dried under vacuum. The resultant solids were purified by recrystalization from ethanol to produce the pure tosyl derivatives **26-35**.

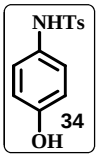
	Cream color crystalline solid, **MP** = 84-86 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.84-7.72 (m, 3H), 7.50-7.40 (m, 2H), 7.36 (t, *J* = 8.1 Hz, 1H), 7.30-7.24 (m, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 145.7, 145.4, 134.7, 132.7, 129.7, 128.4, 127.6, 127.2, 127.0, 126.7, 126.6, 125.1, 121.7, 118.3, 21.6. **IR (film) ν_{max} :** 1599, 1369, 1221, 1183, 1073, 1041, 898, 778, 717, 586, 578 cm^{-1}. **MS(ESI):** *m/z* 316 $[M+H_2O]^+$.
	Yellow crystalline solid, **MP** = 56-58 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 2.44 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 147.4, 145.2, 136.9, 132.4, 130.0, 129.6, 128.5, 122.0, 21.6, 20.8. **IR (film) ν_{max} :** 3030, 2969, 1605, 1501, 1391, 1315, 1172, 1075, 1019, 947, 827, 734, 646, 558 cm^{-1}. **MS(ESI):***m/z* 280 $[M+H_2O]^+$.
	White crystalline solid,**MP =** 74-76 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 8.20 (d, *J* = 9.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 9.1 Hz, 2H), 2.48 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 153.9, 146.2, 146.1, 131.7, 130.1, 128.4, 125.3, 123.1, 21.7. **IR (film) ν_{max} :** 3112, 3052, 2865, 1917, 1682, 1649, 1610, 1583, 1528, 1490, 1446, 1386, 1315, 1200, 1183, 1090, 1041, 1008, 871, 810, 767, 739, 690, 663cm^{-1}. **MS(ESI):** *m/z* 316 $[M+Na]^+$.

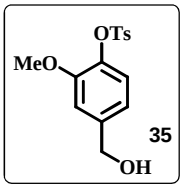
	White crystalline solid, **MP** = 119-121 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 9.93 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.43 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.37-7.27 (m, 4H), 3.64 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 190.8, 152.6, 145.5, 142.9, 135.7, 132.8, 129.5, 128.5, 124.5, 124.3, 111.0, 55.7, 21.7. **IR (film) ν_{max} :** 2832, 2785, 1698, 1589, 1506, 1457, 1369, 1287, 1189, 1145, 1024, 832, 701, 663 $cm^{-1.}$ **MS(ESI):** *m/z* 307$[M+H]^+$.

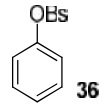
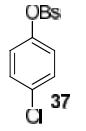
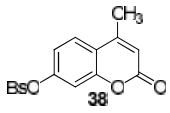
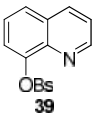
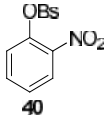
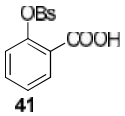
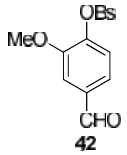
	White crystalline solid, **MP** = 114-116 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.08 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.27 (d, *J* = 1.3 Hz, 1H), 2.48 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 160.0, 153.8, 151.7, 151.5, 146.0, 131.8, 130.0, 128.4, 125.7, 118.8, 118.7, 115.0, 110.8, 21.7, 18.6. **IR (film) ν_{max} :** 1731, 1610, 1561, 1446, 1424, 1260, 1194, 1128, 1063, 1013, 957, 882, 816, 756, 695, 657, 630, 547 cm^{-1}. **MS(ESI):** *m/z* 331 $[M+H]^+$.
	White crystalline solid, **MP =** 119-121 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 8.80 (dd, *J* = 4.4, 1.9 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.72 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.57 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 150.7, 145.5, 145.0, 141.5, 135.6, 133.1, 129.5, 129.3, 128.7, 126.9, **IR (film) ν_{max} :** 3057, 2914, 1599, 1420, 1380, 1309, 1183, 1052, 898, 827, 728, 717, 668, 553 cm^{-1}. 125.9, 122.3, 121.8, 21.6. **MS(ESI):** *m/z* 300 $[M+H]^+$.
	Cream color crystalline solid, **MP** = 122-124 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 2.40 (s, 3H), 2.28 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 143.7, 136.1, 135.2, 133.9, 129.8. 129.6, 127.3, 122.2, 21.5, 20.8. **IR (film) ν_{max} :** 3238, 3040, 2925, 2854, 1512, 1605, 1408, 1331, 1156, 1084, 898, 863, 695, 586 cm^{-1}. **MS(ESI):** *m/z* 260 $[M-H]^+$.

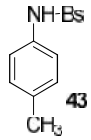
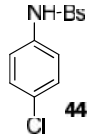
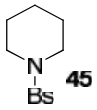
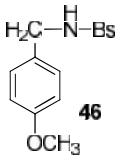
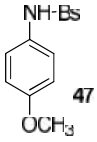
	White crystalline solid, **MP** = 76-78 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.28-7.24 (m, 3H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 2.4 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 144.2, 135.8, 135.2, 130.9, 129.8, 129.4, 127.3, 122.9, 21.5. **IR (film) ν_{max} :** 3249, 2915, 1514, 1495, 1463, 1397, 1326, 1332, 1167, 1084, 915, 810, 717, 673 cm^{-1} **MS(ESI):** *m/z* 299 $[M+H_2O]^+$& 301 $[M+H_2O+2]^+$ in 3:1 ratio.

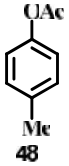
	White crystalline solid,**MP=** 111-113 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** 7.75 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.27-7.24 (m, 3H), 7.21-7.18 (m, 2H), 4.80-4.75 (m, 1H), 4.11 (d, *J* = 6.3 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 143.5, 136.8, 136.3, 129.7, 128.6, 127.8, 127.2, 47.2, 21.5. **IR (film) ν_{max} :** 3271, 3049, 2909, 2849, 2356, 2036, 1660, 1594, 1495, 1457, 1161, 879, 745, 673, 542 cm^{-1}. **MS(ESI):** *m/z* 262 $[M+H]^+$.

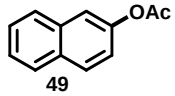
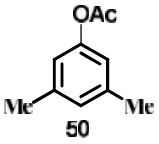
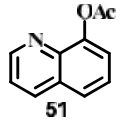
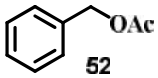
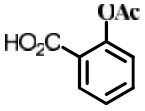
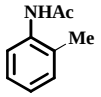
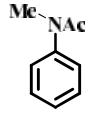
	Pink crystalline solid, **MP**= 142-144 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$ + DMSO-d6):** δ 154.3, 142.1, 136.2, 128.5, 127.9, 126.3, 123.9, 114.9, 20.6. **IR (film) ν_{max} :** 3446, 3249, 3035, 2920, 2367, 1605, 1506, 1468, 1397, 1358, 1320, 1287, 1260, 1205, 1156, 1090, 909, 838, 810, 690 cm^{-1}. **MS(ESI):** *m/z* 281 $[M+H_2O]^+$.

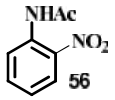
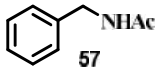
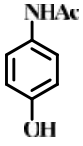
	White crystalline solid, **MP**= 83-84 °C. **^{1}H NMR (500 MHz, $CDCl_3$):**δ 7.72 (d. *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.03 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.87 (bs, 1H), 6.82 (dd, *J* = 8.3, 1.8 Hz, 1H), 4.63 (s, 2H), 3.55 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 151.8, 145.0, 141.1, 137.5, 133.1, 129.3, 128.5, 123.8, 118.6, 111.0, 64.6, 55.5, 21.6. **IR (film) ν_{max} :** 3565-3450, 1589, 1501, 1452, 1374, 1282, 1172, 1030, 832, 750, 695, 663, 547 cm^{-1}. **MS(ESI):** *m/z* 309 $[M+H]^+$.

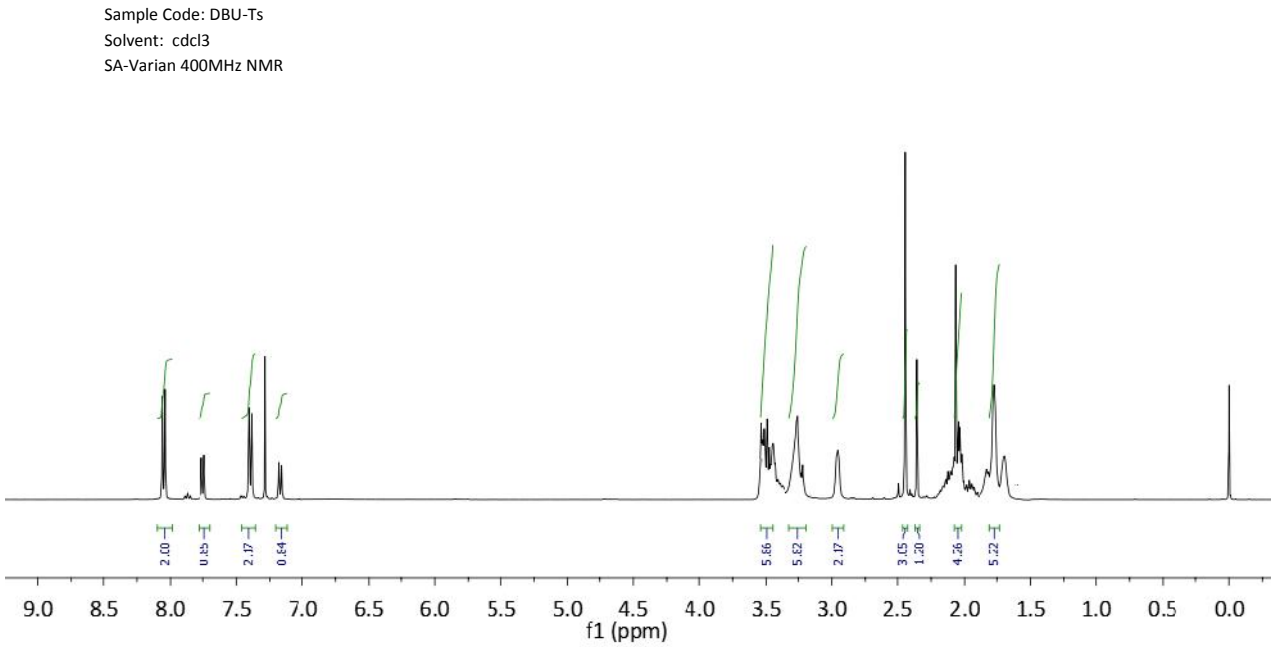
 **36**	**^{1}H NMR (400 MHz, In $CDCl_3$):** δ 7.90 – 7.75 (m, 2H), 7.72 – 7.59 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.17 (m, 3H), 7.10 – 6.79 (m, 2H). **Mass (ESI-MS):** 234.27 [M]+; **CHN**: Expected for $C_{12}H_{10}O_3S$; C, 61.52; H, 4.30; S, 13.69; Found: C, 61.54; H, 4.32; S, 13.65.
 **37**	**^{1}H NMR (400 MHz, , In $CDCl_3$):** δ 7.92 – 7.79 (m, 2H), 7.70 (dd, *J* = 15.6, 8.2 Hz, 1H), 7.63 – 7.47 (m, 2H), 7.35 – 7.20 (m, 2H), 7.03 – 6.83 (m, 2H). **Mass (ESI-MS**): 268.72 [M]+; **CHN:** Expected for $C_{12}H_9ClO_3S$; C, 53.64; H, 3.38; Cl, 13.19; S, 11.95; Found: C, 53.65; H, 3.36; Cl, 13.21; S, 11.91.
 **38**	**MP =** 99-102 °C; **^{1}H NMR (400 MHz, In $CDCl_3$):** δ 8.37 – 7.91 (m, 4H), 7.70 (dt, *J* = 15.7, 7.6 Hz, 6H), 7.26 (s, 1H), 1.69 – 1.02 (m, 6H). **Mass (ESI-MS):** 331.36 [M]+; **CHN:** Expected for $C_{17}H_{15}O_5S$; C, 61.62; H, 4.56; S, 9.68; Found: C, 61.59; H, 4.54; S, 9.71.
 **39**	**MP =** 107–110 °C; **^{1}H NMR (400 MHz, In $CDCl_3$):** δ 8.78 (dd, *J* = 4.2, 1.5 Hz, 2H), 8.12 (dd, *J* = 8.3, 1.5 Hz, 2H), 8.01–7.94 (m, 4H), 7.75 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.61 (ddd, *J* = 12.9, 8.7, 4.3 Hz, 4H), 7.53–7.43 (m, 6H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 2H), 7.26 (s, 1H); **^{13}C NMR (100 MHz, In $CDCl_3$)** δ 150.65 , 145.32 , 141.35 , 135.96, 135.60 , 133.84 , 129.48 , 128.64 , 126.99 , 125.87 , 122.46 , 121.75. **Mass (ESI-MS):** 300.35 [M]+; **CHN:** Expected for $C_{16}H_{14}NO_3S$; C, 63.98; H, 4.70; N, 4.66; S, 10.68; Found: C, 63.96; H, 4.72; N, 4.68; S, 10.69.
 **40**	**MP =** 70°C - 72 °C; **^{1}H NMR (400 MHz, In $CDCl_3$):** δ 7.90 (d, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.71 (t, *J*=7.5 Hz, 1H), 7.69-7.61 (m, 4H), 7.26 (d, *J*=8.3 Hz, 1H). **Mass (ESI-MS):** 279.27 $[M]^+$; **CHN:** Expected for $C_{12}H_9NO_2S$; C, 51.61; H, 3.25; N, 5.02; S, 11.48; Found: C, 51.64; H, 3.27; N, 5.19; S, 11.46.
 **41**	**MP =** 98-100 °C; **^{1}H NMR (400 MHz, In $CDCl_3$):** δ 8.21 (d, *J*=7.6 Hz, 1H), 7.86 (t, *J* = 7.5 Hz, 2H), 7.71-7.65(m, 5H), 7.16 (d, *J*=8.1 Hz, 1H). **Mass (ESI-MS):** 278.28 $[M]^+$; **CHN:** Expected for $C_{13}H_{10}O_5S$; C, 56.11; H, 3.62; S, 11.32; Found: C, 56.09; H, 3.64; S, 11.30.
 **42**	**MP** =60-62 °C; **^{1}H NMR (400 MHz, , In $CDCl_3$):** δ 9.93 (s, 1H), 7.89 (d, *J* = 7.4 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.44 – 7.34 (m, 1H), 7.17 (d, *J* = 13.8 Hz, 2H), 3.60 (s, 3H); **^{13}C NMR (101 MHz, in $CDCl_3$):** δ 152.42 , 142.78 , 135.80 , 134.21 , 128.65 , 128.63 , 124.38 , 124.09 , 110.98 , 55.68.

	Mass (ESI-MS): 292.31 [M]+; **CHN:** Expected for $C_{14}H_{20}O_5S$; C, 57.53; H, 4.14; S, 10.97; Found: C, 57.55; H, 4.15; S, 10.98.
 **43**	**MP** =116-118 °C; **^{1}H NMR (400 MHz, In $CDCl_3$):** δ 7.85 – 7.72 (m, 2H), 7.61 – 7.37 (m, 3H), 6.99 (dd, *J* = 23.7, 8.3 Hz, 5H), 2.26 (s, 3H). **Mass (ESI-MS):** 247.31 [M]+; **CHN:** Expected for $C_{13}H_{13}NO_2S$; C, 63.13; H, 5.30; N, 5.66; S, 12.97; Found: C, 63.11; H, 5.29; N, 5.65; S, 12.95.
 **44**	**MP** =108-110 °C; **^{1}H NMR (400 MHz, , In $CDCl_3$):** δ 7.78 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.59 – 7.41 (m, 3H), 7.22 – 7.16 (m, 2H), 7.05 – 6.99 (m, 2H). **Mass (ESI-MS):** 267.73 [M]+; **CHN:** Expected for $C_{12}H_{10}ClNO_2S$; C, 53.83; H, 3.76; Cl, 13.24; N, 5.23; S, 11.98; Found: C, 53.85; H, 3.72; Cl, 13.25; N, 5.21; S, 11.96.
 **45**	**MP** =80-82 °C; **^{1}H NMR (400 MHz, , In $CDCl_3$):** δ 7.76 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.63 – 7.44 (m, 3H), 3.09 – 2.88 (m, 4H), 1.75 – 1.29 (m, 7H). **Mass (ESI-MS):** 240.34 [M]+; **CHN:** Expected for $C_{12}H_{18}NO_2S$; C, 59.97; H, 7.55; N, 5.82; S, 13.34; Found: C, 59.95; H, 7.56; N, 5.80; S, 13.24.
 **46**	**MP** =70-72 °C; **^{1}H NMR (400 MHz, , In $CDCl_3$):** δ 7.91 – 7.81 (m, 2H), 7.62 – 7.47 (m, 3H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.83 – 6.75 (m, 2H), 4.08 (d, *J* = 6.0 Hz, 2H), 3.77 (s, 3H). **^{13}C NMR (101 MHz, in $CDCl_3$):** δ 159.28, 139.91, 132.61, 129.14, 128.12, 127.06, 114.03, 55.24, 46.77. **Mass (ESI-MS):** 292.37 [M]+; **CHN:** Expected for $C_{15}H_{18}NO_3S$; C, 61.62; H, 6.21; N, 4.79; S, 10.97; Found: C, 61.64; H, 6.20; N, 4.77; S, 10.95.
 **47**	**MP** =80-81°C; **^{1}H NMR (400 MHz, In $CDCl_3$):** δ 7.75 – 7.66 (m, 2H), 7.48 (dt, *J* = 15.5, 7.5 Hz, 3H), 7.03 – 6.91 (m, 2H), 6.80 – 6.73 (m, 2H), 3.76 (s, 3H). **Mass (ESI-MS):** 263.31 [M]+; **CHN:** Expected for $C_{13}H_{13}NO_3S$; C, 59.30; H, 4.98; N, 5.32; S, 12.28; Found: C, 59.31; H, 4.96; N, 5.30; S, 12.30.

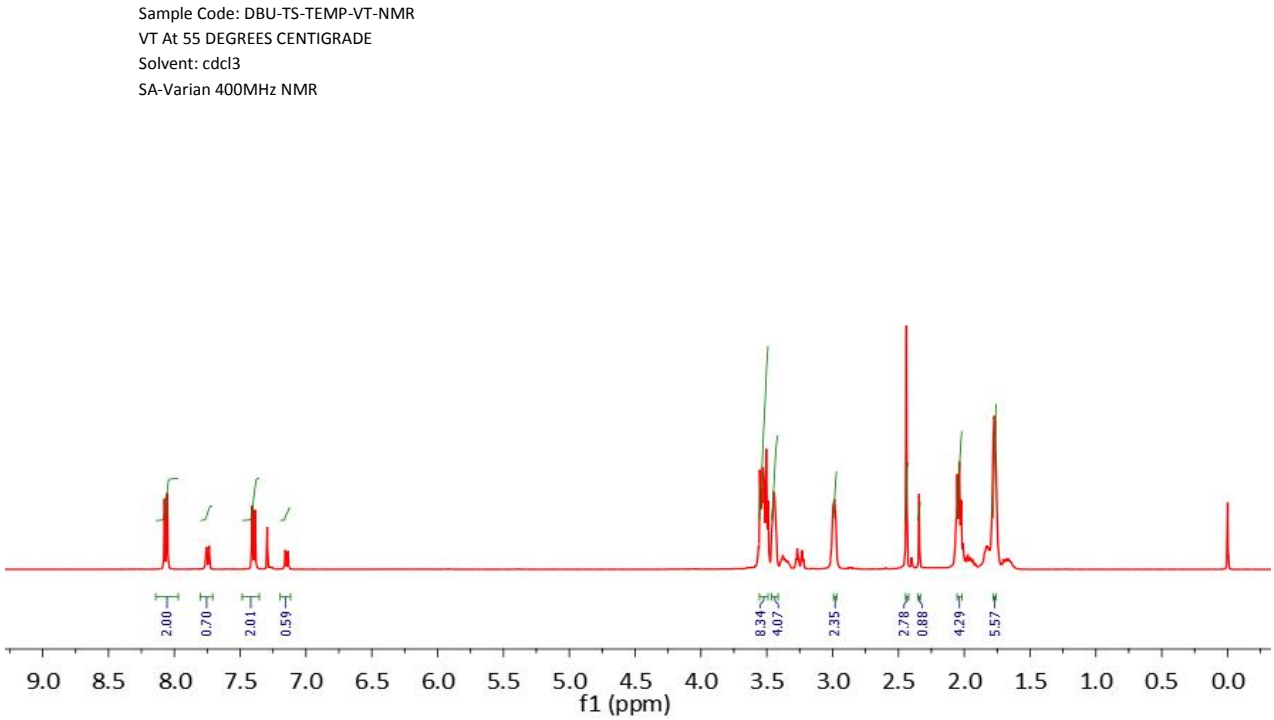
 **48**	**MP** = 40-42 °C; ^{1}H NMR (400 MHz, in $CDCl_3$): δ 7.17 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 2.34 (s, 3H), 2.28 (s, 3H). Mass (ESI-MS): 150.07 [M]+; CHN: Expected for $C_9H_{10}O_2$; C, 71.98; H, 6.71; Found: C, 71.95; H, 6.74.

 49	**MP** = 67-70 °C; ^{1}H NMR (400 MHz, in $CDCl_3$): δ 7.85 (dd, *J* = 7.8, 4.5 Hz, 3H), 7.56 (d, *J* = 1.8 Hz, 1H), 7.48 (td, *J* = 7.1, 3.4 Hz, 2H), 7.22 (d, *J* = 2.2 Hz, 1H), 2.36 (s, 3H). Mass (ESI-MS): 186.07 [M]+; CHN: Expected for $C_{12}H_{10}O_2$; C, 77.40; H, 5.41; Found:C, 77.44; H, 5.38.
 50	**MP** = 61-64 °C; **^{1}H NMR (400 MHz, in $CDCl_3$):** δ6.86 (s, 1H), 6.69 (s, 2H), 2.31 (s, 6H), 2.27 (s, 3H); **Mass (ESI-MS):** 196.07 [M]+. **CHN:** Expected for $C_{10}H_{12}O_4$; C, 61.22; H,6.16; Found: C, 61.18; H, 6.21.
 51	**^{1}H NMR (400 MHz, in $CDCl_3$):**δ 8.94 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.18 (dt, *J* = 11.5, 5.7 Hz, 1H), 7.83 (m, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.49 (m, 1H), 7.45 (m, 1H), 2.52 (s, 3H). **^{13}C NMR (400 MHz, in $CDCl_3$):** 169.8, 150.4, 147.1, 140.7, 136.3, 129.7, 126.3, 125.9, 121.8, 21.0. **Mass (ESI-MS):** 187.06 [M]+; **CHN:** Expected for $C_{11}H_9NO_2$; C, 70.58; H, 4.85; N, 7.48; Found: C, 70.60; H, 4.82; N, 7.50.
 52	**MP** = 8-10 °C; **^{1}H NMR (400 MHz, in $CDCl_3$):** δ 7.48–7.22 (m, 5H), 5.10 (s, 2H), 2.09 (s, 3H); **Mass (ESI-MS): 150**.07 [M]+; CHN: Expected for $C_9H_{10}O_2$; C, 71.98; H, 6.71; Found: C, 71.88; H, 6.69.
 53	MP = 132-134 °C; ^{1}H NMR (400 MHz, in CDCl3):δ10.37 (s, 1H), 7.93 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (m, 1H), 7.01 (dd, *J* = 8.4, 0.4 Hz, 1H), 6.99 (m, 1H), 2.16 (s, 3H).Mass (ESI-MS): CHN: Expected for $C_9H_8O_4$; C, 60.00; H, 4.48; O, 35.52; Found: C, 60.06; H, 4.44; O, 35.56.
 54	MP = 110-112 °C; ^{1}H NMR (400 MHz, in $CDCl_3$): δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.19 (dd, *J* = 7.4, 3.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.01 (s, 1H), 2.26 (s, 3H), 2.20 (s, 3H); Mass (ESI-MS): 149.08[M]+; CHN: Expected for $C_9H_{11}NO$; C, 72.46; H, 7.43; N, 9.39; Found: C, 72.36; H, 7.33; N, 9.35
 55	**MP** = 100-102 °C; **^{1}H NMR (400 MHz, in $CDCl_3$):**7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 2H), 3.27 (s, 3H), 1.87 (s, 3H). **^{13}C NMR (400 MHz, in $CDCl_3$):** 170.5, 144.6, 130.0,129.7, 127.7, 37.1, 22.4. **Mass (ESI-MS):** 149.08[M]+; **CHN:** Expected for $C_9H_{11}NO$; C, 72.46; H, 7.43; N, 9.39; Found: C, 72.48; H, 7.40; N, 9.35

 56	**MP** =146-148 °C; **^{1}H NMR (400 MHz, in $CDCl_3$):** δ 10.33 (s, 1H), 8.77 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.21 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.70 – 7.60 (m, 1H), 7.21 – 7.12 (m, 1H), 2.30 (s, 3H). **Mass (ESI-MS):** 180.05 [M]+. **CHN:** Expected for $C_8H_8N_2O_3$; C, 53.33; H,4.48; O, 26.64; N, 15.55; Found:C, 53.38; H, 4.58; O, 26.60; N, 15.58
 57	MP = 60-62 °C; ^{1}H NMR (400 MHz, in CDCL3) δ 7.36 (m, 2H), 7.27 (dd, *J* = 6.0, 3.1 Hz, 2H), 6.05 (d, *J* = 81.9 Hz, 1H), 4.39 (dd, *J* = 16.3, 6.2 Hz, 2H), 2.01 (s, 3H). ^{13}C NMR (400 MHz, in $CDCl_3$) 172.56, 136.78, 128.65,127.78, 127.44, 43.65, 22.03; Mass (ESI-MS): 149.08 [M]+. CHN: Expected for $C_9H_{11}NO$; C, 72.46; H, 7.43; N, 9.39; Found; C, 72.44; H, 7.45; N, 9.41.
 58	**MP =** 167-169 °C; **^{1}H NMR (400 MHz, in $CDCl_3$):** δ 7.33 (t, *J* = 6.3 Hz, 2H), 7.02 (d, *J* = 12.6 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 2.16 (s, 3H). **Mass (ESI-MS):** 151.06 [M]+; **CHN:** Expected for $C_8H_9NO_2$; C, 63.56; H, 6.00; N, 9.27; Found; C, 63.59; H, 6.07; N, 9.24.

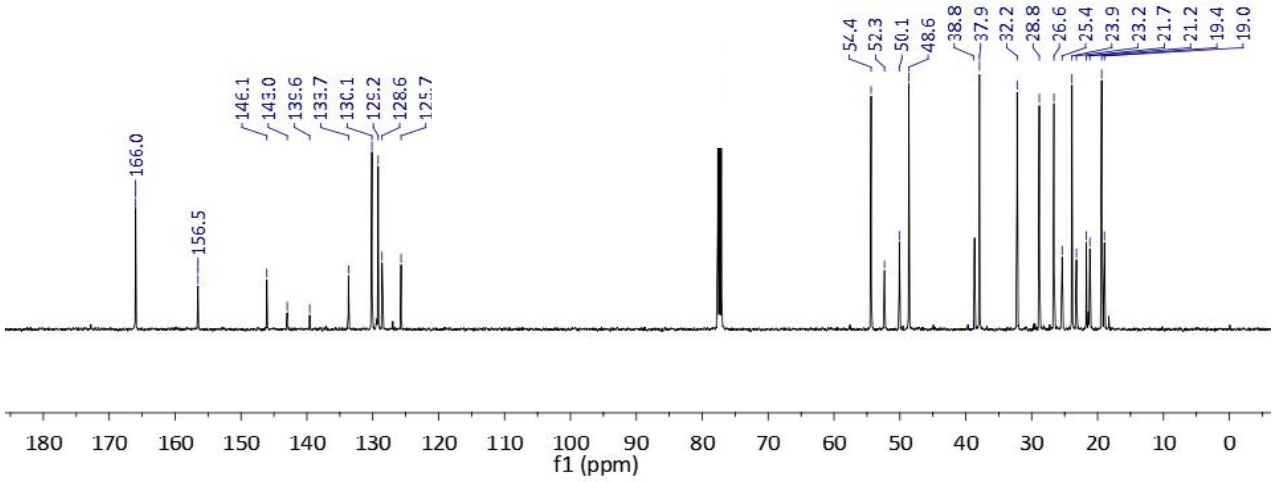


^{1}H-NMR of **8** in $CDCl_3$



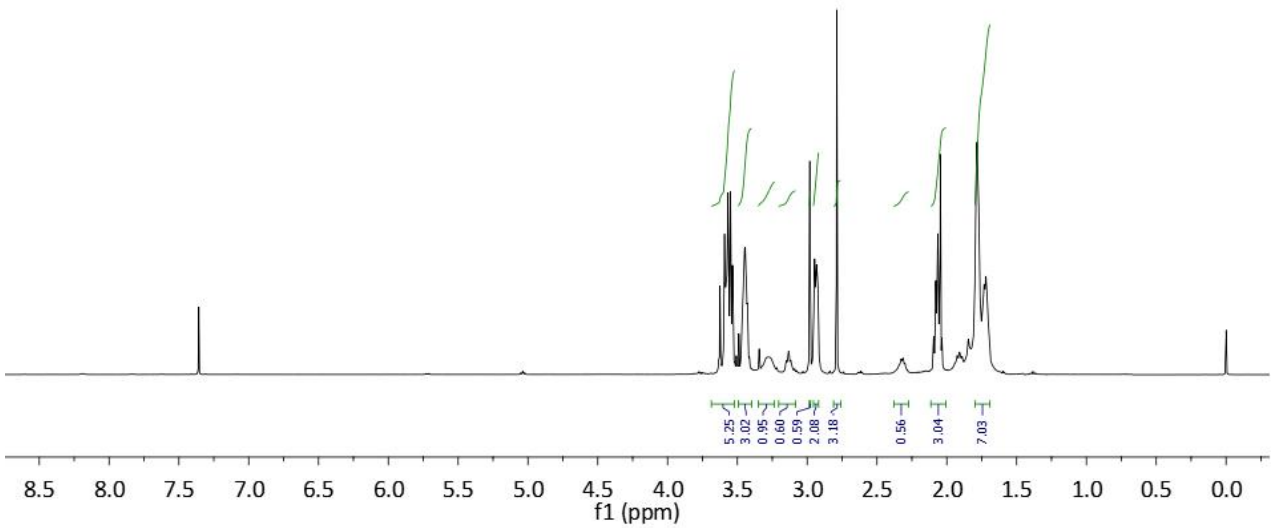
High temperature (55 °C) ^{1}H-NMR of **8** in $CDCl_3$

Sample Code: DBU-Ts
Solvent: cdcl3
SA-Varian 400MHz NMR



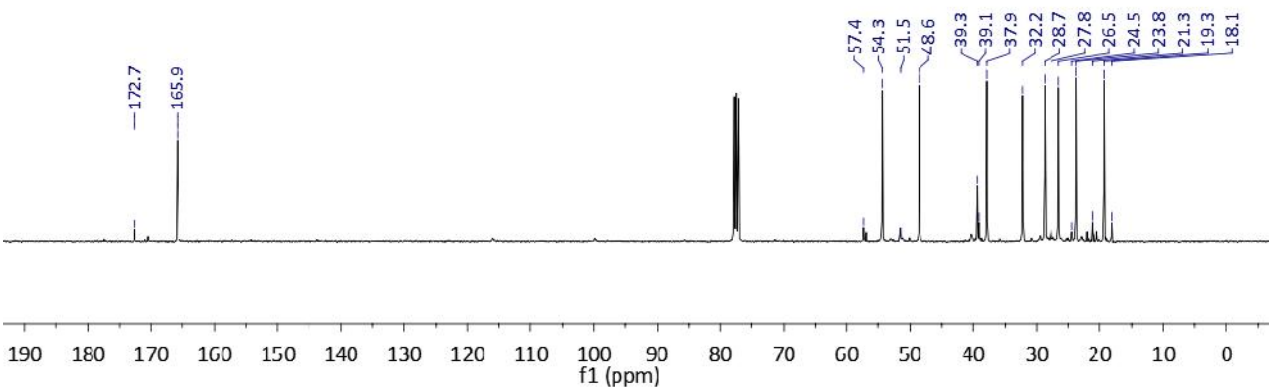
^{13}C-NMR of **8** in $CDCl_3$

Sample Code: DBU-Mes
Solvent: cdcl3
SA-Varian 400MHz NMR



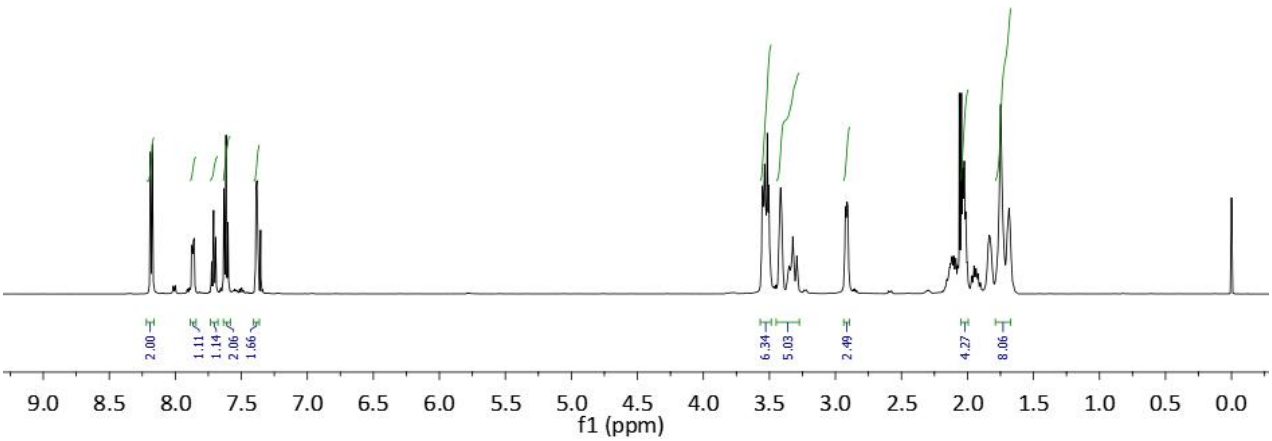
^{1}H-NMR of **9** in $CDCl_3$

Sample Code: DBU-Mes
Solvent: cdcl3
SA-Varian 400MHz NMR

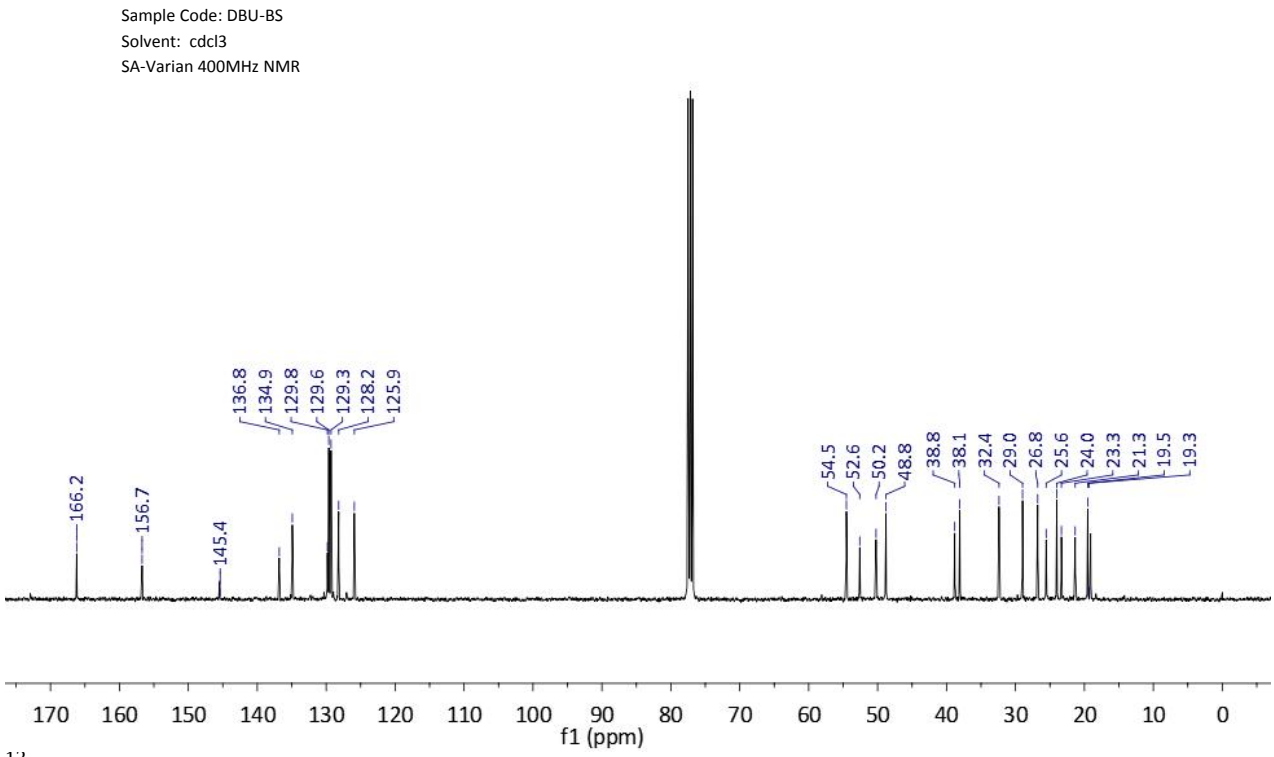


^{13}C-NMR of **9** in $CDCl_3$

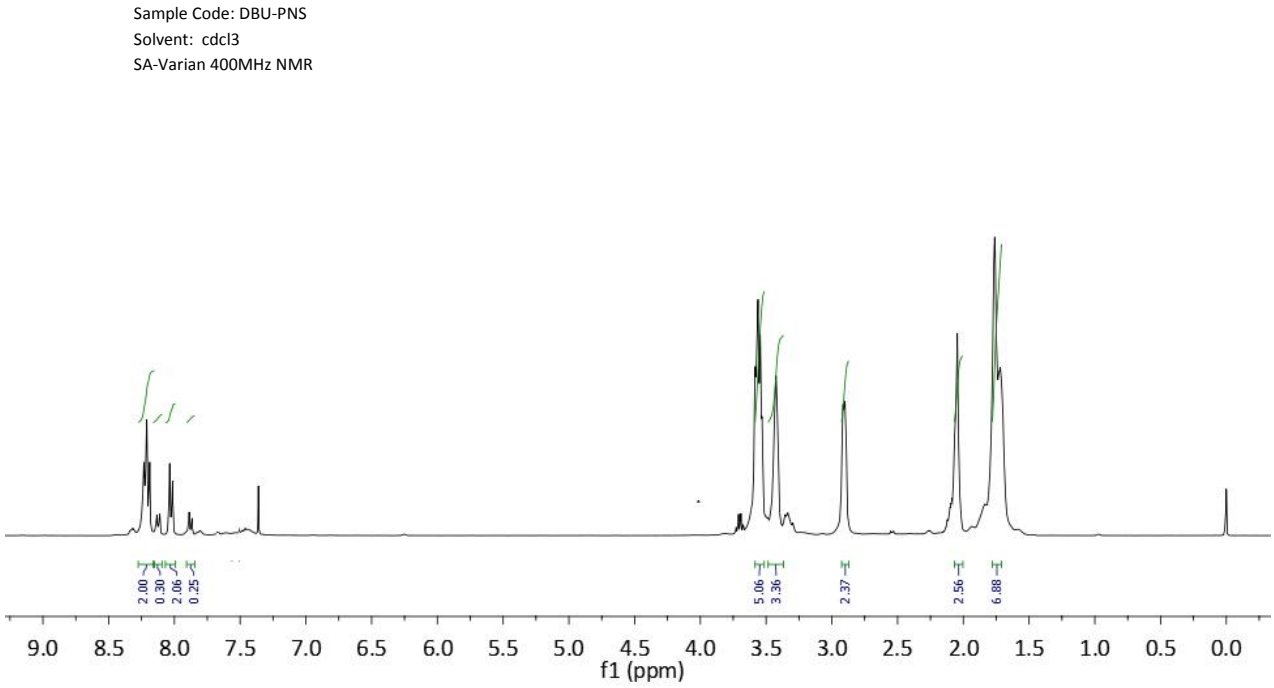
Sample Code: DBU-BS
Solvent: cdcl3
SA-Varian 400MHz NMR



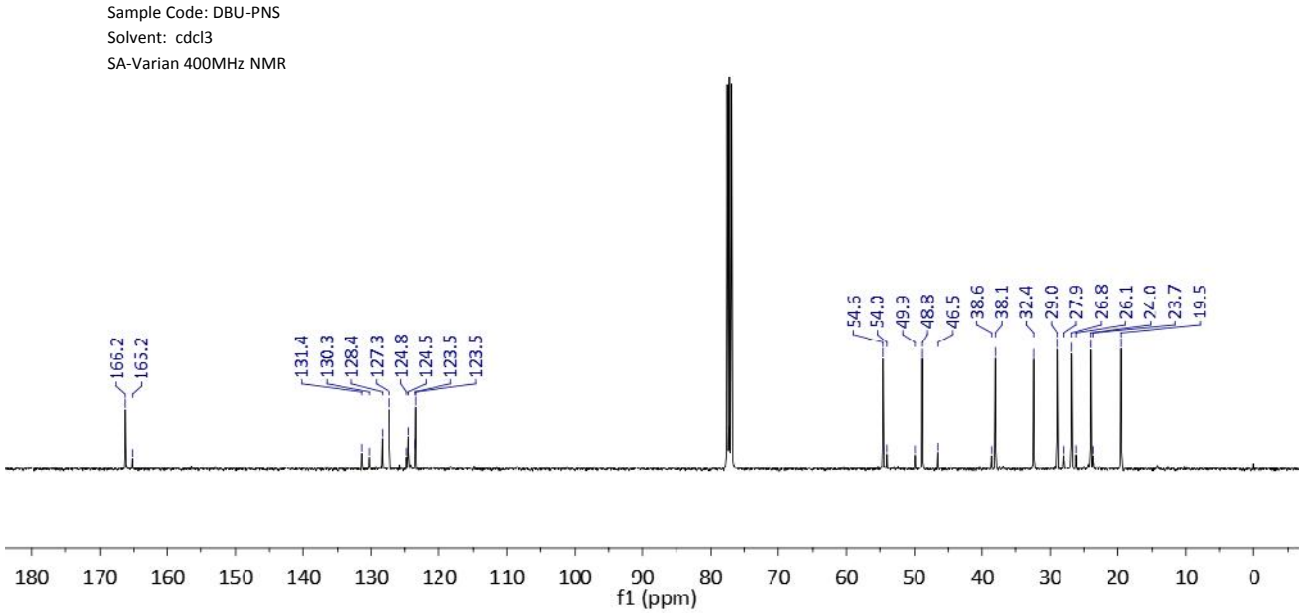
^{1}H-NMR of **10** in $CDCl_3$



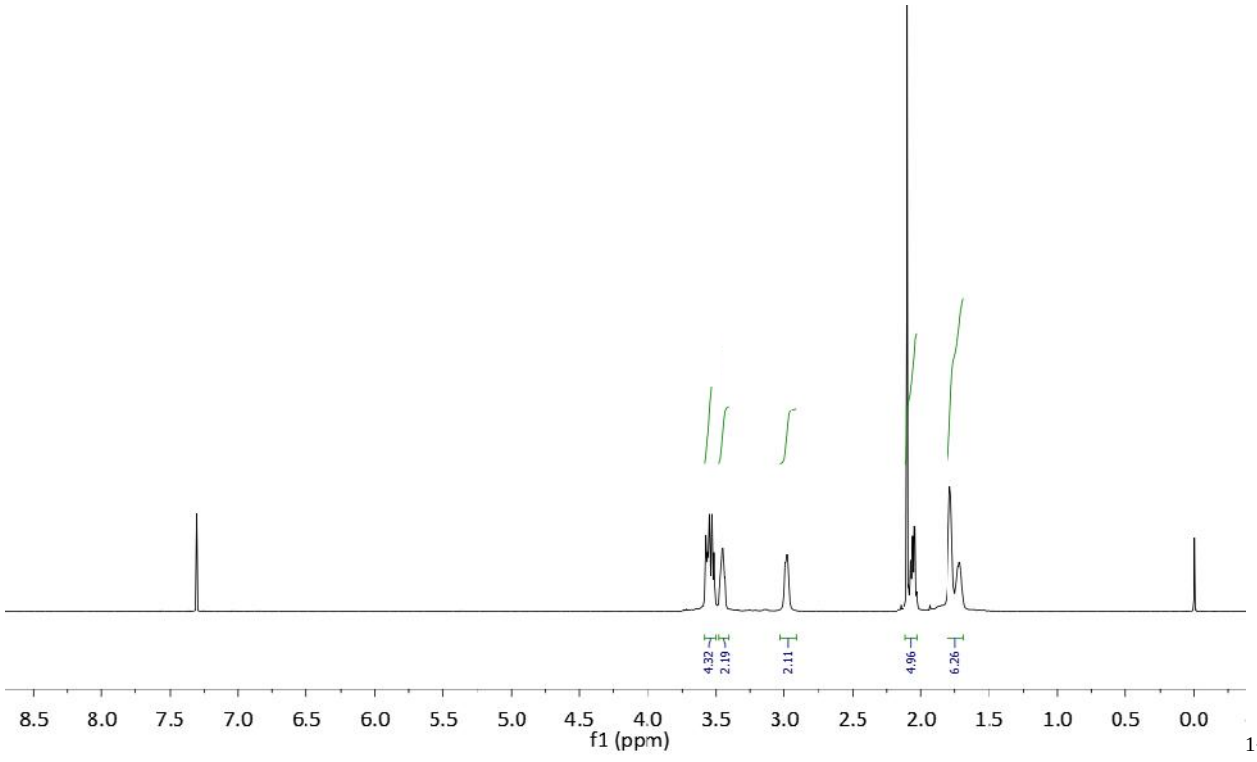
^{13}C-NMR of **10** in $CDCl_3$



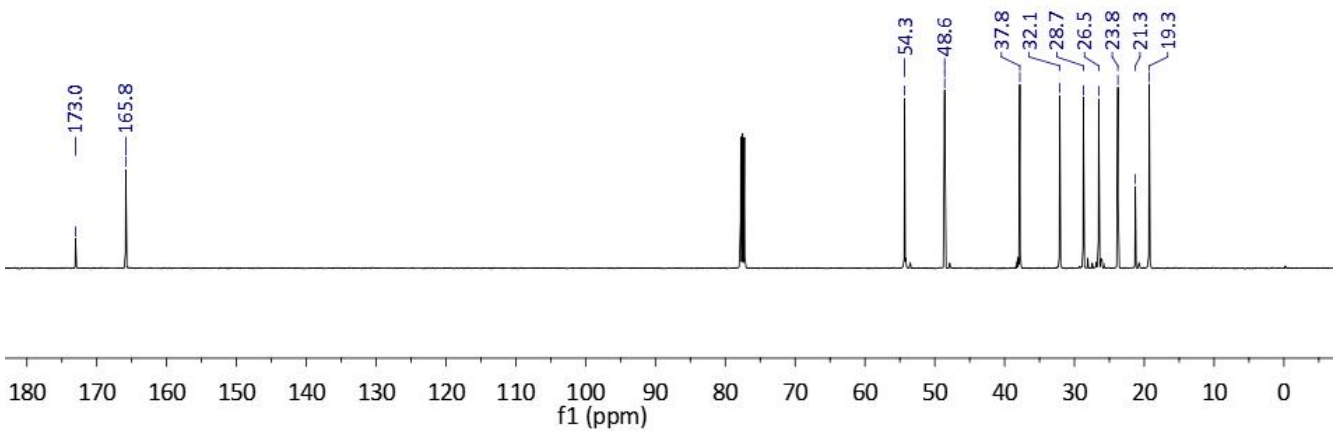
^{1}H-NMR of **11**in $CDCl_3$



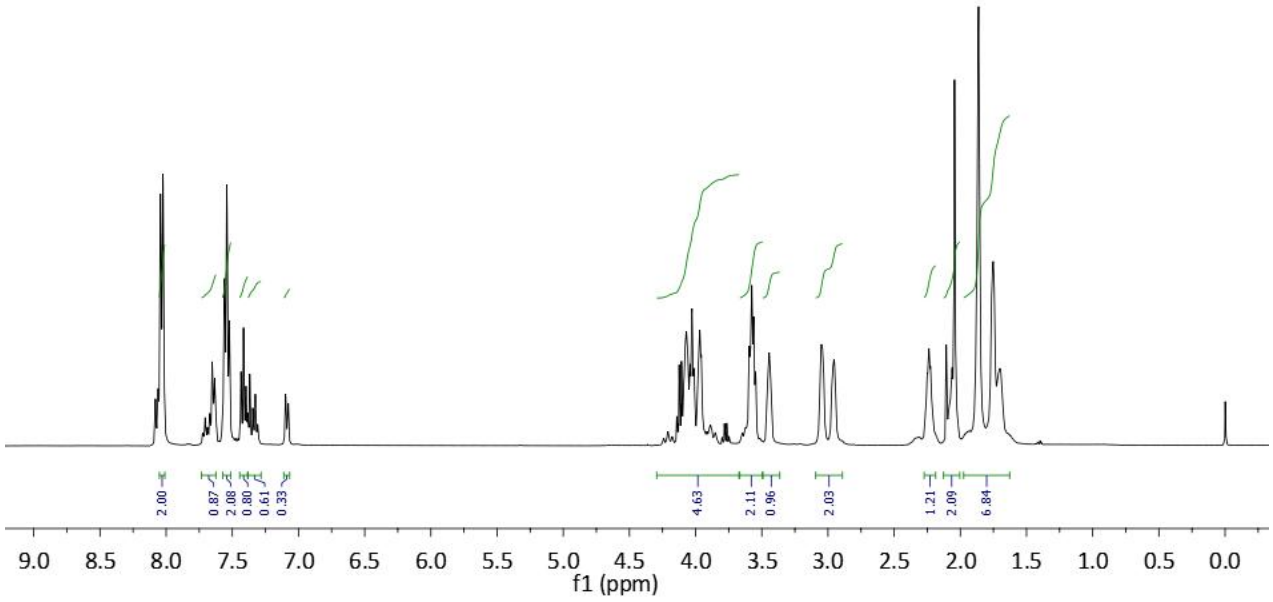
^{13}C-NMR of **11** in $CDCl_3$



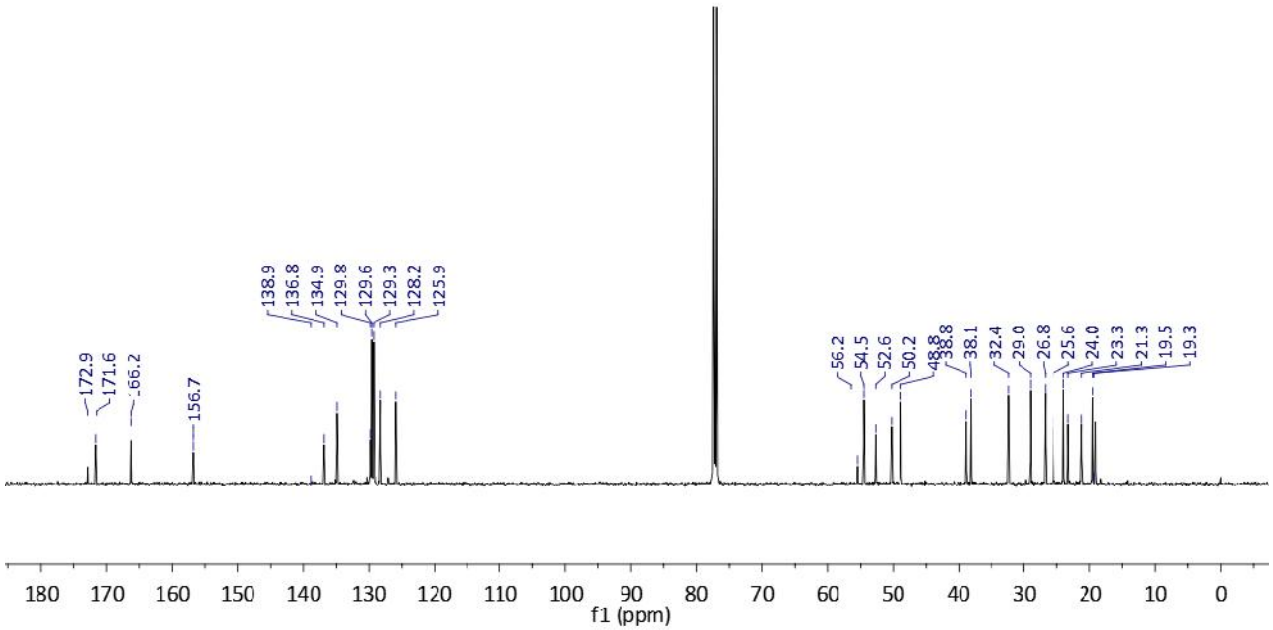
^{1}H-NMR of **12** in $CDCl_3$



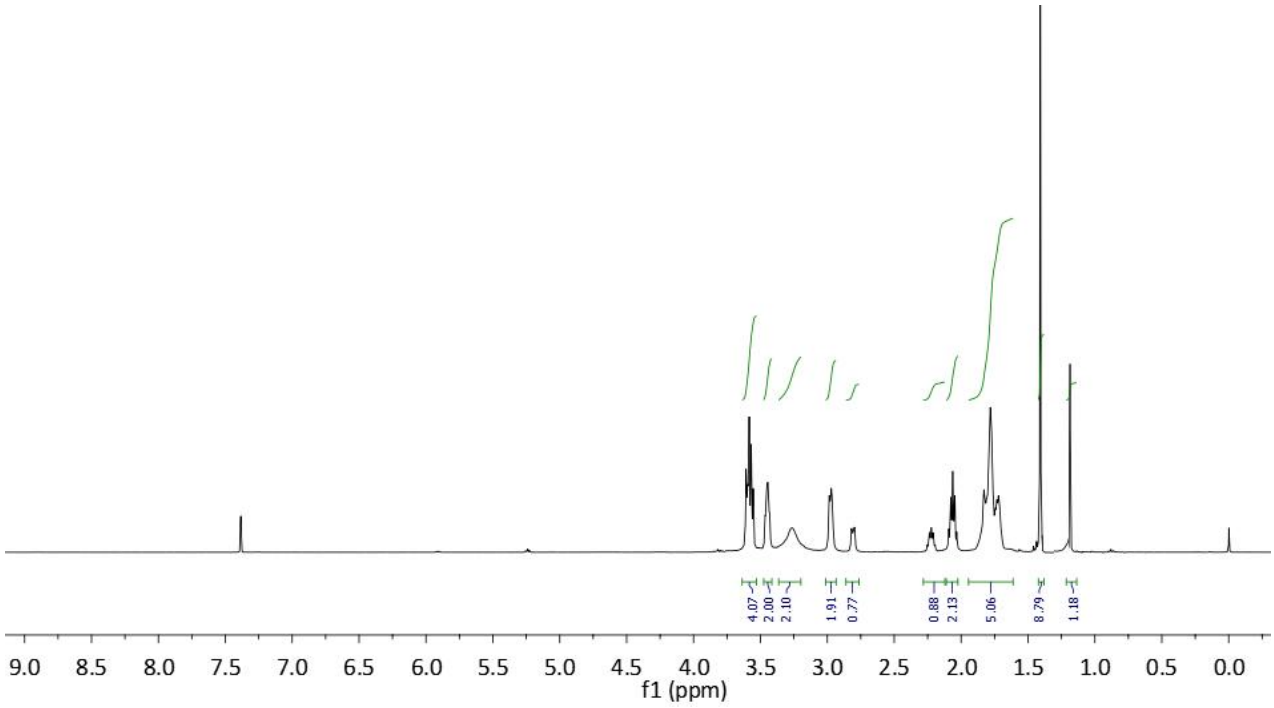
^{13}C-NMR of **12**in $CDCl_3$



^{1}H-NMR of **13** in $CDCl_3$

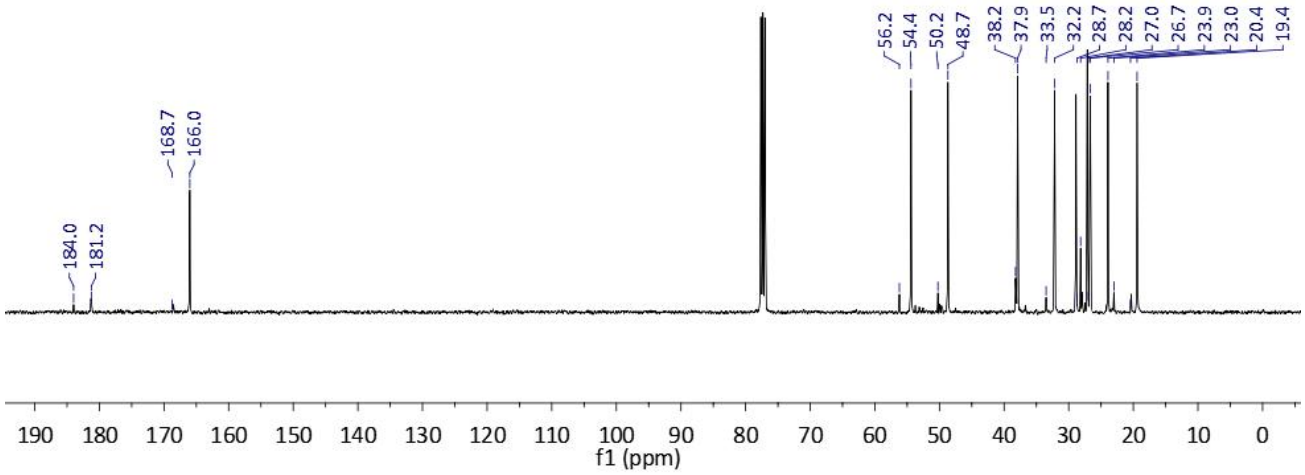


^{13}C-NMR of **13** in $CDCl_3$

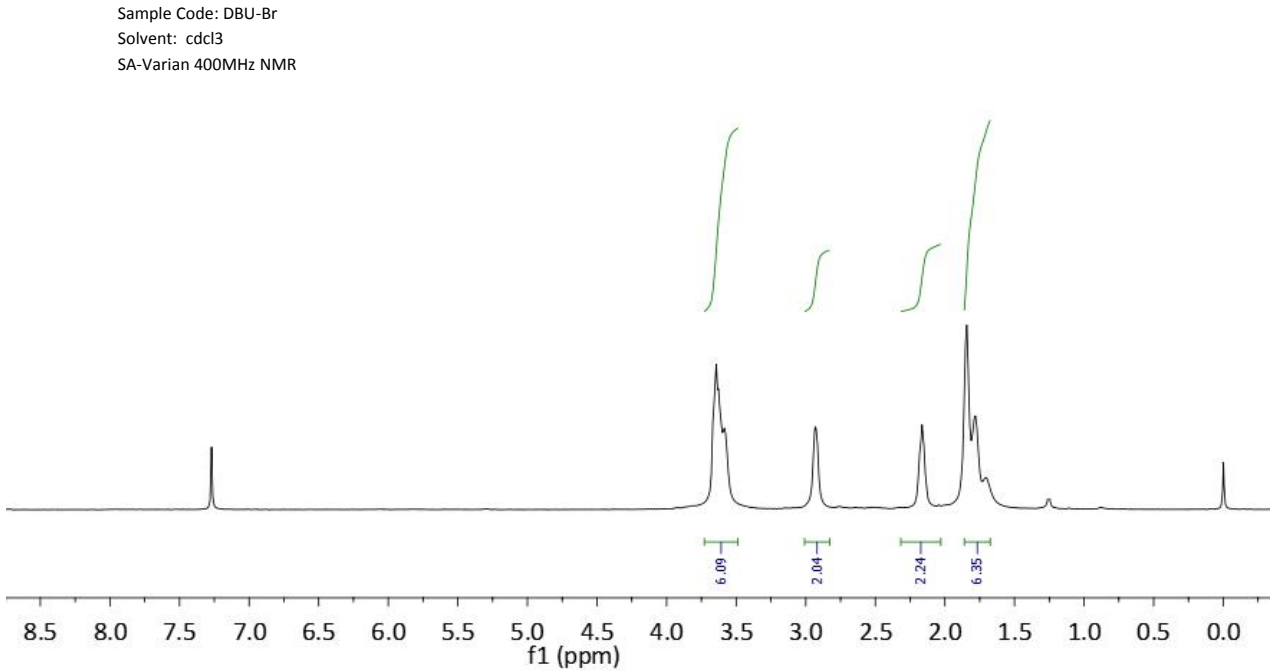


^{1}H-NMR of **14** in $CDCl_3$

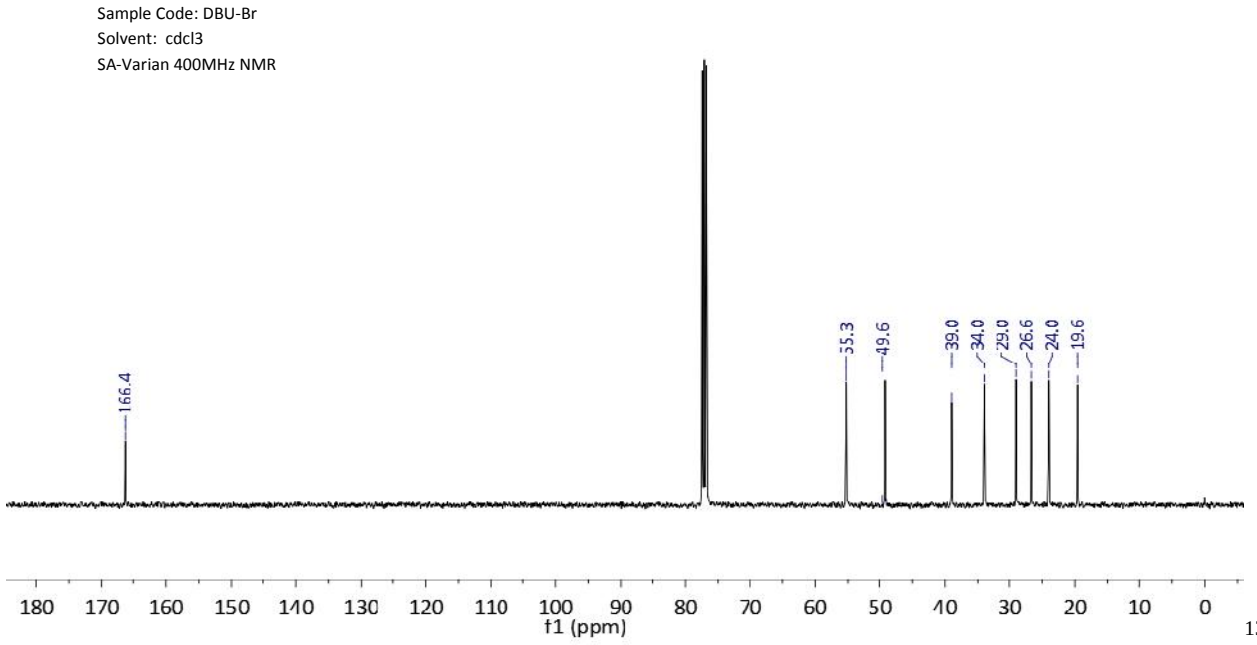
Sample Code: DBU-Piv
Solvent: cdcl3
SA-Varian 400MHz NMR



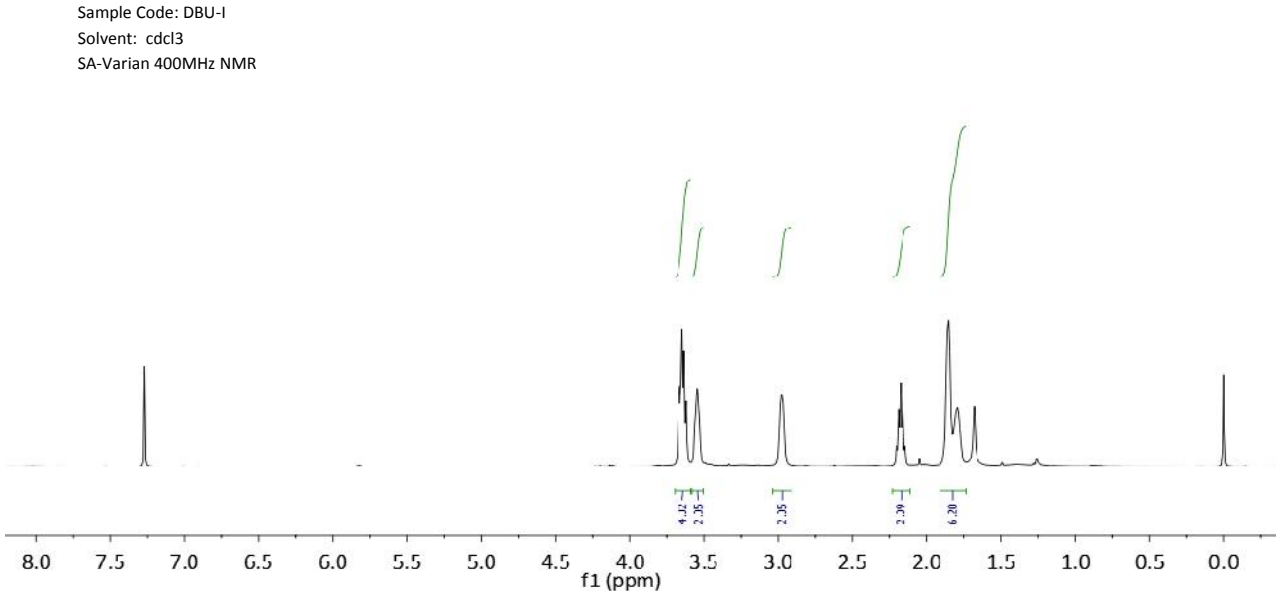
^{13}C-NMR of **14**in $CDCl_3$



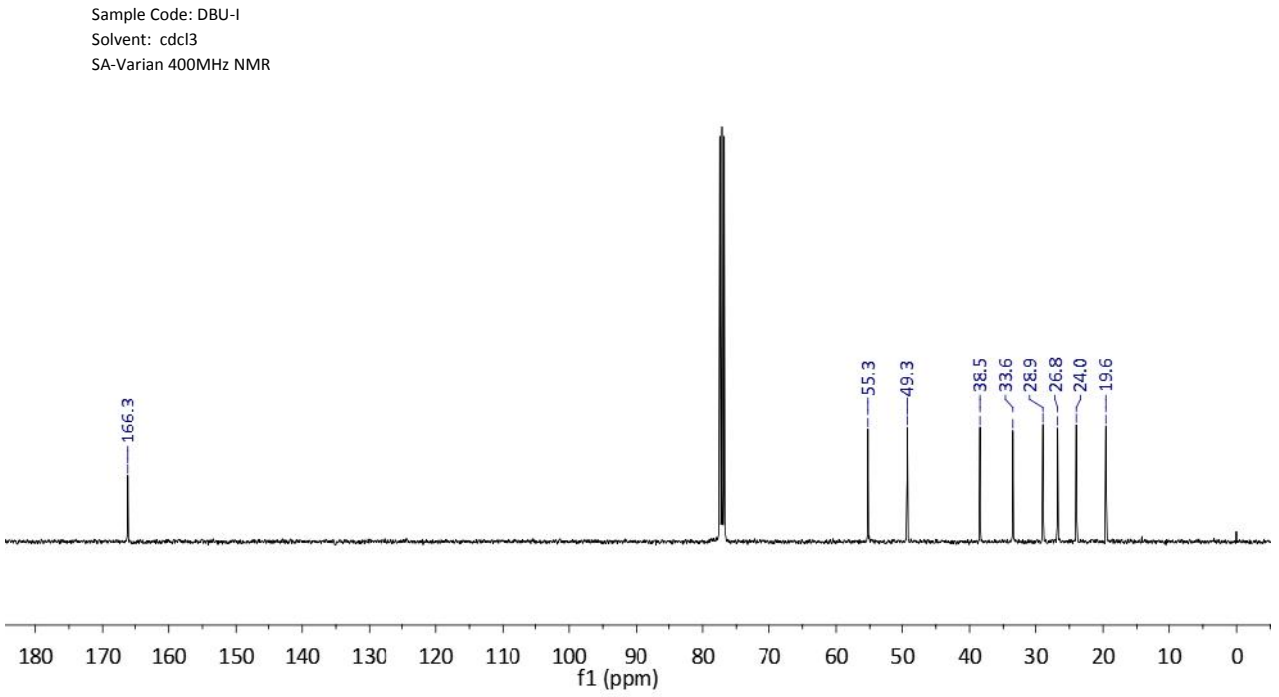
^{1}H-NMR of **15** in $CDCl_3$



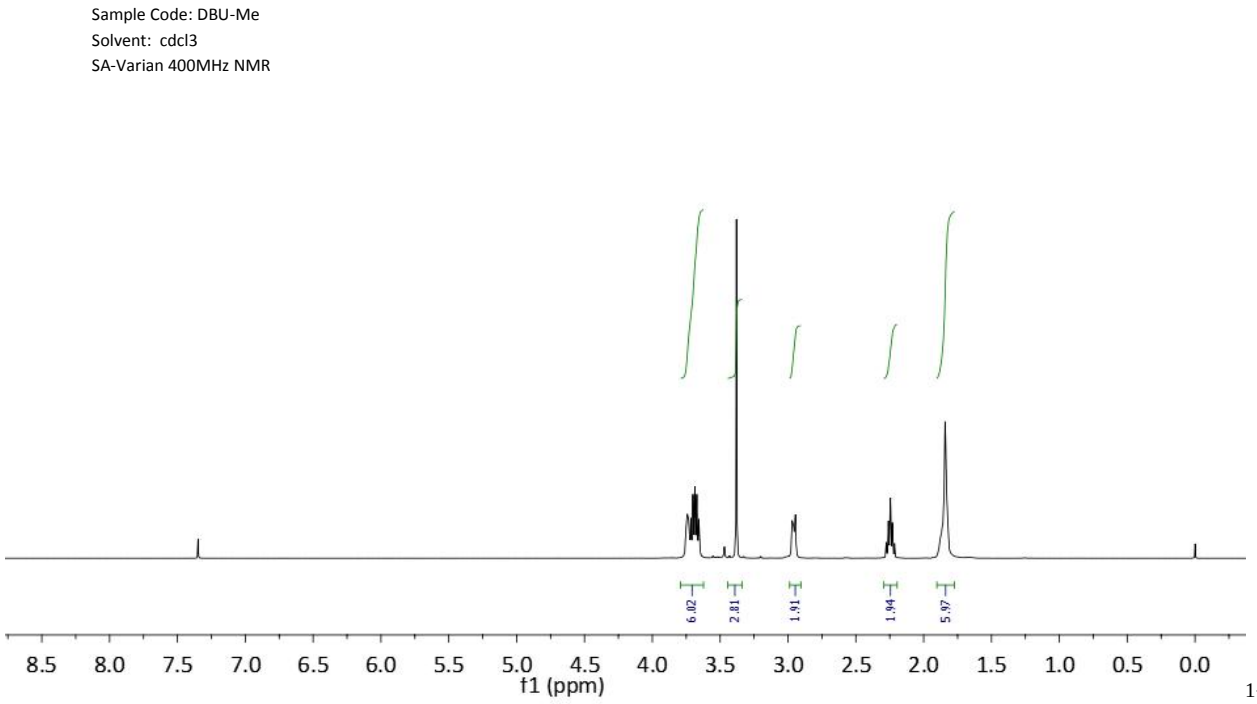
^{13}C-NMR of **15** in $CDCl_3$



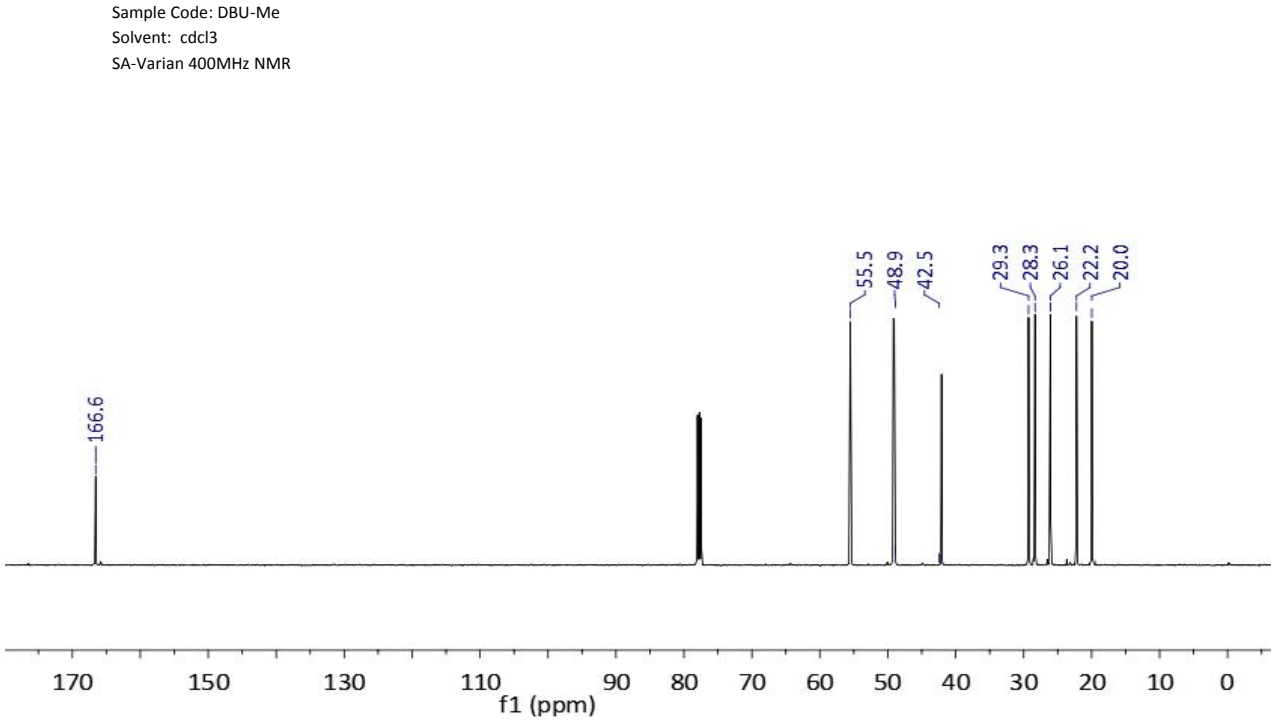
^{1}H-NMR of **16**in $CDCl_3$



^{13}C-NMR of **16** in $CDCl_3$

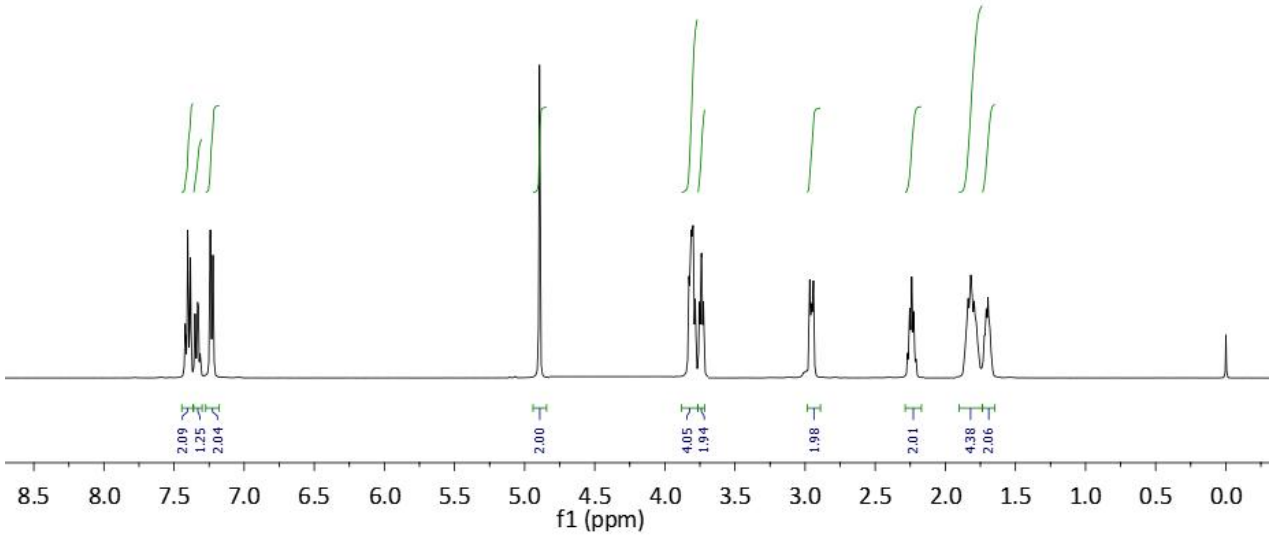


^{1}H-NMR of **17** in $CDCl_3$



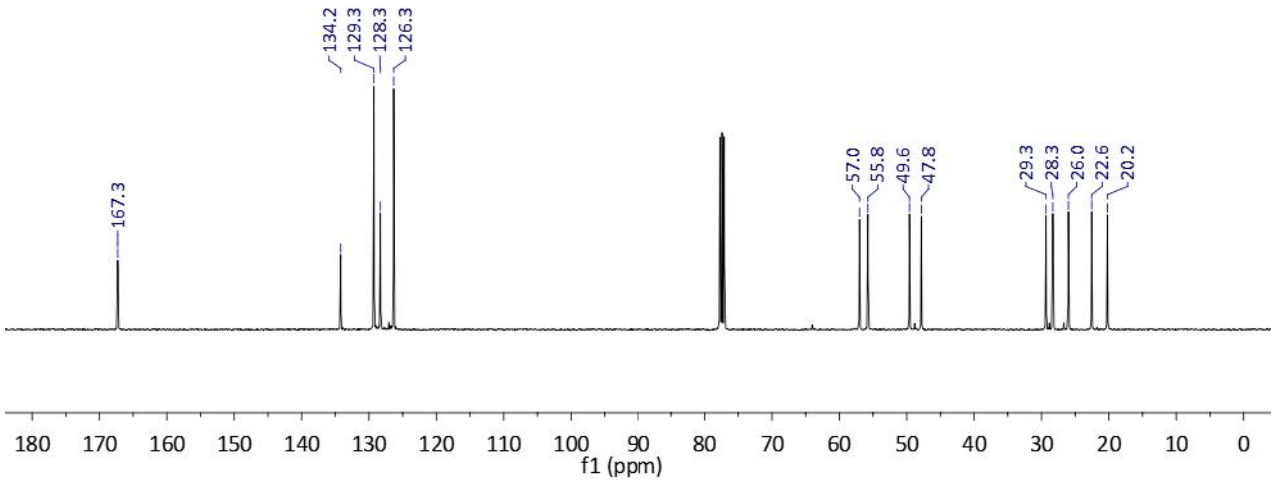
^{13}C-NMR of **17** in $CDCl_3$

Sample Code: DBU-Bn
Solvent: cdcl3
SA-Varian 400MHz NMR

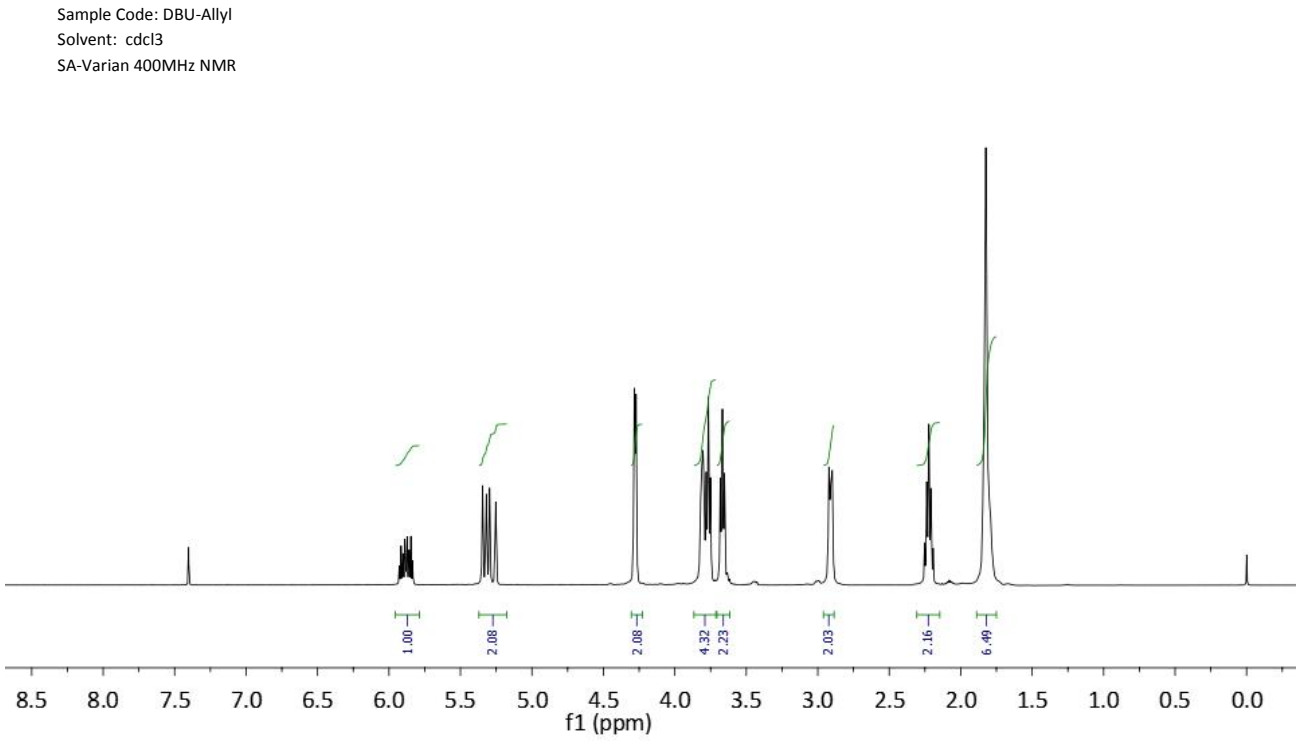


^{1}H-NMR of **18** in $CDCl_3$

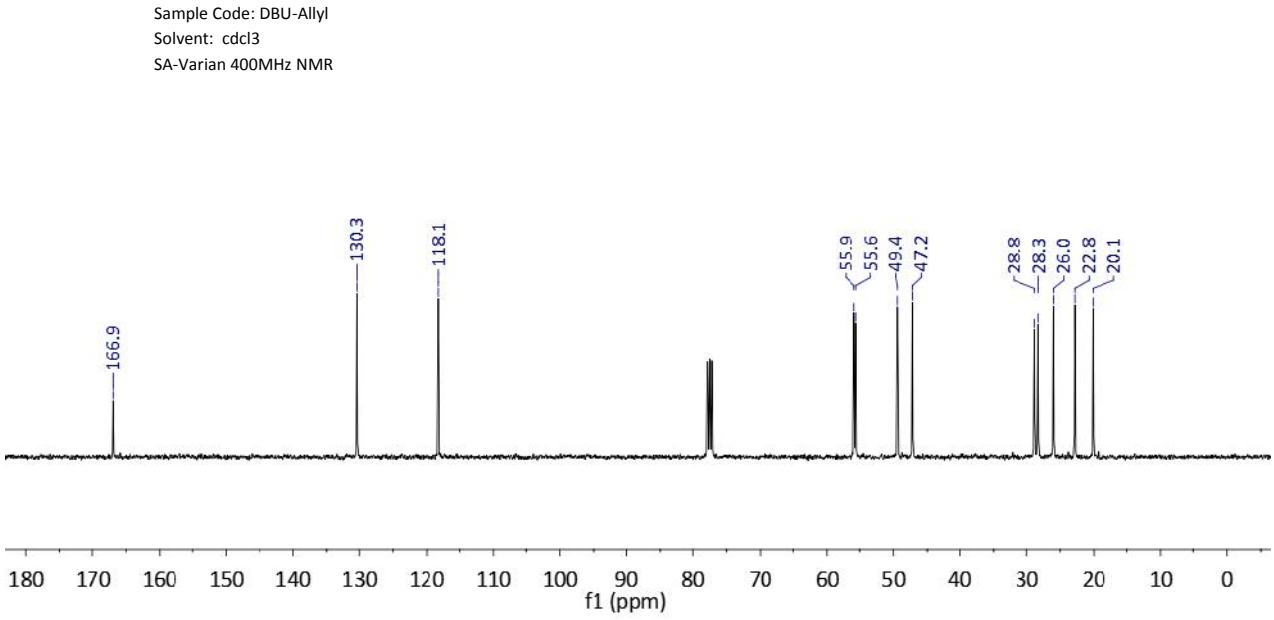
Sample Code: DBU-Bn
Solvent: cdcl3
SA-Varian 400MHz NMR



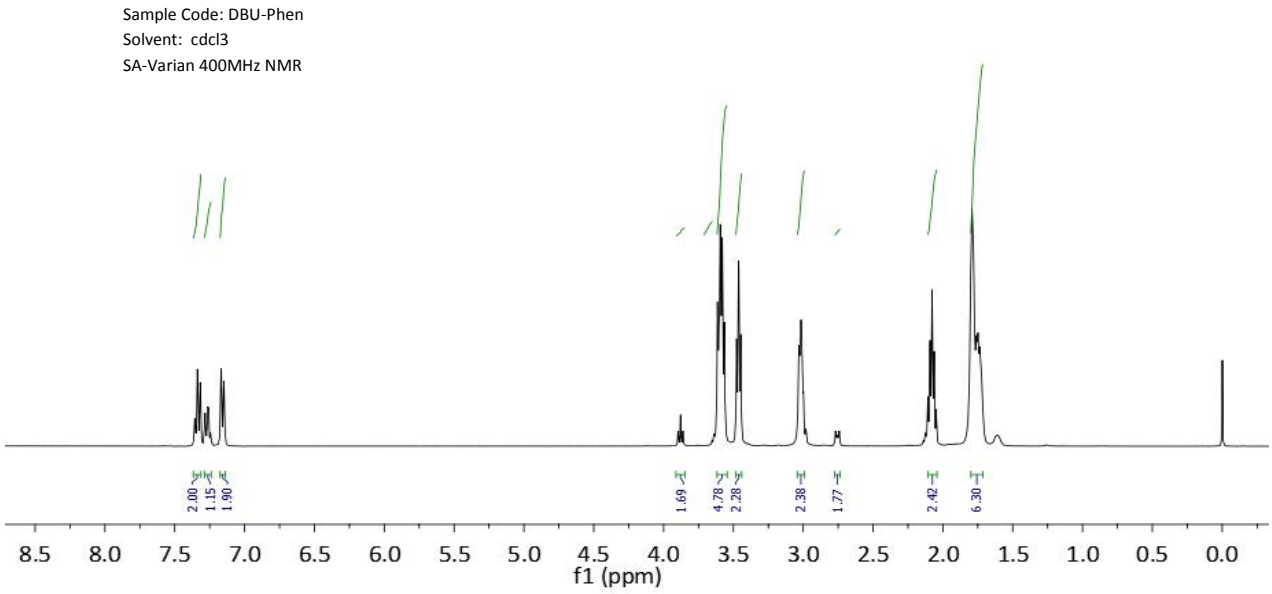
^{13}C-NMR of **18** in $CDCl_3$



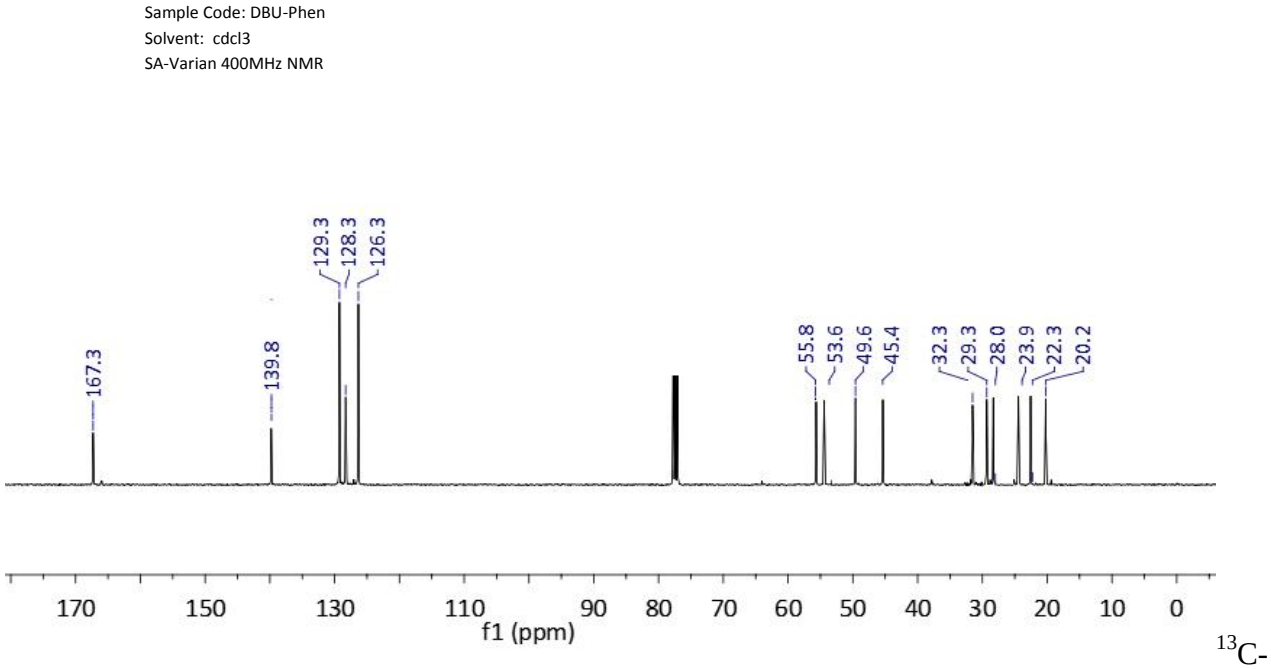
^{1}H-NMR of **19** in $CDCl_3$



^{13}C-NMR of **19** in $CDCl_3$

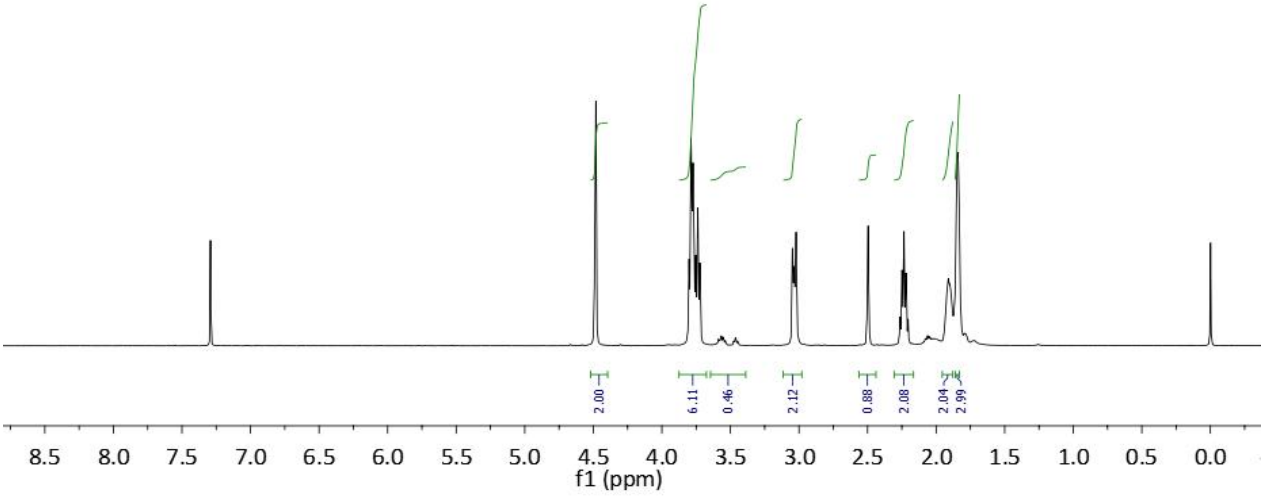


^{1}H-NMR of **20**in $CDCl_3$



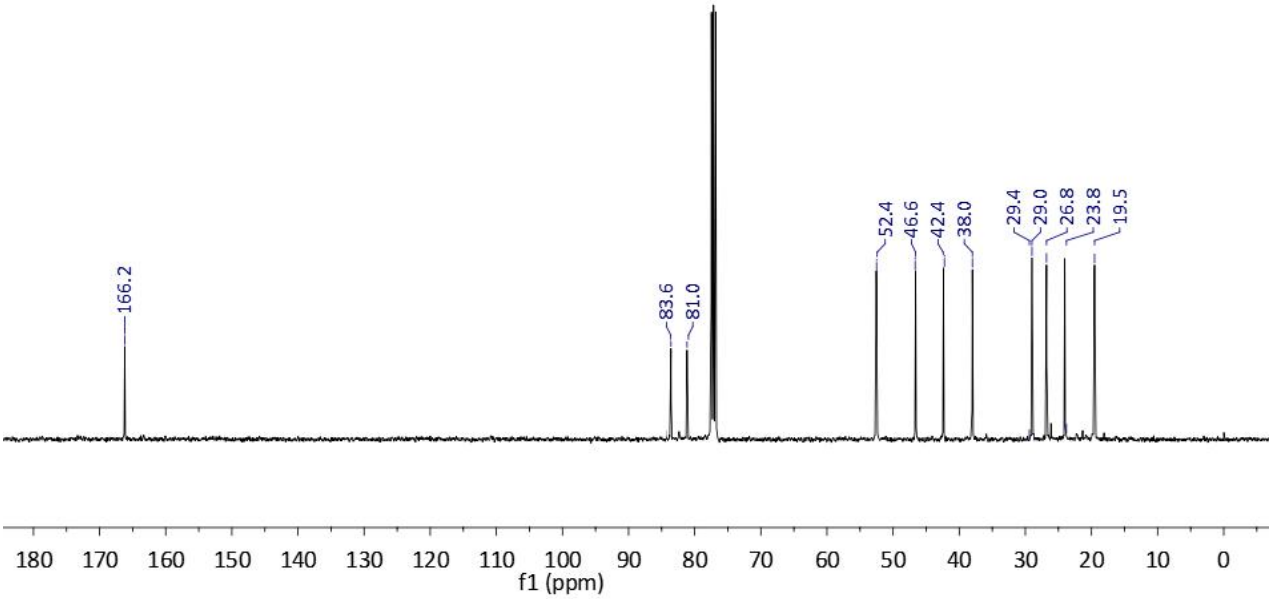
^{13}C-NMR of **20**in $CDCl_3$

Sample Code: DBU-Pro
Solvent: cdcl3
SA-Varian 400MHz NMR



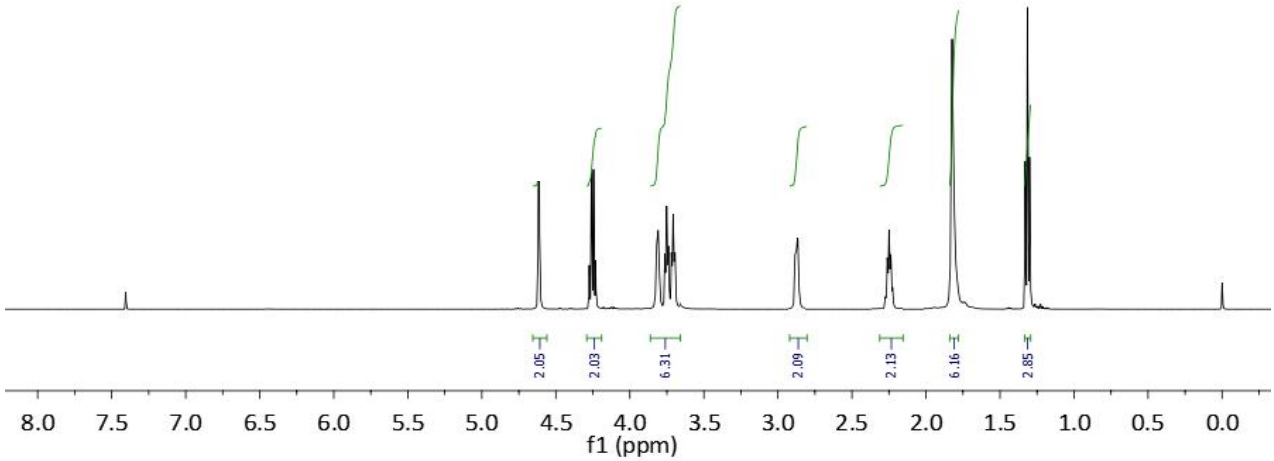
^{1}H-NMR of **21** in $CDCl_3$

Sample Code: DBU-Pro
Solvent: cdcl3
SA-Varian 400MHz NMR



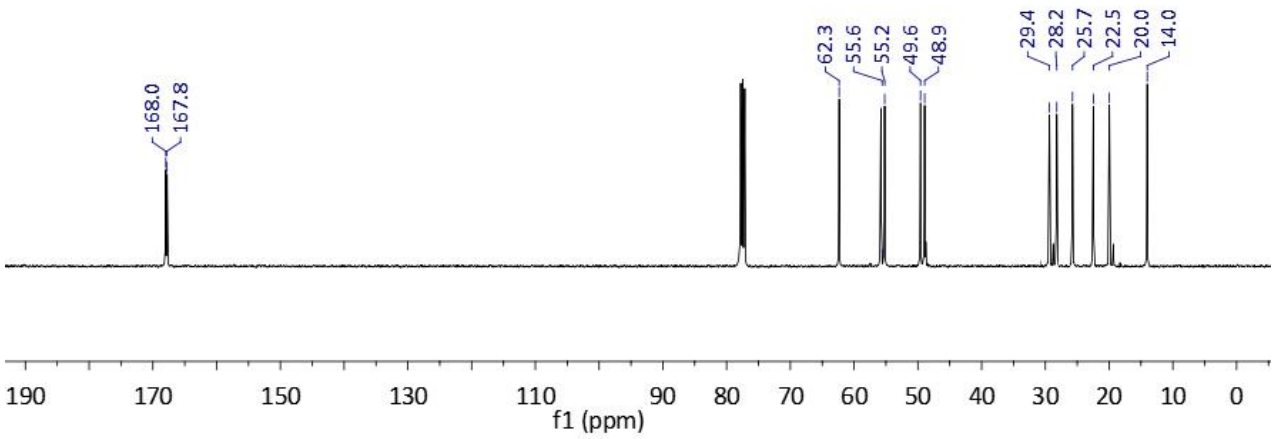
^{13}C-NMR of **21** in $CDCl_3$

Sample Code: DBU-EBr
Solvent: cdcl3
SA-Varian 400MHz NMR



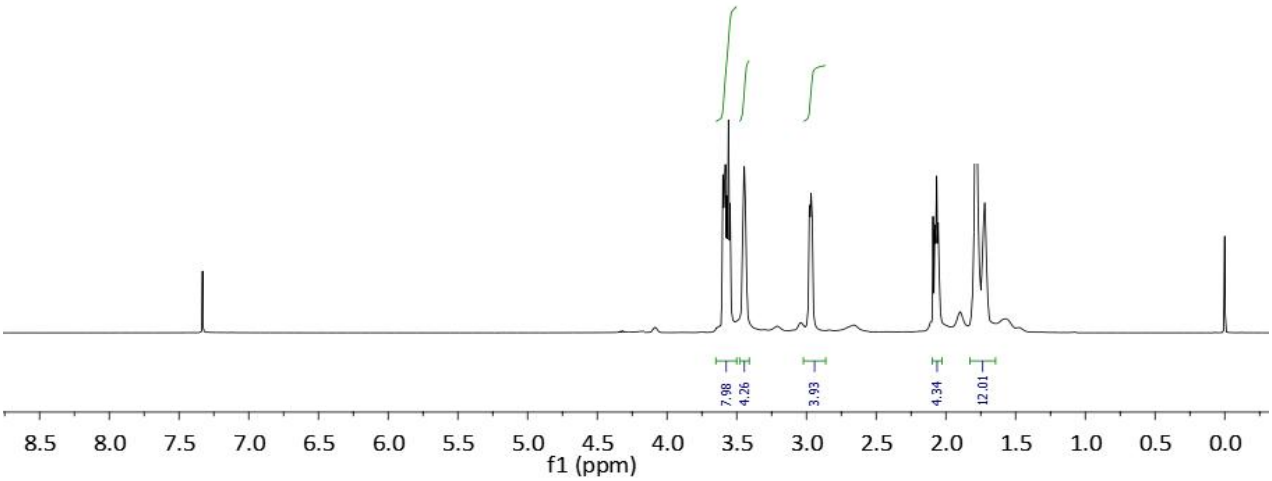
^{1}H-NMR of **22** in $CDCl_3$

Sample Code: DBU-EBr
Solvent: cdcl3
SA-Varian 400MHz NMR



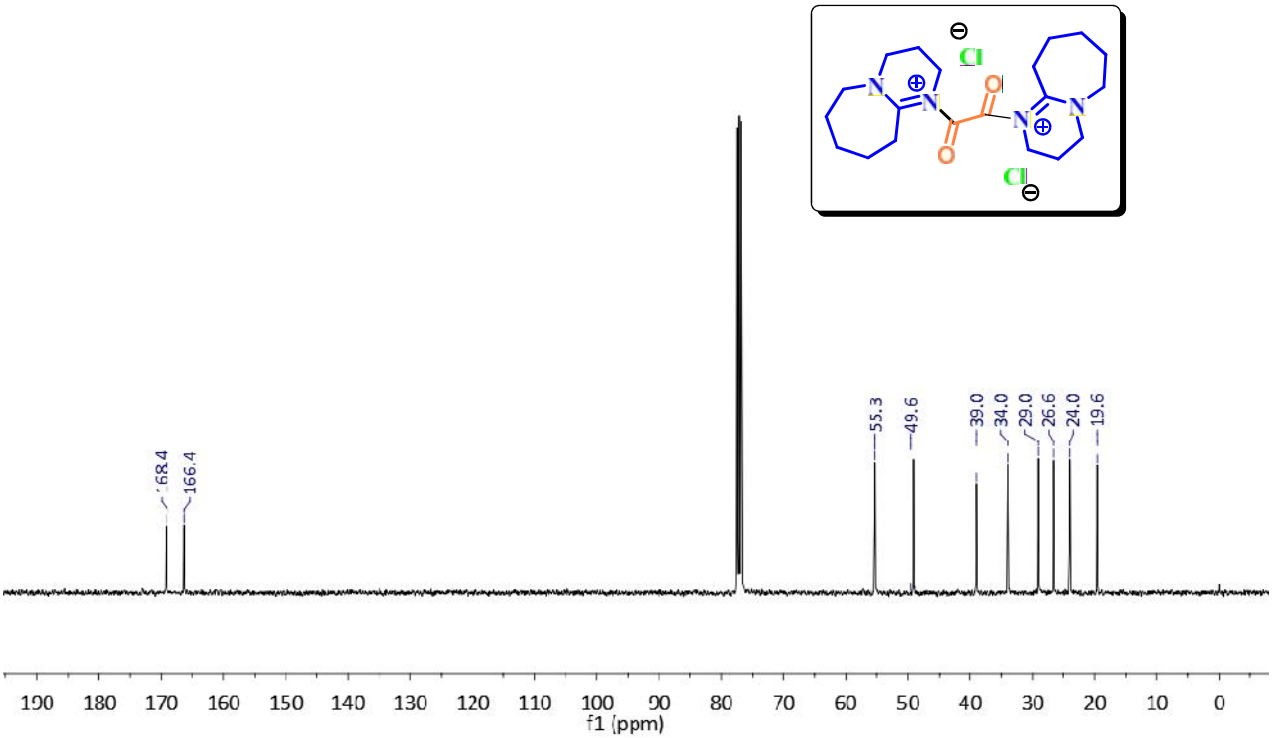
^{13}C-NMR of **22** in $CDCl_3$

Sample Code: DBU-OX
Solvent: cdcl3
SA-Varian 400MHz NMR



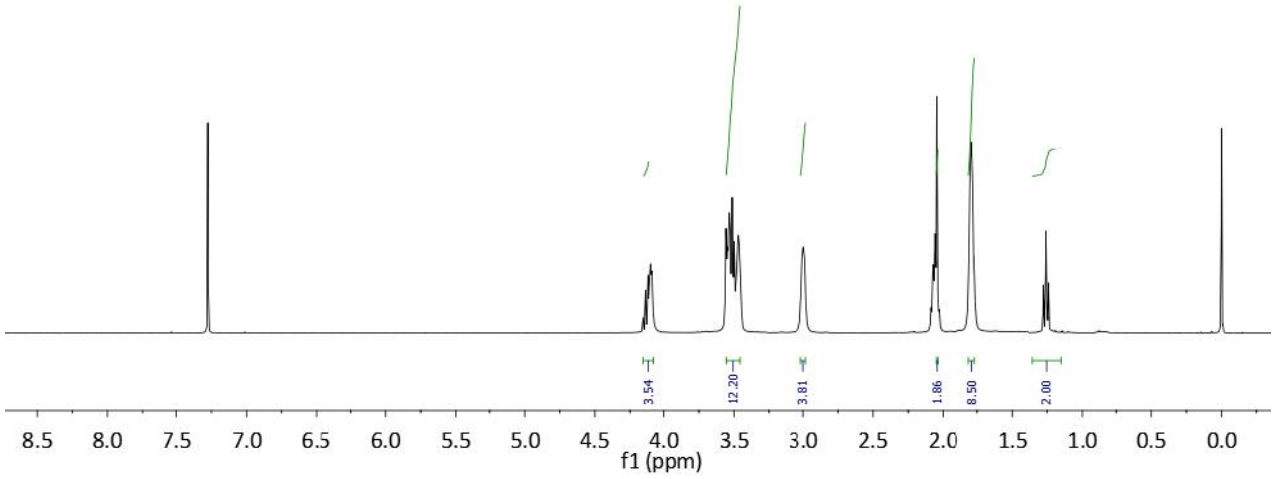
^{1}H-NMR of **23** in $CDCl_3$

Sample Code: DBU-OX
Solvent: cdcl3
SA-Varian 400MHz NMR



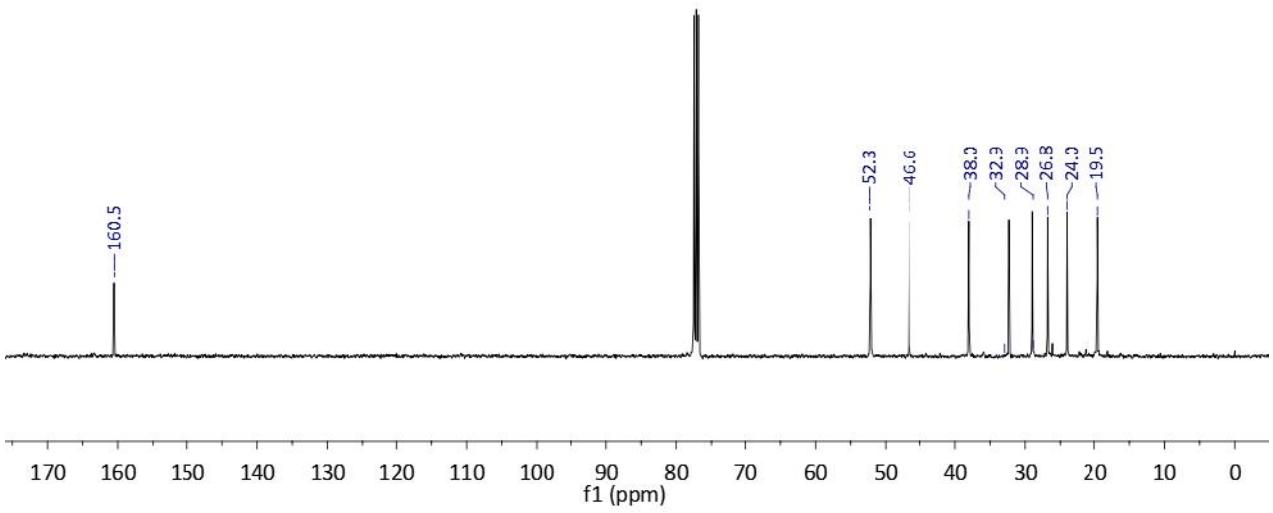
^{13}C-NMR of **23** in $CDCl_3$

Sample Code: DBU-Thio
Solvent: cdcl3
SA-Varian 400MHz NMR



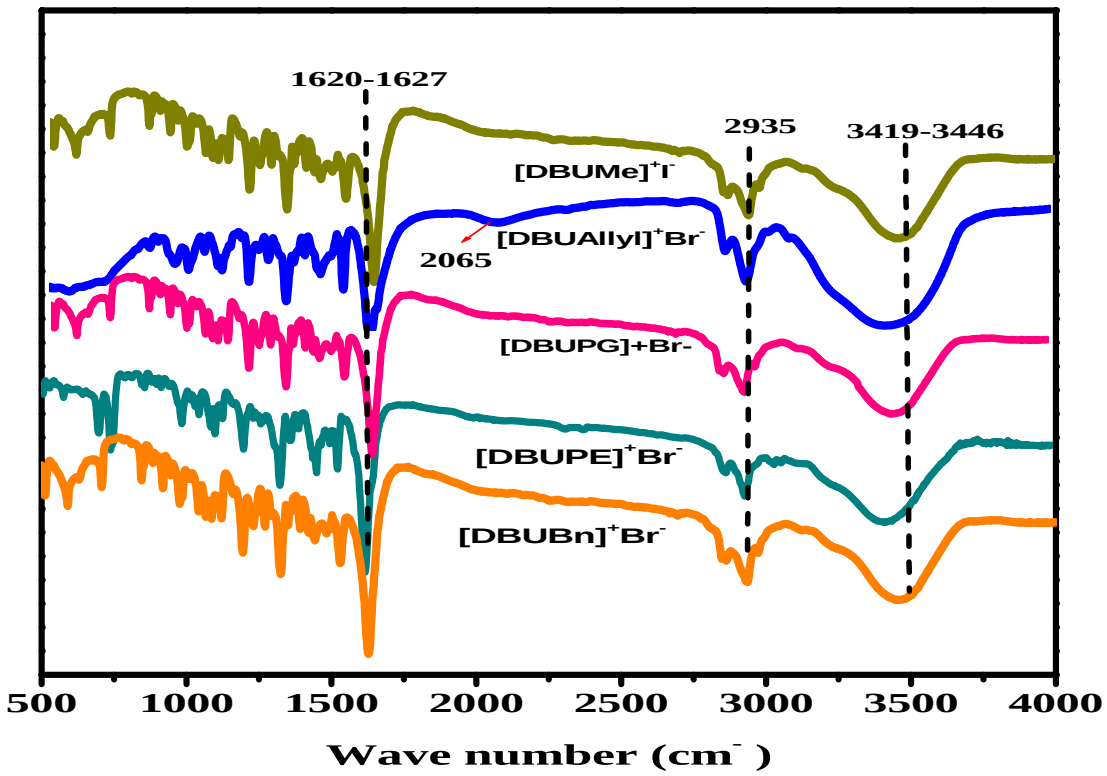
^{1}H-NMR of **24** in $CDCl_3$

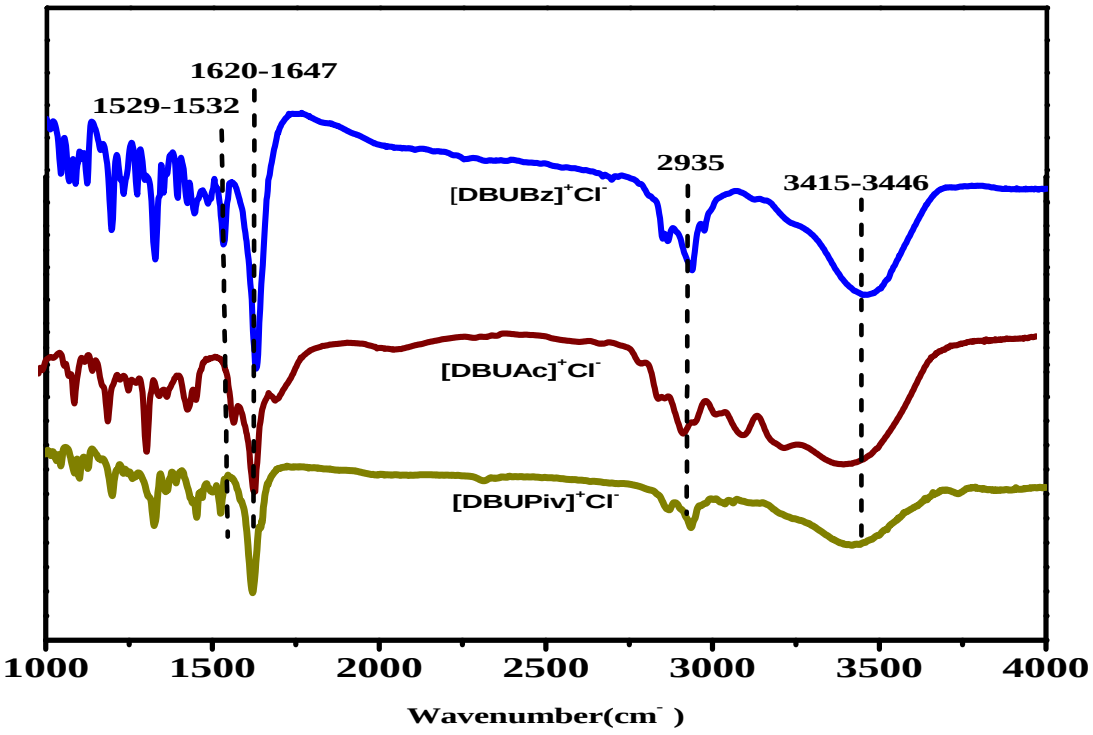
Sample Code: DBU-Thio
Solvent: cdcl3
SA-Varian 400MHz NMR

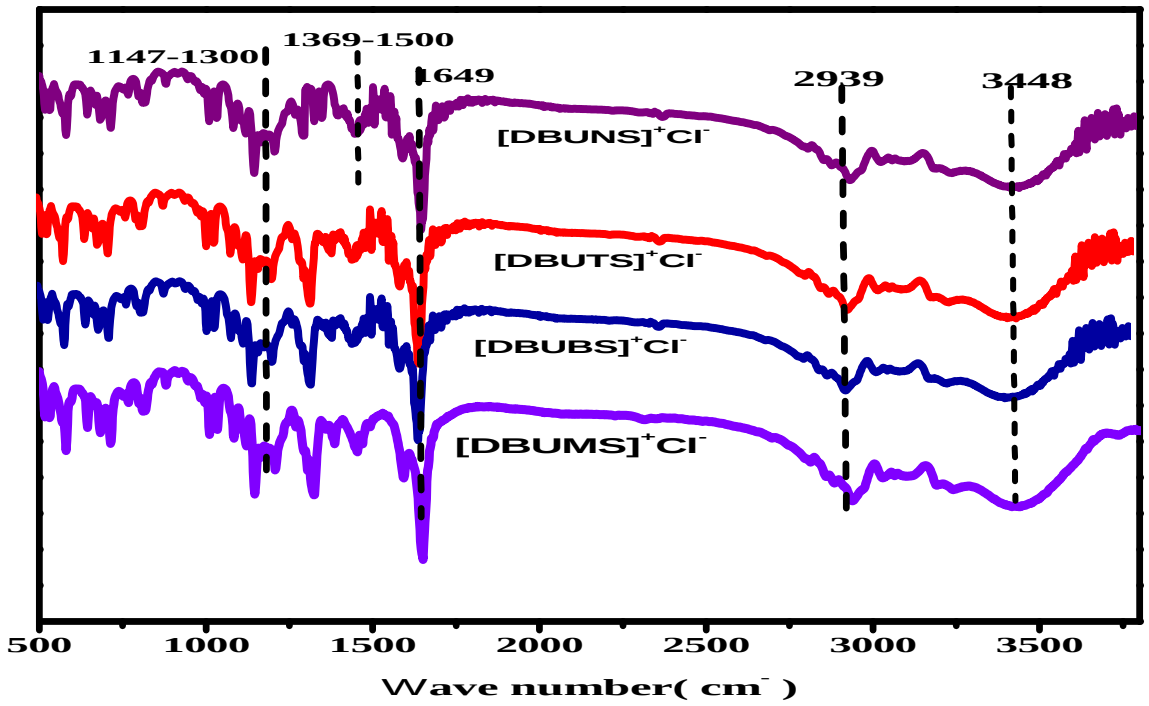


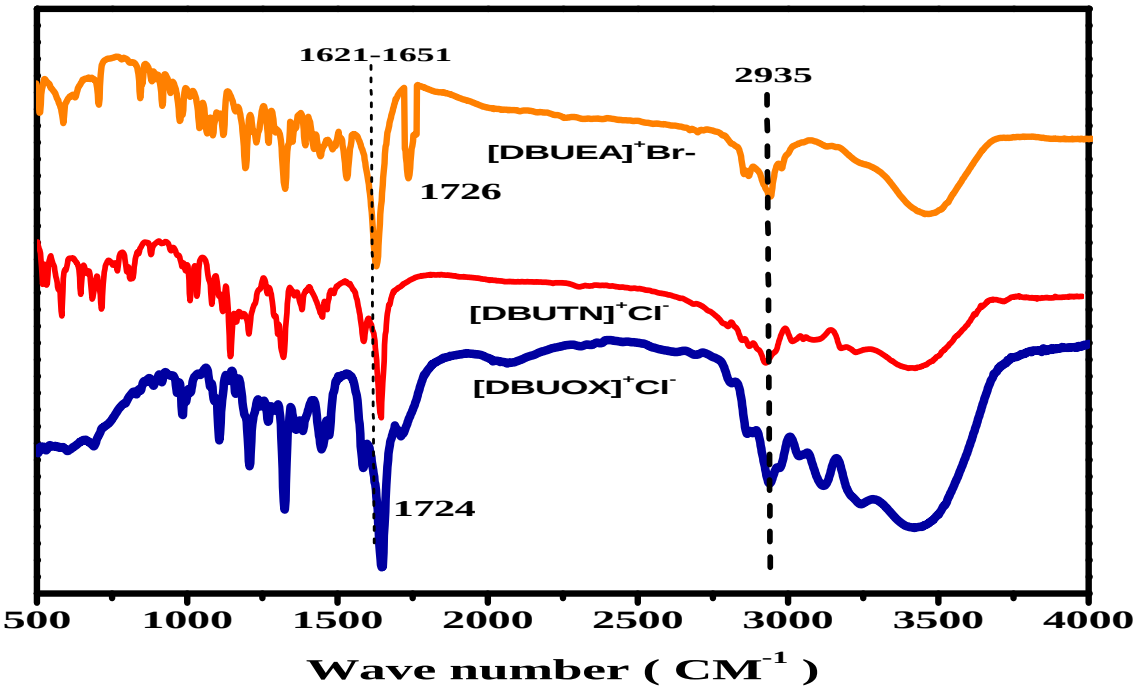
^{13}C-NMR of **24** in $CDCl_3$

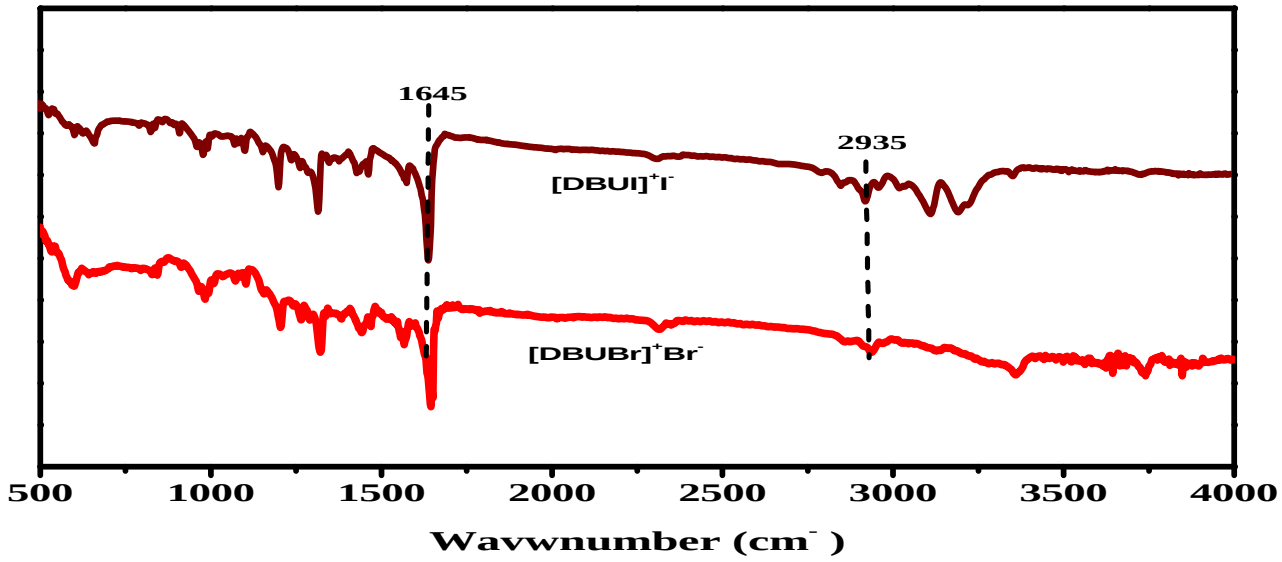
IR spectra of different LBAs of DBU






1147-1300
1369-1500
1649
2939
3448
[DBUNS]+Cl-
[DBUTS]+Cl-
[DBUBS]+Cl-
[DBUMS]+Cl-
500
1000
1500
2000
2500
3000
3500
Wave number(cm-)


1621-1651
2935
[DBUEA]+Br-
1726
[DBUTN]+Cl-
[DBUOX]+Cl-
1724
500
1000
1500
2000
2500
3000
3500
4000
Wave number (CM-1)


1645
2935
[DBUI]+I-
[DBUBr]+Br-
500
1000
1500
2000
2500
3000
3500
4000
Wavwnumber (cm-)

Computational Details : In order to understand the molecular structure and identify the most reactive site in the selected compound density functional theory (DFT) [1] calculations are carried out on the compounds A to G of the main moiety (i.e., 1,8-Diazabicyclo[5.4.0]undec-7-ene or DBU molecule) using the Gaussian-09 program package [2]. The calculations are carried out in the gas phase. The geometry of the target compounds was optimized at the Becke-3, Lee, Yang, Par (B3LYP) functionals with 6-311++g(d,p) basis set [3]. The optimized geometries identified as global minimum as the potential energy surfaces, were verified by the absence of any imaginary frequencies. The optimized geometries of the considered molecules XYZ coordinates and their structures are given in the supplementary information (SI) file. The main moiety (i.e., DBU) of the selected compounds is shown in Fig. 1.

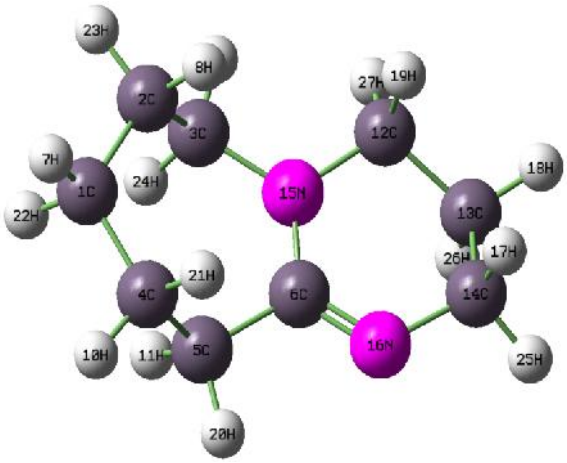


Figure 1. Optimized molecular geometry of DBU.

As discussed in the reaction scheme___, when reactants react with DBU produce a mixture of two compounds. This is because DBU contains two nitrogen atoms both of which might act as electrophilic sites. Among these two compounds, one of the compound is more stable and this can be confirmed with the molecular electrostatic potential (MEP). Because the MEP of a molecule is still a good guide to assessing the reactivity of the molecule towards positively or negatively charged reactants. That is, the MEP surface will illustrate the charge distributions of molecules three dimensionally. These surface analyses allow us to visualize variably charged regions of a molecule. MEP surface also can be intrepret as a map of an area of electron excess and electron deficiency [4,5].

Fig. 2 shows the molecular electrostatic potential surface of DBU moiety. This figure clearly indicates the high electron density at N16 (red in color) and hence the respective N16 site is more favorable for the electrophilic attack. On the other hand, N15 does not favorable for the electrophilic attack. However, these two nitrogen atom sites make a mixture of two compounds. This is a clear agreement with the experiment, but N16 sites will give a more stable compound than the N15 site. Because the N15 site is more steric hindrance, so the attacking electrophile mostly chooses the N16 site.
To further confirmation, we have optimized the two N (15 and 16) site compounds (A to G) with the same level of theory and observed that the N16 site compounds are more stable than the N15 site compounds. We note here that, in case of compound G (-CH_3 substitution) we could only optimize the N16 site compound. Because -CH_3 substitution at N15 site is not feasible (due to strong steric hindrance between -CH_3 group and -CH_2 groups (which are connected to N15). This is conformed by

experiment, that is, during the reaction we found only N16 site compound. The optimized XYZ coordinates are given in SI.

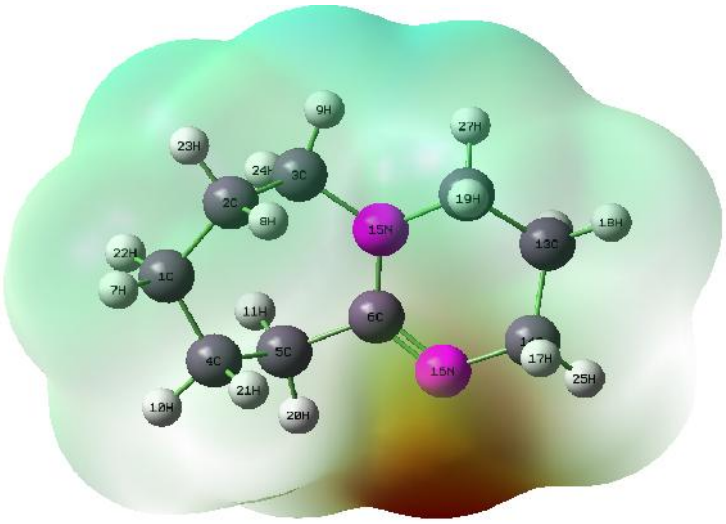
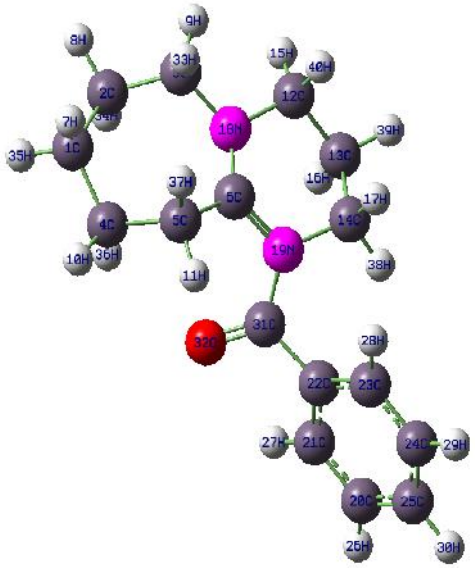
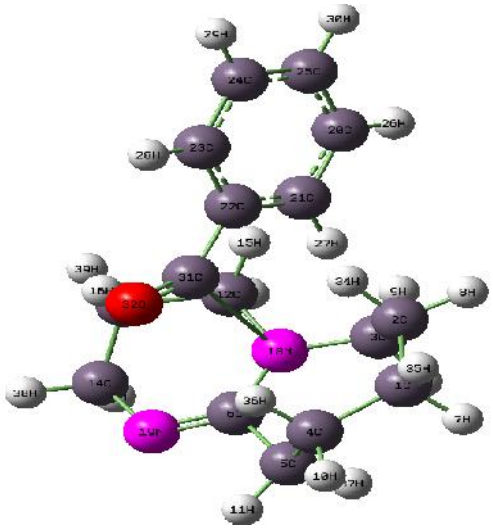
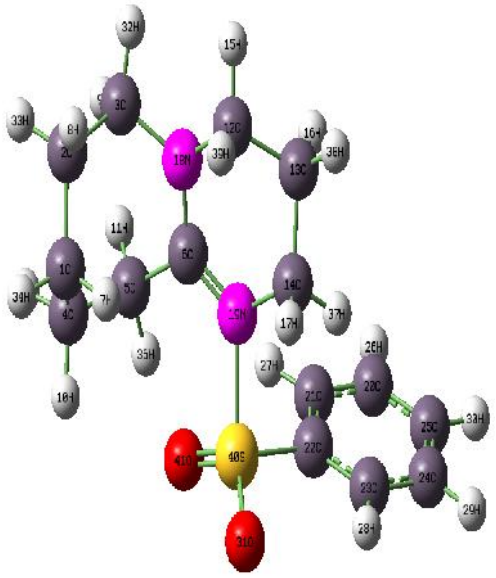


Figure 2. Calculated molecular electrostatic potential surfaces of DFT optimized geometry of the DBU dark red color denotes negative charge density. Where electrophilic attack is more favourable.

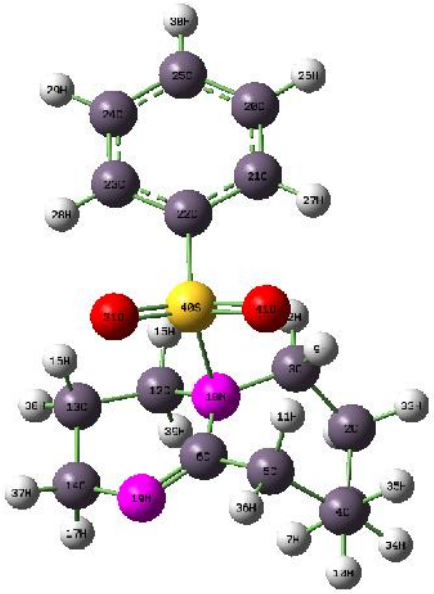




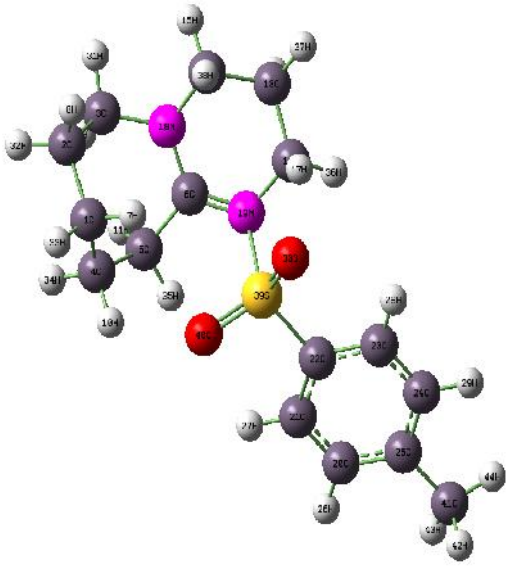
(A1) E=-807.2535 a.u **(A2) E= -807.2349 a.u**



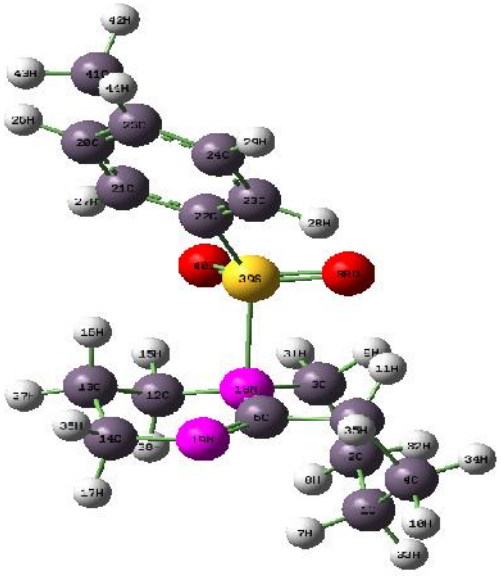
(B1) E= -1242.5497 a.u



(B2) E= -1242.5453 a.u



(C1) E=-1281.8781 a.u



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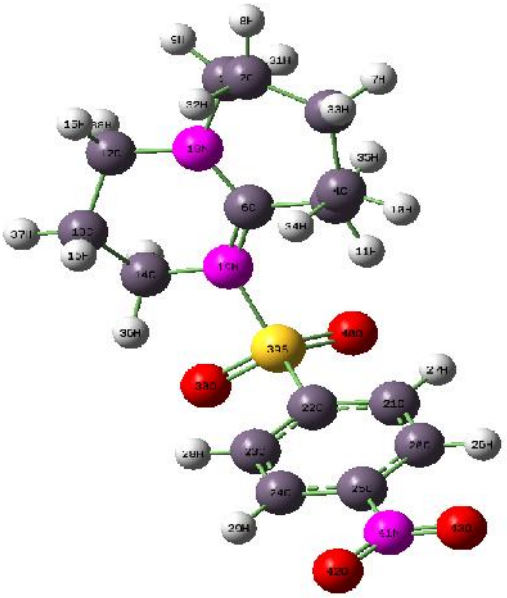

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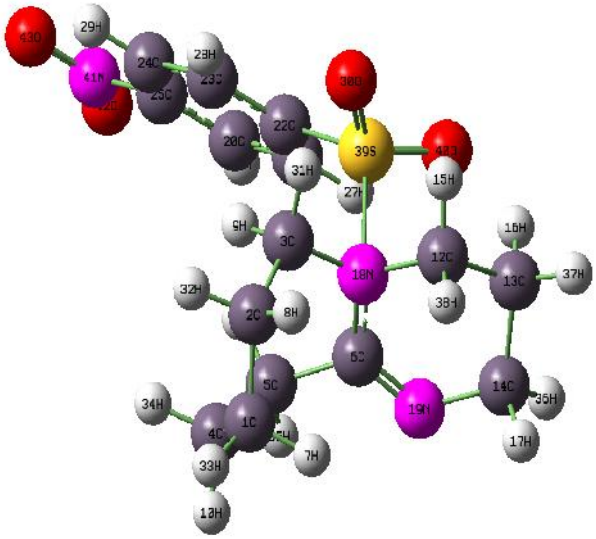

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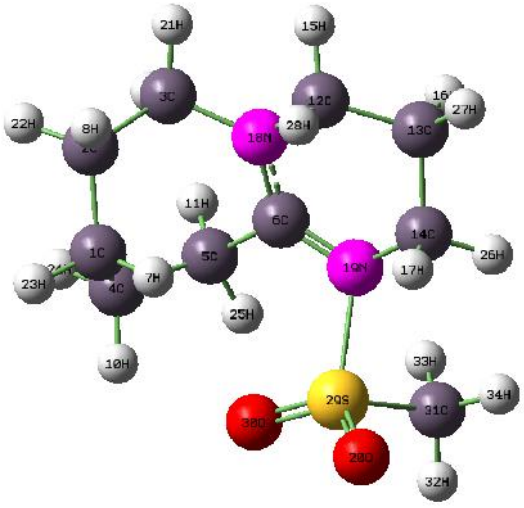
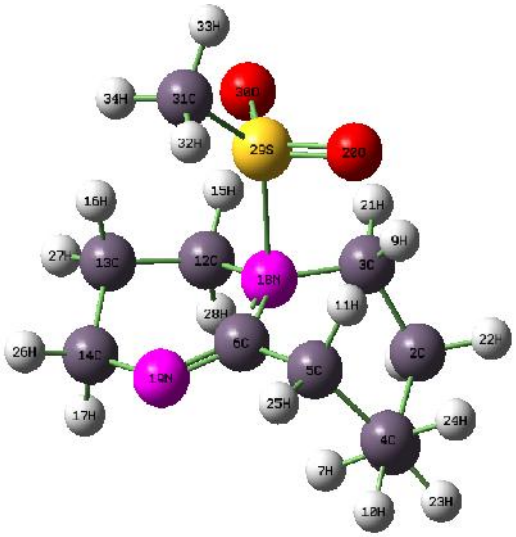
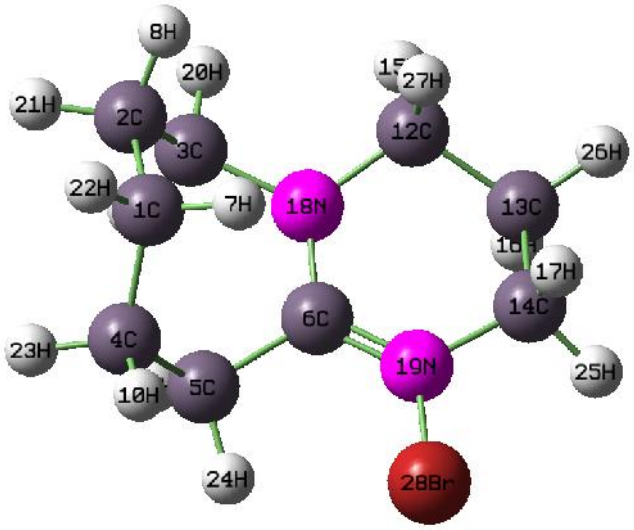


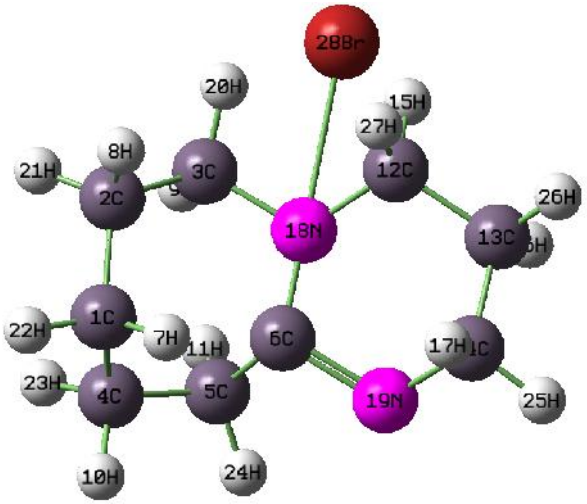
(E1) E = -1050.7724 a.u



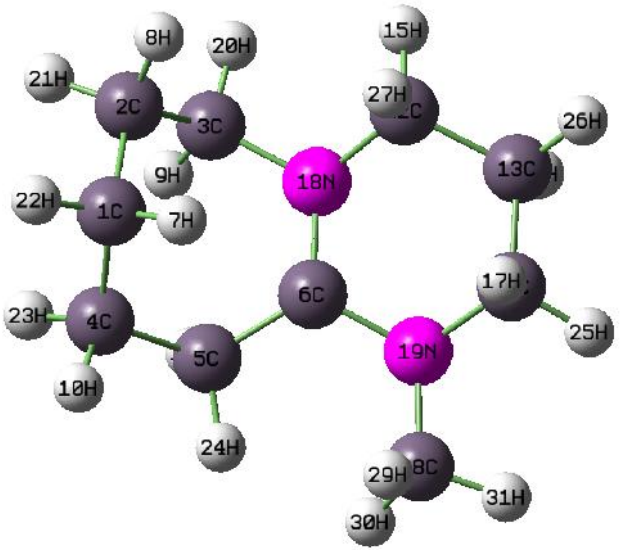
(E2) E= -1050.7685 a.u



(F1) E = -3036.3466 a.u



(F2) E= -3036.3361 a.u



(G1) E = -502.0778 a.u

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5. Dipendra Sharma, S.N. Tiwari, *J. Mol. Liq.***214** (2016) 128-135.

Supplementary Information (SI) file :

C9H16N2 (DBU) :

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.829436	-0.037996	0.294419
2	6	1.963258	-1.288615	0.489773
3	6	0.851880	-1.448659	-0.562488
4	6	2.069489	1.293816	0.334694
5	6	0.930905	1.423627	-0.698739
6	6	-0.352537	0.726027	-0.291671
7	1	3.617329	-0.024400	1.055395
8	1	1.509807	-1.289209	1.488049
9	1	0.533132	-2.492643	-0.590632
10	1	2.785719	2.103432	0.159865
11	1	1.274190	1.066326	-1.677305
12	6	-1.541777	-1.379592	0.148693
13	6	-2.793549	-0.540755	-0.084083
14	6	-2.577723	0.855172	0.501109
15	7	-0.358127	-0.660164	-0.325840
16	7	-1.332713	1.478150	0.067740
17	1	-2.586934	0.806356	1.599326
18	1	-3.662122	-1.030714	0.366164
19	1	-1.446095	-1.625727	1.217266
20	1	0.659789	2.472508	-0.812163
21	1	1.655313	1.462999	1.335425
22	1	3.342346	-0.121119	-0.673309
23	1	2.610255	-2.172195	0.439532
24	1	1.257651	-1.228058	-1.557686
25	1	-3.403184	1.517268	0.221728
26	1	-2.979365	-0.461878	-1.160278
27	1	-1.608245	-2.326992	-0.394922

(A1) C16H21N2O

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.089739	-1.630965	0.025124
2	6	-4.510749	-0.151798	-0.095056
3	6	-3.582979	0.893078	0.561170
4	6	-2.756698	-2.021334	-0.637974
5	6	-1.525545	-1.485644	0.109930
6	6	-1.284565	0.027595	-0.001956
7	1	-4.027698	-1.889502	1.061565
8	1	-5.460643	-0.076302	0.391670
9	1	-4.107101	1.825150	0.523250
10	1	-2.697296	-3.089069	-0.601727
11	1	-0.663916	-1.958484	-0.313056
12	6	-1.810047	2.388484	0.357240
13	6	-0.479789	2.689852	-0.312846
14	6	0.516341	1.673646	0.214141
15	1	-2.520887	3.151586	0.117904
16	1	-0.590474	2.612614	-1.374299
17	1	0.659845	1.842371	1.260964
18	7	-2.314198	1.099768	-0.156168
19	7	-0.003909	0.315817	0.036453
20	6	4.471235	0.419290	-1.066781
21	6	3.095663	0.155206	-1.111324
22	6	2.472169	-0.496400	-0.038669
23	6	3.224246	-0.883922	1.078527
24	6	4.599818	-0.619837	1.123070
25	6	5.223312	0.031770	0.050417
26	1	4.947287	0.916804	-1.885776
27	1	2.521436	0.451085	-1.964329
28	1	2.748195	-1.381440	1.897521
29	1	5.174046	-0.915721	1.976074
30	1	6.273591	0.233405	0.084427
31	6	0.960551	-0.786600	-0.087617
32	8	0.550974	-1.967464	-0.233824
33	1	-3.386650	0.622542	1.577618
34	1	-4.599845	0.097618	-1.131759
35	1	-4.858895	-2.197937	-0.456374
36	1	-2.741483	-1.687682	-1.654510
37	1	-1.624902	-1.748902	1.142269
38	1	1.449352	1.783640	-0.298003
39	1	-0.139795	3.674201	-0.067161
40	1	-1.674564	2.350126	1.417935

Energy = -807.2535 a.u.

(A2) C16H21N2O

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.951314	-2.088940	0.569169
2	6	1.526989	-2.007721	1.150087
3	6	1.021352	-0.614543	1.588655
4	6	3.196502	-1.325516	-0.739462
5	6	3.222421	0.197203	-0.557973
6	6	1.866258	0.860524	-0.271269
7	1	3.644258	-1.724454	1.298469
8	1	1.533764	-2.623784	2.024914
9	1	0.103926	-0.786208	2.111876
10	1	4.168356	-1.610719	-1.084512
11	1	3.573958	0.619221	-1.476244
12	6	-0.080428	1.401133	1.098960
13	6	-0.466972	2.399012	0.020677
14	6	0.814142	3.073481	-0.435973
15	1	-0.960351	0.985274	1.543592
16	1	-0.942310	1.881175	-0.786044
17	1	1.209578	3.656736	0.369225
18	7	0.695438	0.304033	0.479943
19	7	1.804913	2.060454	-0.797818
20	6	-3.875358	-1.161676	-1.037368
21	6	-2.485996	-1.123710	-1.216679
22	6	-1.678431	-0.447254	-0.292467
23	6	-2.260228	0.191237	0.811056
24	6	-3.649591	0.153269	0.990368
25	6	-4.457156	-0.523186	0.066156
26	1	-4.491952	-1.678163	-1.743026
27	1	-2.041780	-1.611210	-2.059245
28	1	-1.643635	0.707728	1.516711
29	1	-4.093806	0.640771	1.832933
30	1	-5.517965	-0.552173	0.203063
31	6	-0.151659	-0.405535	-0.489511
32	8	0.370772	-0.978873	-1.480430
33	1	1.737596	-0.155733	2.237800
34	1	0.838543	-2.390883	0.426120
35	1	3.131405	-3.124194	0.367386
36	1	2.456674	-1.594880	-1.464029
37	1	3.898260	0.425896	0.239423
38	1	0.607409	3.710173	-1.270709
39	1	-1.136399	3.140727	0.403595
40	1	0.496878	1.897599	1.850718

Energy = -807.2349 a.u.

(B1) C15H21N2O2S					(B2) C15H21N2O2S				
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.402529	-0.982669	-0.679165	1	6	-3.557638	-1.016365	0.345600
2	6	4.304261	-0.011545	0.095762	2	6	-3.121128	-1.228449	-1.112420
3	6	3.501335	0.759493	1.172817	3	6	-1.594665	-1.016113	-1.286131
4	6	2.587737	-1.936640	0.214504	4	6	-2.762565	-1.839037	1.374732
5	6	1.781225	-1.079147	1.192043	5	6	-1.281927	-1.512801	1.182434
6	6	1.342070	0.156850	0.410977	6	6	-1.208172	-0.024491	0.845031
7	1	2.699036	-0.392449	-1.228382	7	1	-3.392831	0.015071	0.577716
8	1	4.711431	0.678252	-0.613669	8	1	-3.652215	-0.513309	-1.705229
9	1	3.254393	0.087583	1.968089	9	1	-1.073947	-1.844871	-0.853797
10	1	1.928997	-2.479448	-0.430725	10	1	-3.087728	-1.522069	2.343598
11	1	2.394397	-0.742402	2.001686	11	1	-0.879472	-2.047390	0.347483
12	6	2.353552	2.157430	-0.517848	12	6	-1.804699	1.416458	-1.010052
13	6	0.927121	2.543911	-0.929111	13	6	-1.241898	2.557758	-0.157831
14	6	0.200974	1.266743	-1.397109	14	6	-1.633374	2.297476	1.312677
15	1	2.926132	3.027037	-0.271202	15	1	-1.633098	1.597459	-2.050576
16	1	0.428892	2.974019	-0.085503	16	1	-0.177597	2.578075	-0.266231
17	1	0.663281	0.923598	-2.299009	17	1	-2.695760	2.381491	1.408473
18	7	2.216608	1.310814	0.666186	18	7	-1.093306	0.203819	-0.601393
19	7	0.319233	0.190186	-0.390328	19	7	-1.244871	0.932230	1.724299
20	6	-3.872359	1.020211	1.527562	20	6	3.774951	-1.677446	0.397471
21	6	-2.629621	0.438820	1.242064	21	6	2.503850	-1.350982	-0.094103
22	6	-2.453190	-0.292401	0.059648	22	6	2.176627	-0.014055	-0.357682
23	6	-3.519497	-0.442232	-0.837271	23	6	3.120505	0.996408	-0.129685
24	6	-4.762235	0.139159	-0.551773	24	6	4.391605	0.669943	0.361892
25	6	-4.938666	0.870380	0.630644	25	6	4.718828	-0.666984	0.625471
26	1	-4.007069	1.578514	2.430364	26	1	4.024793	-2.698220	0.598719
27	1	-1.815472	0.553220	1.926881	27	1	1.783178	-2.122492	-0.268183
28	1	-3.384787	-1.000534	-1.740073	28	1	2.870664	2.017181	-0.330936
29	1	-5.576384	0.024760	-1.236590	29	1	5.112277	1.441454	0.535973
30	1	-5.887524	1.314284	0.848629	30	1	5.689341	-0.916247	1.000800
31	8	-0.948271	-1.737012	-1.589706	31	8	0.536405	1.439248	0.057306
32	1	4.120975	1.550509	1.540565	32	1	-1.390723	-0.962240	-2.335133
33	1	5.097353	-0.539167	0.583124	33	1	-3.359887	-2.218924	-1.439305
34	1	4.005627	-1.556976	-1.350987	34	1	-4.597353	-1.253104	0.434184
35	1	3.198388	-2.627520	0.757357	35	1	-2.916619	-2.893496	1.278382
36	1	0.964642	-1.647855	1.585318	36	1	-0.735182	-1.776840	2.063487
37	1	-0.829267	1.488890	-1.581913	37	1	-1.157113	3.022294	1.939347
38	1	0.939898	3.252305	-1.730931	38	1	-1.646646	3.498883	-0.466640
39	1	2.838744	1.636302	-1.316543	39	1	-2.857105	1.322744	-0.841055
40	16	-0.874716	-1.030860	-0.302980	40	16	0.562129	0.400607	-0.982062
41	8	-0.524044	-1.983780	0.759422	41	8	0.496645	-1.066177	-1.045162
Energy = -1242.5497 a.u.					Energy = -1242.5453 a.u.				

(C1) C16H23N2O2S

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.395567	2.677295	-0.000454
2	6	4.339105	1.699083	-0.085337
3	6	4.182268	0.304258	-0.075475
4	6	1.997117	2.574174	0.121117
5	6	1.219387	1.464759	0.185857
6	6	1.617121	0.126402	0.147551
7	1	3.694591	3.264744	0.842391
8	1	5.009140	1.900370	0.724254
9	1	4.638578	-0.029498	-0.983929
10	1	1.762389	3.120735	1.010539
11	1	0.524492	1.568452	-0.621154
12	6	3.197697	-1.940921	0.004191
13	6	2.082876	-2.790336	0.099013
14	6	0.770799	-2.293847	0.214693
15	1	3.702237	-2.190773	-0.905706
16	1	2.099017	-3.416316	-0.768621
17	1	0.363866	-2.707812	1.113547
18	7	3.040359	-0.411849	0.022071
19	7	0.492584	-0.917279	0.242690
20	6	-3.509505	1.610007	-0.039173
21	6	-2.206698	1.124232	-0.154016
22	6	-1.974537	-0.250813	-0.177996
23	6	-3.045371	-1.140785	-0.085913
24	6	-4.347796	-0.655055	0.029378
25	6	-4.579945	0.720441	0.052357
26	1	-3.692368	2.694149	-0.020734
27	1	-1.363068	1.825811	-0.226931
28	1	-2.862070	-2.224917	-0.104783
29	1	-5.191951	-1.356202	0.101976
30	8	-0.953849	-2.144257	0.019839
31	1	4.788664	-0.034196	0.738548
32	1	4.859116	1.905066	-0.997510
33	1	3.544589	3.269439	-0.879123
34	1	1.612355	3.125432	-0.711333
35	1	0.674588	1.563754	1.101442
36	1	0.214344	-2.703132	-0.602463
37	1	2.248538	-3.420997	0.947378
38	1	3.851886	-2.195458	0.811748
39	16	-0.536594	-0.787121	-0.305643
40	8	-0.332486	0.504979	-0.101092
41	6	-6.018071	1.256406	0.179382
42	1	-6.202344	1.546628	1.192651
43	1	-6.140873	2.103794	-0.462297
44	1	-6.710214	0.491186	-0.103951

Energy = -1281.8781 a.u.

(c2) C16H23N2O2S

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.633660	2.399449	-0.479941
2	6	1.261130	2.350905	-1.162626
3	6	0.348303	1.256470	-0.526234
4	6	2.541134	2.571402	1.029544
5	6	1.602652	1.488619	1.537978
6	6	1.900813	0.190247	0.772228
7	1	3.112952	1.461142	-0.666380
8	1	1.437087	2.112755	-2.190840
9	1	-0.017181	1.584641	0.424358
10	1	3.524983	2.443977	1.430425
11	1	0.588029	1.753445	1.325124
12	6	1.827550	-0.442946	-1.471424
13	6	2.507071	-1.753330	-1.064161
14	6	3.500859	-1.444642	0.068113
15	1	1.154434	-0.607094	-2.286820
16	1	1.755268	-2.432731	-0.720501
17	1	4.311286	-0.866285	-0.323820
18	7	1.086259	-0.010946	-0.287314
19	7	2.839496	-0.643706	1.120592
20	6	-3.780393	-0.142933	1.178321
21	6	-2.472423	-0.644386	1.219348
22	6	-1.675509	-0.618266	0.066884
23	6	-2.186569	-0.090708	-1.126608
24	6	-3.494543	0.410729	-1.167640
25	6	-4.291453	0.384627	-0.015173
26	1	-4.388853	-0.162865	2.058255
27	1	-2.082222	-1.047199	2.130604
28	1	-1.578106	-0.070760	-2.006536
29	1	-3.884752	0.813515	-2.078905
30	8	0.117688	-2.358938	-0.842264
31	1	-0.470982	1.098117	-1.196008
32	1	0.760711	3.293879	-1.089941
33	1	3.215191	3.195916	-0.895107
34	1	2.167394	3.532081	1.316449
35	1	1.725703	1.376651	2.594965
36	1	3.877031	-2.361764	0.470954
37	1	3.029217	-2.191701	-1.888838
38	1	2.552756	0.287501	-1.763698
39	16	-0.014170	-1.255160	0.118991
40	8	0.279876	-1.746505	1.472447
41	6	-5.728783	0.935681	-0.060258
42	1	-6.403814	0.149835	-0.327989
43	1	-5.993489	1.320754	0.902316
44	1	-5.787711	1.719331	-0.786429

Energy = -1281.8762 a.u.

(D1) C15H20N3O4S					(D2) C15H20N3O4S				
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.202635	-2.657807	0.208779	1	6	2.944929	2.539114	-0.415599
2	6	-5.200346	-1.514761	0.485515	2	6	1.577182	2.411794	-1.097738
3	6	-4.629691	-0.228969	1.121095	3	6	0.745962	1.238944	-0.489844
4	6	-3.074729	-2.356403	-0.793943	4	6	2.845098	2.663792	1.098059
5	6	-2.008199	-1.398770	-0.239480	5	6	1.987070	1.504156	1.578381
6	6	-2.441762	0.067771	-0.092580	6	6	2.373928	0.251006	0.777757
7	1	-3.749502	-2.952077	1.132309	7	1	3.488785	1.642375	-0.627681
8	1	-5.918020	-1.911538	1.172664	8	1	1.766388	2.214179	-2.132170
9	1	-5.472798	0.373240	1.387745	9	1	0.361104	1.514979	0.469629
10	1	-2.581541	-3.285646	-0.988937	10	1	3.836715	2.595656	1.494232
11	1	-1.188050	-1.401271	-0.926414	11	1	0.955617	1.702112	1.373885
12	6	-3.750999	1.909306	0.841841	12	6	2.338746	-0.325753	-1.481976
13	6	-2.906766	2.826358	-0.027487	13	6	3.110452	-1.595165	-1.110779
14	6	-1.480153	2.315840	0.053813	14	6	4.083390	-1.247227	0.028206
15	1	-4.745606	2.295750	0.922620	15	1	1.676425	-0.515321	-2.300691
16	1	-3.273256	2.800602	-1.032582	16	1	2.409616	-2.334979	-0.784580
17	1	-1.126490	2.438992	1.056148	17	1	4.849698	-0.602736	-0.349026
18	7	-3.814193	0.581107	0.201323	18	7	1.572398	0.020999	-0.285846
19	7	-1.433637	0.889503	-0.276043	19	7	3.370281	-0.523432	1.102548
20	6	3.655773	-1.366331	-0.084892	20	6	-3.268239	-0.494081	1.181439
21	6	2.303388	-1.214949	-0.419183	21	6	-1.927960	-0.902613	1.207470
22	6	1.738246	0.065476	-0.490768	22	6	-1.138430	-0.789438	0.055187
23	6	2.525463	1.194831	-0.227265	23	6	-1.689176	-0.267728	-1.123125
24	6	3.877701	1.043440	0.107727	24	6	-3.029454	0.140806	-1.149154
25	6	4.442990	-0.237041	0.178429	25	6	-3.818985	0.027629	0.003128
26	1	4.087266	-2.343947	-0.030654	26	1	-3.871063	-0.580494	2.061232
27	1	1.702112	-2.077010	-0.619820	27	1	-1.507453	-1.300951	2.107136
28	1	2.094029	2.172532	-0.281779	28	1	-1.086352	-0.181317	-2.002918
29	1	4.478685	1.905598	0.309473	29	1	-3.449962	0.539142	-2.048822
30	8	0.386753	1.676480	-1.009842	30	8	0.770550	-2.374009	-0.902405
31	1	-4.060699	-0.472390	1.994084	31	1	-0.062125	1.040933	-1.162664
32	1	-5.673478	-1.240594	-0.434187	32	1	1.011575	3.314724	-0.999221
33	1	-4.779031	-3.462214	-0.197953	33	1	3.467423	3.385514	-0.809944
34	1	-3.485290	-1.962181	-1.699927	34	1	2.405258	3.587631	1.411048
35	1	-1.695251	-1.768726	0.714476	35	1	2.120962	1.373040	2.631843
36	1	-0.858826	2.872143	-0.616579	36	1	4.524691	-2.145846	0.405881
37	1	-2.939509	3.833909	0.331252	37	1	3.659757	-1.973354	-1.947521
38	1	-3.316105	1.842511	1.817633	38	1	3.009599	0.461704	-1.755413
39	16	0.020269	0.256432	-0.915955	39	16	0.563934	-1.308344	0.088248
40	8	-0.166563	-0.752726	0.135847	40	8	0.896132	-1.813557	1.427699
41	7	5.861673	-0.395657	0.528315	41	7	-5.224872	0.456157	-0.024178
42	8	6.533465	0.568472	0.756428	42	8	-5.899135	0.359501	0.959874
43	8	6.345155	-1.488877	0.585184	43	8	-5.695213	0.901695	-1.030461
Energy = -1447.1145 a.u.					Energy = -1447.1053 a.u.				

(E1) C10H19N2O2S

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.792457	-1.736152	0.956648
2	6	-3.073303	-0.912585	0.751436
3	6	-2.933173	0.148478	-0.358274
4	6	-1.134906	-2.260370	-0.330064
5	6	-0.650519	-1.165427	-1.330171
6	6	-0.489551	0.217874	-0.732004
7	1	-1.058922	-1.130124	1.498721
8	1	-3.344830	-0.432338	1.697831
9	1	-3.072080	-0.321851	-1.334296
10	1	-0.267227	-2.853540	-0.035708
11	1	-1.336151	-1.097151	-2.180529
12	6	-1.566133	2.124095	0.373920
13	6	-0.358102	2.914274	-0.118543
14	6	0.889375	2.031231	-0.040295
15	1	-2.492201	2.680325	0.202373
16	1	-0.530280	3.224194	-1.154333
17	1	1.205005	1.907488	1.003175
18	7	-1.653751	0.857882	-0.353956
19	7	0.699878	0.709089	-0.629677
20	8	2.169063	0.403386	1.442074
21	1	-3.722730	0.898657	-0.267894
22	1	-3.910993	-1.567823	0.484172
23	1	-2.014647	-2.584405	1.611459
24	1	-1.823240	-2.937183	-0.848674
25	1	0.322028	-1.438953	-1.735658
26	1	1.724768	2.513693	-0.557525
27	1	-0.229606	3.820054	0.481064
28	1	-1.486368	1.946785	1.456289
29	16	2.036276	-0.396596	0.193671
30	8	1.518033	-1.792600	0.246051
31	6	3.590811	-0.473112	-0.514613
32	1	4.200219	-1.159000	0.035914
33	1	3.505099	-0.806132	-1.527851
34	1	4.039834	0.497917	-0.495097

Energy = -1050.7724 a.u.

(E2) C10H19N2O2S

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.806416	0.029304	-0.621780
2	6	-2.069013	-1.126027	-1.310040
3	6	-0.703687	-1.423242	-0.614634
4	6	-2.987837	-0.188130	0.873707
5	6	-1.613955	-0.508868	1.440499
6	6	-0.583050	0.403166	0.757513
7	1	-2.206768	0.906566	-0.747212
8	1	-1.893900	-0.820827	-2.320529
9	1	-0.862445	-1.935012	0.311534
10	1	-3.370037	0.721073	1.288645
11	1	-1.346577	-1.517717	1.204633
12	6	0.118518	0.722918	-1.443814
13	6	0.917666	1.933181	-0.952542
14	6	0.112474	2.615634	0.165886
15	1	0.626998	0.240826	-2.252477
16	1	1.856937	1.588244	-0.573480
17	1	-0.764185	3.062190	-0.254777
18	7	0.038150	-0.176402	-0.293590
19	7	-0.322628	1.613903	1.162800
20	8	2.586830	0.121879	-0.711231
21	1	-0.137194	-2.041415	-1.279350
22	1	-2.656885	-2.019993	-1.298584
23	1	-3.762572	0.171343	-1.080573
24	1	-3.662905	-0.987200	1.098807
25	1	-1.628082	-0.384911	2.503201
26	1	0.713756	3.371352	0.626592
27	1	1.091132	2.630687	-1.745193
28	1	-0.855182	1.018204	-1.774896
29	16	1.636367	-0.557923	0.179955
30	8	1.857062	-0.112483	1.562923
31	6	1.851188	-2.100436	0.089927
32	1	1.652249	-2.430595	-0.908230
33	1	2.862570	-2.335379	0.348402
34	1	1.186092	-2.593340	0.767860

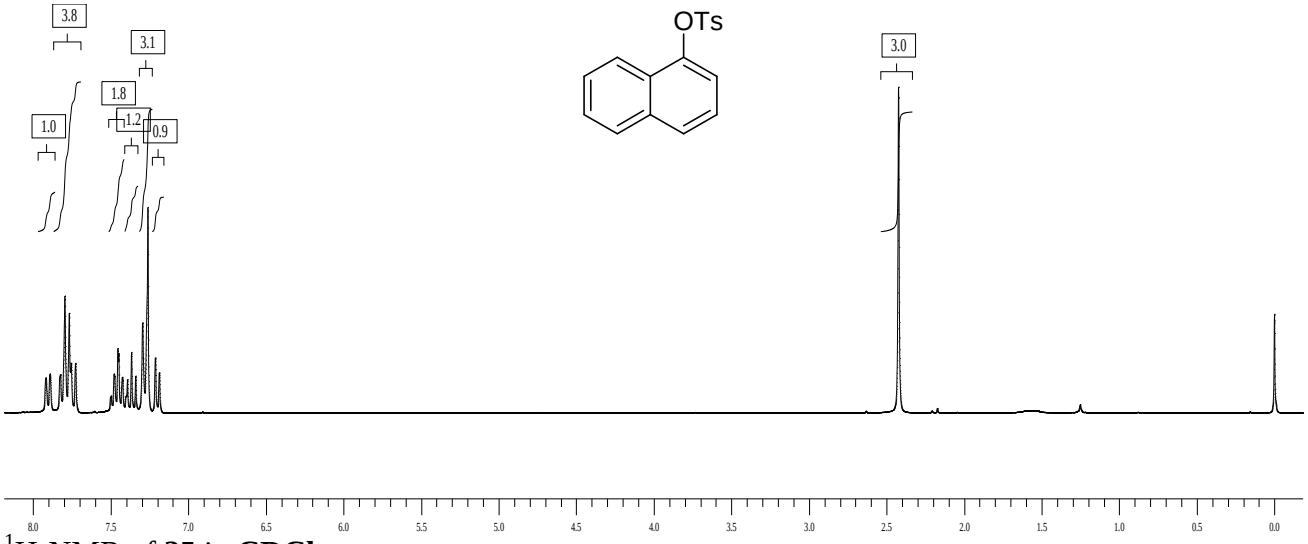
Energy = -1050.7685 a.u.

(F1) C9H16BrN2					(F2) C9H16BrN2				
Center Number	Atomic Number	Coordinates (Angstrom s) X	Y	Z	Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.931004	-1.797441	1.030939	1	6	3.099388	-1.292392	0.779987
2	6	-3.199481	-1.103755	0.510484	2	6	1.757229	-2.002801	1.012488
3	6	-2.921616	-0.074491	-0.605265	3	6	0.577822	-1.405943	0.219336
4	6	-0.976870	-2.336249	-0.047140	4	6	3.455128	-1.015733	-0.688808
5	6	-0.412156	-1.269794	-1.032010	5	6	2.448471	-0.102497	-1.453415
6	6	-0.467665	0.141639	-0.492879	6	6	1.565843	0.736750	-0.557203
7	1	-1.375998	-1.097378	1.664842	7	1	3.098477	-0.341299	1.323086
8	1	-3.705290	-0.616768	1.350997	8	1	1.525304	-1.979271	2.081984
9	1	-2.847394	-0.583525	-1.568188	9	1	0.578935	-1.788168	-0.804912
10	1	-0.131907	-2.807185	0.460927	10	1	4.437889	-0.537796	-0.708778
11	1	-0.957421	-1.296748	-1.979259	11	1	1.815899	-0.703768	-2.112393
12	6	-1.838153	2.029181	0.255259	12	6	-0.493790	0.756490	0.801763
13	6	-0.592838	2.870493	-0.011875	13	6	-0.492823	2.244053	0.481169
14	6	0.657418	2.081697	0.387719	14	6	0.940285	2.768101	0.449812
15	1	-2.730048	2.521596	-0.141003	15	1	-1.472621	0.298069	0.423438
16	1	-0.547066	3.119432	-1.076261	16	1	-0.948732	2.397008	-0.501692
17	1	0.755386	2.027573	1.478476	17	1	1.392104	2.746076	1.453449
18	7	-1.710578	0.725687	-0.401265	18	7	0.582962	0.060221	0.163718
19	7	0.623943	0.732925	-0.147195	19	7	1.792915	1.998712	-0.445152
20	1	-3.757813	0.622379	-0.694309	20	1	-0.373496	-1.709214	0.656221
21	1	-3.903192	-1.844396	0.113269	21	1	1.832124	-3.059334	0.733324
22	1	-2.223925	-2.621351	1.688958	22	1	3.895692	-1.891216	1.232262
23	1	-1.471482	-3.124163	-0.624929	23	1	3.561161	-1.960663	-1.231585
24	1	0.630787	-1.484286	-1.254277	24	1	2.989496	0.599195	-2.086124
25	1	1.561719	2.570000	0.017657	25	1	0.963549	3.812592	0.129013
26	1	-0.646063	3.809056	0.546262	26	1	-1.106439	2.778831	1.208905
27	1	-1.985840	1.904109	1.337457	27	1	-0.513012	0.532978	1.876284
28	35	2.886748	-0.415895	0.072778	28	35	-3.298651	-0.506364	-0.227806
Energy = -3036.3466 a.u.					Energy = -3036.3361 a.u.				

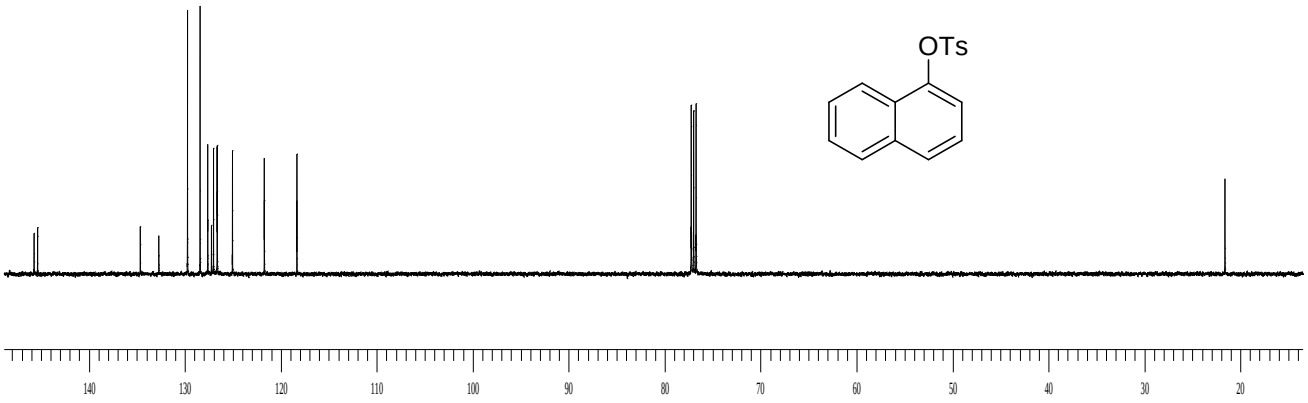
(G1) C10H19N2

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.352677	0.329796	1.021509
2	6	2.486270	-1.020213	0.299681
3	6	1.464056	-1.199029	-0.840082
4	6	2.093546	1.525793	0.093055
5	6	0.731705	1.500942	-0.681416
6	6	-0.250393	0.463115	-0.211362
7	1	1.529047	0.272016	1.739438
8	1	2.390349	-1.833064	1.028043
9	1	1.768725	-0.587604	-1.692119
10	1	2.126129	2.432681	0.704643
11	1	0.926921	1.372666	-1.759932
12	6	-0.668169	-1.910933	0.195442
13	6	-2.161400	-1.648269	0.040741
14	6	-2.478458	-0.224230	0.478758
15	1	-0.402679	-2.882903	-0.228806
16	1	-2.446951	-1.782691	-1.006728
17	1	-2.329190	-0.135080	1.571739
18	7	0.075034	-0.879597	-0.520933
19	7	-1.645356	0.754781	-0.229544
20	1	1.483476	-2.234245	-1.192444
21	1	3.486722	-1.117566	-0.140510
22	1	3.260669	0.519806	1.604369
23	1	2.914215	1.619404	-0.627787
24	1	0.281359	2.486325	-0.592948
25	1	-3.525280	0.011209	0.270472
26	1	-2.736689	-2.355461	0.646313
27	1	-0.406444	-1.932294	1.268647
28	6	-2.041160	2.115505	0.114054
29	1	-1.692874	2.423100	1.115434
30	1	-1.676190	2.834026	-0.619398
31	1	-3.131103	2.168517	0.102634

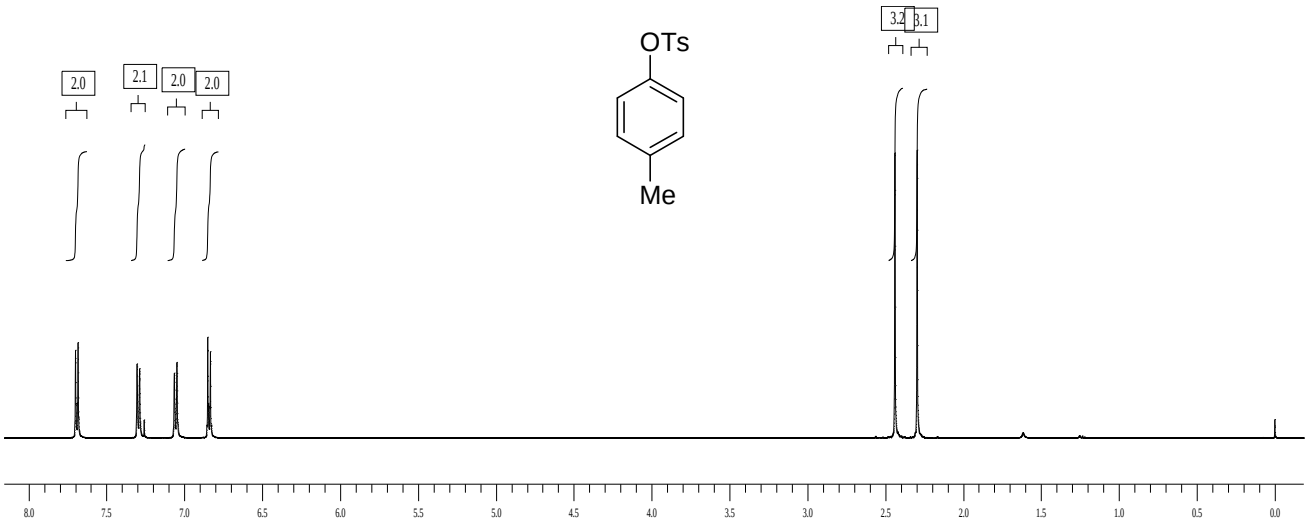
Energy = -502.0778 a.u.



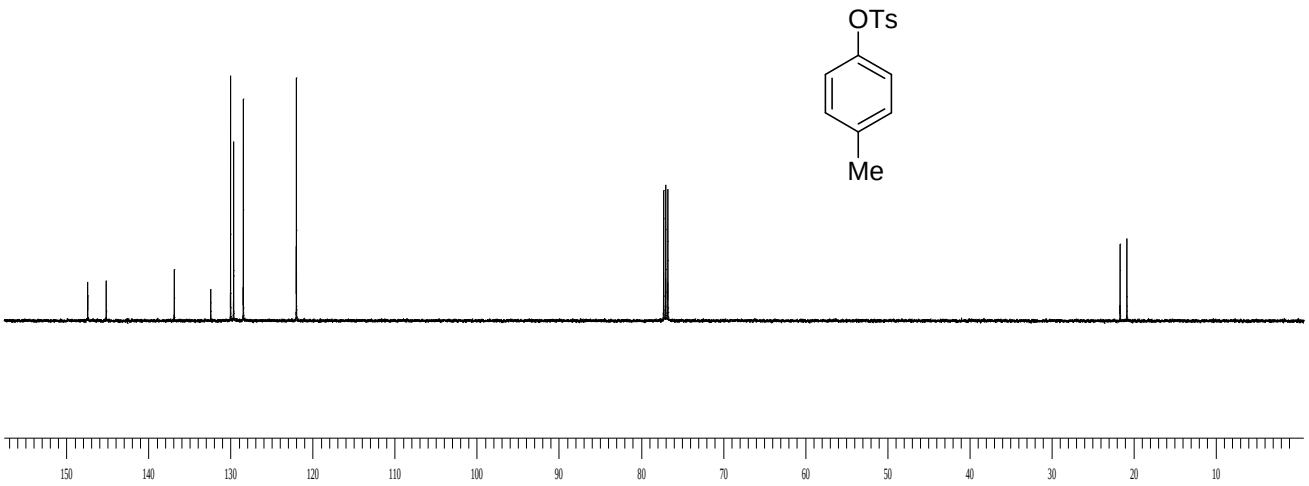
^{1}H-NMR of **25** in **$CDCl_3$**



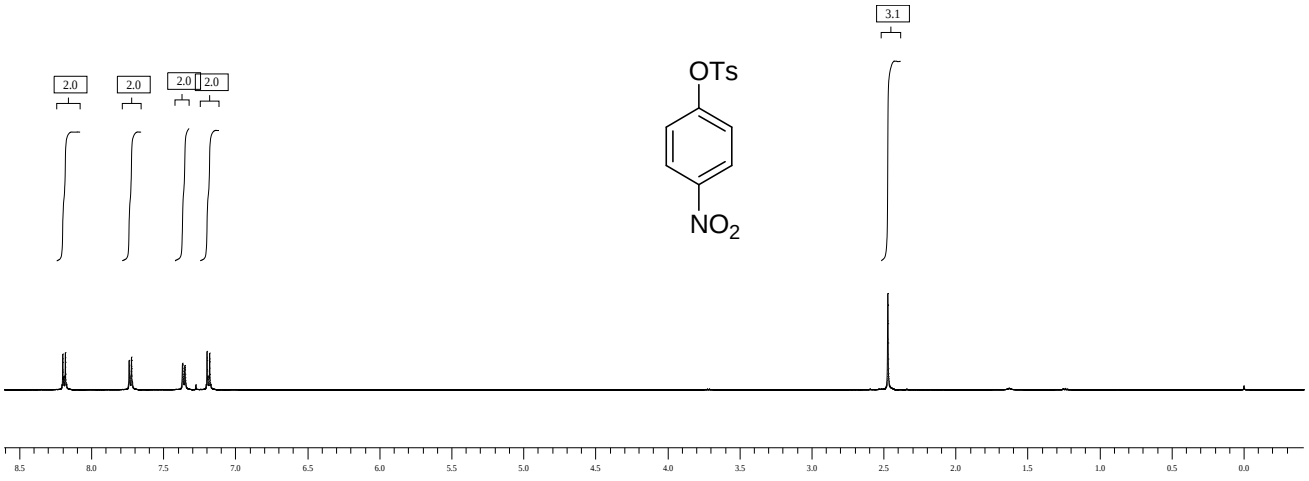
^{13}C-NMR of **25** in DMSO



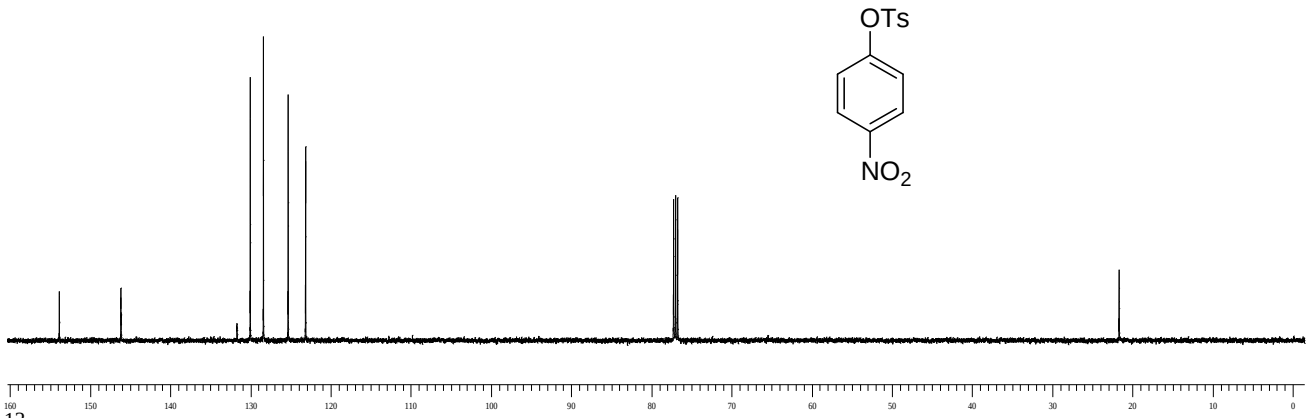
^{1}H-NMR of **26** in **$CDCl_3$**



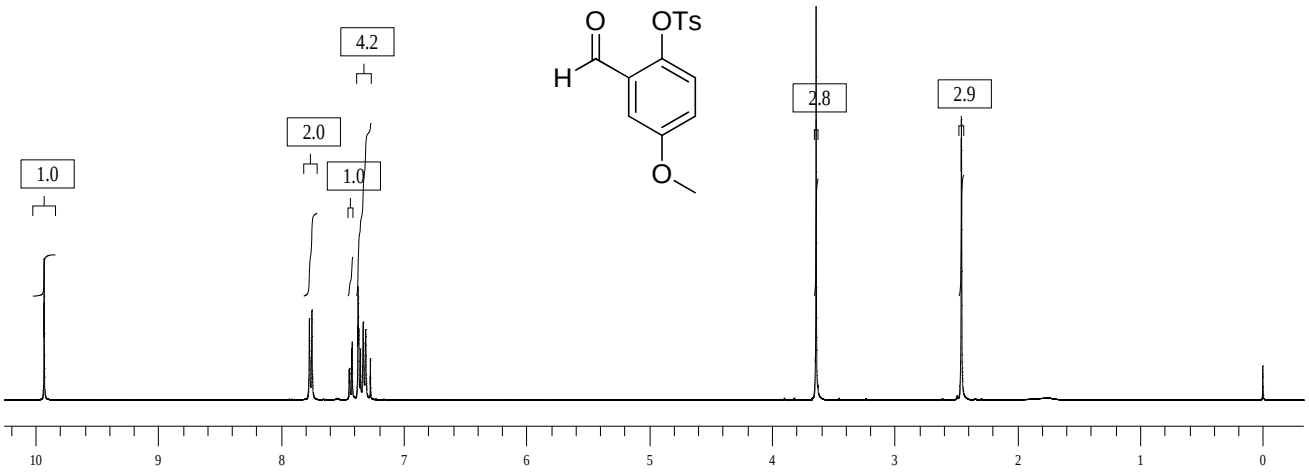
^{13}C-NMR of **26** in **$CDCl_3$**



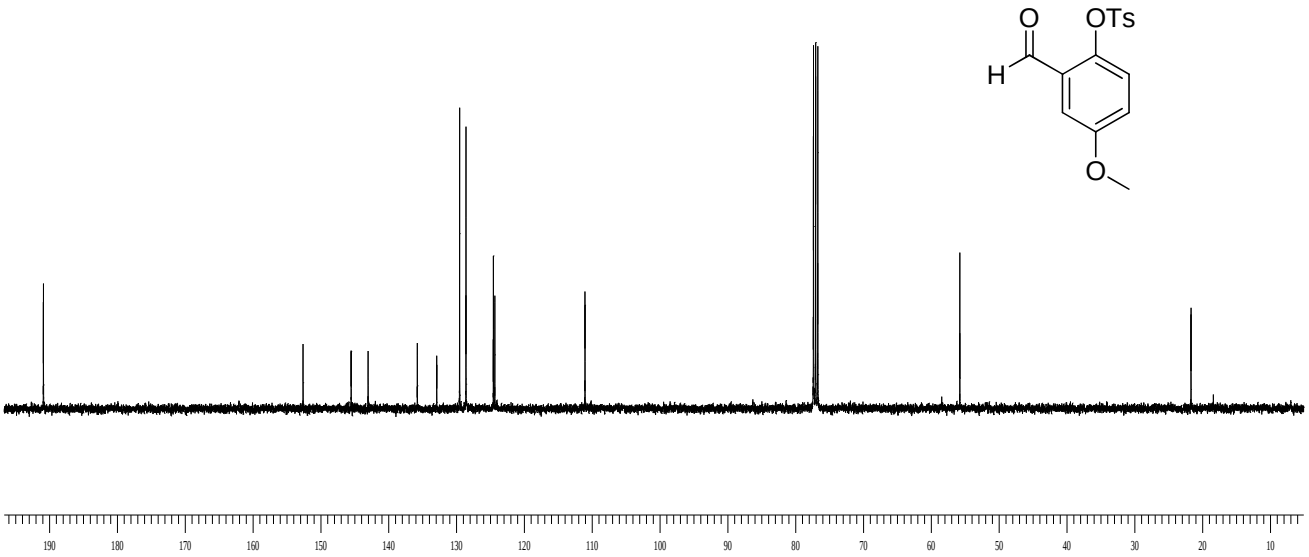
^{1}H-NMR of **27** in **$CDCl_3$**



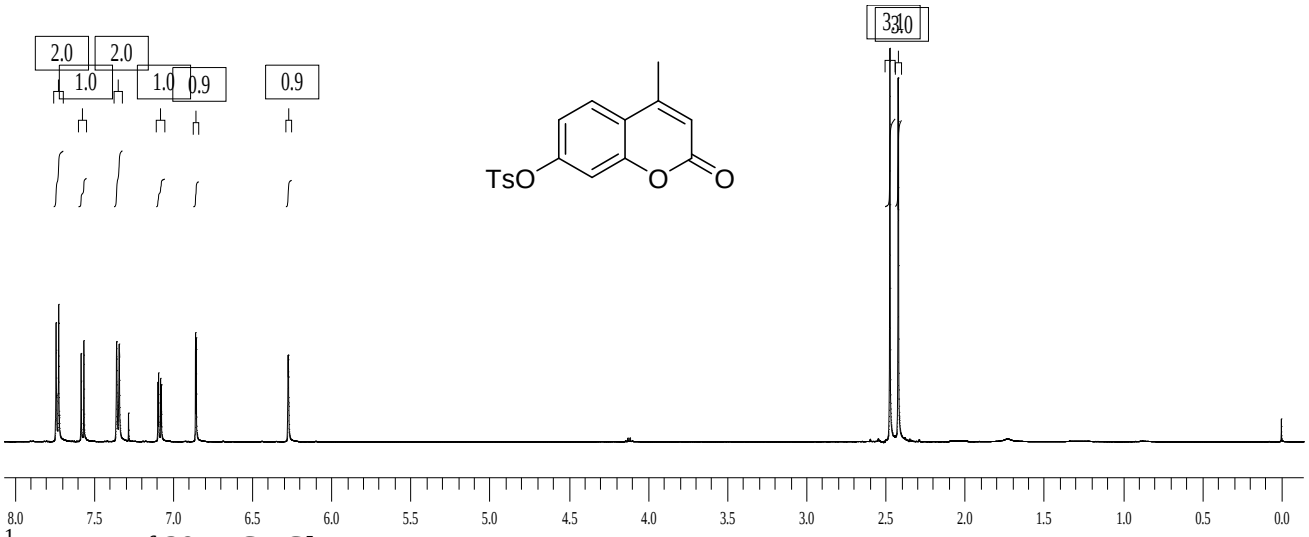
^{13}C-NMR of **27** in **$CDCl_3$**



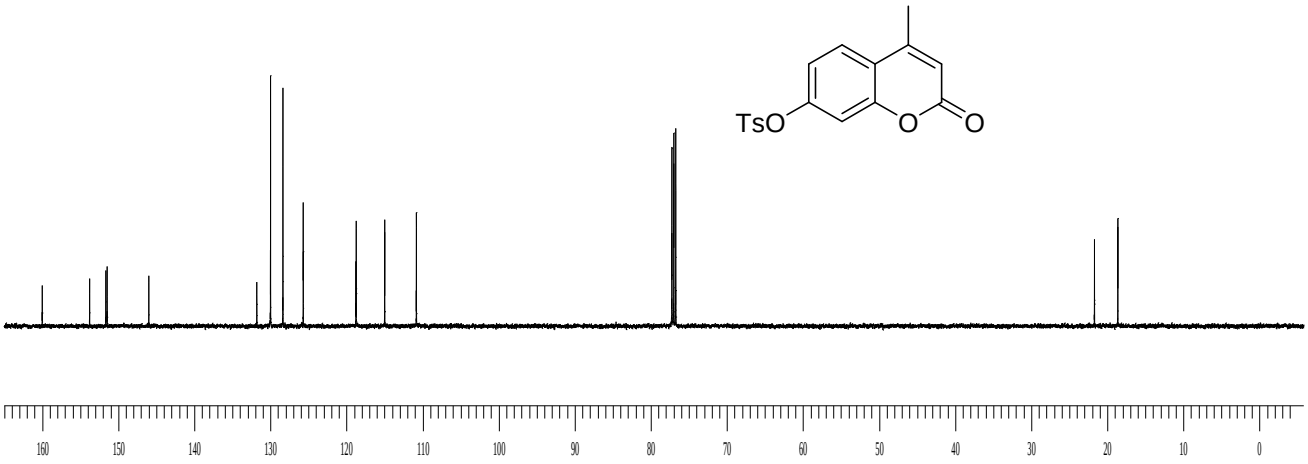
^{1}H-NMR of **28** in **$CDCl_3$**



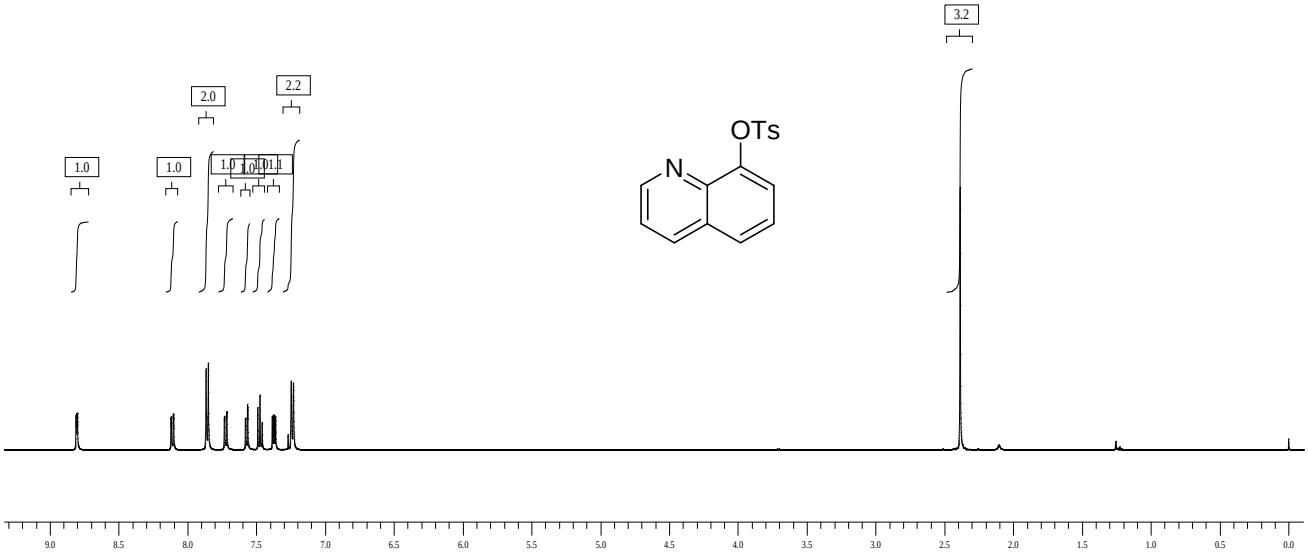
^{13}C-NMR of **28** in **$CDCl_3$**



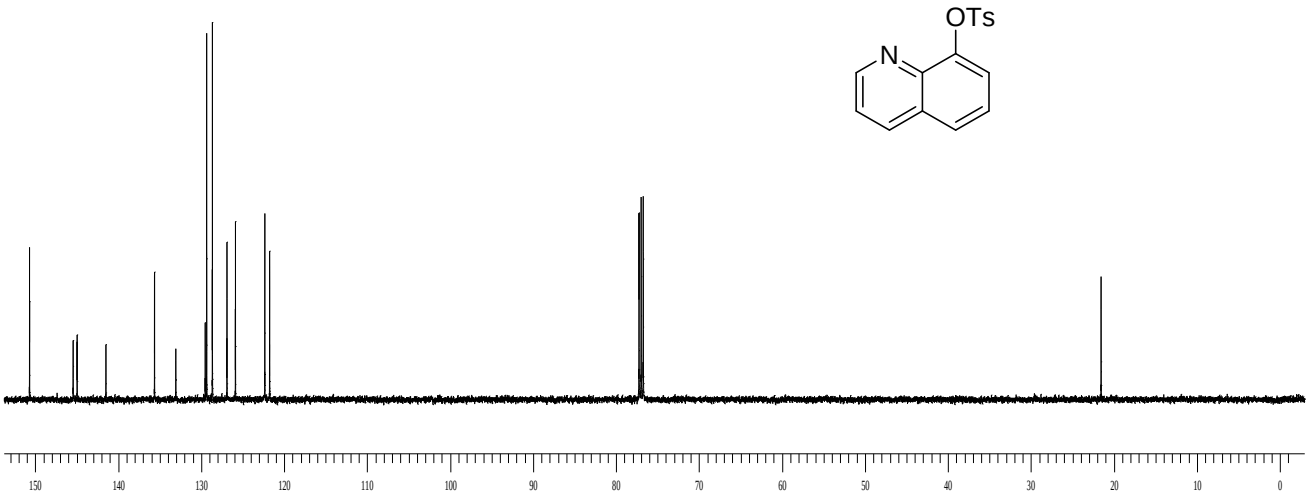
^{1}H-NMR of **29** in **$CDCl_3$**



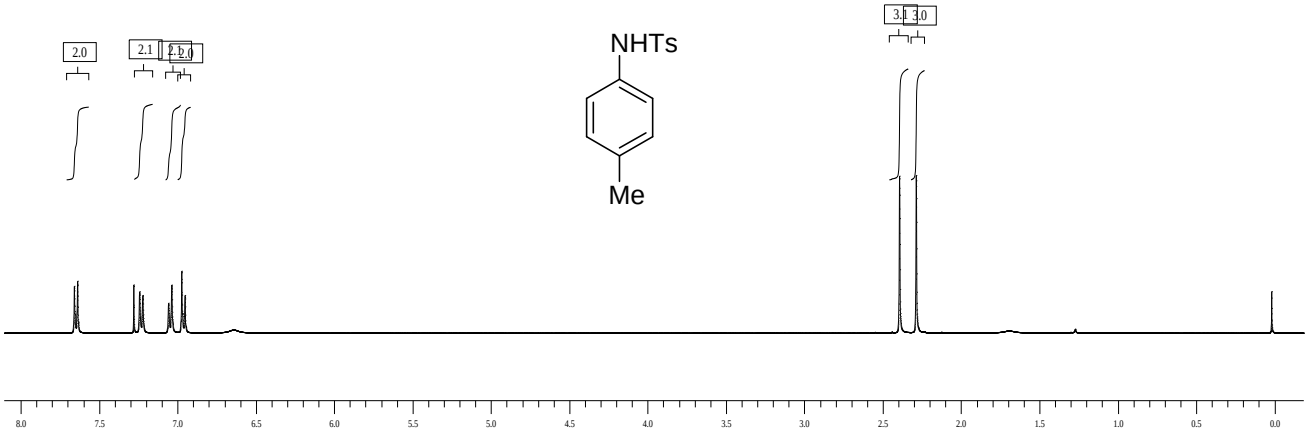
^{13}C-NMR of **29** in **$CDCl_3$**



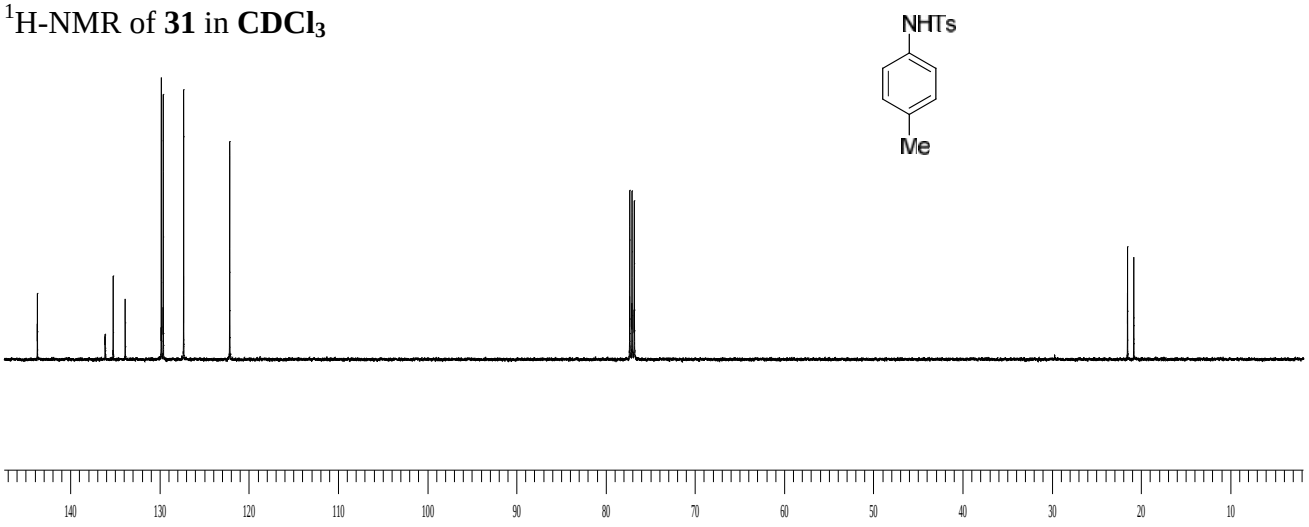
^{1}H-NMR of **30** in **$CDCl_3$**



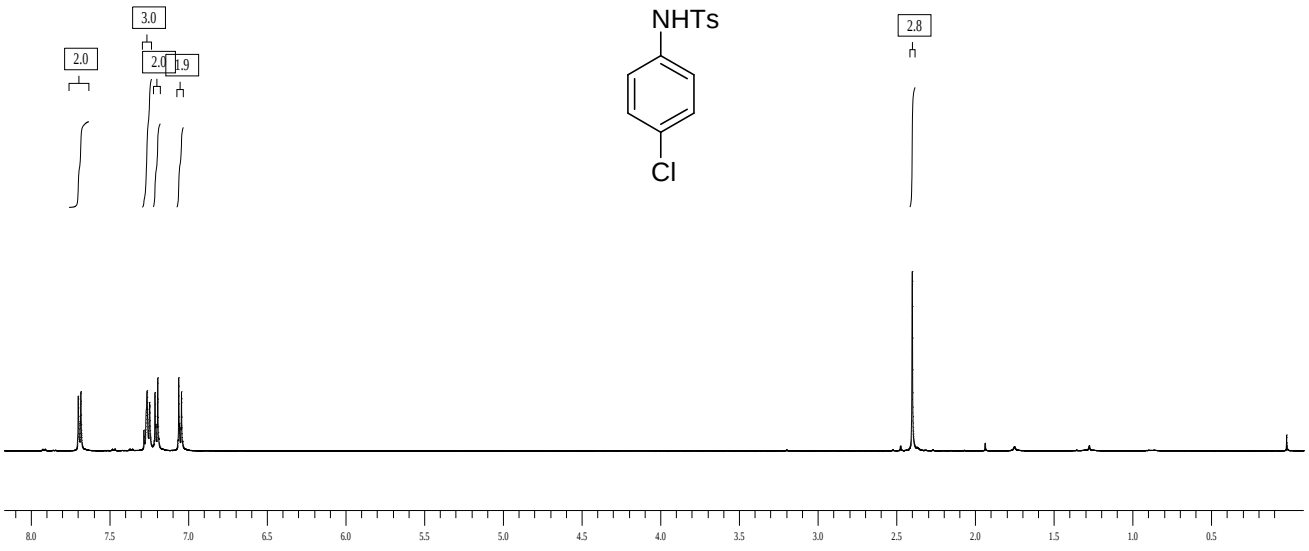
^{13}C-NMR of **30** in **$CDCl_3$**



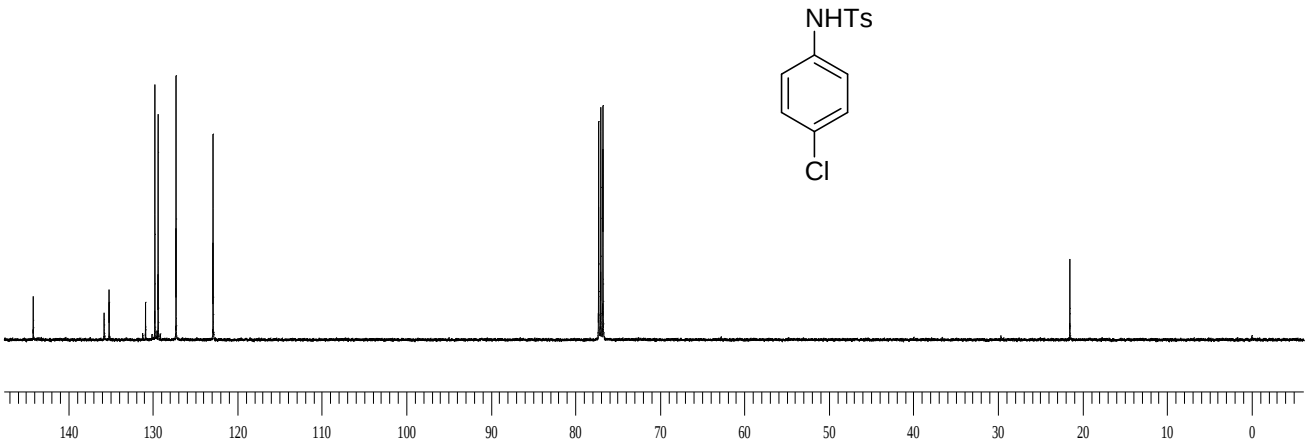
^{1}H-NMR of **31** in **$CDCl_3$**



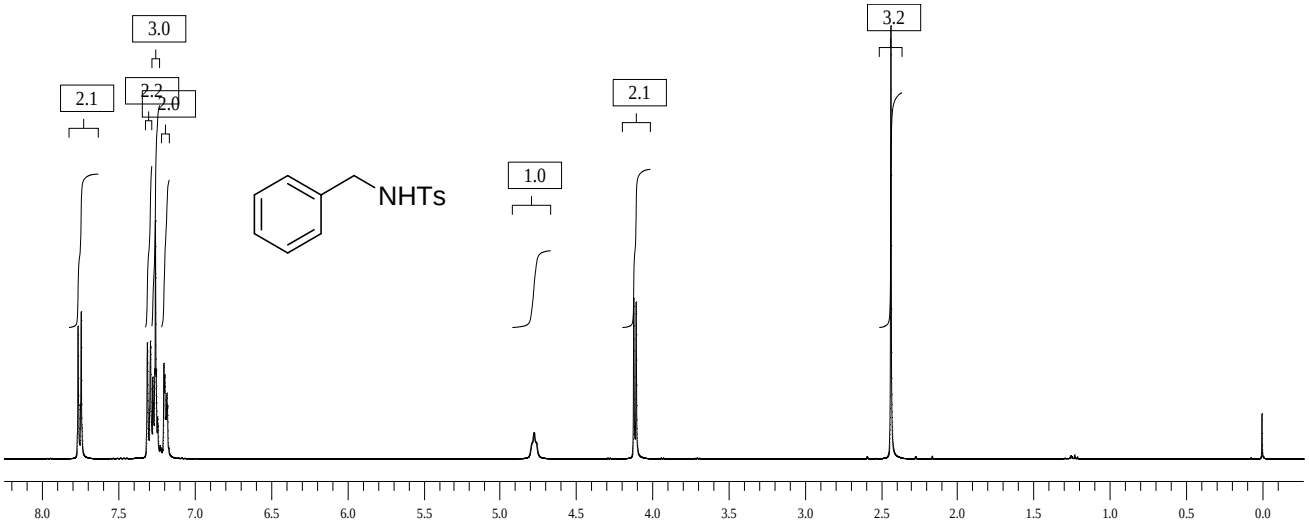
^{13}C-NMR of **31** in **$CDCl_3$**



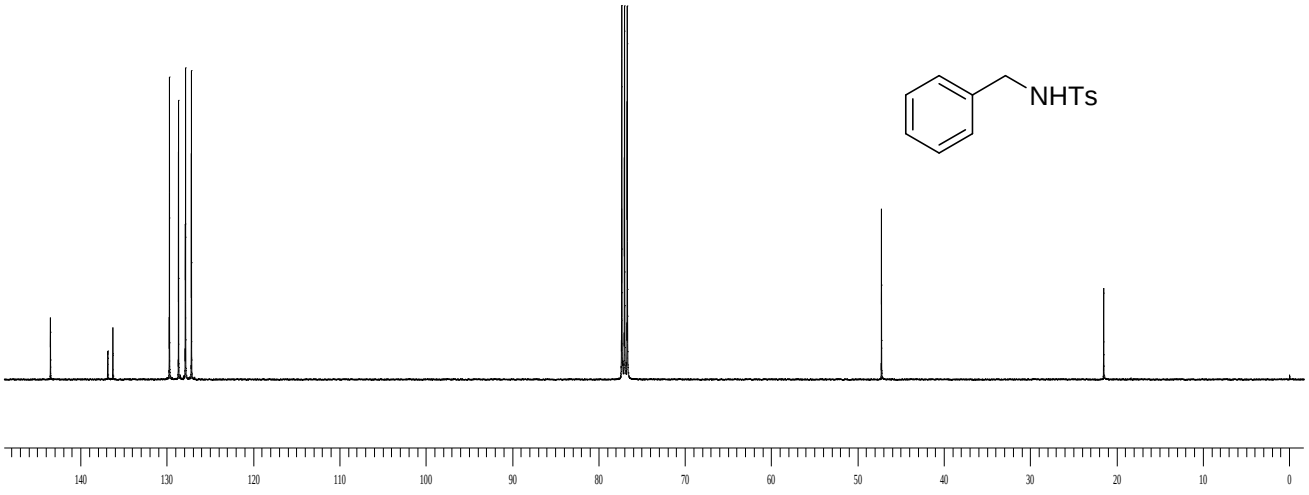
^{1}H-NMR of **32** in **$CDCl_3$**



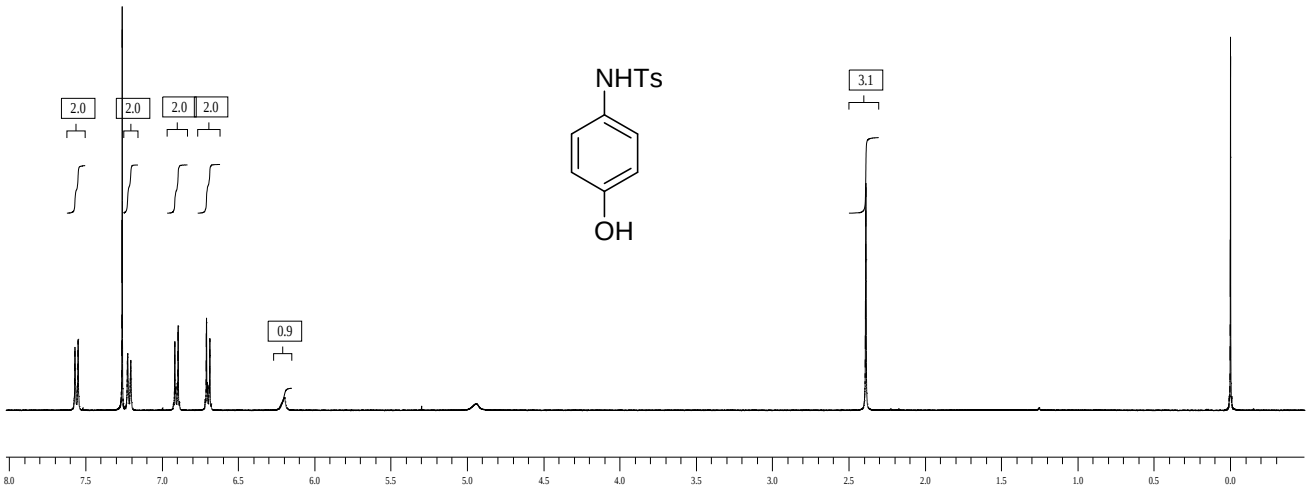
^{13}C-NMR of **32** in **$CDCl_3$**



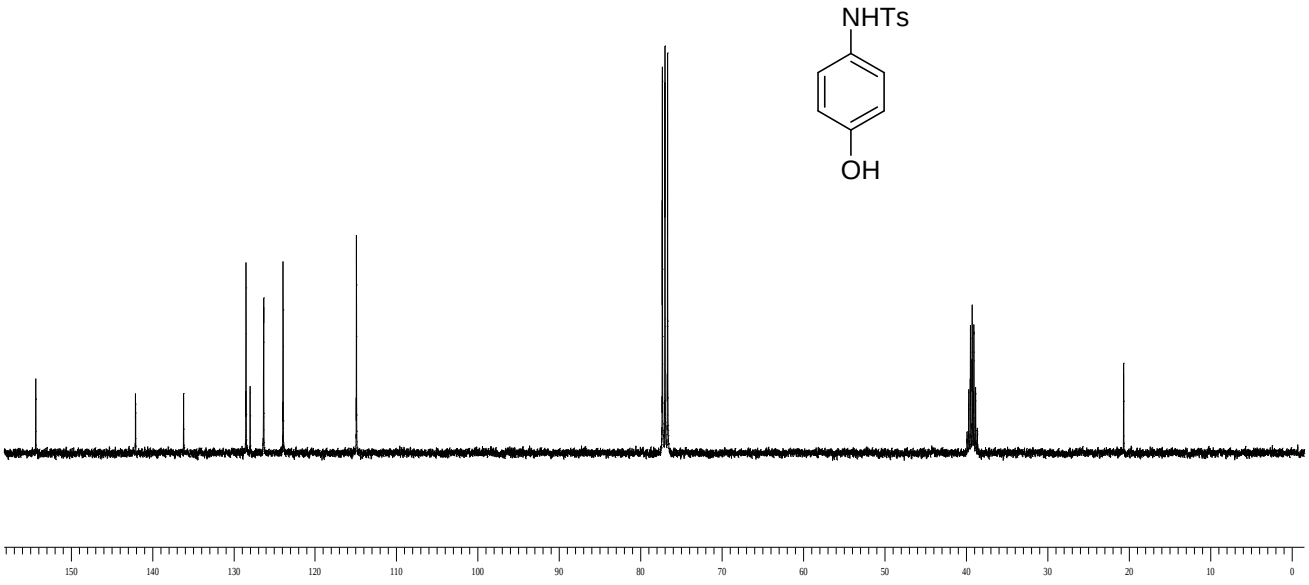
^{1}H-NMR of **33** in **$CDCl_3$**



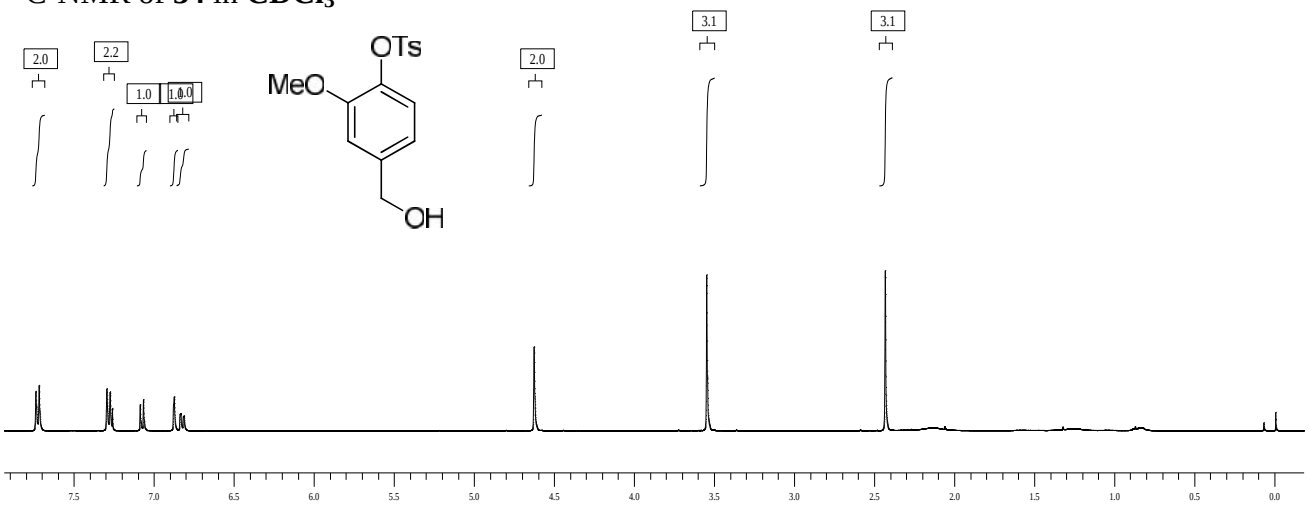
^{13}C-NMR of **33** in **$CDCl_3$**



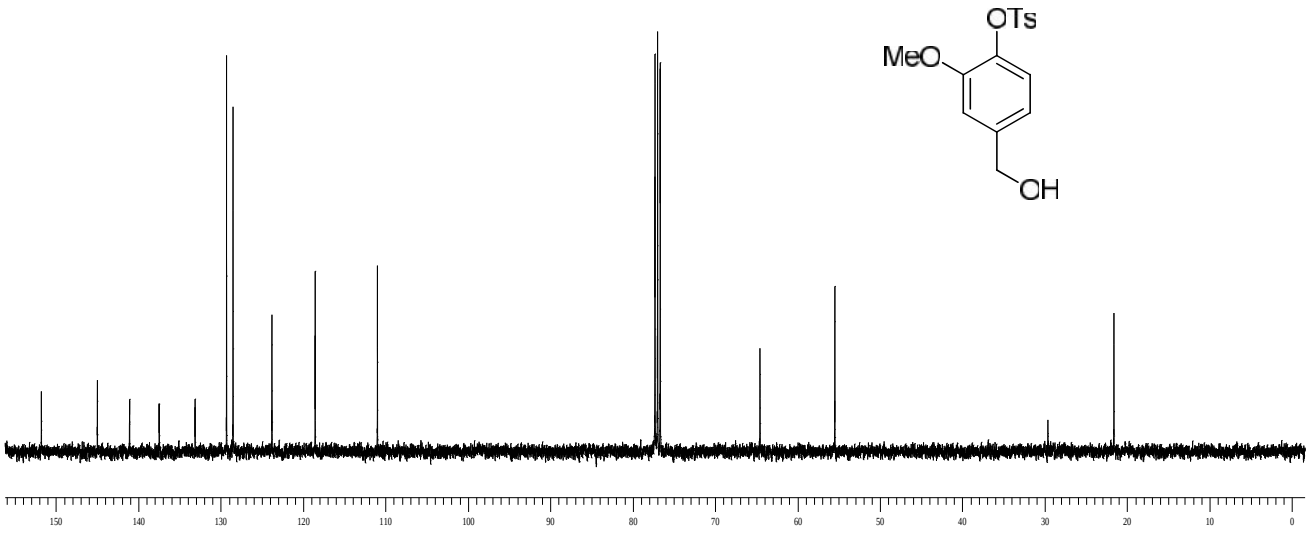
^{1}H-NMR of **34** in **$CDCl_3$**



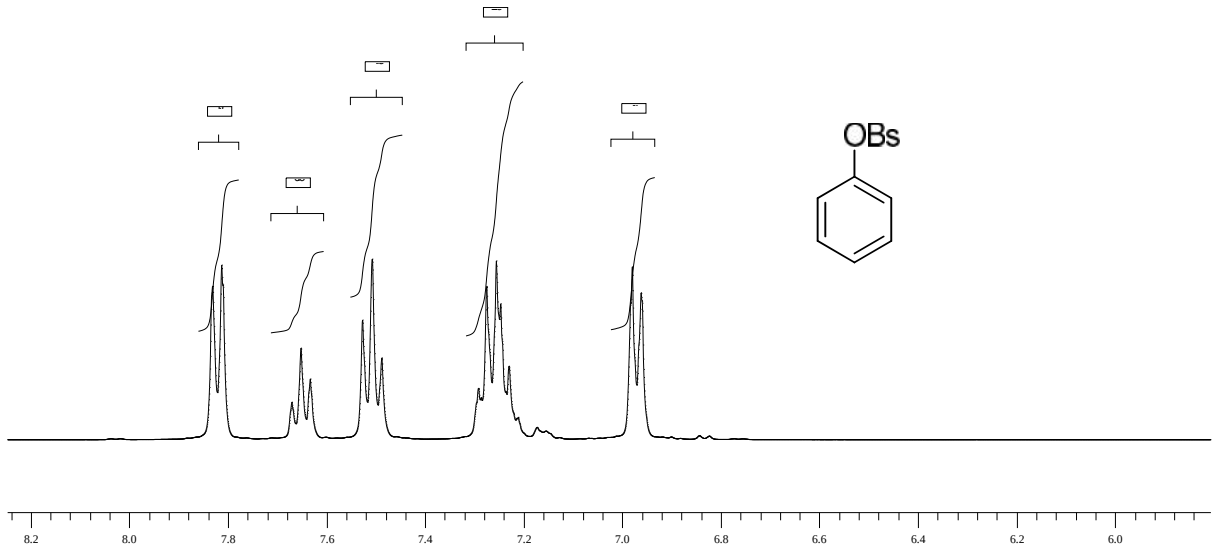
^{13}C-NMR of **34** in **$CDCl_3$**



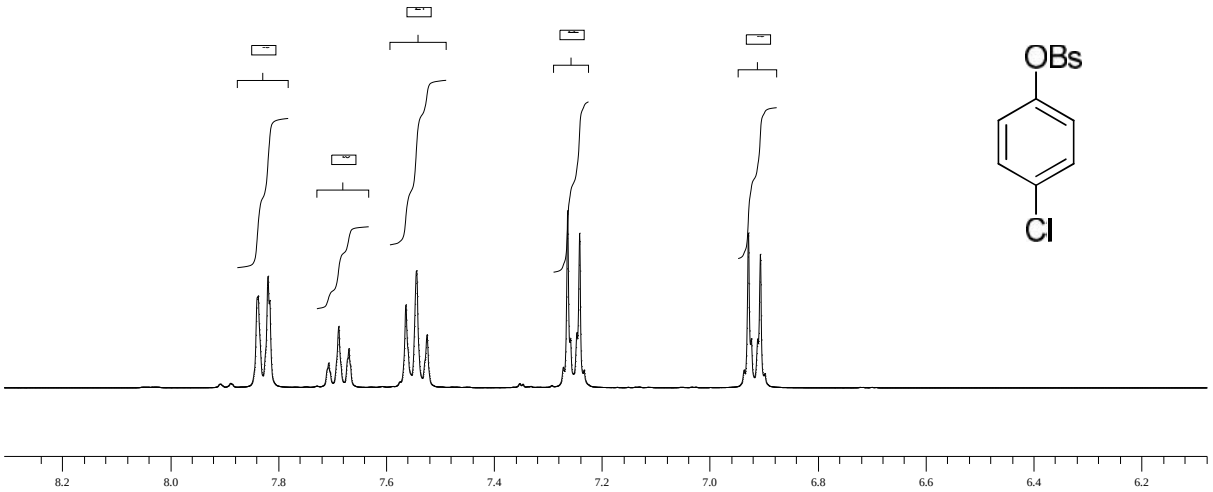
^{1}H-NMR of **35** in **$CDCl_3$**



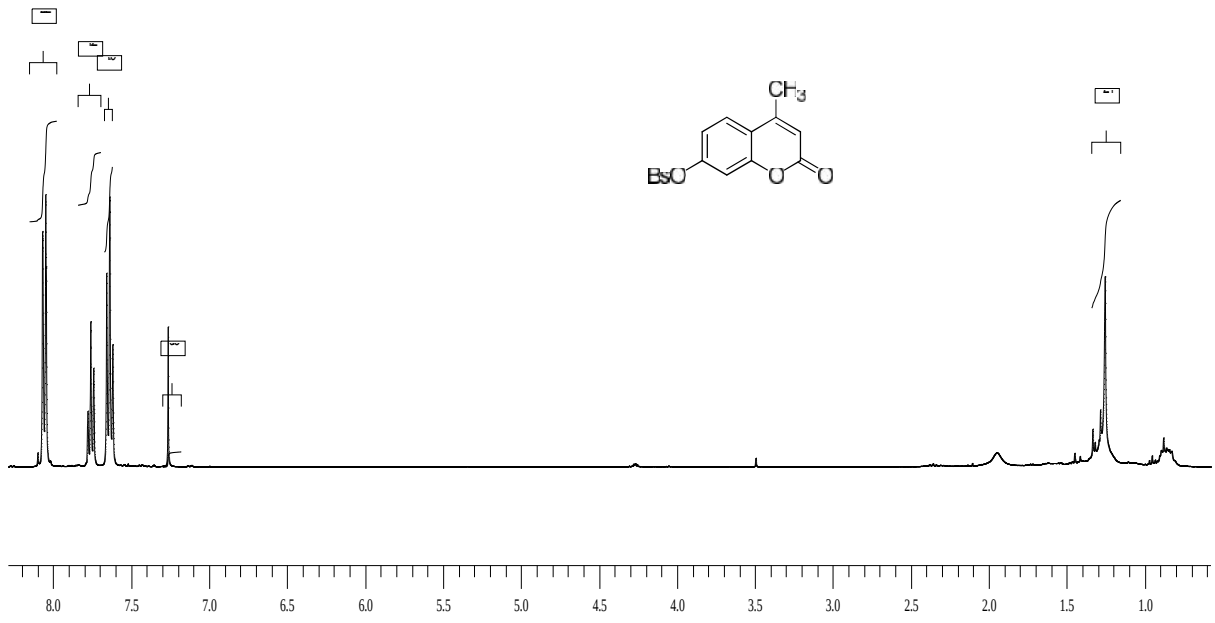
^{13}C-NMR of **35** in **$CDCl_3$**



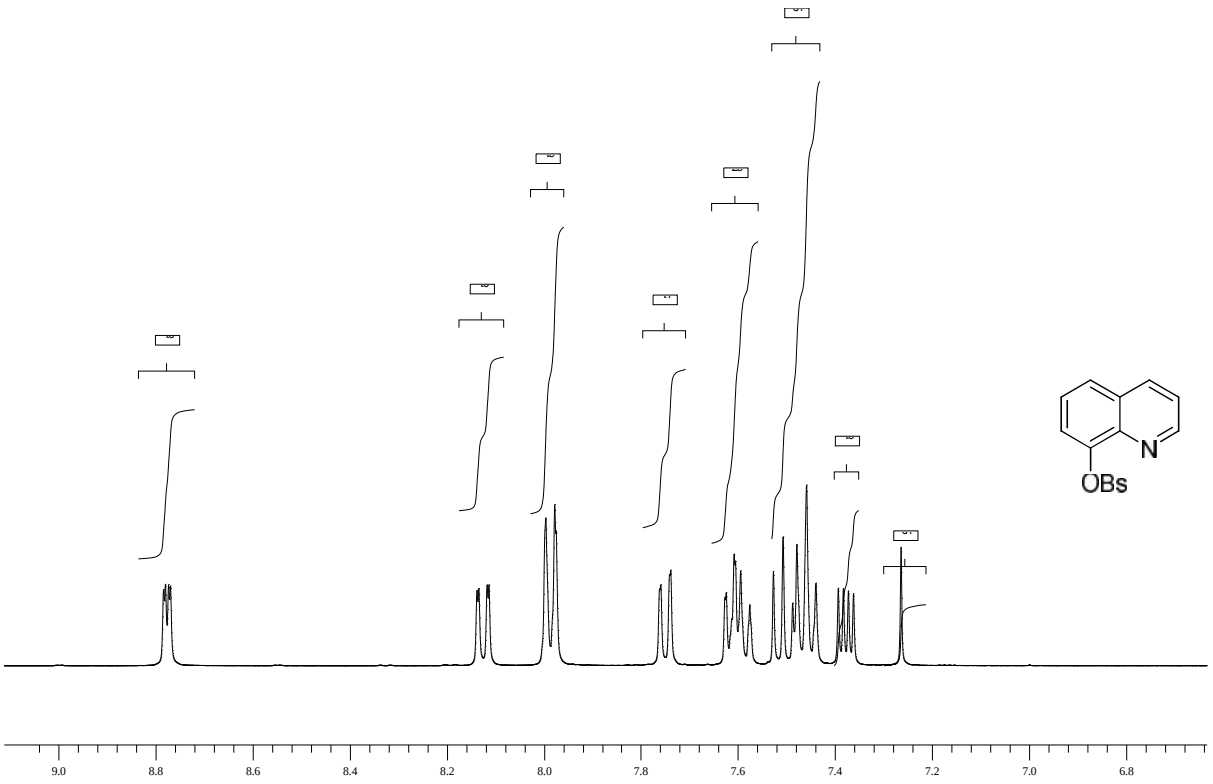
^{1}H-NMR of **36**in $CDCl_3$



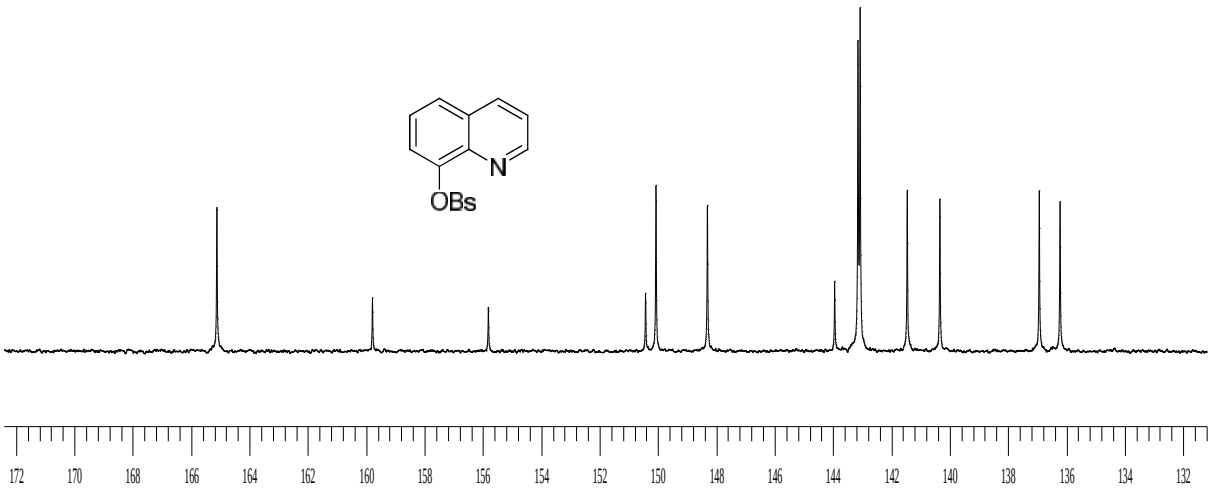
^{1}H-NMR of **37** in $CDCl_3$



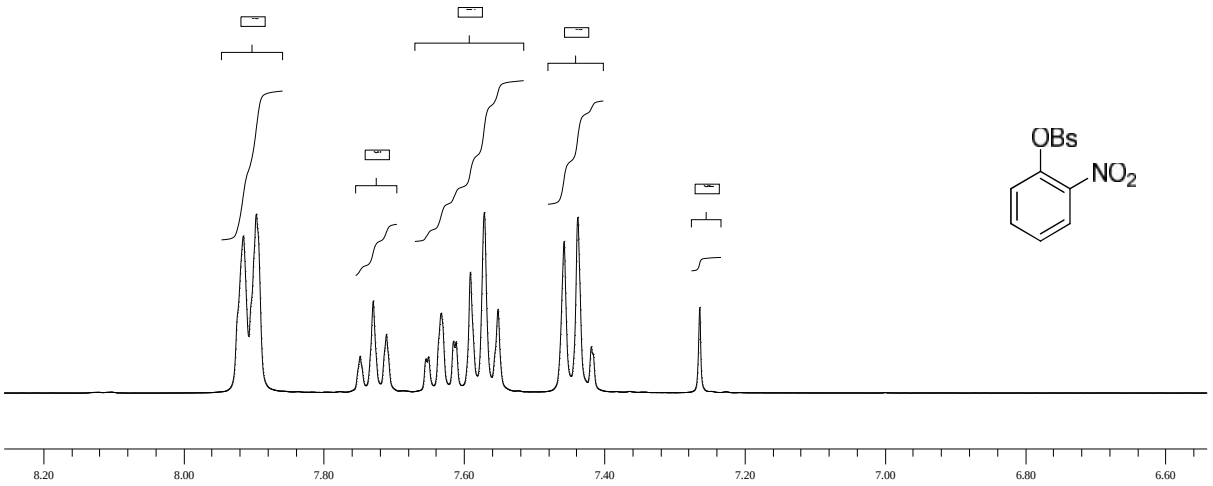
^{1}H-NMR of **38** in $CDCl_3$



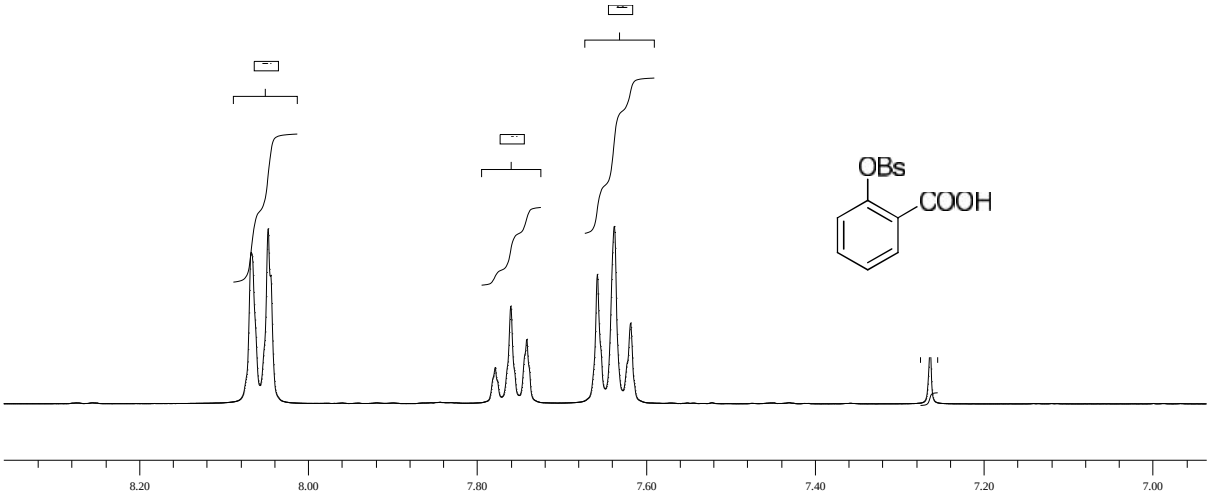
^{1}H-NMR of **39** in $CDCl_3$



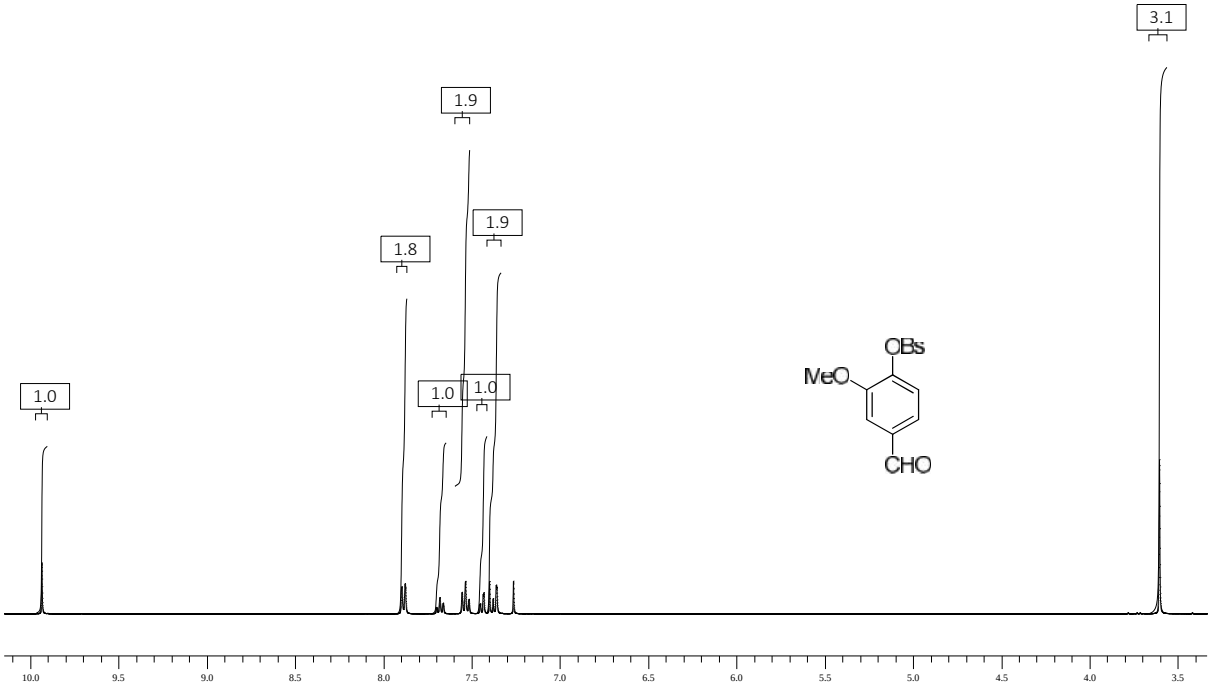
^{13}C-NMR of **39** in $CDCl_3$



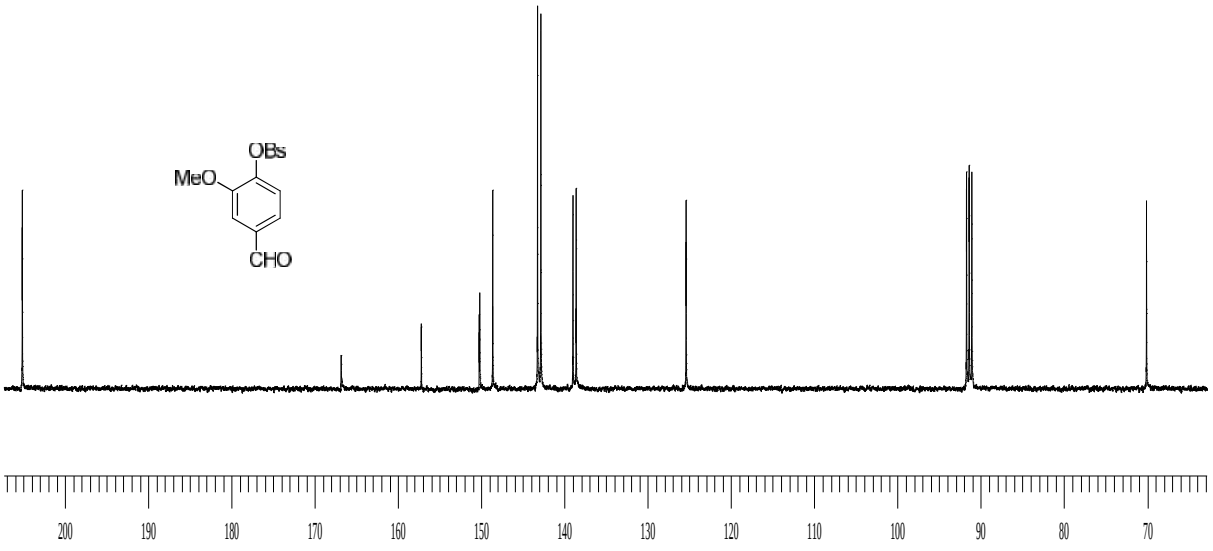
^{1}H-NMR of **40** in $CDCl_3$



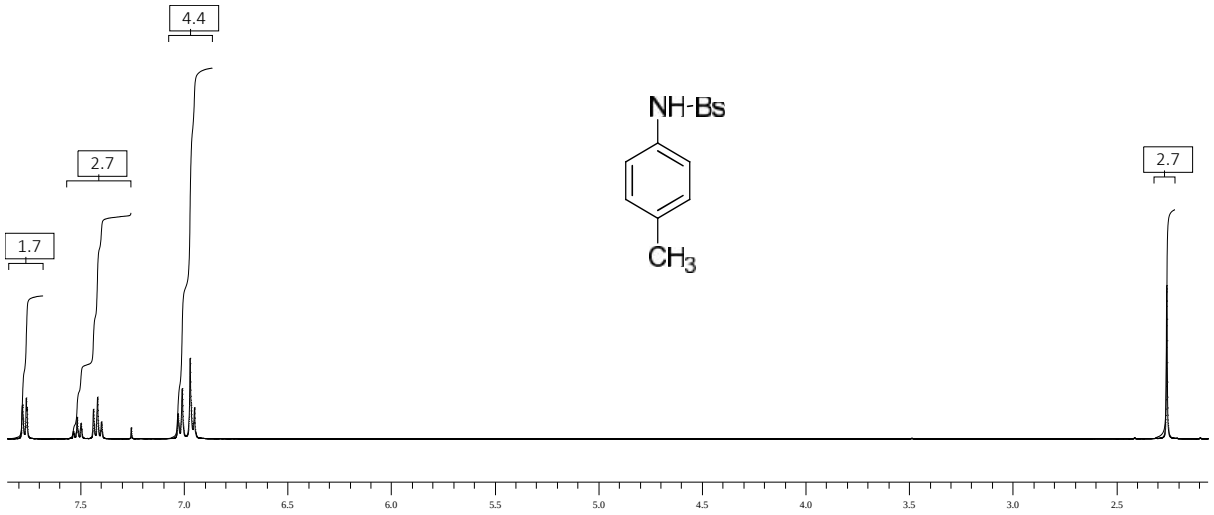
^{1}H-NMR of **41** in $CDCl_3$



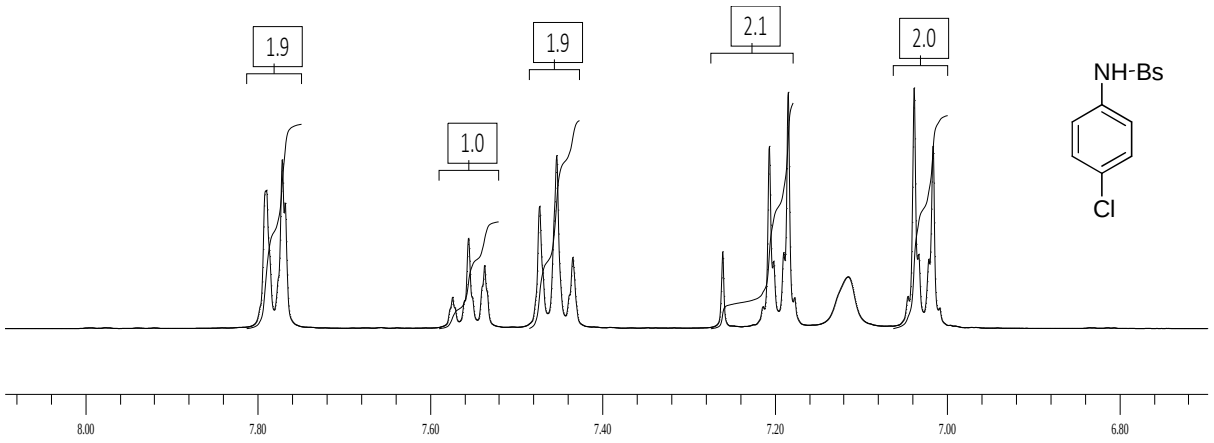
^{1}H-NMR of **42** in $CDCl_3$



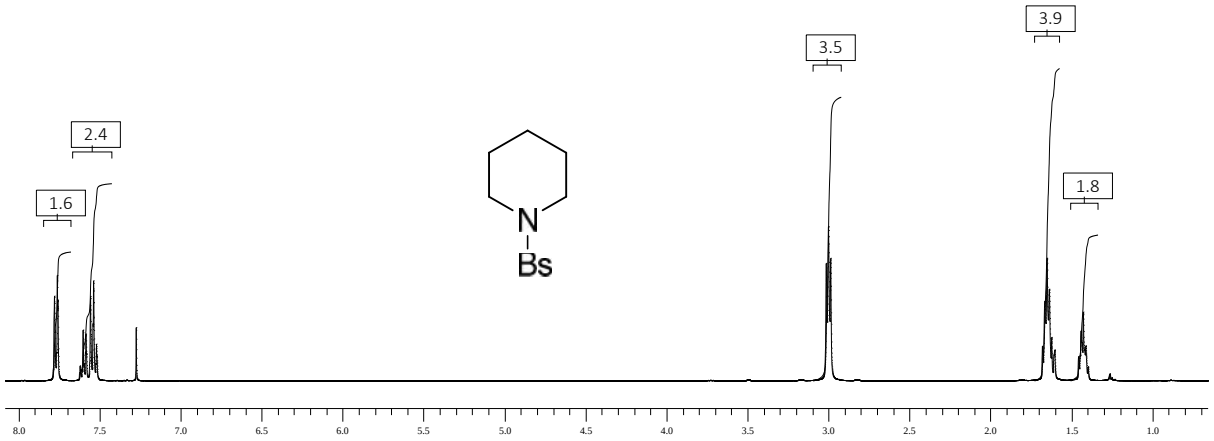
^{13}C-NMR of **42** in $CDCl_3$



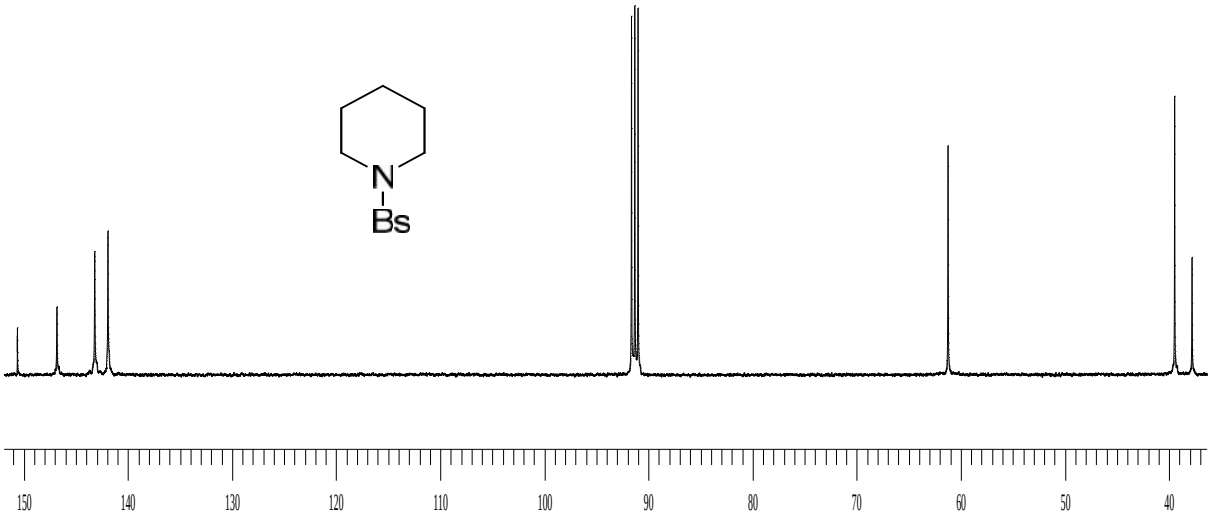
^{1}H-NMR of **43** in $CDCl_3$



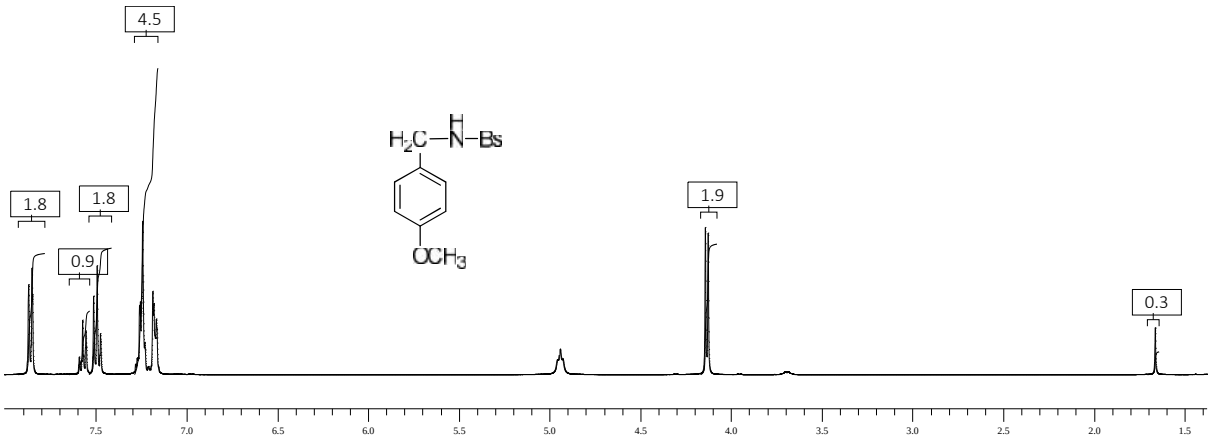
^{1}H-NMR of **44** in $CDCl_3$



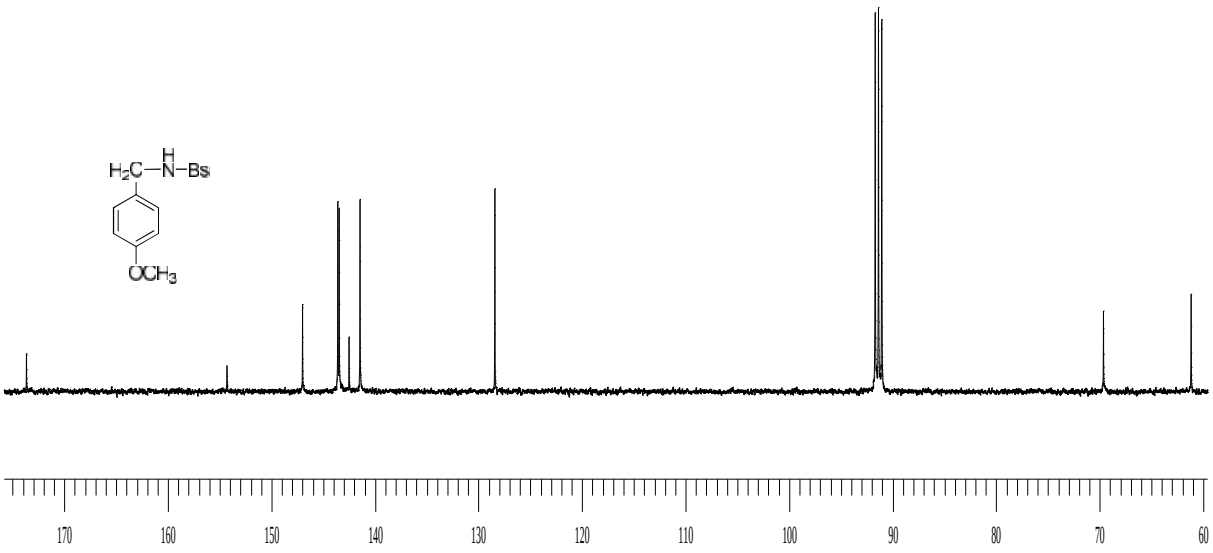
^{1}H-NMR of **45** in $CDCl_3$



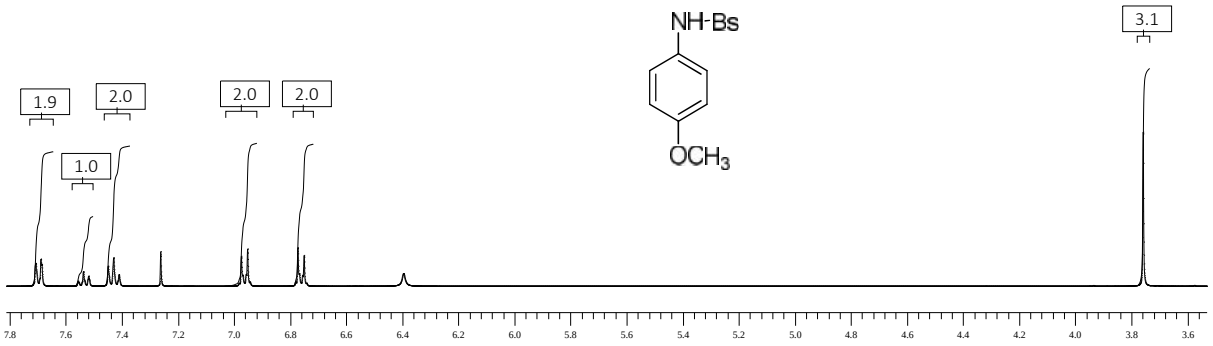
^{13}C-NMR of 45 in $CDCl_3$



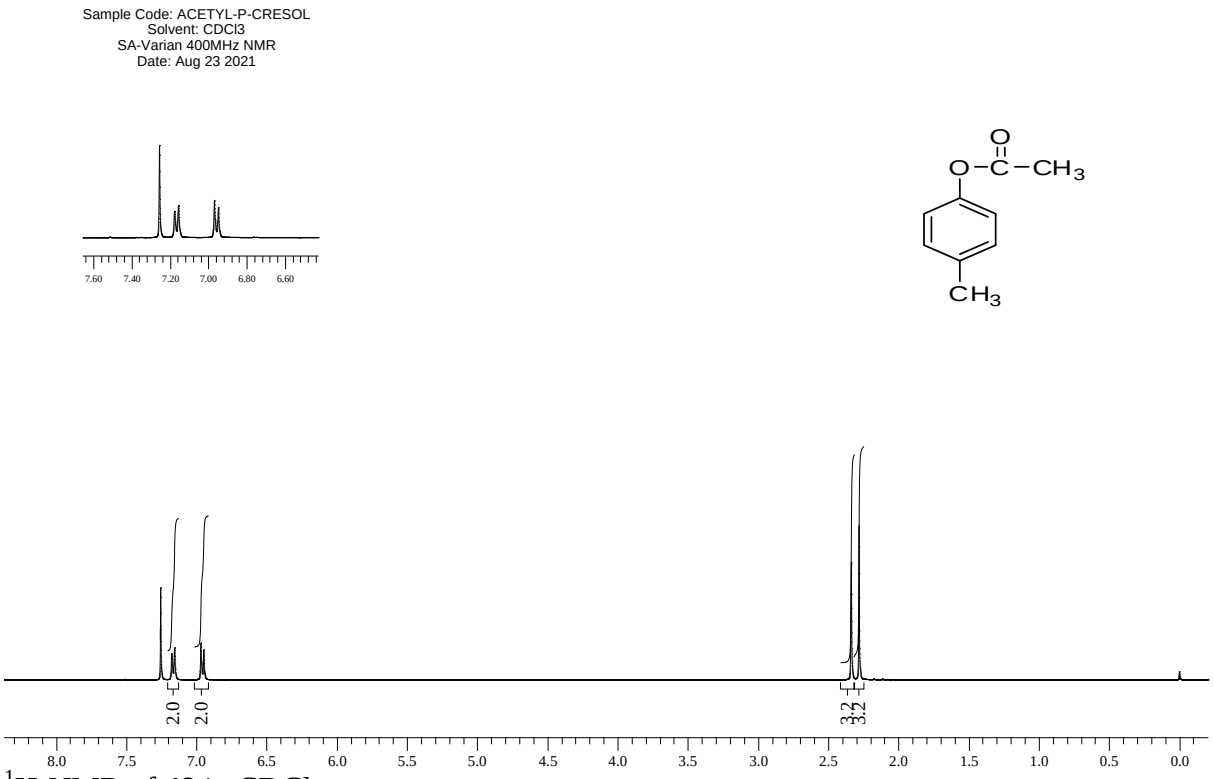
^{1}H-NMR of **46** in $CDCl_3$



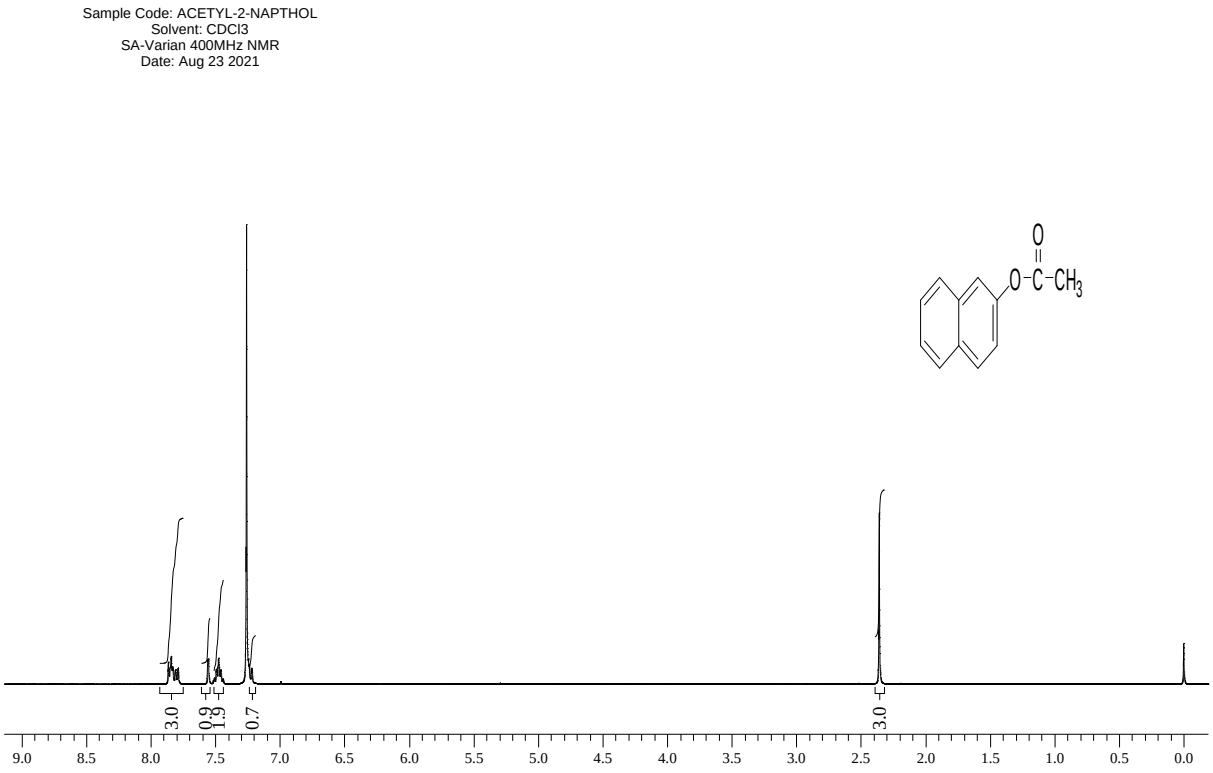
^{13}C-NMR of 46 in $CDCl_3$



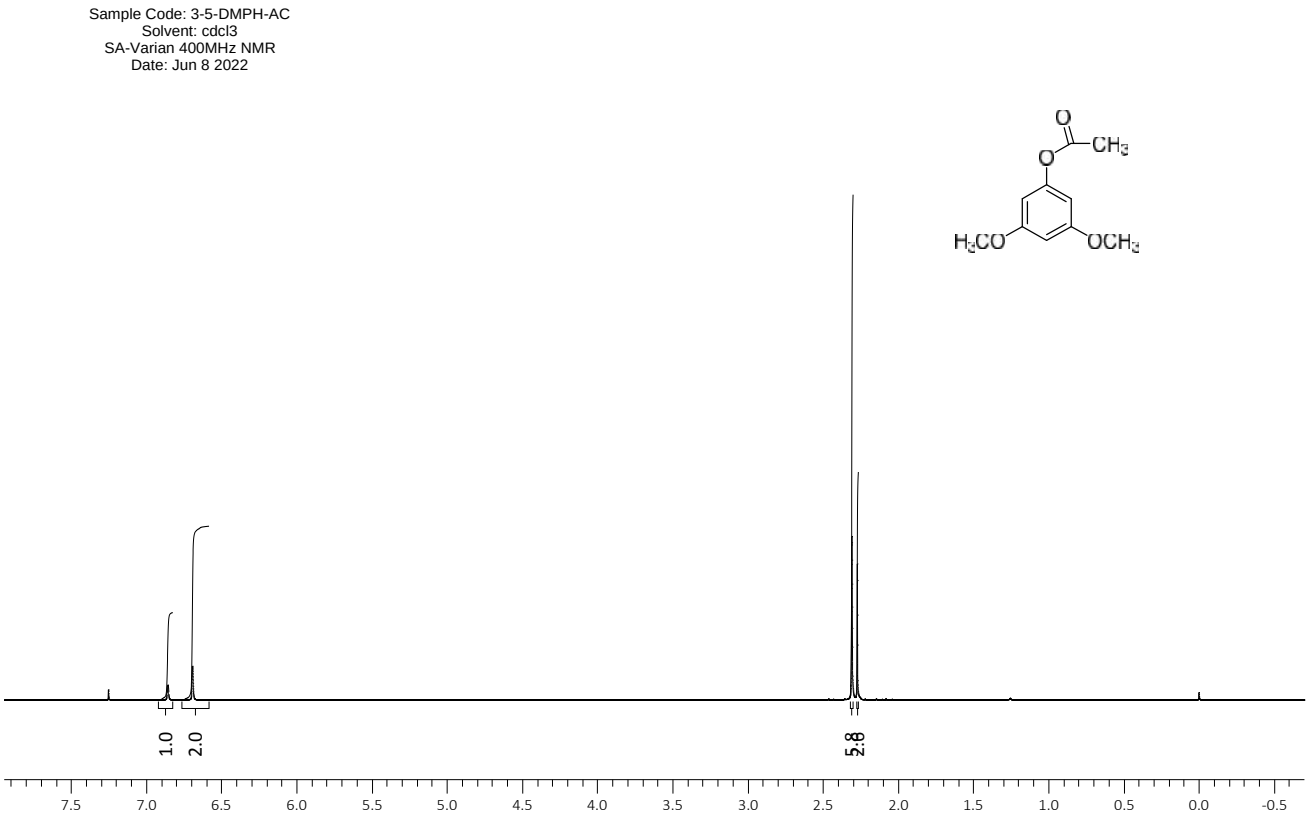
^{1}H-NMR of **47** in $CDCl_3$



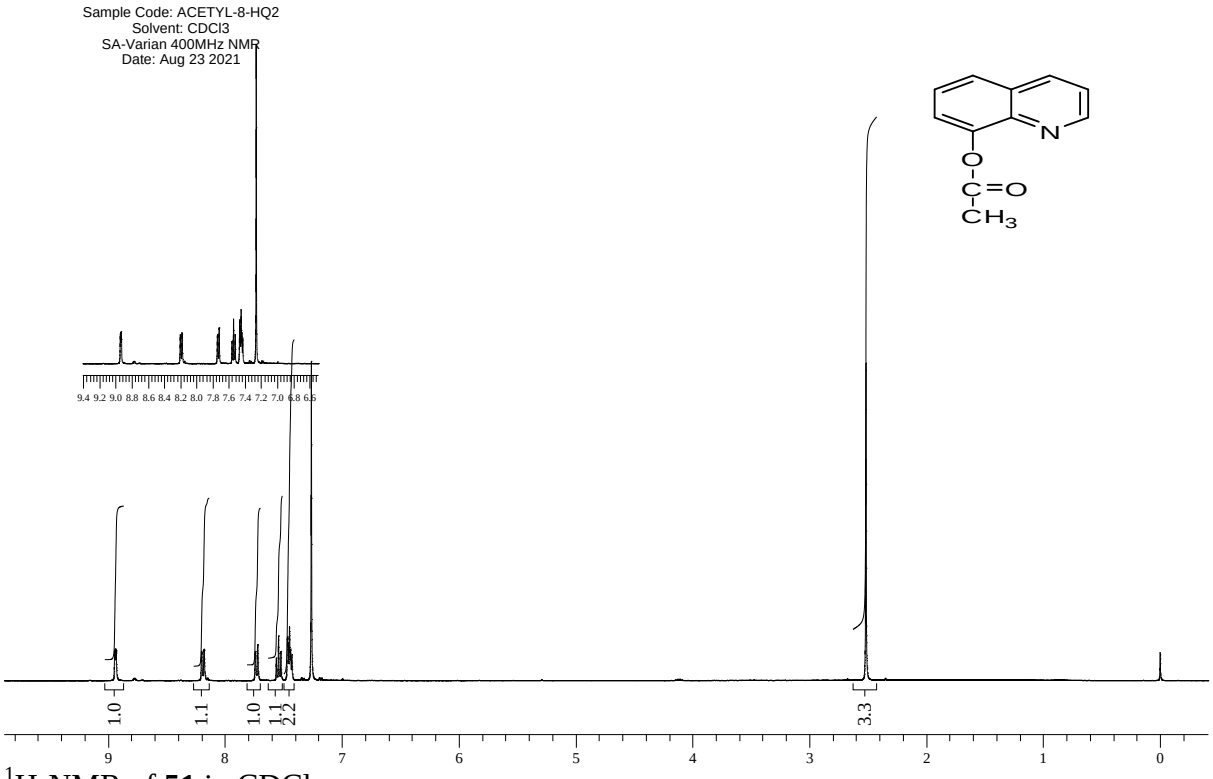
^{1}H-NMR of **48** in $CDCl_3$



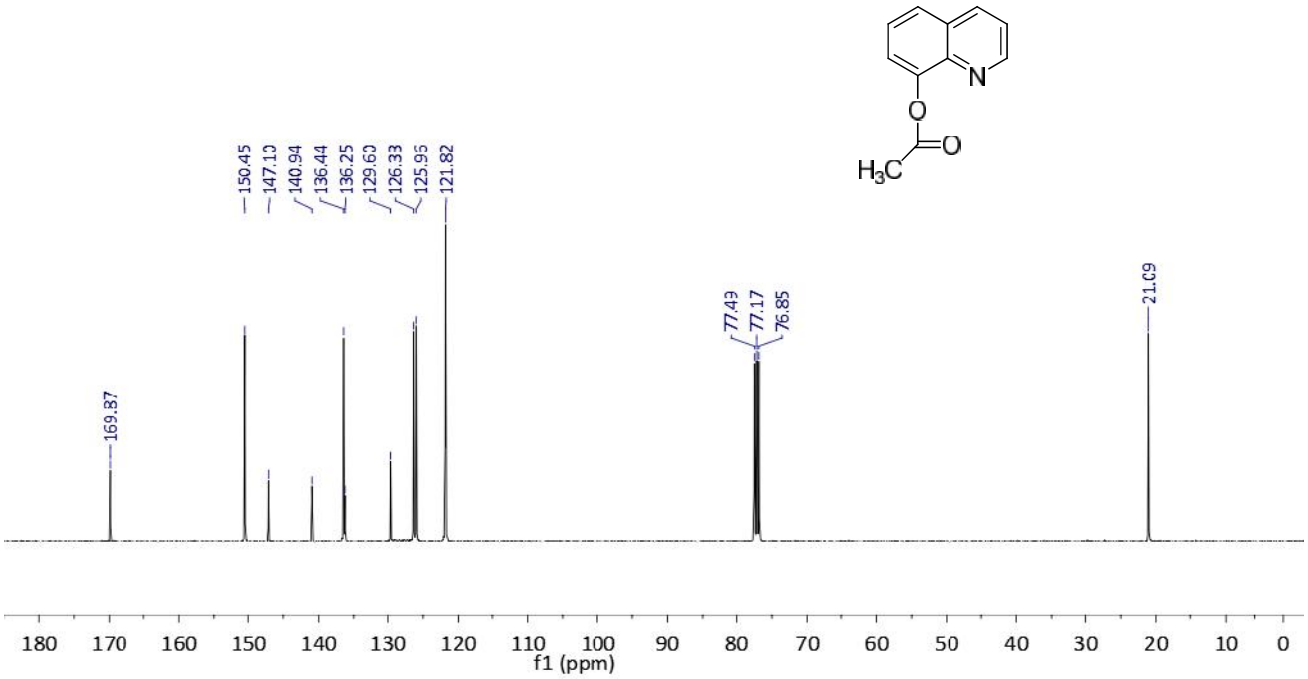
^{1}H-NMR of **49** in $CDCl_3$



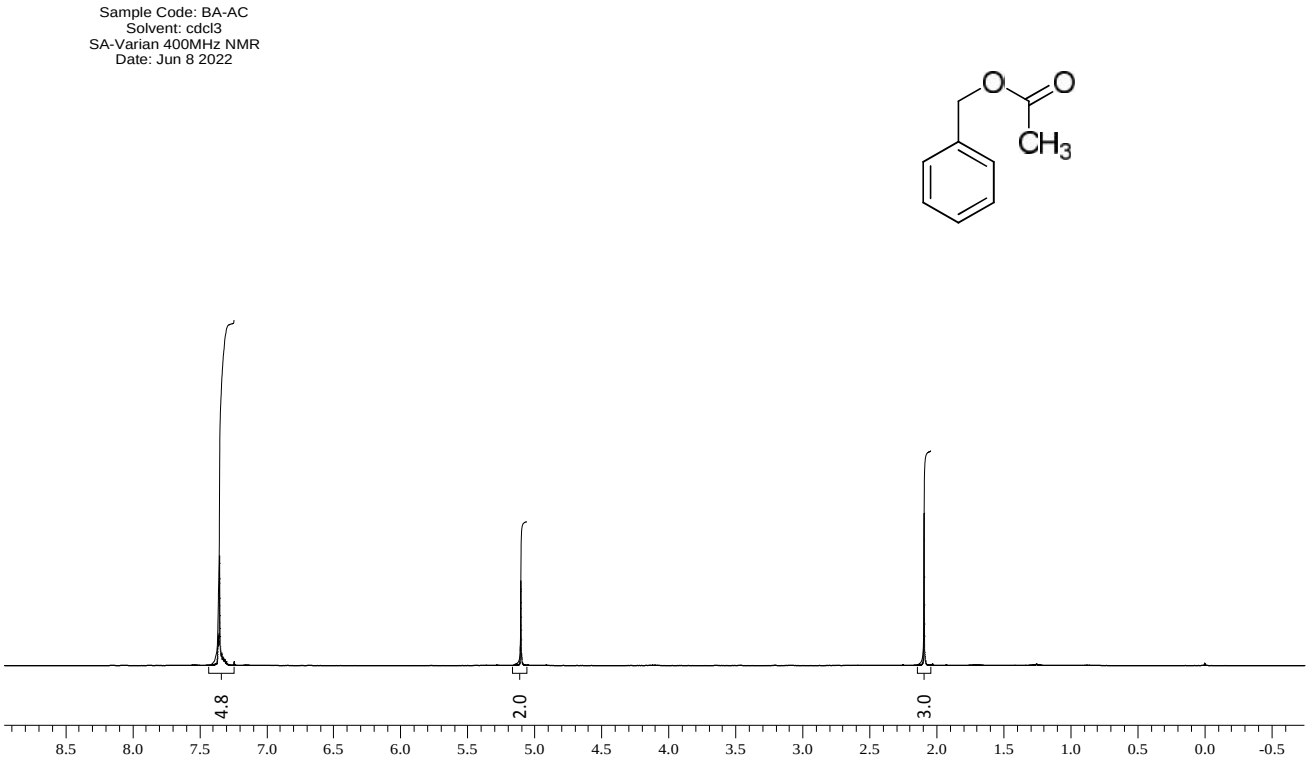
^{1}H-NMR of **50** in $CDCl_3$



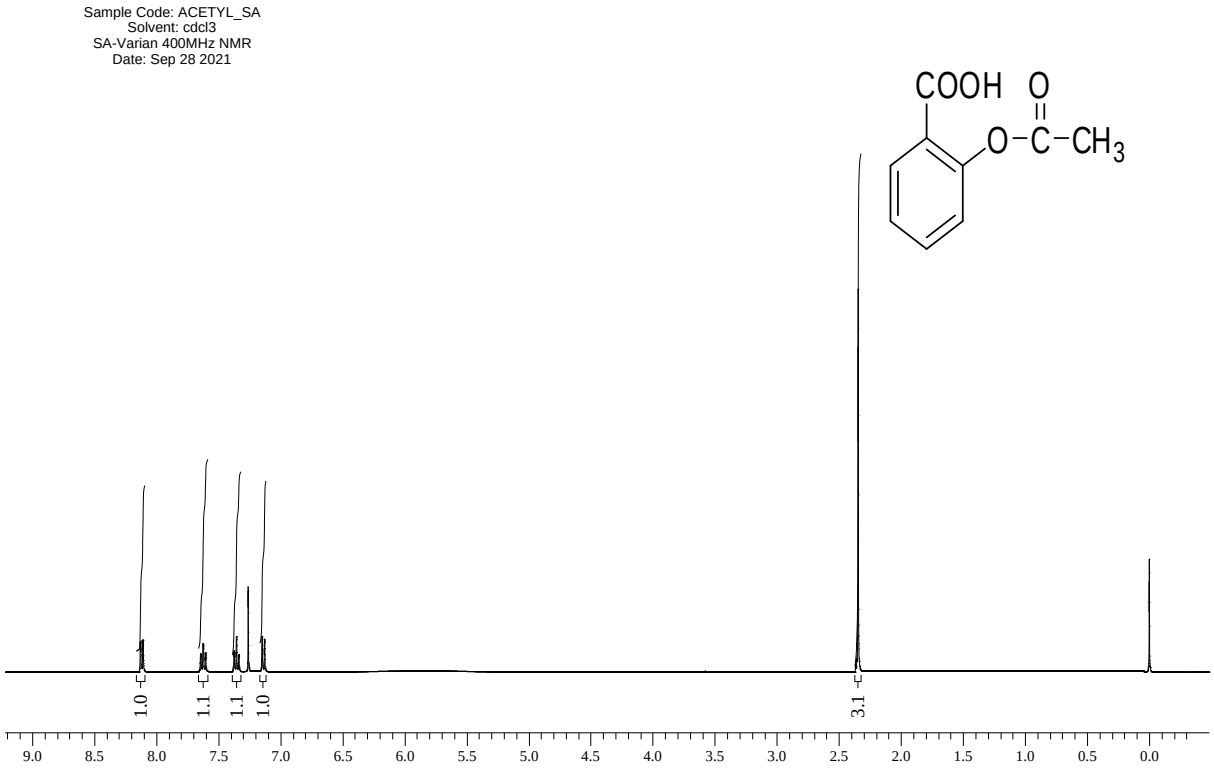
^{1}H-NMR of **51** in $CDCl_3$



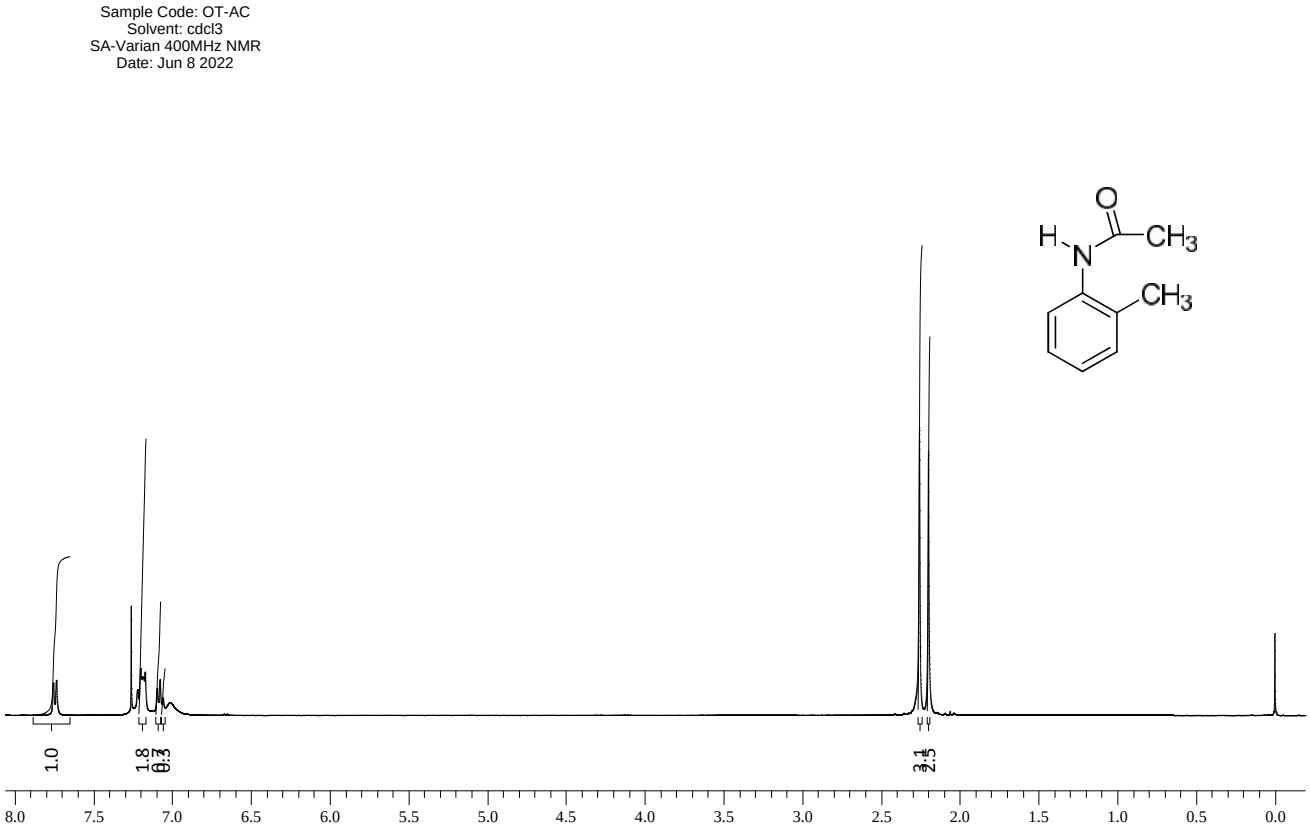
^{13}C-NMR of **51** in $CDCl_3$



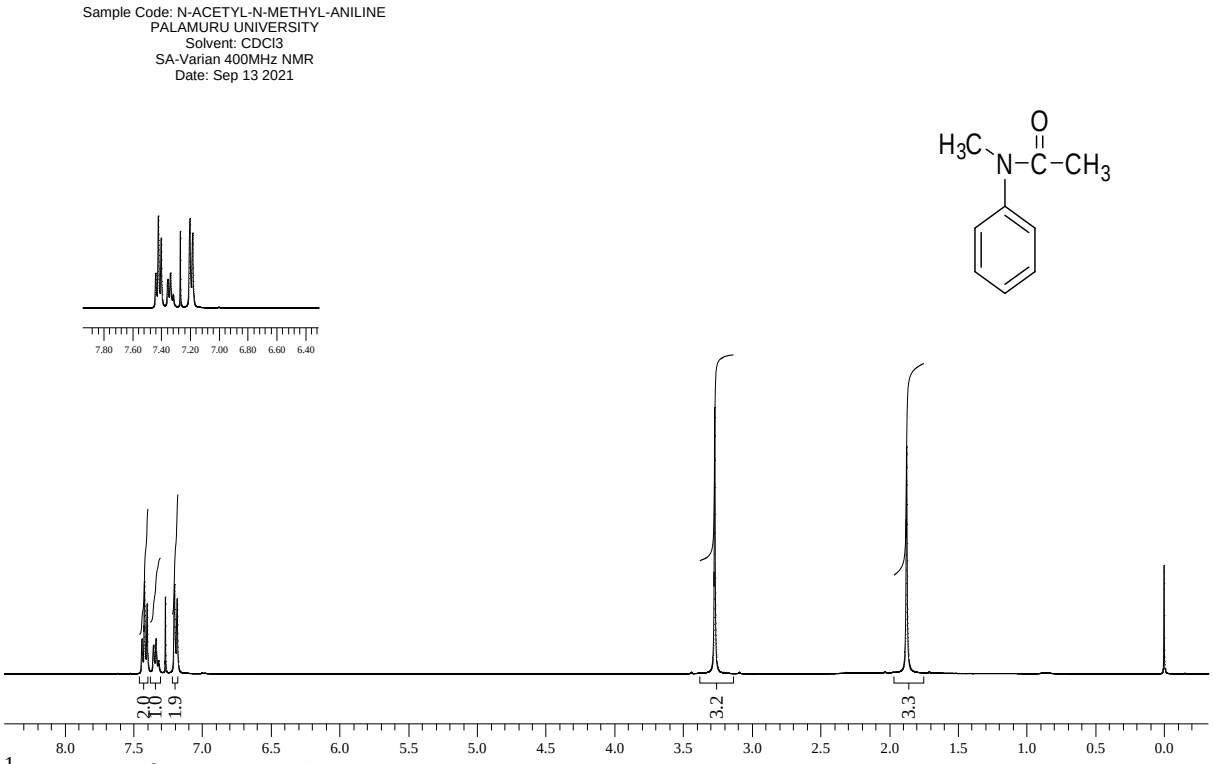
^{1}H-NMR of **52** in $CDCl_3$



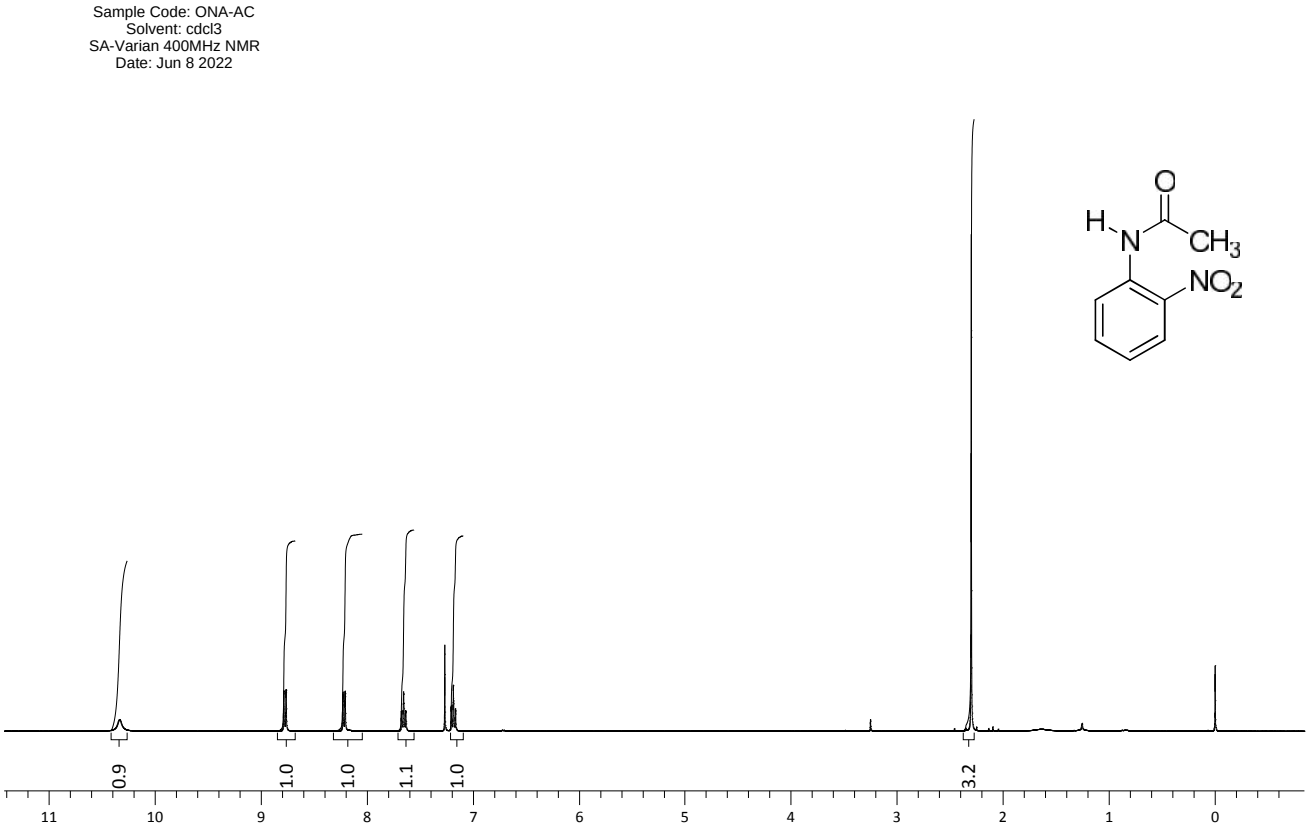
^{1}H-NMR of **53** in $CDCl_3$



^{1}H-NMR of **54** in $CDCl_3$

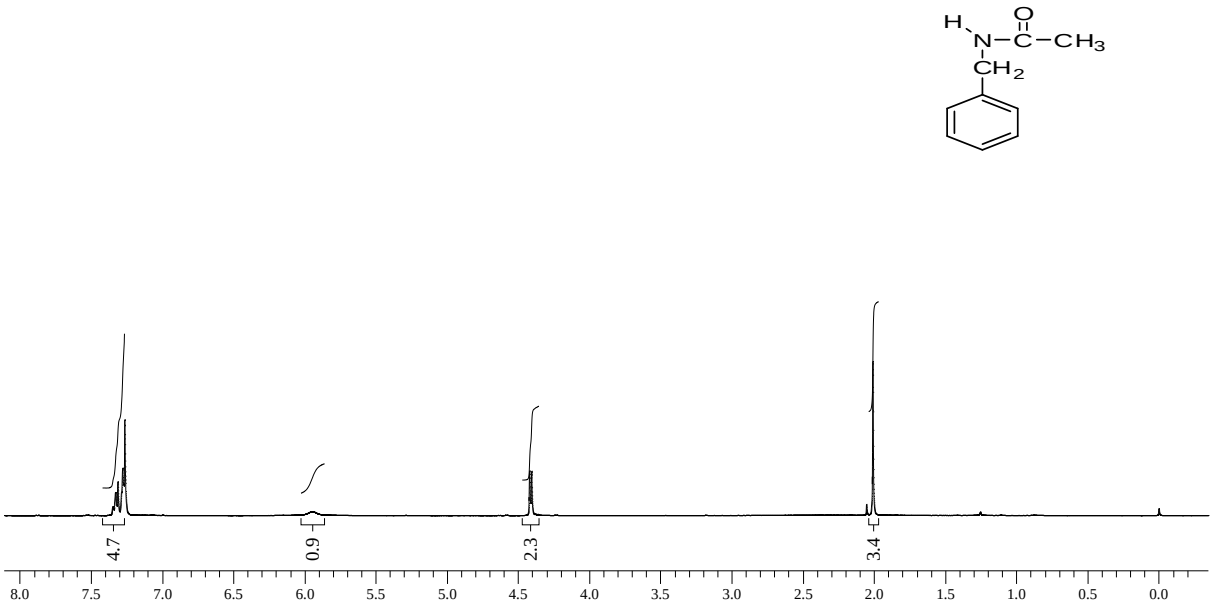


^{1}H-NMR of **55** in $CDCl_3$

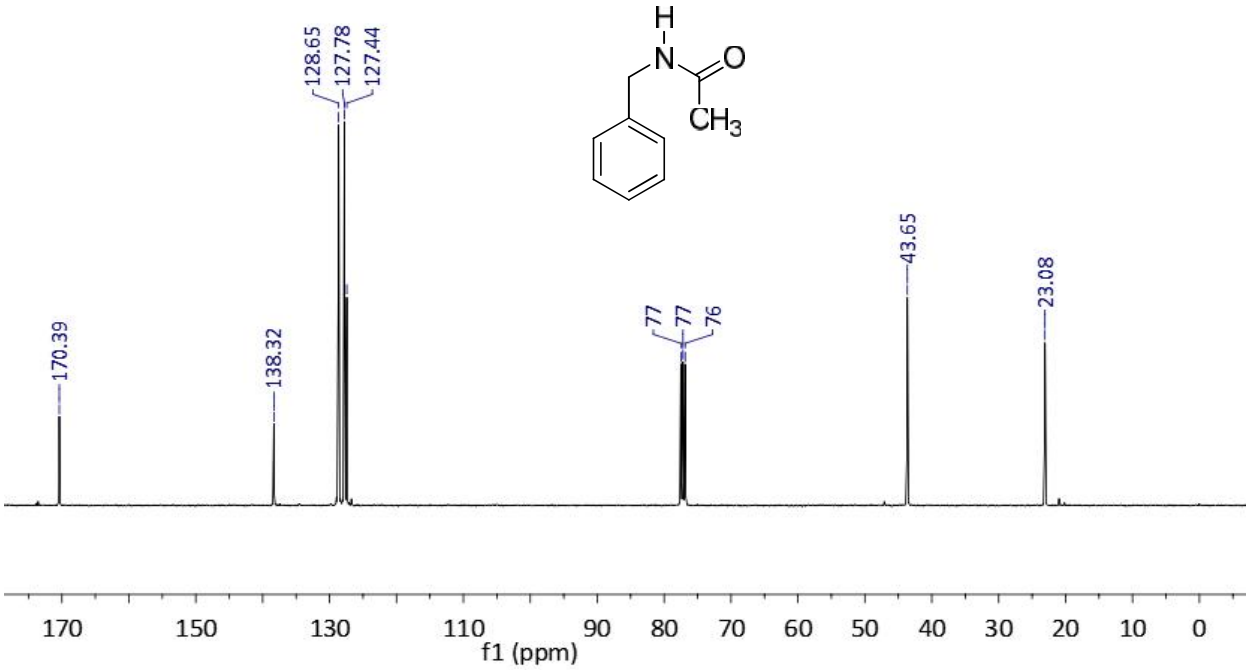


^{1}H-NMR of **56** in $CDCl_3$

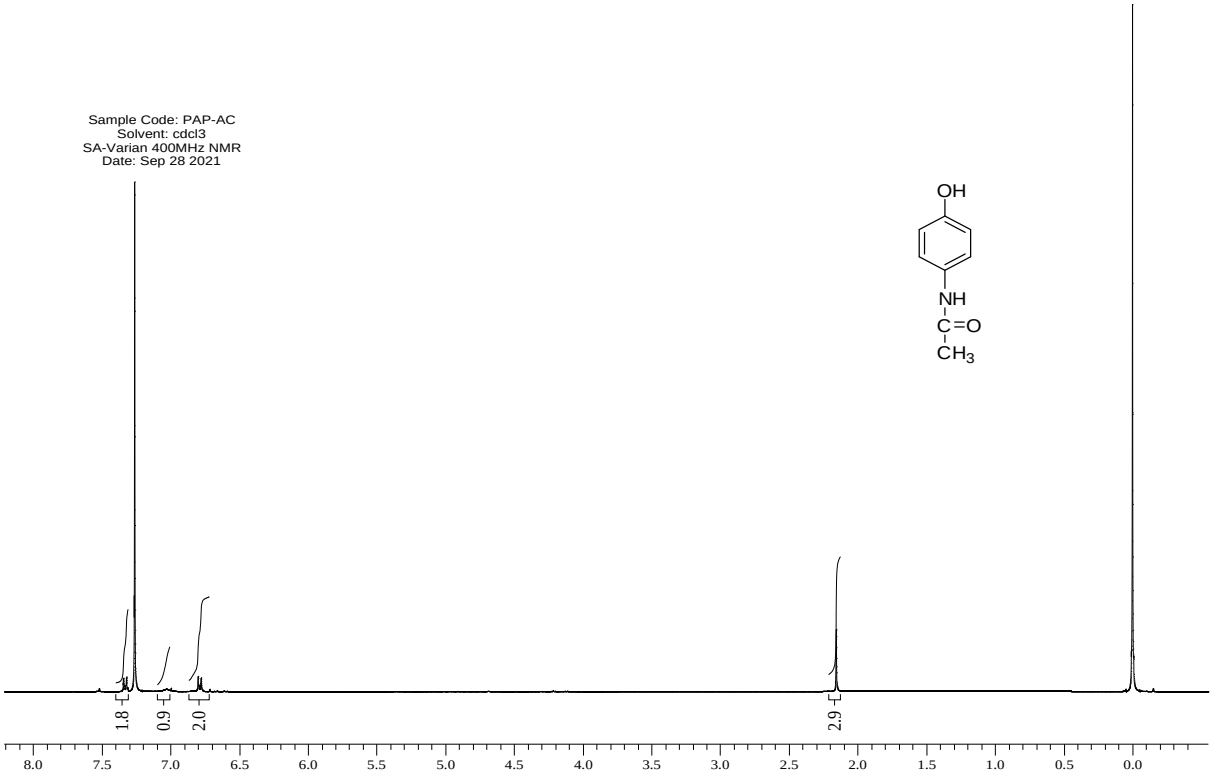
Sample Code: ACETYL-BENZYL-ANILINE
Solvent: CDCl3
SA-Varian 400MHz NMR
Date: Aug 23 2021



^{1}H-NMR of **57** in $CDCl_3$



^{13}C-NMR of **57** in $CDCl_3$



^{1}H-NMR of **58** in $CDCl_3$