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Supporting Information for

A multicomponent synthetic strategy for two-carbon-tethered 1,3-oxathiole/indole pairs

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Experimental

General

Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}. ^1H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in DMSO-d_6 with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-Q Ⅱ HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

General procedure for the synthesis of compounds 4

Preparation of compounds 4

β-oxopropanenitriles (**1**, 1.0 mmol,) was introduced in a 20-mL reaction vial, carbon disulfide (**2**, 2.0 mmol), α-bromo ketones (**3**, 1.1 mmol), K_2CO_3 (2.5 mmol), and DMF (8 mL) were then successively added. Subsequently, the reaction vial was capped and then stirred at room temperature for a given time until TLC (petroleum ether : acetone 4:1) revealed that conversion of the starting material **1** was complete. The reaction mixture was diluted with cold water (50 ml) and then extracted by acetic ester. Next, the organic phase was concentrated by vacuum distillation and dissolved in EtOH (95%) to afford the desired pure 1,3-oxathioles **4**

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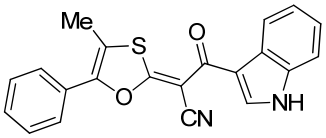
(2Z)-3-(1*H*-indol-3-yl)-2-(4-methyl-5-phenyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4a)



Pale yellow solid, mp: 281-282 ^{o}C

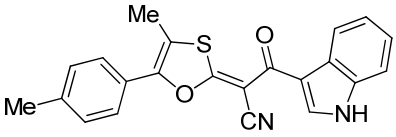
^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.05 (s, 1H, NH), 8.54 (d, J = 3.2 Hz, 1H, Ar-H), 8.30 (d, J = 7.2 Hz, 1H, Ar-H), 7.70 (d, J = 7.2 Hz, 2H, Ar-H), 7.60 (t, J = 7.2 Hz, 2H, Ar-H), 7.54 (d, J = 7.2 Hz, 2H, Ar-H), 7.28-7.20 (m, , 2H, Ar-H), 2.42 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 178.6, 172.0, 145.0, 135.7, 131.2, 129.6, 129.0, 127.1, 126.8, 126.3, 123.0, 122.3, 121.8, 117.1, 115.1, 114.2, 112.0, 10.6,

IR (KBr, ν, cm^{-1}): 3314, 2209, 1560, 1514, 1407, 1221, 729

HRMS (ESI): m/z calcd for: $C_{22}H_{16}N_2O_2S$, 357.0698, found: 357.0689

(2Z)-3-(1*H*-indol-3-yl)-2-(4-methyl-5-*p*-tolyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4b)



Pale yellow solid, mp: 295-296 ^{o}C;

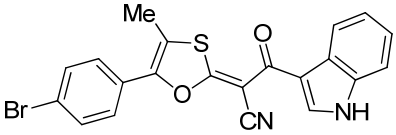
^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.04 (s, 1H, NH), 8.54 (d, J = 3.2 Hz, 1H, Ar-H), 8.29 (d, J = 7.2 Hz, 1H, Ar-H), 7.59 (d, J = 8.0 Hz, 2H, Ar-H), 7.54 (d, J = 8.0 Hz, 1H, Ar-H), 7.40 (d, J = 8.0 Hz, 2H,Ar-H), 7.26-7.22 (m, 2H, Ar-H), 2.40 (s, 3H, CH_3), 2.39 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 192.3, 153.6, 143.2, 136.9, 135.8, 135.2, 133.3, 130.9, 128.2, 127.9, 127.2, 125.4, 119.8, 104.6, 52.8, 25.4, 10.7.

IR (KBr, ν, cm^{-1}): 3320, 2215, 1565, 1519, 1411, 1226, 728

HRMS (ESI): m/z calcd for: $C_{22}H_{16}N_2O_2S$, 371.0853, found: 371.0857.

(2Z)-2-(5-(4-bromophenyl)-4-methyl-1,3-oxathiol-2-ylidene)-3-(1*H*-indol-3-yl)-3-oxopropanenitrile (4c)



Pale yellow solid, mp: >300 ^{o}C;

^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.07 (s, 1H, NH), 8.54 (d, J = 3.2 Hz, 1H, Ar-H), 8.29 (d, J = 7.6 Hz, 1H, Ar-H), 7.81 (d, J = 8.4 Hz, 2H, Ar-H), 7.65 (d, J = 8.4 Hz, 2H, Ar-H), 7.54 (d, J = 8.0 Hz, 1H, Ar-H), 7.29 – 7.20 (m, 2H, Ar-H), 2.42 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 180.8, 178.5, 144.0, 135.9, 135.2, 132.0, 131.4, 128.6, 126.3, 123.0, 121.7, 119.2, 117.0, 116.0, 114.2, 112.1, 10.8.

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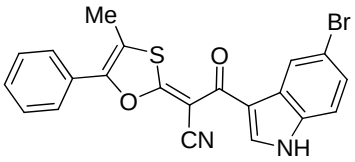
IR (KBr, ν, cm^{-1}): 3220, 2206, 1558, 1421, 1379, 838;

HRMS (ESI): m/z calcd for: $C_{21}H_{13}BrN_2O_2S$, 436.9778, found: 436.9792.

(2Z)-3-(5-bromo-1*H*-indol-3-yl)-2-(4-methyl-5-phenyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4d)



Pale yellow solid, mp: 291-293 °C;

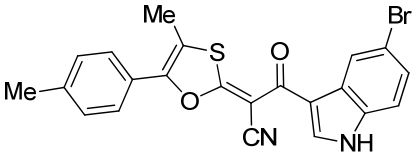
^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.21 (s, 1H, NH), 8.57 (s, 1H, Ar-H), 8.45 (s, 1H, Ar-H), 7.71 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.60 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.56-7.50 (m, 2H, Ar-H), 7.39 (d, *J* = 8.0Hz, 1H, Ar-H), 2.44 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 178.4, 153.2, 145.2, 138.9, 132.3, 128.9, 127.0, 125.9, 124.1, 120.9, 114.9, 114.7, 114.0, 113.8, 105.3, 87.4, 10.8.

IR (KBr, ν, cm^{-1}): 3316, 2209, 1563, 1516, 1417, 1221, 725

HRMS (ESI): m/z calcd for: $C_{22}H_{16}N_2O_2S$, 436.9778, found: 436.9773.

(2Z)-3-(5-bromo-1*H*-indol-3-yl)-2-(4-methyl-5-*p*-tolyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4e)



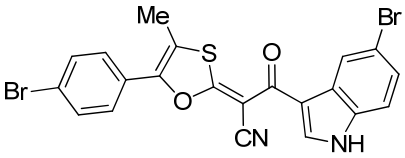
Pale yellow solid, mp: 297-298 °C;

^{1}H NMR (400 MHz, DMSO-d_6) δ:12.20 (s, 1H, NH), 8.56 (d, *J* = 3.2 Hz, 1H, Ar-H), 8.44 (s, 1H, Ar-H), 7.59 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.52 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.39-7.32(m, 3H, Ar-H), 2.41 (s, 3H, CH_3), 2.39 (s, 3H, CH_3).

IR (KBr, ν, cm^{-1}): 3319, 2211, 1561, 1518, 1409, 1223, 732

HRMS (ESI): m/z calcd for: $C_{22}H_{15}BrN_2O_2S$, 450.9935, found: 450.9928.

(2Z)-3-(5-bromo-1*H*-indol-3-yl)-2-(5-(4-bromophenyl)-4-methyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4f)



Pale yellow solid, mp: 292-293 °C;

^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.19 (s, 1H, NH), 8.55 (s, 1H, Ar-H), 8.43 (s, 1H, Ar-H), 7.79 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.62 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.50 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.37 (d, *J* = 7.6 Hz, 1H, Ar-H), 2.40 (s, 3H, CH_3).

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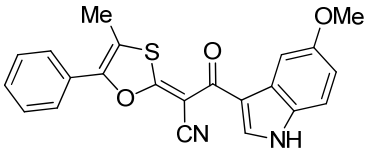
IR (KBr, ν, cm^{-1}): 3225, 2209, 1558, 1423, 1379, 835

HRMS (ESI): m/z calcd for: $C_{21}H_{12}Br_2N_2O_2S$, 514.8883, found: 514.8883

(2Z)-3-(5-methoxy-1*H*-indol-3-yl)-2-(4-methyl-5-phenyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4g)



Pale yellow solid, mp: 271-273 °C;

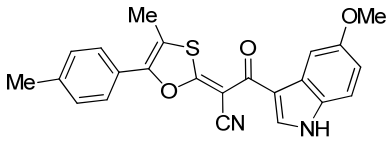
^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.94 (s, 1H, NH), 8.50 (d, J = 3.2 Hz, 1H, Ar-H), 7.82 (d, J = 2.0 Hz, 1H, Ar-H), 7.70 (d, J = 7.2 Hz, 2H, Ar-H), 7.60 (t, J = 7.2 Hz, 2H, Ar-H), 7.54 (d, J = 7.2 Hz, 1H, Ar-H), 7.43 (d, J = 8.8 Hz, 1H, Ar-H), 6.89 (m, 1H, Ar-H), 3.81 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 180.8, 178.5, 155.4, 144.9, 131.5, 130.7, 129.5, 129.0, 127.2, 126.8, 117.1, 115.0, 114.1, 113.1, 112.8, 103.2, 81.0, 55.1, 10.8.

IR (KBr, ν, cm^{-1}): 3318, 2209, 1565, 1514, 1404, 1224, 722

HRMS (ESI): m/z calcd for: $C_{22}H_{16}N_2O_3S$, 387.0803 , found: 387.0803

(2Z)-3-(5-methoxy-1*H*-indol-3-yl)-2-(4-methyl-5-*p*-tolyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4h)



Pale yellow solid, mp: 292-293 °C;

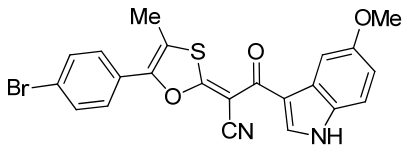
^{1}H NMR (400 MHz, DMSO-d_6) δ :11.95 (s, 1H, NH), 8.49 (d, J = 3.2 Hz, 1H, Ar-H), 7.81 (d, J = 2.0 Hz, 1H, Ar-H), 7.59 (d, J = 8.0 Hz, 2H, Ar-H), 7.44 - 7.39 (m, 3H, Ar-H), 6.91 - 6.86 (m, 1H, Ar-H), 3.81 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3), 2.39 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 180.9, 178.5, 155.4, 145.2, 139.4, 131.5, 130.7, 129.6, 127.2, 126.7, 124.4, 121.7, 116.5, 114.1, 113.1, 112.9, 103.2, 55.1, 21.0, 10.7.

IR (KBr, ν, cm^{-1}): 3269, 2207, 1586, 1474, 1431, 846

HRMS (ESI): m/z calcd for: $C_{23}H_{18}N_2O_3S$, 401.0950, found: 401.0943.

(2Z)-2-(5-(4-bromophenyl)-4-methyl-1,3-oxathiol-2-ylidene)-3-(5-methoxy-1*H*-indol-3-yl)-3-oxopropanenitrile (4i)



Pale yellow solid, mp: 295-297 °C;

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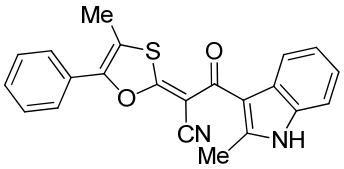
^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.81 (s, 1H, NH), 8.50 (d, J = 3.2 Hz, 1H, Ar-H), 7.85 (d, J = 2.4 Hz, 1H, Ar-H), 7.71 (d, J = 8.4 Hz, 2H, Ar-H), 7.59 (d, J = 8.4 Hz, 2H, Ar-H), 7. 37 (d, J = 8.8 Hz, 1H, Ar-H), 6.85 (dd, J = 8.8 Hz, 2.4Hz, 1H, Ar-H), 3.84 (s, 3H, OCH_3), 2.41 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 180.8, 178.6, 145.2, 139.3, 135.9, 131.2, 129.4, 126.6, 126.4, 122.8, 121.8, 121.6, 117.0, 114.3, 113.8, 112.0, 81.1, 21.0, 10.7.

IR (KBr, ν, cm^{-1}): 3265, 2203, 1579, 1477, 1421, 827

HRMS (ESI): m/z calcd for: $C_{22}H_{15}BrN_2O_3S$, 466.9884, found: 466.9888.

(2Z)-3-(2-methyl-1*H*-indol-3-yl)-2-(4-methyl-5-phenyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4j)



Pale yellow solid, mp: 251-252 °C;

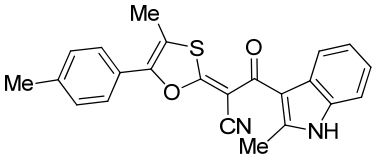
^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.79 (s, 1H, NH), 7.72 (d, J = 7.2Hz, 2H, Ar-H), 7.66 (d, J = 7.6 Hz, 1H, Ar-H), 7.60 (t, J = 7.2 Hz, 2H, Ar-H), 7.55 (d, J = 7.2 Hz, 1H, Ar-H), 7.37 (d, J = 7.6 Hz, 1H, Ar-H), 7.15-7.07 (m, 2H, Ar-H), 2.58 (s, 3H, CH_3), 2.44 (s, 3H, CH_3).

IR (KBr, ν, cm^{-1}): 3265, 2203, 1579, 1477, 1421, 827

IR (KBr, ν, cm^{-1}): 3314, 2208, 1561, 1513, 1407, 1223, 726

HRMS (ESI): m/z calcd for: $C_{22}H_{16}N_2O_2S$, 371.0853, found: 371.0853.

(2Z)-3-(2-methyl-1*H*-indol-3-yl)-2-(4-methyl-5-*p*-tolyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4k)



Pale yellow solid, mp: 263-265 °C;

^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.00 (s, 1H, NH), 8.55 (d, J = 3.2 Hz, 1H, Ar-H), 7.56 (d, J = 8.0 Hz, 2H, Ar-H), 7.52 (d, J = 8.0 Hz, 1H, Ar-H), 7.42 (d, J = 8.0 Hz, 2H, Ar-H), 7.26-7.22 (m, 2H, Ar-H), 2.56 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.39 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 182.0, 181.5, 178.8, 142.3, 138.2, 134.8, 129.0, 126.5, 126.2, 121.8, 120.6, 120.0, 117.5, 112.7, 112.5, 111.2, 99.6, 96.9, 57.5, 20.7, 13.8, 10.0.

IR (KBr, ν, cm^{-1}): 3265, 2203, 1579, 1477, 1421, 827

HRMS (ESI): m/z calcd for: $C_{23}H_{18}N_2O_2S$, 385.1010, found: 385.1003.

(2Z)-2-(5-(4-bromophenyl)-4-methyl-1,3-oxathiol-2-ylidene)-3-(2-methyl-1*H*-indol-3-yl)-3-oxopropanenitrile (4l)

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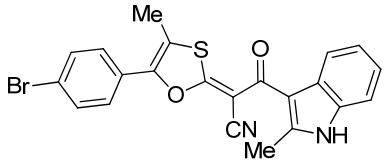


Pale yellow solid, mp: 265-266 °C;

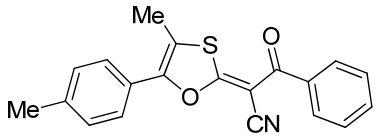
^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.79 (s, 1H, NH), 7.80 (d, J = 8.0 Hz, 2H, Ar-H), 7.66 (d, J = 8.0 Hz, 3H, Ar-H), 7.37 (d, J = 7.6 Hz, 1H, Ar-H), 7.16 – 7.06 (m, 2H, Ar-H), 2.58 (s, 3H, CH_3), 2.43 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 182.7, 181.1, 144.2, 140.4, 134.9, 132.1, 128.7, 126.1, 121.5, 119.9, 115.8, 112.5, 111.0, 84.5, 13.8, 10.8.

IR (KBr, ν, cm^{-1}): 3263, 2207, 1578, 1473, 1437, 800

HRMS (ESI): m/z calcd for: $C_{22}H_{15}BrN_2O_2S$, 450.9928, found: 450.9928.

(2Z)-2-(4-methyl-5-p-tolyl-1,3-oxathiol-2-ylidene)-3-oxo-3-phenylpropanenitrile (4m)



Pale yellow solid, mp: 189-190 °C;

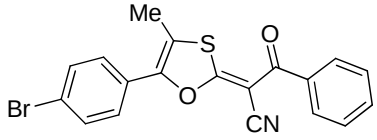
^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.78 (d, J = 7.2 Hz, 1H, Ar-H), 7.69-7.62 (m, 1H, Ar-H), 7.55 (d, J = 6.4 Hz, 1H, Ar-H), 7.29 (d, J = 8.0 Hz, 1H, Ar-H), 2.34 (s, 3H, CH_3), 1.19 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 186.0, 185.5, 183.9, 138.3, 137.0, 134.5, 133.9, 132.2, 128.9, 128.2, 127.9, 126.4, 117.6, 100.7, 57.7, 20.7, 9.7.

IR (KBr, ν, cm^{-1}): 3262, 2207, 1579, 1475, 1432, 805

HRMS (ESI): m/z calcd for: $C_{20}H_{15}NO_2S$, 332.0744, found: 332.0747.

(2Z)-2-(5-(4-bromophenyl)-4-methyl-1,3-oxathiol-2-ylidene)-3-oxo-3-phenylpropanenitrile (4n)



Pale yellow solid, mp: 186-188 °C;

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 (d, J = 7.6 Hz, 2H, Ar-H), 7.74 (s, 1H, Ar-H), 7.70 (t, J = 7.6 Hz, 3H, Ar-H), 7.63 (d, J = 8.0 Hz, 1H, Ar-H), 7.55 (d, 2H, J = 8.0 Hz, Ar-H), 1.20 (s, 3H, CH_3),

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 186.0, 185.6, 183.7, 137.0, 132.3, 131.4, 131.3, 128.8, 128.0, 122.5, 117.5, 100.0, 93.7, 57.5, 9.7.

IR (KBr, ν, cm^{-1}): 3260, 2257, 1576, 1473, 1432, 799

HRMS (ESI): m/z calcd for: $C_{19}H_{12}BrNO_2S$, 395.9693, found: 395.9692.

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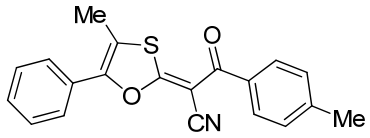
(2Z)-2-(4-methyl-5-phenyl-1,3-oxathiol-2-ylidene)-3-oxo-3-*p*-tolylpropanenitrile (4o)



Pale yellow solid, mp: 171-173 ^{o}C;

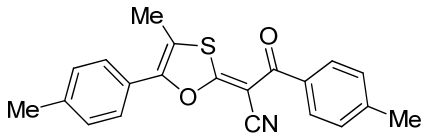
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ: 7.81 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.71 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.60 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.57 – 7.53 (m, 1H, Ar-H), 7.37 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.46 (s, 3H, CH_3), 2.40 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) (δ, ppm): 185.2, 182.8, 177.1, 146.0, 143.6, 142.3, 134.4, 129.8, 129.1, 128.9, 127.9, 126.9, 120.4, 118.5, 117.3, 116.1, 115.6, 21.1, 10.8.

IR (KBr, ν, cm^{-1}): 3250, 2255, 1576, 1472, 1433, 800

HRMS (ESI): m/z calcd for: $C_{20}H_{15}NO_2S$, 332.0744,found: 332.0746

(2Z)-2-(4-methyl-5-*p*-tolyl-1,3-oxathiol-2-ylidene)-3-oxo-3-*p*-tolylpropanenitrile (4p)



Pale yellow solid, mp: 174-176 ^{o}C;

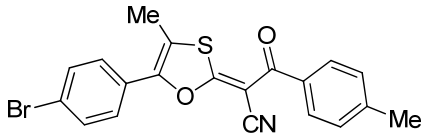
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ: 7.81 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.59 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.41 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.43 (s, 3H ,CH_3), 2.40 (s, 3H ,CH_3), 2.39 (s, 3H ,CH_3).

^{13}C NMR (100 MHz, DMSO-d$_6$) (δ, ppm): 185.3, 182.9, 166.9, 156.1, 142.5, 134.4, 129.2, 129.0, 127.9, 127.0, 115.7, 112.7, 86.5, 55.7, 21.1, 10.8.

IR (KBr, ν, cm^{-1}): 3313, 2209, 1561, 1514, 1405, 1221, 725

HRMS (ESI): m/z calcd for: $C_{21}H_{17}NO_2S$, 346.0901, found: 346.0914.

(2Z)-2-(5-(4-bromophenyl)-4-methyl-1,3-oxathiol-2-ylidene)-3-oxo-3-*p*-tolylpropanenitrile (4q)



Pale yellow solid, mp: 173-175 ^{o}C;

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ: 7.81 (d, *J* = 7.2 Hz, 4H, Ar-H), 7.65 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.37 (d, *J* = 7.6 Hz, 2H, Ar-H), 2.45 (s, 3H, CH_3), 2.40 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d$_6$) (δ, ppm): 185.1, 182.4, 145.0, 142.3, 134.1, 132.2, 128.9, 128.2, 127.8, 125.6, 123.5, 116.3, 115.8, 112.7, 86.5, 82.1, 21.2, 10.9.

IR (KBr, ν, cm^{-1}): 3313, 2209, 1561, 1514, 1405, 1221, 725

HRMS (ESI): m/z calcd for: $C_{20}H_{14}BrNO_2S$, 409.9850, found: 409.9834.

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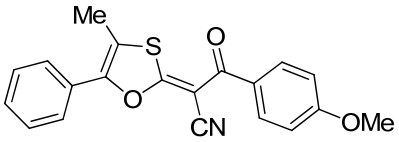
(2Z)-3-(4-methoxyphenyl)-2-(4-methyl-5-phenyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4r)



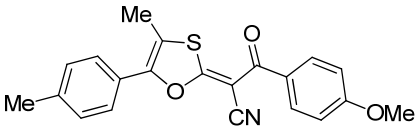
Pale yellow solid, mp: 168-169 ^{o}C;

^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.84 (d, J = 6.8 Hz, 2H, Ar-H), 7.78 (t, J = 8.4 Hz, 2H, Ar-H), 7.50-7.43 (m, 3H, Ar-H), 7.08 (d, J = 8.8 Hz, 2H, Ar-H), 3.85 (s, 3H, OCH_3), 1.19. (s, 3H, CH_3)

IR (KBr, ν, cm^{-1}): 3312, 2211, 1563, 1515, 1409, 1220, 727

HRMS (ESI): m/z calcd for: $C_{20}H_{15}NO_3S$, 348.0695, found: 348.0682.

(2Z)-3-(4-methoxyphenyl)-2-(4-methyl-5-*p*-tolyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4s)



Pale yellow solid, mp: 165-166 ^{o}C;

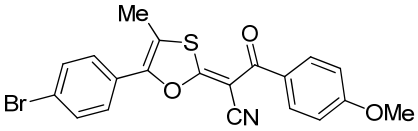
^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.84 (d, J = 8.8 Hz, 2H, Ar-H), 7.65 (t, J = 8.8 Hz, 2H, Ar-H), 7.28 (d, J = 8.0 Hz, 2H, Ar-H), 7.08 (d, J = 8.8 Hz, 2H, Ar-H), 3.85 (s, 3H, OCH_3), 2.34 (s, 3H,CH_3), 1.18. (s, 3H, CH_3)

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 184.0, 162.4, 139.7, 138.4, 134.6, 134.1, 130.5, 130.1, 129.7, 129.1, 129.0, 126.9, 126.5, 113.8, 100.4, 57.4, 55.5, 20.7, 9.8.

IR (KBr, ν, cm^{-1}): 3315, 2218, 1569, 1513, 1409, 1223, 729

HRMS (ESI): m/z calcd for: $C_{21}H_{17}NO_3S$, 362.0850, found: 362.0853.

(2Z)-2-(5-(4-bromophenyl)-4-methyl-1,3-oxathiol-2-ylidene)-3-(4-methoxyphenyl)-3-oxopropanenitrile (4t)



Pale yellow solid, mp: 169-171 ^{o}C;

^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.84 (d, J = 8.8 Hz, 2H, Ar-H), 7.75-7.68 (m, 4H, Ar-H), 7.08 (d, J = 8.8 Hz, 2H, Ar-H), 3.85 (s, 3H, OCH_3), 1.18. (s, 3H, CH_3)

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 184.4, 184.0, 182.6, 162.7, 137.0, 136.6, 131.3, 130.5, 130.4, 129.1, 128.7, 122.4, 117.7, 113.6, 99.5, 93.7, 57.4, 55.4, 9.7.

IR (KBr, ν, cm^{-1}): 3319, 2209, 1565, 1514, 1409, 1221, 729

HRMS (ESI): m/z calcd for: $C_{20}H_{14}BrNO_3S$, 425.9799, found: 425.9793.

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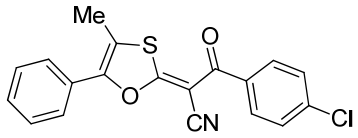
(2Z)-3-(4-chlorophenyl)-2-(4-methyl-5-phenyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4u)



Pale yellow solid, mp: 163-165 ^{o}C;

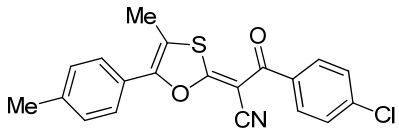
^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.87 – 7.84 (m, 2H, Ar-H), 7.72 (d, J = 7.2 Hz, 3H, Ar-H), 7.62-7.54 (m, 4H, Ar-H), 2.47 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm):185.6, 183.7, 137.0, 136.9, 132.3, 132.2, 131.4, 131.3, 128.8, 128.3, 128.0, 127.9, 122.5, 117.5, 57.5, 9.7.

IR (KBr, ν, cm^{-1}): 3314, 2209, 1560, 1514, 1407, 1221, 729

HRMS (ESI): m/z calcd for: $C_{19}H_{12}ClNO_2S$, 352.0198, found: 352.0183.

(2Z)-3-(4-chlorophenyl)-2-(4-methyl-5-*p*-tolyl-1,3-oxathiol-2-ylidene)-3-oxopropanenitrile (4v)



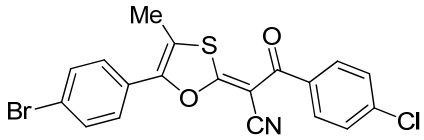
Pale yellow solid, mp: 160-162 ^{o}C;

^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.80 – 7.78 (m, 2H, Ar-H), 7.69-7.59 (m, 4H, Ar-H), 7.29 (d, J = 8.0 Hz, 2H, Ar-H), 2.34 (s, 3H, CH_3), 1.20 (s, 3H, CH_3).

IR (KBr, ν, cm^{-1}): 3315 ,2212, 1563, 1515, 1409, 1223, 725

HRMS (ESI): m/z calcd for: $C_{20}H_{14}ClNO_2S$, 366.0355, found: 366.0343.

(2Z)-2-(5-(4-bromophenyl)-4-methyl-1,3-oxathiol-2-ylidene)-3-(4-chlorophenyl)-3-oxopropanenitrile (4w)



Pale yellow solid; mp: 167-169 ^{o}C;

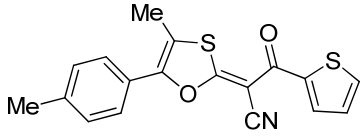
^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.82 (d, J = 7.2 Hz,2H, Ar-H), 7.74-7.68 (m, 4H, Ar-H), 7.62 (d, J = 6.4 Hz, 2H, Ar-H), 1.20 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 184.2, 136.9, 136.4, 131.4, 131.3, 129.9, 129.8, 128.7, 128.4, 122.5, 117.4, 112.7, 100.1, 93.5, 57.6, 9.7.

IR (KBr, ν, cm^{-1}): 3318 ,2209, 1563, 1517, 1407, 1225, 725

HRMS (ESI): m/z calcd for: $C_{20}H_{14}ClNO_2S$, 431.9277, found: 431.9255.

(2Z)-2-(4-methyl-5-*p*-tolyl-1,3-oxathiol-2-ylidene)-3-oxo-3-(thiophen-2-yl)propanenitrile (4x)



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Pale yellow solid, mp: 166-168 ^{o}C;

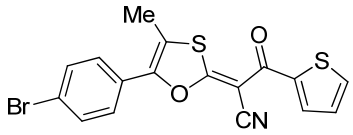
^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.15 (d, J = 4.8 Hz, 1H, Ar-H), 8.06 (s, 1H, Ar-H), 7.68-7.63 (m, 2H, Ar-H), 7.28 (d, J = 7.6 Hz, 3H, Ar-H), 2.34 (s, 3H, CH_3), 1.18 (s, 3H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 184.3, 175.6, 142.1, 138.4, 135.3, 134.5, 133.9, 132.5, 129.1, 128.7, 126.5, 117.7, 100.6, 91.9, 57.5, 20.7, 9.7.

IR (KBr, ν, cm^{-1}): 3315, 2214, 1565, 1518, 1407, 1226, 735.

HRMS (ESI): m/z calcd for: $C_{18}H_{13}NO_2S_2$, 338.0309, found:.338.0294

(2Z)-2-(5-(4-bromophenyl)-4-methyl-1,3-oxathiol-2-ylidene)-3-oxo-3-(thiophen-2-yl)propanenitrile (4y)



Pale yellow solid, mp: 159-160 ^{o}C;

^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.21-8.13 (m, 1H, Ar-H), 8.08 (d, J = 4.4 Hz, 1H Ar-H), 7.82-7.59 (m, 4H, Ar-H), 7.30 (d, J = 4.0 Hz, 1H, Ar-H), 1.19 (s, 3H,CH_3).

^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 183.9, 175.6, 142.0, 137.0, 135.3, 132.5, 131.4, 131.3, 128.8, 122.4, 117.5, 99.7, 57.4, 9.7.

IR (KBr, ν, cm^{-1}): 3312, 2225, 1565, 1514, 1407, 1221, 723

HRMS (ESI): m/z calcd for: $C_{17}H_{10}BrNO_2S_2$, 401.9257, found:.401.9243.

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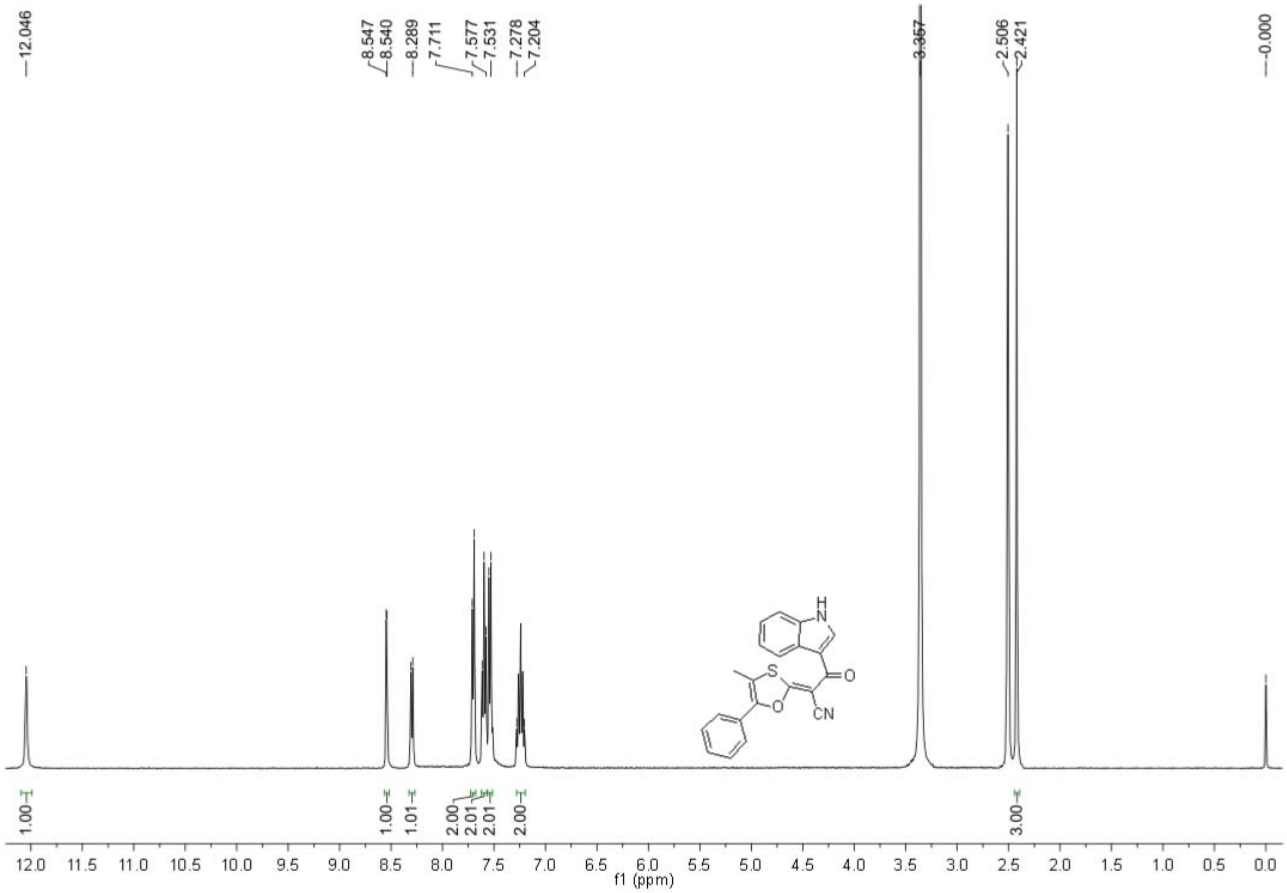
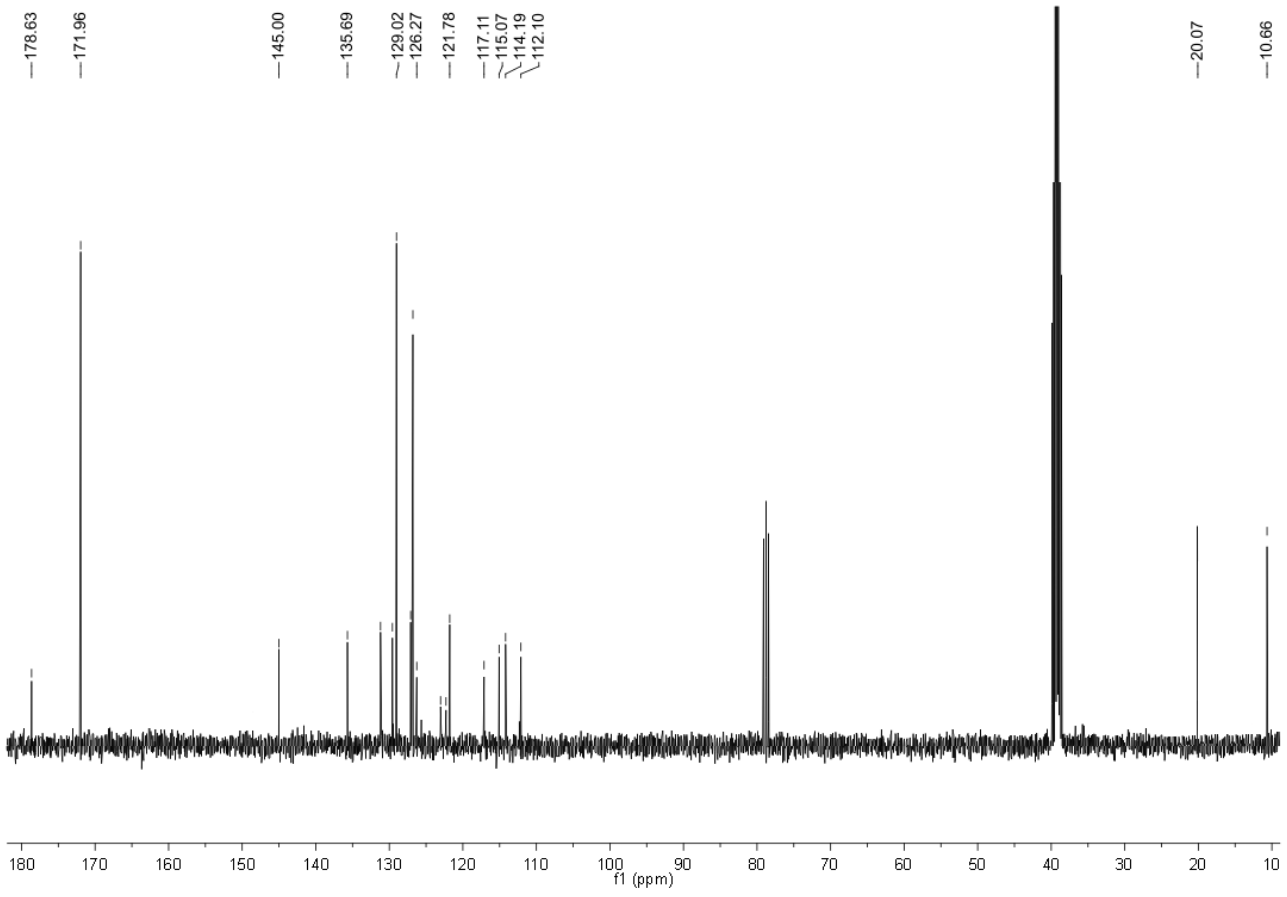


^{1}H NMR Spectrum of Compound 4a



^{13}C NMR Spectrum of Compound 4a

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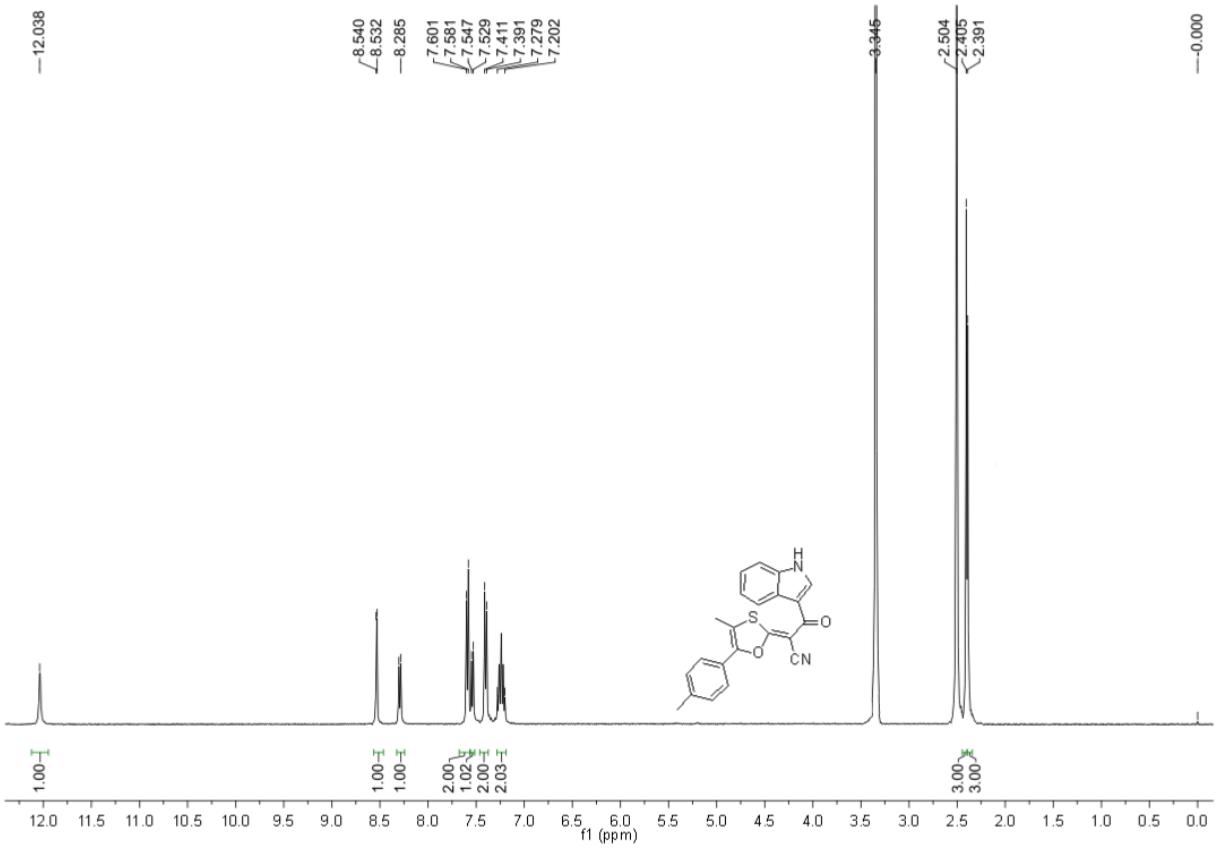
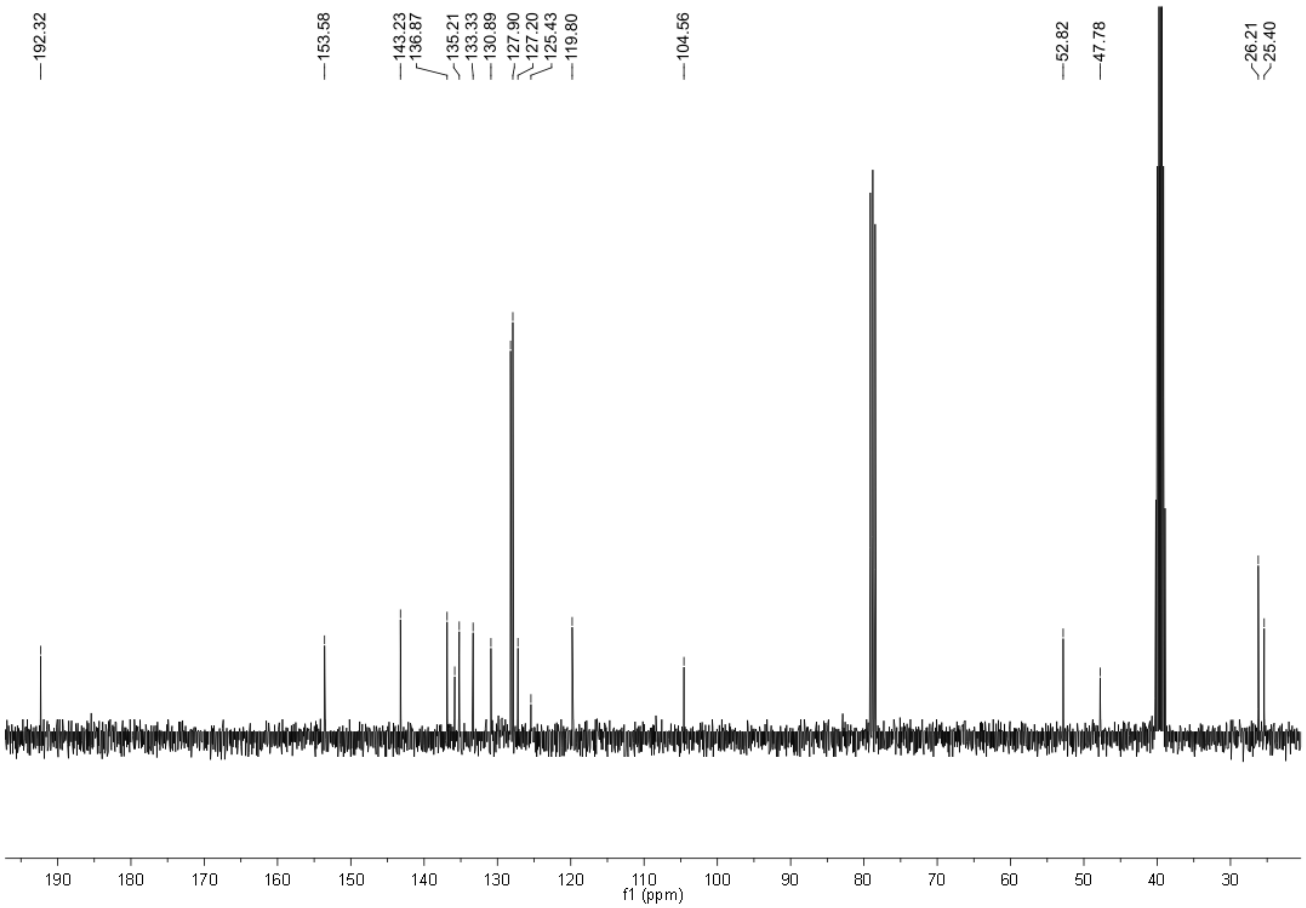


^{1}H NMR Spectrum of Compound 4b



^{13}C NMR Spectrum of Compound 4b

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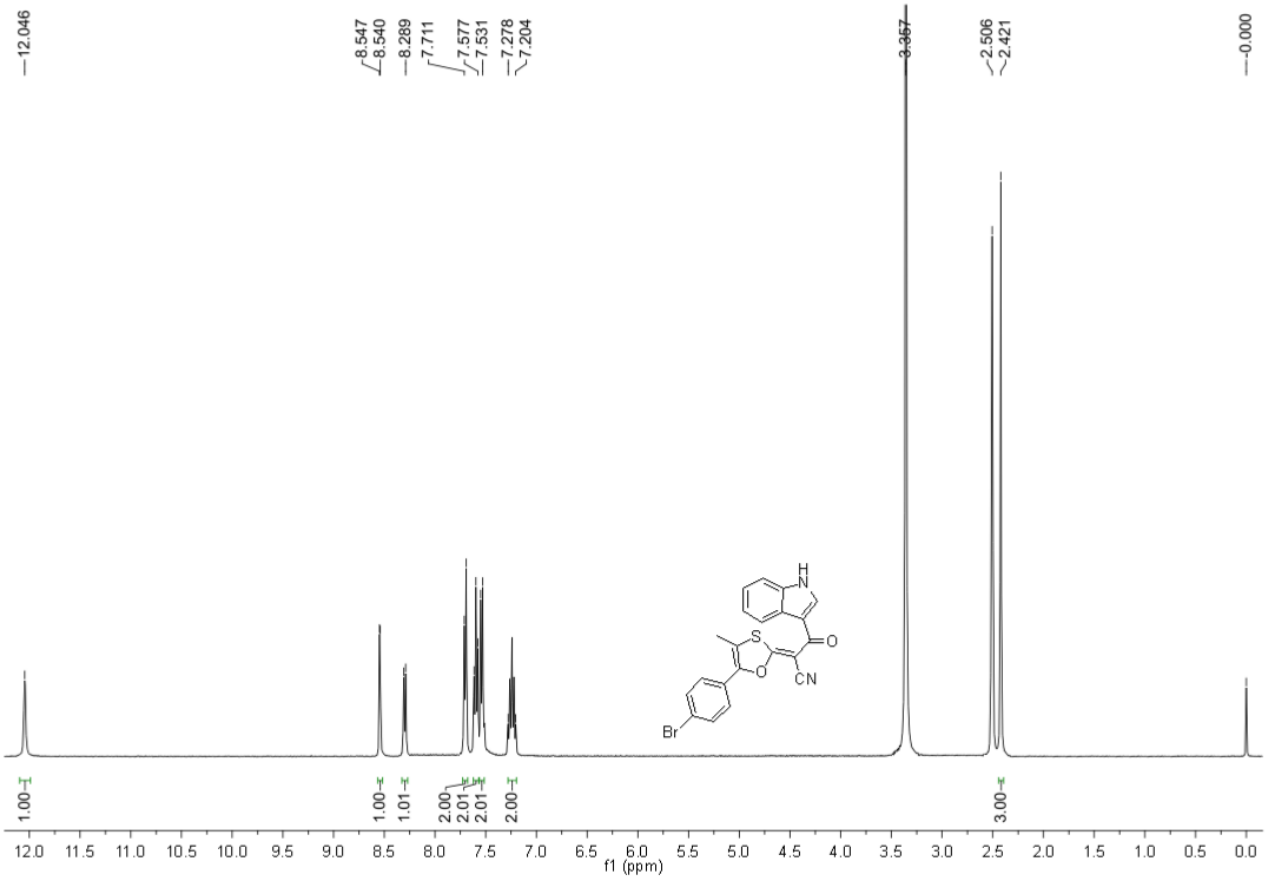
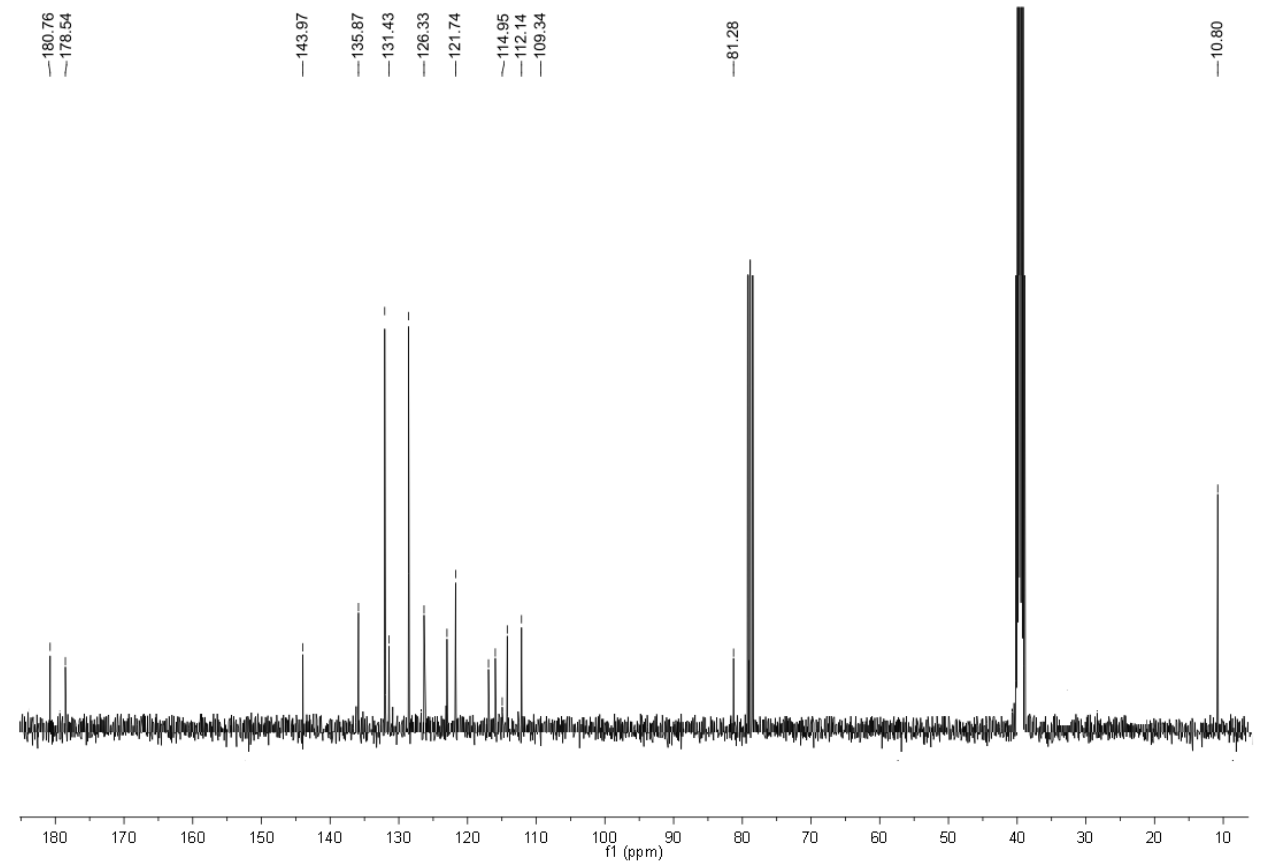


^{1}H NMR Spectrum of Compound 4c



^{13}C NMR Spectrum of Compound 4c

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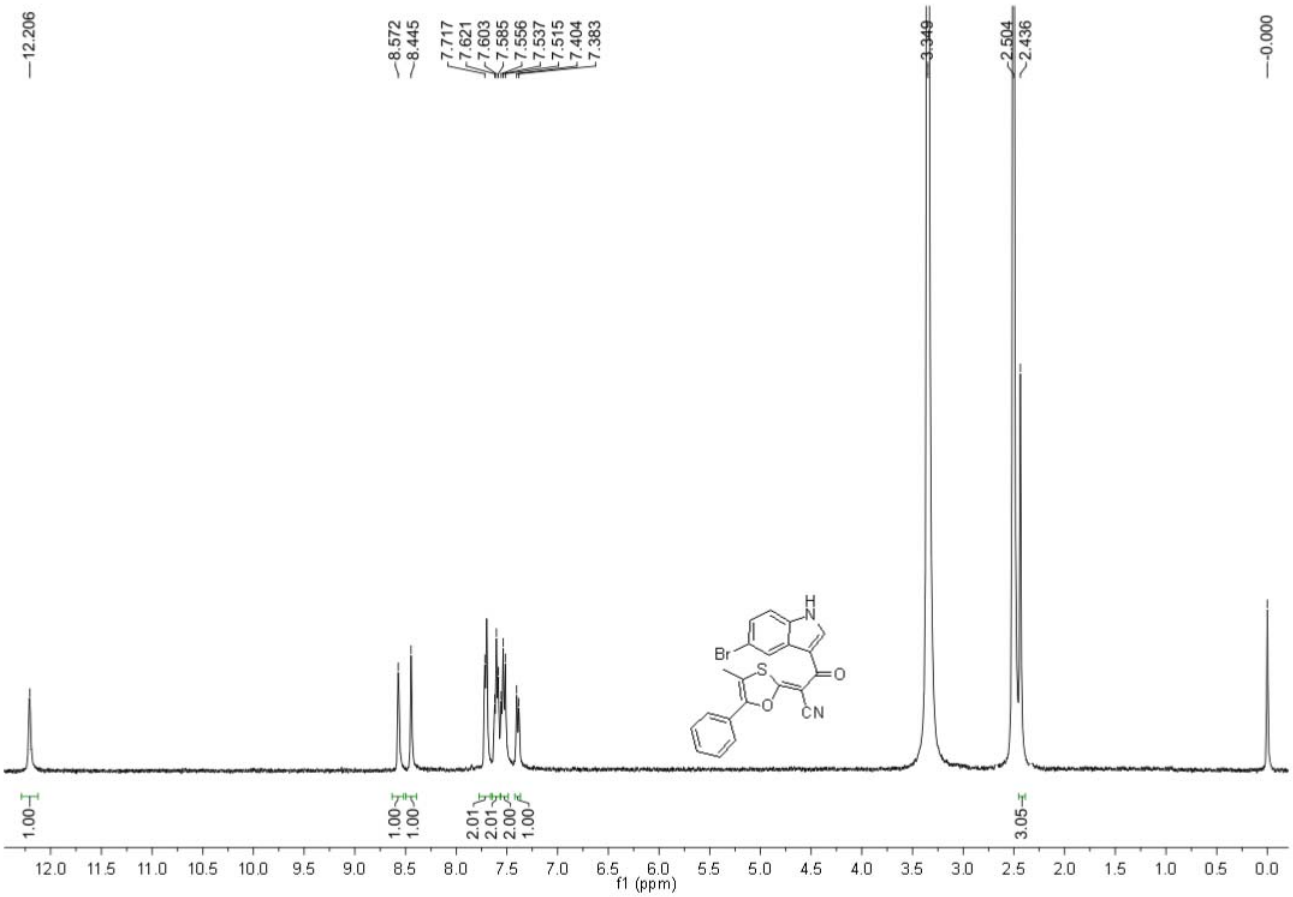
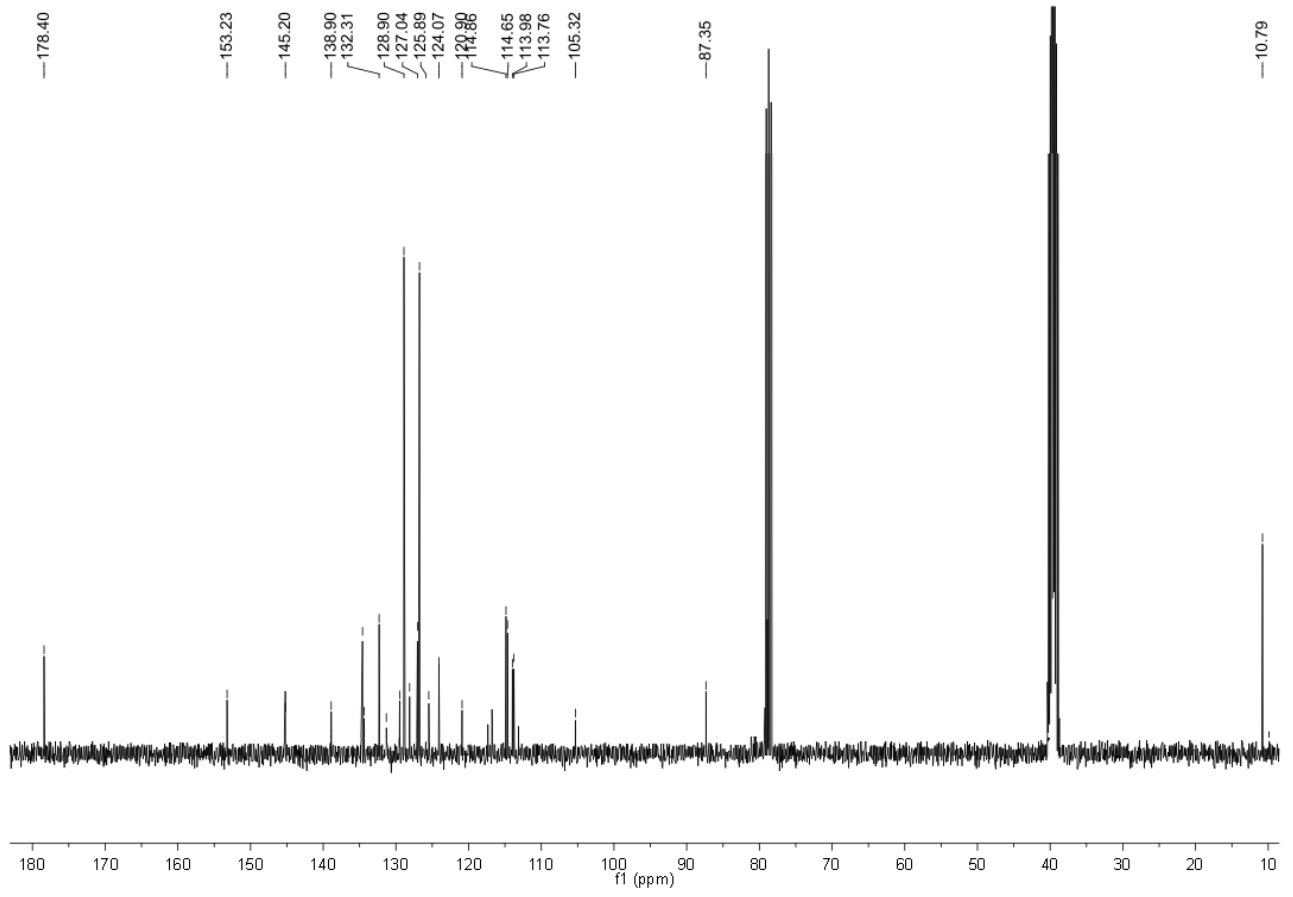


^{1}H NMR Spectrum of Compound 4d



^{13}C NMR Spectrum of Compound 4d

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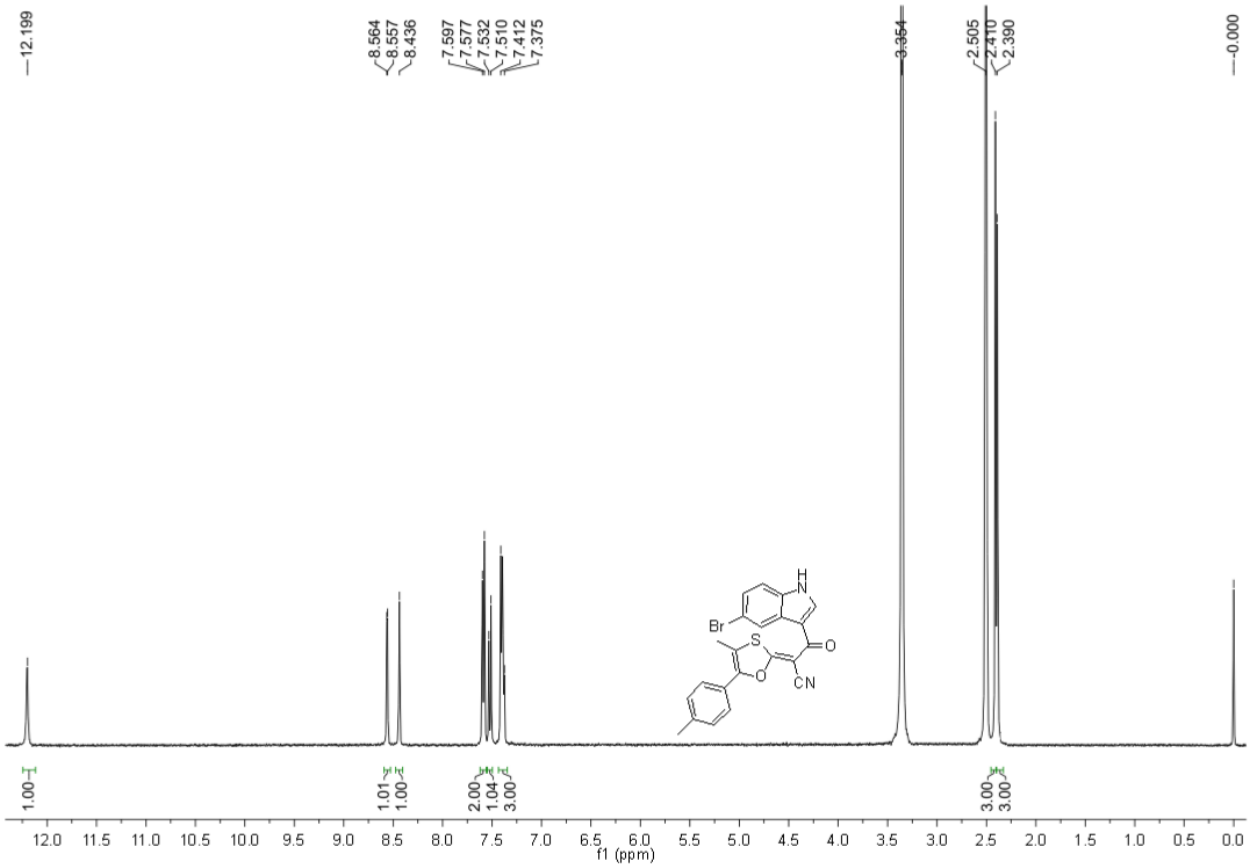
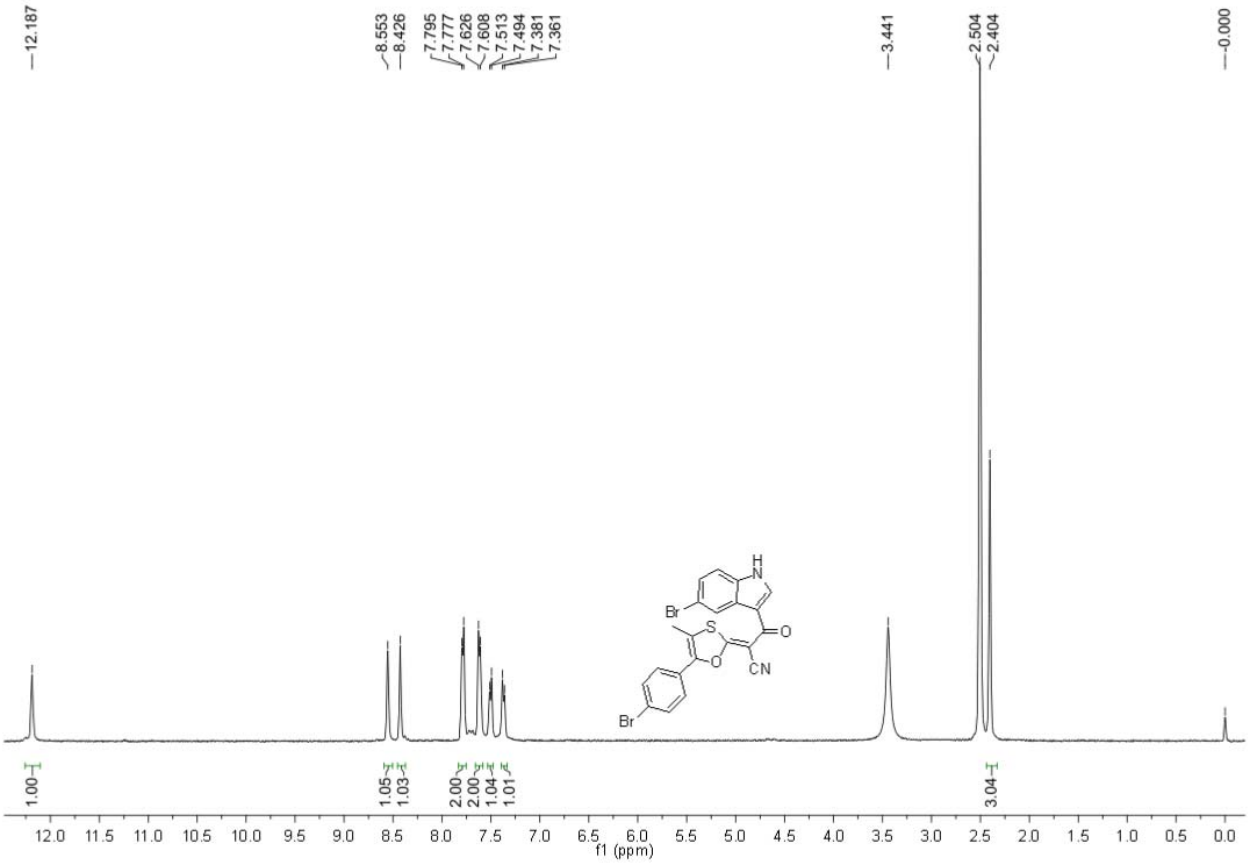


^{1}H NMR Spectrum of Compound 4e



^{1}H NMR Spectrum of Compound 4f

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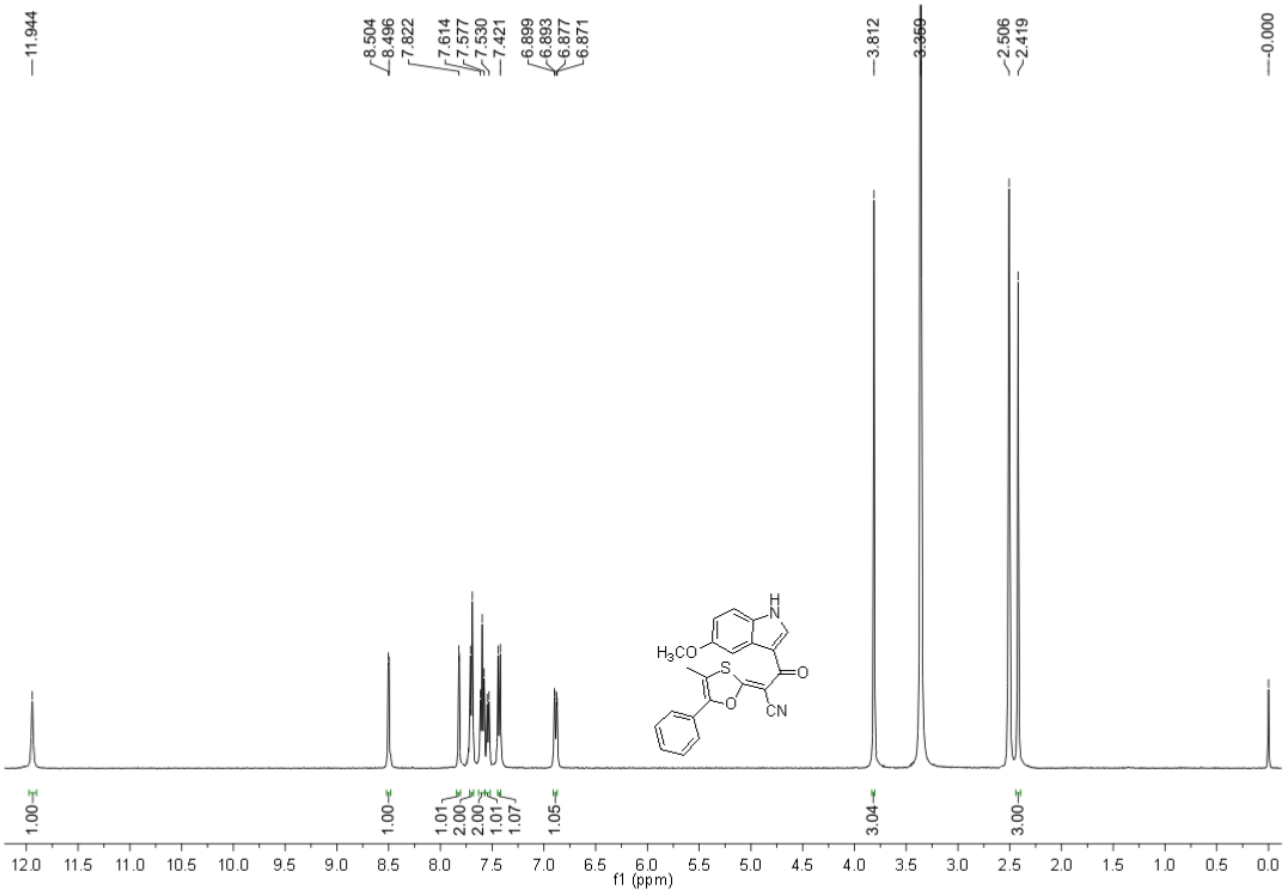
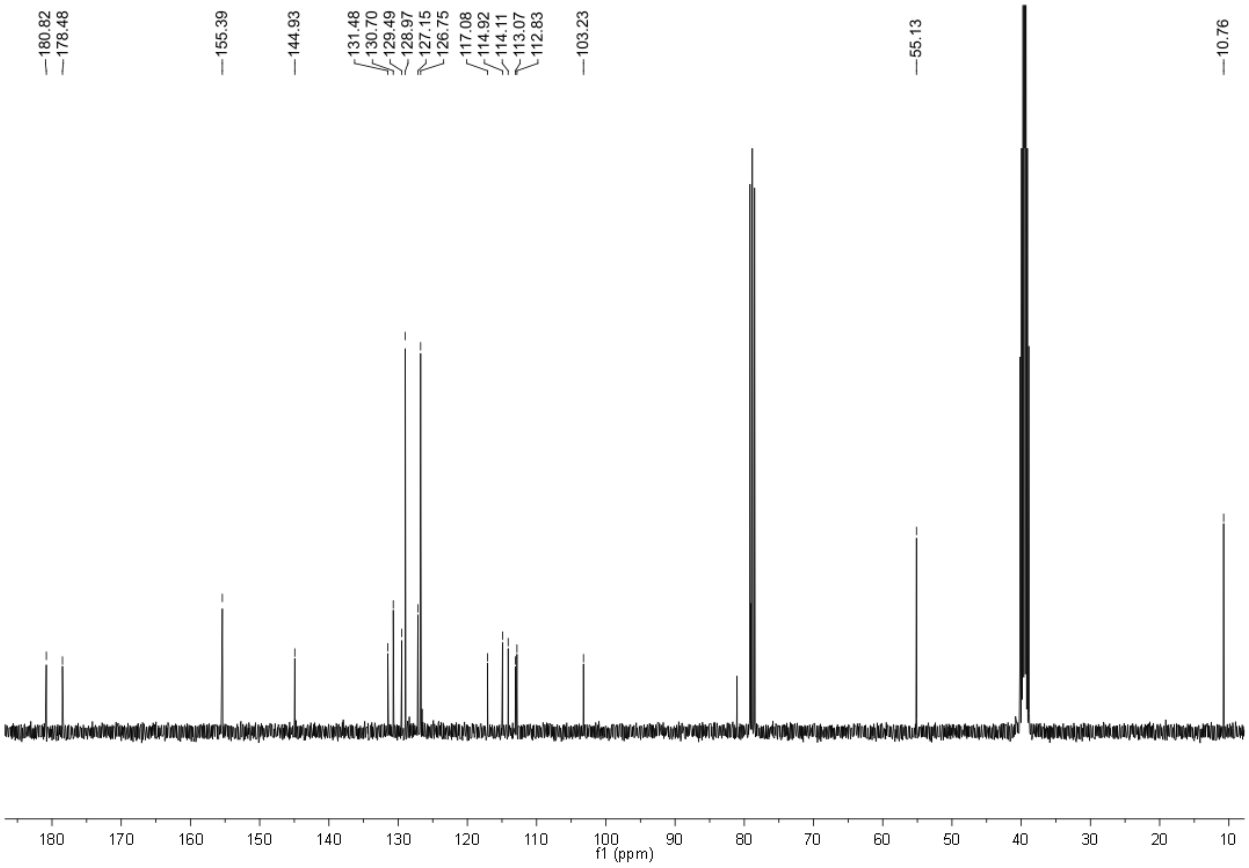


^{1}H NMR Spectrum of Compound 4g



^{13}C NMR Spectrum of Compound 4g

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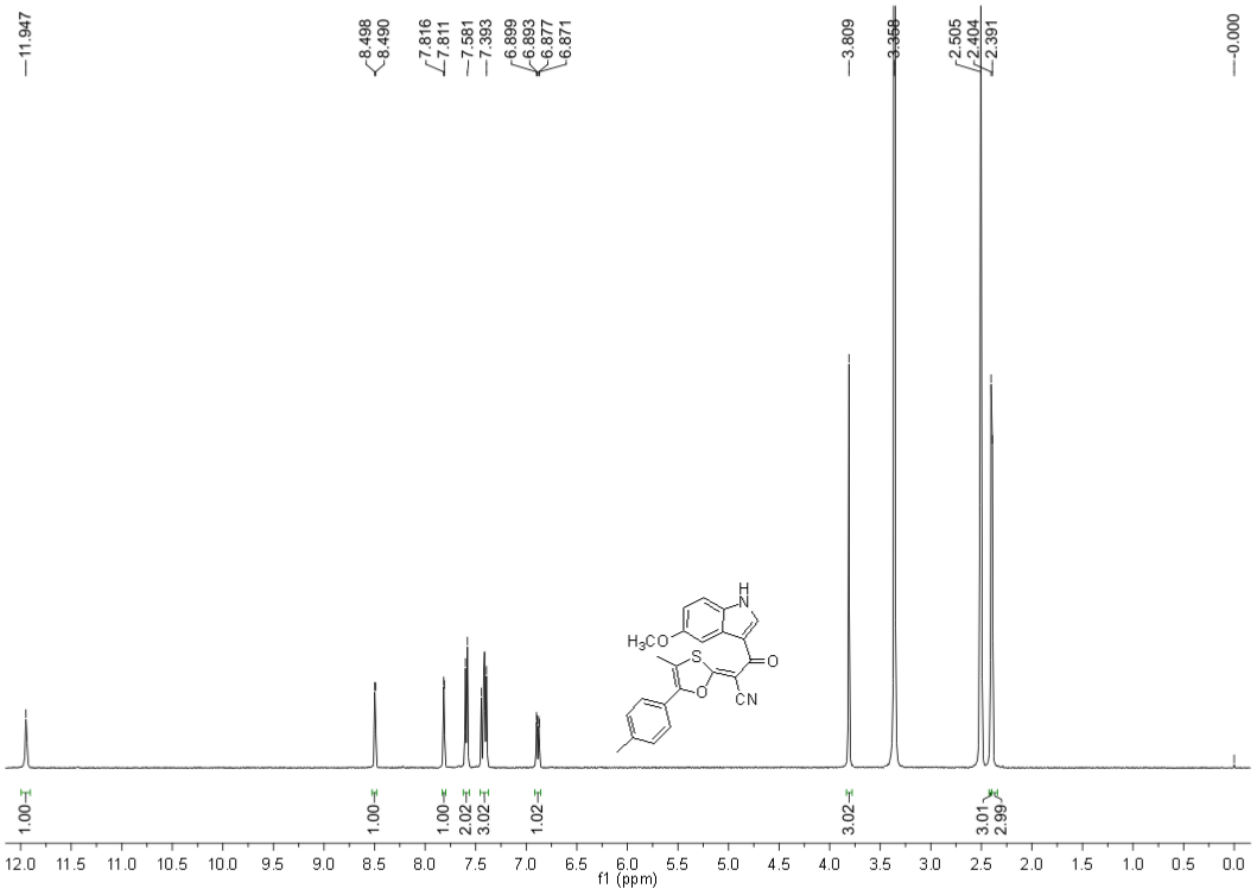
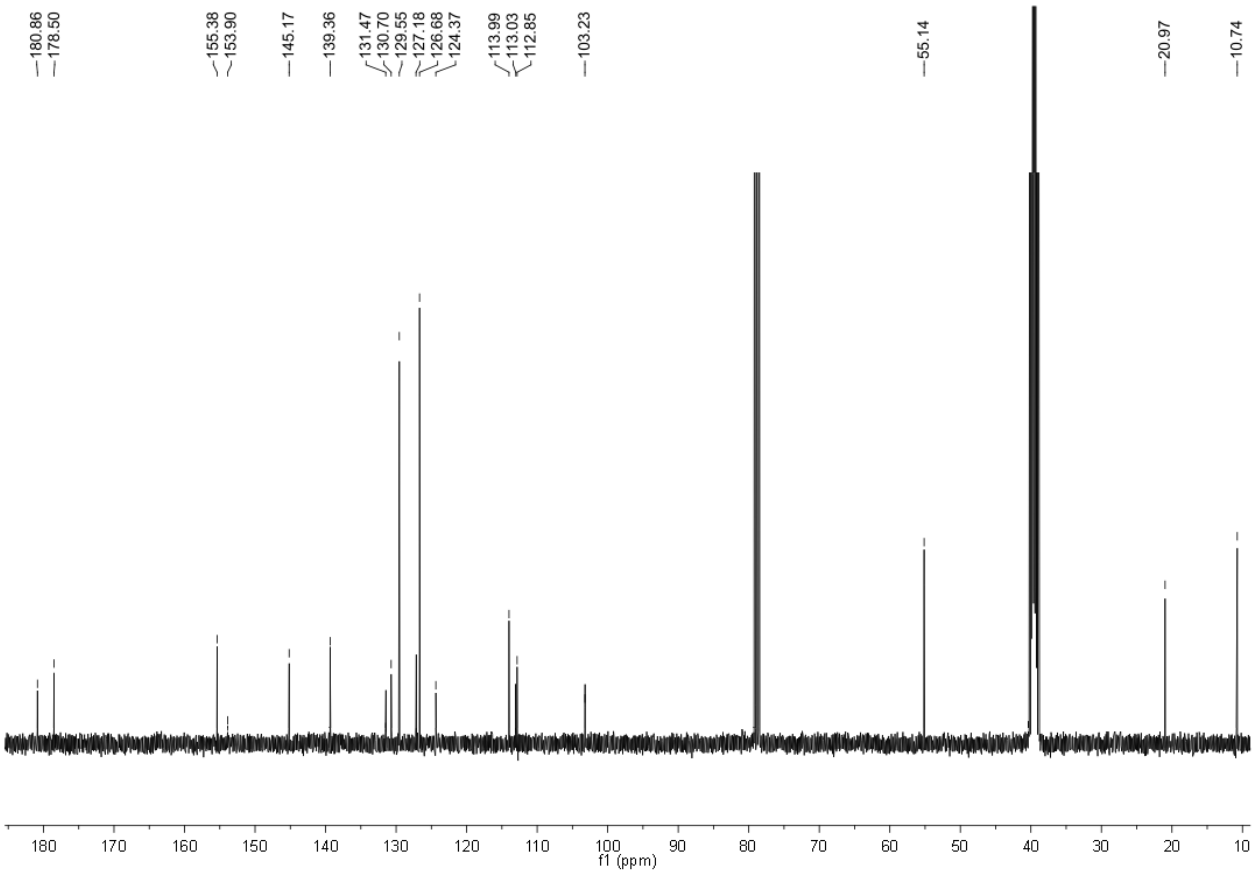


^{1}H NMR Spectrum of Compound 4h



^{13}C NMR Spectrum of Compound 4h

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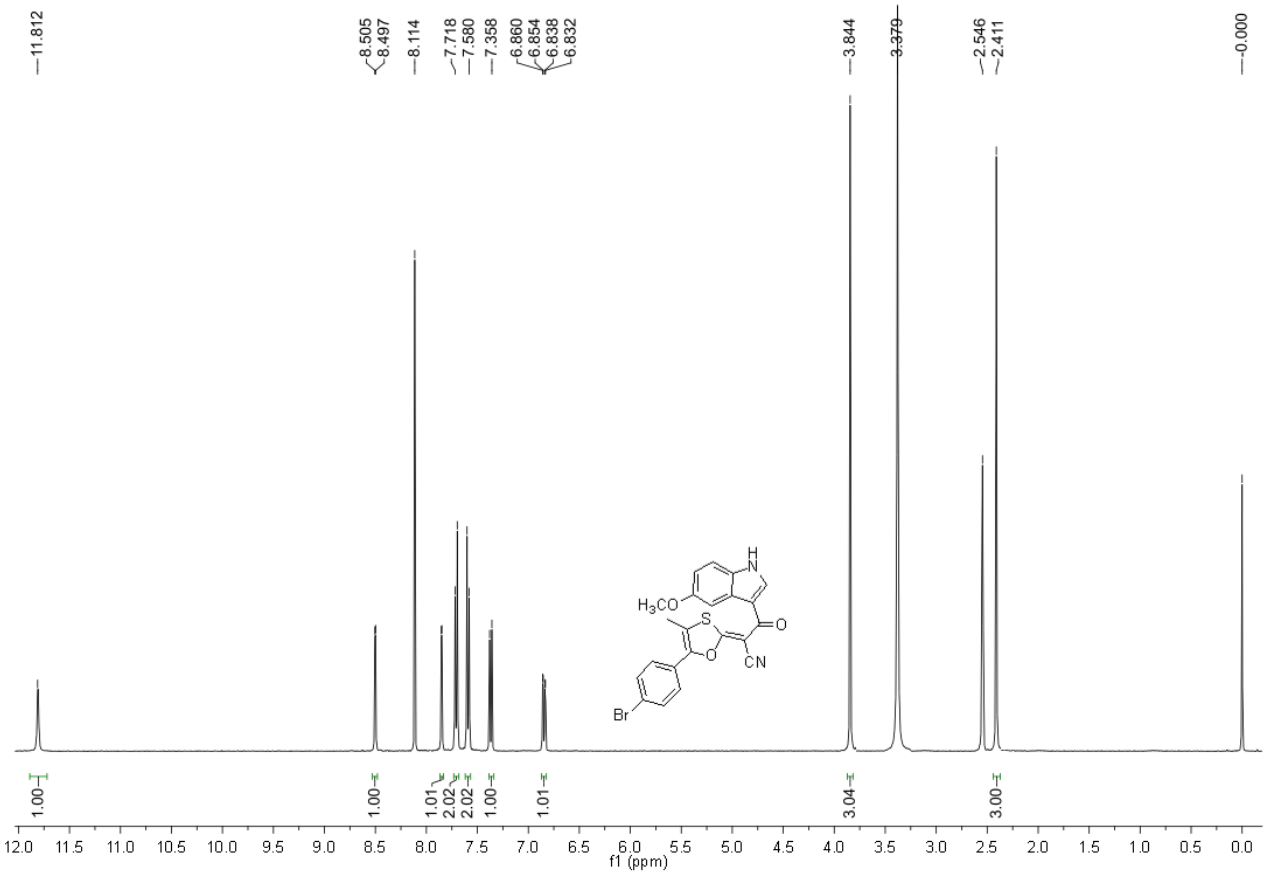
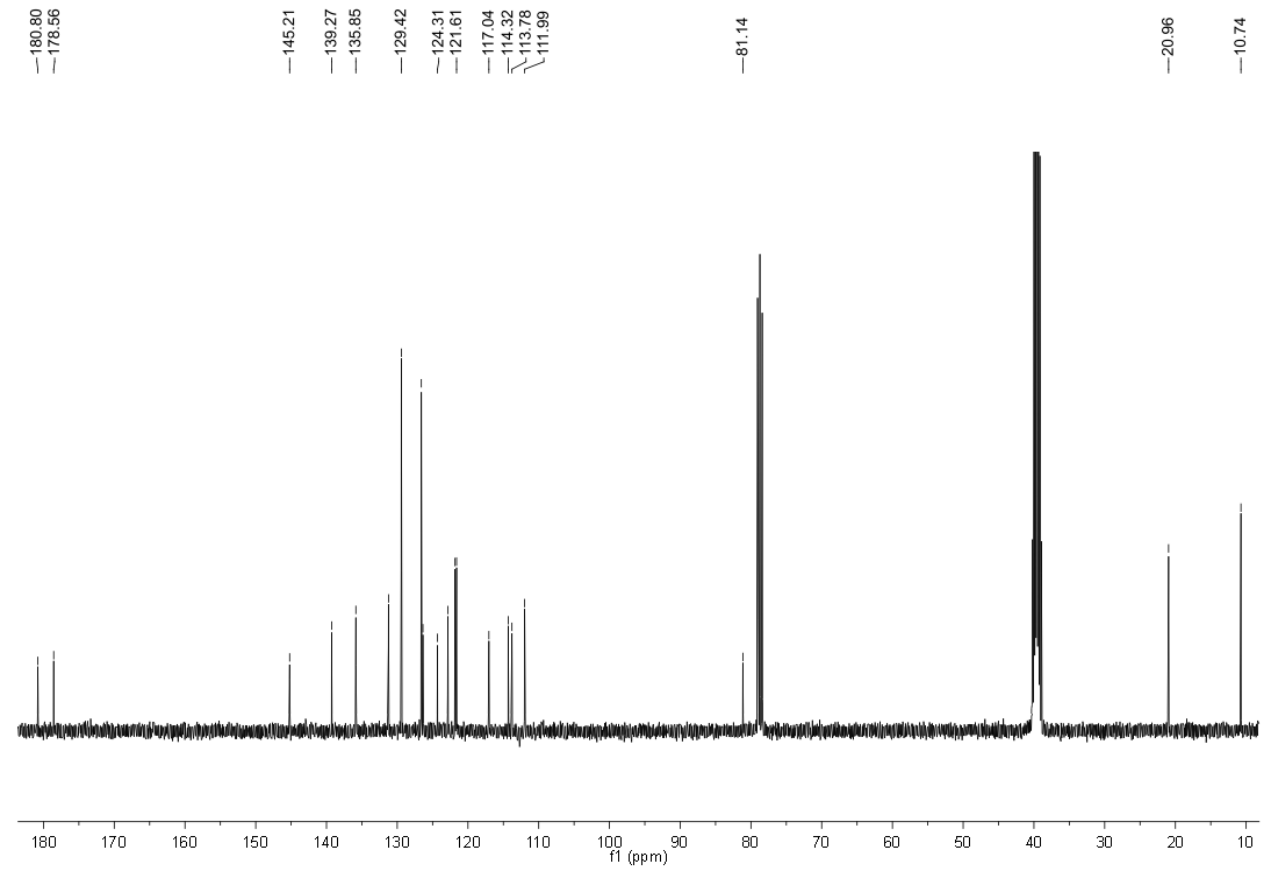


^{1}H NMR Spectrum of Compound 4i



^{13}C NMR Spectrum of Compound 4i

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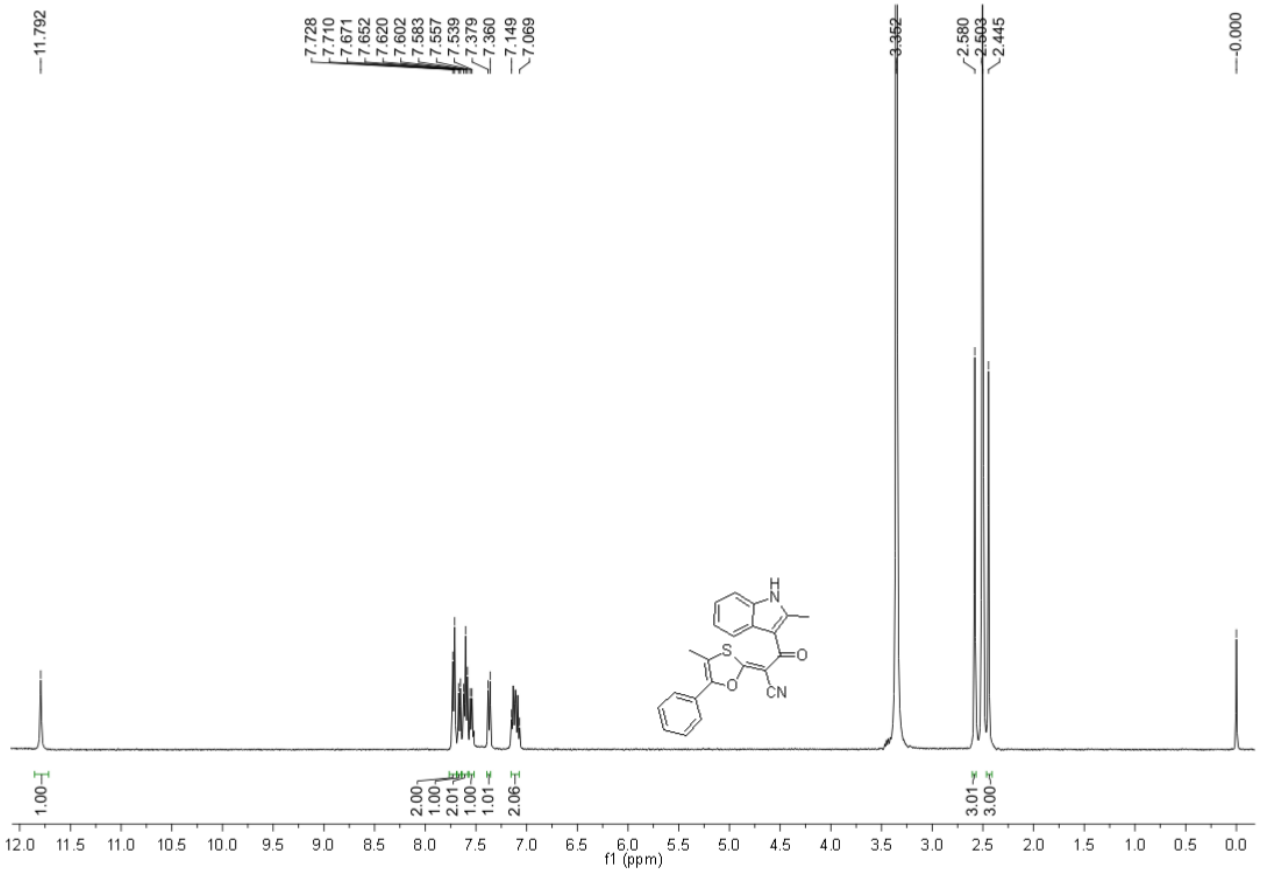
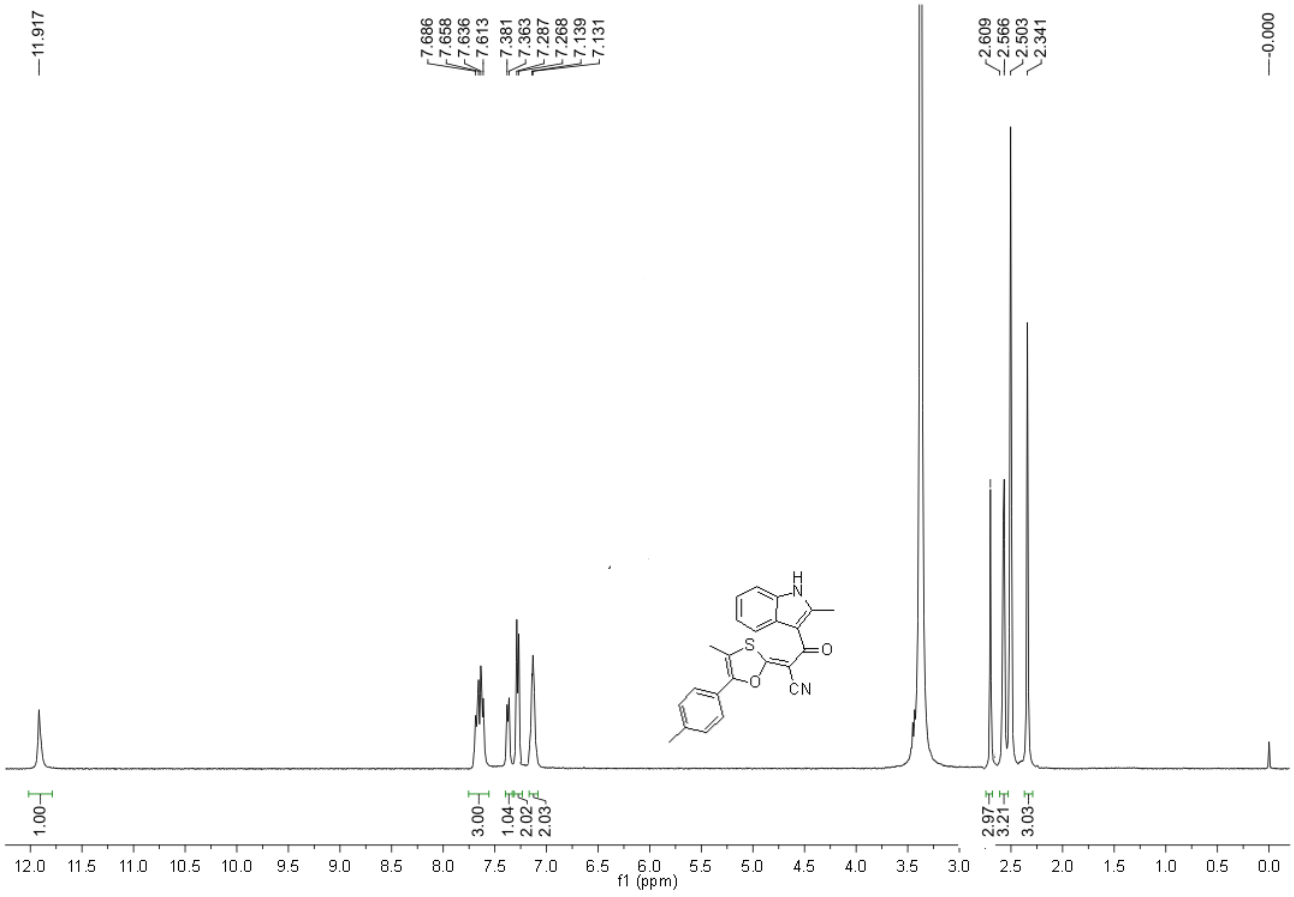


^{1}H NMR Spectrum of Compound 4j



^{1}H NMR Spectrum of Compound 4k

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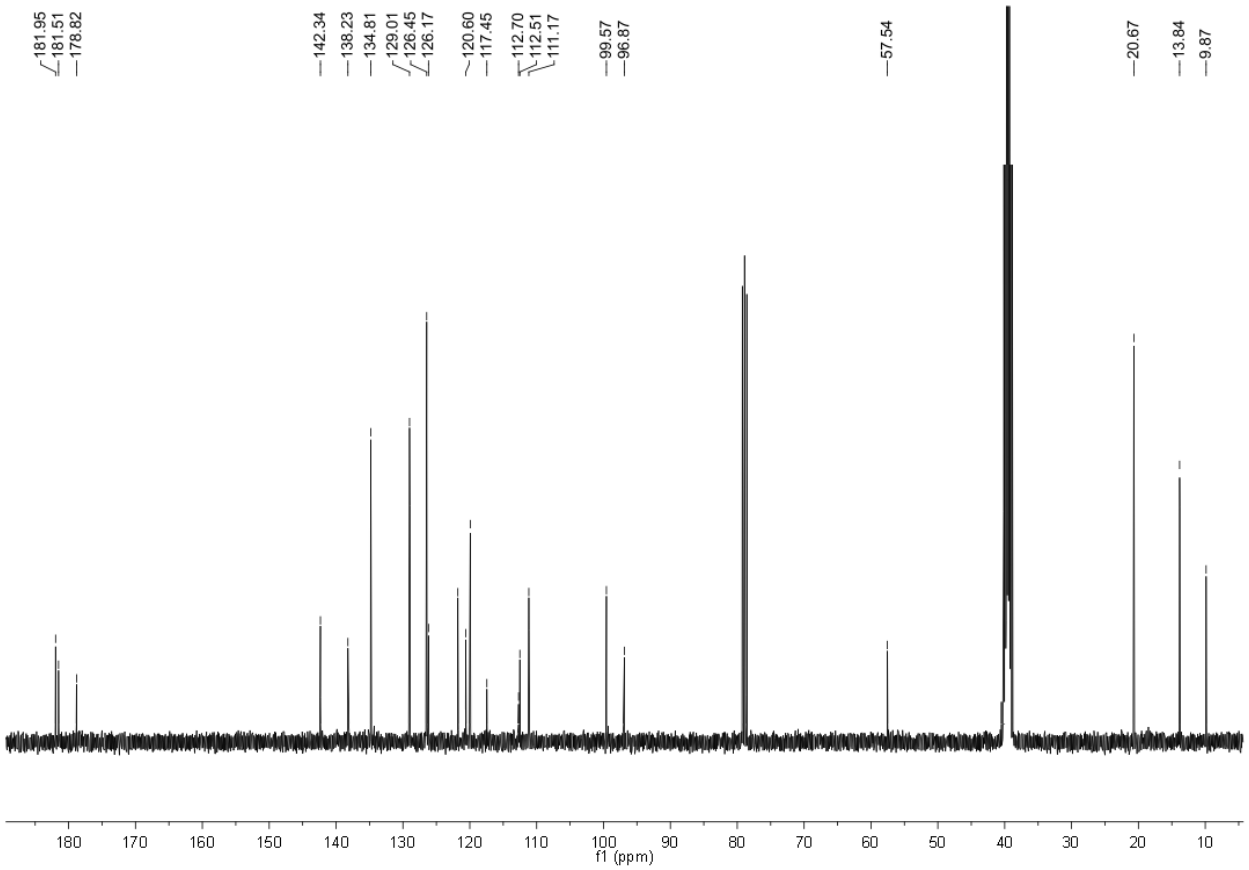
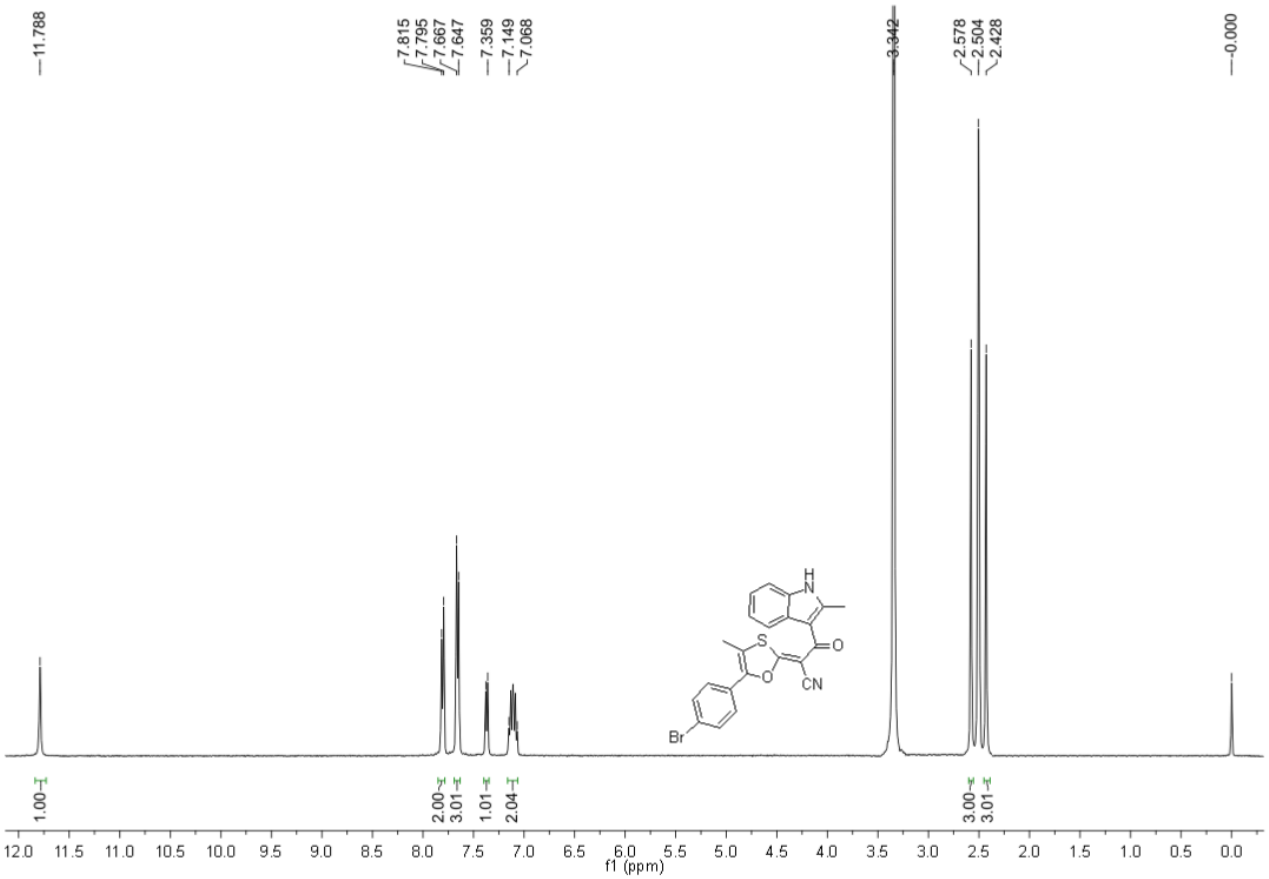


^{13}C NMR Spectrum of Compound 4k



^{1}H NMR Spectrum of Compound 4l

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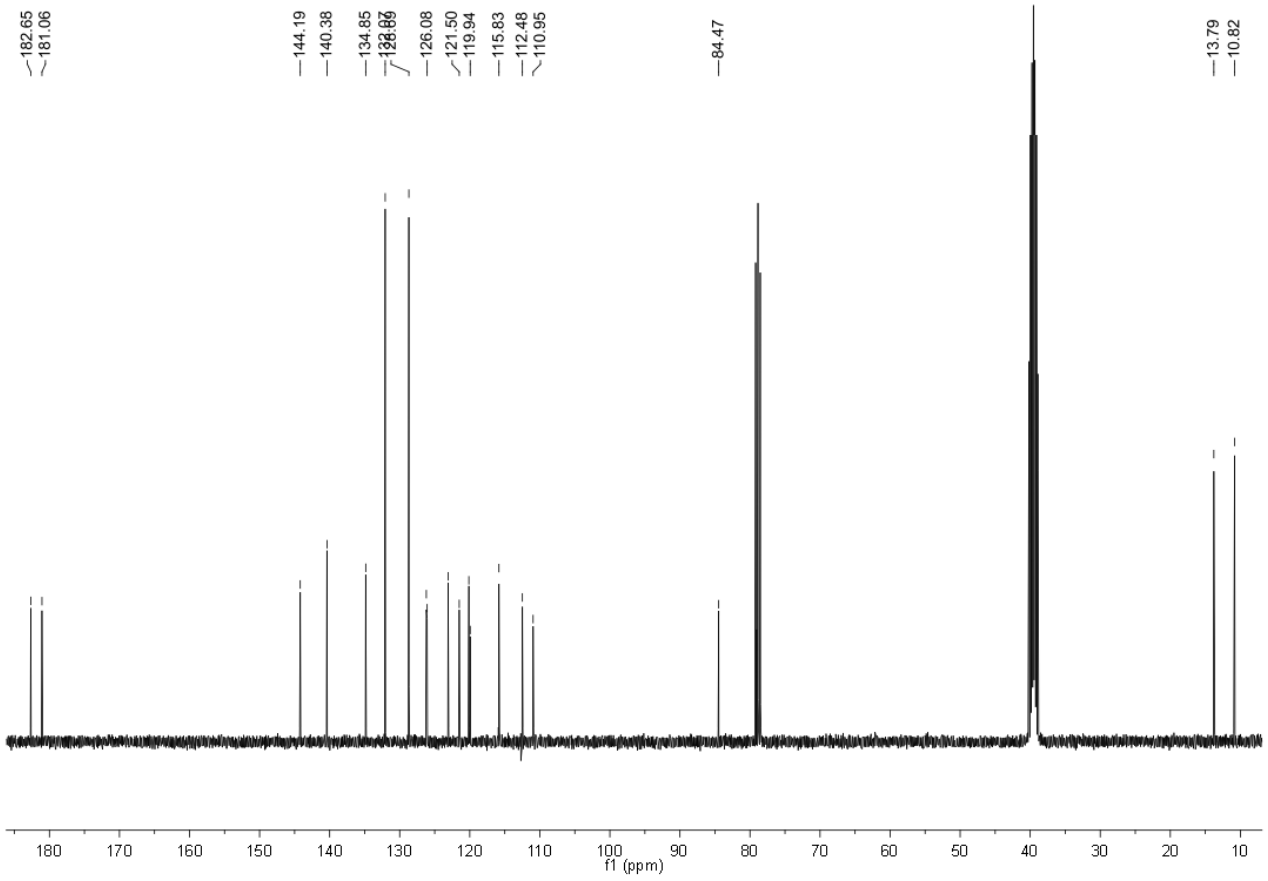
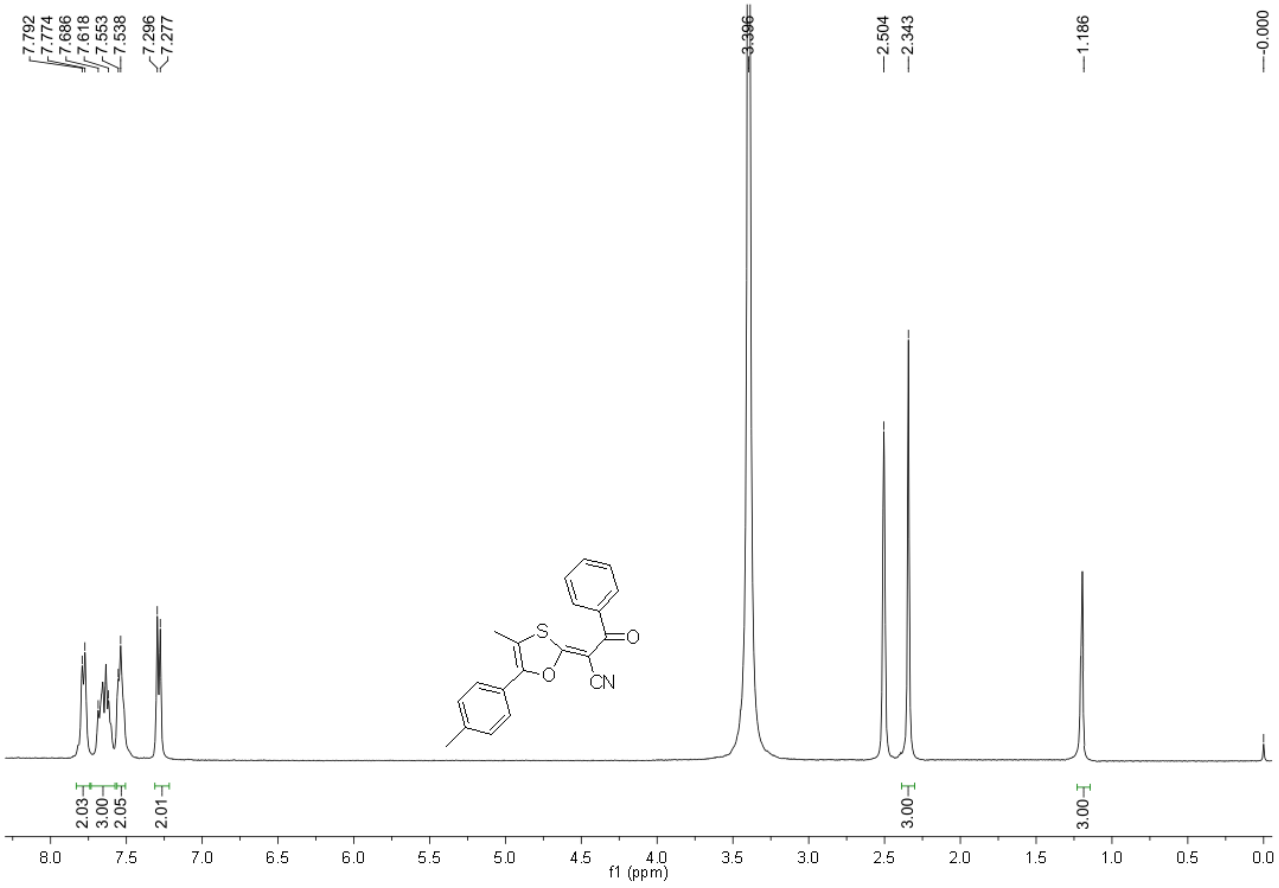


^{13}C NMR Spectrum of Compound 4l



^{1}H NMR Spectrum of Compound 4m

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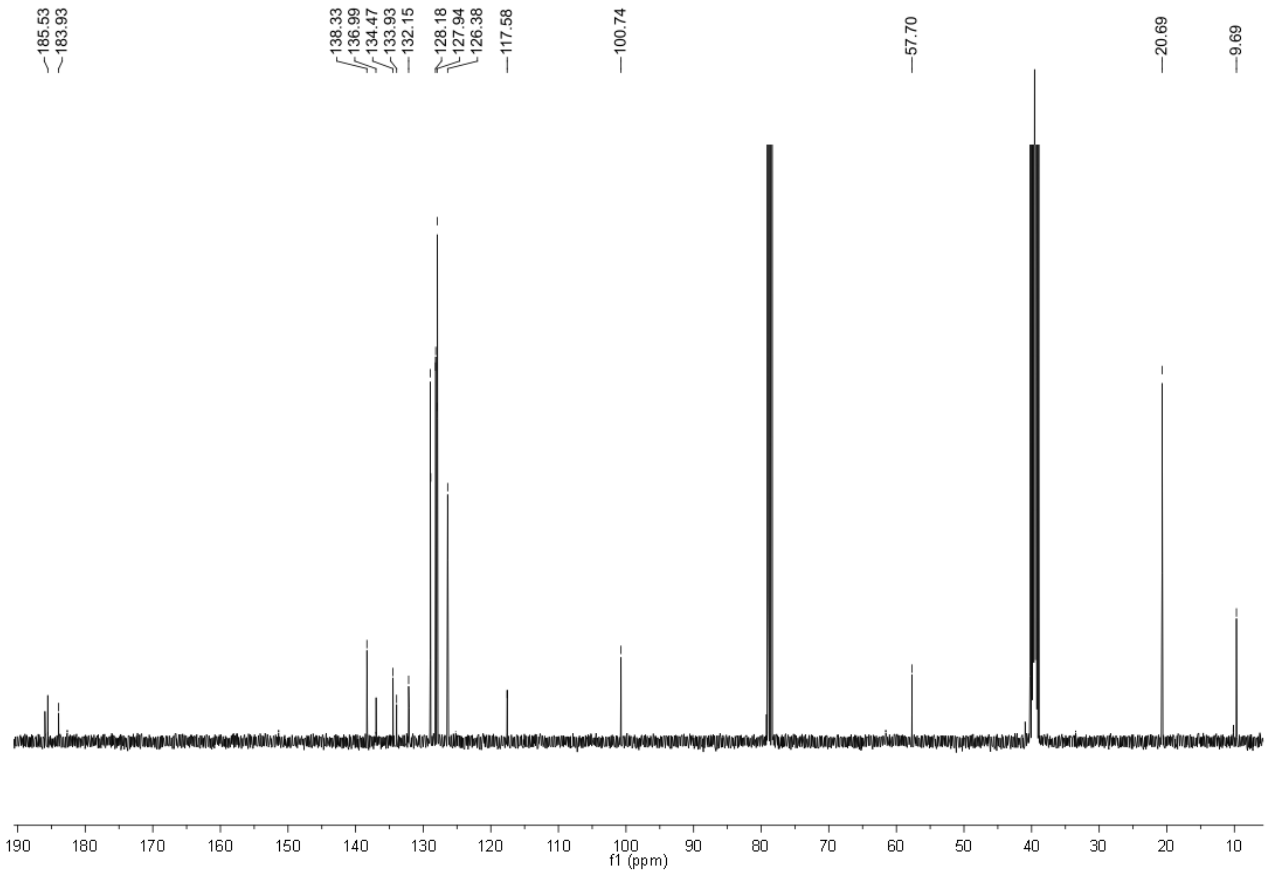
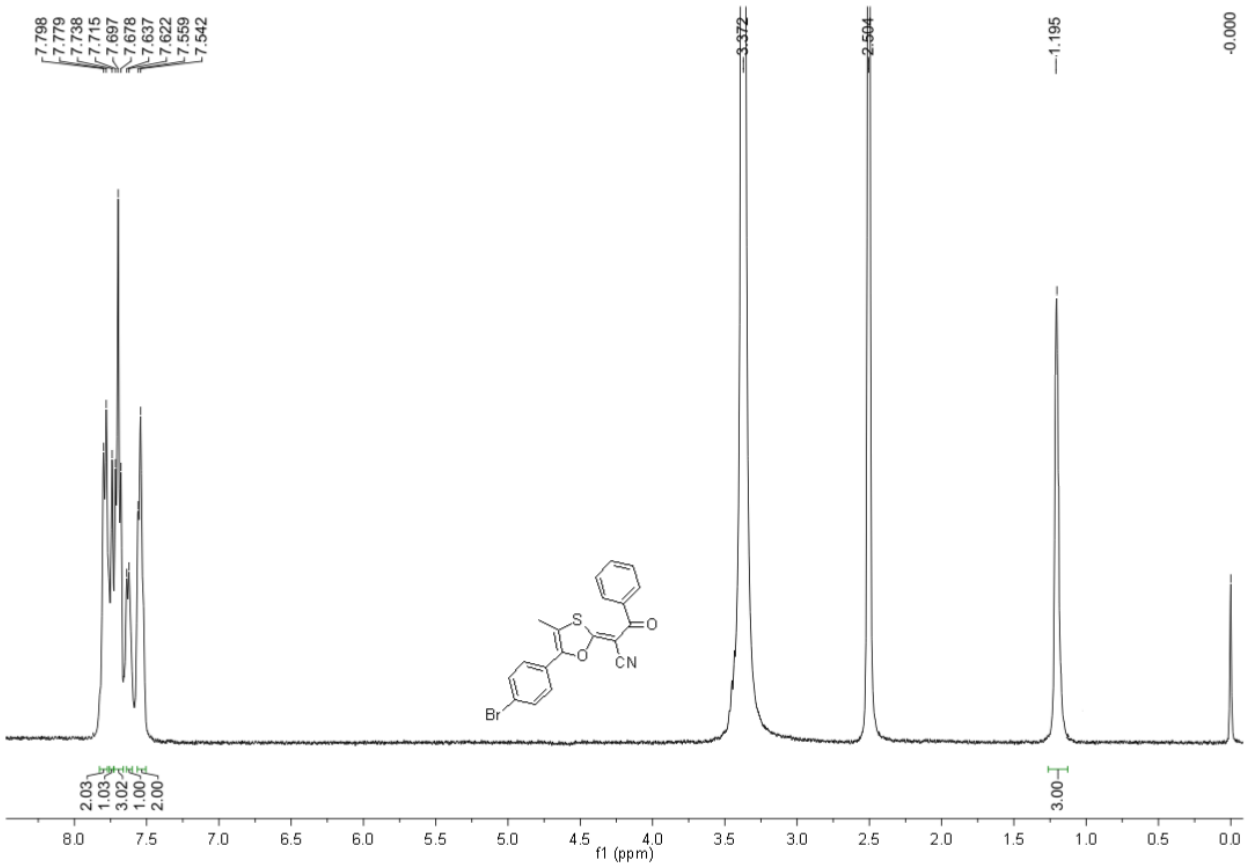


^{13}C NMR Spectrum of Compound 4m



^{1}H NMR Spectrum of Compound 4n

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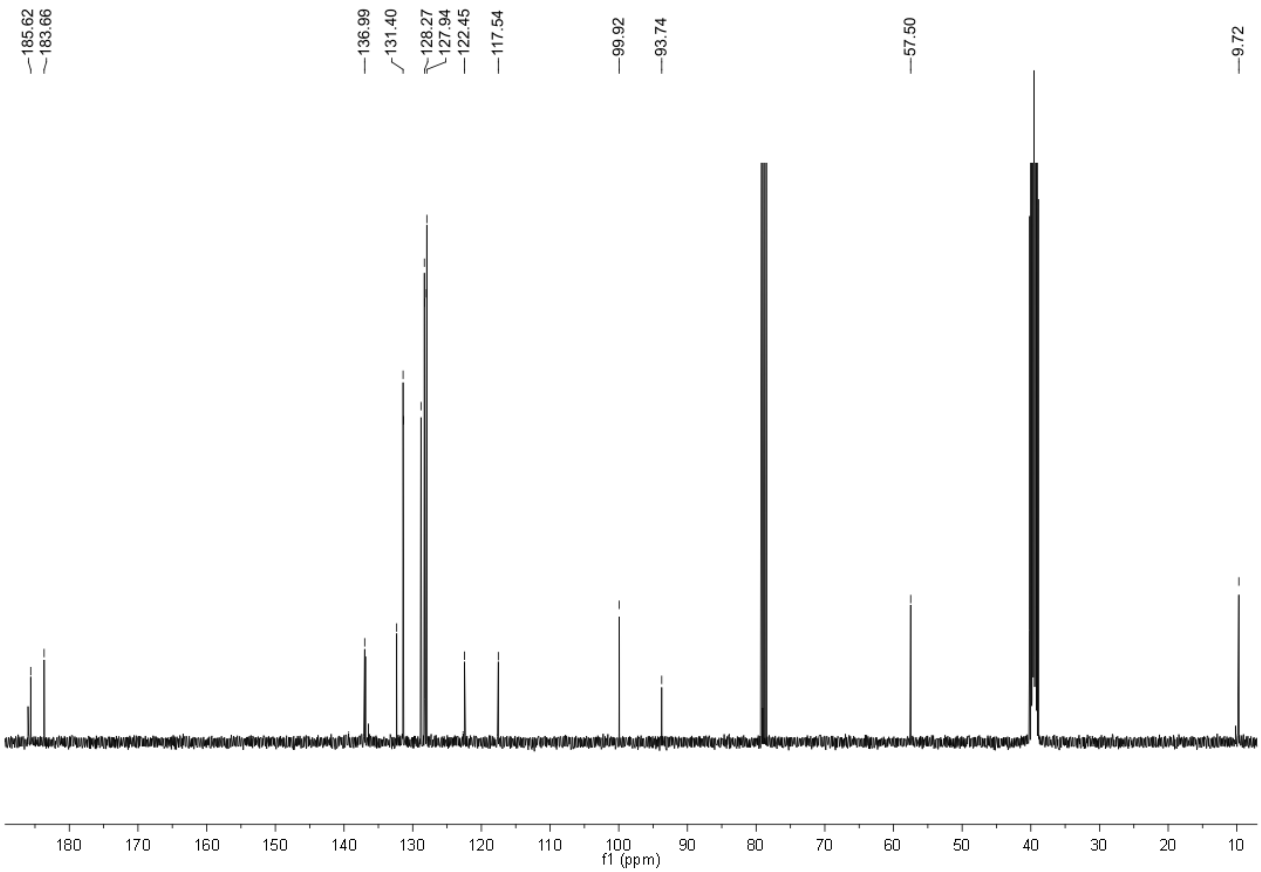
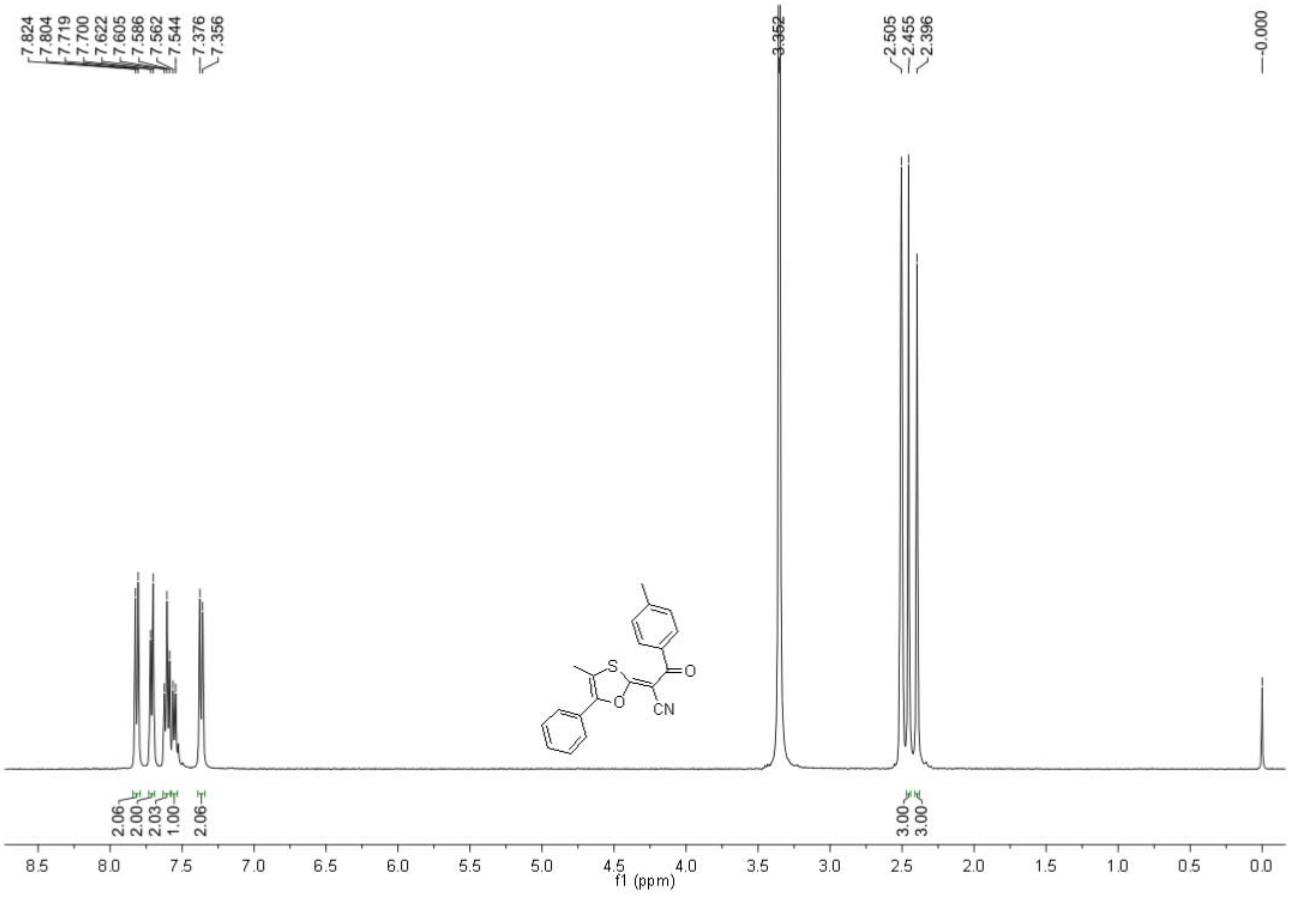


^{13}C NMR Spectrum of Compound 4n



^{1}H NMR Spectrum of Compound 4o

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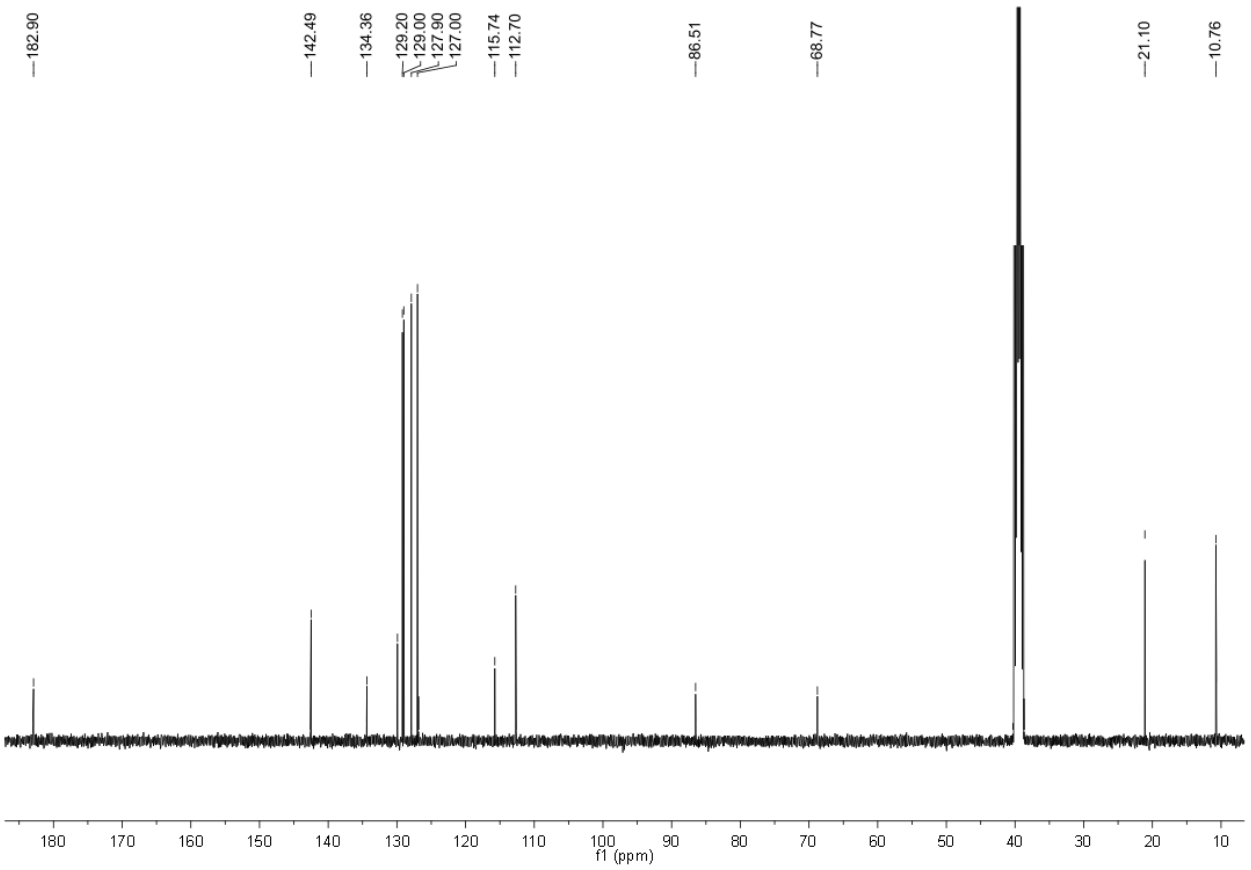
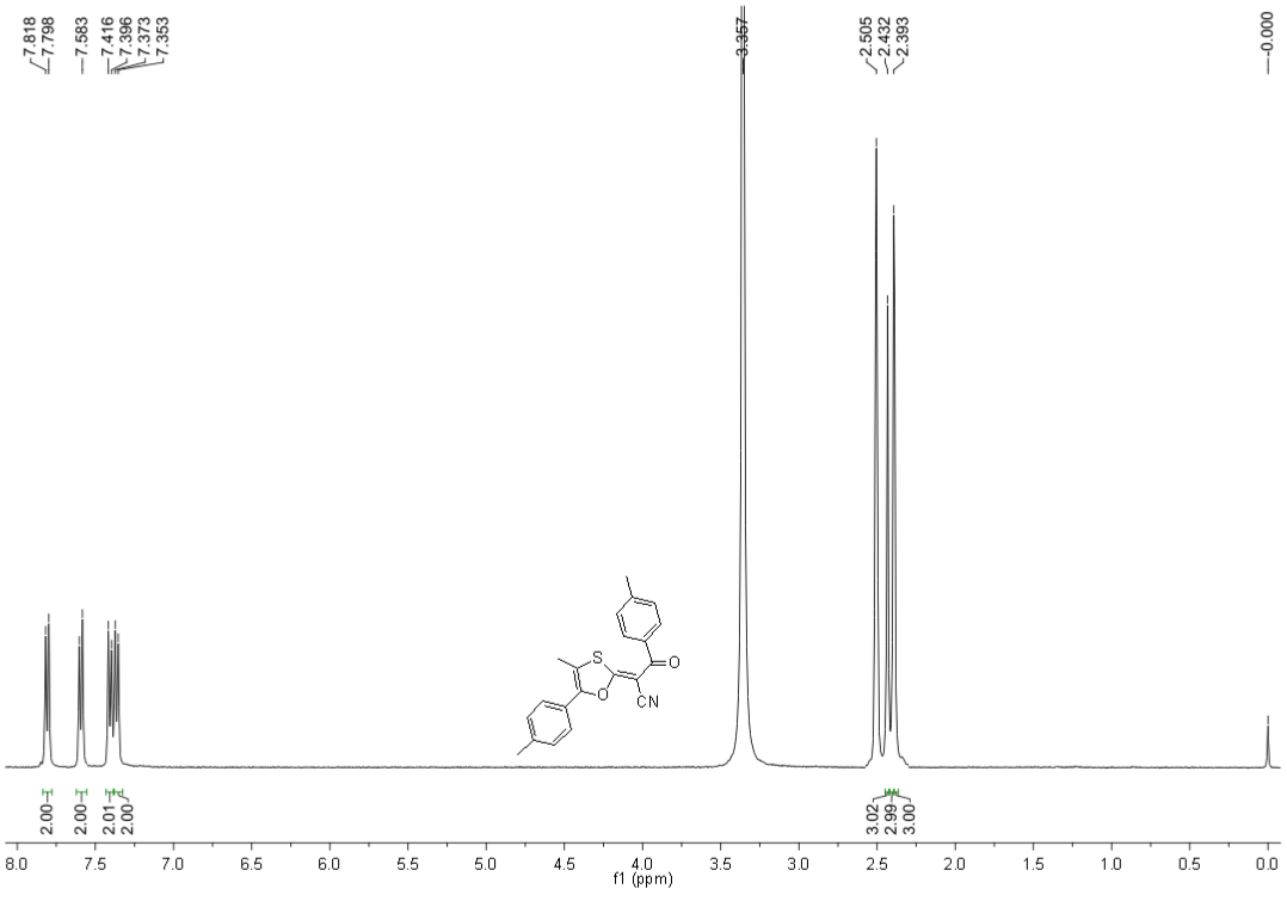


^{13}C NMR Spectrum of Compound 4o



^{1}H NMR Spectrum of Compound 4p

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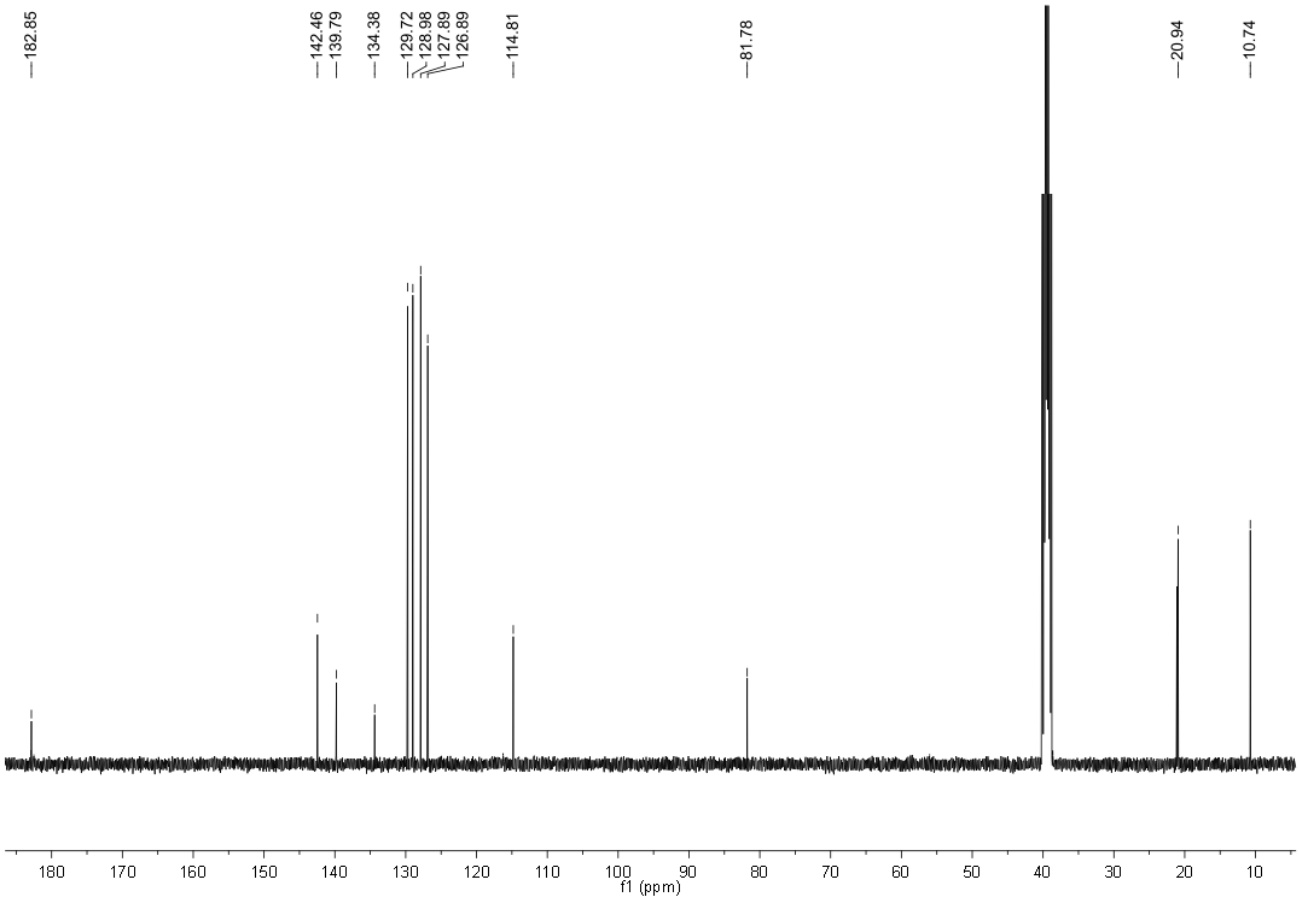
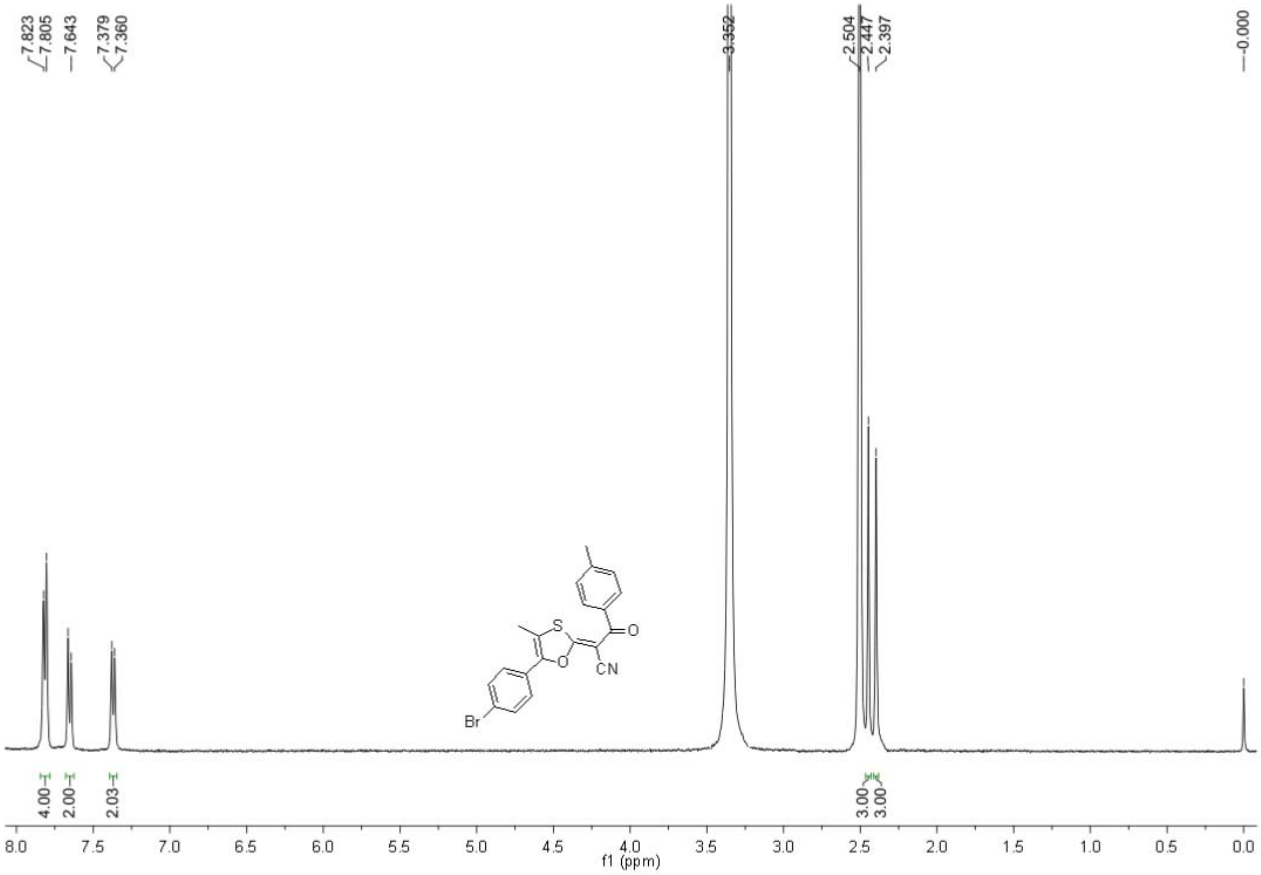


^{13}C NMR Spectrum of Compound 4p



^{1}H NMR Spectrum of Compound 4q

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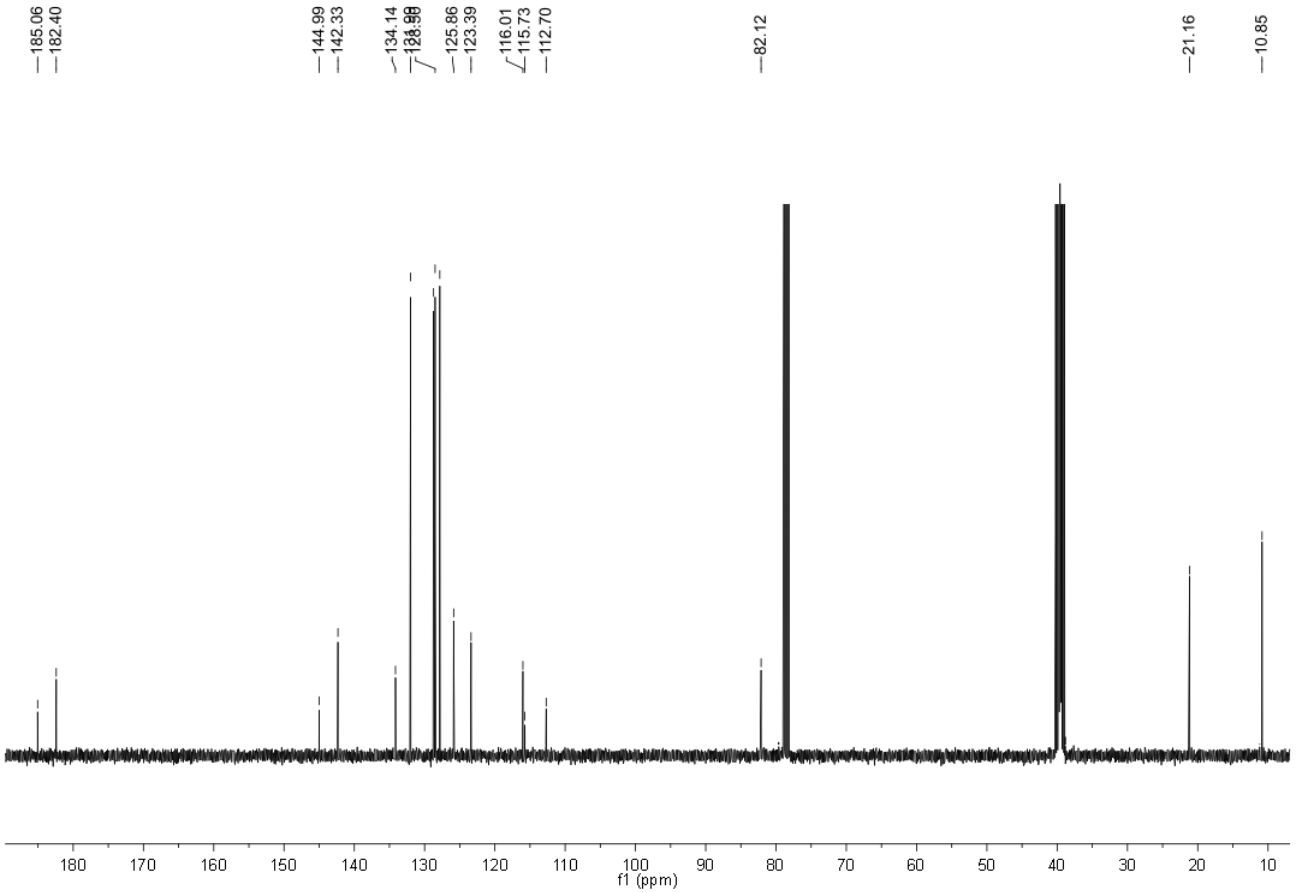
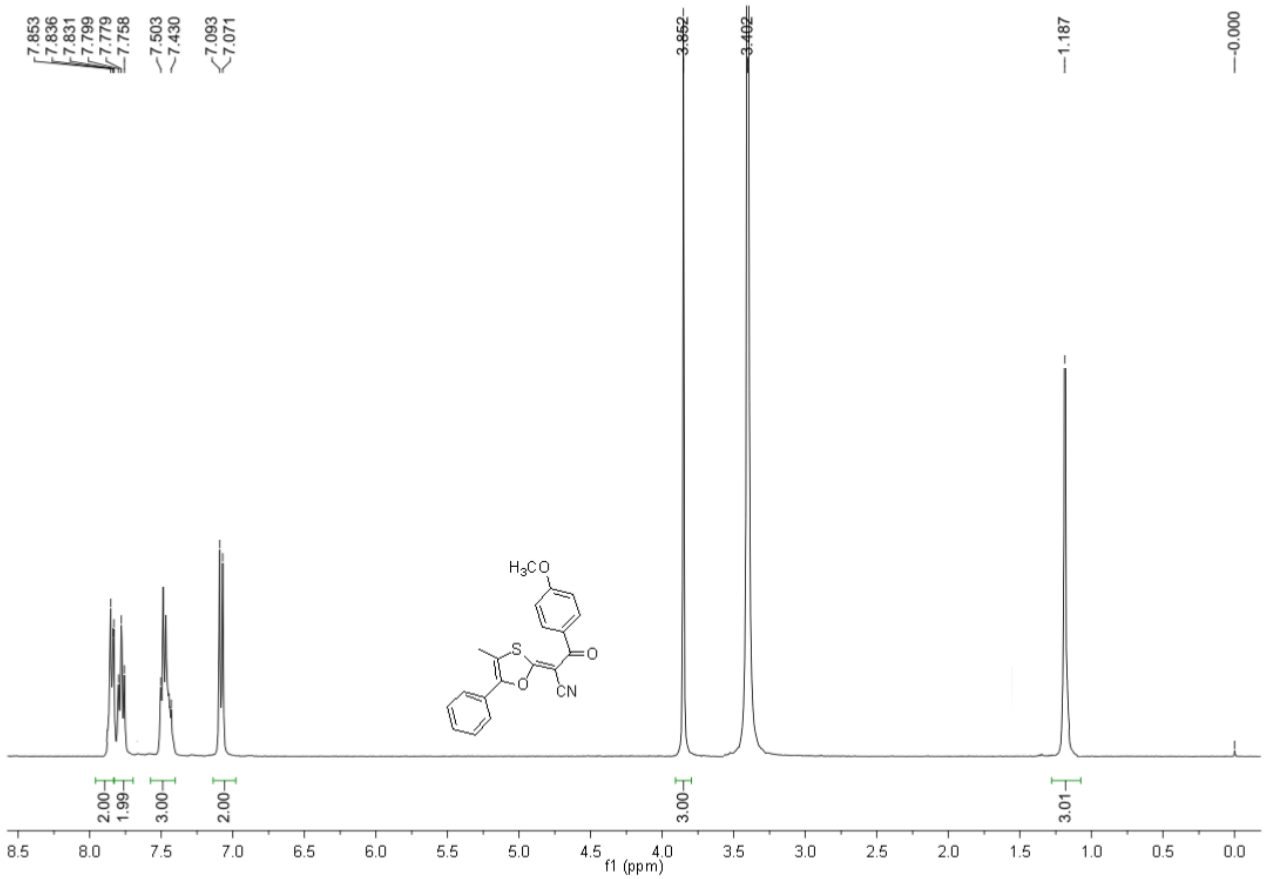


^{13}C NMR Spectrum of Compound 4q



^{1}H NMR Spectrum of Compound 4r

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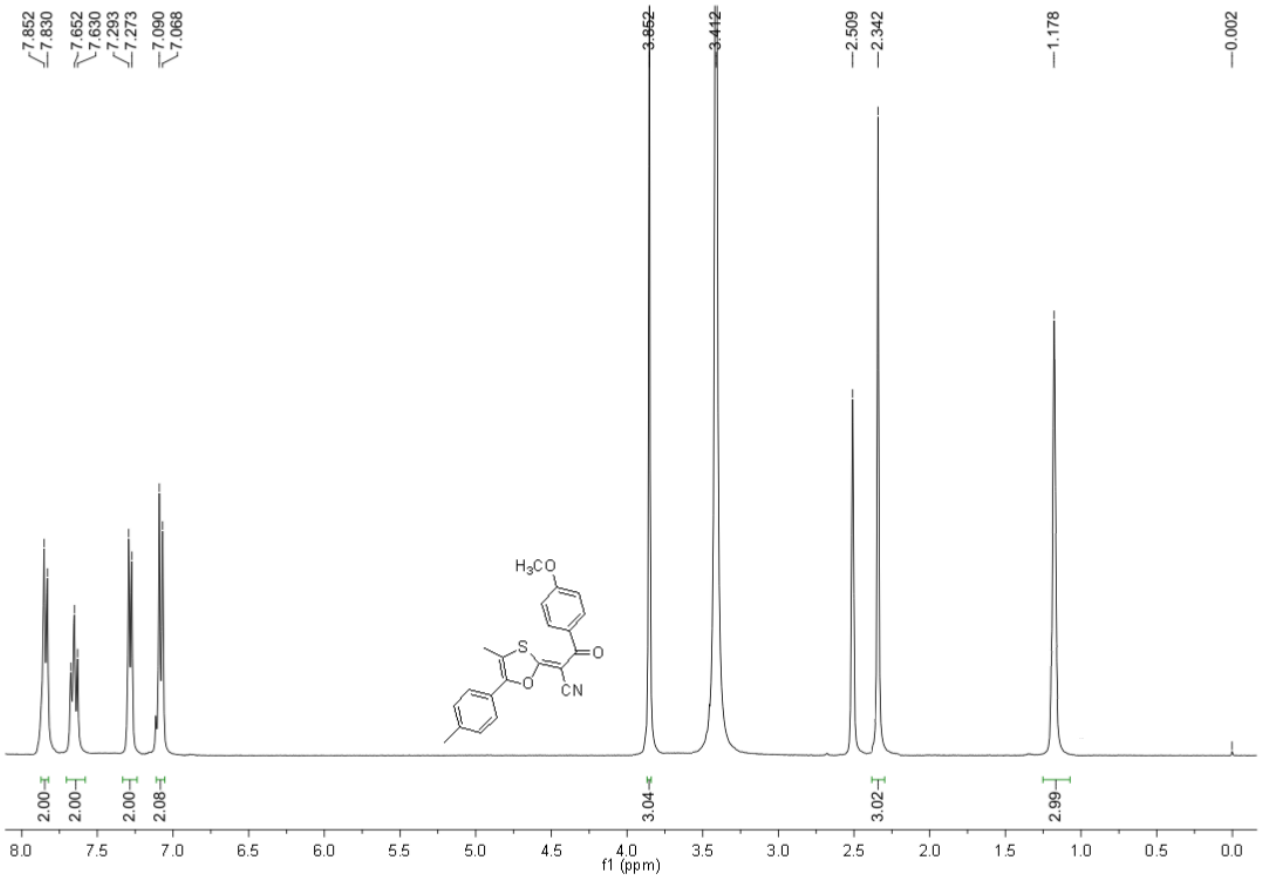
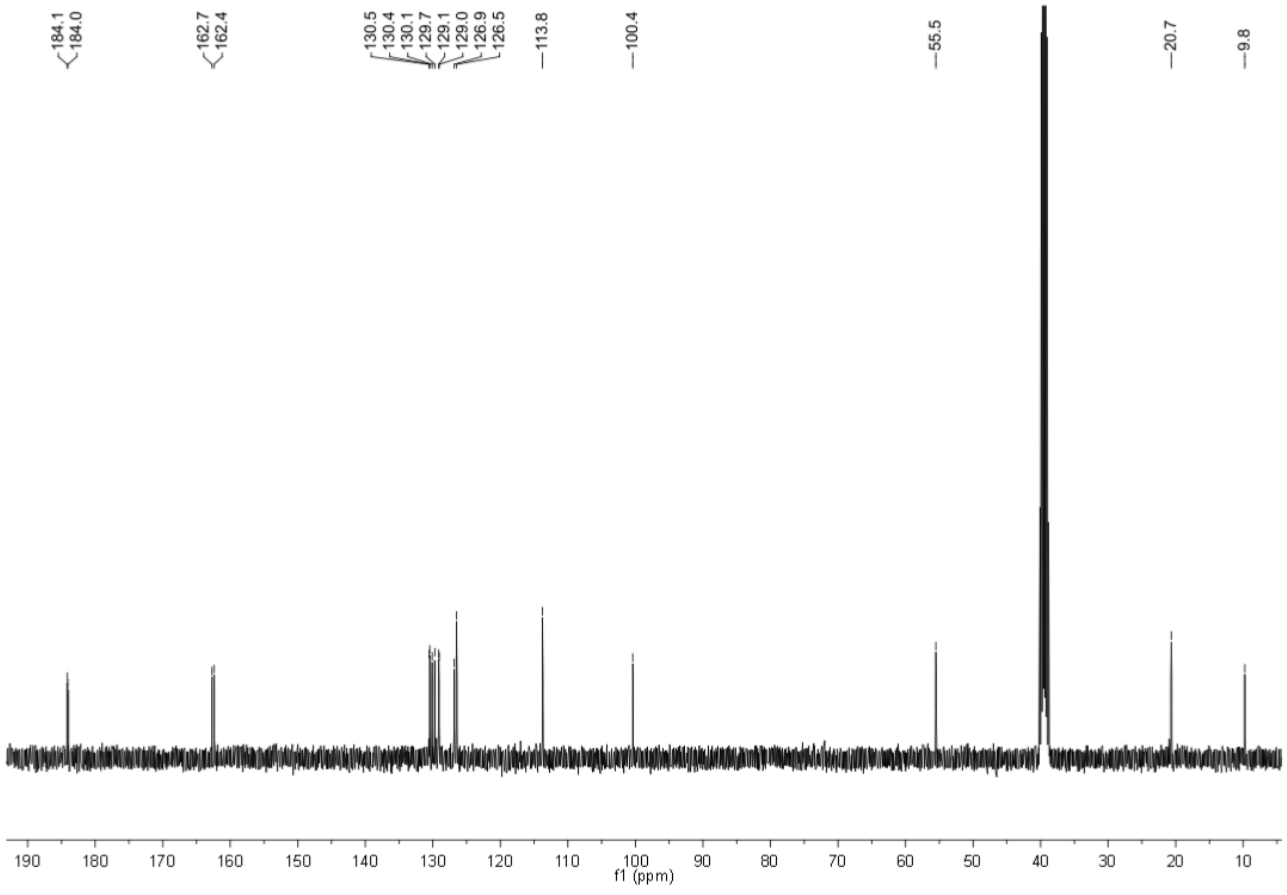


^{1}H NMR Spectrum of Compound 4s



^{13}C NMR Spectrum of Compound 4s

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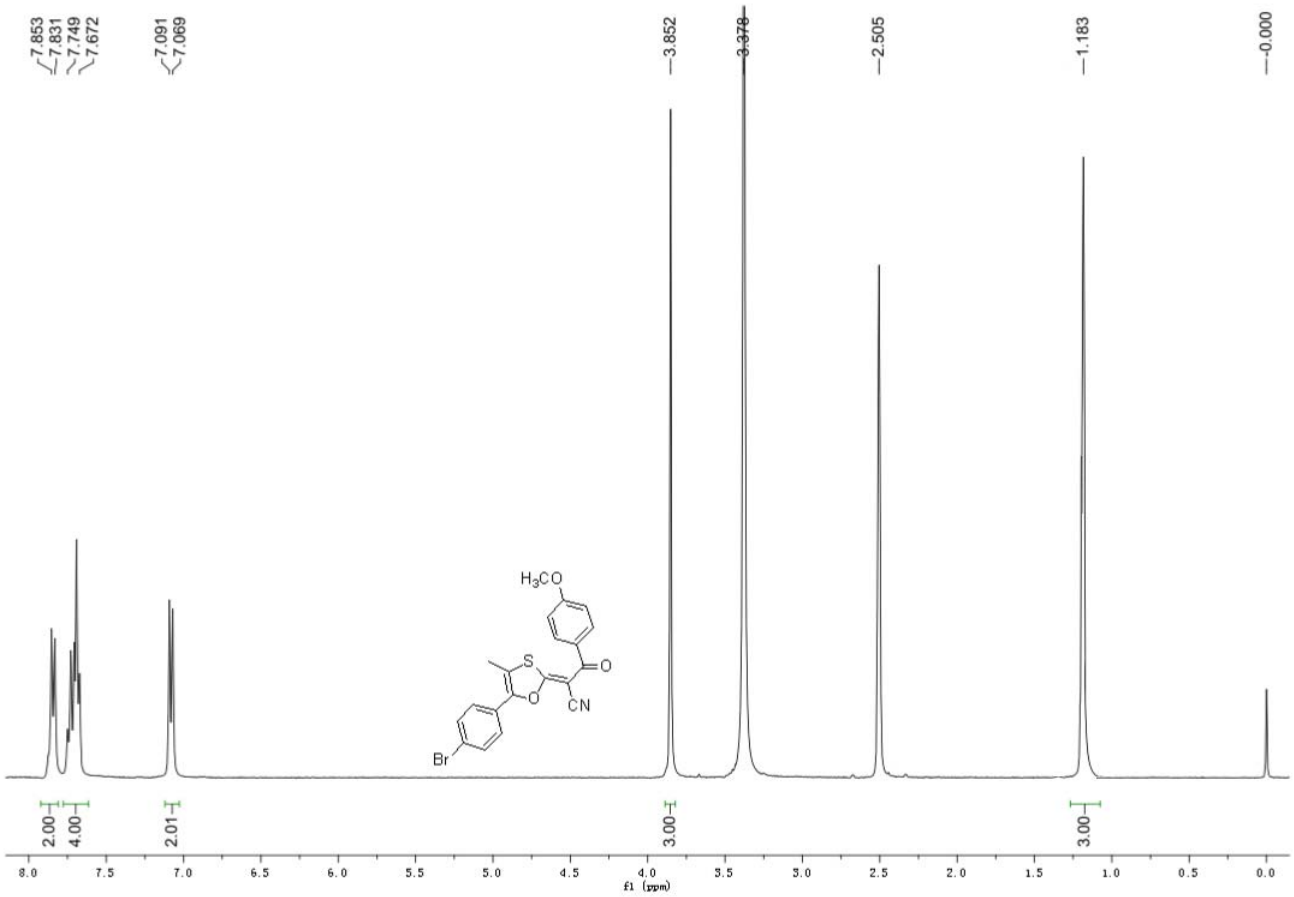
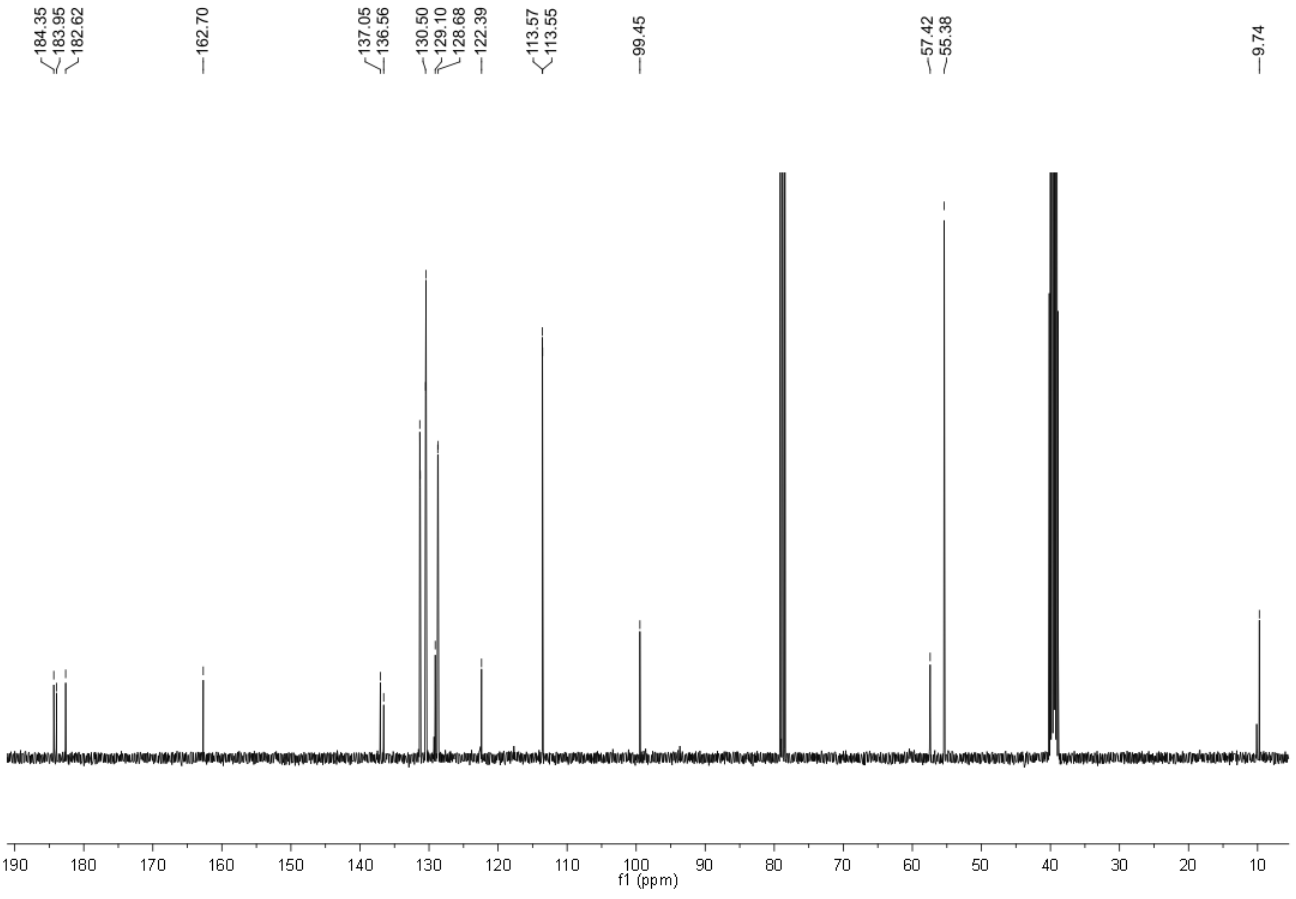


^{1}H NMR Spectrum of Compound 4t



^{13}C NMR Spectrum of Compound 4t

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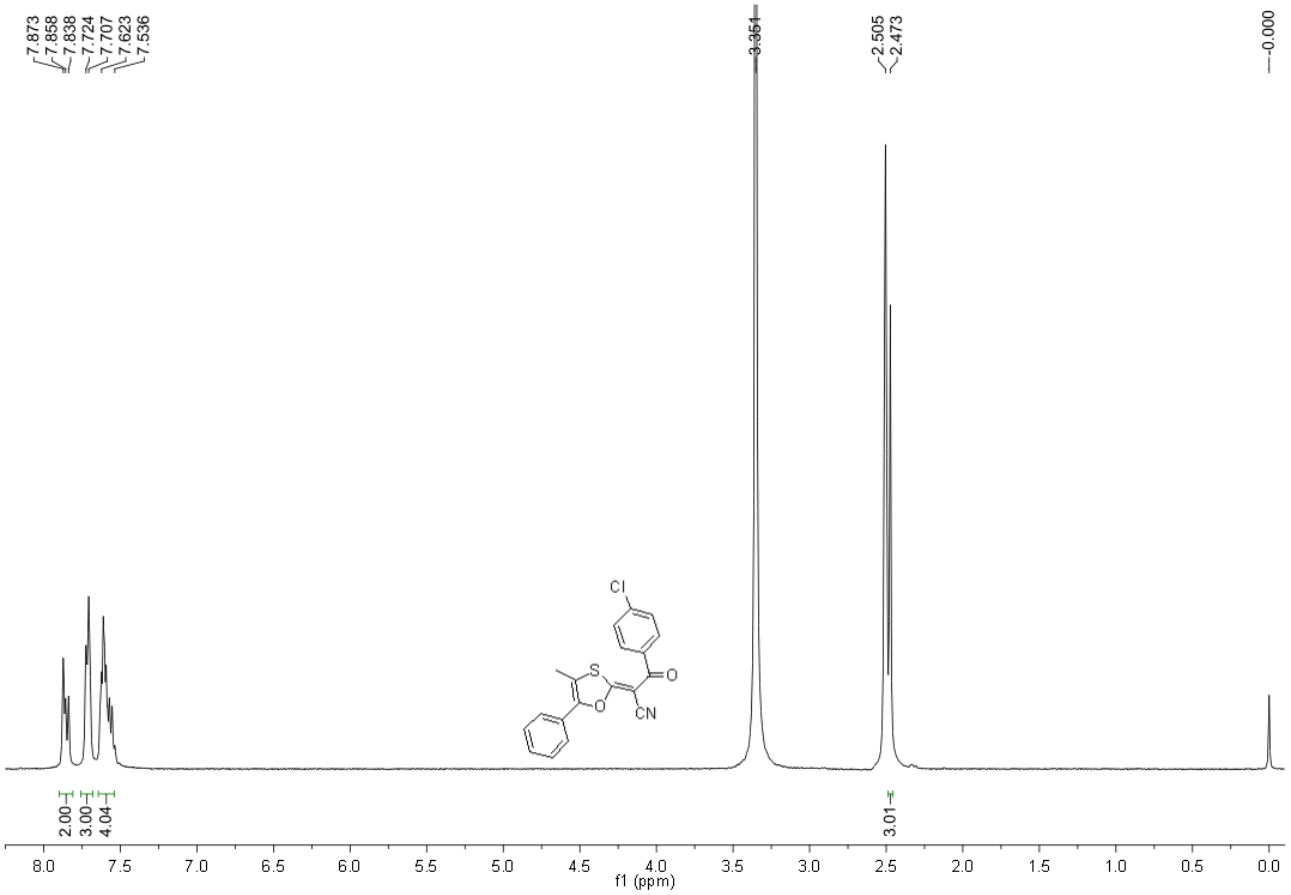
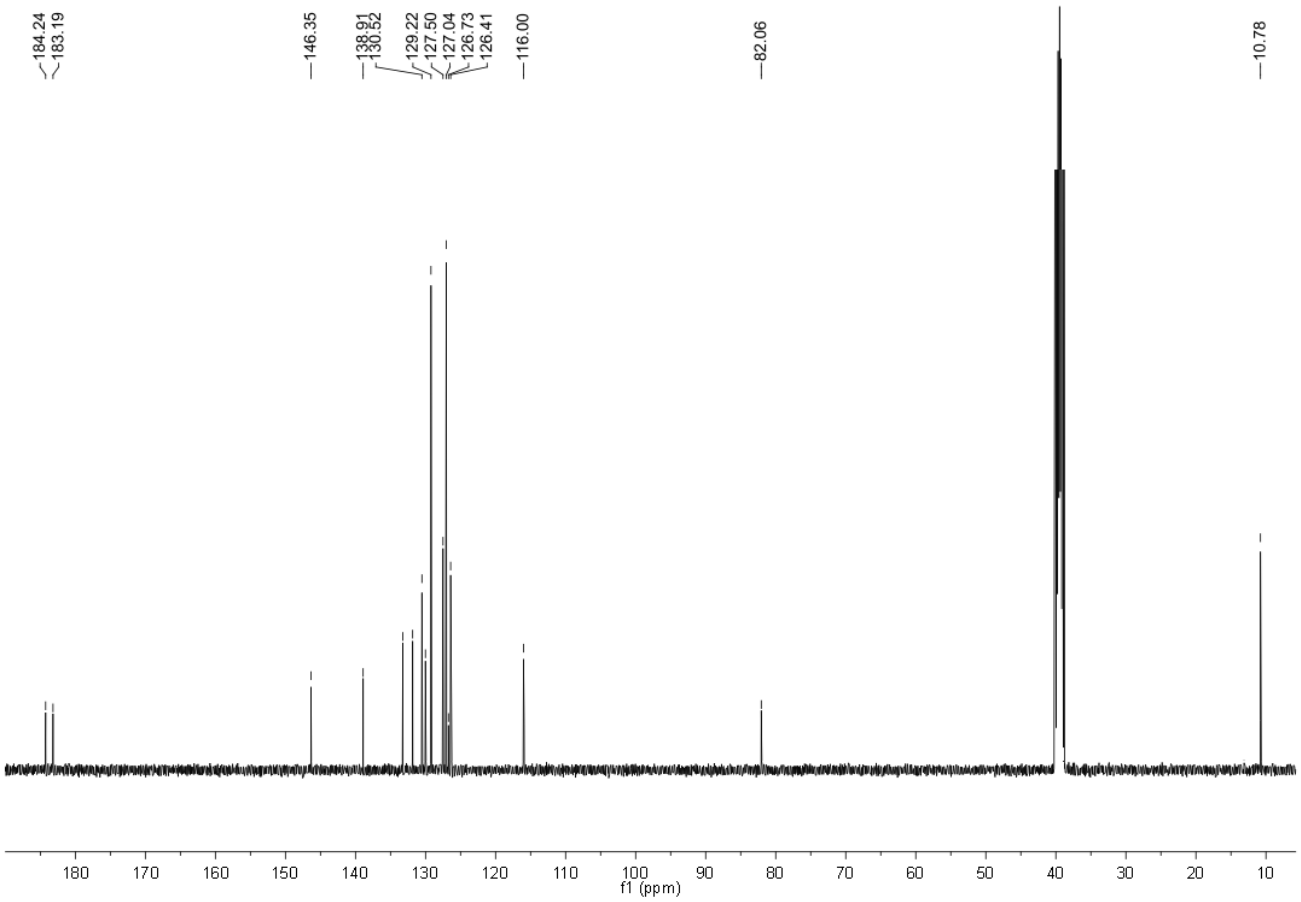


^{1}H NMR Spectrum of Compound 4u



^{13}C NMR Spectrum of Compound 4u

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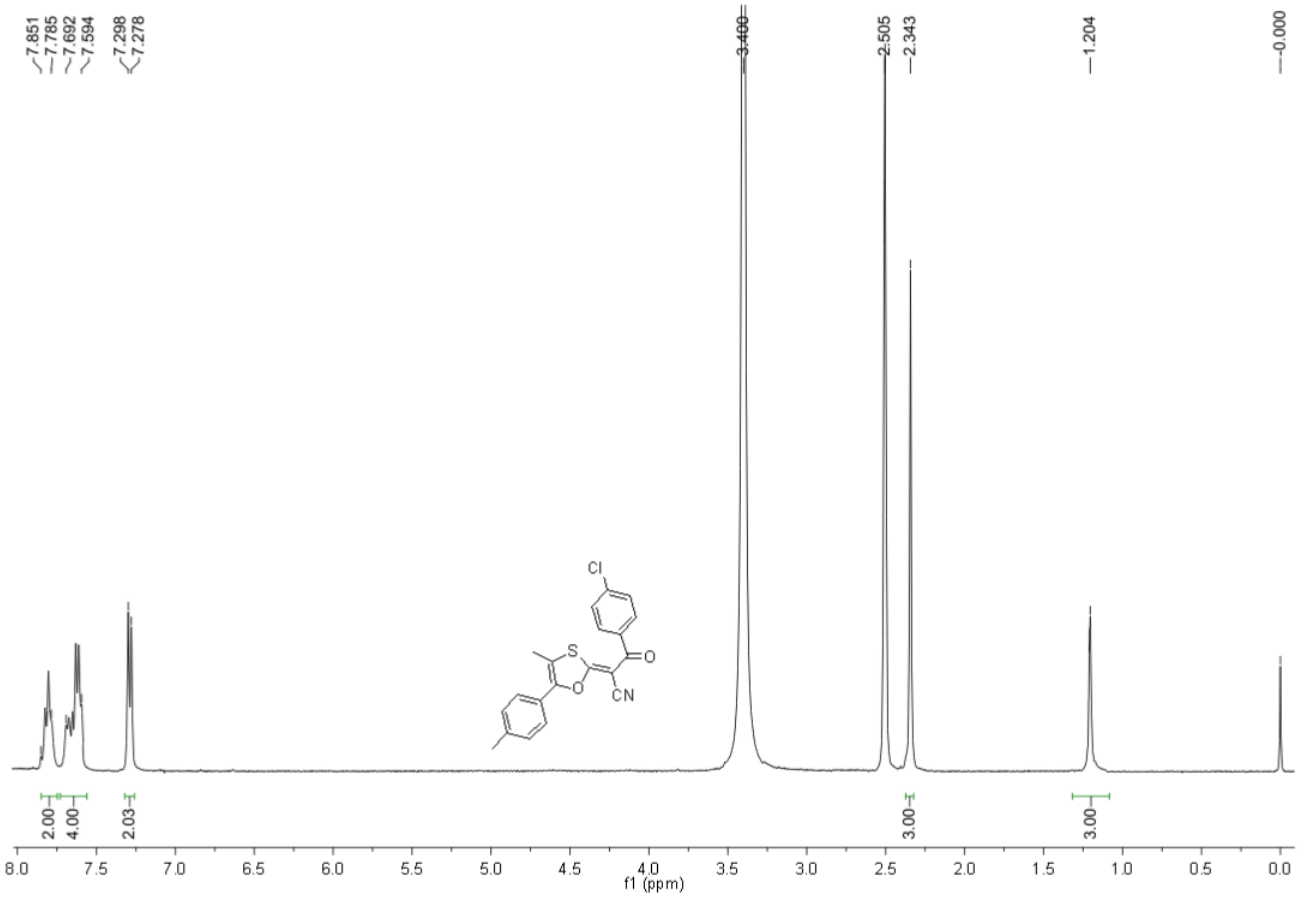
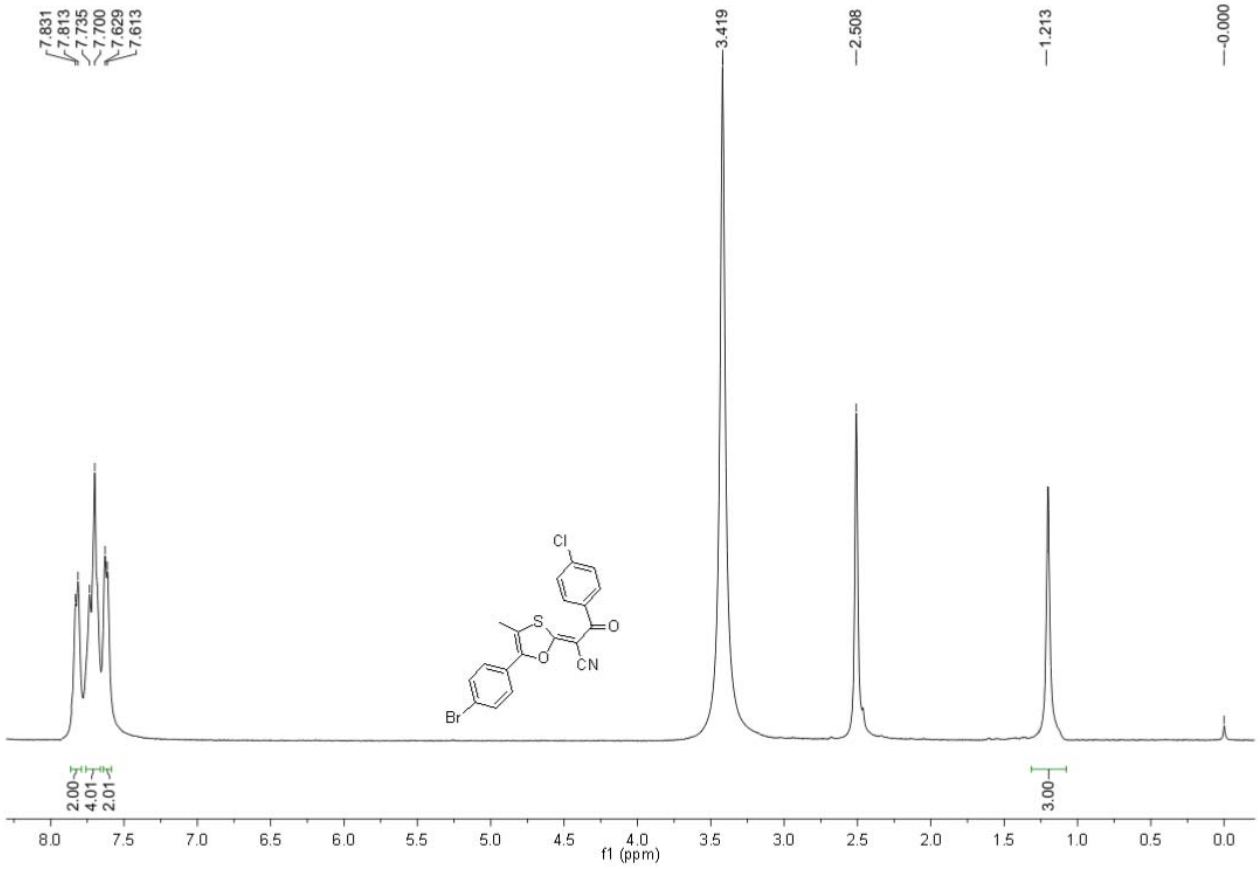


^{1}H NMR Spectrum of Compound 4v



^{1}H NMR Spectrum of Compound 4w

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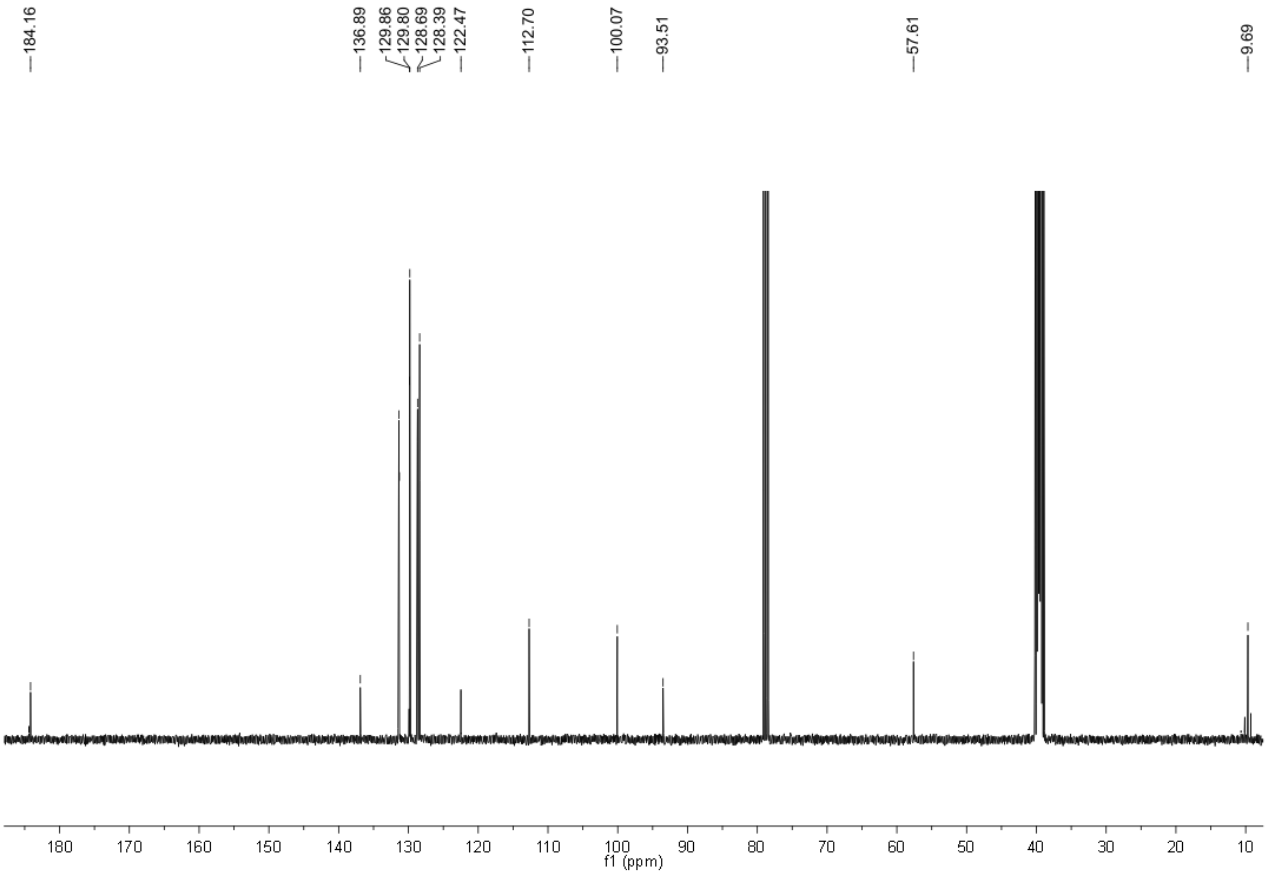
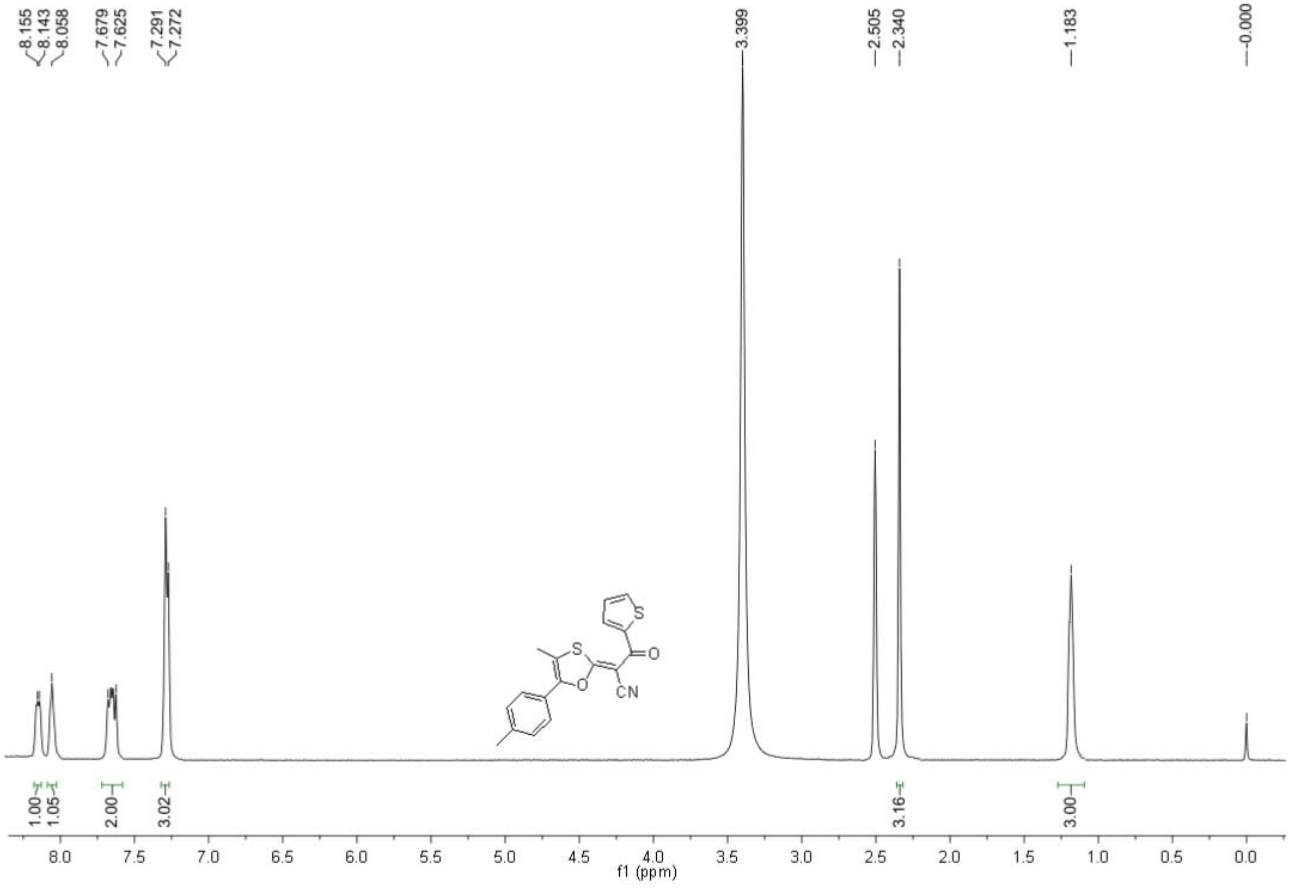


^{13}C NMR Spectrum of Compound 4w



^{1}H NMR Spectrum of Compound 4x

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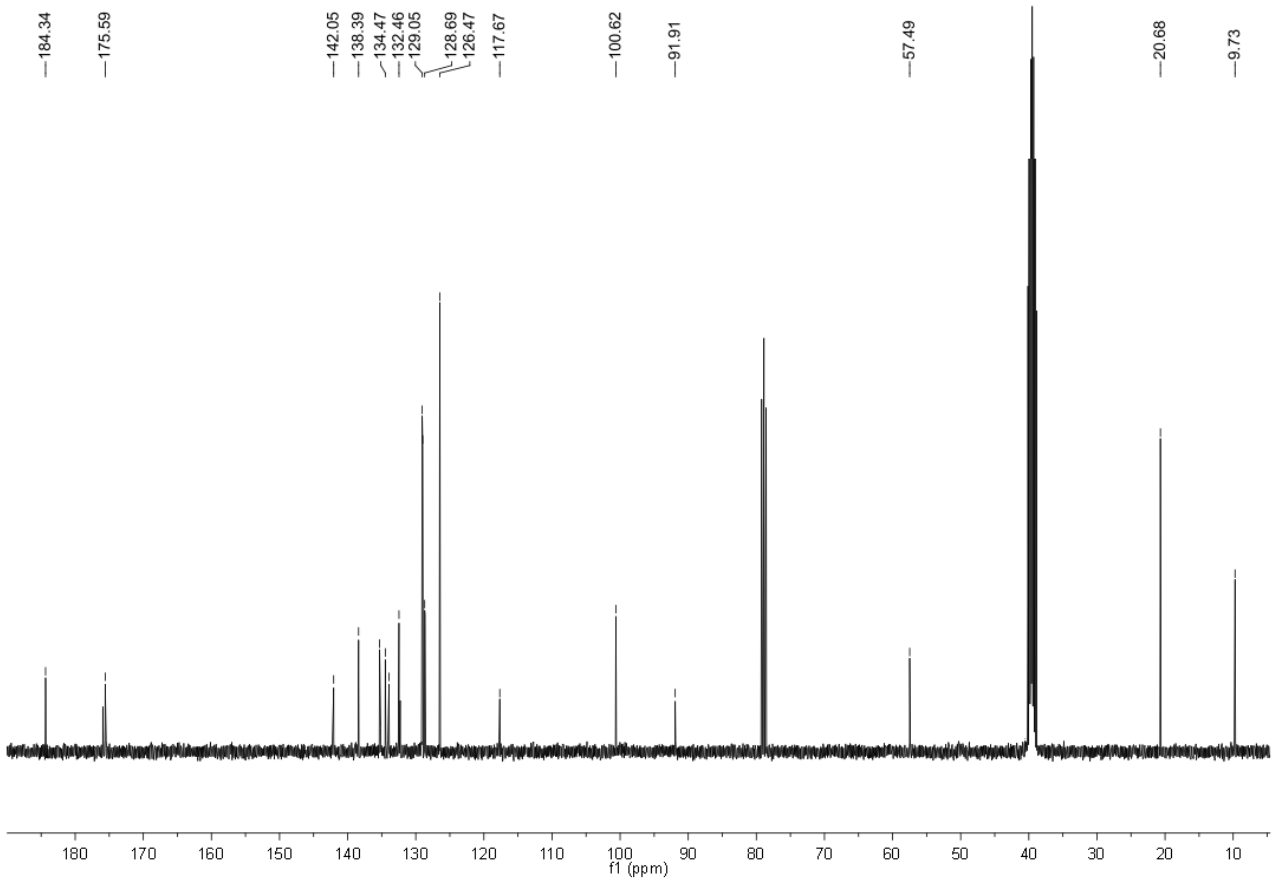
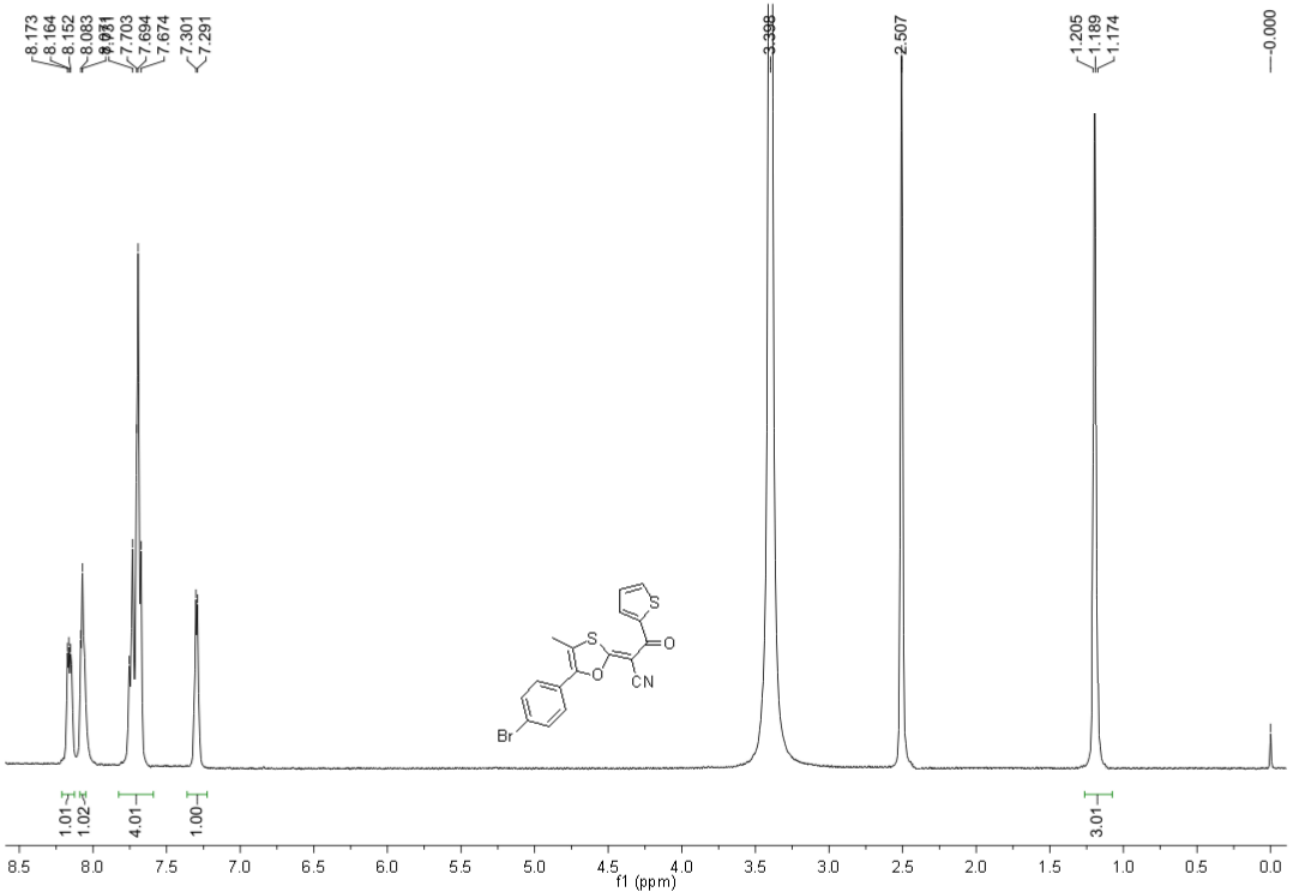


^{13}C NMR Spectrum of Compound 4x



^{1}H NMR Spectrum of Compound 4y

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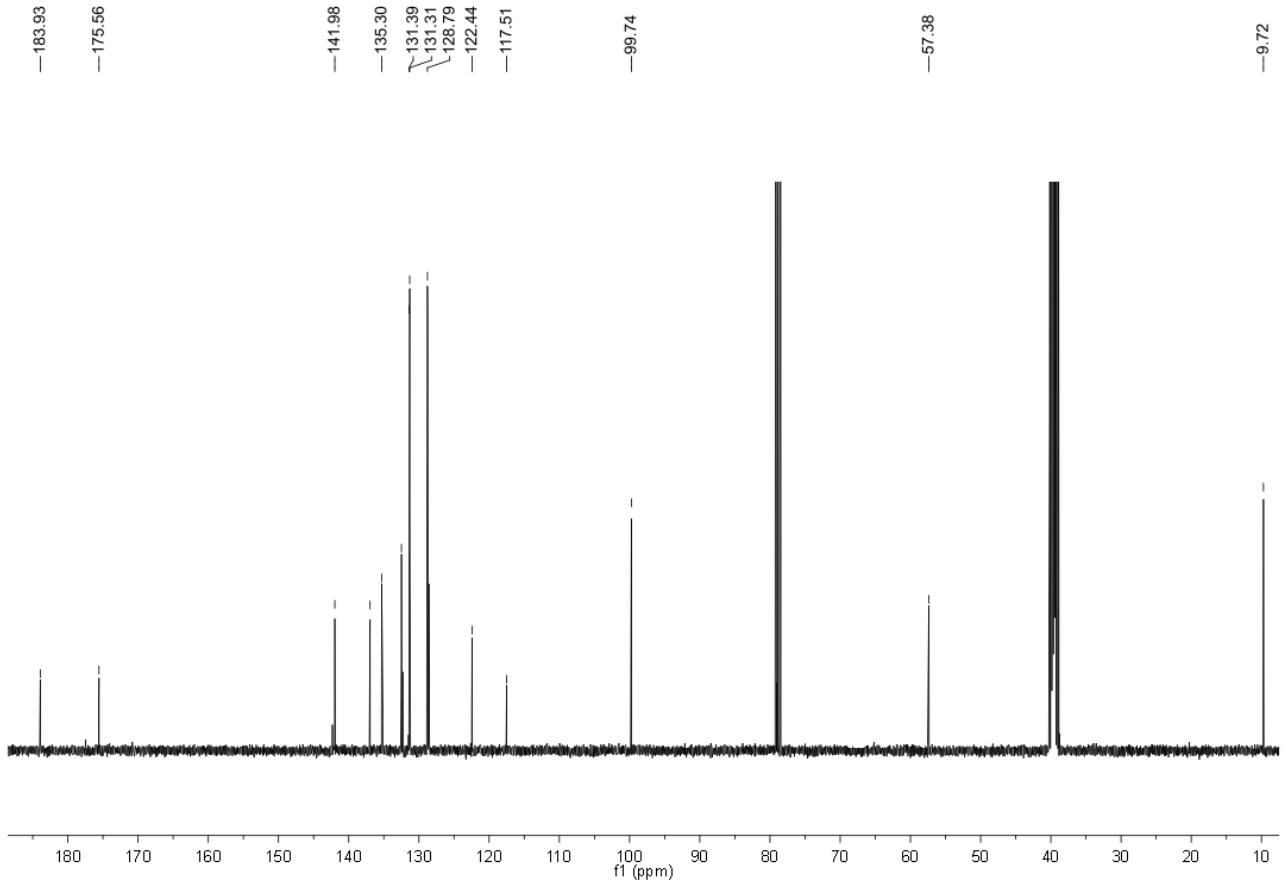

^{13}C NMR Spectrum of Compound 4y