

Supporting Information

Solid support mediated chemo and regioselective synthesis of 3H-1,5 benzodiazepines from diversely substituted α -oxo ketene dithioacetals

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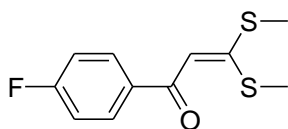
Experimental Section

General. The ^1H -NMR spectra were recorded in CDCl_3 & DMSO-d_6 solution on a Jeol JNM-ECX400P at 400 MHz using TMS as internal standard. The ^{13}C -NMR spectra were recorded in CDCl_3 & DMSO-d_6 solution on Jeol JNM-ECX400P at 100 MHz. Thin-layer chromatography was performed using commercially prepared 100-mesh silica gel plates, and visualization was effected with short wavelength UV light (254 nm) and all melting points are uncorrected. Mass spectra were recorded on a micromass instrument (WATERS-KC455, ESI-MS). IR spectra was recorded in CHCl_3 on a Perkin Elmer Spectrum RX-1 FT-IR spectrophotometer.

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Anhydrous forms of diethylether, THF, toluene, ethanol, hexanes, ethyl acetate, and CH_2Cl_2 were purchased from Merck Chemical Co. Aromatic and heterocyclic ketones, o-phenylenediamine, 3,4-Diaminotoluene, Silica gel, Neutral alumina, Basic alumina, Acidic alumina and Montmorillonite KSF were purchased from Aldrich Chemical Co., Inc.

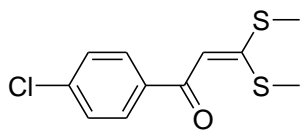
General procedure for the synthesis of α -oxo ketene dithioacetals (2a-l) : The procedure for the synthesis of α -oxo ketene dithioacetals is previously reported.¹

The compounds **2a**, **2b**, **2e**, **2f** are previously reported².



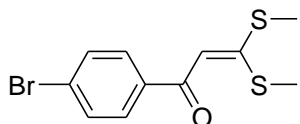
1-(4-Fluoro-phenyl)-3,3-bis-methylsulfanyl-propenone (2a). The

compound was obtained as a yellow crystalline solid, mp 83-85°C: ^1H NMR (400 MHz, CDCl_3): 7.92-7.88 (multiplet, 2H), 7.08 (t, $J = 8.79\text{Hz}$, 2H), 6.68 (s, 1H), 2.51 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): 184.05, 166.9, 166.1, 163.6, 135.3, 129.8, 115.3, 108.9, 17.3, 15.0.



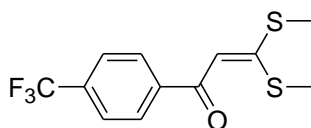
1-(4-Chloro-phenyl)-3,3-bis-methylsulfanyl-propenone (2b). The

compound was obtained as a brown crystalline solid, mp 107-109°C: ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 8.05$ Hz, 2H), 7.38 (d, $J = 8.79$ Hz, 2H), 6.68 (s, 1H), 2.54 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 184.1, 167.4, 137.8, 137.5, 129.0, 128.6, 108.7, 17.3, 15.0.



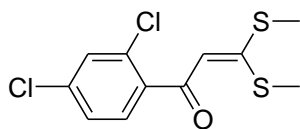
1-(4-Bromo-phenyl)-3,3-bis-methylsulfanyl-propenone (2c). The

compound was obtained as a brown solid, mp 88-90°C: ^1H NMR (400 MHz, CDCl_3): 7.76 (d, $J = 8.79$ Hz, 2H), 7.55 (d, $J = 8.79$ Hz, 2H), 6.67 (s, 1H), 2.54 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 184.2, 167.6, 138.02, 131.6, 129.2, 126.5, 108.6, 17.3, 15.0.



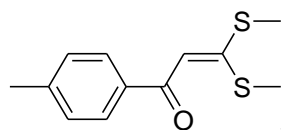
3,3-Bis-methylsulfanyl-1-(4-trifluoromethyl-phenyl)-propenone (2d).

The compound was obtained as a dark yellow solid, mp 84-86°C: ^1H NMR (400 MHz, CDCl_3): 7.98 (d, $J = 8.05$ Hz, 2H), 7.67 (d, $J = 8.05$ Hz, 2H), 6.7 (s, 1H), 3.85 (s, 3H), 2.56 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 184.1, 168.8, 142.0, 127.9, 125.4, 108.6, 17.3, 15.0.



1-(2,4-Dichloro-phenyl)-3,3-bis-methylsulfanyl-propenone (2e). The

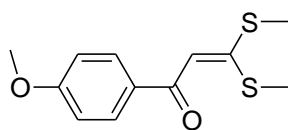
compound was obtained as a off-white solid, mp 113-115°C: ^1H NMR (400 MHz, CDCl_3): 7.47 (d, $J = 8.05$ Hz, 1H), 7.39 (d, $J = 2.2$ Hz, 1H), 7.27 (dd, $J = 6.59, 2.2$ Hz, 1H), 6.46 (s, 1H), 2.52 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 185.02, 167.7, 138.8, 136.2, 131.6, 130.8, 129.9, 127.2, 112.5, 17.2, 15.0.



3,3-Bis-methylsulfanyl-1-p-tolyl-propenone (2f). The compound was

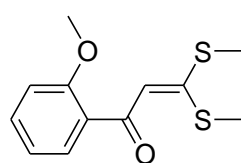
obtained as a dark orange brown solid, mp 96-98°C: ^1H NMR (400 MHz, CDCl_3): 7.81 (d, $J =$

8.79 Hz, 2H), 7.22 (d, $J = 8.05$ Hz, 2H), 6.75 (s, 1H), 2.54 (s, 3H), 2.52 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 185.3, 165.5, 142.2, 136.58, 129.0, 127.7, 109.4, 21.4, 17.2, 14.9.



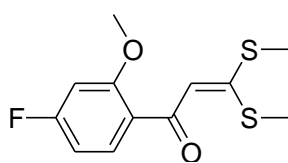
1-(4-methoxy-phenyl)-3,3-bis-methylsulfanyl-propenone (2g). The

compound was obtained as a yellow solid, mp 98-100°C: ^1H NMR (400 MHz, CDCl_3): 7.89 (d, $J = 8.79$ Hz, 2H), 6.91 (d, $J = 8.79$ Hz, 2H), 6.73 (s, 1H), 3.83 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 184.4, 164.8, 162.4, 131.9, 129.7, 113.5, 109.3, 55.3, 17.2, 14.9.



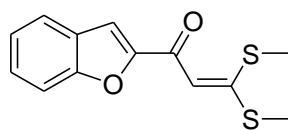
1-(2-Methoxy-phenyl)-3,3-bis-methylsulfanyl-propenone (2h). The

compound was obtained as a yellow crystalline solid, mp 66-68°C: ^1H NMR (400 MHz, CDCl_3): 7.71 (dd, $J = 9.52, 2.20$ Hz, 1H), 7.38 (dt, $J = 6.59, 2.20$ Hz, 1H), 6.99 (t, $J = 7.32$ Hz, 1H), 6.92 (d, $J = 8.05$ Hz, 1H), 6.85 (s, 1H), 3.85 (s, 3H), 2.49 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 185.9, 163.5, 157.3, 132.2, 130.8, 129.7, 120.7, 114.7, 55.5, 17.1, 14.9.



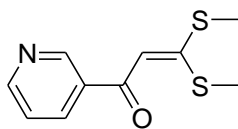
1-(4-Fluoro-2-methoxy-phenyl)-3,3-bis-methylsulfanyl-propenone (2i).

The compound was obtained as a pale yellow solid, mp 96-98°C: ^1H NMR (400 MHz, CDCl_3): 7.77 (dd, $J = 8.79, 7.32$ Hz, 1H), 6.84 (s, 1H), 6.68 (td, $J = 8.79, 8.05$ Hz, 2.2, 1H), 6.62 (dd, $J = 10.98, 2.2$ Hz, 1H), 3.8 (s, 3H), 2.48 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 184.3, 166.5, 164.0, 158.8, 132.6, 125.7, 114.4, 107.7, 99.4, 55.7, 17.2, 15.0.

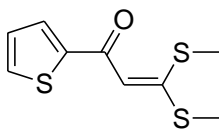


1-Benzofuran-2-yl-3,3-bis-methylsulfanyl-propenone (2j). The

compound was obtained as a dark yellow solid, mp 114-116°C: ^1H NMR (400 MHz, CDCl_3): 7.61 (d, $J = 7.32$ Hz, 1H), 7.48 (d, $J = 8.05$ Hz, 1H), 7.41 (s, 1H), 7.36 (t, $J = 8.05$ Hz, 1H), 7.20 (t, $J = 8.79$ Hz, 1H), 6.82 (s, 1H), 2.56 (s, 1H), 2.48 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 175.6, 168.1, 155.1, 154.4, 127.7, 127.0, 123.5, 122.7, 112.0, 110.7, 108.8, 17.3, 15.1.



3,3-Bis-methylsulfanyl-1-pyridin-3-yl-propenone (2k). The compound was obtained as a yellow solid, mp 103-105°C: ^1H NMR (400 MHz, DMSO- d_6): 9.14 (d, $J = 2.54$ Hz, 1H), 8.72 (dd, $J = 6.59, 2.2$ Hz, 1H), 8.28 (td, $J = 8.05, 2.2$ Hz, 1H), 7.52 (dd, $J = 8.05, 2.2$ Hz, 1H), 6.87 (s, 1H), 2.67 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 182.8, 167.9, 152.2, 148.8, 135.2, 133.9, 123.7, 108.9, 16.8, 14.6.

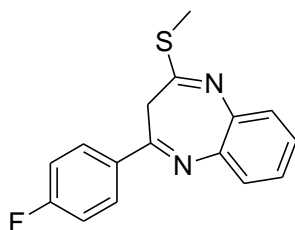


3,3-Bis-methylsulfanyl-1-thiophen-2-yl-propenone (2l). The compound was obtained as a dark brown solid, mp 90-92°C: ^1H NMR (400 MHz, DMSO- d_6): 7.98 (d, $J = 2.93$ Hz, 1H), 7.90 (dd, $J = 5.13$ Hz, 1H), 7.22 (t, $J = 5.13$ Hz, 1H), 6.79 (s, 1H), 2.66 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 177.5, 165.1, 146.2, 133.3, 130.6, 128.4, 108.9, 16.7, 14.4.

General Procedure for the synthesis of substituted 3H- 1,5-benzodiazepines (4a-x).

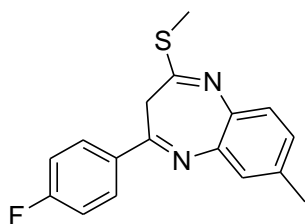
α -oxo ketene dithioacetal **2(a-l)** (1 mmol) and amine (**3a/3b**) (1.5 mmol) were dissolved in diethyl ether (5mL). Basic alumina (1g) was then added to the mixture and stirred for a while followed by removal of the solvent under reduced pressure. The mixture was stirred at 90°C for 4 hr. After completion of the reaction (monitored by TLC), reaction mass was directly purified by column chromatography on neutral alumina using hexane–ethyl acetate 9.5 : 0.5 as eluent to afford the desired pure product.

Compounds **4c**, **4e**, **4k**, **4m** are previously reported ³.



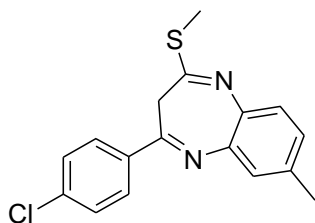
2-(4-Fluoro-phenyl)-4-methylsulfanyl-3H-benzo[*b*][1,5]diazepine (4a). The compound was obtained as a yellow solid, mp 95-97°C; IR ($\nu_{\text{max}}\text{cm}^{-1}$) (CHCl_3): 2924, 1599, 1584; ^1H NMR (400 MHz, CDCl_3): 8.09 (t, $J = 8.79$ Hz, 2H), 7.49 (t, $J = 9.52$, 1H), 7.40 (t,

$J = 9.52$, 1H), 7.25 (t, $J = 6.59$, 2H), 7.15 (t, $J = 8.79$, 2H), 3.38 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.6, 163.1, 156.1, 152.8, 140.5, 139.6, 133.3, 130.2, 128.8, 127.6, 125.7, 124.5, 115.6, 39.4, 13.8; ESI-MS (m/z): 285.41 (M+1).



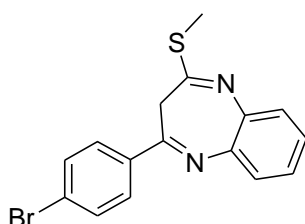
4-(4-Fluoro-phenyl)-7-methyl-2-methylsulfanyl-3H-

benzo[*b*][1,5]diazepine (4b) The compound was obtained as a yellow solid, mp 66-68°C; IR ($\nu_{\text{max}}\text{cm}^{-1}$) (CHCl_3): 2924, 1600, 1584; ^1H NMR (400 MHz, CDCl_3): 8.07 (dd, $J = 8.79$, 3.66, 2H), 7.29 (d, $J = 8.05$, 1H), 7.24 (s, 1H), 7.13 (t, $J = 8.79$, 2H), 7.06 (d, $J = 8.79$, 1H), 3.36 (s, 2H), 2.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.6, 163.0, 155.3, 152.4, 139.4, 138.3, 134.4, 130.0, 128.4, 127.5, 126.9, 126.0, 115.7, 115.5, 39.4, 20.9, 13.8; ESI-MS (m/z): 299.37 (M+1).



4-(4-Chloro-phenyl)-7-methyl-2-methylsulfanyl-3H-

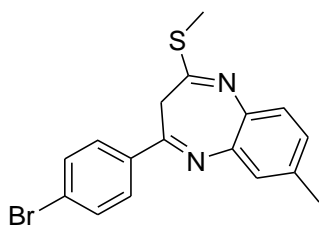
benzo[*b*][1,5]diazepine (4d) The compound was obtained as yellow solid, mp 96-98°C; IR ($\nu_{\text{max}}\text{cm}^{-1}$) (CHCl_3): 2923, 1590; ^1H NMR (400 MHz, CDCl_3): 7.96 (d, $J = 8.05$ Hz, 2H), 7.38 (d, $J = 8.79$ Hz, 2H), 7.24 (d, $J = 8.05$ Hz, 1H), 7.19 (s, 1H), 7.03 (dd, $J = 8.05$, 1.46, 1H), 3.31 (s, 2H), 2.40 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.2, 152.3, 139.2, 138.4, 136.9, 134.5, 129.2, 128.8, 128.4, 127.5, 127.0, 126.1, 39.3, 20.9, 13.8; ESI-MS (m/z): 315.37, 317.37 (M+1, M+3).



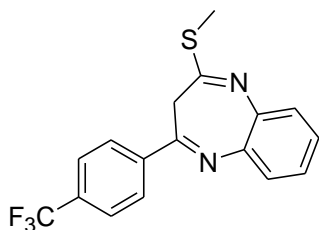
2-(4-Bromo-phenyl)-4-methylsulfanyl-3H-benzo[*b*][1,5]diazepine (4e)

The compound was obtained as light yellow solid, mp 92-94°C; IR ($\nu_{\text{max}}\text{cm}^{-1}$) (CHCl_3): 2924, 1586; ^1H NMR (400 MHz, CDCl_3): 7.95 (d, $J = 8.79$ Hz, 2H), 7.59 (d, $J = 8.05$ Hz, 2H), 7.50 (m, 1H), 7.40 (m, 1H), 7.26-7.24 (m, 2H), 3.35 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz,

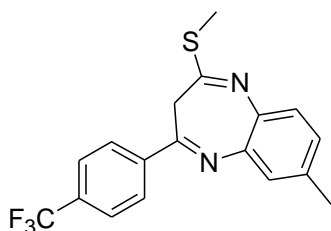
CDCl₃): δ 156.2, 152.7, 140.5, 139.6, 135.9, 131.8, 129.5, 128.6, 127.7, 125.7, 125.5, 124.7, 39.3, 13.9; ESI-MS (*m/z*): 345.31, 347.31 (*M*+1, *M*+3).



4-(4-Bromo-phenyl)-7-methyl-2-methylsulfanyl-3H-benzo[*b*][1,5]diazepine (4f) The compound was obtained as a light yellow solid, mp 100-102°C; IR (ν_{\max} cm⁻¹) (CHCl₃): 2923, 1585 ; ¹H NMR (400 MHz, CDCl₃): 7.93 (d, *J* = 8.79 Hz, 2H), 7.58 (d, *J* = 8.79 Hz, 2H), 7.28 (d, *J* = 8.05 Hz, 1H), 7.20 (s, 1H), 7.07 (dd, *J* = 8.05 Hz, 2.2, 1H), 3.34 (s, 2H), 2.45 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 155.2, 152.4, 139.2, 138.3, 136.0, 134.5, 131.7, 129.4, 128.4, 127.5, 127.0, 126.1, 125.4, 39.3, 20.9, 13.8; ESI-MS (*m/z*): 359.25, 361.25 (*M*+1, *M*+3).

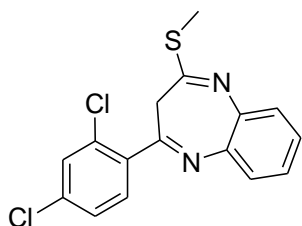


2-Methylsulfanyl-4-(4-trifluoromethyl-phenyl)-3H-benzo[*b*][1,5]diazepine (4g) The compound was obtained as a yellow solid, mp 96-98°C; IR (ν_{\max} cm⁻¹) (CHCl₃): 2925, 1577, 1315 ; ¹H NMR (400 MHz, CDCl₃): 8.19 (d, *J* = 8.05 Hz, 2H), 7.71 (d, *J* = 8.05 Hz, 2H), 7.50 (dd, *J* = 7.32, 2.93 Hz, 1H), 7.41 (dd, *J* = 7.32, 2.93 Hz, 1H), 7.28-7.25 (m, 2H), 3.4 (s, 2H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 156.1, 152.3, 140.6, 140.3, 139.4, 132.2, 131.9, 128.7, 128.1, 127.7, 126.0, 125.5, 124.7, 39.5, 13.9; ESI-MS (*m/z*): 335.34 (*M*+1).



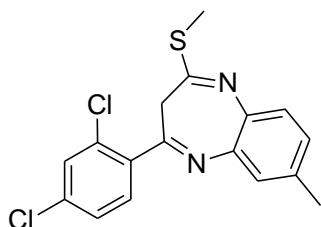
7-Methyl-2-methylsulfanyl-4-(4-trifluoromethyl-phenyl)-3H-benzo[*b*][1,5]diazepine (4h) The compound was obtained as a yellow viscous material, IR (ν_{\max} cm⁻¹) (CHCl₃): 2924, 1578, 1313 ; ¹H NMR (400 MHz, CDCl₃): 8.12 (d, *J* = 8.05 Hz, 2H), 7.65 (d, *J* = 8.05 Hz, 2H), 7.24 (d, *J* = 7.32 Hz, 1H), 7.17 (d, *J* = 7.32 Hz, 1H), 7.02 (t, *J* = 7.32 Hz,

1H), 3.32 (s, 2H), 2.40 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.1, 151.9, 140.4, 139.2, 138.4, 137.2, 136.1, 134.6, 128.6, 128.1, 127.6, 127.4, 126.1, 125.5, 39.5, 20.9, 13.8; ESI-MS (m/z): 349.28 (M+1).



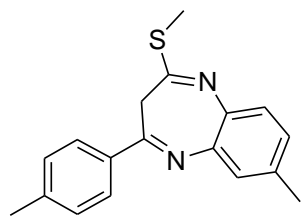
2-(2,4-Dichloro-phenyl)-4-methylsulfanyl-3H-benzo[b][1,5]diazepine

(4i) The compound was obtained as a yellow solid, mp 108-110°C; IR ($\nu_{\text{max}}\text{cm}^{-1}$) (CHCl_3): 2924, 1601, 1580; ^1H NMR (400 MHz, CDCl_3): 7.47 (dd, $J = 7.32, 1.46$ Hz, 2H), 7.40 (dd, $J = 7.32, 1.46$ Hz, 1H), 7.30-7.23 (m, 4H), 3.43 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.3, 155.0, 139.9, 139.2, 136.9, 136.2, 133.4, 131.5, 129.8, 128.6, 127.5, 126.2, 124.6, 43.7, 14.0; ESI-MS (m/z): 335.26, 337.26 (M+1, M+3).



4-(2,4-Dichloro-phenyl)-7-methyl-2-methylsulfanyl-3H-

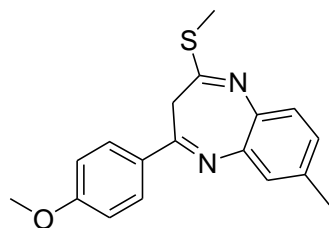
benzo[b][1,5]diazepine (4j) The compound was obtained as a yellow viscous material, IR ($\nu_{\text{max}}\text{cm}^{-1}$) (CHCl_3): 2923, 1584; ^1H NMR (400 MHz, CDCl_3): 7.47 (s, 1H), 7.37-7.20 (m, 4H), 7.11-7.04 (dddd, $J = 8.05, 2.2$ Hz, 1H), 3.41 (s, 2H), 2.45 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.9, 154.6, 139.7, 138.9, 137.7, 137.0, 136.1, 134.4, 133.4, 131.5, 129.8, 128.5, 127.5, 126.0, 43.6, 20.9, 13.9; ESI-MS (m/z): 349.29, 351.29 (M+1, M+3).



7-Methyl-2-methylsulfanyl-4-p-tolyl-3H-benzo[b][1,5]diazepine (4l)

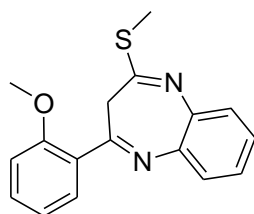
The compound was obtained as a light yellow solid, mp 64-66°C; IR ($\nu_{\text{max}}\text{cm}^{-1}$) (CHCl_3): 2922, 1594, 1574; ^1H NMR (400 MHz, CDCl_3): 7.94 (d, $J = 8.05$ Hz, 2H), 7.28-7.24 (m, 4H), 7.04 (d, $J = 8.79$ Hz, 1H), 3.35 (s, 2H), 2.42 (s, 3H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ

156.1, 155.5, 141.1, 138.3, 134.3, 129.3, 128.4, 128.0, 127.4, 126.6, 125.9, 39.3, 21.4, 20.9, 13.8;
ESI-MS (m/z) : 295.39 (M+1).



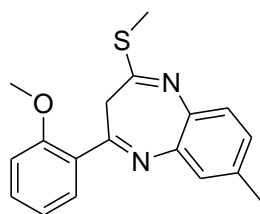
4-(4-Methoxy-phenyl)-7-methyl-2-methylsulfanyl-3H-

benzo[*b*][1,5]diazepine (4n) The compound was obtained as a off white solid, mp 92-94°C; IR (ν_{\max} cm⁻¹) (CHCl₃): 2923, 1593 ; ¹H NMR (400 MHz, CDCl₃): 8.05 (d, *J* = 8.05 Hz, 2H), 7.36-7.20 (m, 2H), 7.06 (d, *J* = 8.05 Hz, 1H), 6.97 (d, *J* = 8.79 Hz, 2H), 3.85 (s, 3H), 3.37 (s, 2H), 2.43 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 161.9, 155.5, 138.4, 134.4, 130.0, 128.3, 127.3, 126.6, 126.0, 114.0, 55.4, 39.2, 20.8, 13.8; ESI-MS (m/z) : 311.41 (M+1).



2-(2-Methoxy-phenyl)-4-methylsulfanyl-3H-benzo[*b*][1,5]diazepine (4o)

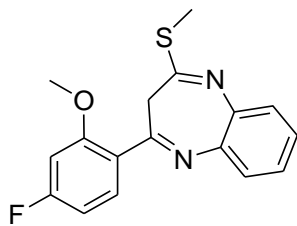
The compound was obtained as a yellow viscous material, IR (ν_{\max} cm⁻¹) (CHCl₃): 2924, 1597, 754 ; ¹H NMR (400 MHz, CDCl₃): 7.57 (d, *J* = 6.59 Hz, 1H), 7.44 (d, *J* = 8.05 Hz, 2H), 7.39 (dd, *J* = 8.05, 2.2 Hz, 1H), 7.27 (dd, *J* = 7.32, 2.2 Hz, 1H), 7.21 (dt, *J* = 7.32, 2.2 Hz, 1H), 6.98 (d, *J* = 8.05 Hz, 2H), 3.92 (s, 3H), 3.51 (s, 2H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 140.3, 131.7, 131.3, 128.7, 127.5, 125.6, 124.5, 120.9, 111.1, 55.3, 43.0, 14.0; ESI-MS (m/z) : 297.37 (M+1).



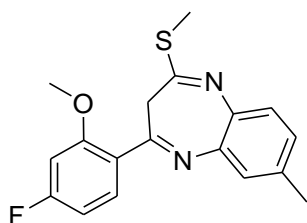
4-(2-Methoxy-phenyl)-7-methyl-2-methylsulfanyl-3H-

benzo[*b*][1,5]diazepine (4p) The compound was obtained as a yellow viscous material, IR (ν_{\max} cm⁻¹) (CHCl₃): 2923, 1599, 753 ; ¹H NMR (400 MHz, CDCl₃): 7.40 (t, *J* = 8.05 Hz, 2H), 7.33-7.19 (m, 2H), 7.05 (t, *J* = 8.79 Hz, 1H), 6.97 (t, *J* = 7.32 Hz, 2H), 3.9 (s, 3H), 3.46 (s, 2H), 2.43 (s, 3H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 157.7, 157.0, 140.0, 138.0, 134.1,

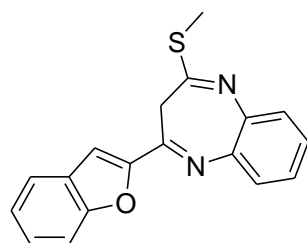
131.5, 131.2, 128.7, 127.3, 126.8, 125.7, 120.8, 111.0, 55.3, 43.0, 20.9, 13.9; ESI-MS (m/z) : 311.36 (M+1).



2-(4-Fluoro-2-methoxyphenyl)-4-methylsulfanyl-3H-benzo[b][1,5]diazepine (4q) The compound was obtained as a off white solid, mp 128-130°C; IR (ν_{\max} cm⁻¹) (CHCl₃): 2923, 1596 ; ¹H NMR (400 MHz, CDCl₃): 7.51 (d, *J* = 7.32 Hz, 1H), 7.44 (t, *J* = 8.05 Hz, 1H), 7.38 (dd, *J* = 7.32, 2.2 Hz, 1H), 7.27-7.19 (m, 2H), 6.71-6.66 (m, 2H), 3.91 (s, 3H), 3.47 (s, 2H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.2, 163.7, 159.5, 157.8, 156.3, 140.2, 132.9, 128.7, 127.5, 125.6, 124.4, 107.6, 99.4, 55.7, 42.9, 14.0; ESI-MS (m/z) : 315.34 (M+1).

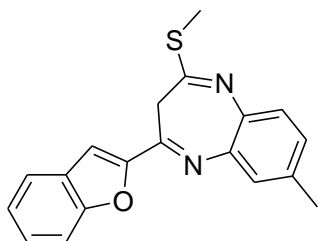


4-(4-Fluoro-2-methoxyphenyl)-7-methyl-2-methylsulfanyl-3H-benzo[b][1,5]diazepine (4r) The compound was obtained as a light yellow solid, mp 76-78°C; IR (ν_{\max} cm⁻¹) (CHCl₃): 2924, 1596 ; ¹H NMR (400 MHz, CDCl₃): 7.38-7.31 (m, 1H), 7.22-7.13 (m, 2H), 7.01-6.96 (m, 1H), 6.63-6.58 (m, 2H), 3.81 (s, 3H), 3.39 (s, 2H), 2.37 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.2, 163.7, 159.6, 157.4, 156.8, 140.0, 138.0, 135.6, 134.2, 132.7, 128.6, 127.3, 126.9, 125.8, 124.3, 107.6, 99.4, 55.6, 42.8, 20.9, 13.9; ESI-MS (m/z) : 329.35 (M+1).

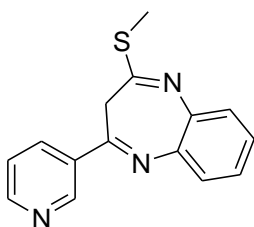


2-Benzofuran-2-yl-4-methylsulfanyl-3H-benzo[b][1,5]diazepine (4s) The compound was obtained as a fluorescent yellow solid, mp 109-111°C; IR (ν_{\max} cm⁻¹) (CHCl₃): 2923, 1592, 751 ; ¹H NMR (400 MHz, CDCl₃): 7.62 (d, *J* = 7.32 Hz, 1H), 7.56-7.53 (m, 2H), 7.39-7.32 (m, 3H), 7.23-7.19 (m, 3H), 3.33 (s, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz,

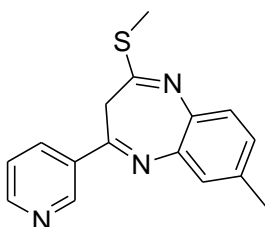
CDCl₃): δ 156.4, 156.0, 152.4, 144.9, 140.5, 139.2, 129.0, 127.7, 126.9, 125.9, 124.7, 123.5, 122.2, 112.1, 110.9, 39.5, 13.8; ESI-MS (*m/z*): 307.54 (*M*+1).



2-Benzofuran-2-yl-7-methyl-4-methylsulfanyl-3H-benzo[*b*][1,5]diazepine (4t) The compound was obtained as a yellow solid, mp 119-121 °C; IR (ν_{\max} cm⁻¹) (CHCl₃): 2923, 1592, 751 ; ¹H NMR (400 MHz, CDCl₃): 7.61 (d, *J* = 8.05 Hz, 1H), 7.55 (d, *J* = 8.79 Hz, 1H), 7.37-7.31 (m, 2H), 7.25-7.16 (m, 3H), 7.03 (dd, *J* = 8.05, 1.46 Hz, 1H), 3.31 (s, 2H), 2.39 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 156.0, 155.4, 152.5, 144.5, 140.5, 139.0, 138.5, 134.5, 128.9, 127.9, 127.6, 127.3, 126.9, 126.1, 123.5, 122.2, 112.1, 110.7, 39.5, 20.9, 13.9; ESI-MS (*m/z*): 321.55 (*M*+1).

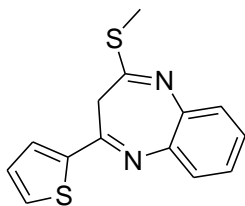


2-Methylsulfanyl-4-pyridin-3-yl-3H-benzo[*b*][1,5]diazepine (4u) The compound was obtained as a yellow viscous material, IR (ν_{\max} cm⁻¹) (CHCl₃): 2923, 2852, 1598, 1574 ; ¹H NMR (400 MHz, DMSO-*d*₆): 9.28 (s, 1H), 8.71 (dd, *J* = 5.13, 2.2, 1H), 8.46 (dd, *J* = 8.05, 2.2, 1H), 7.55 (q, *J* = 8.05 Hz, 1H), 7.46 (dd, *J* = 7.32, 2.2, 1H), 7.36 (dd, *J* = 7.32, 2.2, 1H), 7.33-7.26 (m, 2H), 3.56 (s, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 157.5, 152.8, 152.0, 149.7, 140.6, 139.8, 136.0, 132.3, 129.1, 128.0, 126.5, 125.3, 124.3, 39.5, 13.9; ESI-MS (*m/z*): 268.56 (*M*+1).



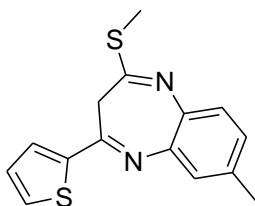
7-Methyl-2-methylsulfanyl-4-pyridin-3-yl-3H-benzo[*b*][1,5]diazepine (4v) The compound was obtained as a peach coloured solid, mp 86-88 °C; IR (ν_{\max} cm⁻¹) (CHCl₃): 2923, 1596, 1576 ; ¹H NMR (400 MHz, DMSO-*d*₆): 9.23 (t, *J* = 2.2 Hz, 1H), 8.67 (td, *J* = 5.13, 1.46 Hz, 1H), 8.41 (dd, *J* = 8.05, 2.2 Hz, 1H), 7.51 (q, *J* = 8.05 Hz, 1H), 7.33-7.22 (m,

2H), 7.08 (td, $J = 8.79, 2.2$ Hz, 1H), 3.50 (s, 2H), 2.36 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 156.3, 152.2, 151.7, 149.4, 140.3, 139.4, 138.3, 135.7, 134.4, 132.2, 128.6, 127.7, 124.1, 39.5, 20.9, 13.7; ESI-MS (m/z): 282.56 (M+1).



2-Methylsulfanyl-4-thiophen-2-yl-3H-benzo[*b*][1,5]diazepine (4w) The

compound was obtained as a fluorescent yellow solid, mp 142-144°C; IR ($\nu_{\text{max}}\text{cm}^{-1}$) (CHCl_3): 2923, 1588, 712; ^1H NMR (400 MHz, CDCl_3): 7.65 (s, 1H), 7.49 (t, 2H), 7.40-7.38 (m, 1H), 7.25-7.22 (m, 2H), 7.12 (t, 1H), 3.35 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.5, 148.8, 143.7, 140.8, 139.4, 131.7, 129.5, 128.7, 128.0, 127.8, 125.6, 124.8, 40.3, 14.0; ESI-MS (m/z): 273.52 (M+1).



7-Methyl-2-methylsulfanyl-4-thiophen-2-yl-3H-benzo[*b*][1,5]diazepine (4x) The

compound was obtained as a yellow viscous material, IR ($\nu_{\text{max}}\text{cm}^{-1}$) (CHCl_3): 2923, 1588, 710; ^1H NMR (400 MHz, DMSO- d_6): 7.91 (td, $J = 5.13, 1.46$, 1H), 7.78 (t, $J = 5.13$, 1H), 7.24-7.14 (m, 3H), 7.06 (td, $J = 8.05, 2.2$, 1H), 3.47 (s, 2H), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 157.5, 156.9, 143.7, 140.6, 139.4, 138.6, 133.2, 131.7, 128.9, 128.6, 128.0, 127.1, 126.5, 39.5, 21.0, 13.9; ESI-MS (m/z): 287.50 (M+1).

X-Ray crystallographic data

The crystals of **4c** of suitable quality were obtained from dichloromethane. The compound **4c** crystallized in Monoclinic crystal system with space group P 21/c. The single-crystal Xray data were collected on an Oxford XCalibur CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures was solved using SIR- 92 and refined by full matrix least square technique on F2 using the SHELXL-97⁴⁻⁵ program within the WinGX v 1.80.05 software package. In **4c** hydrogens are mixed and all non-hydrogen atoms were refined anisotropically. Atomic coordinates, bond lengths, bond angles,

and thermal parameters for compounds **4c** has been deposited at the Cambridge Crystallographic Data Centre. CCDC deposit number for **4c** is 920827.

The main crystallographic data and structural refinement details for **4c** are given in table 1.

Table 1. Crystallographic data and structural refinement parameters for compound **4c**

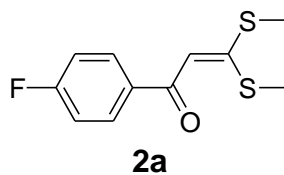
	4c
Empirical formula	C ₁₆ H ₁₃ ClN ₂ S
Formula weight	300.79
Temperature (K)	298(2) K
Wavelength [Å]	0.71073
Crystal System	Monoclinic
Space Group	P 21/c
a [Å]	4.2750(4)
b [Å]	19.7528(15)
c [Å]	17.138(2)
α [°]	90°
β [°]	92.163(9)°
γ [°]	90°
V [Å ³]	1446.1(3)
Z, D calcd [Mg/m ³]	4, 1.382
Abs. coefficient [mm ⁻¹]	0.399
F [000]	624
Crystal size [mm ³]	0.18 x 0.14 x 0.12
Theta range for data collection [°]	3.15 to 25.00
Index ranges	-5 ≤ h ≤ 5, -23 ≤ k ≤ 23, -14 ≤ l ≤ 19
Reflections collected	7718
Independent reflections	2419 [R(int) = 0.0234]
Completeness to theta = 25.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9537 and 0.9317
Refinement method	Full-matrix least-squares on F ²

Data / restraints / parameters	2419 / 0 / 182
Goodness-of-fit on F^2	1.076
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0457$, $wR_2 = 0.1045$
R indices (all data)	$R_1 = 0.0566$, $wR_2 = 0.1102$
Largest diff. peak and hole [\AA^{-3}]	0.185 and -0.194 e

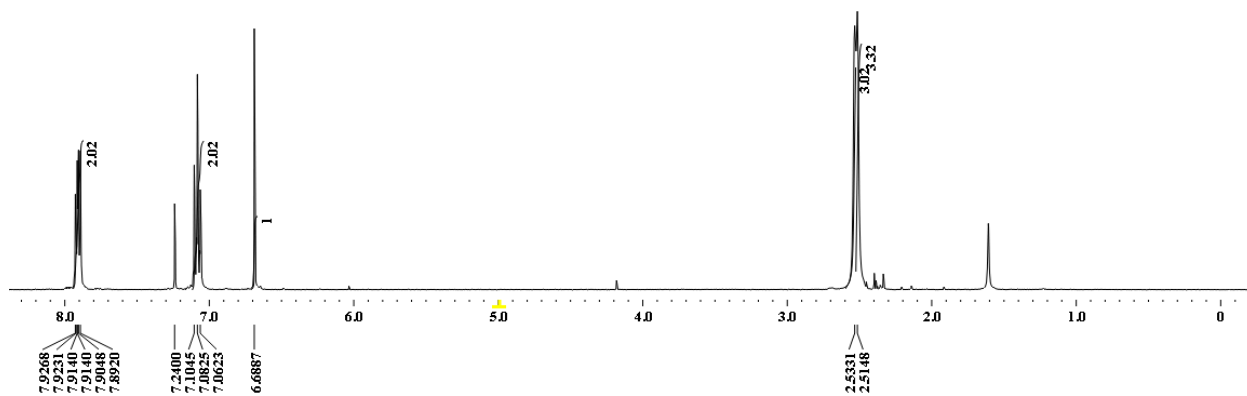
References

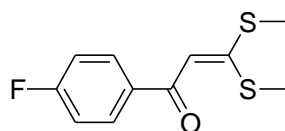
1. K.T. Potts, P.A. Winslow, *Synthesis*, 1987, 839.
2. M. Lubbe, R. Klassen, T. Trabhardt, A. Villinger, P. Langer, *Synlett*, 2008, **15**, 2331.
3. Z.F. Li, Y.M. Zhang, *Chinese Journal of Chemistry*, 2001, **19**, 996.
4. G.M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
5. G.M. Sheldrick, *SHELXL-97, Computer program for crystal structure refinement*.
University of Göttingen, Germany, 1997.

COPIES OF ^1H NMR & ^{13}C NMR DATA



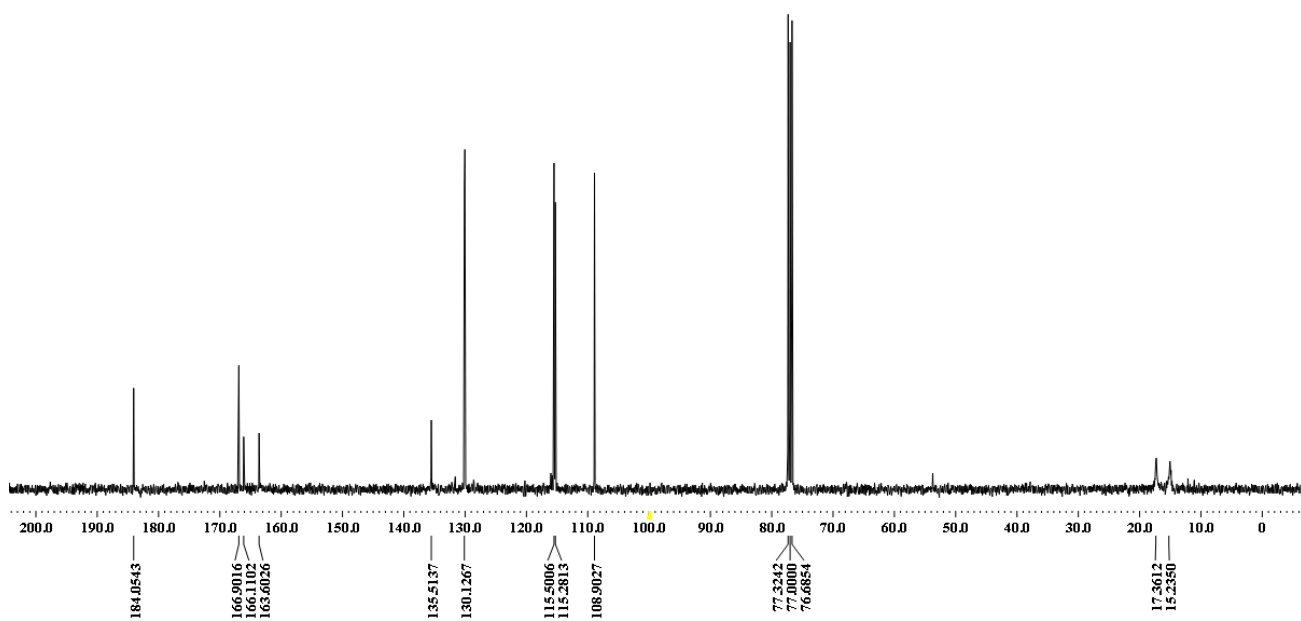
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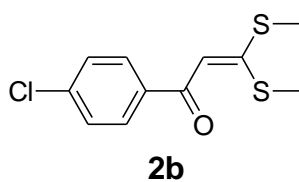




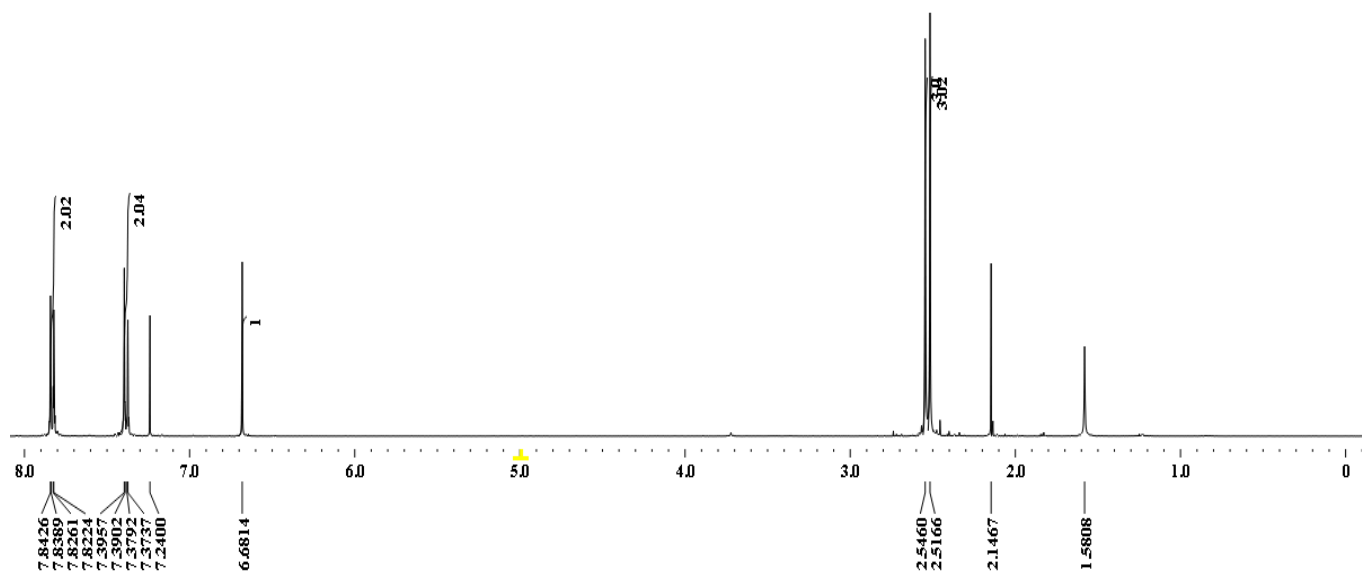
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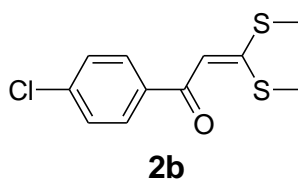
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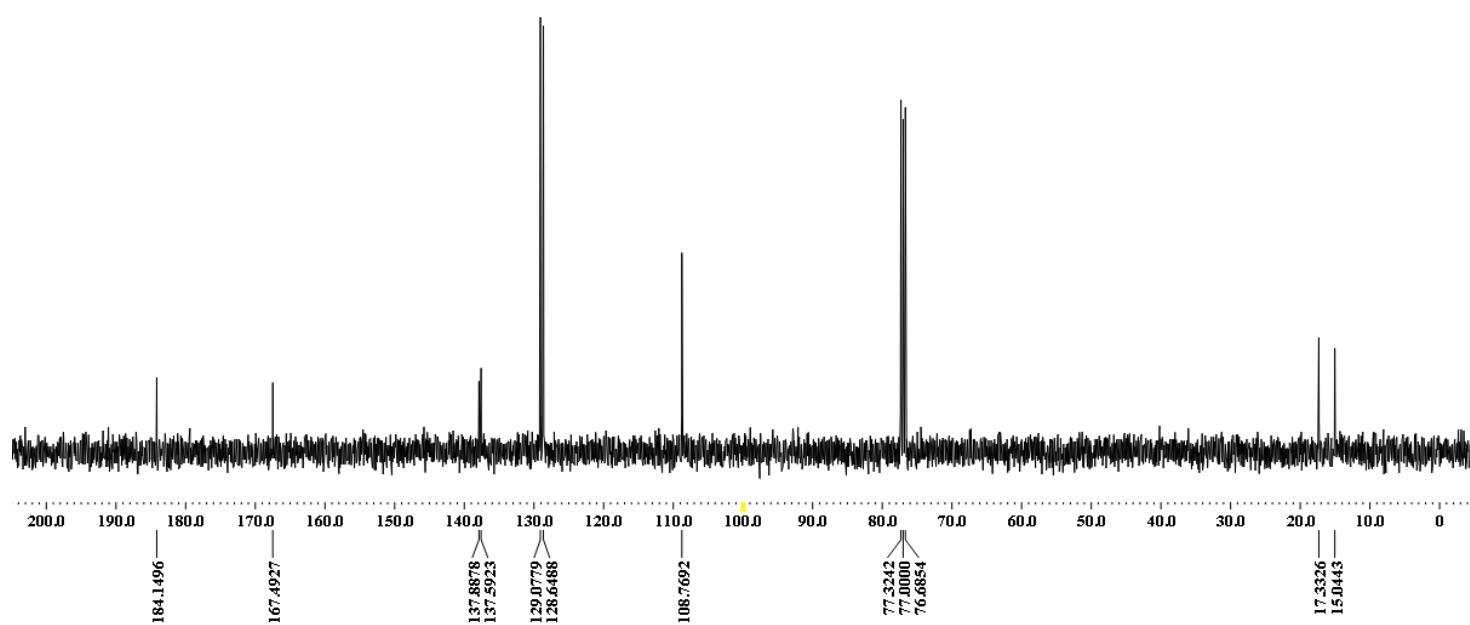


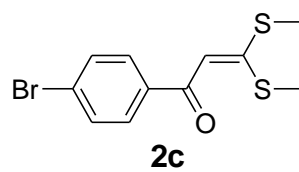
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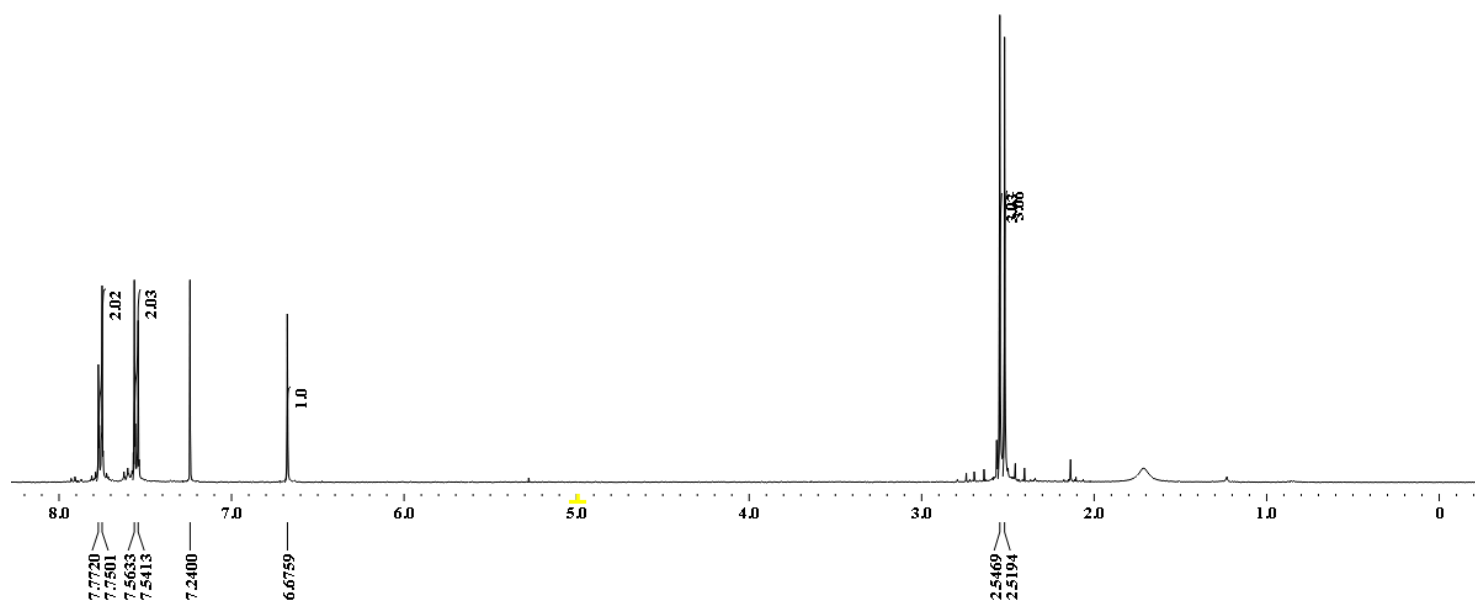


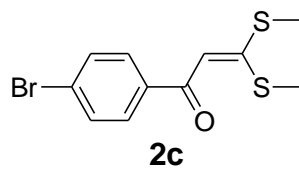
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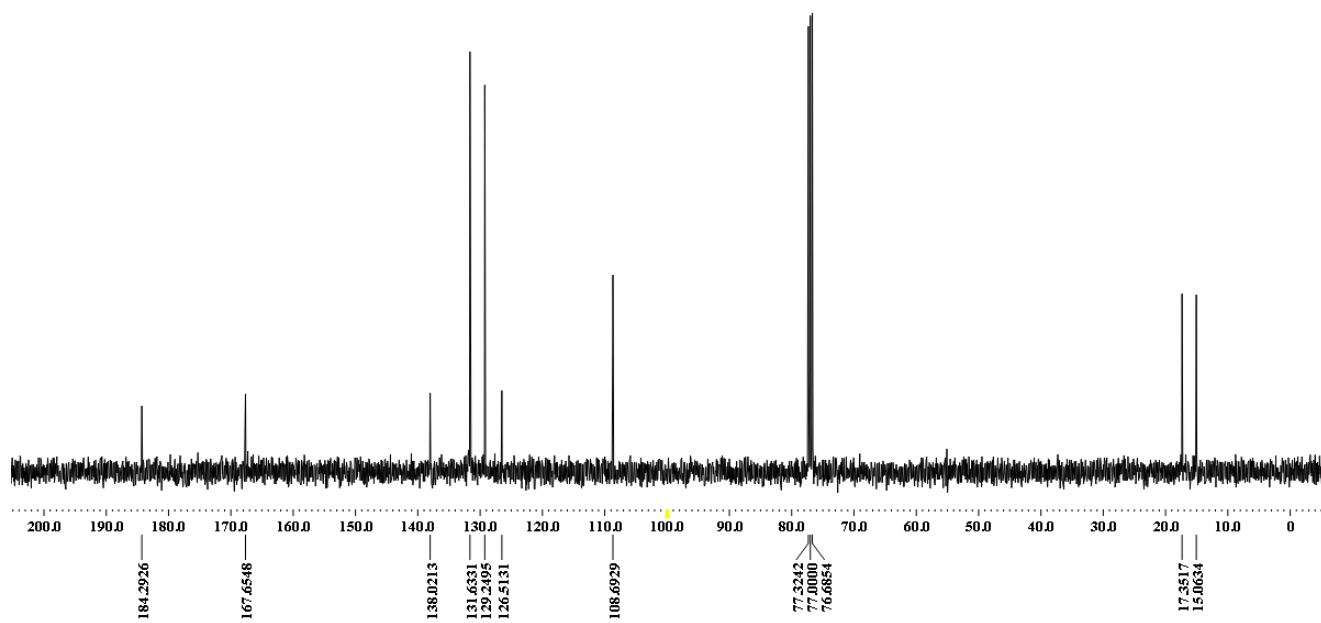


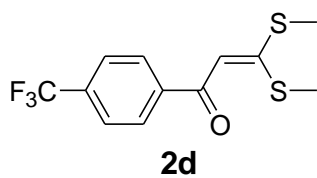
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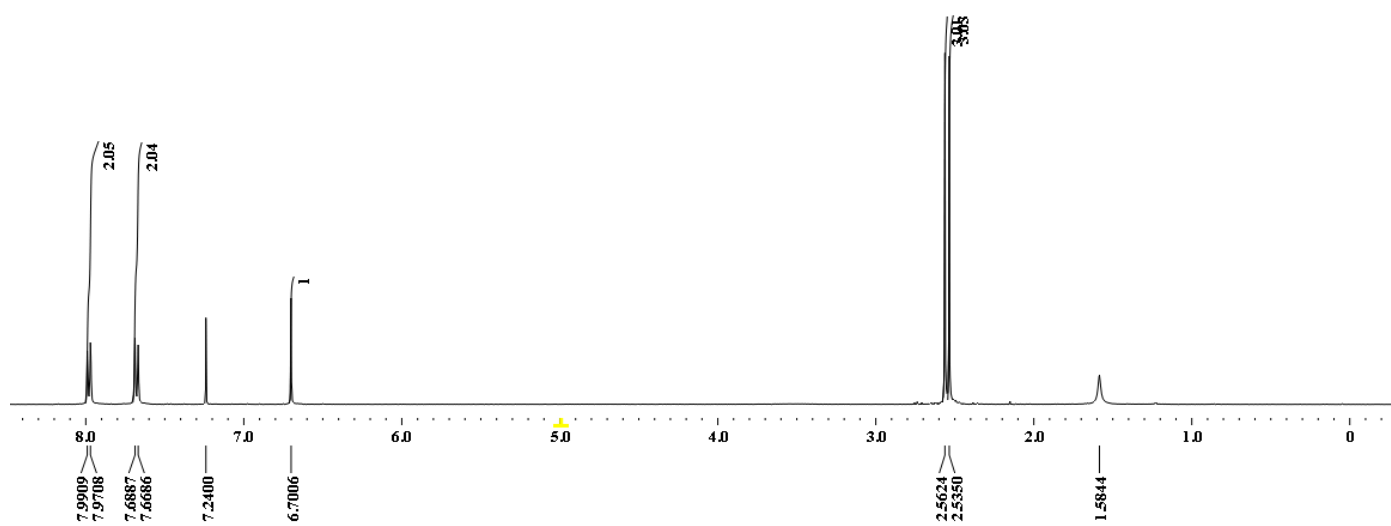


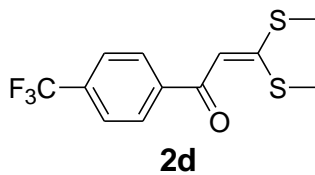
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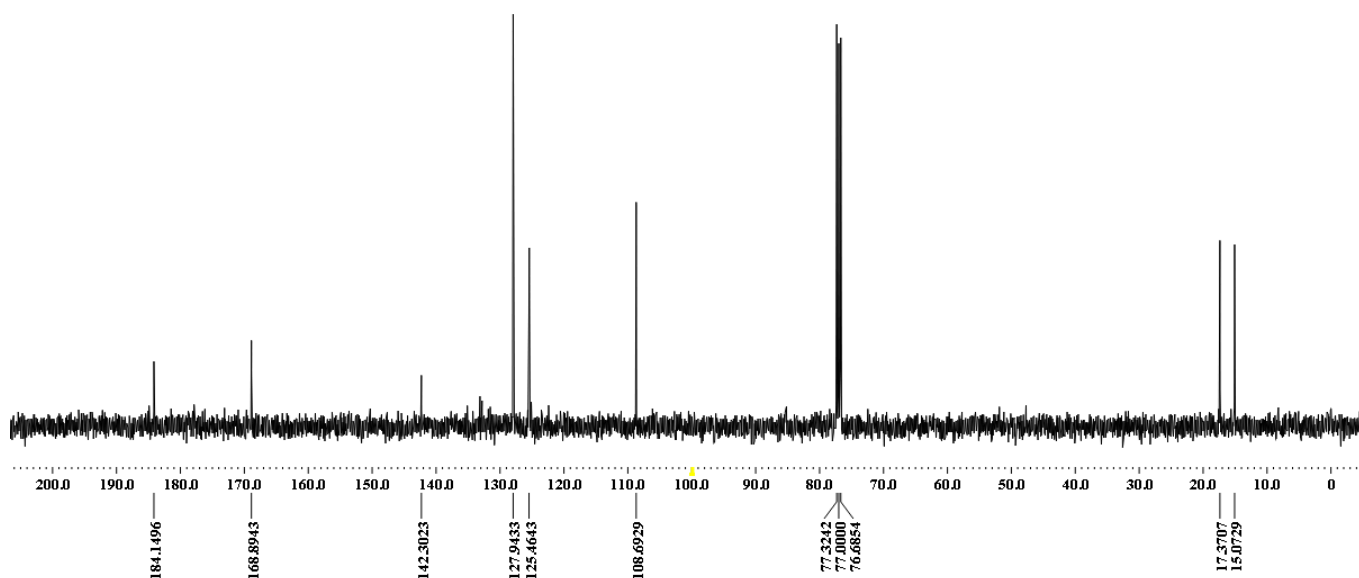


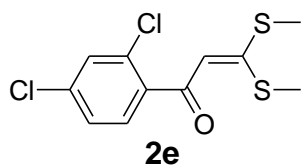
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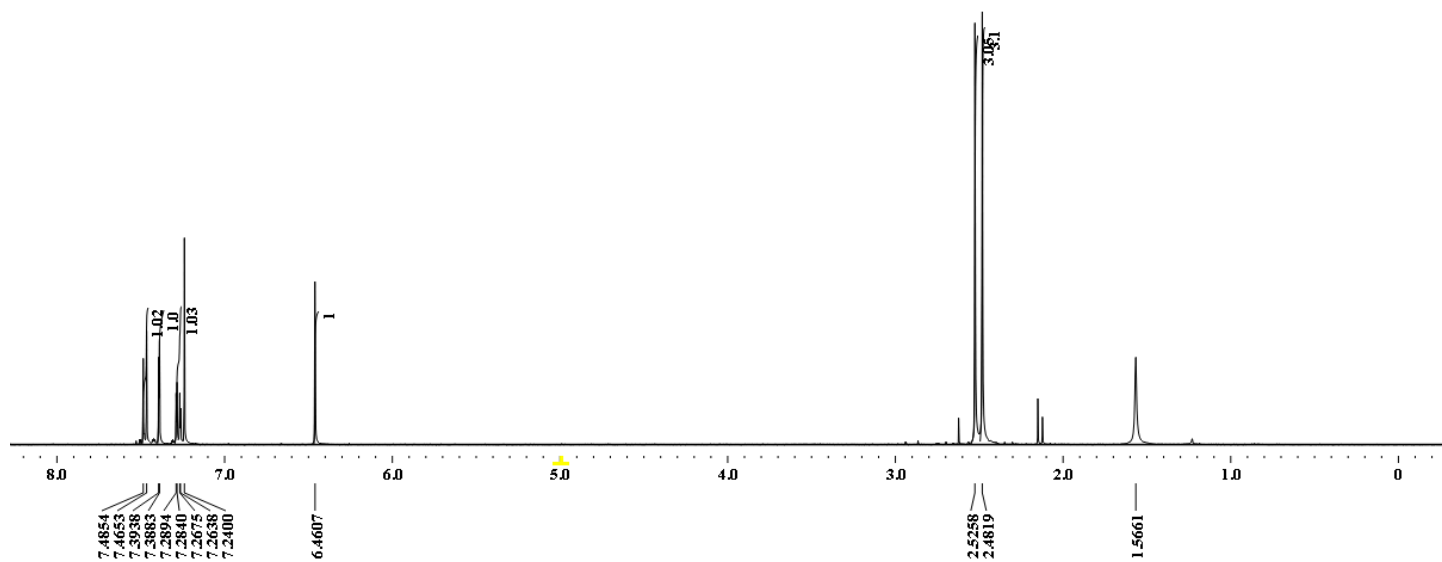


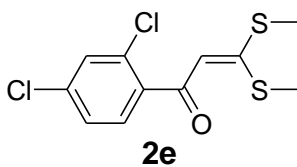
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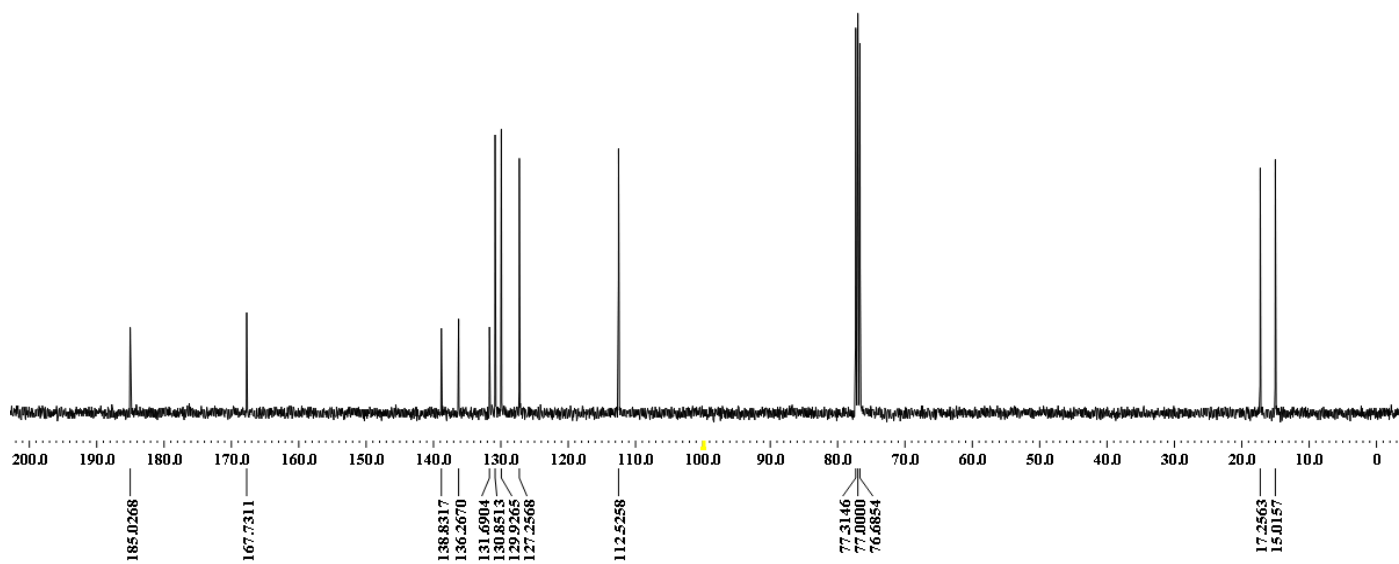


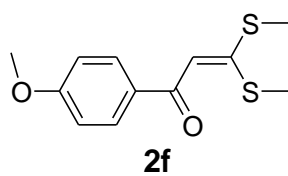
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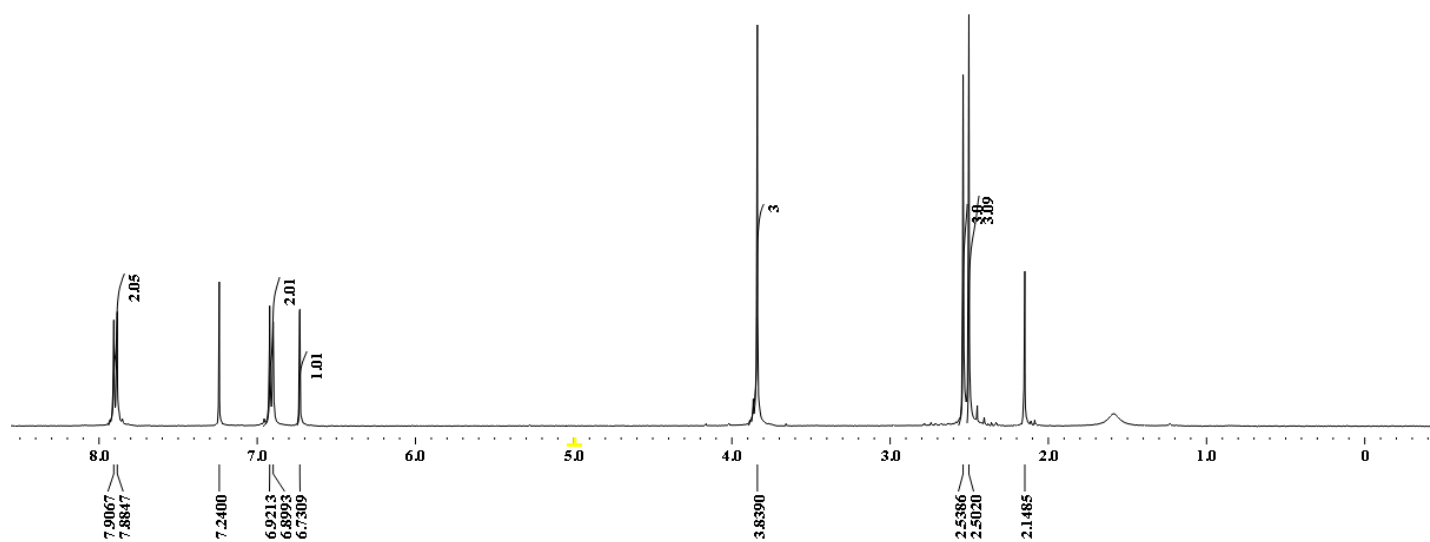


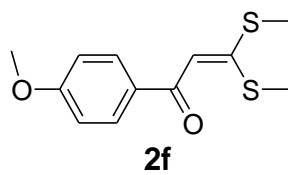
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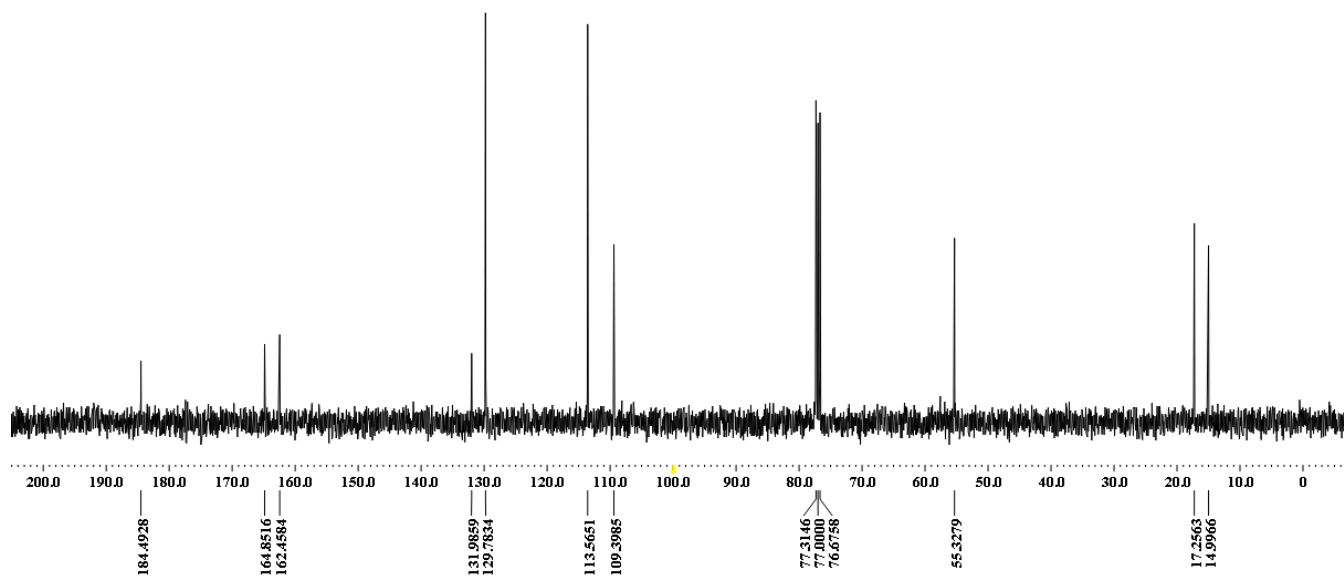


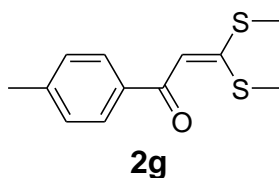
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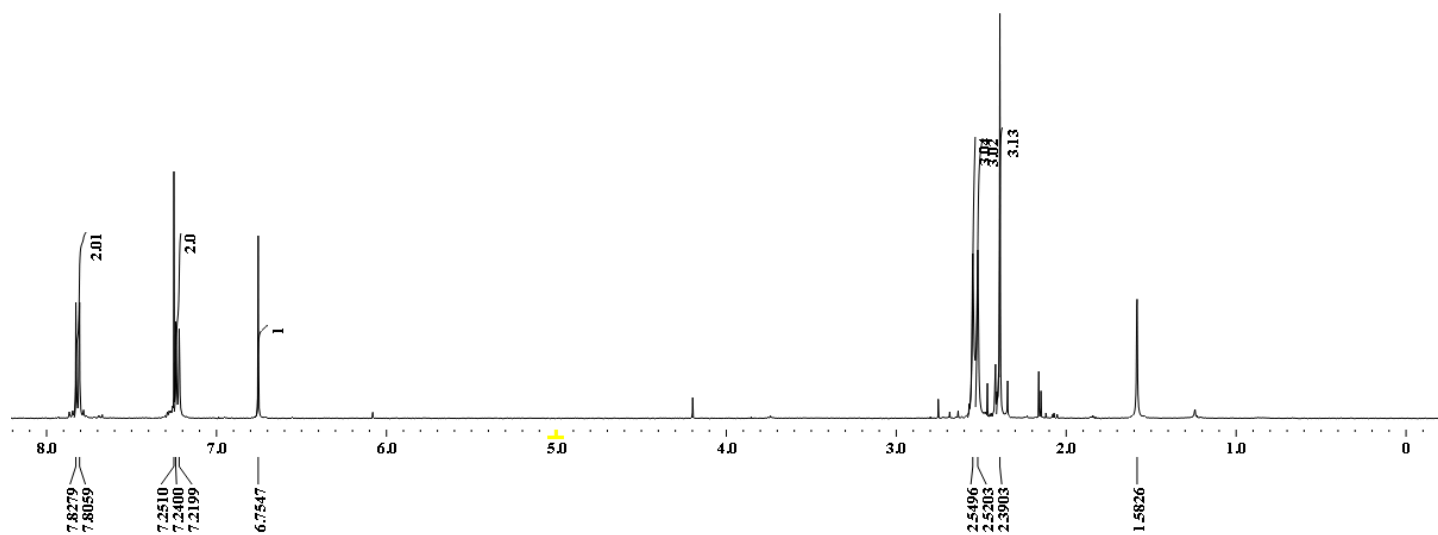


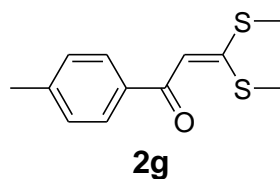
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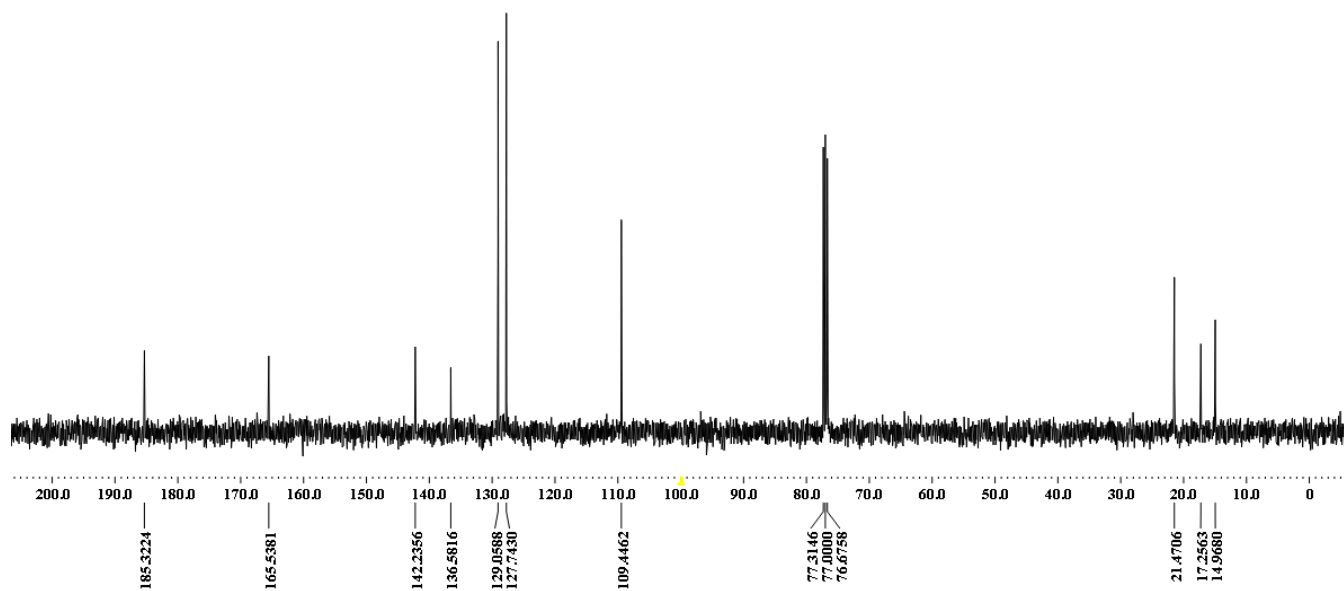


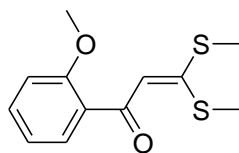
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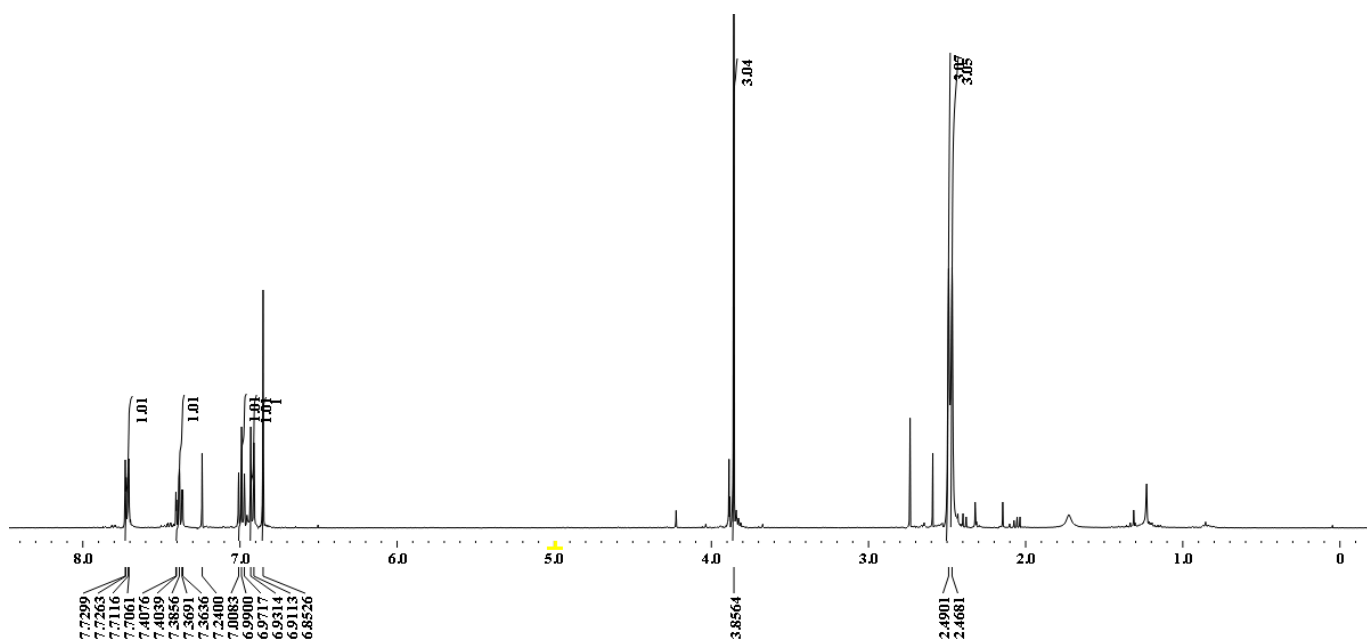
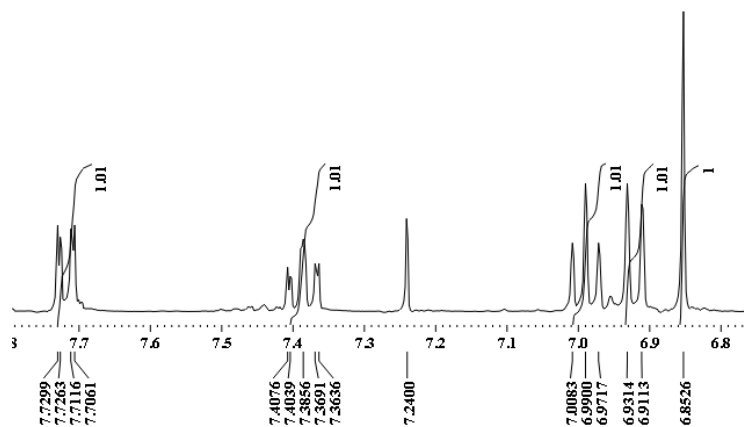
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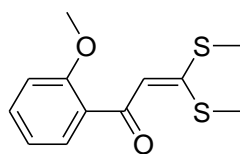




2h

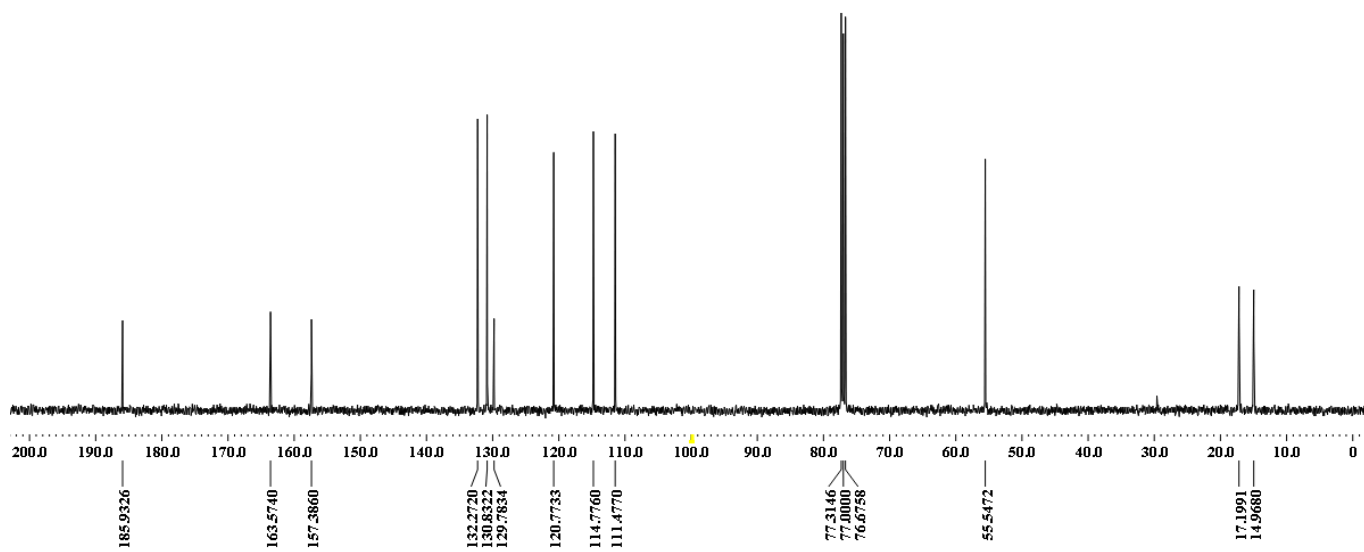
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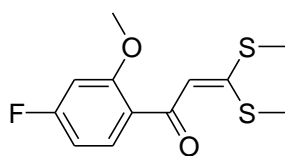




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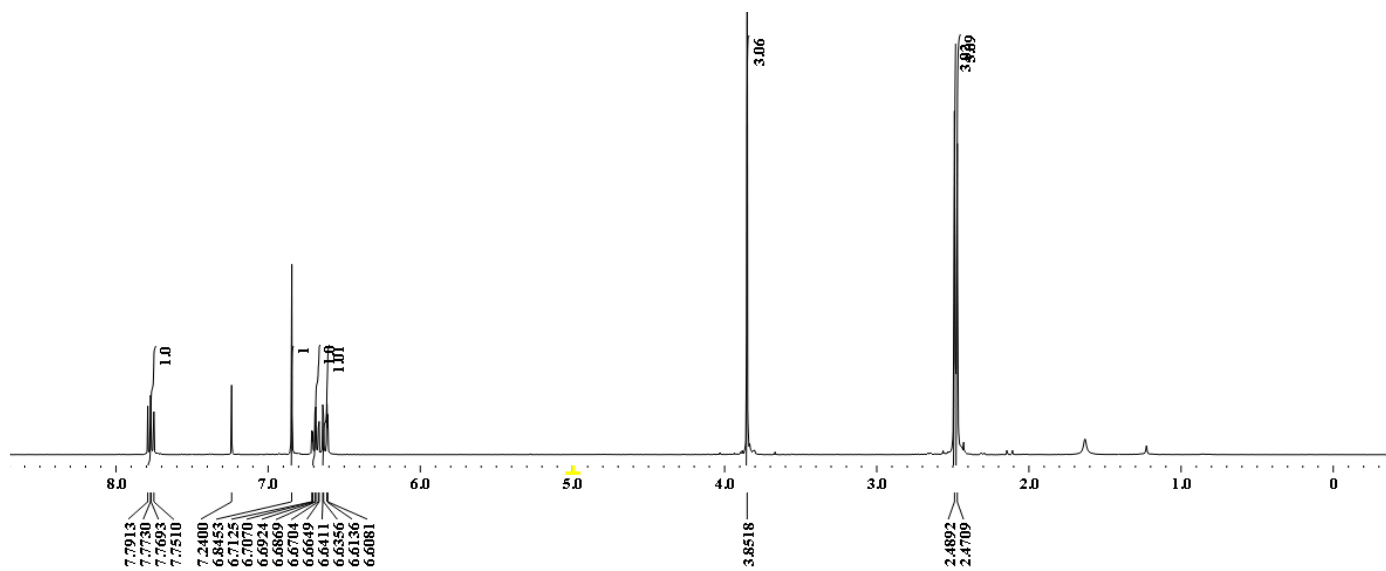
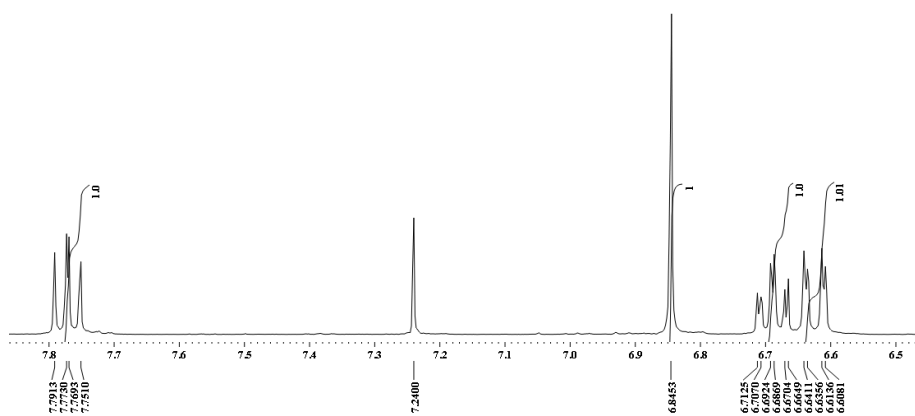
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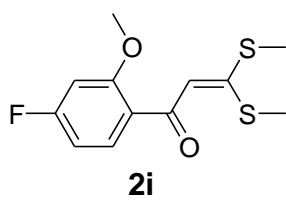




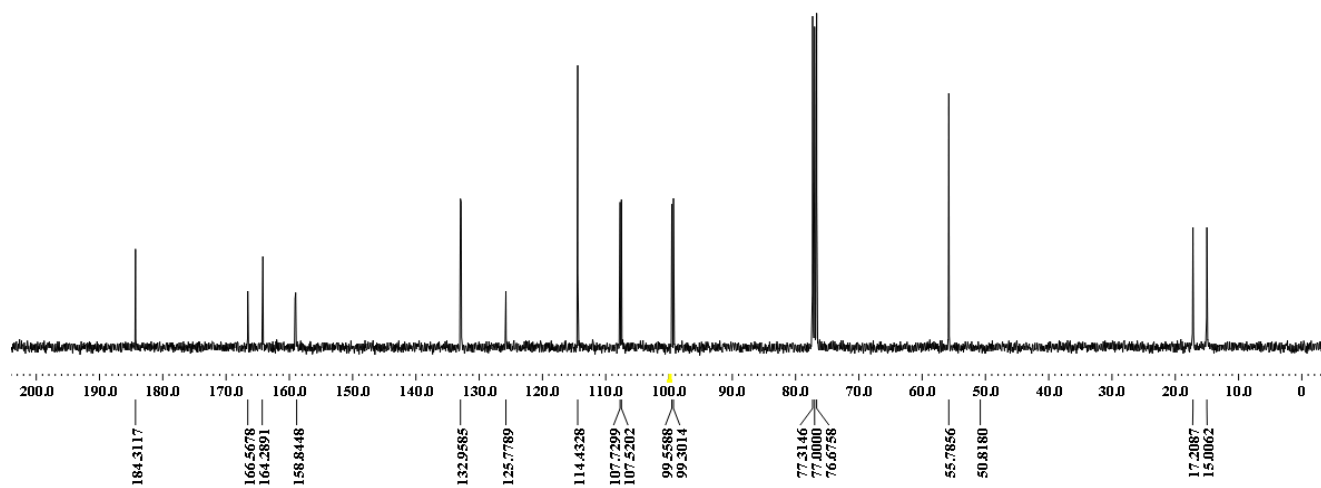
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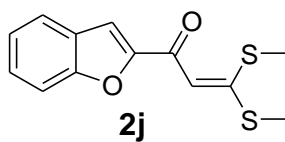
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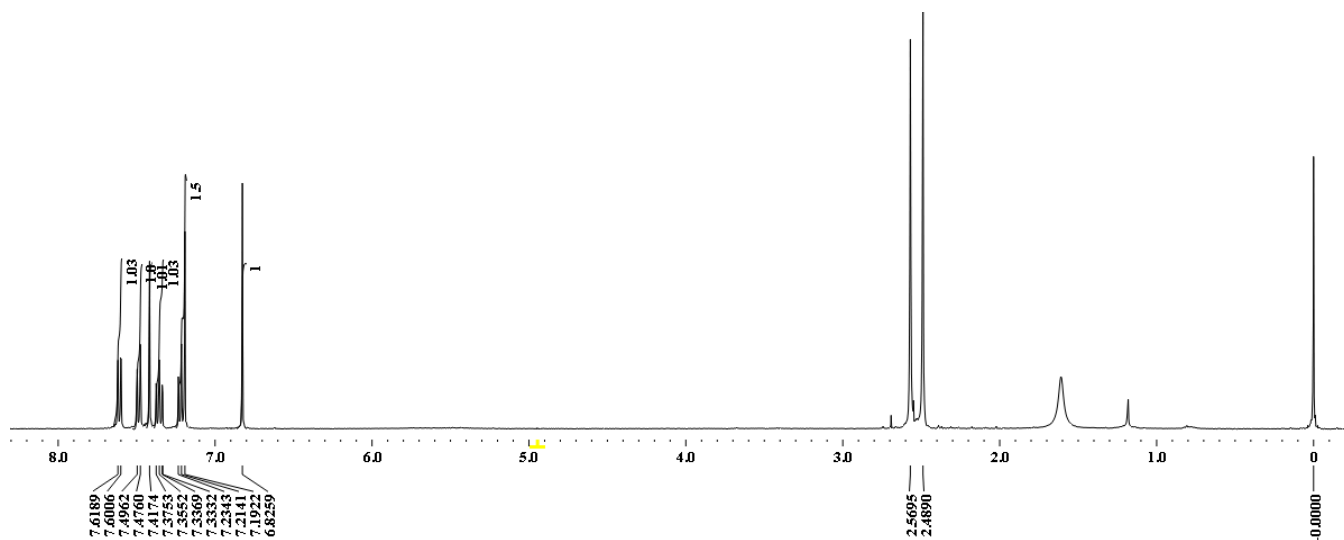
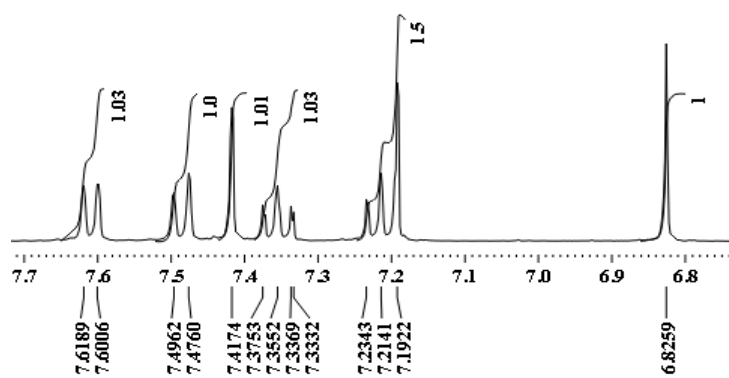


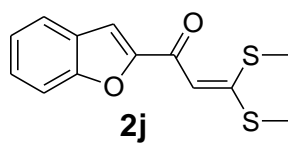
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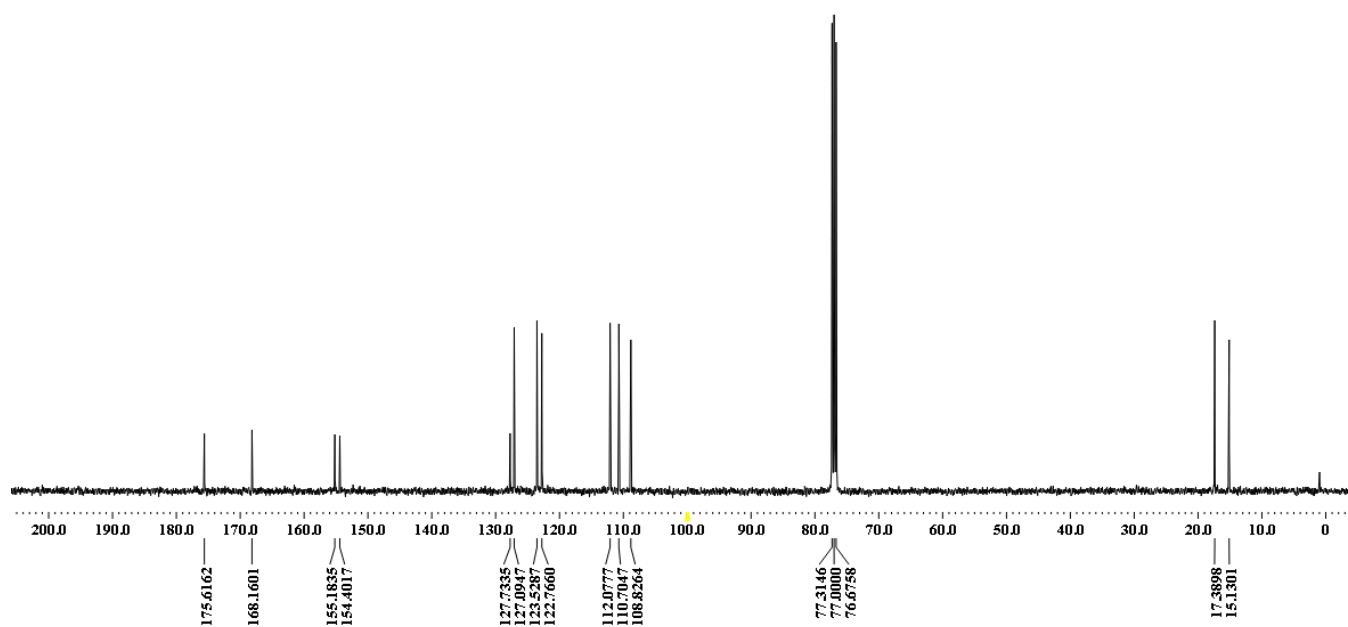


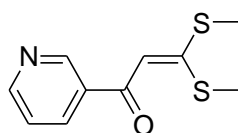
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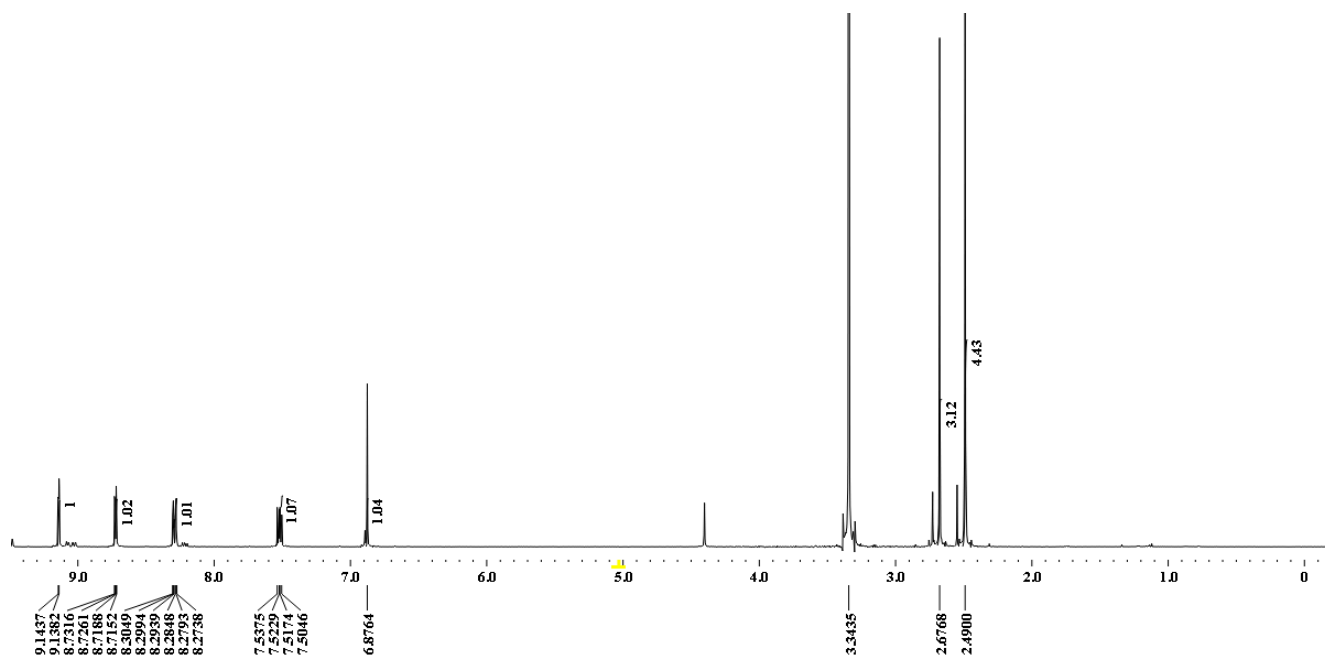
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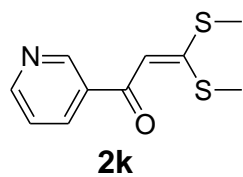




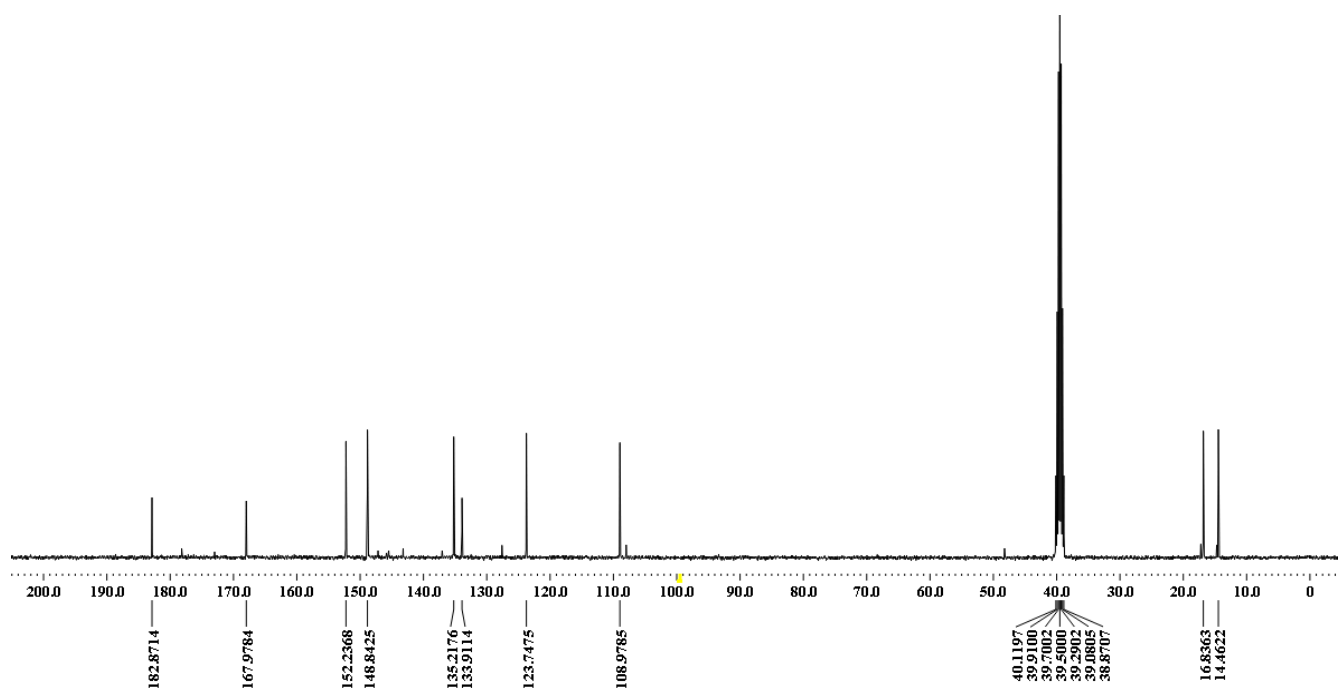
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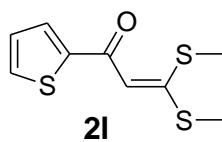
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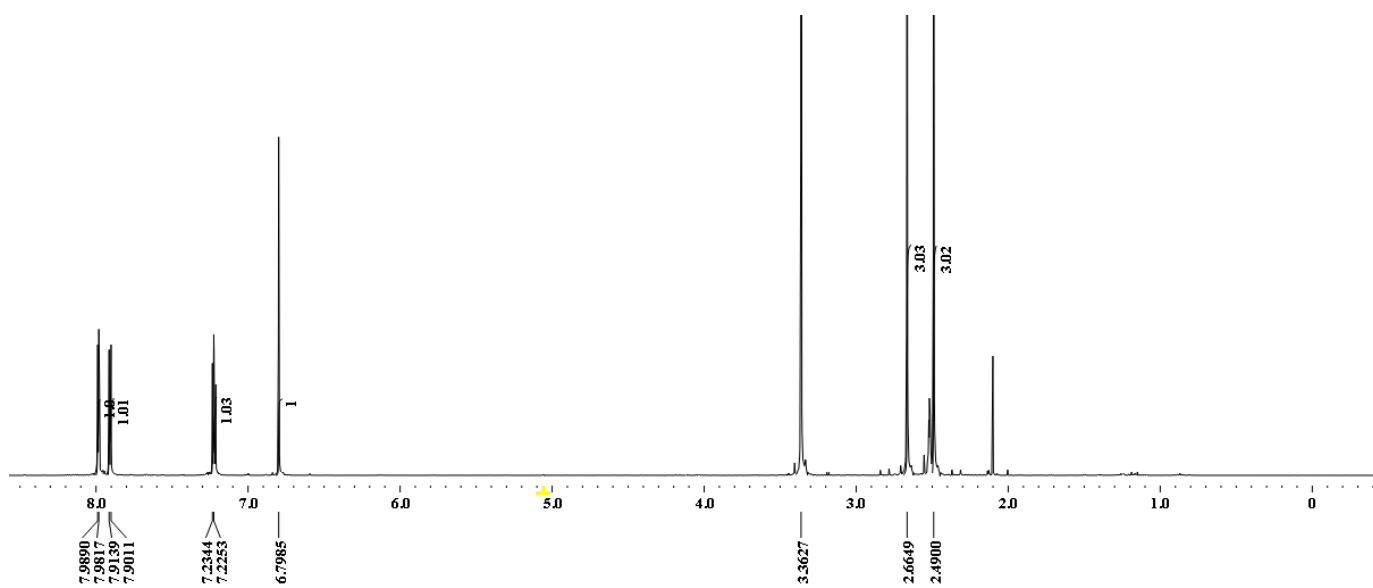


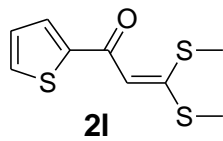
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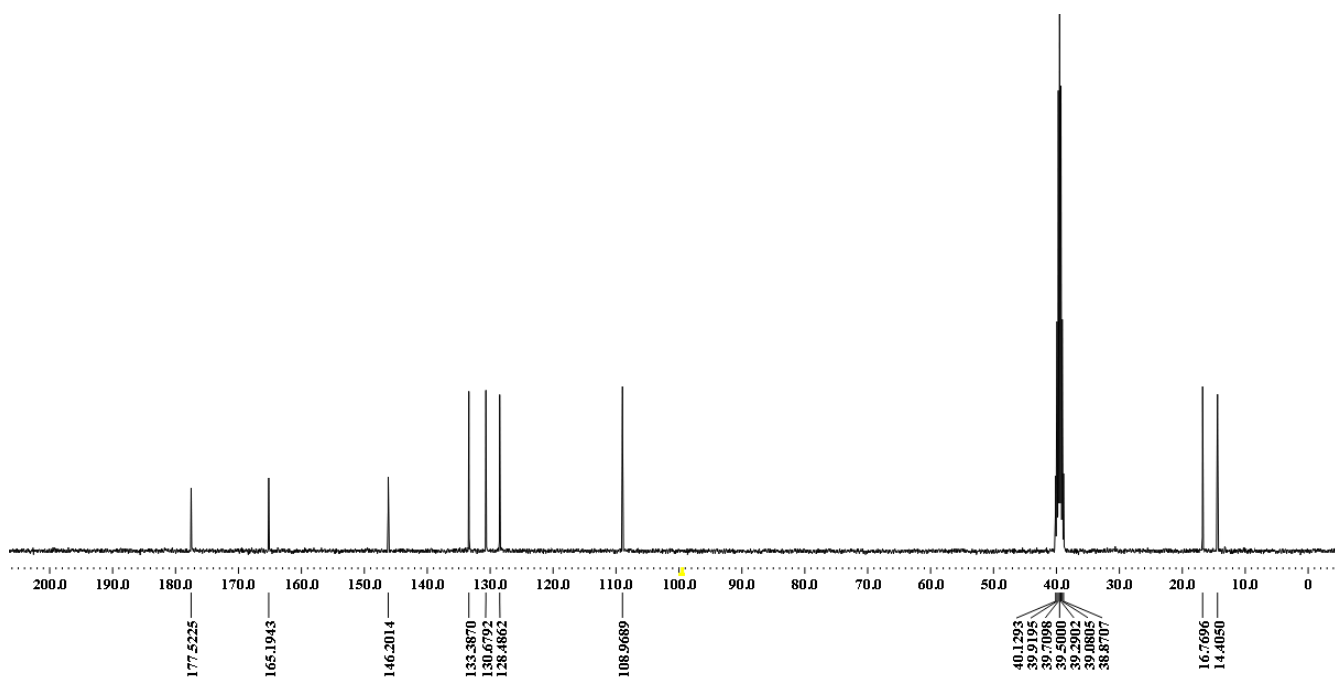


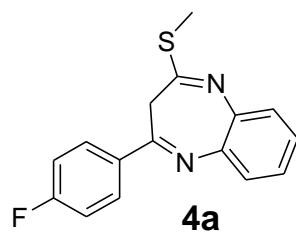
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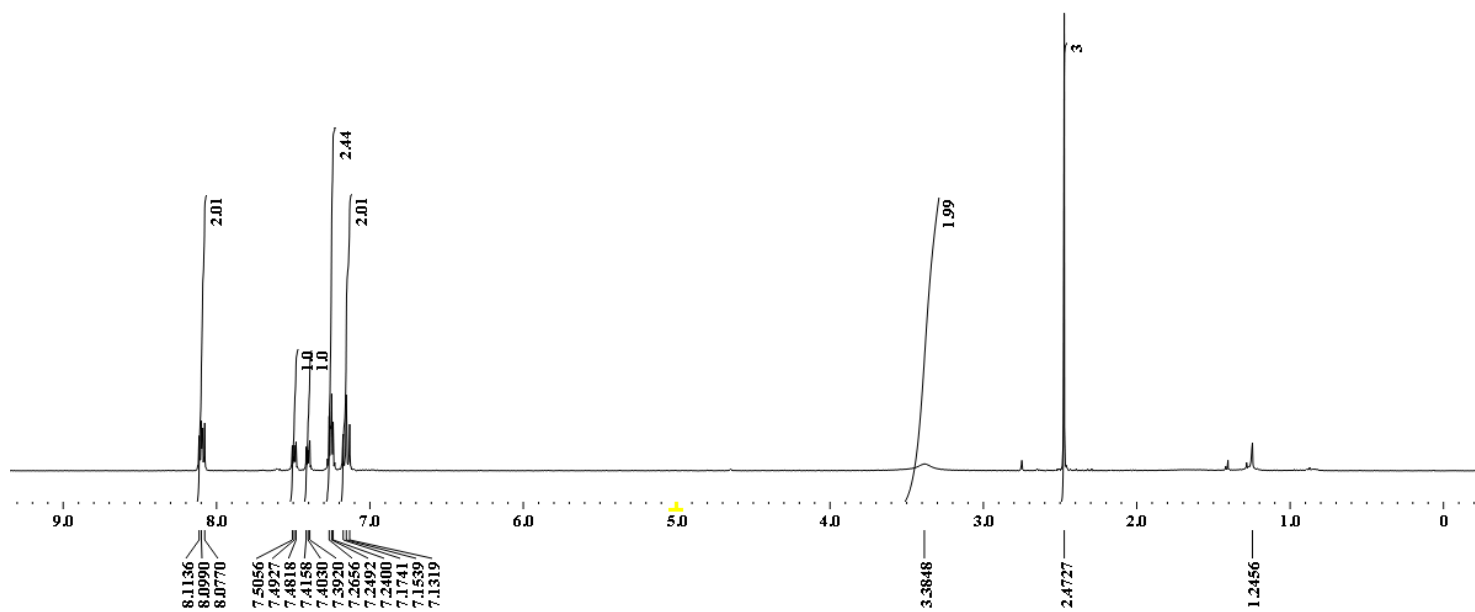


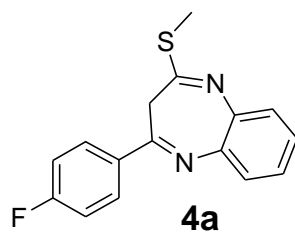
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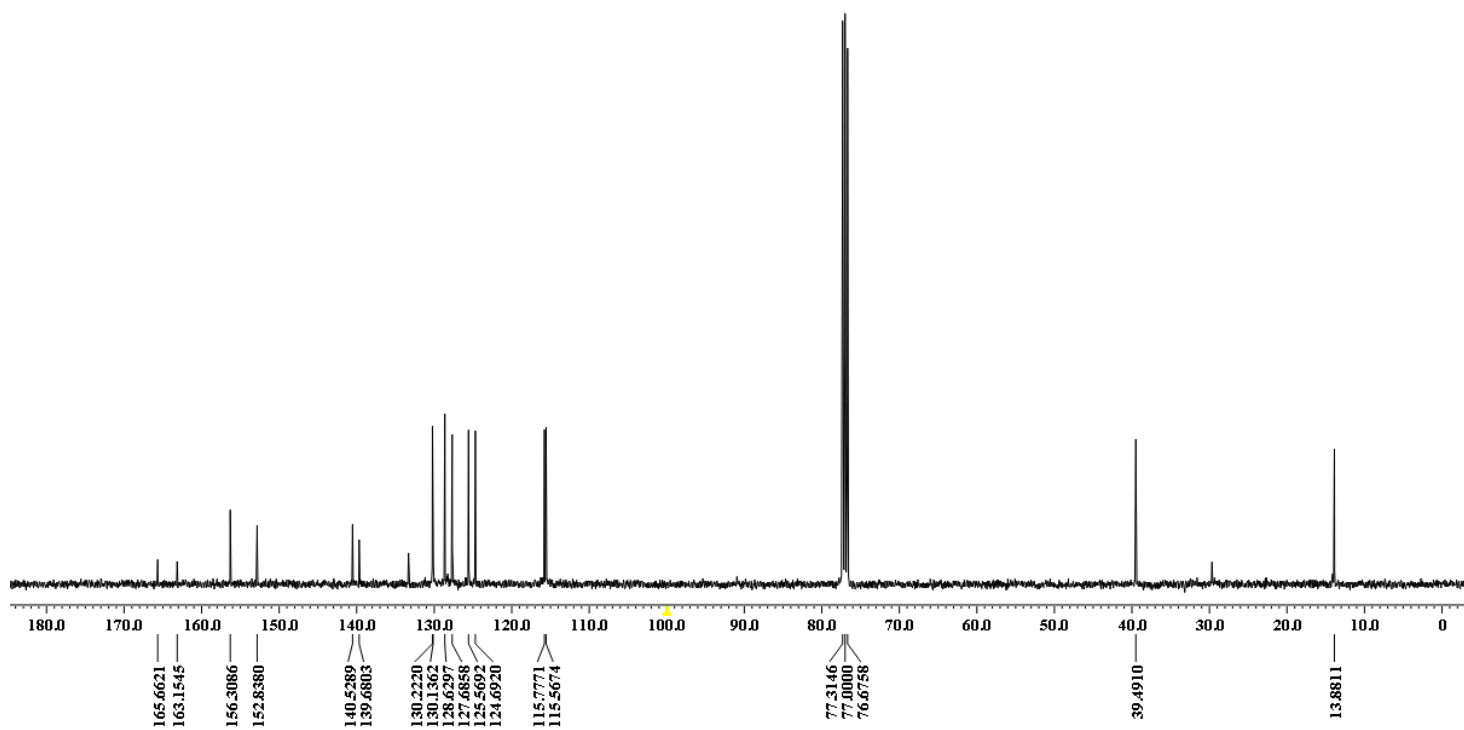


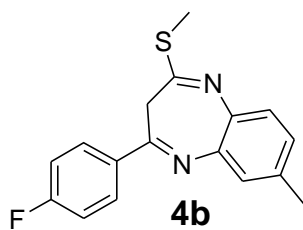
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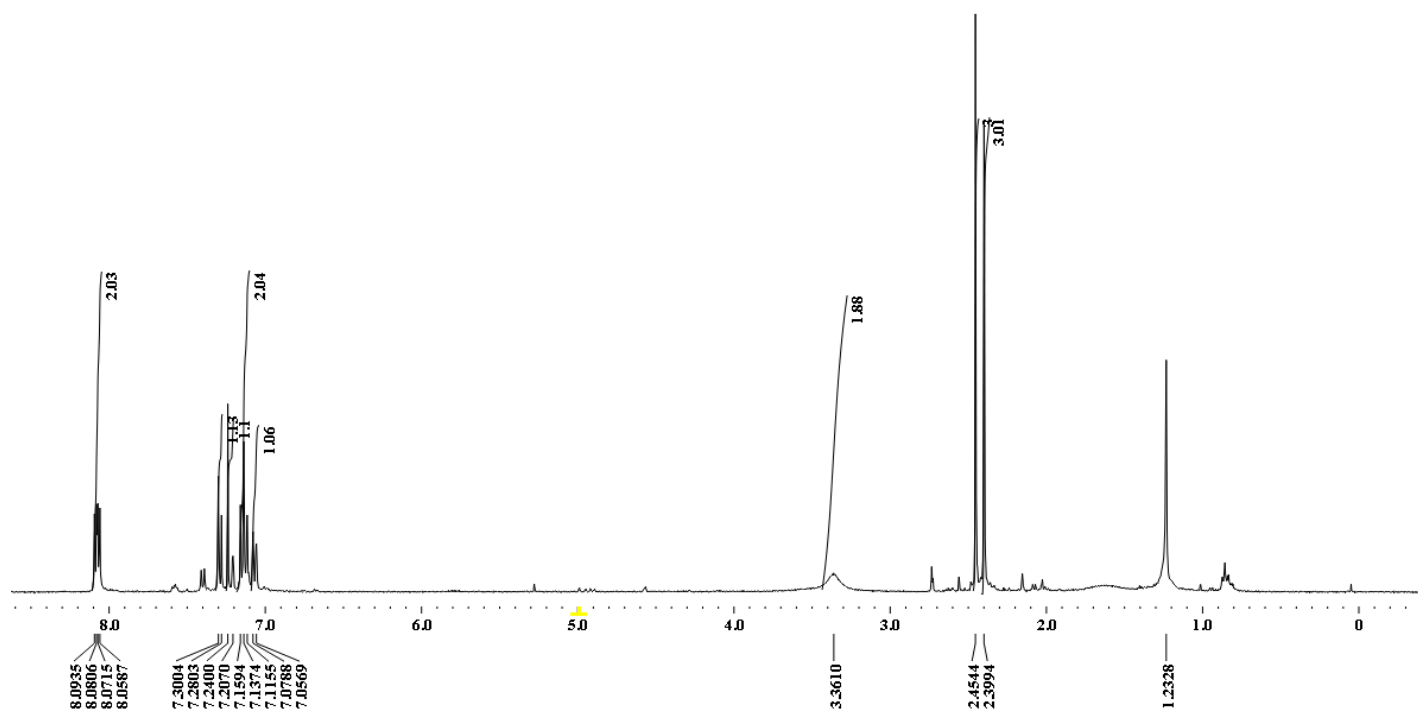


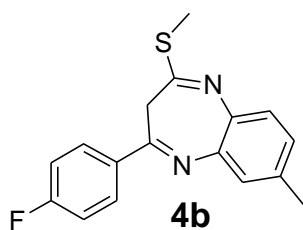
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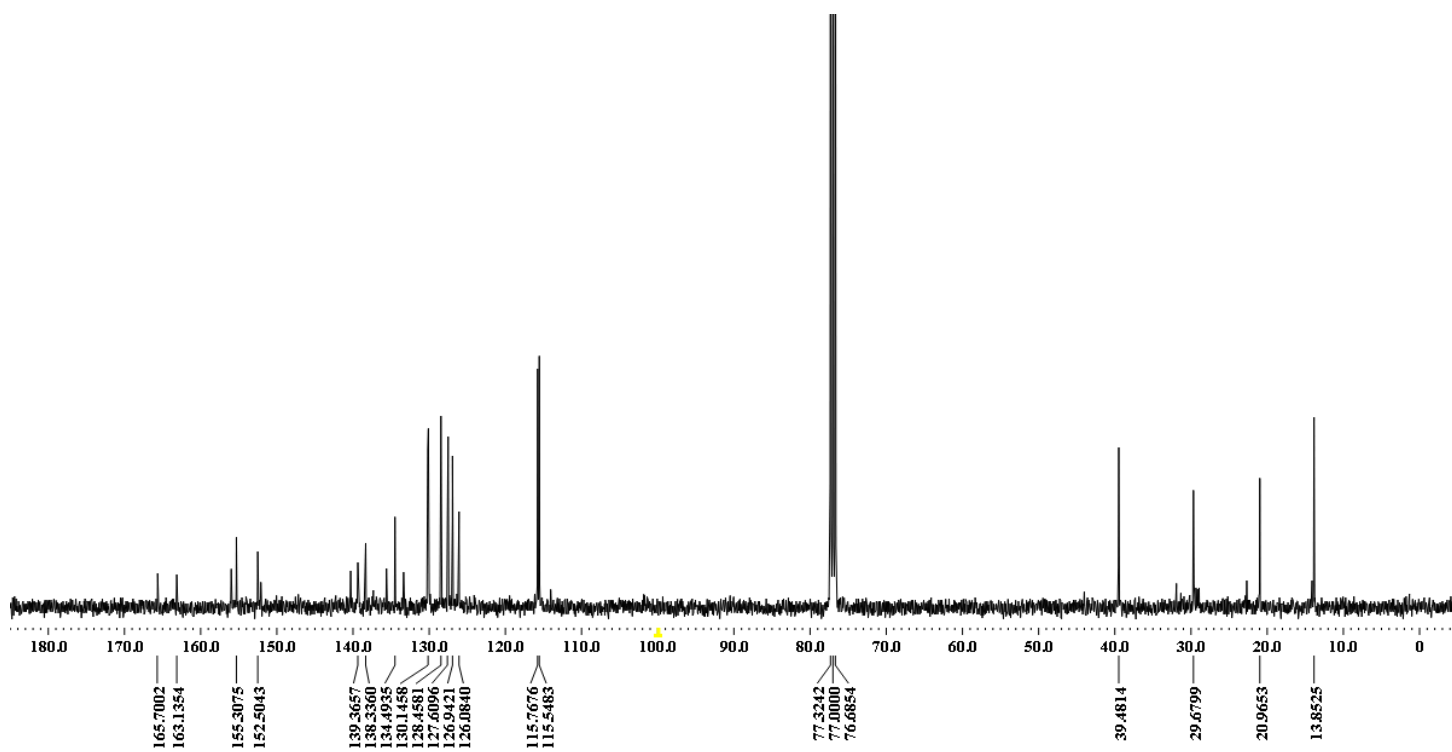


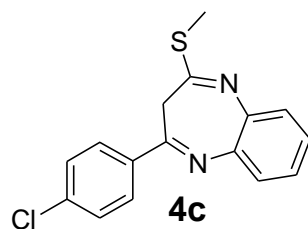
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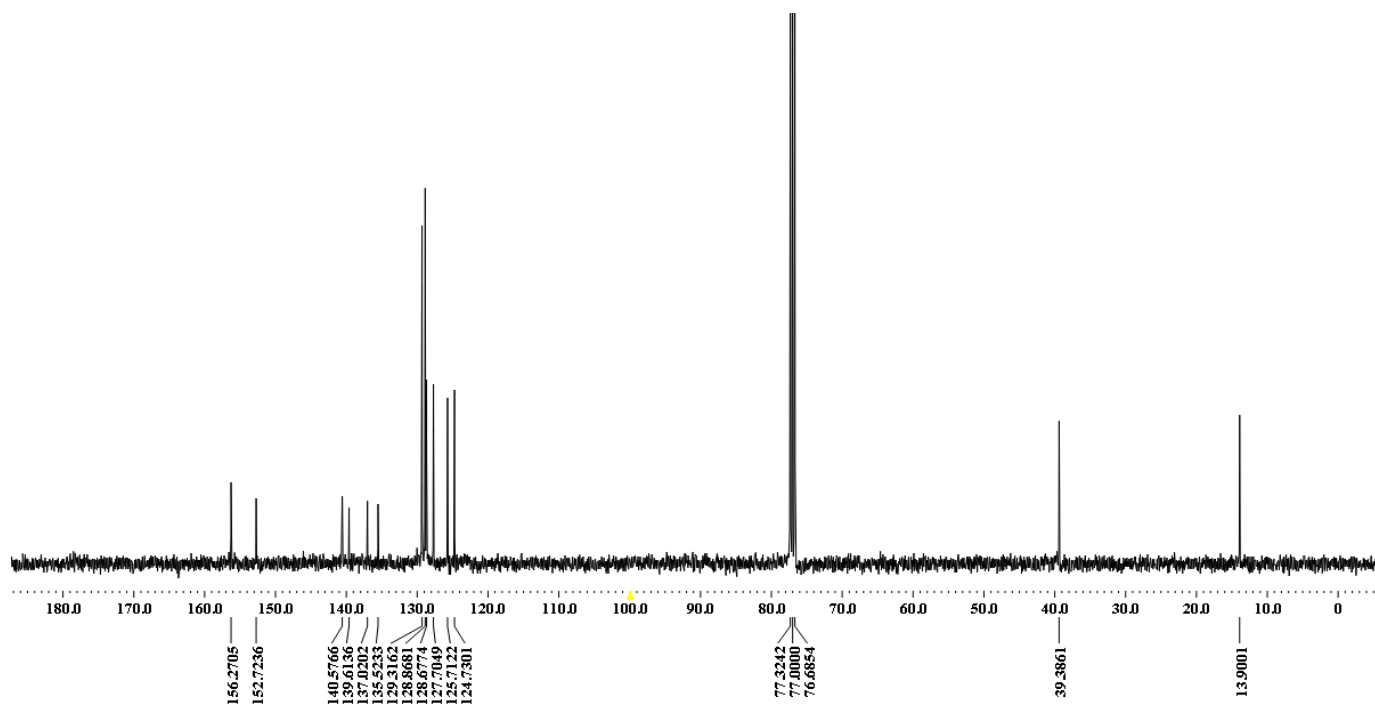


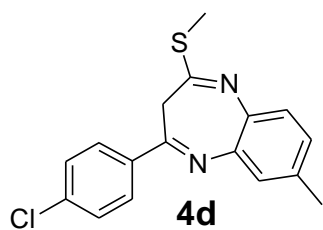
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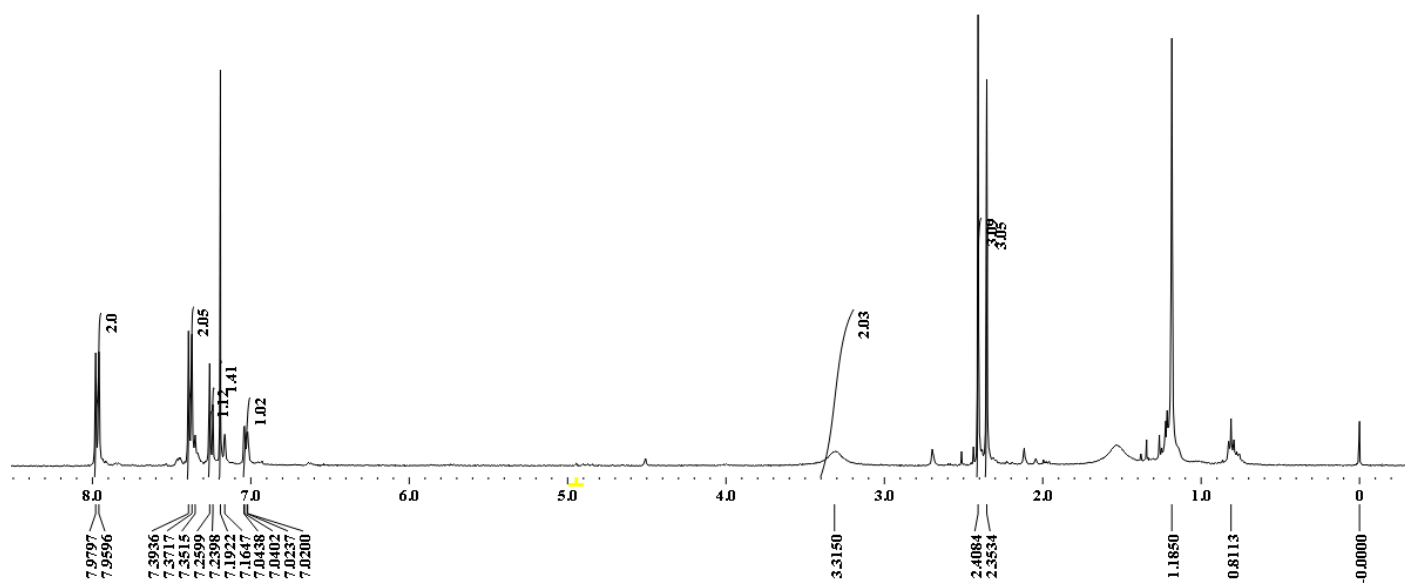


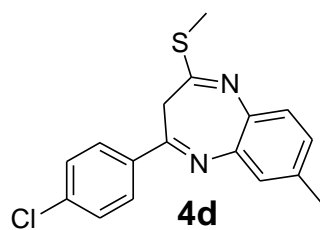
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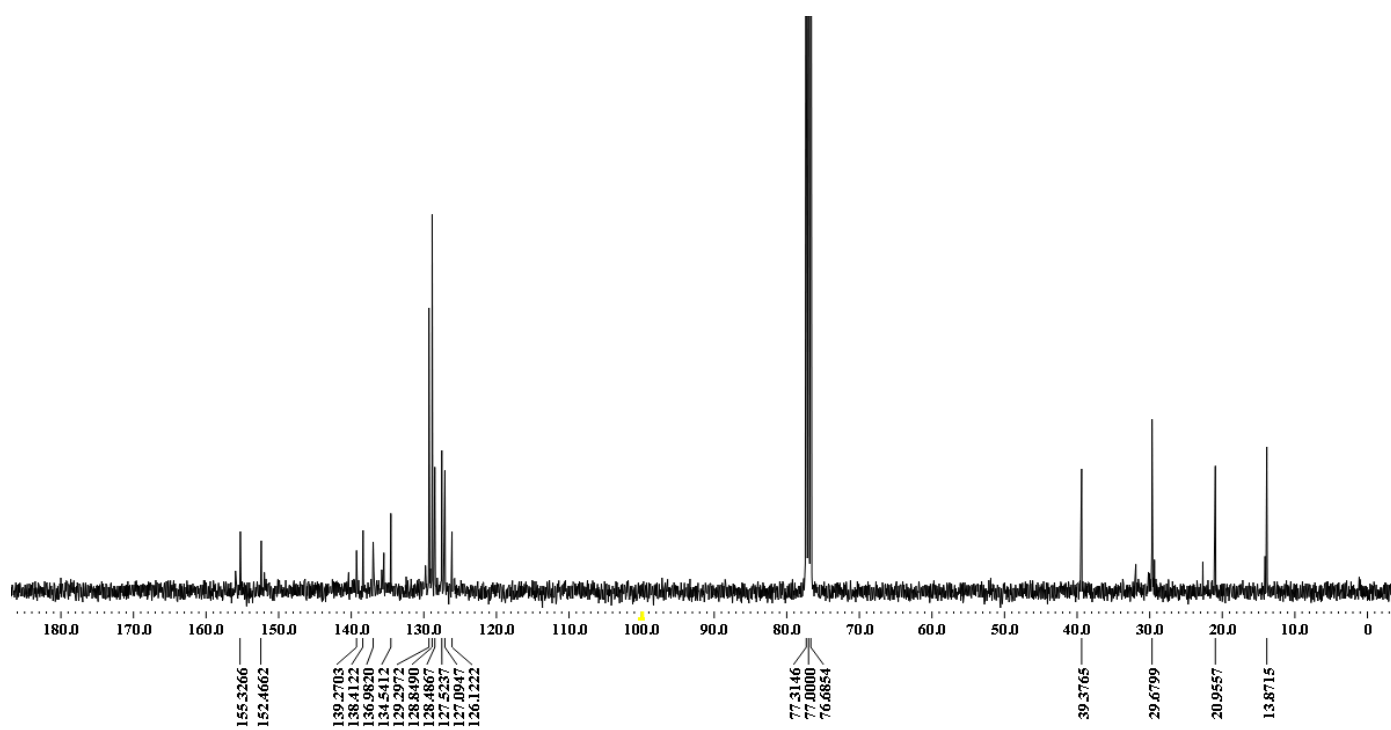


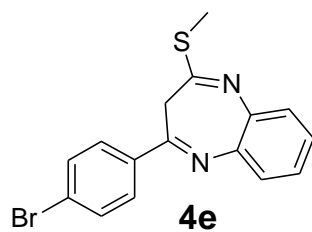
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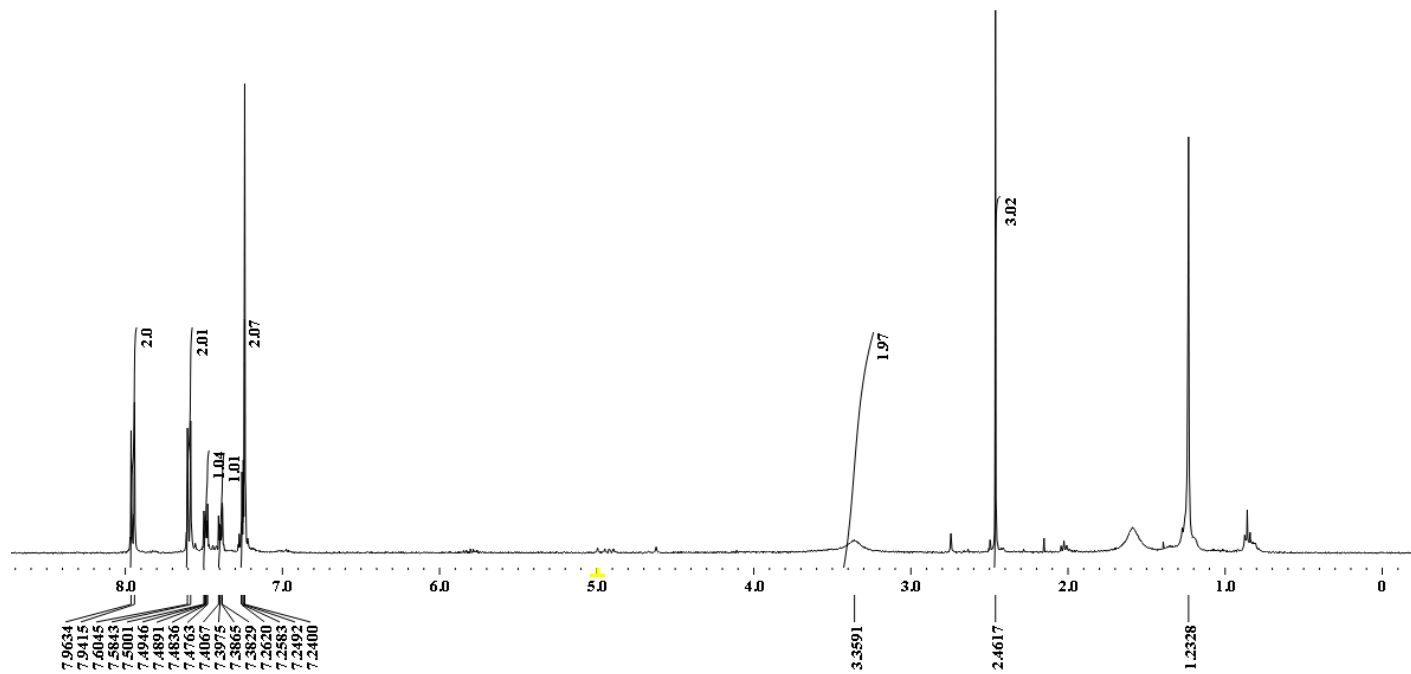


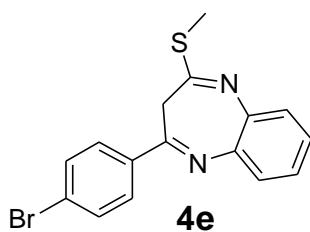
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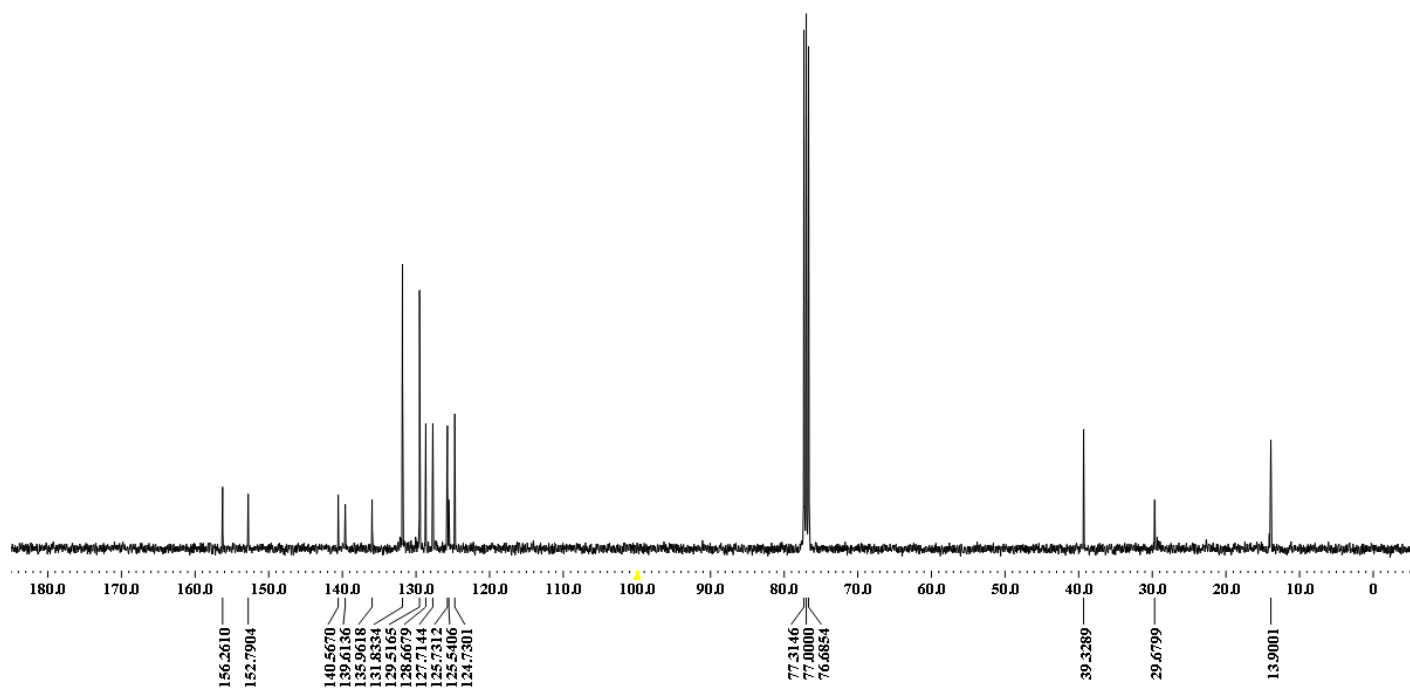


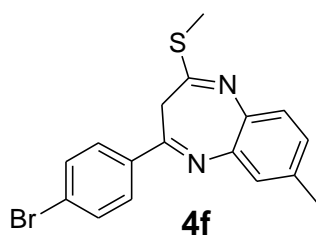
$^1\text{H NMR}$



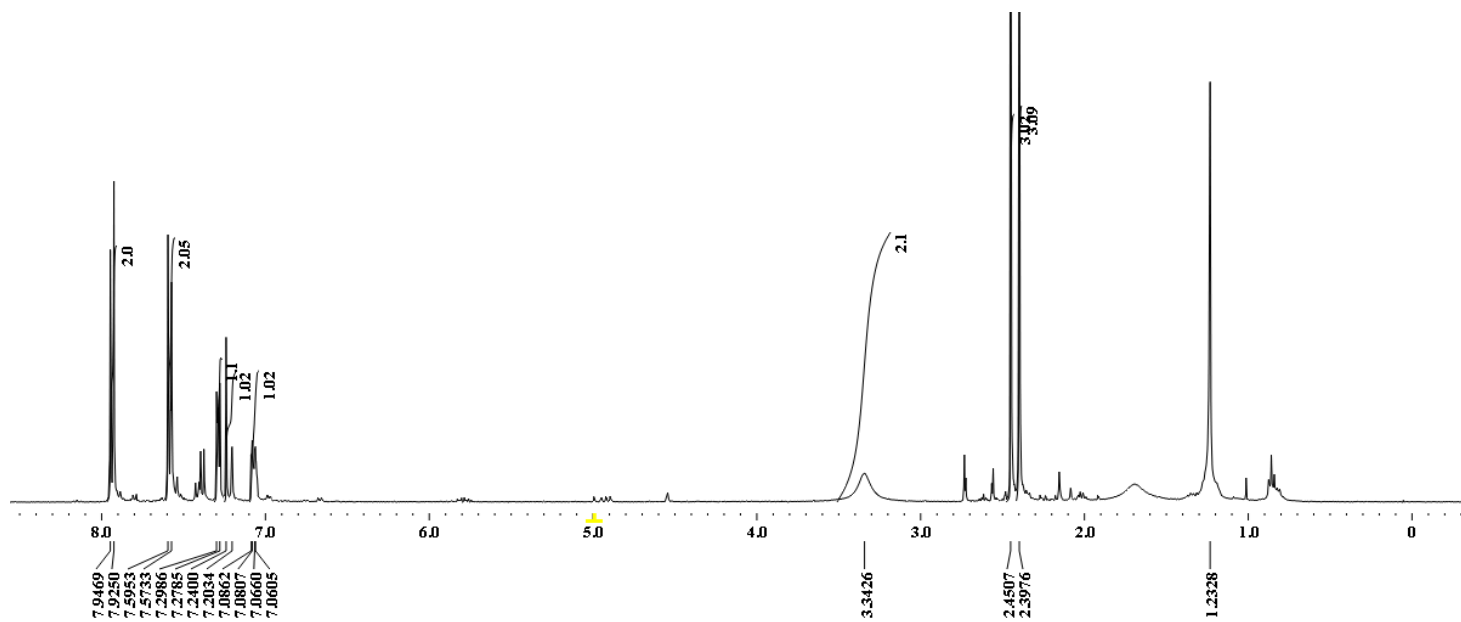


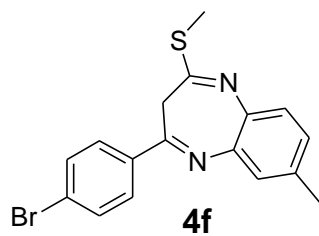
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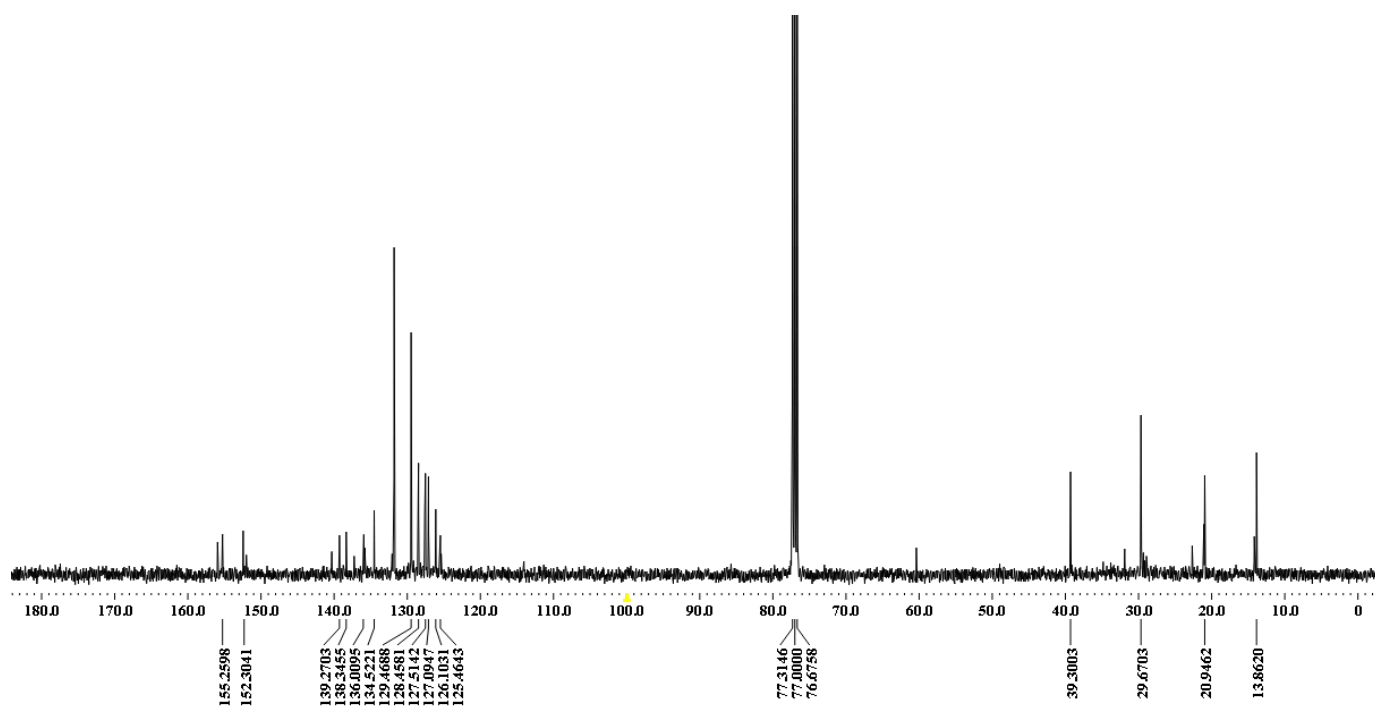


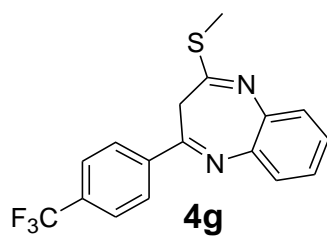
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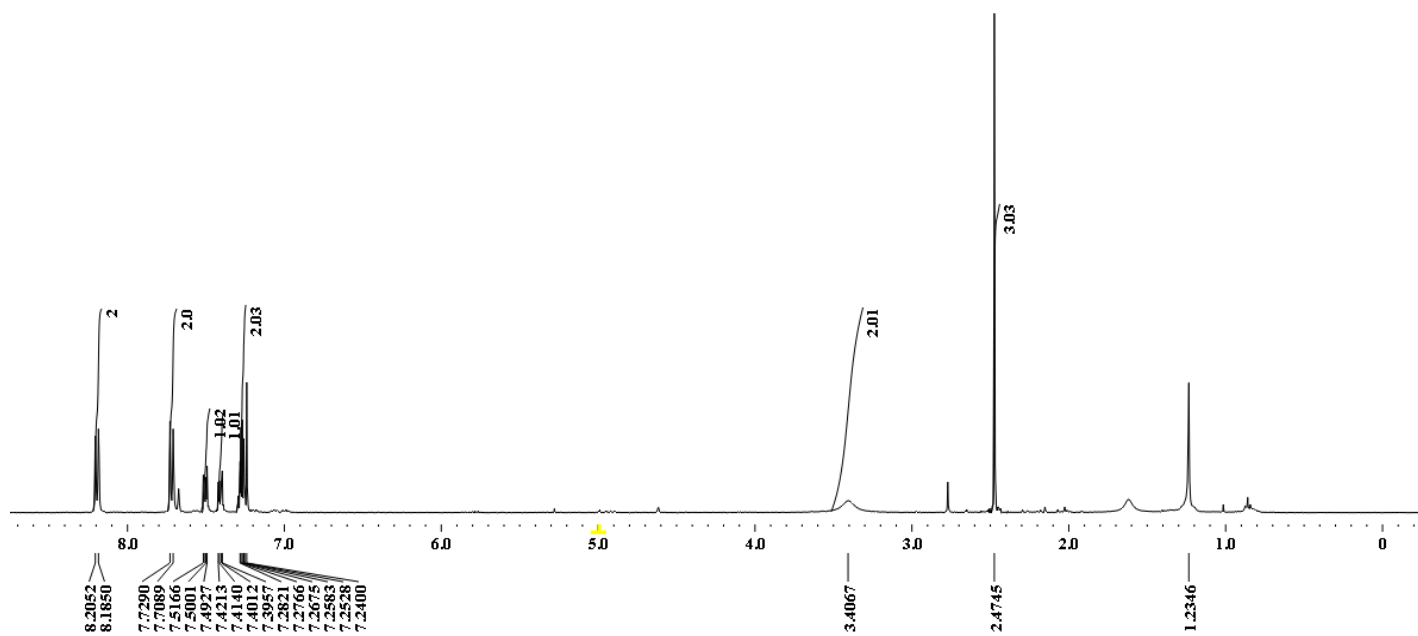


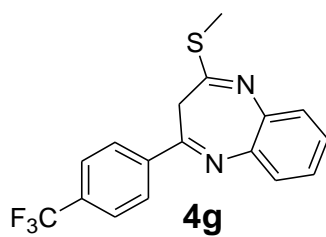
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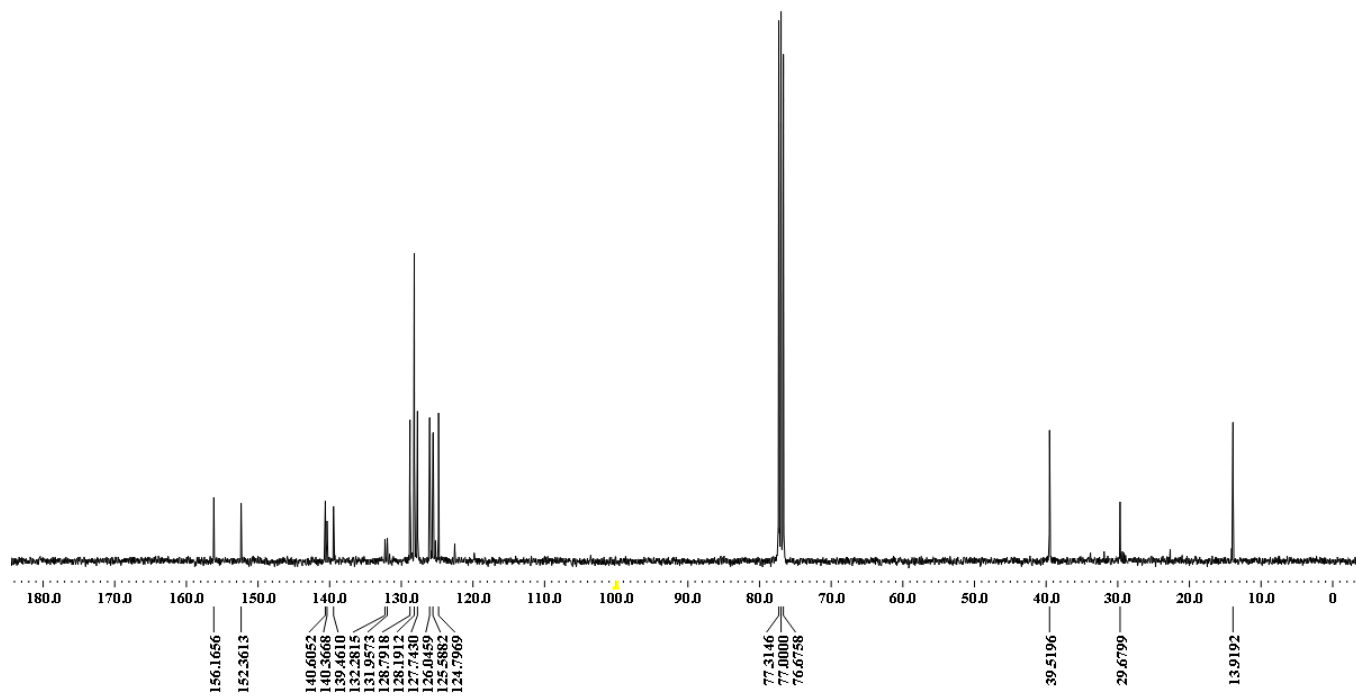


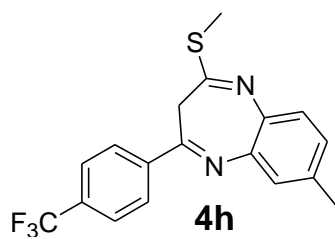
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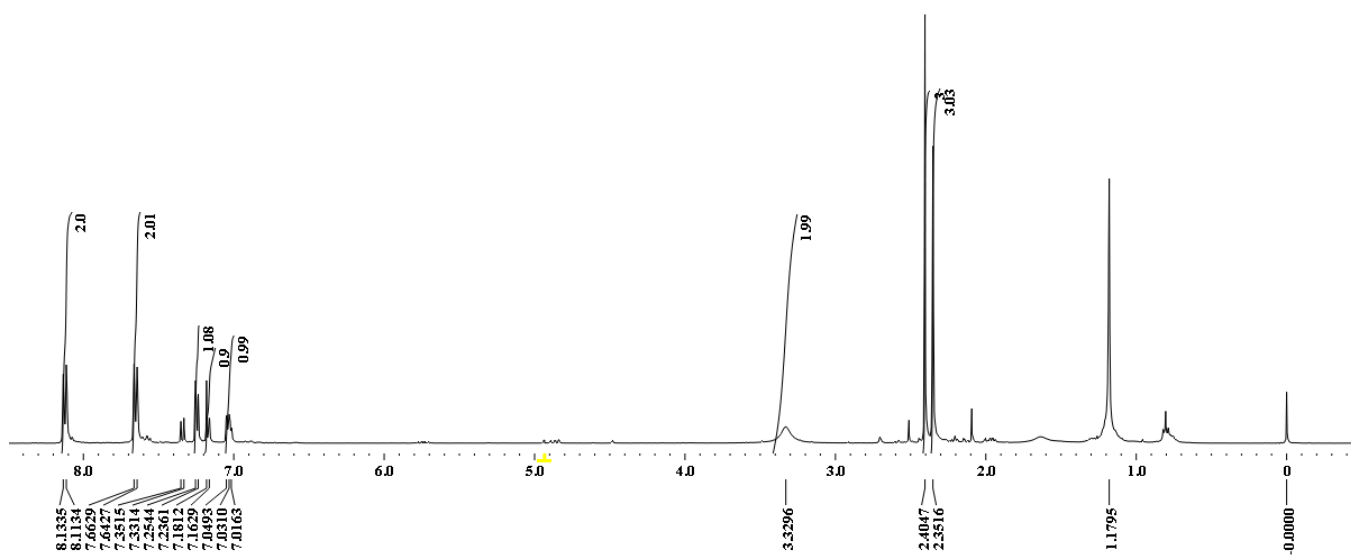


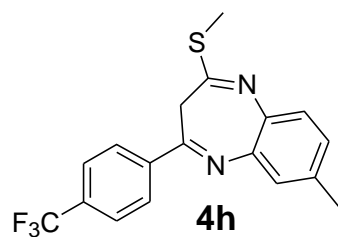
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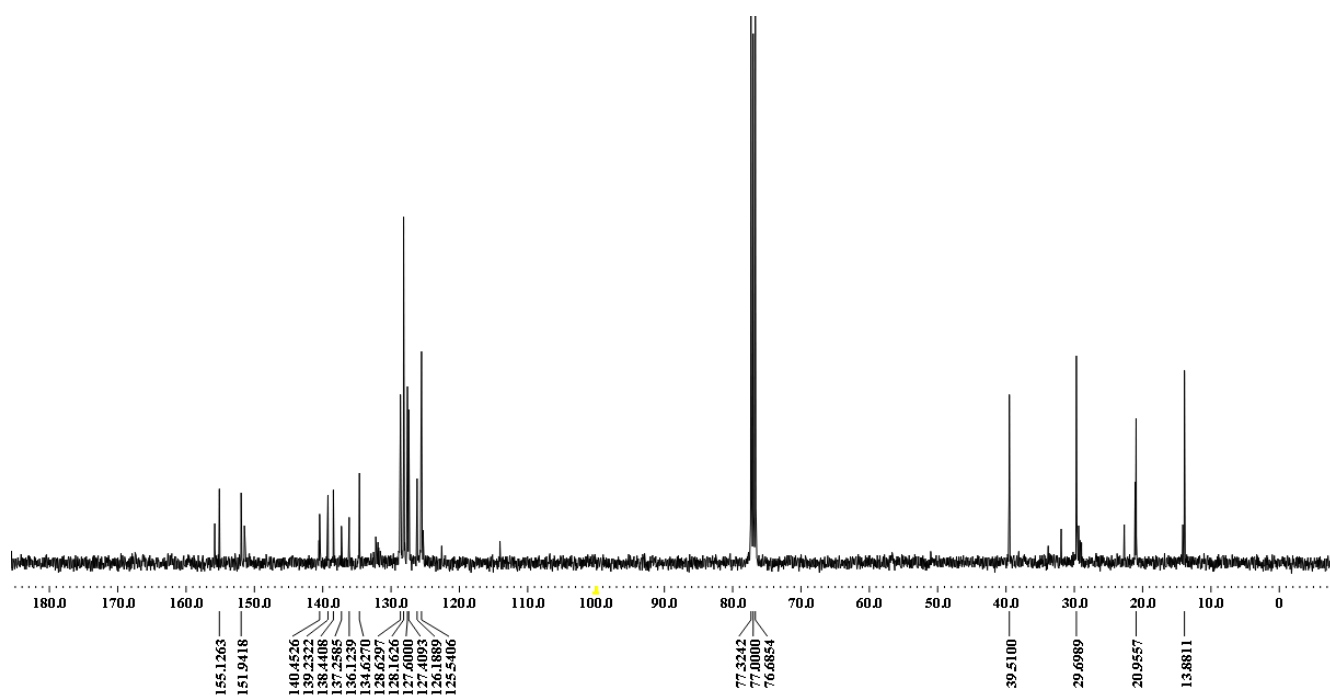


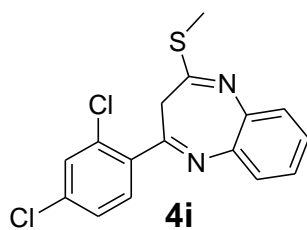
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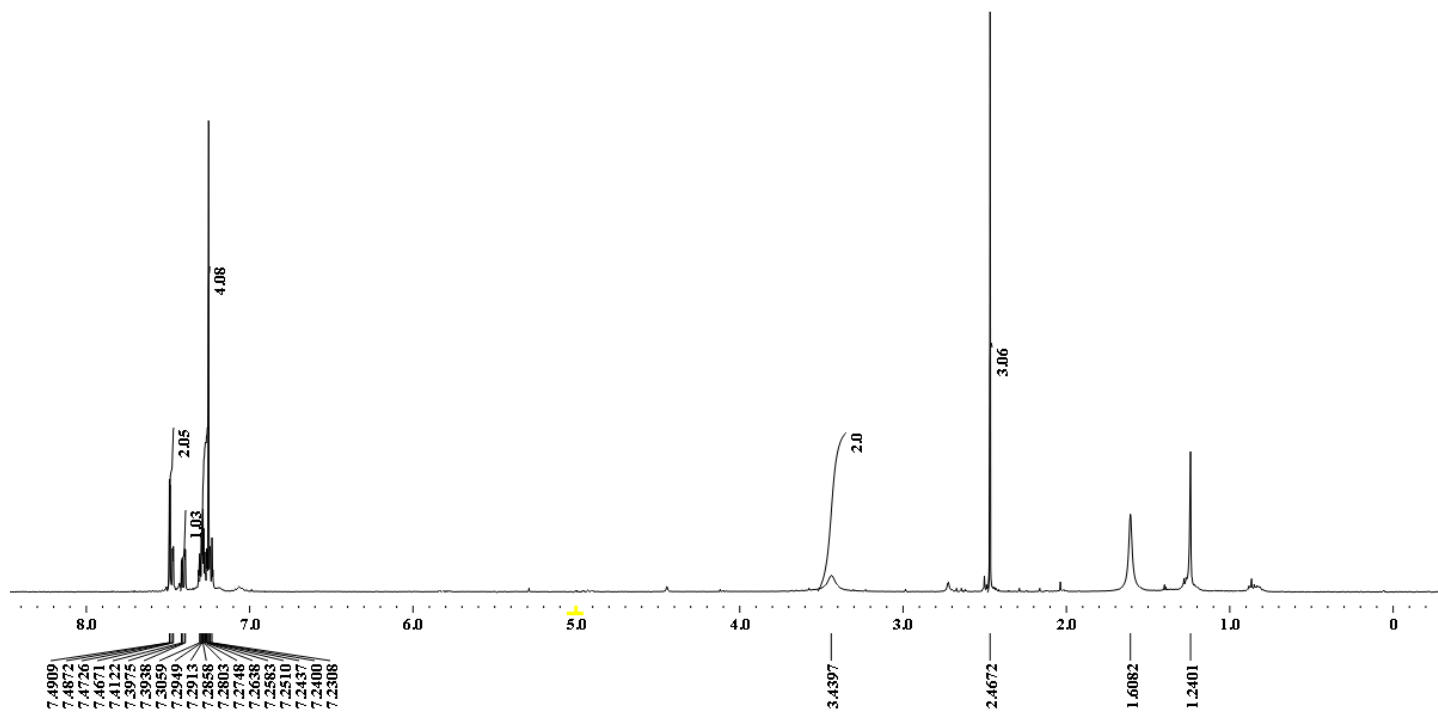


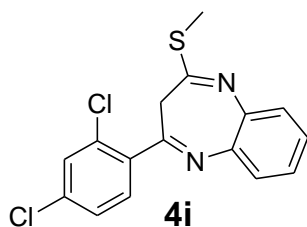
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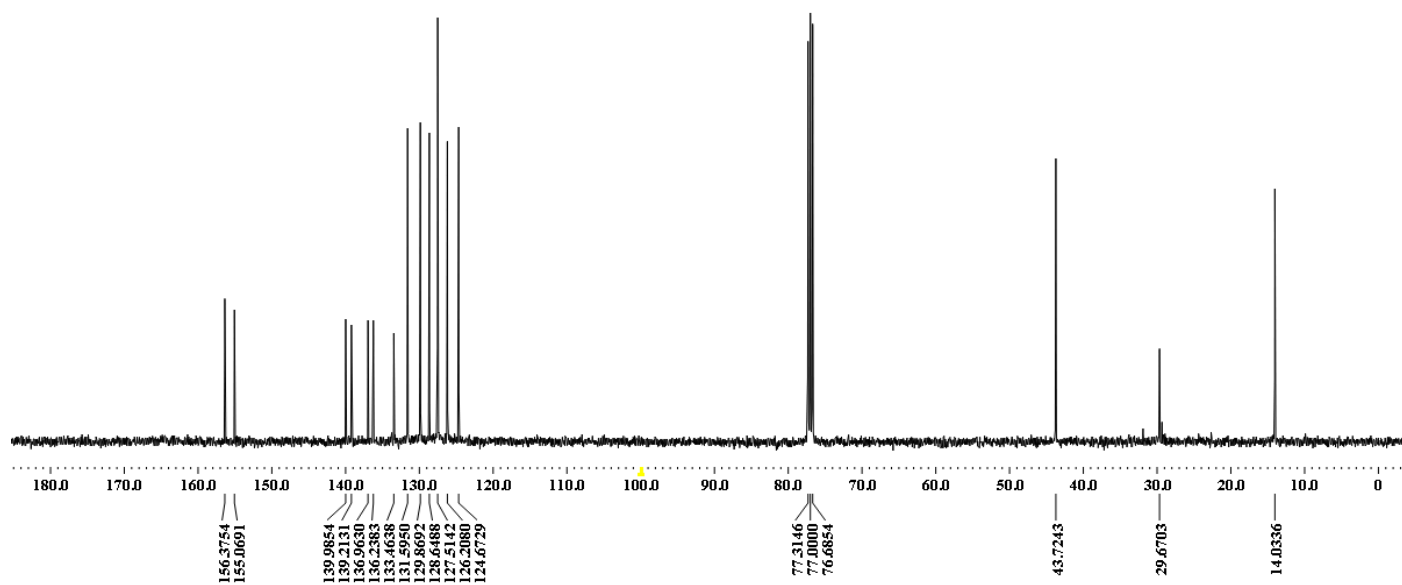


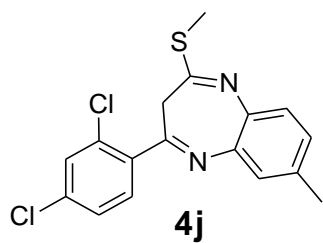
$^1\text{H NMR}$



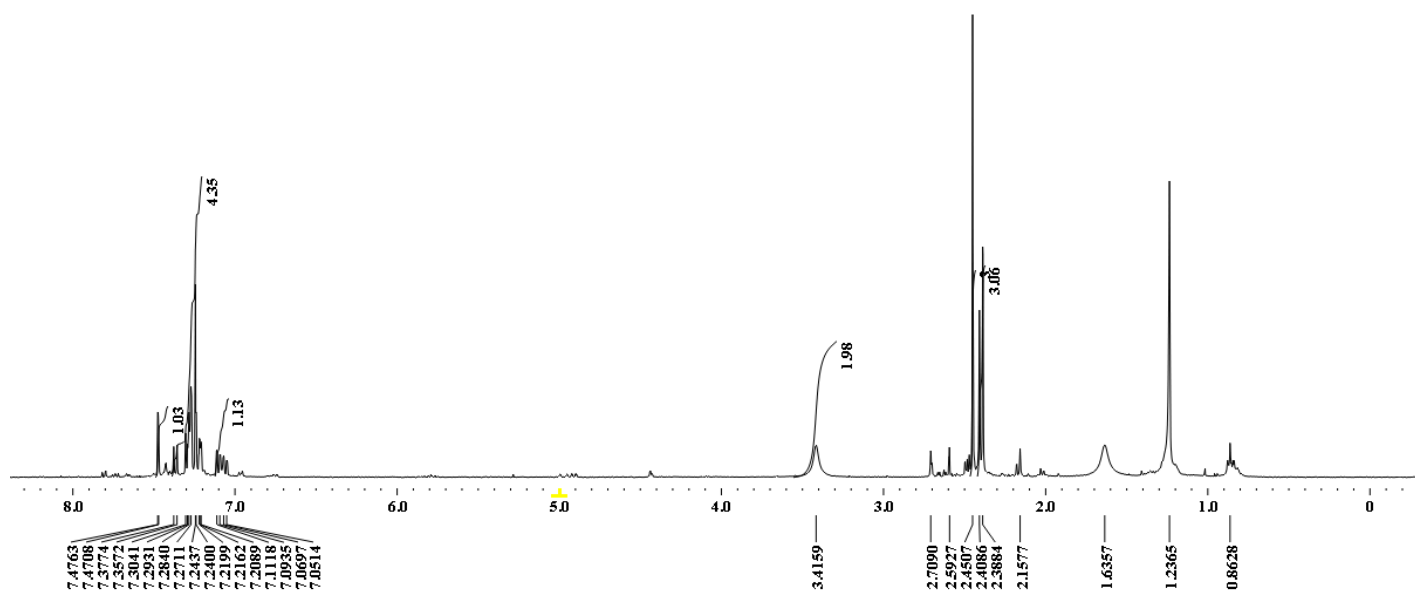


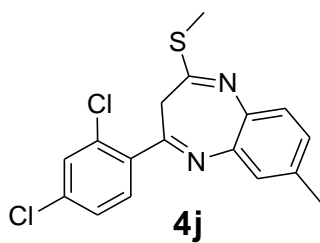
^{13}C NMR



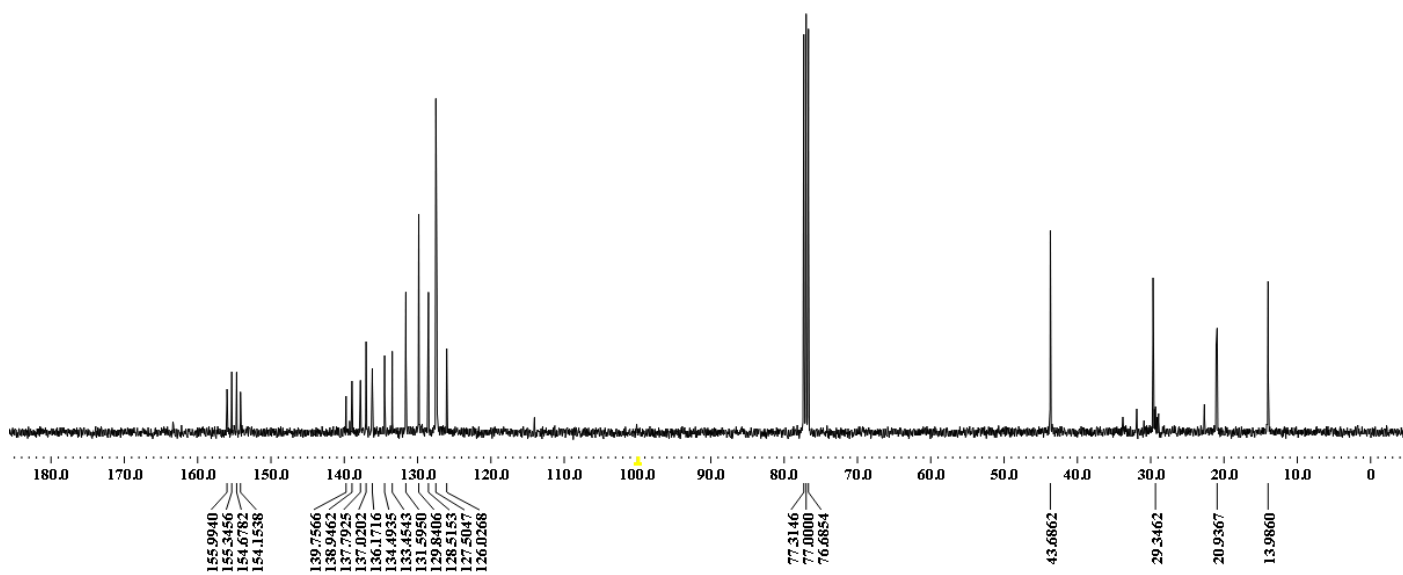


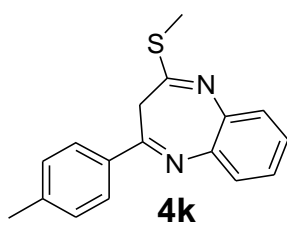
$^1\text{H NMR}$



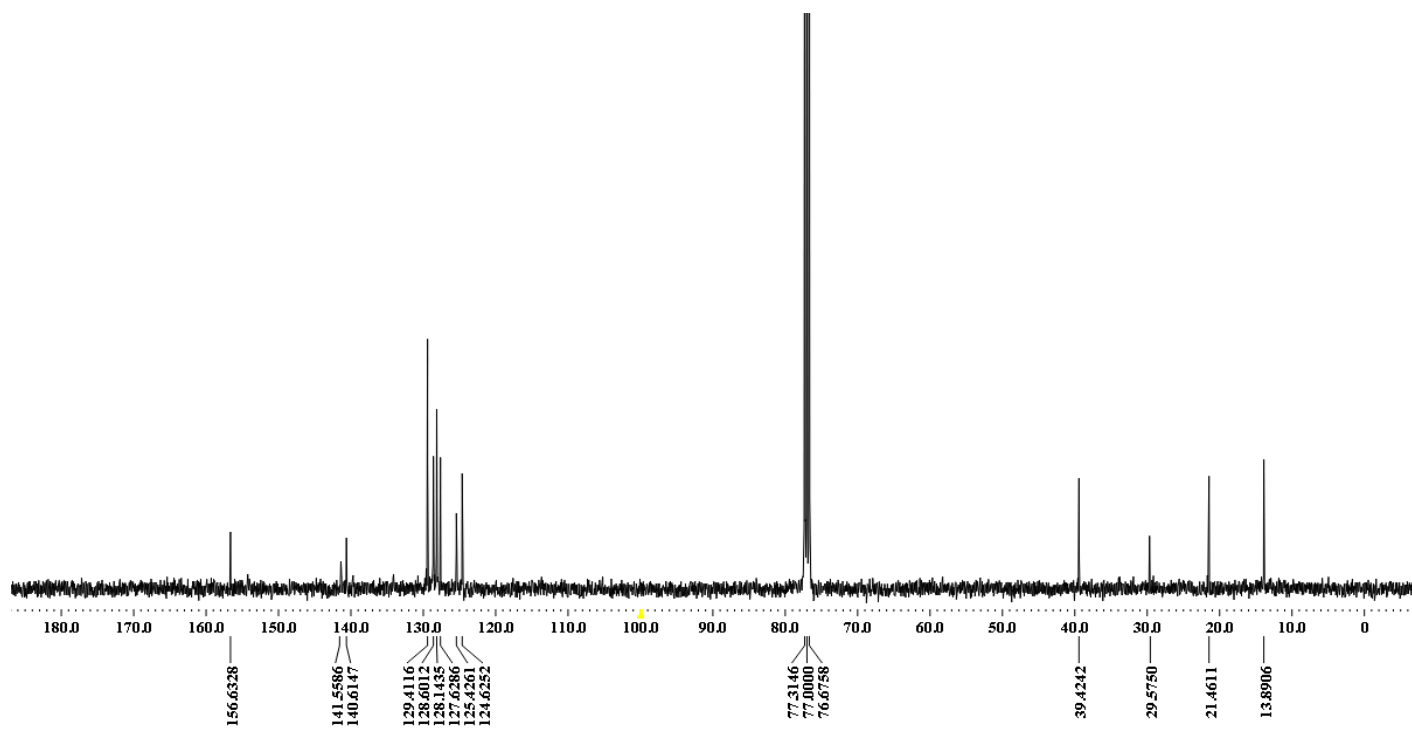


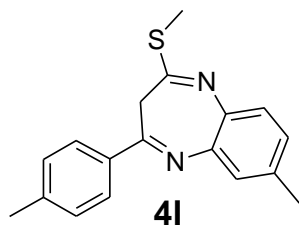
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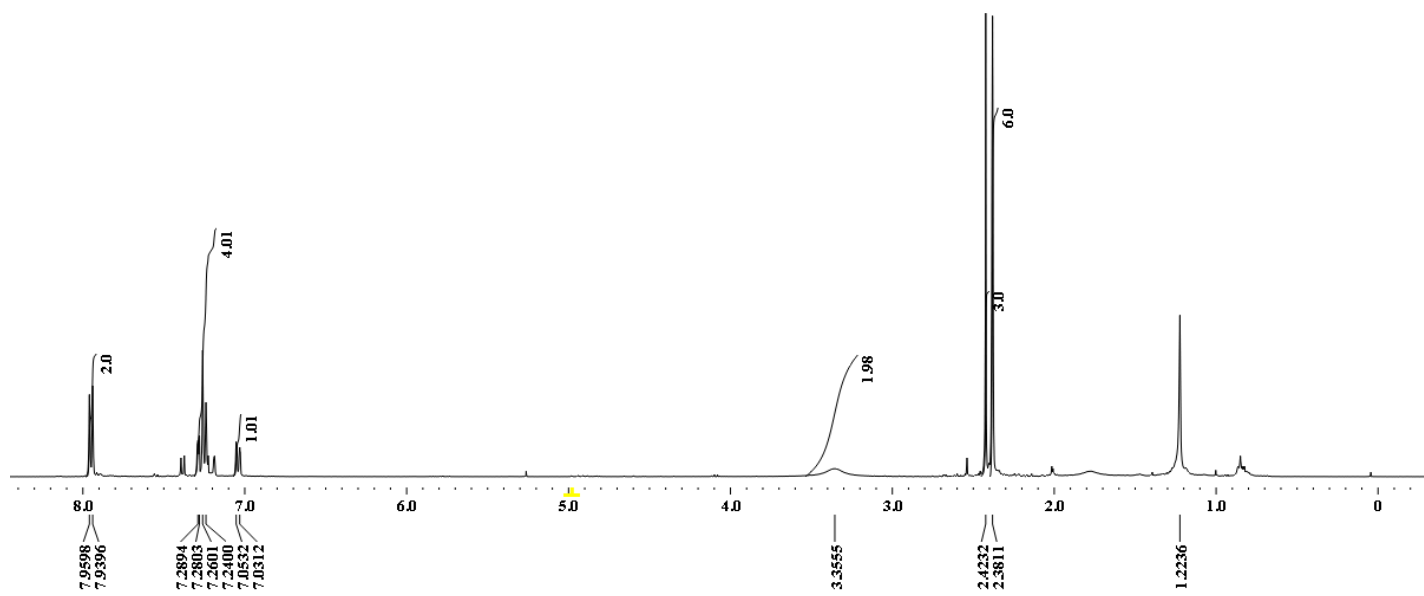


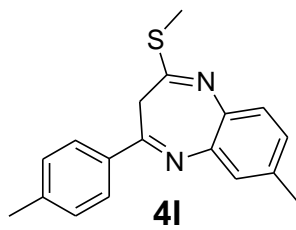
^{13}C NMR



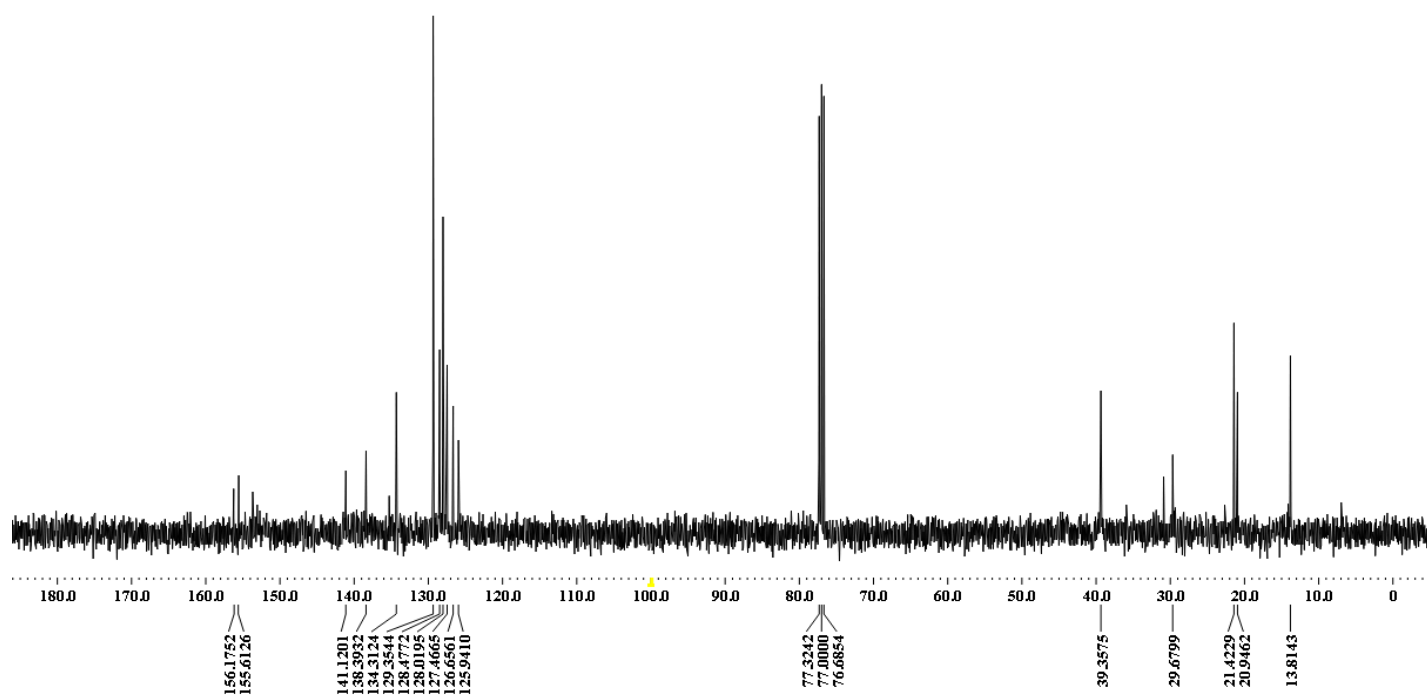


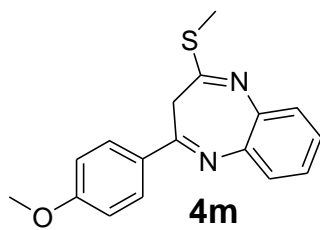
¹H NMR



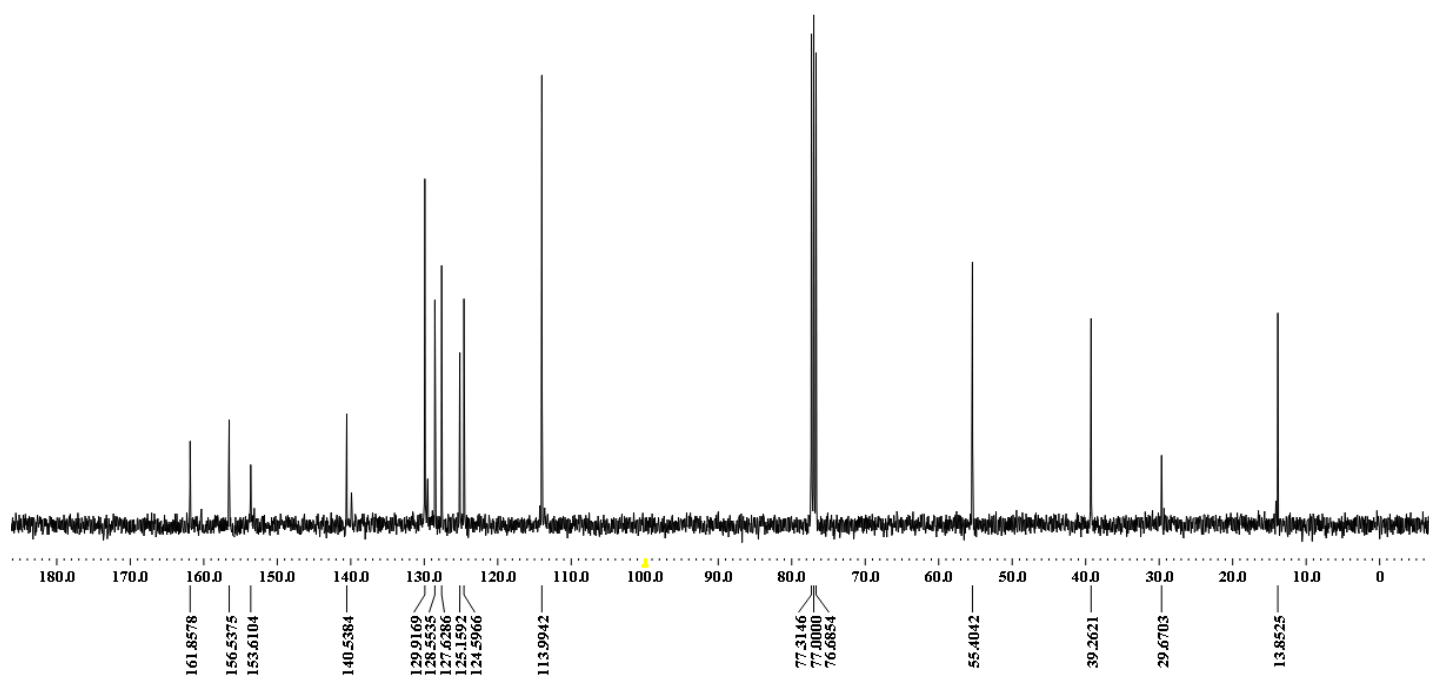


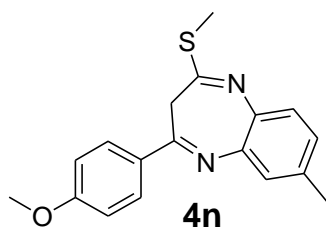
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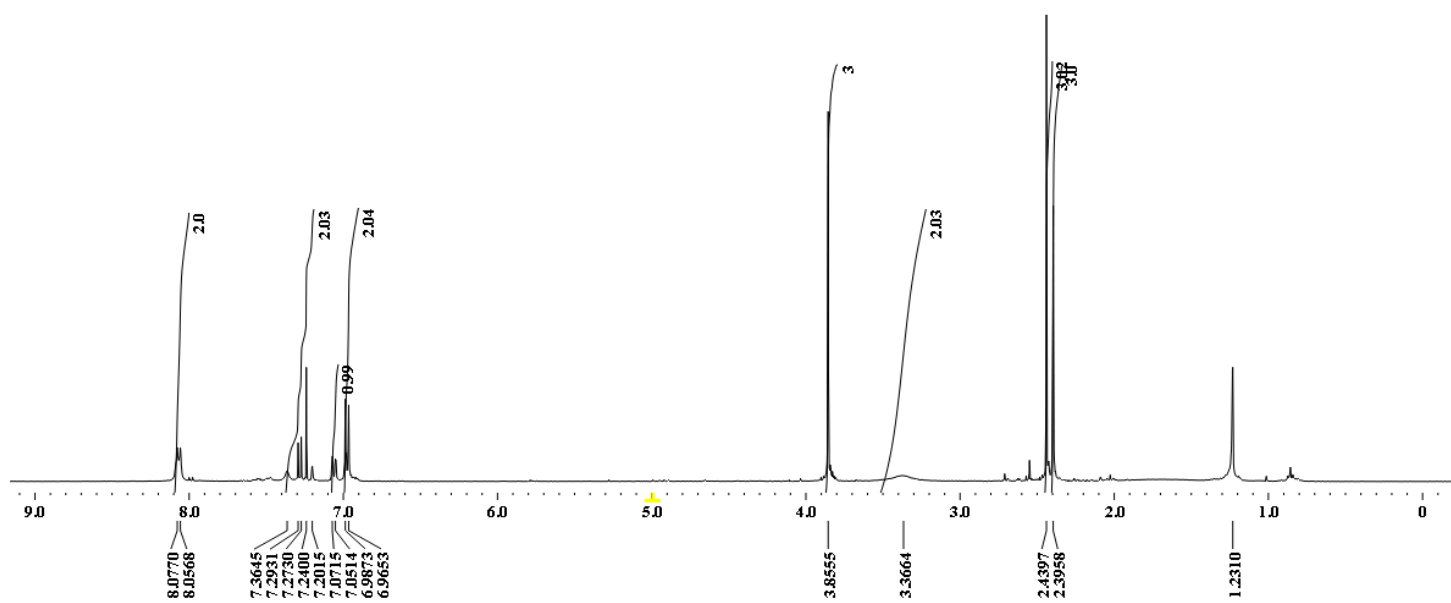


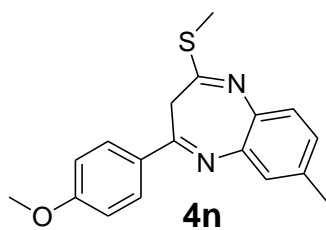
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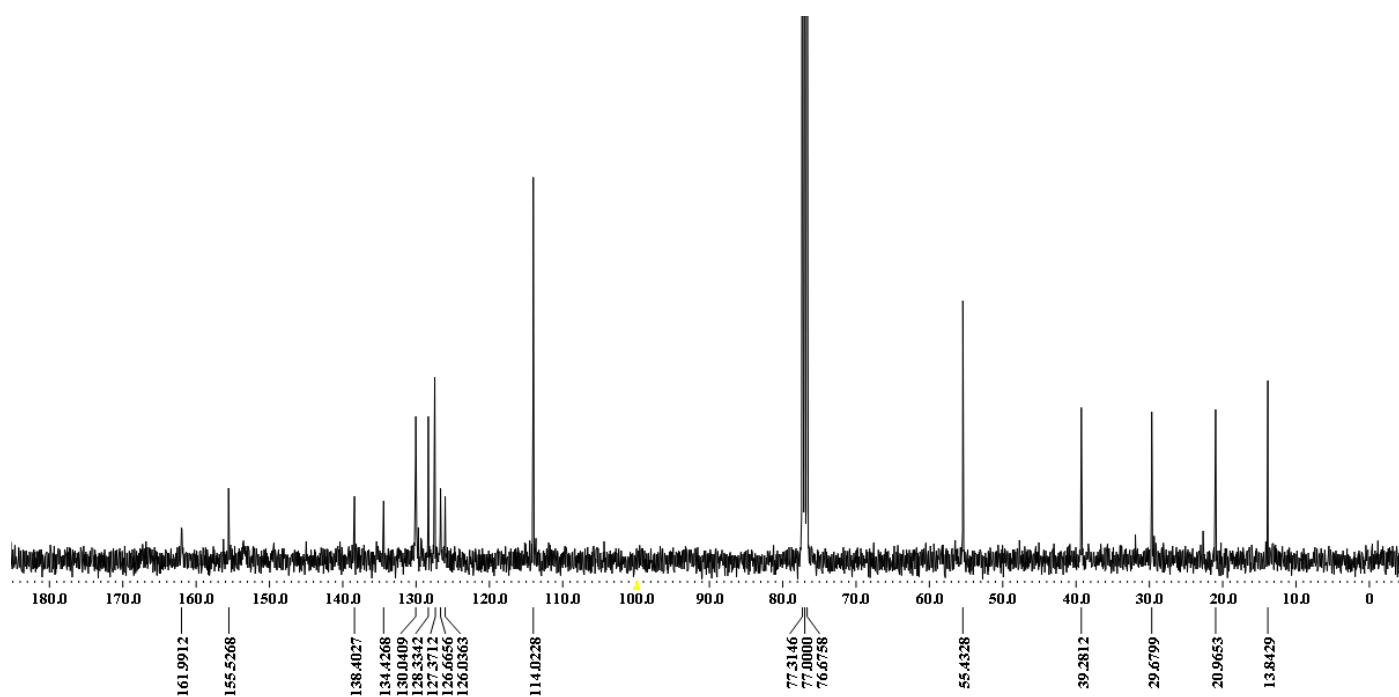


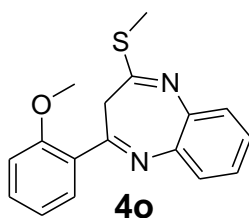
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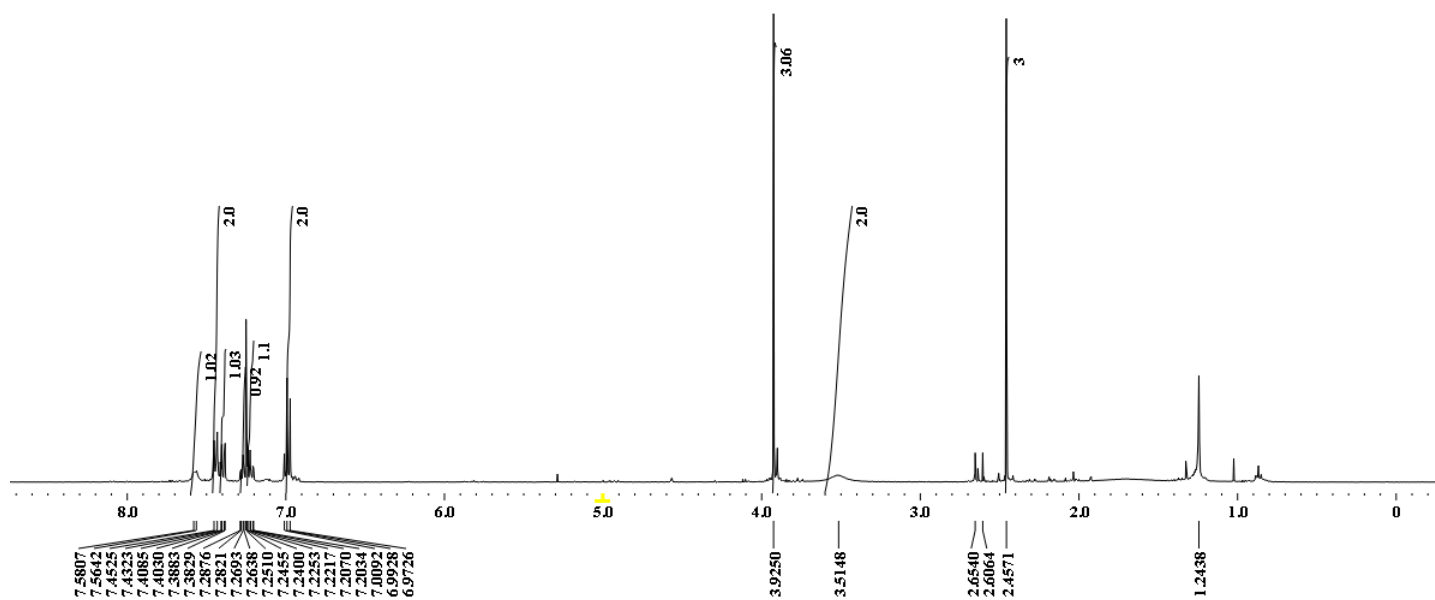


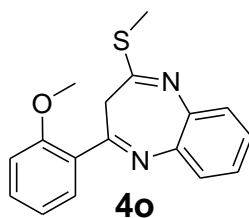
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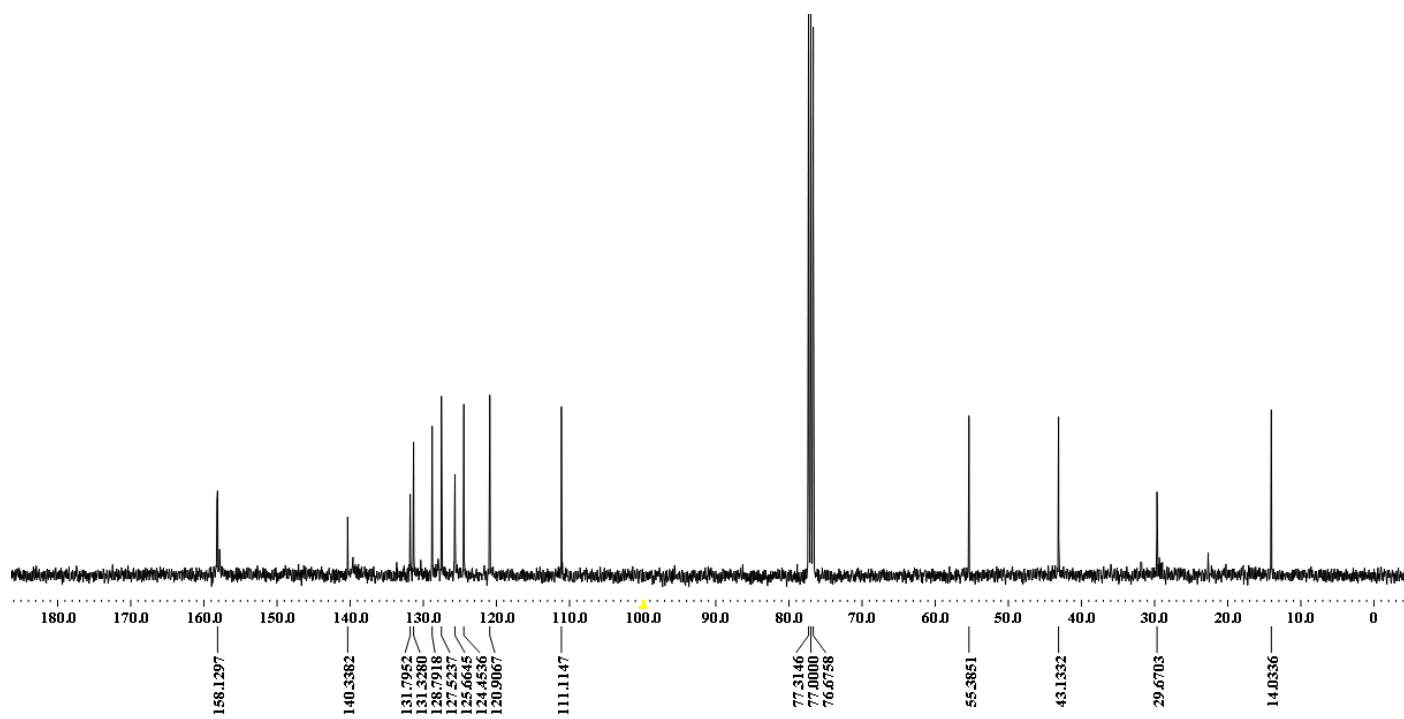


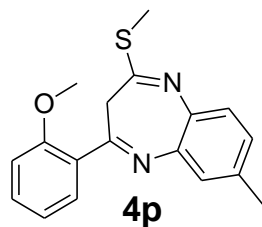
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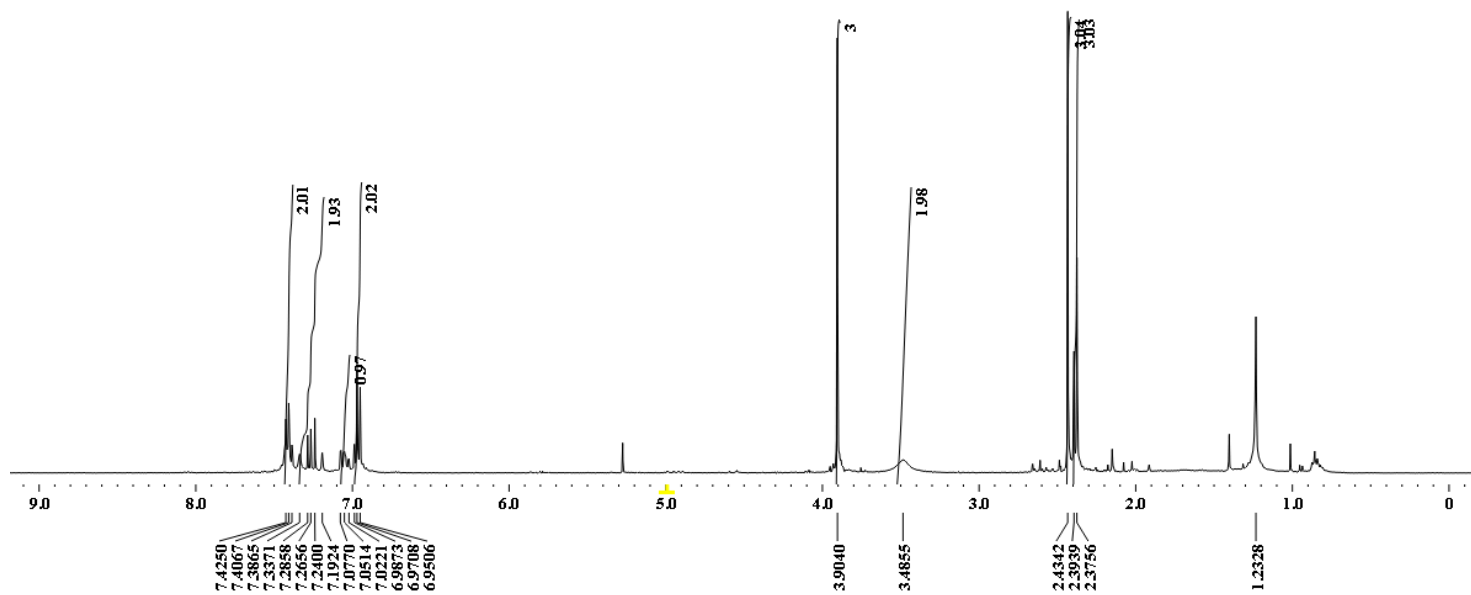


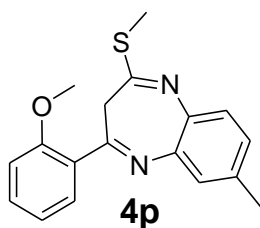
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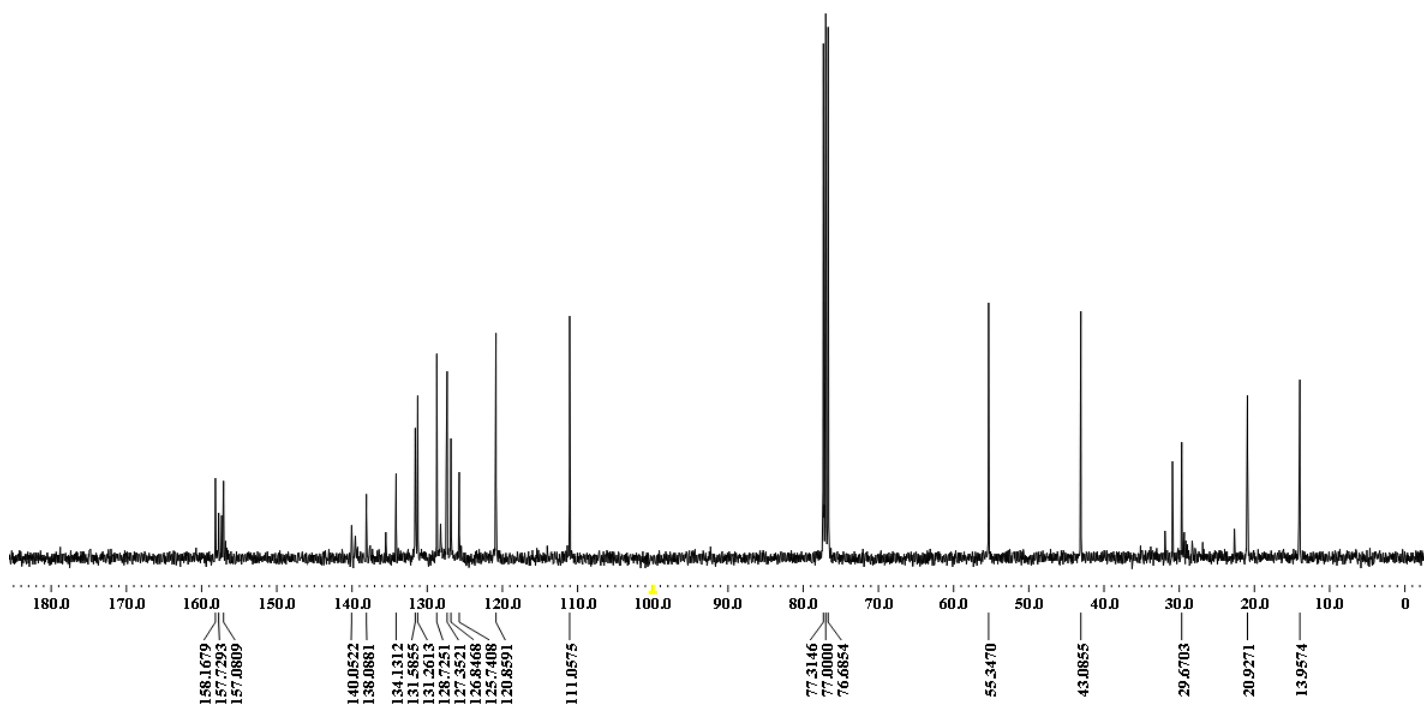


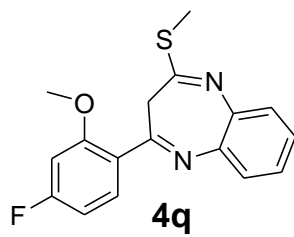
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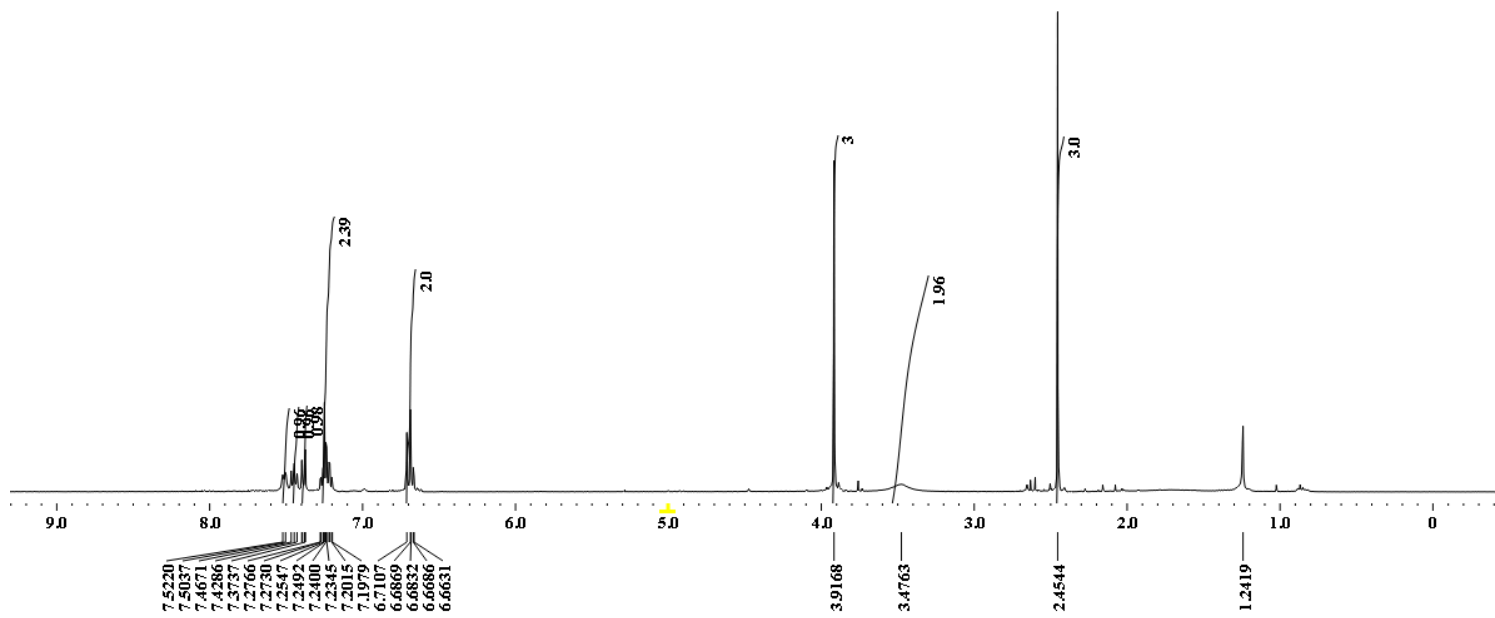
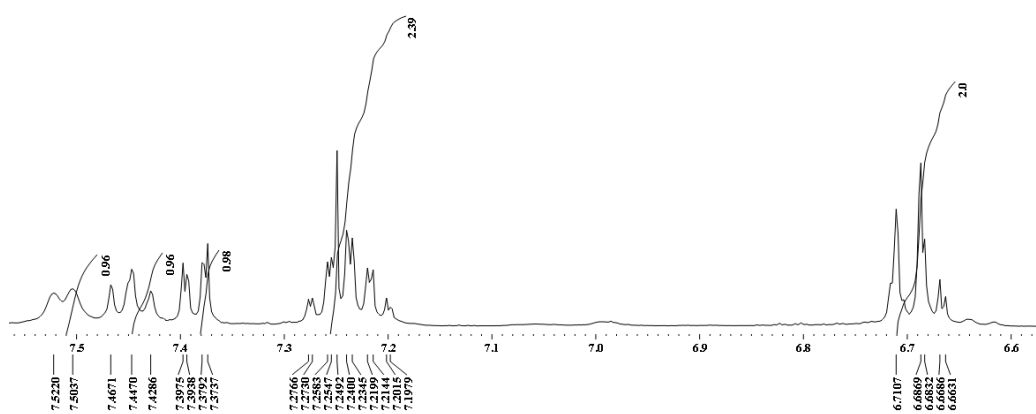


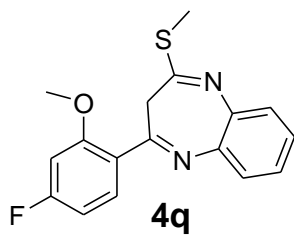
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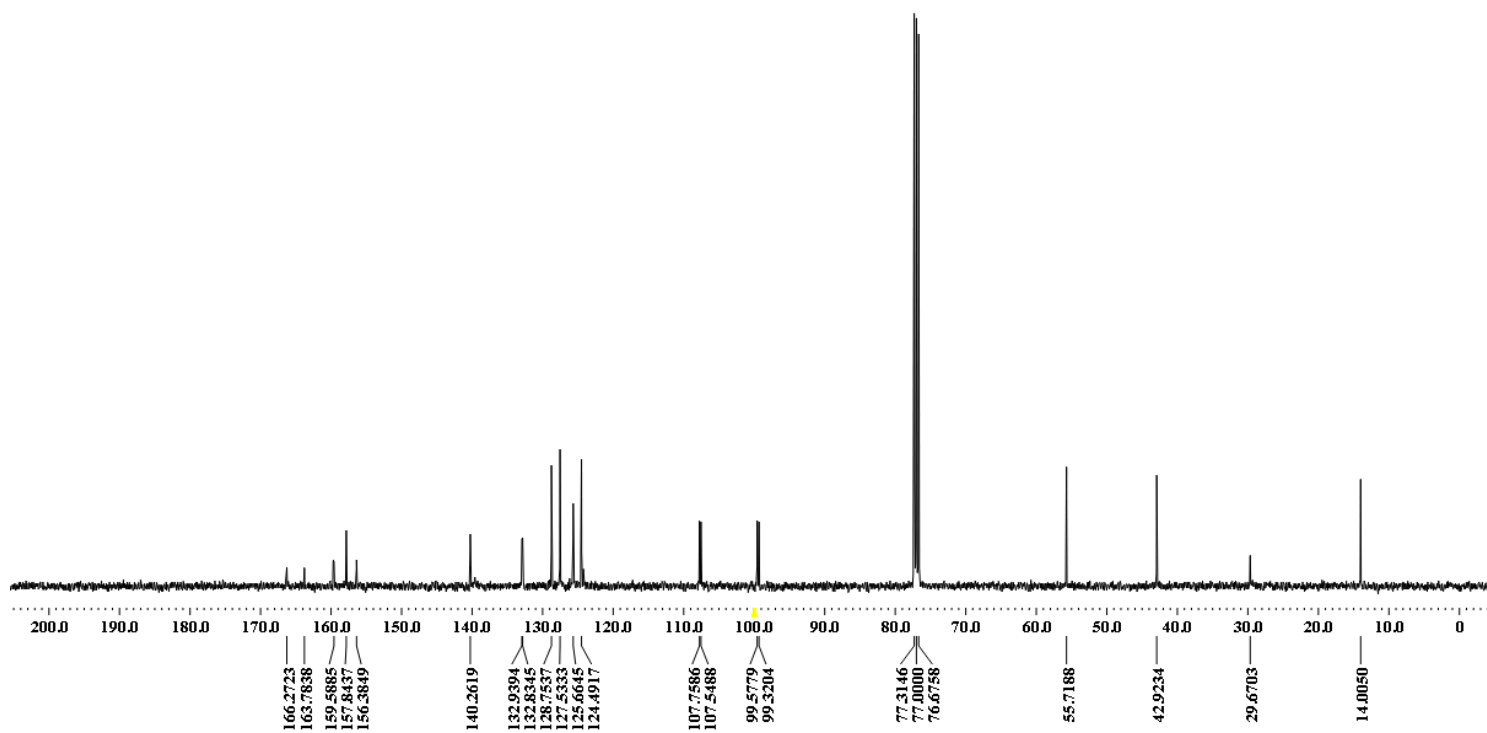


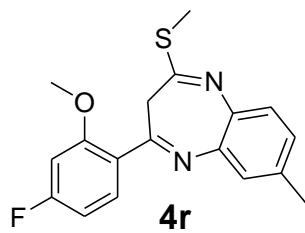
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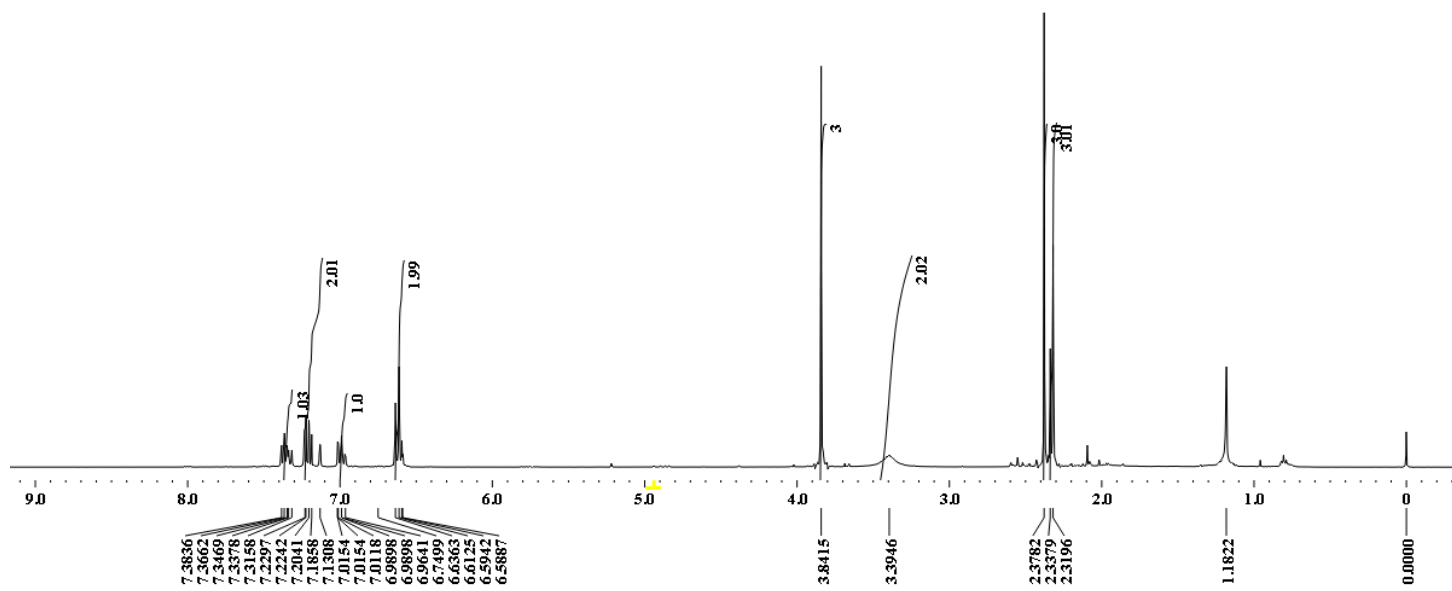


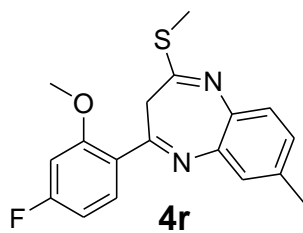
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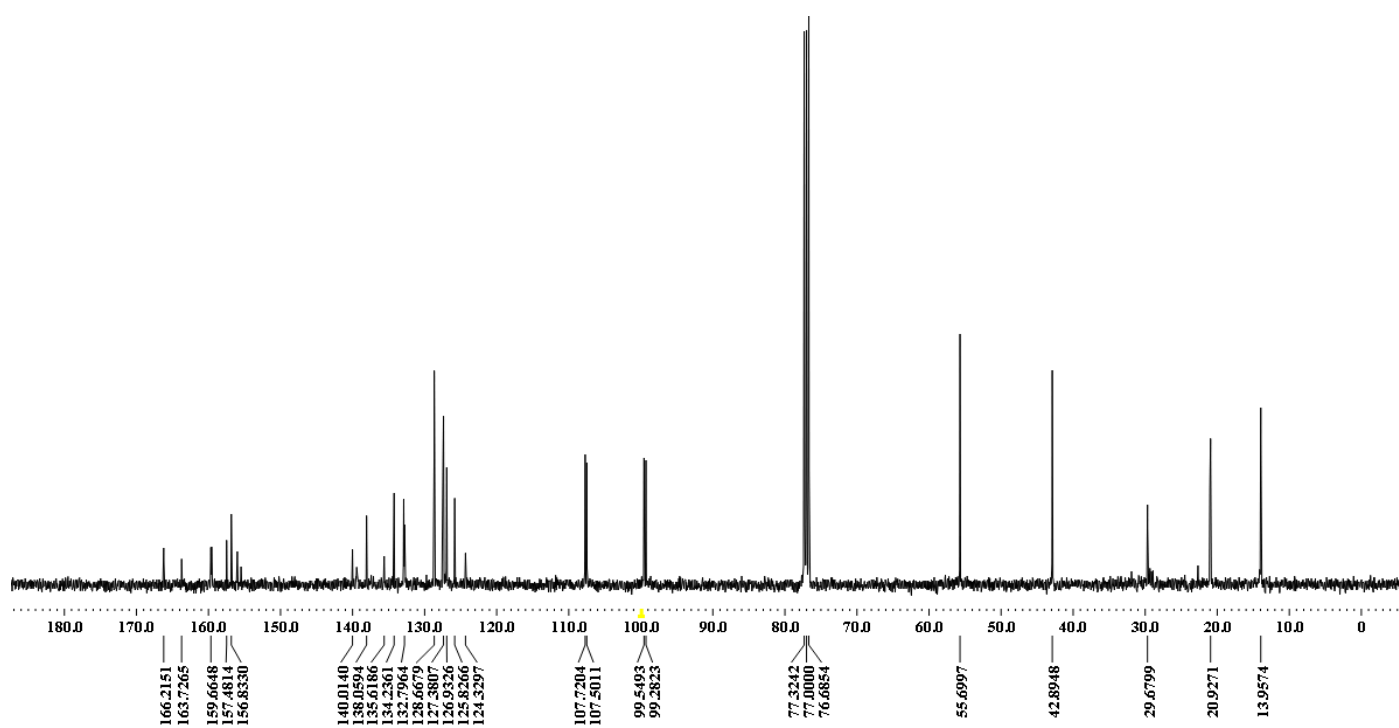


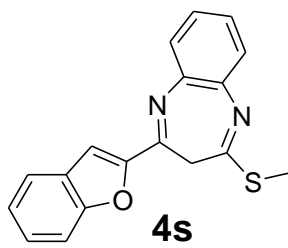
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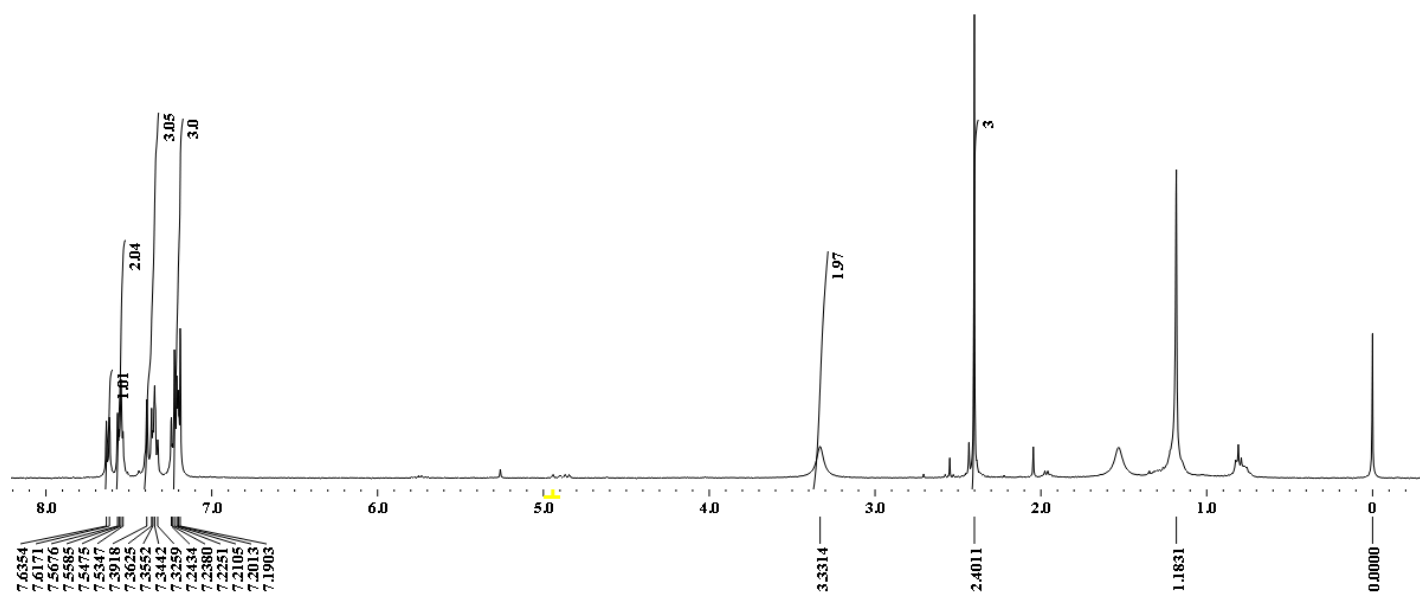


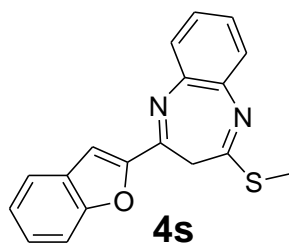
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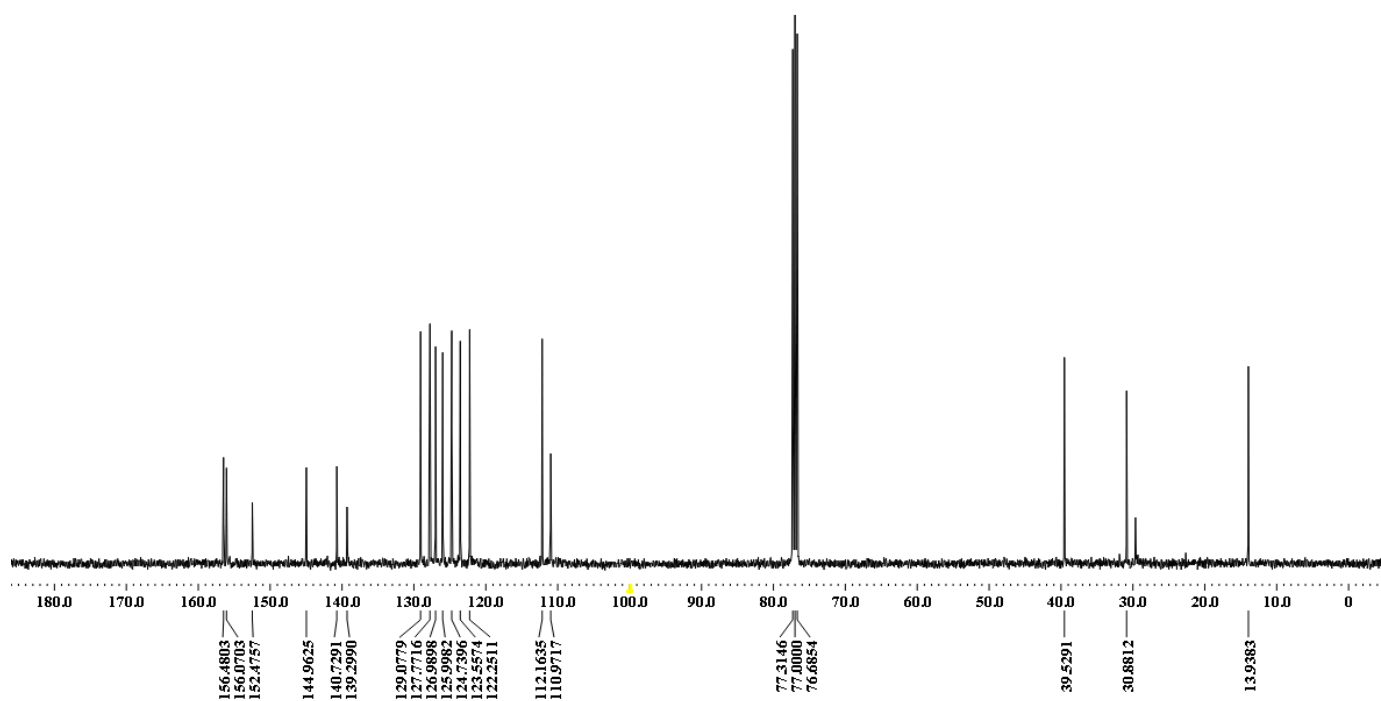


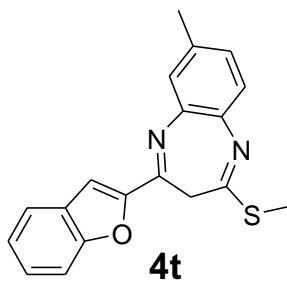
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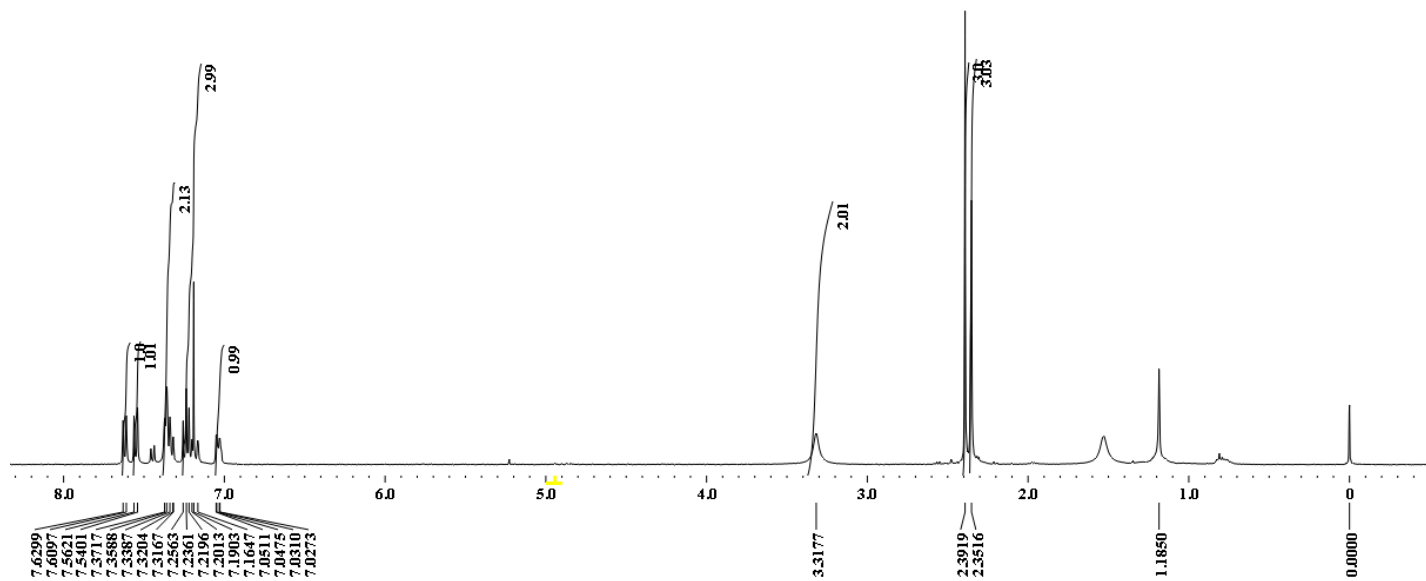


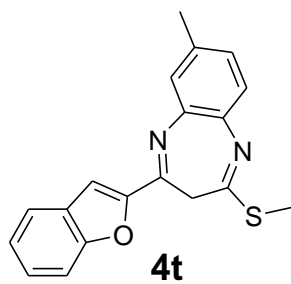
¹³C NMR



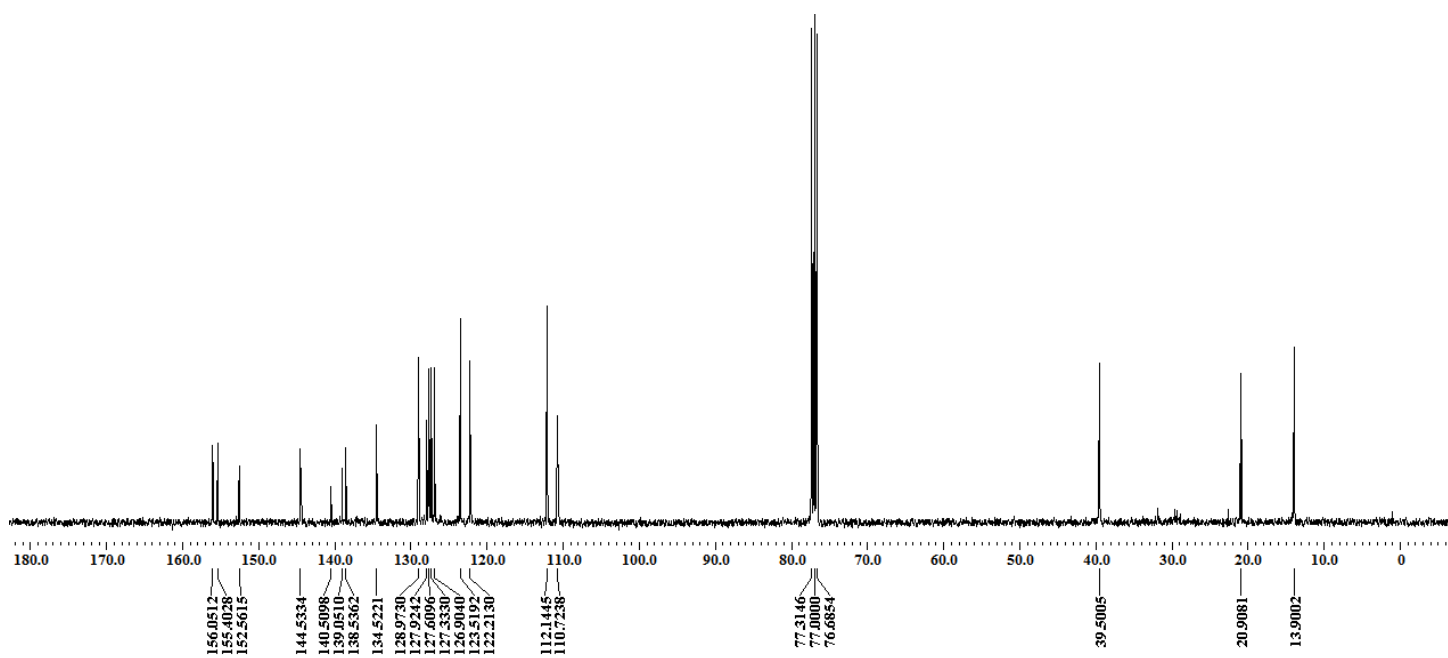


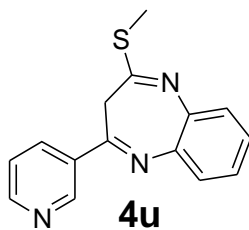
¹H NMR



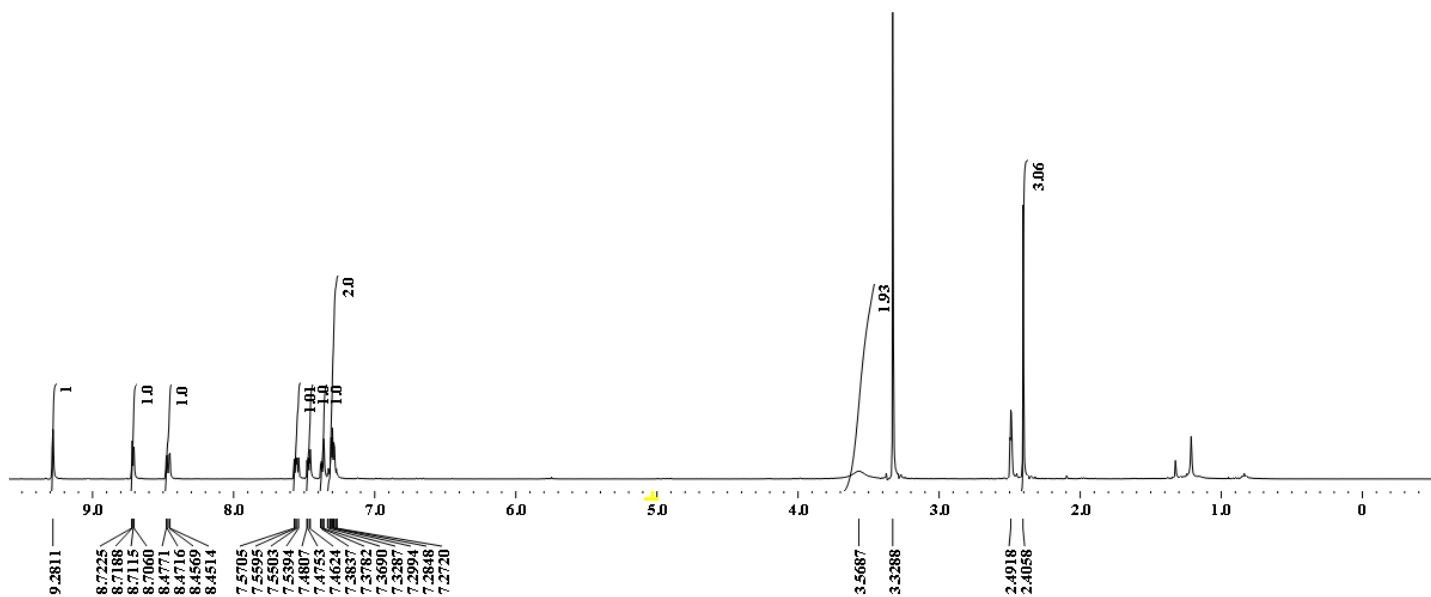
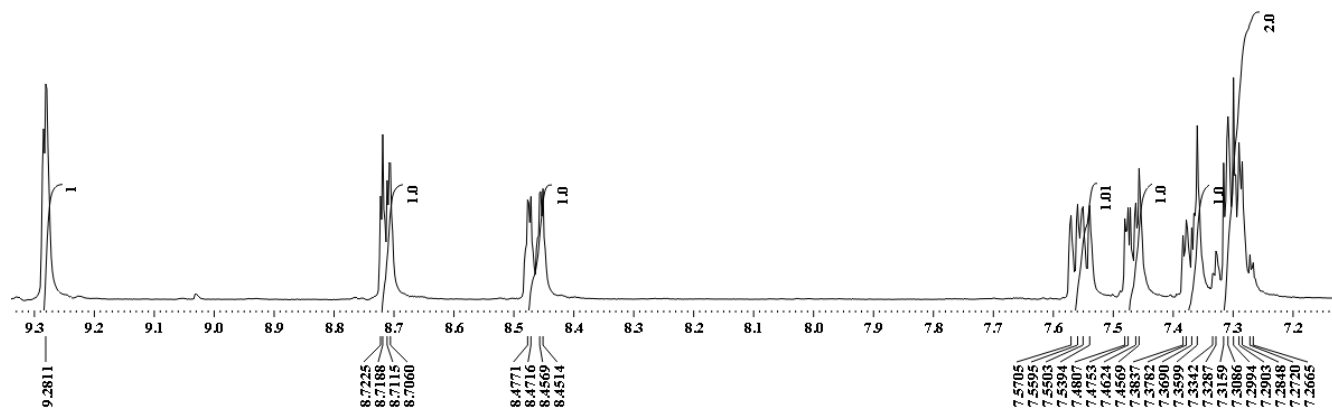


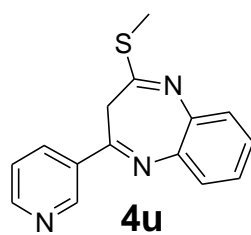
¹³C NMR



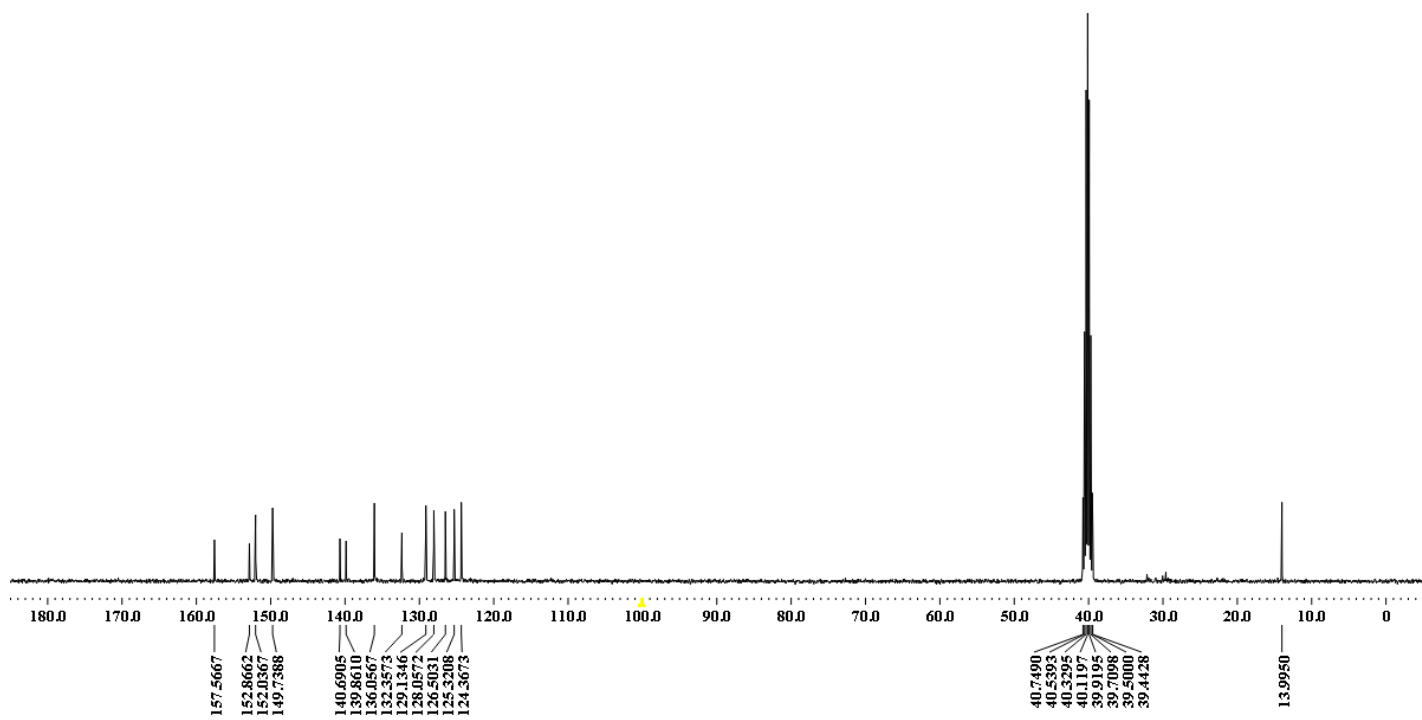


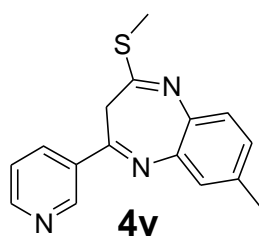
¹H NMR



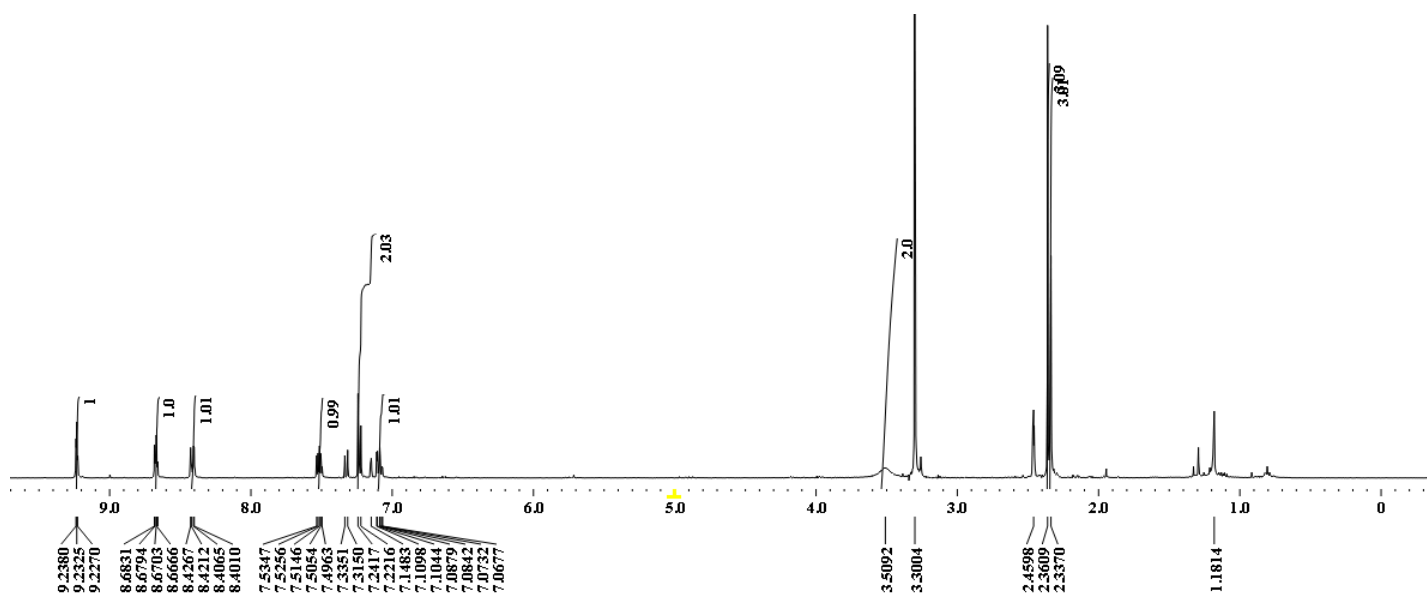


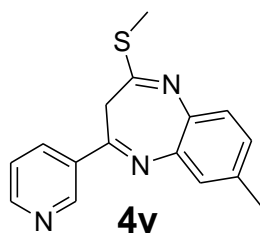
¹³C NMR



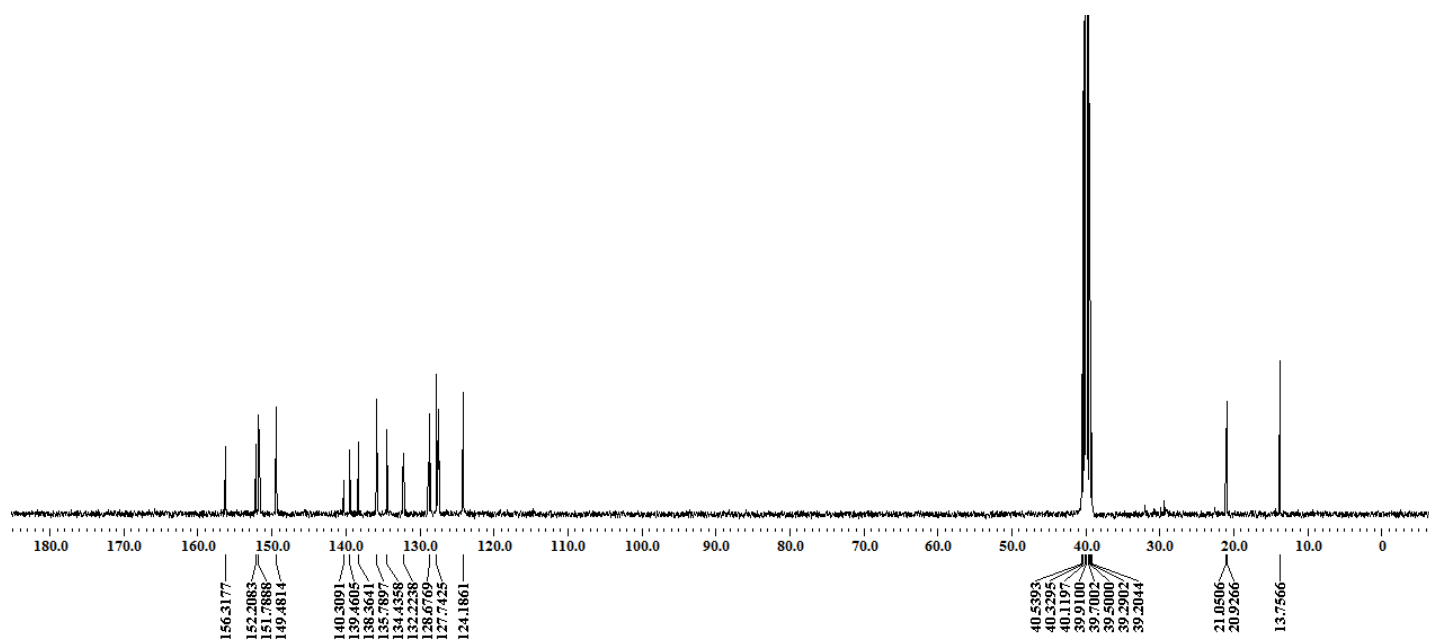


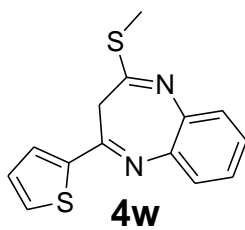
¹H NMR



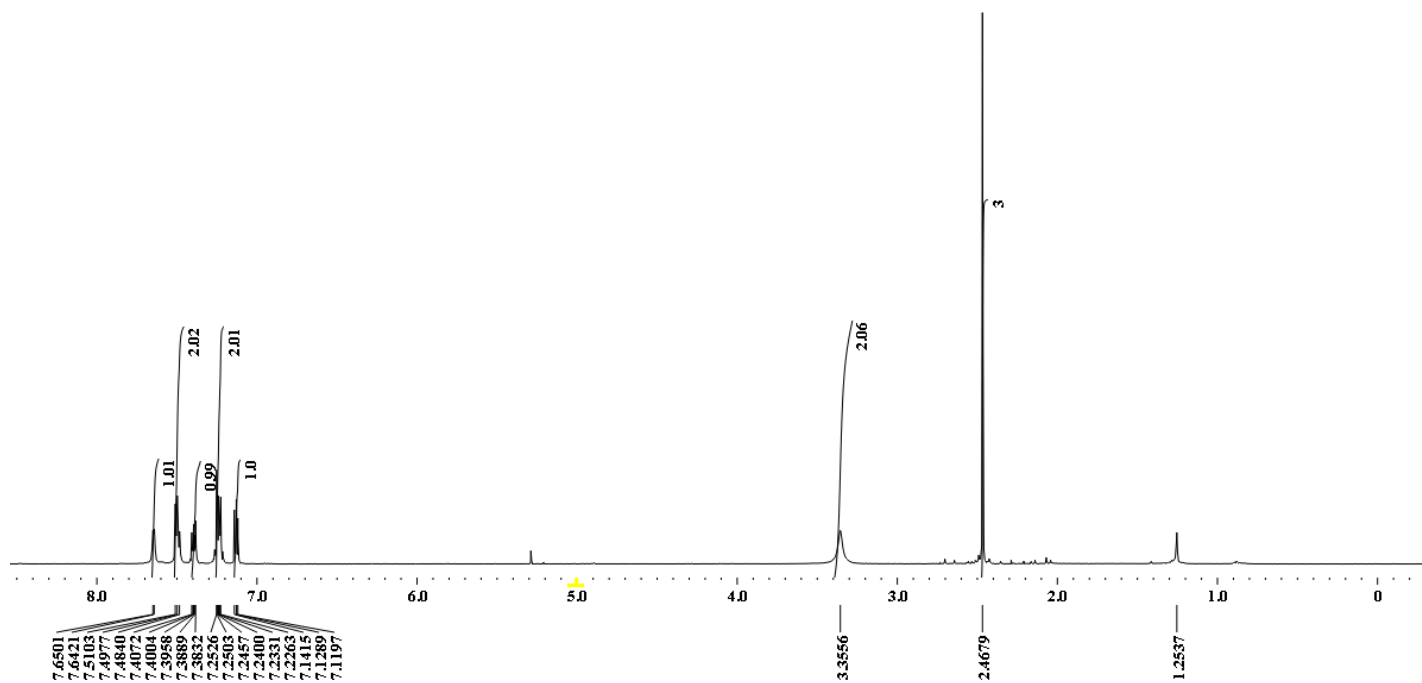


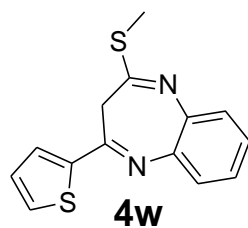
¹³C NMR



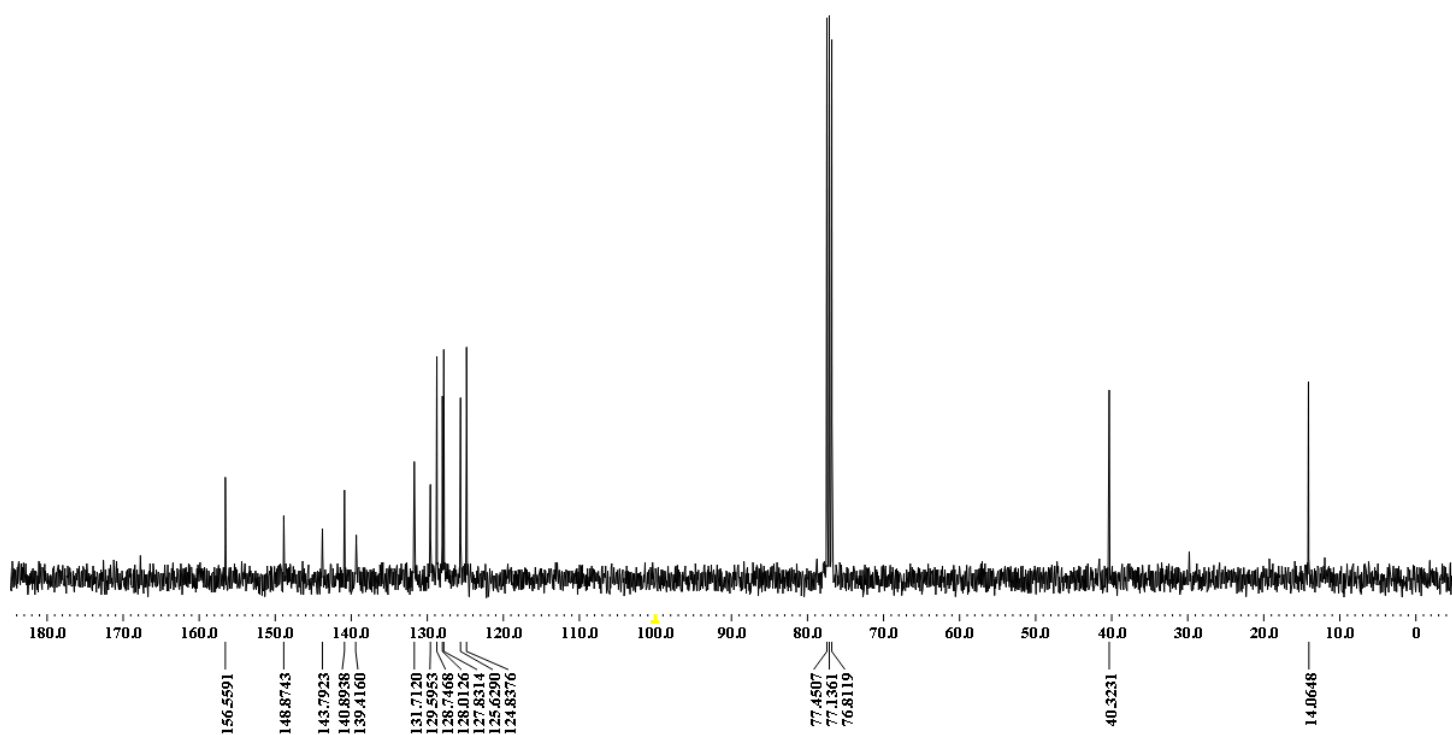


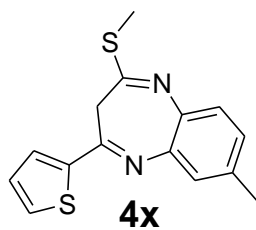
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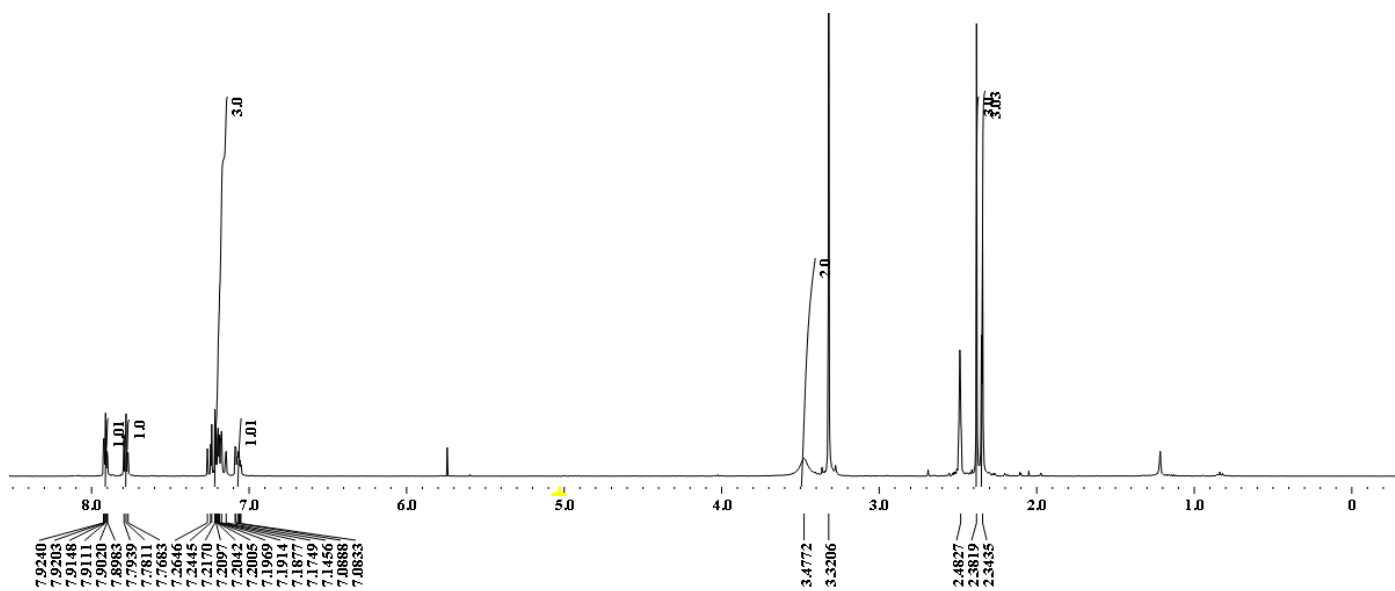


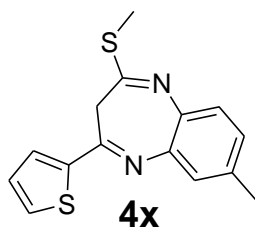
^{13}C NMR





¹H NMR





¹³C NMR

