Supporting Information

Scope and Mechanistic Study of the Ruthenium-Catalyzed *Ortho*-C-H Bond Activation and Cyclization Reactions of Arylamines with Terminal Alkynes

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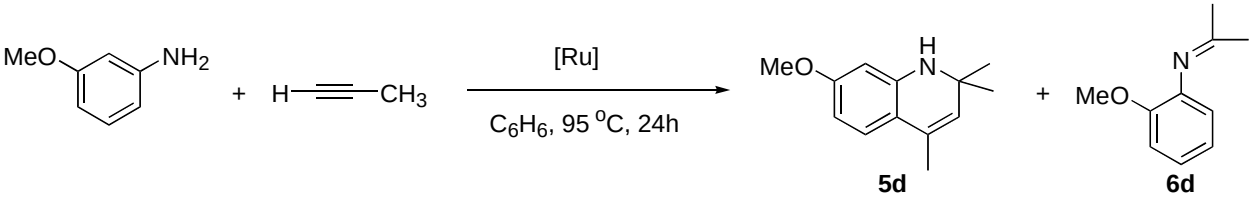
Table S1. Catalyst Activity Survey of Selected Ruthenium Complexes.[a]



Entry	Catalyst	Additive	% yield (**5d:6d**)[b]
1	$(PCy_3)_2(CO)RuHCl$	none	0
2		NH_4PF_6	35:39
3		HBF_4OEt_2	43:28
4		$AlCl_3$	0
5	$Ru_3(CO)_{12}$ (**4**)	none	0
6		NH_4PF_6	82:7
7		HBF_4OEt_2	92:2
8	$(PPh_3)_3RuCl_2$	none	0
9		NH_4PF_6	15:40
10		HBF_4OEt_2	21:38

[a]Reaction conditions: 3-methoxyanilne (0.4 mmol), propyne (2 mmol), Ru catalyst (2 mol%), additive (6 mol%), benzene (2 mL), 95 °C, 24 h. [b]Determined by GC.

Figure S1. Pseudo first-order plots of $-ln([aniline]_t/[aniline]_0)$ vs time. The $k_{obs} = 9.6 \times 10^{-2}$ h^{-1} for $C_6H_5NH_2$ ((●), $R^2 = 0.99$) and $k_{obs} = 3.9 \times 10^{-2}$ h^{-1} for $C_6D_5NH_2$ ((■), $R^2 = 0.98$).

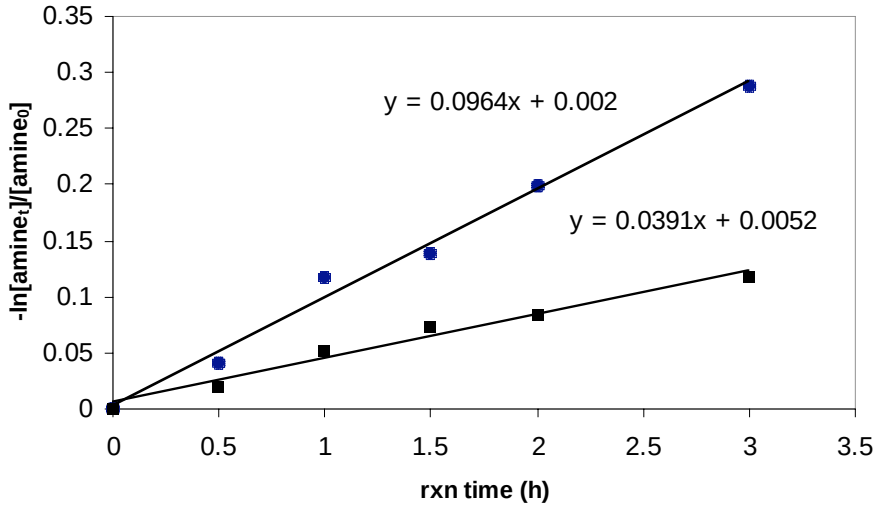


Figure S2. PCy_3 inhibition study for the coupling reaction of indoline with propyne (no PCy_3 (●), 5 mol % PCy_3 (○)).

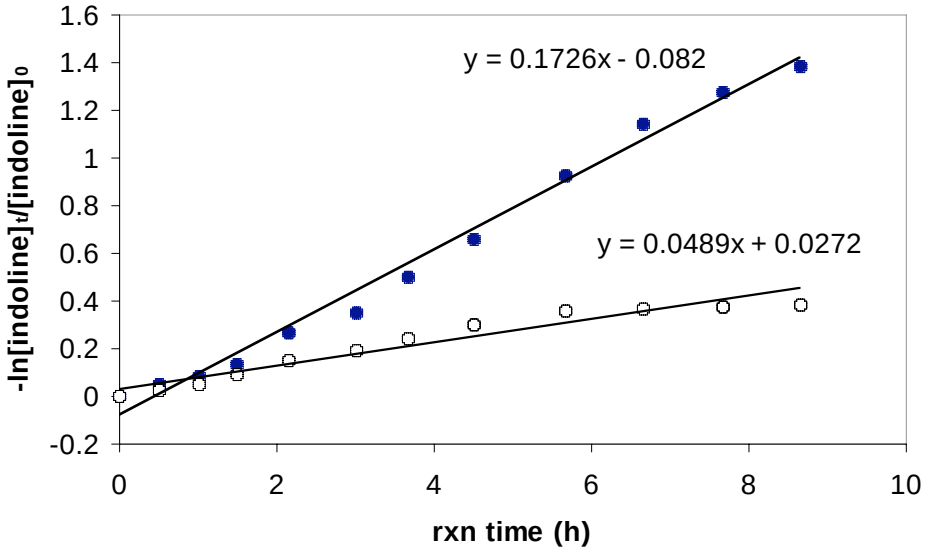


Figure S3. First order plots of $-ln([p\text{-X-}C_6H_5NH_2]_t/[p\text{-X-}C_6H_5NH_2]_0)$ vs time. X = OMe ($k_{obs} = 8.5 \times 10^{-1}$ h^{-1}), Me ($k_{obs} = 2.1 \times 10^{-1}$ h^{-1}), H ($k_{obs} = 6.1 \times 10^{-2}$ h^{-1}), CF_3 ($k_{obs} = 1.1 \times 10^{-2}$ h^{-1}).

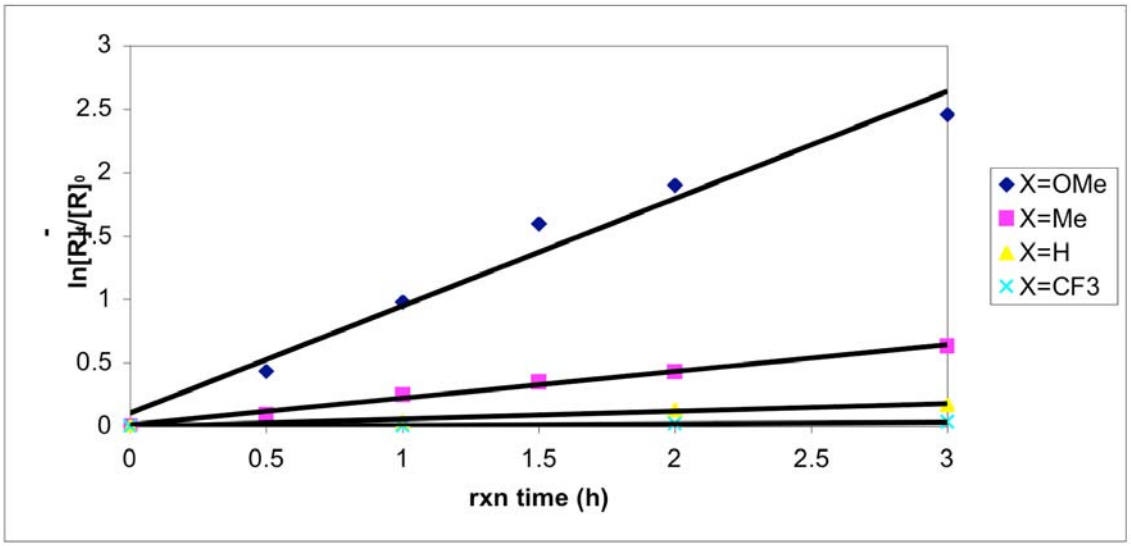
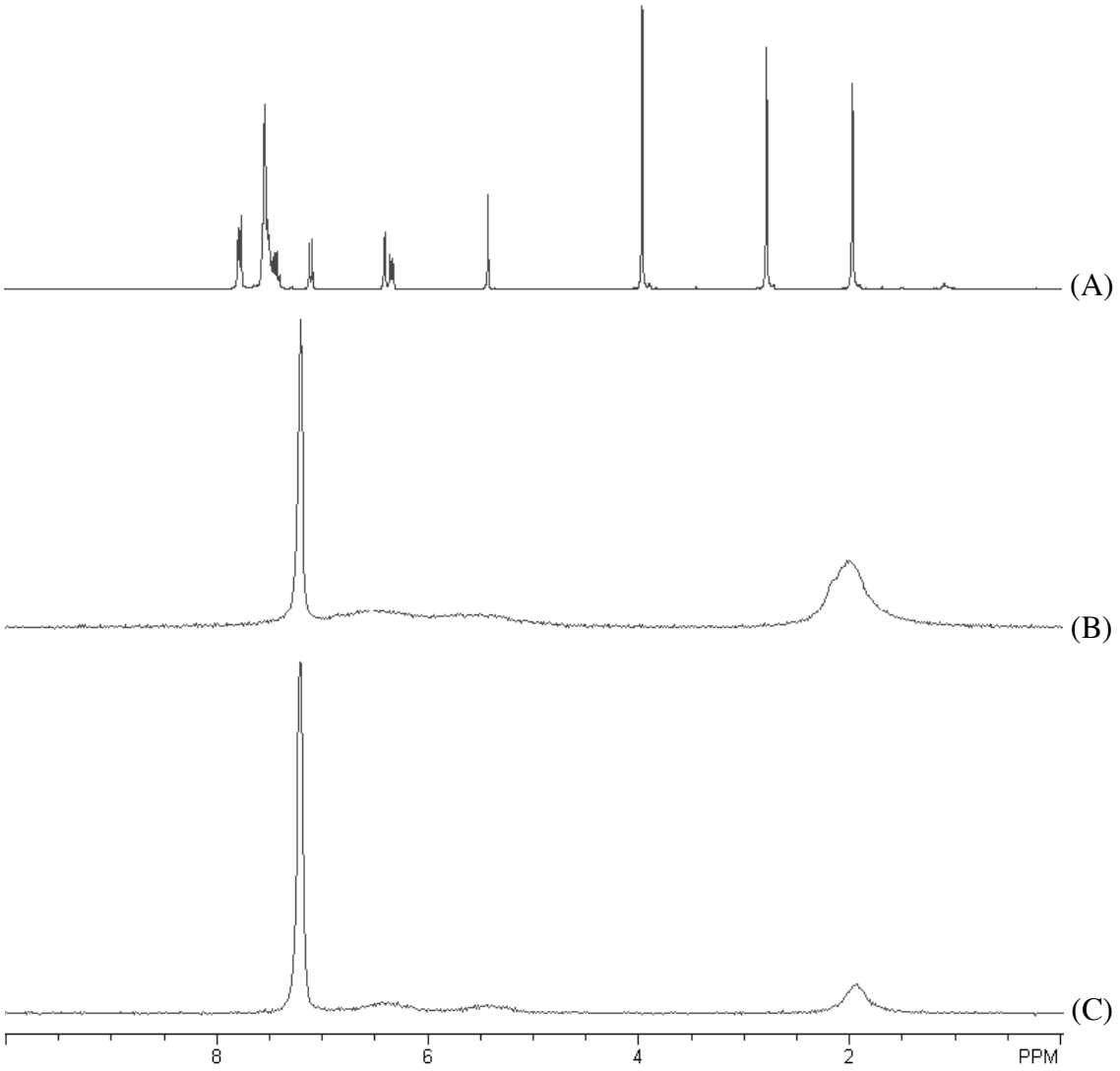
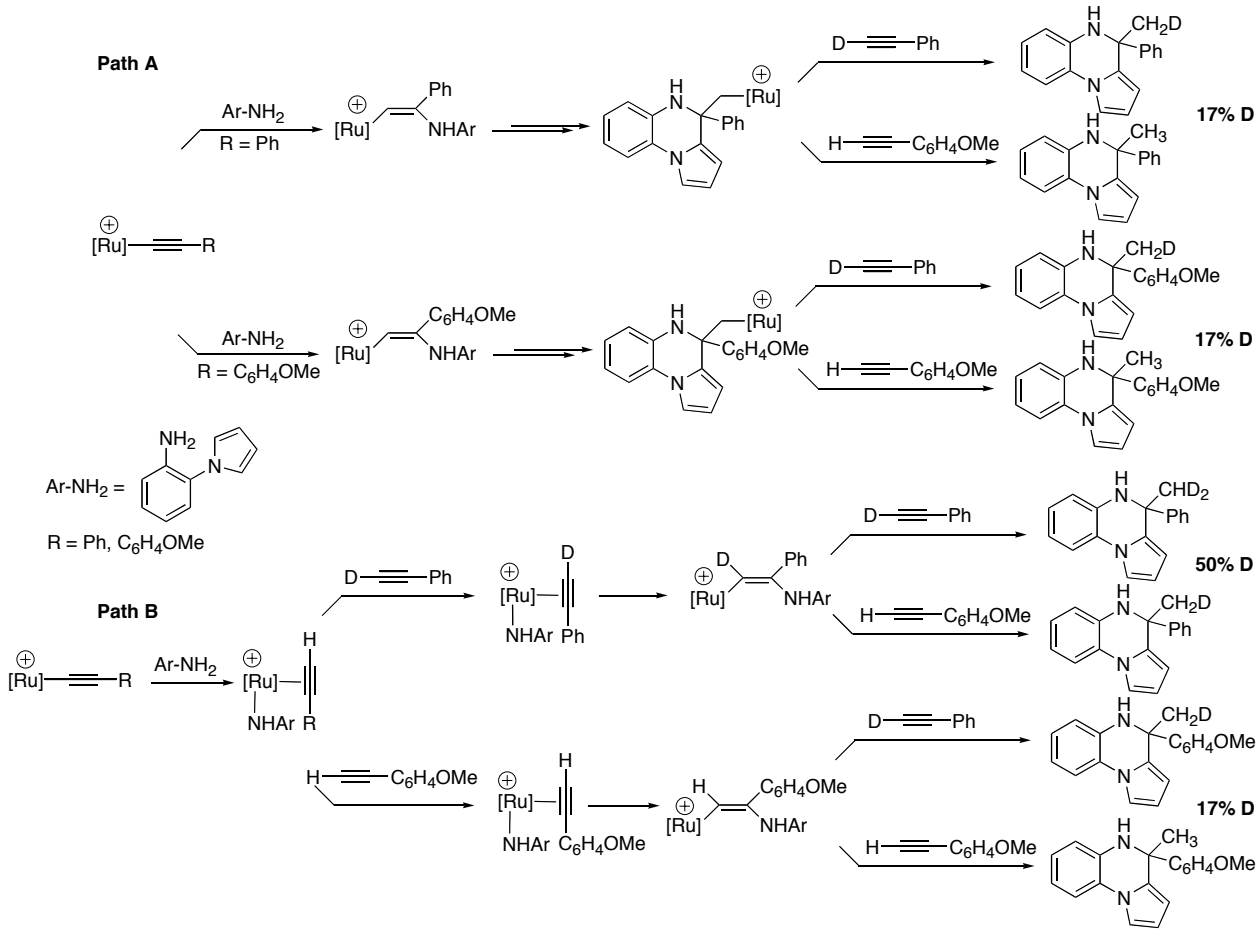


Figure S4. The ^{1}H and ^{2}H NMR Spectra of Deuterium-Labeled **5i**.



(A) ^{1}H NMR spectrum of **5i**; (B) ^{2}H NMR spectrum of **5i-*d*** obtained from the reaction of *m*-OMe-$C_6H_4NHCH_3$ and DC≡CPh; (C) ^{2}H NMR spectrum of **5i-*d*** obtained from the reaction of *m*-OMe-$C_6H_4NDCH_3$ and HC≡CPh.

Scheme S1. Deuterium incorporation analysis for the reaction of 1-(2-aminophenyl)pyrrole with DC≡CPh and HC≡CC_6H_4-*p*-OMe.



Spectroscopic Data of Organic Products.

For **5a**: ^{1}H NMR (C_6D_6, 300 MHz) δ 7.03 (m, 2H, Ar), 6.68 (td, *J* = 7.8, 1.2 Hz, 1H, Ar), 6.24 (dd, *J* = 8.1, 1.2 Hz, 1H, Ar), 5.09 (s, CH_3C=C*H*), 3.16 (br s, NH), 1.83 (d, *J* = 1.2 Hz, C*H*$_3$C=CH), 1.04 (s, NC(CH_3)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz) δ 144.2, 129.2, 129.1, 128.8, 124.4, 122.0, 117.6, 113.5, 52.2 (N*C*(CH_3)$_2$), 31.5 (2CH_3), 19.3 (CH_3); GC-MS (M^+ = 173); Anal. Calcd for $C_{12}H_{15}N$: C, 83.24; H, 10.42. Found C, 83.31; H, 10.39.

For **5b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01 (d, *J* = 7.5 Hz, 1H, Ar), 6.51 (d, *J* = 6.3 Hz, 1H, Ar), 6.23 (s, 1H, Ar), 5.29 (q, *J* = 1.2 Hz, CH_3C=C*H*), 3.64 (br s, NH), 2.27 (s, ArCH_3), 2.02 (d, *J* = 1.2 Hz, C*H*$_3$C=CH), 1.30 (s, NC(CH_3)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 143.4, 138.4, 128.6, 127.5, 123.7, 119.2 118.1, 113.7, 51.9 (N*C*(CH_3)$_2$), 31.1 (NC(*C*H_3)$_2$), 21.5 (ArCH_3), 18.7 (CH_3); HRMS (m/z): calcd for $C_{13}H_{17}N$ (M^+), 187.1361; found, 187.1361.

For **5c**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.90 (d, *J* = 8.1 Hz, 1H, Ar), 6.36 (d, *J* = 7.8 Hz, 1H, Ar), 6.18 (s, 1H, Ar), 5.01 (s, CH_3CH_2C=C*H*), 3.43 (br s, NH), 2.62 (m, C*H*(CH_3)$_2$), 2.24 (q, *J* = 7.5 Hz, CH_2), 1.38 (m, CH_2), 1.08 (s, CH_3), 1.07 (d, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.03 (t, *J* = 7.5 Hz, CH_2C*H*$_3$), 0.78 (t, *J* = 7.6 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 149.4, 144,0, 134.8, 124.3, 123.2, 118.6, 115.0, 110.9, 54.8 (N*C*(CH_3)CH_2CH_3), 36.7 (CH), 36.8 (CH_2), 34.1 (CH_2), 24.8 (CH_3), 24.1 (CH(*C*H_3)$_2$), 13.1 (CH_3), 8.8(CH_3); HRMS (m/z): calcd for $C_{19}H_{29}NO$ $(M)^+$, 243.1987; found, 243.1969.

For **5d**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01 (d, *J* = 8.4 Hz, 1H, Ar), 6.23 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar), 6.04 (d, *J* = 2.1 Hz, 1H, Ar), 5.21 (q, *J* = 1.5 Hz, CH_3C=C*H*), 3.75 (s, OCH_3), 3.70 (br s, NH), 1.98 (d, *J* = 1.2 Hz, C*H*$_3$C=CH), 1.27 (s, NC(CH_3)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 160.2, 144.7, 128.2, 126.1, 124.7, 115.4, 102.2, 98.6, 55.1 (OCH_3), 51.9 (*C*(CH_3)$_2$), 31.1 (C(*C*H_3)$_2$), 18.73 (*C*H_3C=CH); GC-MS (M^+ = 203); Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found C, 76.76; H, 8.48.

For **5e**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02 (d, *J* = 8.4 Hz, 1H, Ar), 6.17 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar), 6.01 (d, *J* = 2.4 Hz, 1H, Ar), 5.10 (s, CH_3C=C*H*), 3.75 (s, OCH_3), 3.65 (br s, NH), 2.35 (m, CH_2), 1.57–1.29 (m, 10 H), 1.23 (CH_3), 0.96 (t, *J* = 7.5 Hz, CH_3), 0.91 (t, *J* = 6.6 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 160.1, 145.5, 132.8, 124.5, 124.2, 114.2, 101.8, 98.5, 55.1 (OCH_3), 54.7 (N*C*(CH_3)$_2$), 44.1, 31.9, 30.7, 30.2, 26.6, 23.3, 22.8, 14.3, 14.2; HRMS (m/z): calcd for $C_{19}H_{29}NO$ (M^+), 287.2249; found, 287.2227.

For **5f**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38 (t, *J* = 7.8 Hz, 2H, Ar), 7.18–7.07 (m, 4H, Ar), 6.36 (dd, *J* =

8.4, 1.8 Hz, 1H, Ar), 6.16 (d, *J* = 2.1 Hz, 1H, Ar), 5.31 (s, CH_3C=C*H*), 3.73 (br s, NH), 2.06 (s, CH_3), 1.33 (s, $(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 157.8, 157.2, 144.8, 129.7, 128.1, 127.0, 124.9, 123.2, 119.2, 117.2, 107.3, 103.0, 52.0 (N*C*$(CH_3)_2$), 31.2 (NC$(CH_3)_2$), 18.8 (*C*H_3C=CH); GC-MS (M^+ = 265); Anal. Calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22. Found C, 81.19; H, 7.18.

For **5g**: ^1H NMR ($CDCl_3$, 300 MHz) δ 6.90 (d, *J* = 8.4 Hz, 1H, Ar), 6.11 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar), 5.90 (d, *J* = 2.4 Hz, 1H, Ar), 5.16 (q, *J* = 1.5 Hz, CH_3C=C*H*), 4.54 and 4.23 (br s, NH and OH), 1.92 (d, *J* = 1.4 Hz, 1H, C*H*$_3$C=CH), 1.22 (s, NC$(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 156.3, 144.9, 128.4, 126.2, 125.8, 125.0, 104.6, 100.4, 52.1 (N*C*$(CH_3)_2$), 31.3 ($(CH_3)_2$), 18.8 (*C*H_3C=CH); HRMS (m/z): calcd for $C_{12}H_{15}NO$ (M^+), 189.2568; found, 189.2573.

For **5h**: ^1H NMR ($CDCl_3$, 300 MHz) δ 6.99 (d, *J* = 8.4 Hz, 1H, Ar), 6.21 (dd, *J* = 8.1, 2.4 Hz, 1H, Ar), 6.12 (d, *J* = 2.4 Hz, 1H, Ar), 5.18 (s, CH_3C=C*H*), 3.79 (s, OCH_3), 2.79 (s, NCH_3), 1.97 (d, *J* = 1.2 Hz CH_3C=C*H*), 1.30 (s, $(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 160.8, 146.9, 128.1, 127.9, 124.3, 117.5, 99.8, 98.4, 56.5 (OCH_3), 55.35 (N*C*$(CH_3)_2$), 30.9 (NCH_3), 27.5 ($(CH_3)_2$), 18.9 (*C*H_3C=CH); HRMS (m/z): calcd for $C_{14}H_{19}NO$ (M^+), 217.1467; found, 217.1464.

For **5i**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.77 (d, *J* = 7.2 Hz, 2H, Ar), 7.55–7.41 (m, 8H, Ar), 7.10 (d, *J* = 8.1 Hz, 1H, Ar), 6.40–6.32 (m, 2H, Ar), 5.42 (s, CH_3C=C*H*), 3.96 (s, OCH_3), 2.79 (s, NCH_3), 1.97 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 161.2, 147.6, 146.6, 139.7, 133.5, 129.1, 128.4, 128.2, 128.1, 128.0, 127.3, 127.0, 126.8, 115.0, 99.6, 97.6, 63.5 (OCH_3), 55.2 (N*C*$(CH_3)_2$), 33.1 (NCH_3), 23.5 (CH_3); GC-MS (M^+ = 341); Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79. Found C, 84.31; H, 6.88.

For **5j**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.55 (d, *J* = 8.7 Hz, 2H, Ar), 7.34 (d, *J* = 8.7 Hz, 2H, Ar), 6.96–6.92 (m, 5H, Ar), 6.22–6.17 (m, 2H Ar), 5.24 (s, CH_3C=C*H*), 3.86 (s, OCH_3), 3.85 (s, OCH_3), 3.84 (s, OCH_3), 2.64 (s, NCH_3), 1.80, (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 161.1, 158.9, 158.5, 146.7, 139.9, 132.9, 132.2, 130.2, 128.1, 128.0, 126.9, 115.3, 113,6, 113.5, 99.5, 97.6, 62.9 (N*C*$(CH_3)_2$), 55.4 (OCH_3), 55.3 (OCH_3), 55.2 (OCH_3), 32.9 (NCH_3), 23.6 (CH_3); HRMS (m/z): calcd for $C_{26}H_{27}NO_3$ (M^+), 401.1991; found, 401.1985.

For **5k**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.64 (d, *J* = 8.7 Hz, 2H, Ar) 7.34 (d, *J* = 7.2 Hz, 2H, Ar), 7.25–7.21 (m, 3H, Ar), 7.10 (m, 2H, Ar), 5.45 (s, CH_3C=C*H*), 3.86 (s, OCH_3), 2.78 (s, NCH_3), 1.96 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 161.2, 147.3, 146.8, 139.5, 133.5, 129.3, 128.1, 128.0, 127.8, 127.5, 127.3, 127.0, 126.5, 115.0, 99.8, 98.6, 55.3 (OCH_3), 53.2 (N*C*$(CH_3)_2$), 32.3 (NCH_3), 23.5 (CH_3); GC-MS (M^+ = 353); Anal.

Calcd for $C_{20}H_{19}NOS_2$: C, 67.95; H, 5.42. Found C, 67.46; H, 5.63.

For **5l**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.11 (s, 1H, Ar), 6.12 (s, 1H, Ar), 5.33 (s, CH_3C=C*H*), 3.78 (s, OCH_3), 3.76 (s, OCH_3), 3.65 (br s, NH), 1.97 (d, *J* = 1.2 Hz, C*H*$_3$C=CH), 1.32 (NC(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 145.0, 144.6, 128.7, 128.3, 124.3, 122.5, 121.2, 114.3, 59.2 (OCH_3), 59.1 (OCH_3), 52.1 (N*C*(CH$_3$)$_2$), 31.3 (NC(*C*H$_3$)$_2$), 18.4 (*C*H$_3$C=CH); GC-MS (M^+ = 233); Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21. Found C, 72.35; H, 8.51.

For **5m**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01 (s, 1H, Ar), 6.32 (s, 1H, Ar), 5.31 (s, CH_3C=C*H*), 3.64 (br s, NH), 2.26 (s, ArCH_3), 1.97 (d, *J* = 1.2 Hz, C*H*$_3$C=CH)), 1.27 (NC(CH$_3$)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 142.0, 135.6, 128.8, 127.8, 124.0, 122.1, 121.2, 115.2, 52.1 (N*C*(CH$_3$)$_2$), 31.0 (NC(CH$_3$)$_2$), 20.1 (ArCH_3), 18.6 (*C*H$_3$C=CH); HRMS (m/z): calcd for $C_{13}H_{16}NCl$ (M^+), 221.0971; found, 211.0965.

For **5n**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38 (d, *J* = 8.4 Hz, 1H, Ar), 7.06–6.85 (m, 5H, Ar), 4.84 (q, *J* = 1.5 Hz, CH_3C=C*H*), 3.85 (br s, NH), 1.64 (d, *J* = 1.5 Hz, C*H*$_3$C=CH), 0.83 (s, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 138.9, 135.1, 129.9, 129.4, 126.7, 126.0, 125.1, 123.3, 122.7, 120.7, 116.9, 116.2, 52.5 (N*C*(CH$_3$)$_2$), 31.6 (NC(*C*H$_3$)$_2$), 19.8 (*C*H$_3$C=CH); GC-MS (M^+ = 223).

For **5o**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02 (s, 1H, Ar), 6.42 (s, 1H, Ar), 5.34 (s, CH_3C=C*H*), 3.58 (br s, NH), 2.88 (t, *J* = 7.2 Hz, 2C*H*$_2$), 2.09 (m, CH_2), 2.06 (d, *J* = 0.9 Hz, C*H*$_3$C=CH), 1.30 (s, NC(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 144.5, 142.1, 132.8, 128.9, 127.7, 120.2, 119.4, 109.2, 51.7 (N*C*(CH$_3$)$_2$), 33.1, 32.2, 30.8, 25.7, 18.9 (*C*H$_3$C=CH); GC-MS (M^+ = 213); Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98. Found C, 84.36; H, 8.84.

For **5p**: ^{1}H NMR (C_6D_6, 300 MHz) δ 6.90 (br s, NH), 6.83 (d, *J* = 8.7 Hz, 1H, Ar), 6.70 (s, 1H, Ar), 6.61 (t, *J* = 2.7 Hz, 1H, Ar), 6.38 (d, *J* = 8.1 Hz, 1H, Ar), 5.22 (s, CH_3C=C*H*), 3.59 (br s, NH), 2.34 (s, CH_3), 1.16 (s, NC(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz) δ 138.1, 131.5, 131.1, 127.8, 125.5, 123.8, 113.4, 111.5, 111.3, 102.6, 51.0 (N*C*(CH$_3$)$_2$), 29.5 (NC(*C*H$_3$)$_2$), 22.6 (*C*H$_3$C=CH); HRMS (m/z): calcd for $C_{14}H_{16}N_2$ (M^+), 212.1313; found, 212.1307.

For **5q**: ^{1}H NMR (C_6D_6, 300 MHz) δ 6.91, (s, 1H Ar), 6.10 (s, 1H, Ar), 5.06 (q, *J* = 0.9 Hz, CH_3C=C*H*), 3.66 (m, 2CH_2), 1.77 (d, *J* = 1.5 Hz, C*H*$_3$C=CH), 1.05 (s, NC(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz) δ 144.6, 138.4, 136.2, 128.8, 127.8, 116.8, 113.3, 102.1, 65.2 and 64.5 (O*C*H$_2$*C*H$_2$O), 51.9 ((N*C*(CH$_3$)$_2$), 30.8 (NC(*C*H$_3$)$_2$), 19.1 (*C*H$_3$C=CH); HRMS (m/z): calcd for $C_{14}H_{17}NO_2$ (M)$^+$, 231.1259; found, 231.1273.

For **7a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26 (dd, *J* = 7.8, 1.5 Hz, 1H, Ar), 7.12 (dd, *J* = 3.0, 1.8 Hz, 1H, Ar), 6.92 (td, *J* = 7.8, 1.5 Hz, 1H, Ar), 6.77 (td, *J* = 7.8, 1.2 Hz, 1H, Ar), 6.69 (dd, *J* = 8.1, 1.2 Hz, 1H, Ar), 6.28 (t, *J* = 3.3 Hz, 1H, Ar), 5.96 (dd, *J* = 3.3, 1.8 Hz, 1H, Ar) 3.74 (br s, NH), 1.69 (m, CH_2), 1.47 (s, CH_3), 0.85 (t, *J* = 7.2 Hz, $CH_2C\mathit{H}_3$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 135.5, 133.5, 125.2, 124.8, 118.8, 115.5, 114.6, 114.0, 109.9, 103.2, 54.5 ($NC(CH_3)(CH_2CH_3)$), 34.6 (CH_2), 26.7 (CH_3), 8.9 (CH_3); GC-MS (M^+ = 212); Anal. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60. Found C, 79.25; H, 7.58.

For **7b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29–7.13 (m, 7H, Ar), 6.91 (td, *J* = 7.8, 1.2 Hz, 1H, Ar), 6.74 (m, 2H, Ar), 6.32 (t, *J* = 3 Hz, 1H, Ar), 6.05 (dd, *J* = 3.6, 1.5 Hz, 1H, Ar), 4.36 (br s, NH), 1.86 (s, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 146. 5, 135.3, 133.1, 128.4, 127.1, 125.9, 125.8, 124.9, 119.4, 115.9, 114.8, 114.5, 110.1, 104.7, 57.0 ($NC(CH_3)(Ph)$), 29.5 (CH_3); GC-MS (M^+ = 260).

For **7c**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12–7.02 (m, 4H, Ar), 6.78 (t, *J* = 7.2 Hz, 1H, Ar), 6.59 (m, 4H, Ar), 6.20 (t, *J* = 3 Hz, 1H, Ar), 5.88 (dd, *J* = 3.3, 1.2 Hz, 1H, Ar), 4.18 (br s, NH), 3.54 (s, OCH_3), 1.71 (s, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 158.4, 138.6, 135.4, 133.5, 127.1, 125.7, 124.8, 119.3, 115.9, 114.7, 114.3, 113.5, 110.1, 104.5, 56.5 (($NC(CH_3)(C_6H_4$-*p*-OMe)), 55.2 (OCH_3), 29.3 (CH_3); HRMS (m/z): calcd for $C_{19}H_{18}N_2O$ (M^+), 290.1419; found, 290.1420.

For **7d**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.19 (dd, *J* = 7.8, 1.2 Hz, 1H, Ar), 7.08 (q, *J* = 1.5 Hz, 1H, Ar), 7.04 (dd, *J* = 5.4, 2.7 Hz, 1H, Ar), (dd, *J* = 4.8, 1.5 Hz, 1H, Ar), 6.88–6.83 (m, 2H, Ar), 6.71 (td, *J* = 7.5, 1.2 Hz, 1H, Ar), 6.58 (dd, *J* = 8.1, 1.2 Hz, 1H, Ar), 6.25 (t, *J* = 3.3 Hz, 1H, Ar), 5.94 (dd, *J* = 3.6, 1.5 Hz, 1H, Ar), 4.11 (br s, NH), 1.78 (s, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 148.4, 135.1, 133.1, 126.3, 125.9, 125.2, 124.8, 120.5, 119.3, 115.6, 114.6, 114.1, 110.1, 103.9, 54.8 ($NC(CH_3)(2$-$SC_4H_3)$), 28.9 (CH_3); HRMS (m/z): calcd for $C_{16}H_{14}N_2S(M^+)$, 266.0878; found, 266.0875.

For **8a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (d, *J* = 8.1 Hz, 1H, Ar), 7.78 (m, 1H, Ar), 7.53 (d, *J* = 7.8 Hz, 1H, Ar), 7.14–7.04 (m, 2H, Ar), 6.87–6.84 (m, 2H, Ar), 6.64 (m, 1H, Ar), 6.25 (s, 1H, Ar), 3.51 (br s, NH), 1.40 (s, $(CH_3)_2$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 143.3, 136.4, 134.1, 129.9, 126.9, 124.2, 122.3, 121.0, 120.9, 119.8, 116.7, 116.5, 111.9, 96.2, 51.8 ($NC(CH_3)_2$), 28.6 ($NC(\mathit{C}H_3)_2$); GC-MS (M^+ = 243).

For **8b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.97 (d, *J* = 8.1 Hz, 1H, Ar), 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H, Ar), 7.65 (d, *J* = 6.9 Hz, 1H, Ar), 7.27–7.16 (m, 4H, Ar), 6.99–6.85 (m, 4H, Ar), 6.76 (dd, *J* = 7.2, 1.8 Hz, 1H, Ar), 6.39 (s, 1H, Ar), 4.32 (br s, NH), 2.21 (s, $ArCH_3$), 1.88 (s, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 142.1,

141.9, 136.9, 136.4, 134.2, 129.7, 129.1, 127.4, 126.1, 124.2, 122.6, 121.2, 121.0, 119.9, 116.9, 116.6, 111.9, 99.0, 57.6 (N*C*(CH_3)(*p*-tol)), 29.2 (CH_3), 21.1 (CH_3); HRMS (m/z): calcd for $C_{23}H_{20}N_2$ (M^+), 324.1626; found, 324.1632.

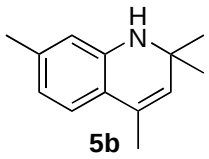
For **8c**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (d, *J* = 7.8 Hz, 1H, Ar), 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H, Ar), 7.69 (d, *J* = 6.9 Hz, 1H, Ar), 7.15–7.04 (m, 4H, Ar), 6.88–6.75 (m, 4H, Ar), 6.54 (dd, *J* = 7.8, 1.5 Hz, 1H, Ar), 6.33 (s, 1H, Ar), 4.37 (br s, NH), 1.88 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 152.1, 142.5, 135.6, 136.2, 133.4, 128.9, 128.1, 127.3, 126.6, 125.2, 123.4, 122.5, 121.0, 119.6, 117.1, 116.7, 111.9, 98.9, 55.3 (N*C*(CH_3)(*p*-tol)), 23.5 (CH_3); GC-MS (M^+ = 344). Anal. Calcd for $C_{22}H_{17}N_2Cl$: C, 76.73; H, 4.98. Found C, 76.15; H, 5.12.

For **8d**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, *J* = 8.1 Hz, 1H, Ar), 7.22 (dd, *J* = 7.8, 1.2 Hz, 1H, Ar), 7.13 (d, *J* = 7.5 Hz, 1H, Ar), 7.10–7.02 (m, 2H, Ar), 6.91–6.85 (m, 2H, Ar), 6.38 (s, 1H, Ar), 4.38 (br s, NH), 3.75 (s, OCH_3), 1.70 (m, CH_2), 1.47 (s, CH_3), 0.92 (t, *J* = 7.2 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 152.1, 136.2, 135.8, 133.4, 128.4, 128.1, 127.3, 126.5, 124.2, 122.6, 117.9, 116.9, 111.9, 99.0, 58.1 (OCH_3), 56.9 (N*C*(CH_3)(CH_2CH_3)), 34.8 (CH_2), 26.9 (CH_3), 9.8 (CH_3); GC-MS (M^+ = 292); Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.08; H, 6.85. Found C, 78.15; H, 6.72.

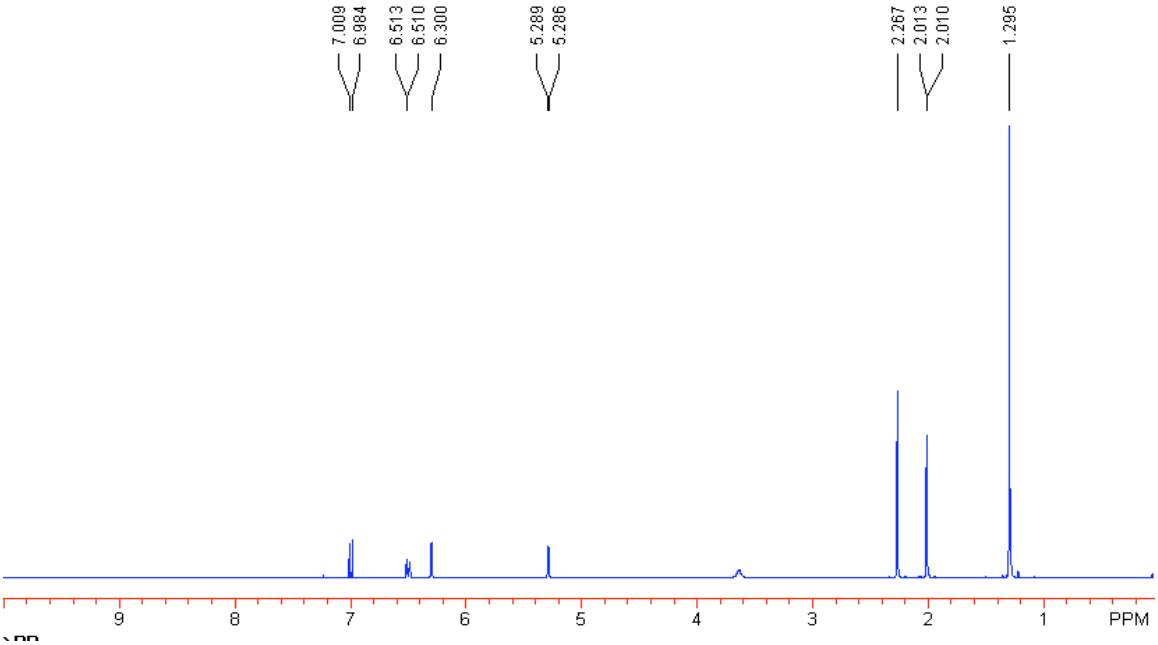
For **9a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.13 (br s, NH), 7.57 (d, *J* = 7.8 Hz, 1H, Ar), 7.35 (d, *J* = 8.1 Hz, 1H, Ar), 7.23–6.96 (m, 4H, Ar), 6.61 (t, *J* = 7.5 Hz, 1H, Ar), 6.51 (d, *J* = 7.8 Hz, 1H, Ar), 3.70 (br s, NH), 2.24 (m, 1H, CH_2), 1.70 (s, CH_3), 1.66–1.17 (m, 3H), 0.93–0.76 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 143.9, 137.4, 130.9, 128.8, 125.9, 122.0, 120.2, 120.1, 119.6, 116.7, 113.5, 113.4, 113.0, 111.4, 57.9 (N*C*(CH_3)(Bu)), 44.4 (CH_2), 31.4 (CH_2), 27.1 (CH_2), 23.3 (CH_3), 14.4 (CH_3); HRMS (m/z): calcd for $C_{20}H_{22}N_2$ (M^+), 290.1783; found, 290.1779.

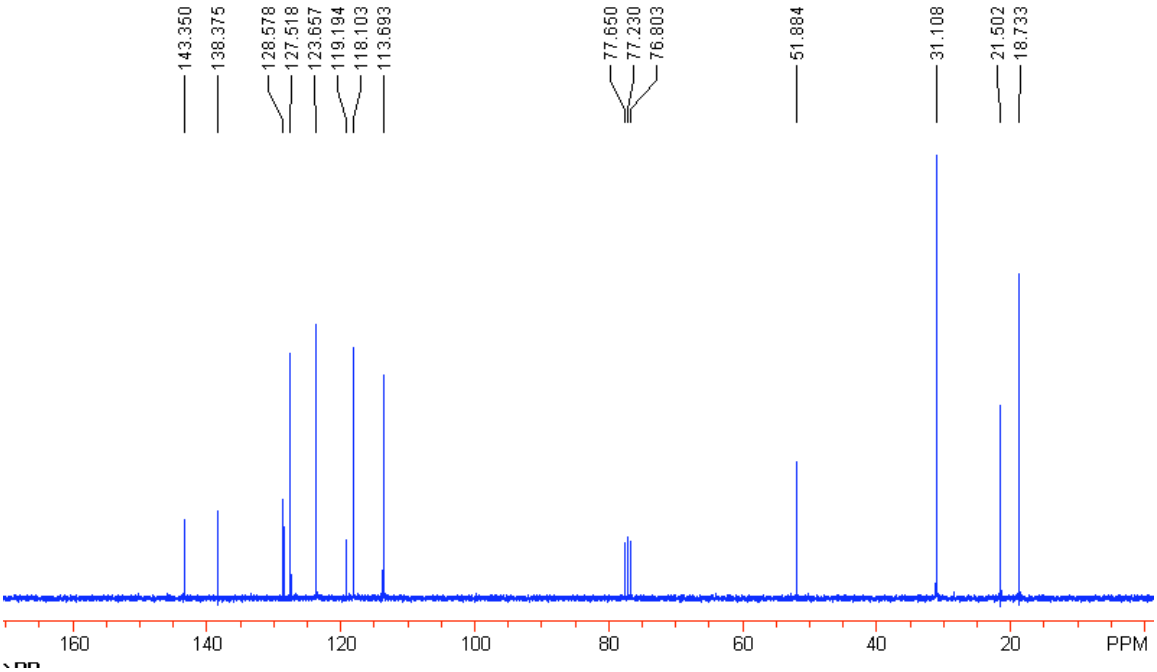
For **9b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.17 (br s, NH), 7.82 (d, *J* = 7.5 Hz, 2H, Ar), 7.46 (t, *J* = 7.8 Hz, 2H, Ar), 7.39 (t, *J* = 6.9 Hz, 2H, Ar), 7.25 (t, *J* = 6.0 Hz, 2H, Ar), 7.19–7.09 (m, 3H, Ar), 6.82 (t, *J* = 7.2 Hz, 1H, Ar), 6.66 (d, *J* = 7.5 Hz, 1H, Ar), 4.33 (br s, NH), 2.24 (CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 144.7, 139.2, 133.7, 126. 9, 125.3, 124.8, 123.6, 123.2, 123.1, 122.2, 118.5, 116.9, 116.6, 115.9, 113.8, 110.9, 109.9, 107.8, 55.7 (N*C*(CH_3)(Ph)), 25.6 (CH_3); HRMS (m/z): calcd for $C_{22}H_{18}N_2$ (M^+), 310.1470; found, 310.1467.

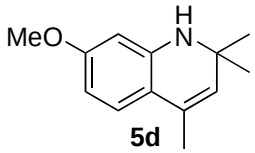
The ^{1}H and ^{13}C NMR Spectra of Selected Organic Products



5b



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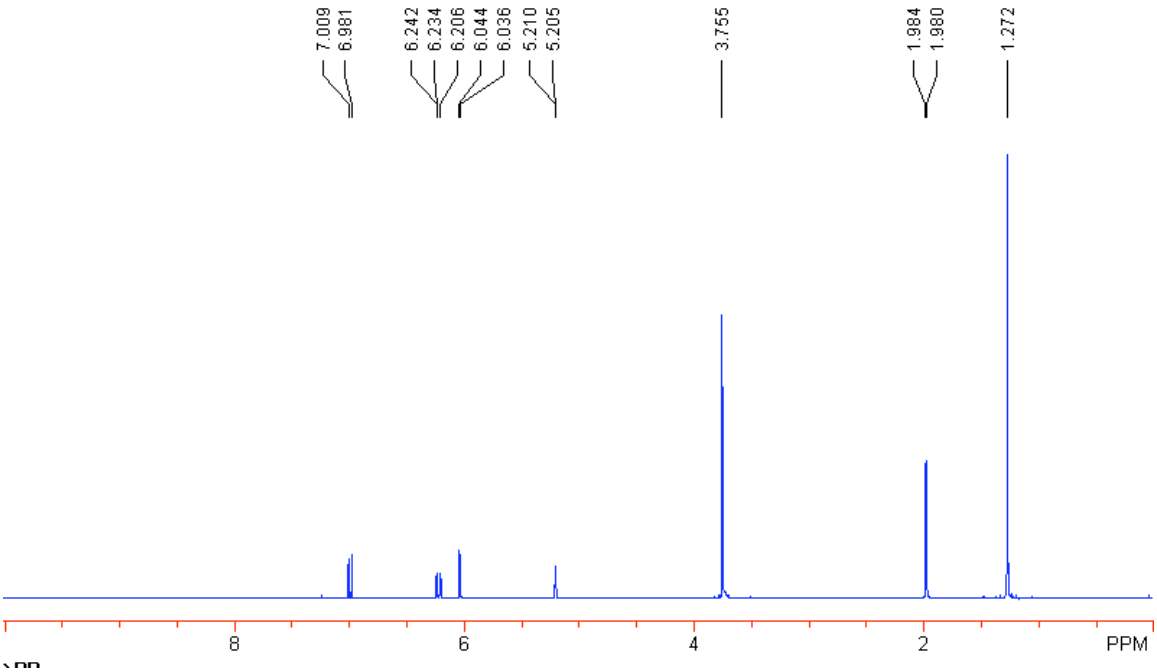
H
N

5d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6.234
6.206
6.044
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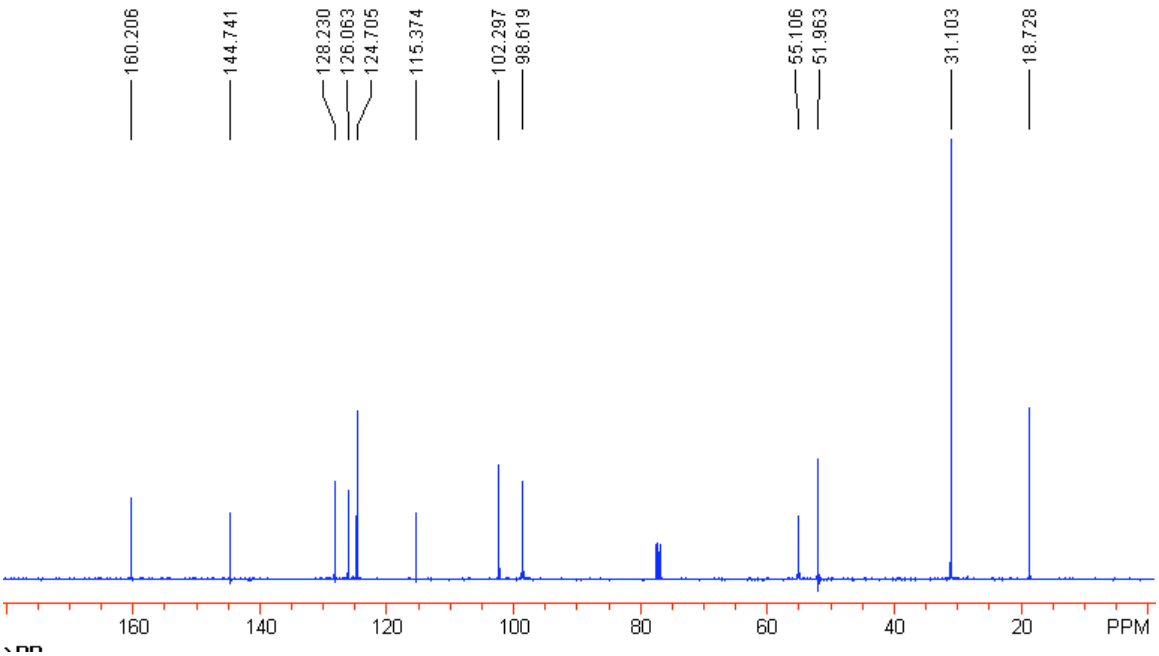
5.210
5.205
3.755
1.984
1.980
1.272
8
6
4
2
PPM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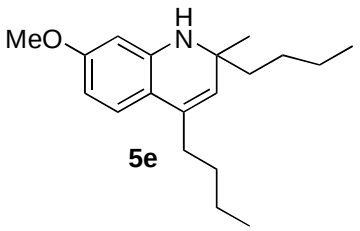
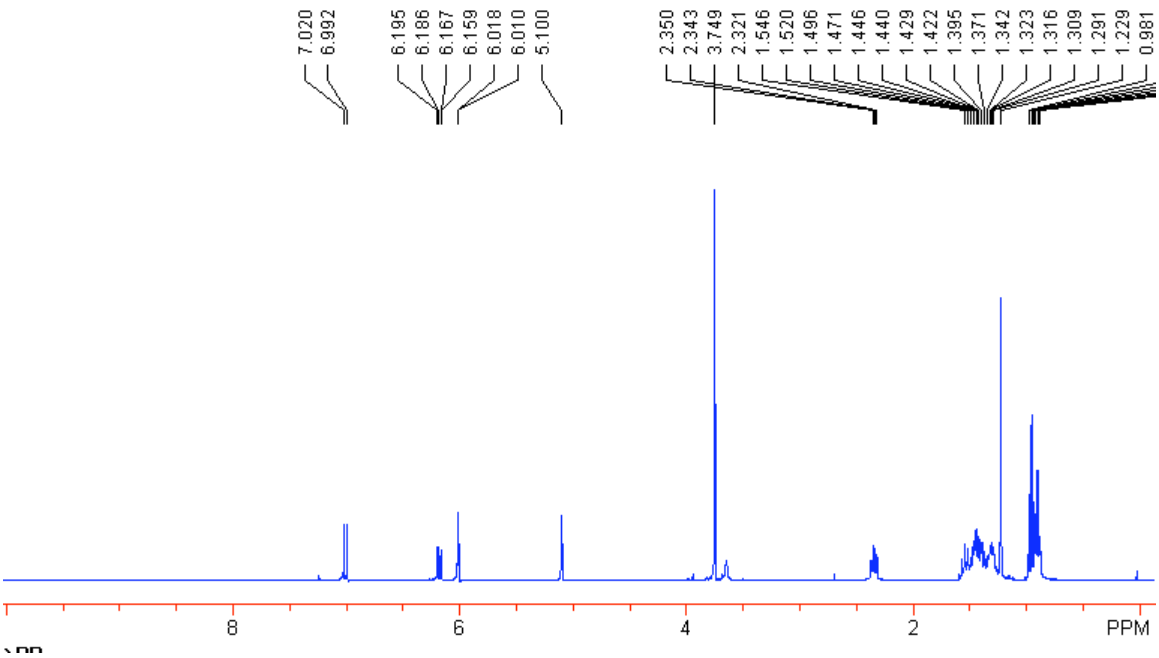
144.741
128.230
126.063
124.705
115.374
102.297
98.619
55.106
51.963
31.103
18.728
160
140
120
100
80
60
40
20
PPM


MeO
H
N

5e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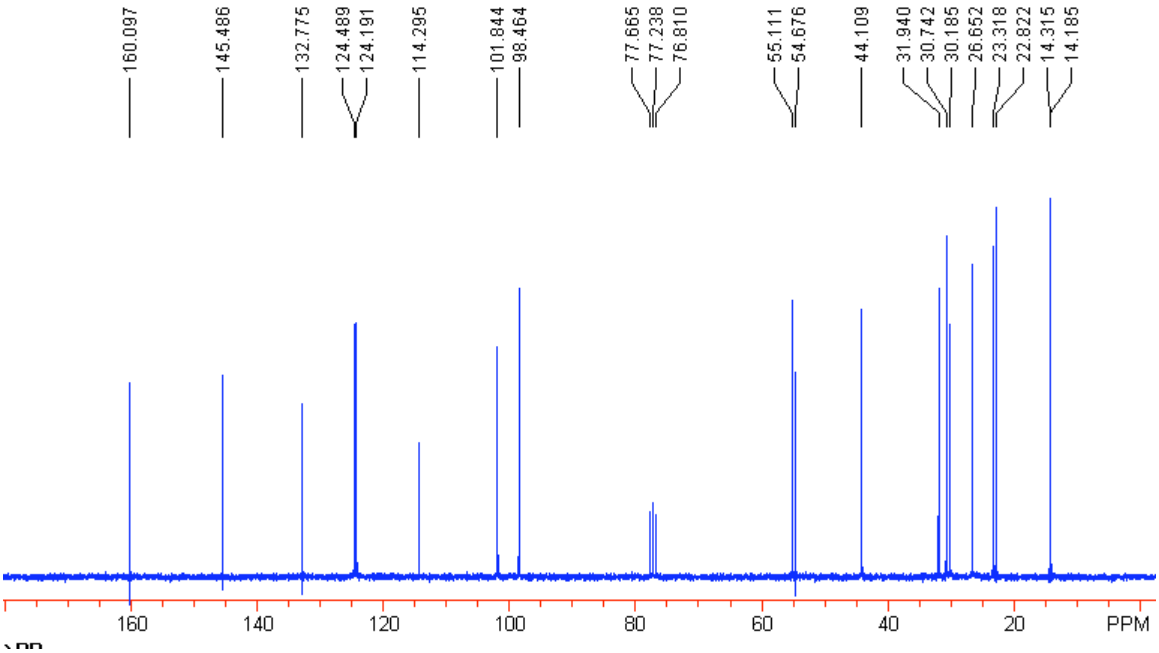
6.159
6.018
6.010
5.100
2.350
2.343
3.749
2.321
1.546
1.520
1.496
1.471
1.446
1.440
1.429
1.422
1.395
1.371
1.342
1.323
1.316
1.309
1.291
1.229
0.981
8
6
4
2
PPM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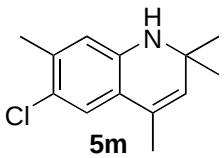
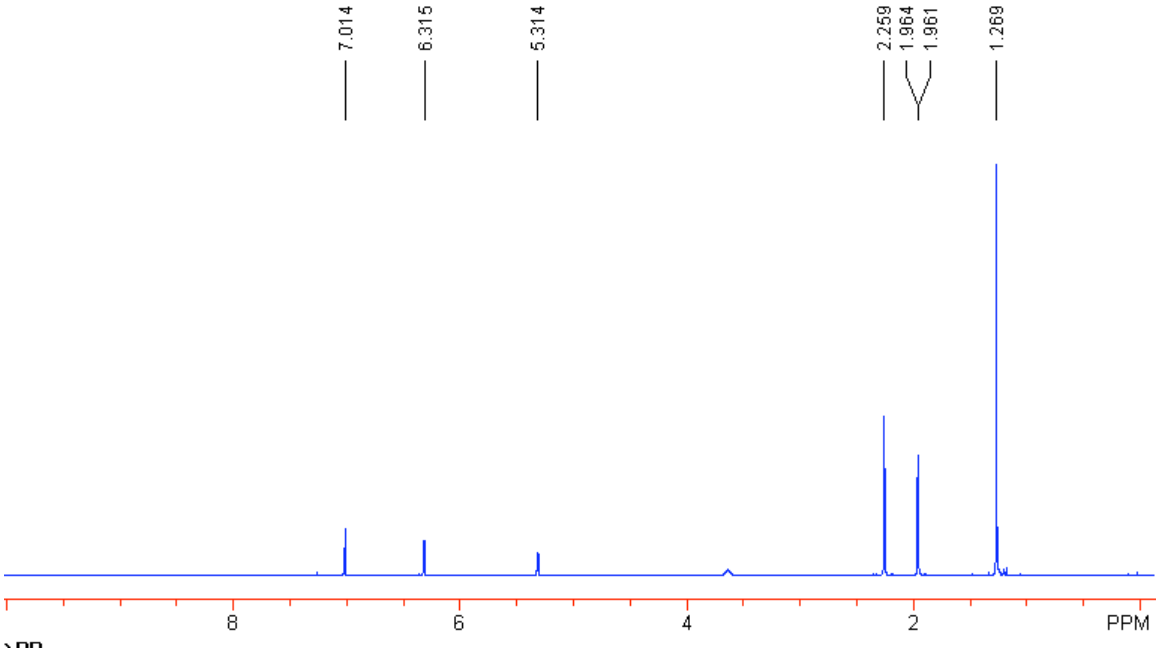
124.489
124.191
114.295
101.844
98.464
77.665
77.238
76.810
55.111
54.676
44.109
31.940
30.742
30.185
26.652
23.318
22.822
14.315
14.185
160
140
120
100
80
60
40
20
PPM


H
N
Cl

5m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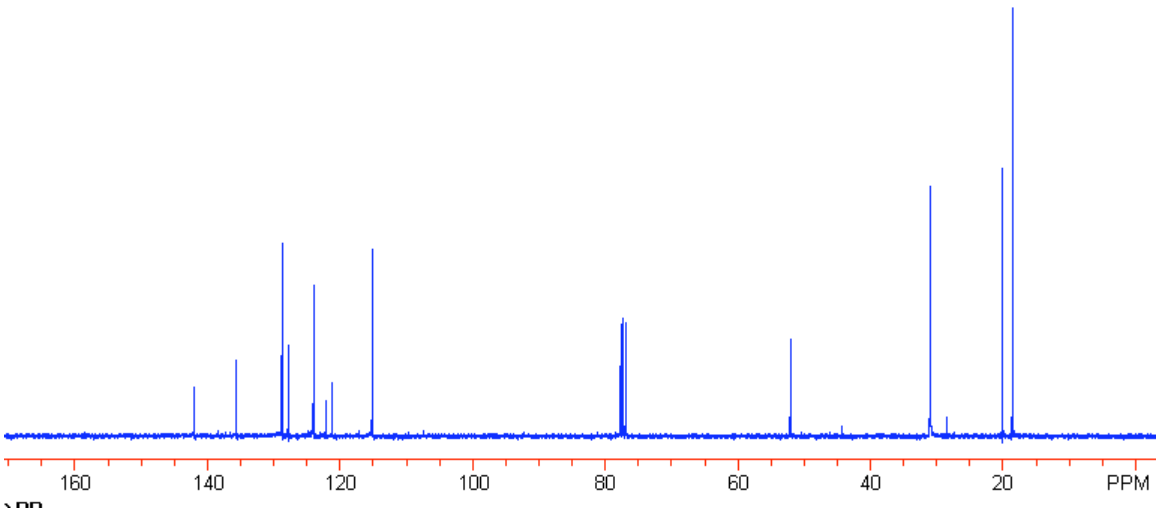
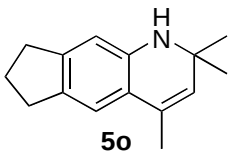
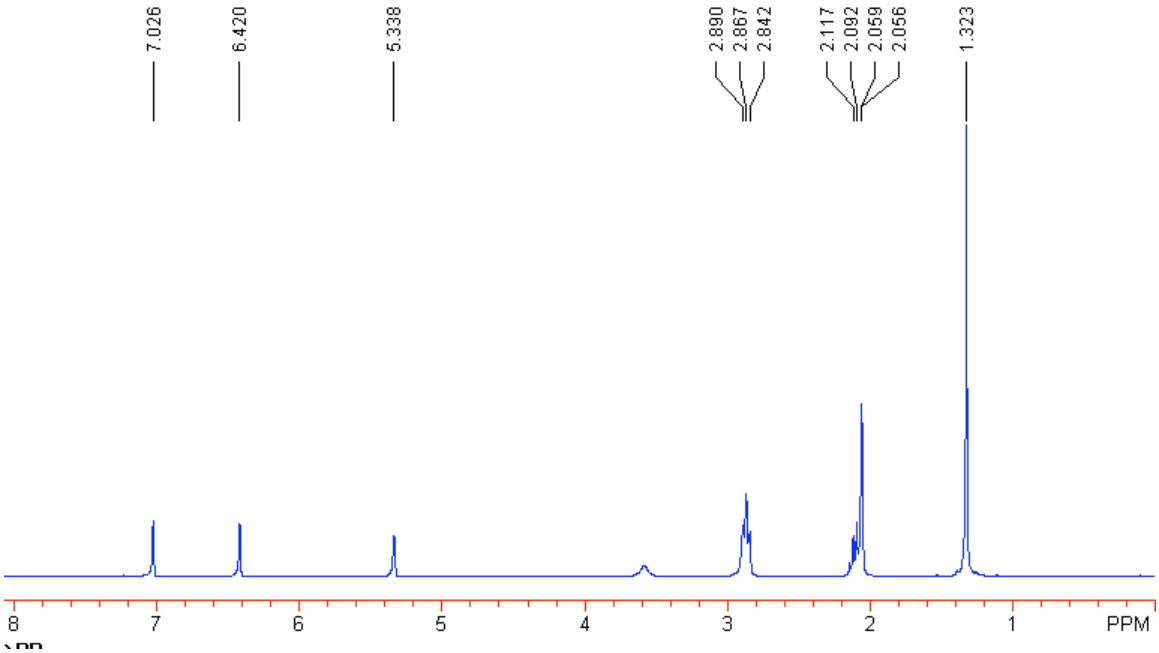
5.314
2.259
1.964
1.961
1.269
8
6
4
2
PPM


160
140
120
100
80
60
40
20
PPM


H
N

5o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2.056
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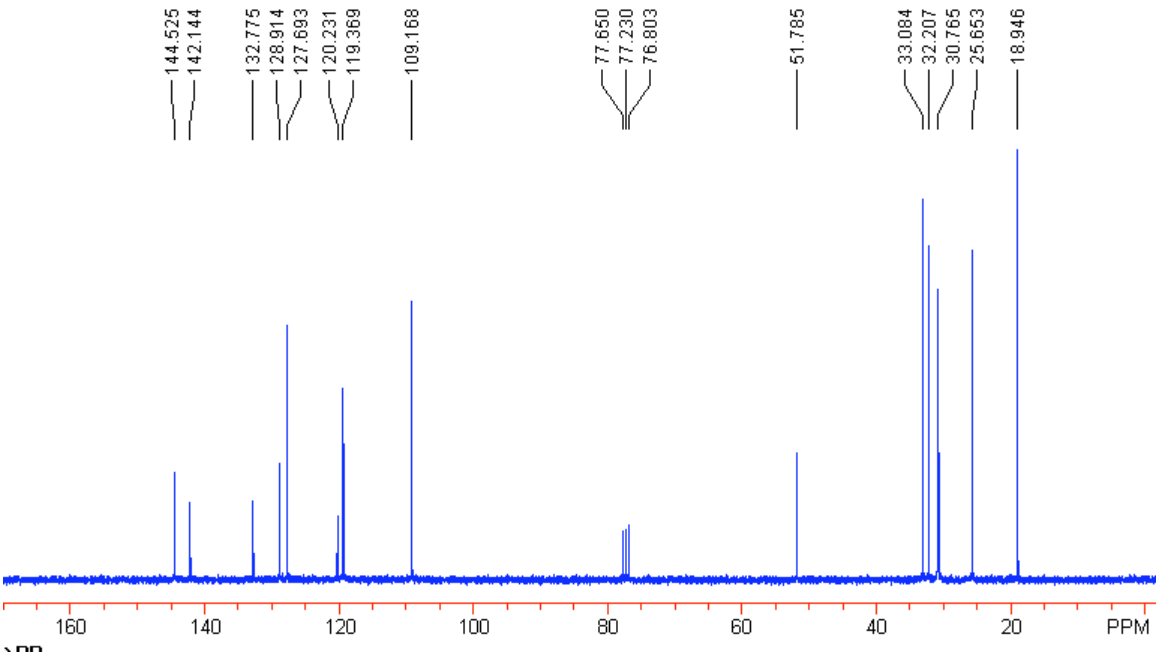
8
7
6
5
4
3
2
1
PPM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109.168
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77.230
76.803
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32.207
30.765
25.653
18.946
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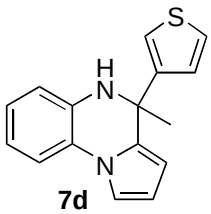
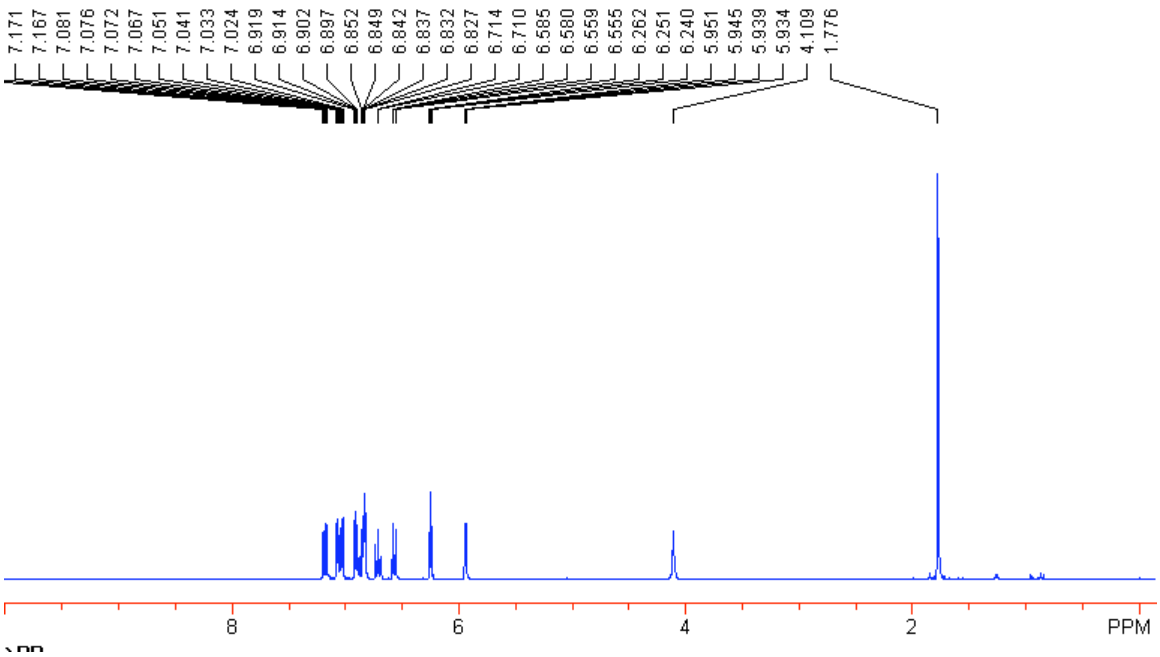
140
120
100
80
60
40
20
PPM


S
H
N
N

7d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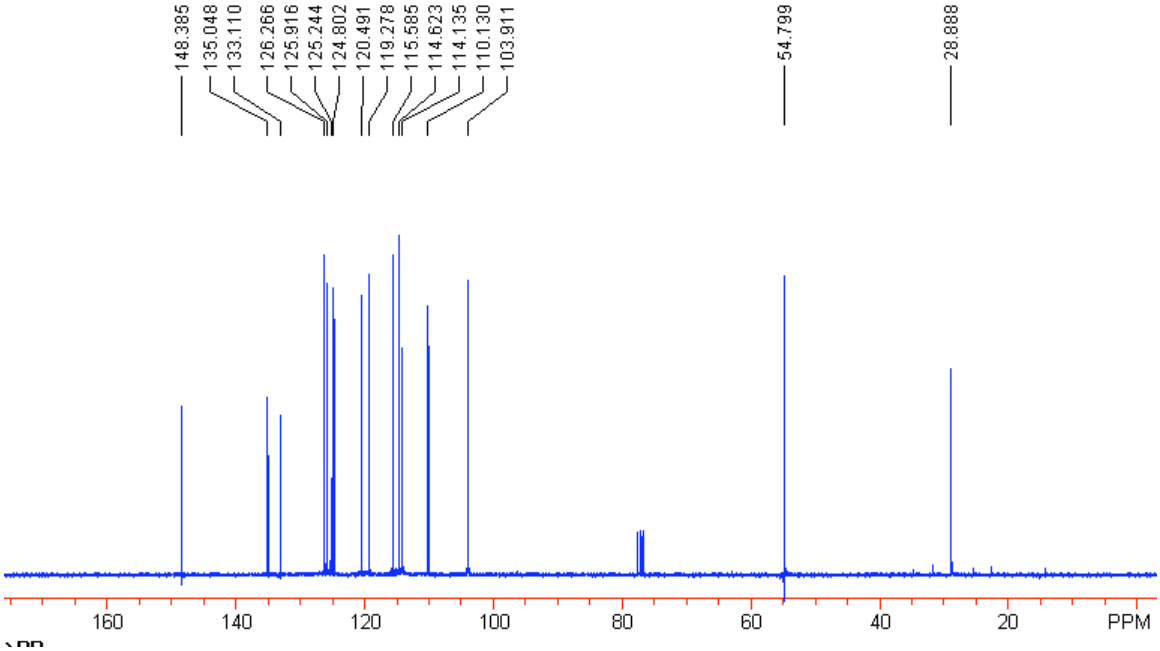
7.067
7.051
7.041
7.033
7.024
6.919
6.914
6.902
6.897
6.852
6.849
6.842
6.837
6.832
6.827
6.714
6.710
6.585
6.580
6.559
6.555
6.262
6.251
6.240
5.951
5.945
5.939
5.934
4.109
1.776
8
6
4
2
PPM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125.244
124.802
120.491
119.278
115.585
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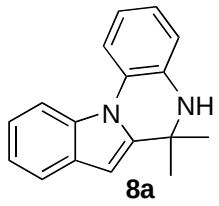
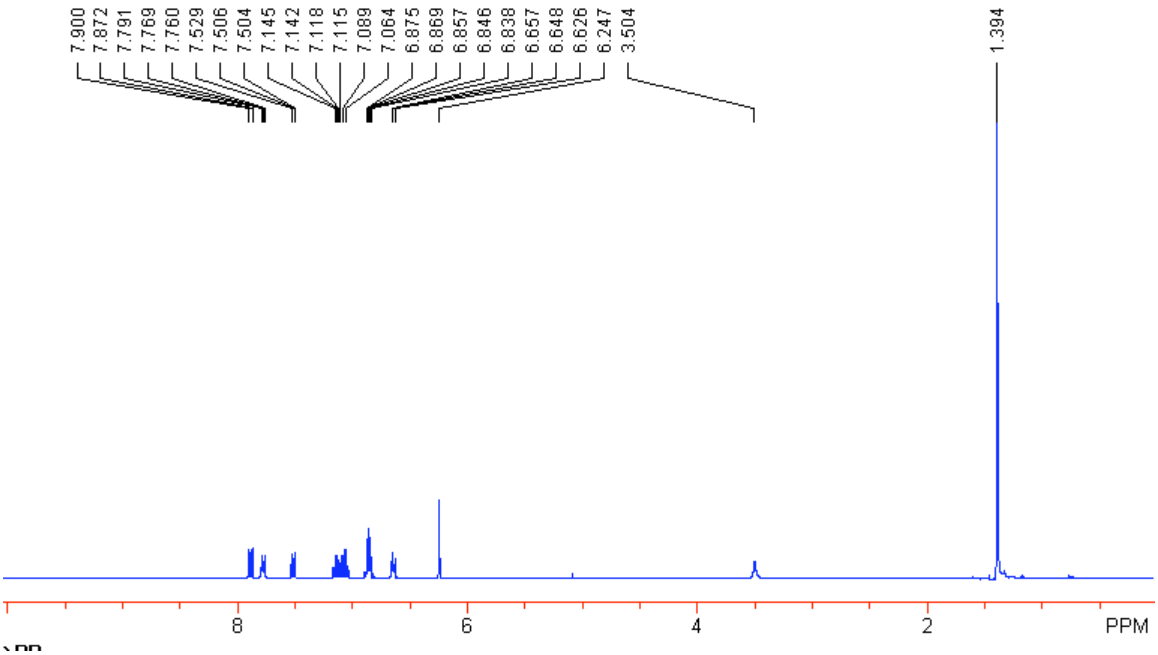
110.130
103.911
54.799
28.888
160
140
120
100
80
60
40
20
PPM


N
NH

8a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6.875
6.869
6.857
6.846
6.838
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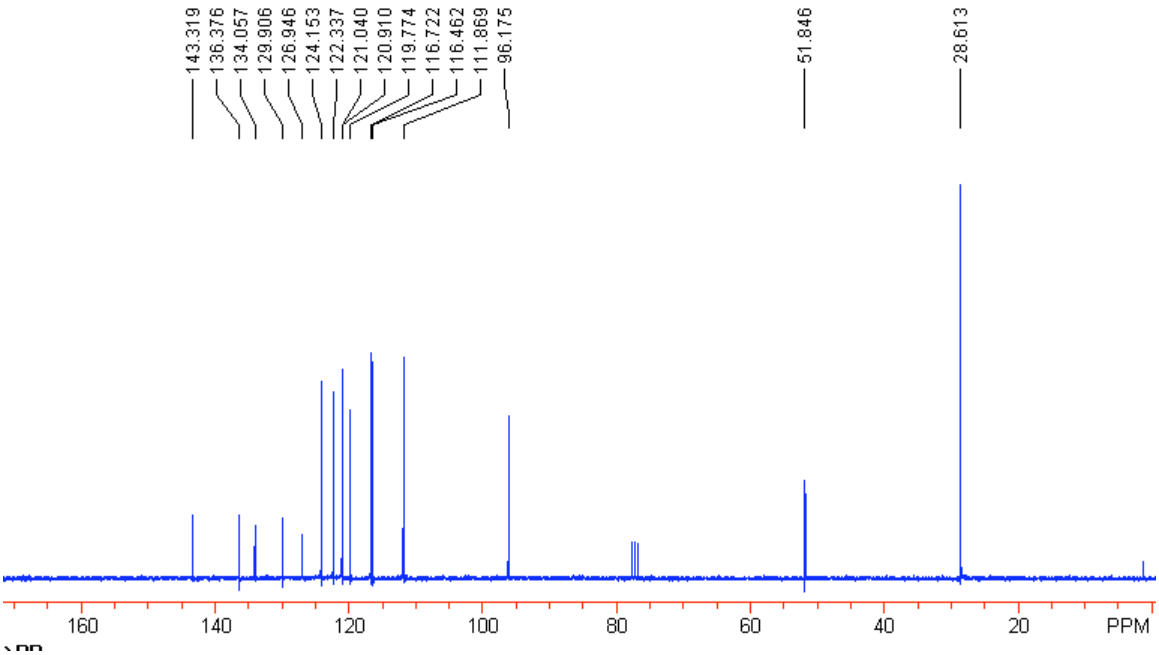
6.626
6.247
3.504
1.394
8
6
4
2
PPM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121.040
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119.774
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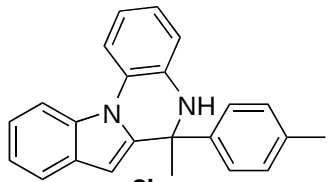
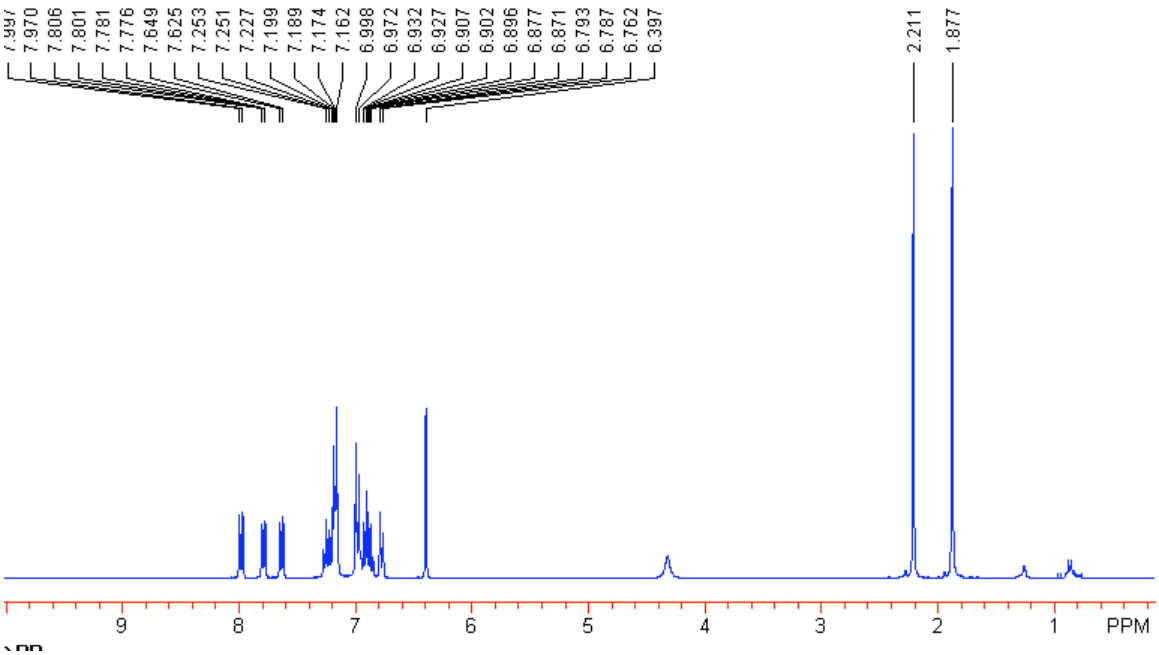
51.846
28.613
160
140
120
100
80
60
40
20
PPM


N
NH

8b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6.972
6.932
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6.907
6.902
6.896
6.877
6.871
6.793
6.787
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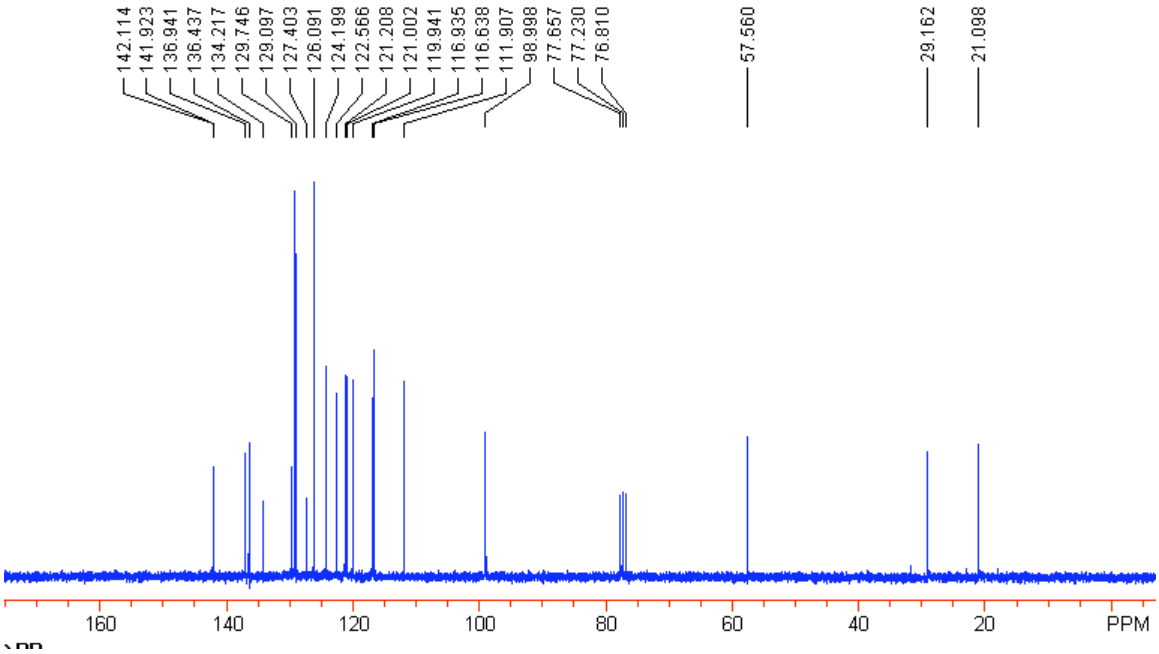
2.211
1.877
9
8
7
6
5
4
3
2
1
PPM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77.657
77.230
76.810
57.560
29.162
21.098
160
140
120
100
80
60
40
20
PPM