Supporting Information

NCS-Promoted Thiocyanation and Selenocyanation of Pyrrolo[1,2-a]quinoxalines

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Experimental section

General Information Unless otherwise noted, all synthetic steps were performed under the air atmosphere using Schlenk tubes. The materials obtained from commercial sources were used without further purification. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Brucker Advance III HD 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 solution. All chemical shifts were reported in ppm (δ) relative to the internal standard TMS (0 ppm). High-resolution mass spectra (HRMS) were acquired in electrospray ionization (ESI/APCI) mode using a TOF mass analyzer.

General procedure for NCS-promoted thiocyanation of pyrrolo[1,2-*a*]quinoxaline and KSCN or NH_4SCN.

A Schlenk tube (25 mL) was charged with pyrrolo[1,2-*a*]quinoxaline **1** (0.5 mmol), KSCN or NH_4SCN **2** (1 mmol), NCS (1.5 equiv.), and MeCN (2 mL) in air. Then the mixture was stirred at room temperature for 24 h. After reaction completion, the solution was extracted with dichloromethane (3 × 10 mL). Then, the combined organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final products **3**.

1-Thiocyanatopyrrolo[1,2-a]quinoxaline **(3a)**

Yield: 96%; Yellow solid; mp 146.2−147.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (dd, J = 8.5, 0.9 Hz, 1H), 8.86 (s, 1H), 8.07 (dd, J = 8.0, 1.5 Hz, 1H), 7.71–7.63 (m, 1H), 7.63–7.55 (m, 1H), 7.28 (d, J = 4.3 Hz, 1H), 6.95 (d, J = 4.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.3, 137.2, 131.6, 131.0, 129.4, 128.8, 127.6, 126.6, 115.7, 109.1, 108.0, 104.5. HRMS (ESI): m/z calcd for $C_{12}H_7N_3S$ $[M+H]^+$ 226.04342, found: 226.04344.

8-Methyl-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3b)**

Yield: 83%; Yellow solid; mp 149.7−150.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.77 (s, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.37 (dd, J = 8.2, 1.1 Hz, 1H), 7.23 (d, J = 4.3 Hz, 1H), 6.89 (d, J = 4.3 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

144.4, 139.4, 135.3, 131.7, 130.7, 129.2, 127.8, 127.5, 115.7, 109.2, 107.6, 103.9, 22.4. HRMS (APCI): m/z calcd for $C_{13}H_9N_3S$ $[M+H]^+$ 240.05899, found: 240.05865.

8-Fluoro-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3c)**

Yield: 76%; Yellow solid; mp 162.8−163.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 10.6, 2.6 Hz, 1H), 8.79 (s, 1H), 8.02 (dd, J = 9.0, 6.2 Hz, 1H), 7.34 – 7.24 (m, 2H), 6.93 (d, J = 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, $J_{C\text{-}F}$ = 249.7 Hz), 144.5 (d, $J_{C\text{-}F}$ = 2.9 Hz), 134.0 (d, $J_{C\text{-}F}$ = 2.4 Hz), 132.8 (d, $J_{C\text{-}F}$ = 9.9 Hz), 131.3 , 129.7 (d, $J_{C\text{-}F}$ = 11.6 Hz), 128.1 , 114.6 (d, $J_{C\text{-}F}$ = 23.3 Hz), 108.7 , 108.0 , 104.6 , 102.7 (d, $J_{C\text{-}F}$ = 29.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.03. HRMS (APCI): m/z calcd for $C_{12}H_6FN_3S$ $[M+H]^+$ 244.03392, found:244.03362.

7-Methyl-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3d)**

Yield: 82%; Yellow solid; mp 174.2−175.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, J = 8.7 Hz, 1H), 8.84 (s, 1H), 7.85 (s, 1H), 7.48 (dd, J = 8.7, 1.9 Hz, 1H), 7.25 (d, J = 4.3 Hz, 1H), 6.93 (d, J = 4.3 Hz, 1H), 2.54 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.3, 137.3, 136.6, 131.5, 130.8, 129.9, 127.3, 127.2, 115.4, 109.2, 107.8, 104.0, 21.1. HRMS (APCI): m/z calcd for $C_{13}H_9N_3S$ $[M+H]^+$ 240.05899, found: 240.05855.

7-Thiocyanatoindolo[1,2-a]quinoxaline **(3e)**

Yield: 87%; Yellow solid; mp 183.7−184.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.51 (d, J = 8.7 Hz, 1H), 8.49–8.46 (m, 1H), 8.16 (dd, J = 5.9, 3.1 Hz, 1H), 8.12 (dd, J = 8.0, 1.3 Hz, 1H), 7.76–7.70 (m, 1H), 7.69–7.62 (m, 2H), 7.59–7.54 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3, 136.4, 132.6, 131.5, 131.3, 129.9, 129.7, 129.7, 125.9, 125.6, 124.9, 120.4, 115.2, 115.2, 110.3, 88.0. HRMS (APCI): m/z calcd for $C_{16}H_9N_3S$ $[M+H]^+$ 276.05899, found: 276.05884.

3-Iodo-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3f)**

Yield: 65%; Yellow solid; mp 202.3−204.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (dd, J = 8.5, 1.1 Hz, 1H), 8.79 (s, 1H), 8.10 (dd, J = 8.0, 1.6 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.64 – 7.59 (m, 1H), 7.41 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 137.6, 133.6, 131.6, 131.4, 129.2, 128.9, 127.2, 115.4, 108.6, 106.3, 61.0. HRMS (APCI): m/z calcd for $C_{12}H_6IN_3S$ $[M+H]^+$ 351.93999, found: 351.93954.

3-Bromo-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3g)**

Yield: 29%; White solid; mp 197.3−198.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (dd, J = 8.5, 0.9 Hz, 1H), 8.89 (s, 1H), 8.10 (dd, J = 8.0, 1.6 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.64 – 7.59 (m, 1H), 7.32 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 137.5, 131.4, 129.2, 129.0, 128.9, 128.5, 127.2, 115.6, 108.5, 104.8, 95.3. HRMS (APCI): m/z calcd for $C_{12}H_6BrN_3S$ $[M+H]^+$ 303.95386, found: 303.95346.

3-Phenyl-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3h)**

Yield: 56%; Yellow solid; mp 154.2−155.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (dd, J = 8.6, 1.1 Hz, 1H), 9.04 (s, 1H), 8.06 (dd, J = 8.0, 1.6 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.60 – 7.47 (m, 5H), 7.45 – 7.40 (m, 1H), 7.38 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 137.5, 132.4, 131.0, 129.3, 128.8, 128.7, 128.1, 127.8, 126.7, 126.6, 124.0, 115.7, 109.0, 104.5. HRMS (APCI): m/z calcd for $C_{18}H_{11}N_3S$ $[M+H]^+$ 302.07464, found: 302.07413.

1-Thiocyanato-3-(4-vinylphenyl)pyrrolo[1,2-a]quinoxaline **(3i)**

Yield: 61%; Yellow solid; mp 150.1−151.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (dd, J = 8.6, 1.2 Hz, 1H), 9.02 (s, 1H), 8.04 (dd, J = 8.0, 1.6 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.60 – 7.48 (m, 5H), 7.36 (s, 1H), 6.77 (dd, J = 17.6, 10.9 Hz, 1H), 5.83 (d, J = 17.6 Hz, 1H), 5.33 (d, J = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 137.5, 137.3, 136.2, 131.8, 131.0, 129.3, 128.8, 128.7, 127.8, 127.1, 126.6, 126.6, 123.6, 115.7, 114.7, 109.0, 104.6. HRMS (APCI): m/z calcd for $C_{20}H_{13}N_3S$ $[M+H]^+$ 328.09029, found: 328.08993.

4-Phenyl-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3j)**

Yield: 81%; Yellow solid; mp 159.2−159.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (dd, J = 8.5, 1.3 Hz, 1H), 8.14 (dd, J = 8.0, 1.7 Hz, 1H), 7.93–7.89 (m, 2H), 7.69–7.64 (m, 1H), 7.62–7.54 (m, 4H), 7.29 (d, J = 4.4 Hz, 1H), 7.02 (d, J = 4.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.2, 137.5, 137.5, 131.2, 131.0, 130.3, 128.9, 128.8, 128.6, 128.3, 127.6, 126.7, 115.5, 109.4, 109.3, 104.8. HRMS (ESI): m/z calcd for $C_{18}H_{11}N_3S$ $[M+H]^+$ 302.07458, found: 302.07455.

4-(4-Fluorophenyl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3k)**

Yield: 90%; Yellow solid; mp 168.3−170.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (dd, J = 8.5, 1.0 Hz, 1H), 8.12 (dd, J = 8.0, 1.6 Hz, 1H), 7.95–7.90 (m, 2H), 7.69–7.64 (m, 1H), 7.62–7.57 (m, 1H), 7.30 (d, J = 4.4 Hz, 1H), 7.26 (d, J = 5.3 Hz, 1H), 7.24 (d, J = 8.7 Hz, 1H), 6.99 (d, J = 4.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 165.4, 162.9, 153.1, 137.4, 133.6, 133.6, 131.2, 130.9, 130.8, 130.8, 128.5, 128.5, 127.7, 126.8, 116.1, 115.9, 115.6, 109.2, 109.2, 105.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.15. HRMS (ESI): m/z calcd for $C_{18}H_{10}FN_3S$ $[M+H]^+$ 320.0652, found: 320.0657.

4-(4-Chlorophenyl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3l)**

Yield: 68%; Yellow solid; mp 190.2−190.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, J = 8.5 Hz, 1H), 8.11 (dd, J = 8.0, 1.5 Hz, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.70–7.64 (m, 1H), 7.62–7.57 (m, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 4.3 Hz, 1H), 6.98 (d, J = 4.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.0, 137.4, 136.5, 135.9, 131.2, 130.7, 130.2, 129.2, 128.6, 128.6, 127.7, 126.8, 115.6, 109.2, 109.2, 105.2. HRMS (APCI): m/z calcd for $C_{18}H_{10}ClN_3S$ $[M+H]^+$ 336.03567, found: 336.03491.

4-(4-Bromophenyl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3m)**

Yield: 74%; Yellow solid; mp 191.3−192.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (dd, J = 8.6, 0.8 Hz, 1H), 8.11 (dd, J = 8.0, 1.5 Hz, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.66 (dd, J = 8.6, 1.5 Hz, 1H), 7.62–7.56 (m, 1H), 7.29 (d, J = 4.4 Hz, 1H), 6.98 (d, J = 4.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.0, 137.4, 136.4, 132.1, 131.2, 130.6, 130.4, 128.6, 128.5, 127.7, 126.8, 124.8, 115.6, 109.2, 109.1, 105.2. HRMS (ESI): m/z calcd for $C_{18}H_{10}BrN_3S$ $[M+Na]^+$ 401.9671, found: 401.9675.

1-Thiocyanato-4-(p-tolyl)pyrrolo[1,2-a]quinoxaline **(3n)**

Yield: 80%; Yellow solid; mp 179.5−180.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (dd, J = 8.5, 1.1 Hz, 1H), 8.13 (dd, J = 8.0, 1.6 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.68–7.62 (m, 1H), 7.61–7.56 (m, 1H), 7.36 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 4.3 Hz, 1H), 7.03 (d, J = 4.4 Hz, 1H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.2, 140.5, 137.6, 134.7, 131.1, 131.1, 129.6, 128.8, 128.5, 128.2, 127.6, 126.6, 115.5,

109.4, 109.4, 104.6, 21.6. HRMS (ESI): m/z calcd for $C_{19}H_{13}N_3S$ $[M+H]^+$ 316.0903, found: 316.0908.

4-(4-Methoxyphenyl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3o)**

Yield: 78%; Yellow solid; mp 173.1−174.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (dd, J = 8.5, 1.1 Hz, 1H), 8.12 (dd, J = 7.9, 1.5 Hz, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.66–7.61 (m, 1H), 7.60–7.55 (m, 1H), 7.28 (d, J = 4.3 Hz, 1H), 7.07 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 4.4 Hz, 1H), 3.90 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.4, 153.7, 137.6, 131.0, 131.0, 130.3, 130.0, 128.4, 128.0, 127.6, 126.6, 115.5, 114.3, 109.4, 104.6, 55.6. HRMS (ESI): m/z calcd for $C_{19}H_{13}N_3OS$ $[M+H]^+$ 332.0852, found: 332.0854.

4-(1-Thiocyanatopyrrolo[1,2-a]quinoxalin-4-yl)benzonitrile **(3p)**

Yield: 51%; Yellow solid; mp 221.2−222.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (dd, J = 8.6, 1.0 Hz, 1H), 8.14 (dd, J = 8.0, 1.5 Hz, 1H), 8.06 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 7.76–7.68 (m, 1H), 7.66–7.61 (m, 1H), 7.34 (d, J = 4.4 Hz, 1H), 6.98 (d, J = 4.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.1, 141.7, 137.2, 132.7, 131.4, 130.3, 129.6, 129.2, 128.6, 127.8, 127.0, 118.5, 115.6, 114.0, 109.0, 108.9, 105.7. HRMS (APCI): m/z calcd for $C_{18}H_{10}N_4O_2S$ $[M+H]^+$ 327.06989, found: 327.06940.

4-(4-Nitrophenyl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3q)**

Yield: 61%; Yellow solid; mp 194.7−195.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (dd, J = 8.6, 0.8 Hz, 1H), 8.42 (d, J = 8.8 Hz, 2H), 8.15 (dd, J = 8.2, 1.5 Hz, 1H), 8.12 (d, J = 8.8 Hz, 2H), 7.76 – 7.70 (m, 1H), 7.67 – 7.60 (m, 1H), 7.35 (d, J = 4.4 Hz, 1H), 6.99 (d, J = 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 148.9, 143.4, 137.2, 131.5, 130.3, 129.9, 129.3, 128.6, 127.9, 127.0, 124.1, 115.7, 109.0, 108.9, 105.8. HRMS (APCI): m/z calcd for $C_{18}H_{10}N_4O_2S$ [M+H]+ 347.05972, found: 347.05942.

2-(1-Thiocyanatopyrrolo[1,2-a]quinoxalin-4-yl)phenol **(3r)**

Yield: 59%; Yellow solid; mp 183.1−184.2 °C; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.27 (s, 1H), 9.35 (d, J = 8.4 Hz, 1H), 8.05 (dd, J = 8.0, 1.3 Hz, 1H), 7.82–7.74 (m, 1H), 7.70–7.62 (m, 1H), 7.53 (dd, J = 7.6, 1.5 Hz, 1H), 7.45 (d, J = 4.3 Hz, 1H), 7.43–

7.32 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 4.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-*d6*) δ 155.8, 153.2, 136.2, 131.2, 130.3, 130.1, 129.9, 128.4, 128.0, 127.0, 126.5, 123.2, 119.1, 116.5, 115.7, 111.3, 109.6, 107.2. HRMS (APCI): m/z calcd for $C_{18}H_{11}N_3OS$ $[M+H]^+$ 318.06956, found: 318.06918.

4-(2,4-Dichlorophenyl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3s)**

Yield: 73%; Yellow solid; mp 209.7−210.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (dd, *J* = 8.6, 1.0 Hz, 1H), 8.13 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.76–7.70 (m, 1H), 7.65–7.60 (m, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.52–7.41 (m, 2H), 7.27 (d, *J* = 4.3 Hz, 1H), 6.60 (d, *J* = 4.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.9, 137.0, 136.3, 134.5, 134.0, 131.7, 131.3, 130.9, 130.2, 129.1, 128.9, 127.7, 127.7, 126.8, 115.6, 109.2, 109.1, 105.1. HRMS (APCI): m/z calcd for $C_{18}H_9Cl_2N_3S$ $[M+H]^+$ 369.99670, found: 369.99634.

4-(Furan-2-yl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3t)**

Yield: 81%; Yellow solid; mp 169.3−170.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.08 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.72 (d, *J* = 0.8 Hz, 1H), 7.64–7.59 (m, 1H), 7.59–7.53 (m, 2H), 7.43 (d, *J* = 3.4 Hz, 1H), 7.33 (d, *J* = 4.4 Hz, 1H), 6.66 (dd, *J* = 3.5, 1.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.8, 144.9, 142.9, 137.0, 130.8, 128.6, 128.3, 128.1, 127.9, 126.6, 115.4, 113.6, 112.3, 109.3, 109.2, 104.5. HRMS (APCI): m/z calcd for $C_{16}H_9N_3OS$ $[M+H]^+$ 292.05391, found: 292.05350.

7-Chloro-4-(4-methoxyphenyl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3u)**

Yield: 71%; mp 161.2−162.7 °C; Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, *J* = 9.1 Hz, 1H), 8.05 (d, *J* = 2.5 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.55 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.27 (d, *J* = 4.4 Hz, 1H), 7.09–7.03 (m, 3H), 3.90 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.6, 154.7, 138.6, 131.8, 130.7, 130.36, 130.1, 129.5, 127.8, 127.7, 126.9, 116.6, 114.3, 109.9, 109.1, 105.1, 55.6. HRMS (APCI): m/z calcd for $C_{19}H_{12}ClN_3OS$ $[M+H]^+$ 366.04624, found: 366.04596.

7-Chloro-4-(4-nitrophenyl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3v)**

Yield: 70%; Yellow solid; mp 210.5−211.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.36 (d, J = 9.2 Hz, 1H), 8.44 (d, J = 8.9 Hz, 2H), 8.20 (d, J = 8.9 Hz, 2H), 8.14 (d, J = 2.5 Hz, 1H), 7.88 (dd, J = 9.2, 2.6 Hz, 1H), 7.59 (d, J = 4.4 Hz, 1H), 7.19 (d, J = 4.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 152.7, 148.5, 142.3, 137.6, 130.5, 130.2, 129.4, 128.7, 128.6, 127.5, 126.9, 123.9, 117.6, 110.9, 109.8, 109.4. HRMS (APCI): m/z calcd for $C_{18}H_9ClN_4O_2S$ $[M+H]^+$ 381.02075, found: 381.02008.

4-(4-Methoxyphenyl)-7-methyl-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3w)**

Yield: 84%; Yellow solid; mp 175.3−176.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, J = 8.7 Hz, 1H), 7.86 (d, J = 8.7 Hz, 3H), 7.38 (dd, J = 8.7, 1.9 Hz, 1H), 7.18 (d, J = 4.3 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 4.4 Hz, 1H), 3.88 (s, 3H), 2.49 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.2, 153.4, 137.4, 136.4, 130.6, 130.5, 130.2, 130.0, 129.1, 127.0, 126.1, 115.0, 114.1, 109.4, 109.0, 104.0, 55.5, 21.0. HRMS (APCI): m/z calcd for $C_{20}H_{15}N_3OS$ $[M+H]^+$ 346.10086, found: 346.10049.

7-Methyl-4-(4-nitrophenyl)-1-thiocyanatopyrrolo[1,2-a]quinoxaline **(3x)**

Yield: 49%; Yellow solid; mp 221.8−222.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, J = 8.7 Hz, 1H), 8.42 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 7.95–7.93 (m, 2H), 7.54 (dd, J = 8.8, 1.8 Hz, 1H), 7.31 (d, J = 4.4 Hz, 1H), 6.97 (d, J = 4.4 Hz, 1H), 2.56 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.6, 148.8, 143.5, 138.6, 137.2, 137.1, 133.3, 131.1, 130.5, 130.2, 129.9, 127.5, 126.5, 124.1, 115.3, 109.1, 108.7, 105.3, 21.1. HRMS (APCI): m/z calcd for $C_{19}H_{12}N_4O_2S$ $[M+H]^+$ 361.07537, found: 361.07471.

General procedure for NCS-promoted selenocyanation of pyrrolo[1,2-*a*]quinoxaline and KSeCN.

A Schlenk tube (25 mL) was charged with pyrrolo[1,2-*a*]quinoxaline **1** (0.5 mmol), KSeCN (1 mmol), NCS (1.5 equiv.), and EtOAc (2 mL) in air. Then the mixture was stirred at room temperature for 24 h. After reaction completion, the solution was extracted with dichloromethane (3 × 10 mL). Then, the combined organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and

the crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final products **4**.

1-Selenocyanatopyrrolo[1,2-a]quinoxaline **(4a)**

Yield: 72%; Yellow solid; mp 167.7−168.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.08 (dd, J = 8.0, 1.5 Hz, 1H), 8.02 (d, J = 2.8 Hz, 1H), 7.92 (dd, J = 8.2, 1.2 Hz, 1H), 7.68–7.62 (m, 1H), 7.60–7.54 (m, 1H), 7.17 (d, J = 2.9 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.9, 136.2, 130.9, 129.2, 128.4, 127.1, 126.7, 120.9, 115.4, 113.9, 101.12, 92.4. HRMS (APCI): m/z calcd for $C_{12}H_7N_3Se$ $[M+H]^+$ 273.98780, found: 273.98737.

7-Methyl-1-selenocyanatopyrrolo[1,2-a]quinoxaline **(4b)**

Yield: 47%; Yellow solid; mp 180.1−181.9 °C; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 9.29 (d, J = 8.7 Hz, 1H), 8.98 (s, 1H), 7.80 (s, 1H), 7.55 (dd, J = 8.8, 2.0 Hz, 1H), 7.34 (d, J = 4.1 Hz, 1H), 7.13 (d, J = 4.2 Hz, 1H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-*d6*) δ 145.6, 136.6, 135.6, 130.0, 129.8, 129.0, 127.6, 126.9, 115.6, 108.5, 106.1, 105.2, 20.4. HRMS (APCI): m/z calcd for $C_{13}H_9N_3Se$ $[M+H]^+$ 288.00345, found: 288.00290.

8-Fluoro-1-selenocyanatopyrrolo[1,2-a]quinoxaline **(4c)**

Yield: 40%; Yellow solid; mp 147.1−148.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (dd, J = 10.7, 2.6 Hz, 1H), 8.84 (s, 1H), 8.05 (dd, J = 9.0, 6.2 Hz, 1H), 7.33 (d, J = 4.1 Hz, 1H), 7.32 – 7.28 (m, 1H), 6.97 (d, J = 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, $J_{C\text{-}F}$ = 249.4 Hz), 144.5 (d, $J_{C\text{-}F}$ = 2.5 Hz), 134.0, 132.8 (d, $J_{C\text{-}F}$ = 9.9 Hz), 131.6, 130.1 (d, $J_{C\text{-}F}$ = 11.1 Hz), 129.7, 114.6 (d, $J_{C\text{-}F}$ = 23.3 Hz), 108.5, 102.8 (d, $J_{C\text{-}F}$ = 29.6 Hz), 100.6, 99.7. HRMS (APCI): m/z calcd for $C_{12}H_6FN_3Se$ $[M+H]^+$ 291.97837, found: 291.97837.

4-Phenyl-1-selenocyanatopyrrolo[1,2-a]quinoxaline **(4d)**

Yield: 68%; Yellow solid; mp 170.5−171.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (dd, J = 8.5, 1.0 Hz, 1H), 8.08 (dd, J = 7.9, 1.6 Hz, 1H), 7.93–7.87 (m, 2H), 7.62–7.56 (m, 1H), 7.55–7.50 (m, 4H), 7.23 (d, J = 4.3 Hz, 1H), 6.97 (d, J = 4.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.9, 137.4, 137.3, 130.9, 130.8, 130.2, 128.9, 128.7,

128.7, 128.5, 127.9, 126.3, 115.4, 109.6, 100.7, 100.4. HRMS (APCI): m/z calcd for $C_{18}H_{11}N_3Se$ $[M+H]^+$ 350.01910, found: 350.01868.

4-(4-Methoxyphenyl)-1-selenocyanatopyrrolo[1,2-a]quinoxaline **(4e)**

Yield: 50%; Yellow solid; mp 197.0−197.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.32 (dd, J = 8.4, 1.1 Hz, 1H), 8.10 (dd, J = 7.9, 1.6 Hz, 1H), 7.89 (d, J = 8.9 Hz, 2H), 7.64–7.59 (m, 1H), 7.58–7.53 (m, 1H), 7.29 (d, J = 4.3 Hz, 1H), 7.07 (d, J = 8.9 Hz, 2H), 7.04 (d, J = 4.3 Hz, 1H), 3.90 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.3, 153.6, 137.5, 131.1, 130.9, 130.3, 130.1, 129.1, 128.6, 127.8, 126.5, 115.5, 114.3, 109.7, 100.6, 100.5, 55.6. HRMS (APCI): m/z calcd for $C_{19}H_{13}N_3OSe$ $[M+H]^+$ 380.02966, found: 380.02905.

4-(4-Bromophenyl)-1-selenocyanatopyrrolo[1,2-a]quinoxaline **(4f)**

Yield: 42%; Yellow solid; mp 181.1−182.9 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.35 (dd, J = 8.5, 1.1 Hz, 1H), 8.11 (dd, J = 8.0, 1.6 Hz, 1H), 7.81 (d, J = 8.5 Hz, 2H), 7.72–7.63 (m, 3H), 7.62–7.56 (m, 1H), 7.31 (d, J = 4.3 Hz, 1H), 6.99 (d, J = 4.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.9, 137.4, 136.5, 132.1, 131.2, 130.8, 130.4, 129.2, 128.7, 128.4, 126.7, 124.8, 115.6, 109.5, 101.1, 100.3. HRMS (APCI): m/z calcd for $C_{18}H_{10}BrN_3Se$ $[M+H]^+$ 427.92961, found: 427.92892.

4-(4-Nitrophenyl)-1-selenocyanatopyrrolo[1,2-a]quinoxaline **(4g)**

Yield: 38%; Yellow solid; mp 185.9−186.9 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 8.8 Hz, 2H), 8.22 – 8.05 (m, 3H), 7.74 – 7.69 (m, 1H), 7.66 – 7.59 (m, 1H), 7.36 (d, J = 4.3 Hz, 1H), 6.99 (d, J = 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 148.9, 143.5, 137.2, 131.4, 130.4, 129.9, 129.4, 129.1, 128.8, 126.9, 124.1, 115.7, 109.3, 101.6, 100.1. HRMS (APCI): m/z calcd for $C_{18}H_{10}N_4O_2Se$ $[M+H]^+$ 395.00417, found: 395.00354.

General procedure for gram-scale experiment.

A 50 mL round-bottomed flask was charged with **1a** (6 mmol), 2a (12 mmol), NCS (1.5 equiv.), and MeCN (20 mL). The solution was stirred at room temperature for 24 h. After reaction completion, the solvent was removed under reduced pressure and the

crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final product **3a** (1.128 g, 83% yield).

Typical procedure for the synthesis of 3aa.

To a 25 mL Schlenk tube equipped with a magnetic stirring bar, **3a** (0.2 mmol), concentrated sulfuric acid (18 M) (0.1 mL), and CH_2Cl_2 (2 mL) were added. The reaction vessel was allowed to stir under the ice bath condition for 4 h. After completion of the reaction, the mixture was washed with the saturated $NaHCO_3$ aqueous solution (10 mL) and extracted with dichloromethane (3 × 10 mL). The organic phase was dried over Na_2SO_4 and concentrated in a vacuum. The crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final product pyrrolo[1,2-a]quinoxaline-1-thiol **3aa** in 84% yield.

Pyrrolo[1,2-a]quinoxaline-1-thiol **(3aa)**

Yield: 84%; Yellow solid; mp 126.3−127.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, J = 8.0 Hz, 1H), 8.57 (s, 1H), 7.74 (dd, J = 8.1, 1.4 Hz, 1H), 7.26–7.21 (m, 1H), 6.94 (d, J = 4.2 Hz, 1H), 6.93–6.87 (m, 1H), 6.73 (d, J = 4.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.8, 136.7, 131.2, 130.2, 129.4, 127.9, 127.1, 125.5, 120.6, 115.4, 107.5. HRMS (APCI): m/z calcd for $C_{11}H_7N_2S$ $[M\text{-}H]^+$ 199.03245, found 199.03285.

Typical procedure for the synthesis of 3ab.

To a 25 mL Schlenk tube equipped with a magnetic stirring bar, **3a** (0.2 mmol), $TMSCF_3$ (2 equiv.), Cs_2CO_3 (2 equiv.) and MeCN (2 mL) were added. The reaction vessel was allowed to stir at room temperature for 15 h. After reaction completion, the solvent was removed under reduced pressure and the crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final product **3ab** in 45% yield.

1-((Trifluoromethyl)thio)pyrrolo[1,2-a]quinoxaline **(3ab)**

Yield: 45%; White solid; mp 94.2−94.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (dd, J = 8.7, 0.8 Hz, 1H), 8.84 (s, 1H), 8.02 (dd, J = 7.9, 1.8 Hz, 1H), 7.61–7.56 (m, 1H), 7.56–7.50 (m, 1H), 7.25 (d, J = 4.2 Hz, 1H), 6.94 (d, J = 4.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.5, 137.2, 131.7, 130.8, 129.9, 129.8, 129.5, 128.2, 126.7,

126.2, 116.4, 107.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.44. HRMS (APCI): m/z calcd for $C_{12}H_7F_3N_2S$ $[M+H]^+$ 269.03548, found: 269.03510.

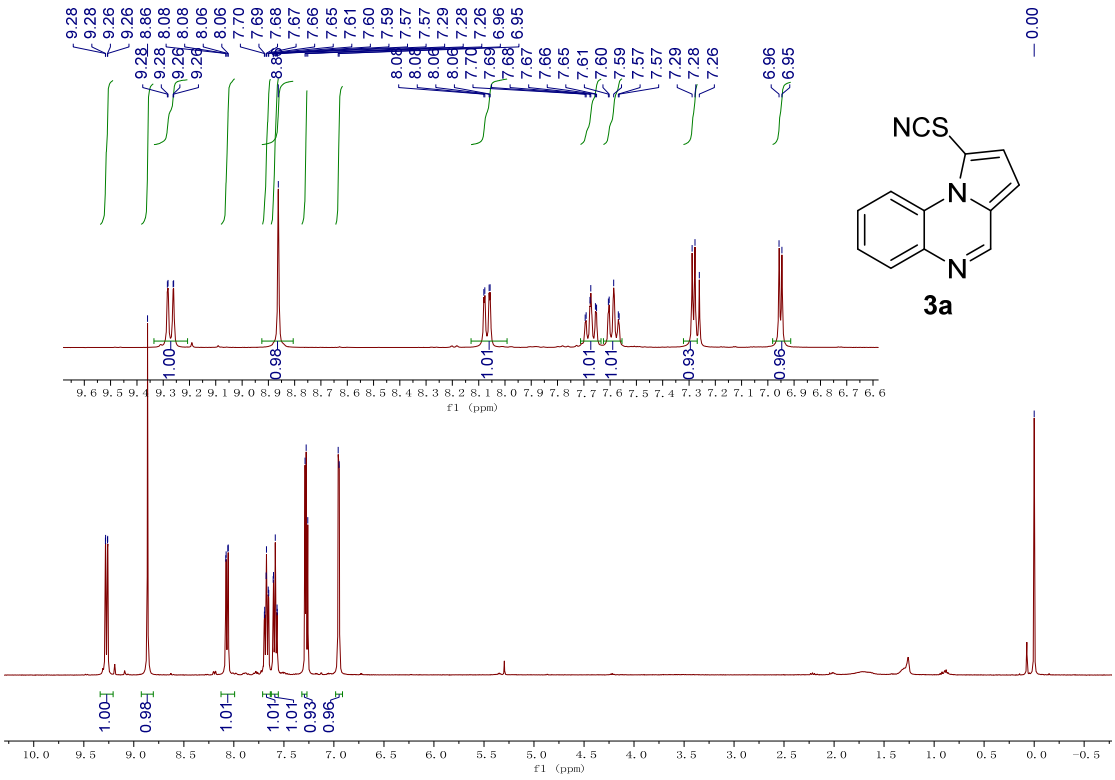
Typical procedure for the synthesis of 4aa.

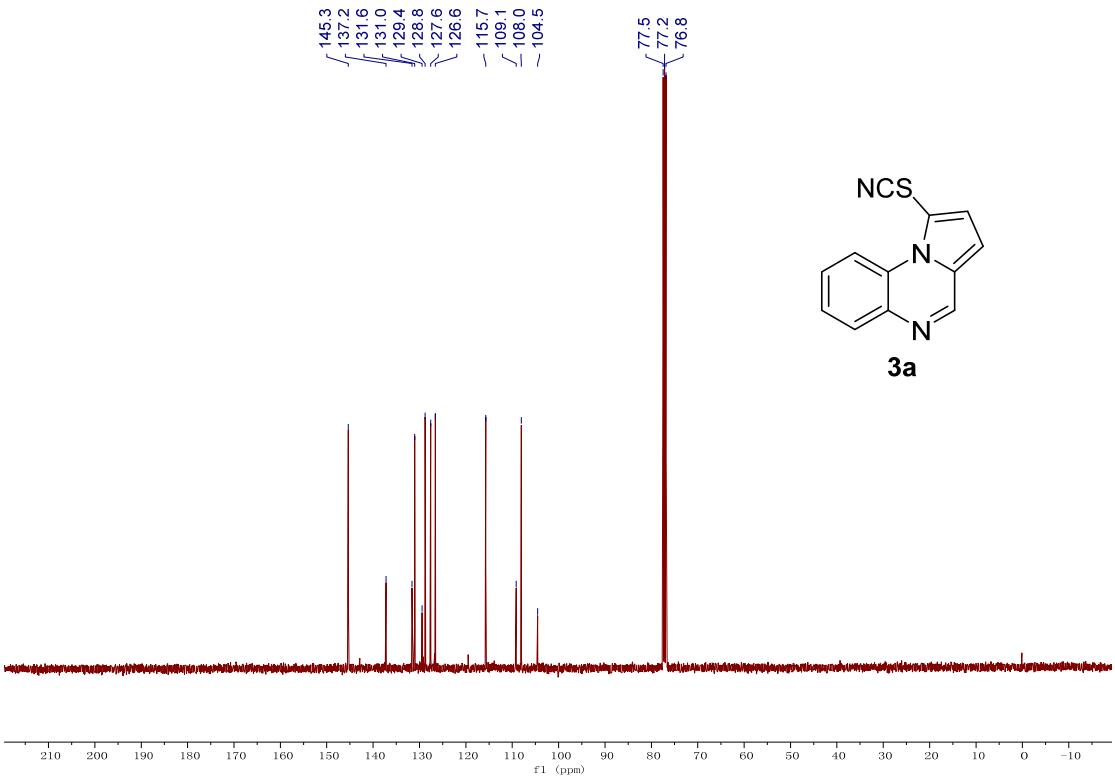
To a 25 mL Schlenk tube equipped with a magnetic stirring bar, **4a** (0.1 mmol), phenylacetylene (0.1 mmol), $Cu(OAc)_2$ (5 mol%), Ag_2CO_3 (20 mol%), Cs_2CO_3 (1 equiv.), and NMP (1.5 mL) were added. The reaction vessel was allowed to stir at 100 ^oC for 8 h under argon atmosphere. After completion of the reaction, the mixture was washed with the saturated solution of NaCl (3 × 10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic phase was dried over Na_2SO_4 and concentrated in a vacuum. The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether as eluent to give the final product **4aa** in 44% yield.

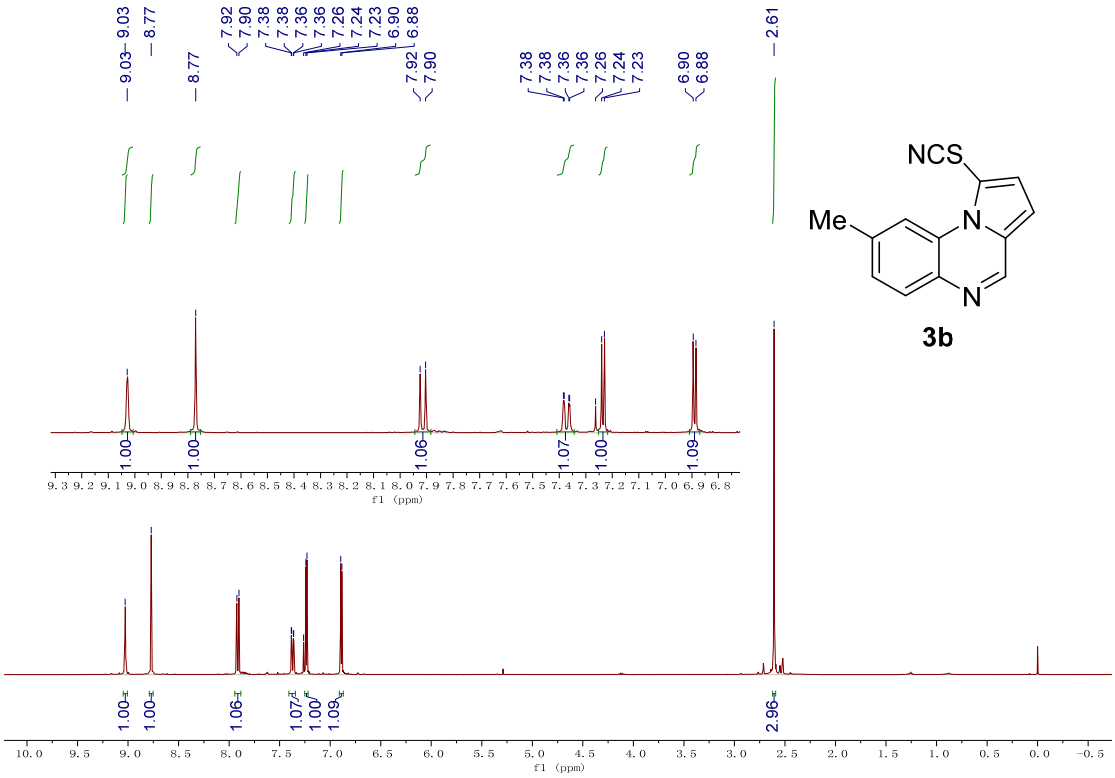
1-((Phenylethynyl)selanyl)pyrrolo[1,2-a]quinoxaline **(4aa)**

Yield: 44%; White solid; mp 169.7−170.9 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.02 (dd, J = 8.0, 1.4 Hz, 1H), 7.94 (d, J = 2.6 Hz, 1H), 7.86 (dd, J = 8.2, 1.2 Hz, 1H), 7.54–7.60 (m, 1H), 7.53–7.47 (m, 1H), 7.41–7.37 (m, 2H), 7.27 (d, J = 2.1 Hz, 2H), 7.26 (d, J = 1.8 Hz, 1H), 7.13 (d, J = 2.8 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.0, 136.1, 131.8, 130.5, 128.5, 128.5, 128.4, 127.6, 127.1, 126.0, 123.2, 119.6, 114.6, 113.8, 100.7, 97.7, 70.5. HRMS (APCI): m/z calcd for $C_{19}H_{12}N_2Se$ $[M+H]^+$ 349.02385, found: 349.02347.

^{1}H, ^{13}C NMR, and ^{19}F NMR Spectra for Products



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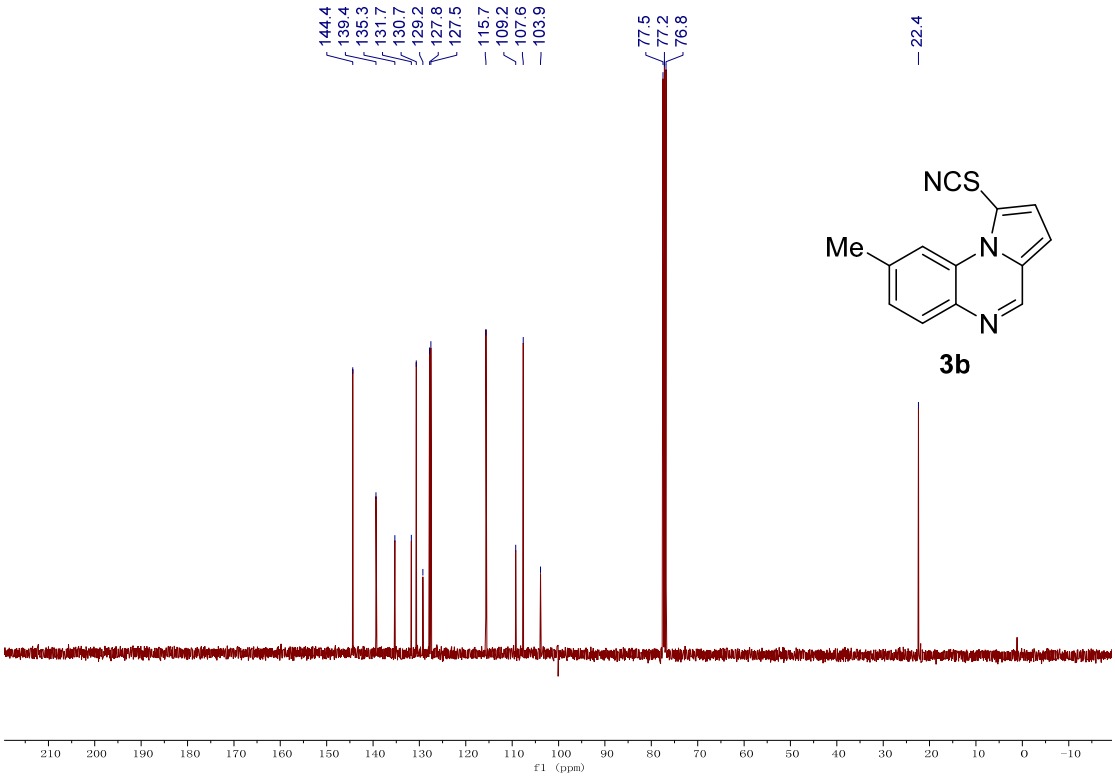
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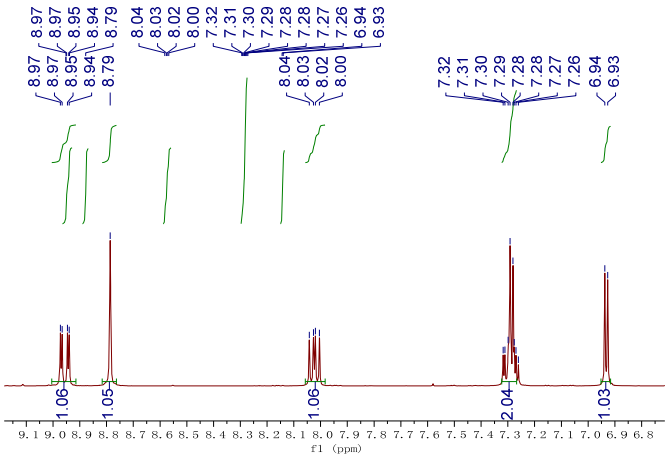
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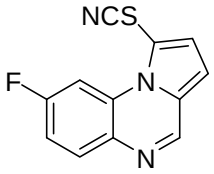
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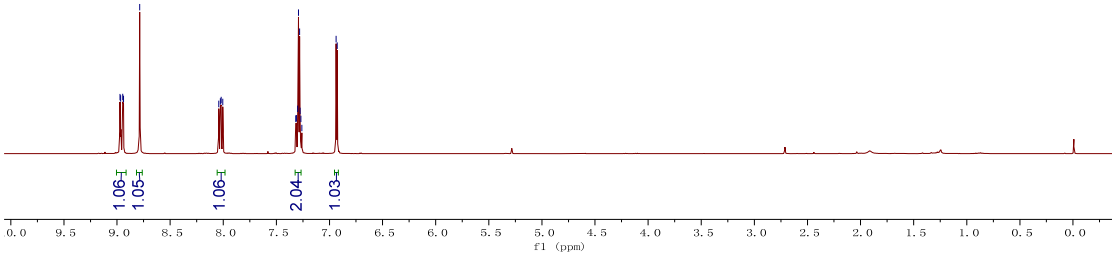
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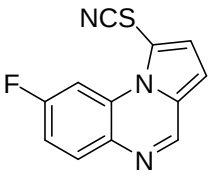
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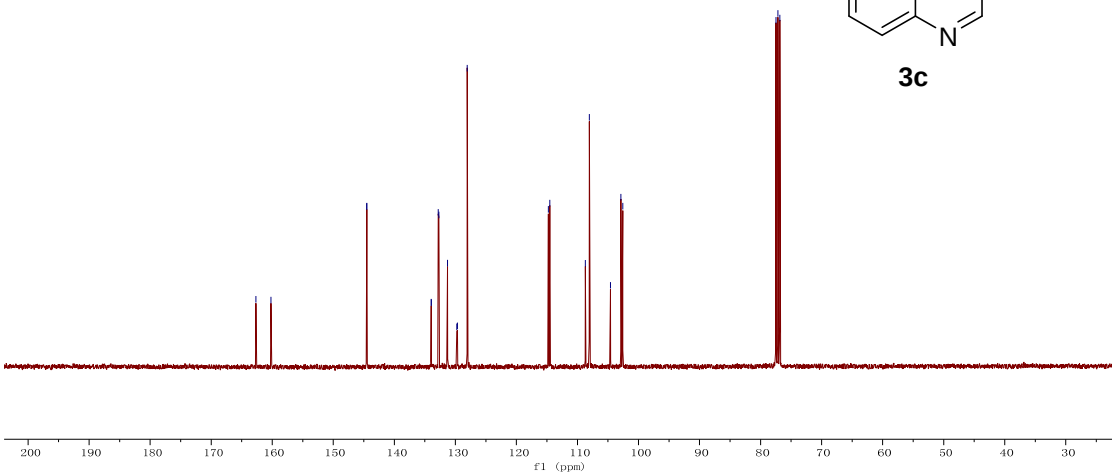
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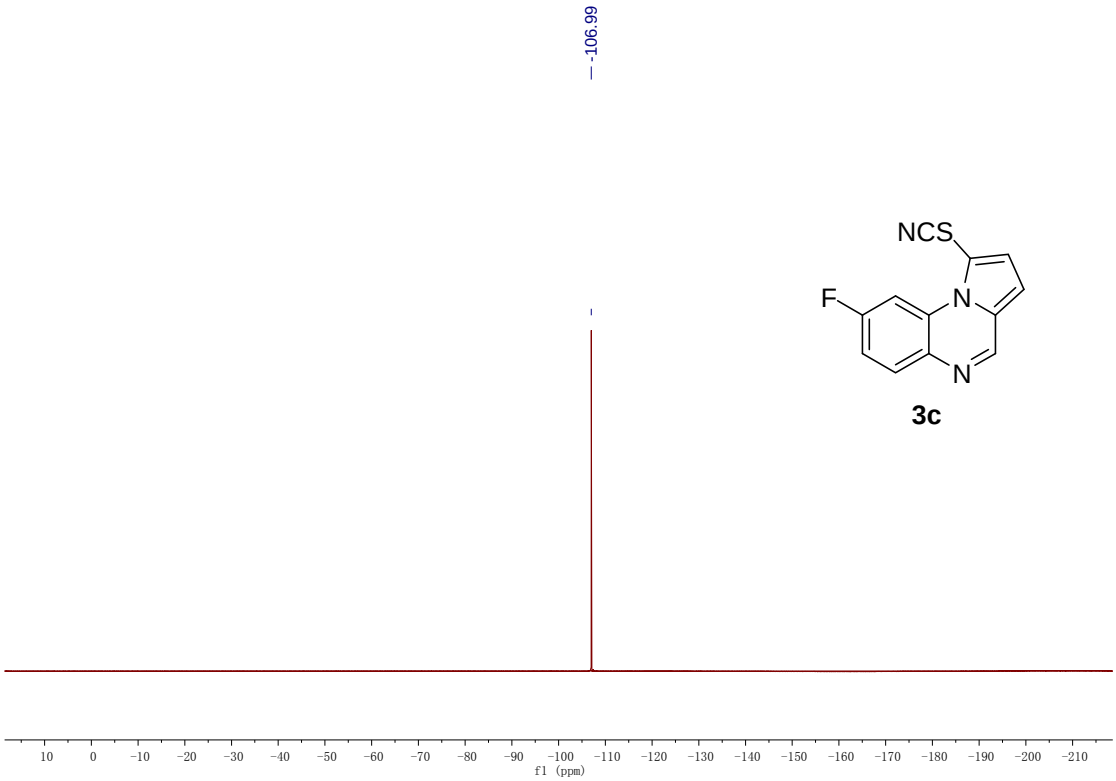
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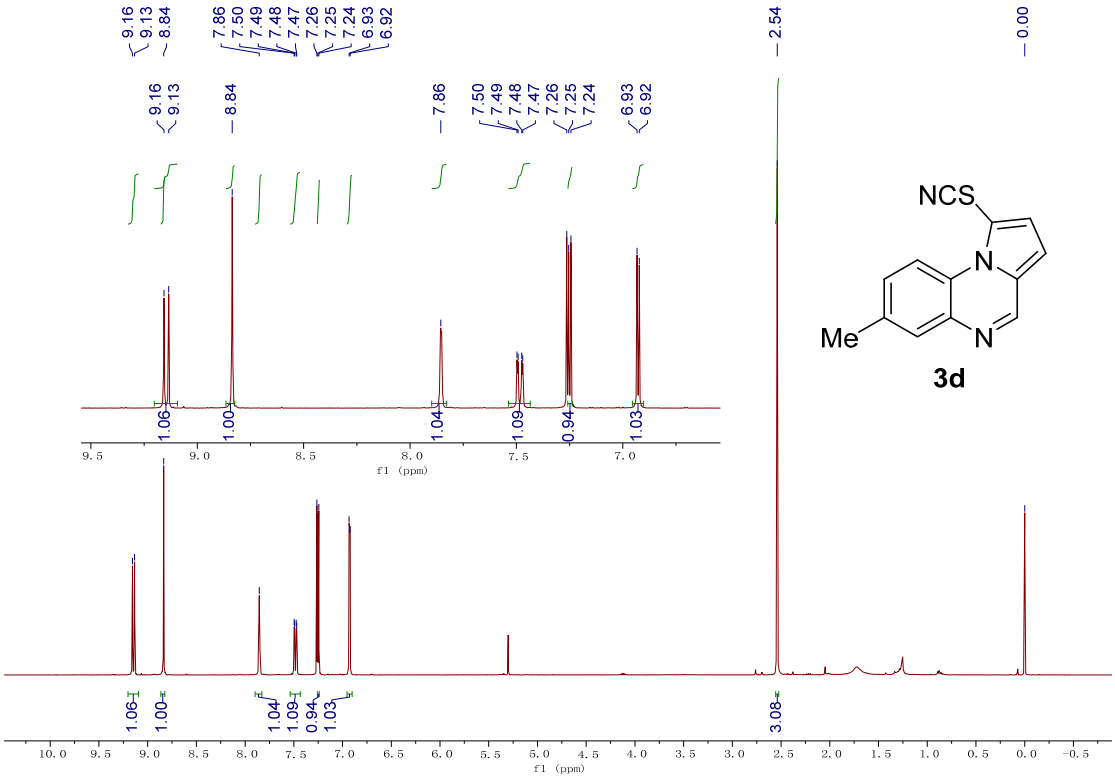
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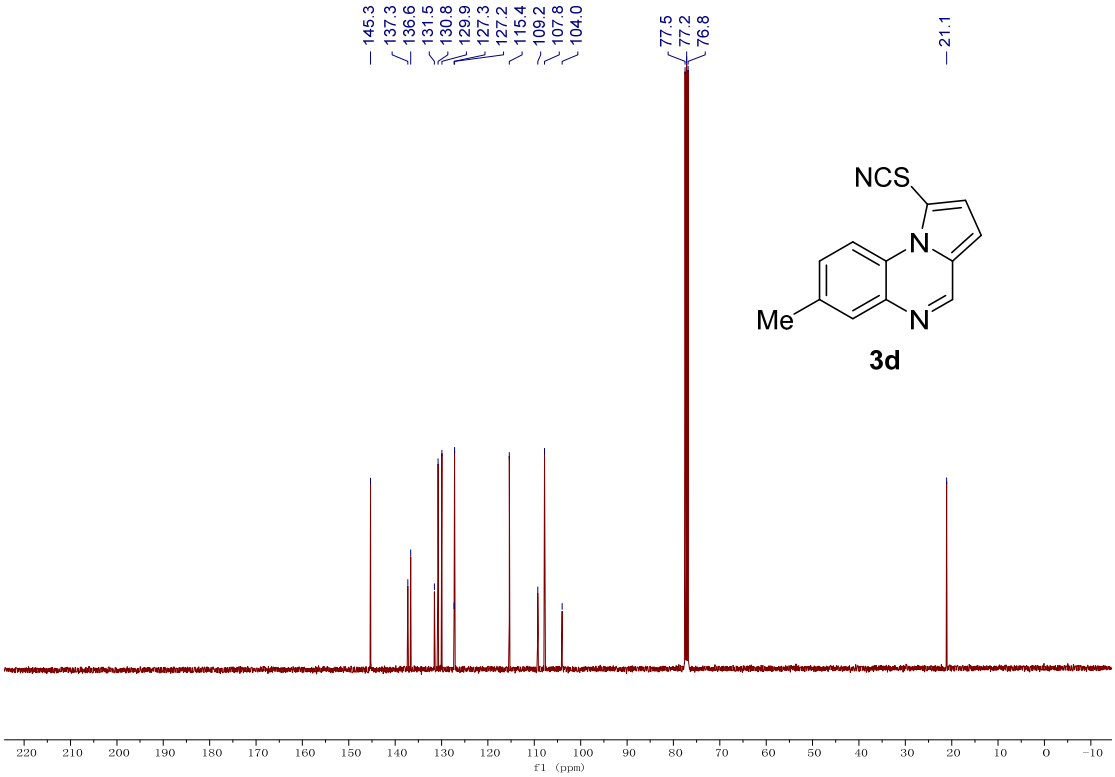
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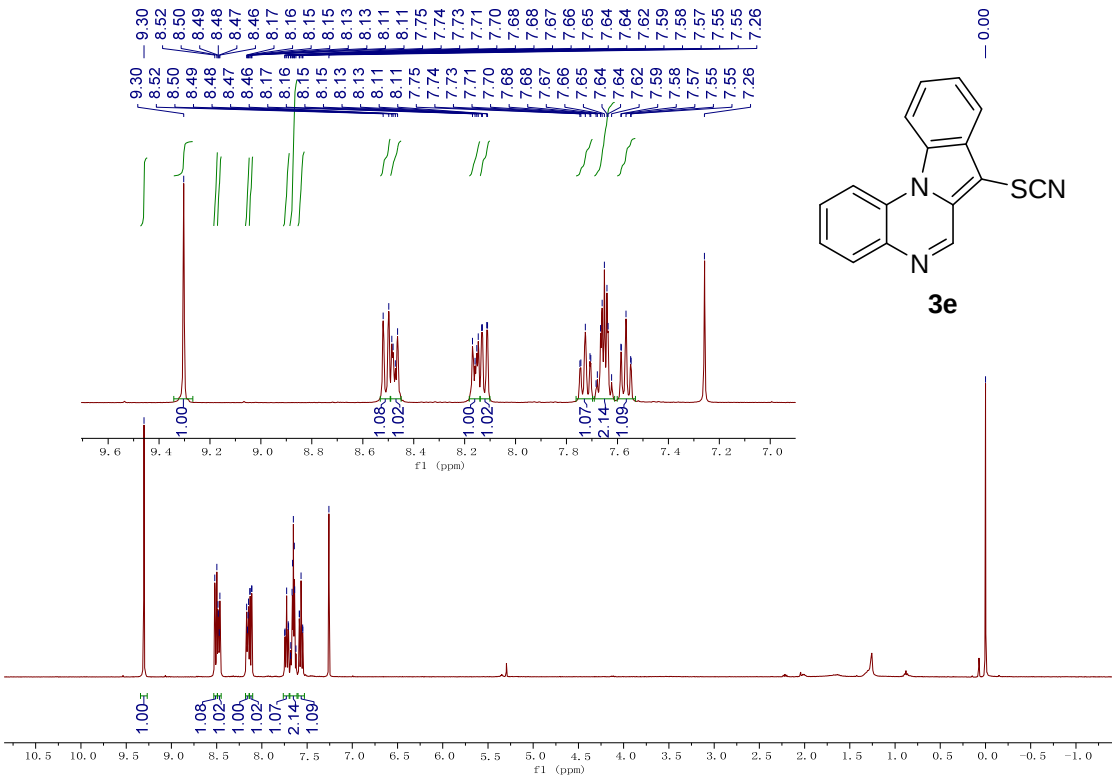
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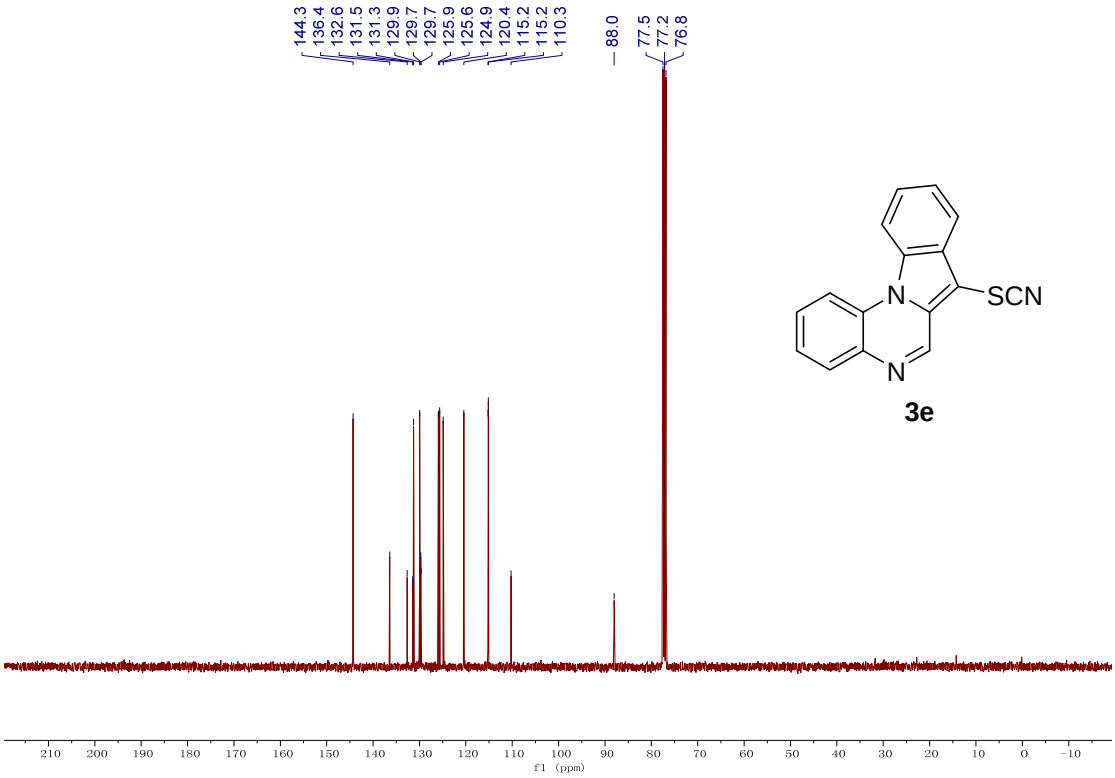
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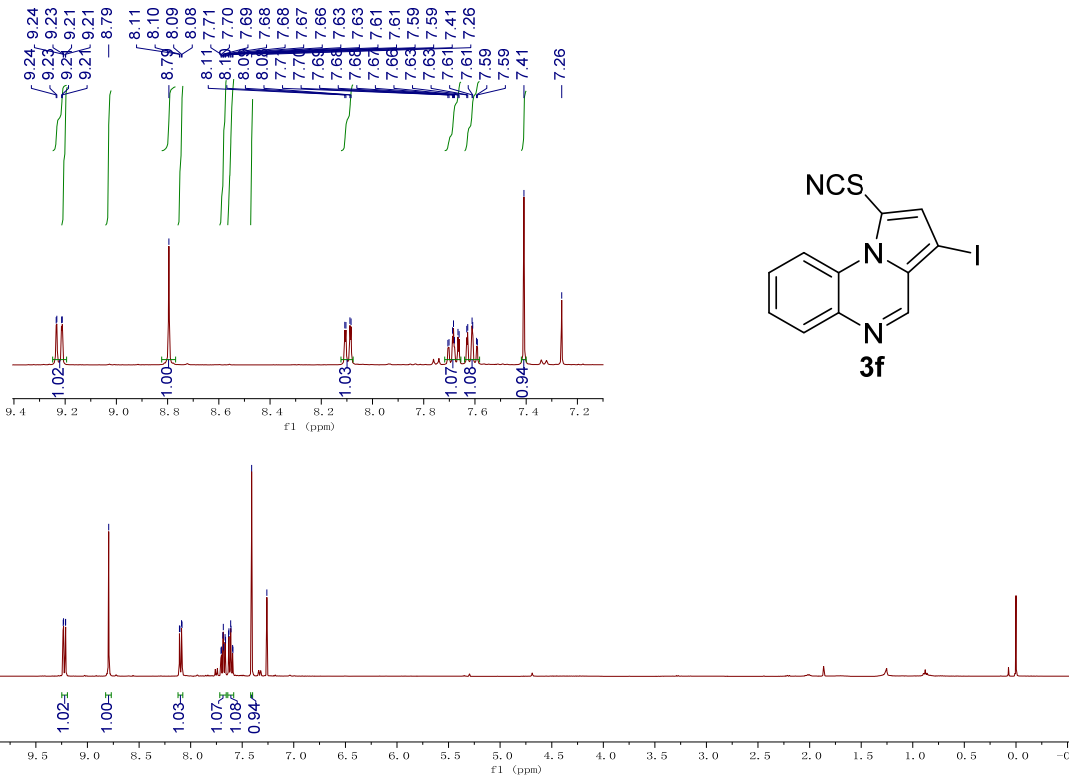
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N

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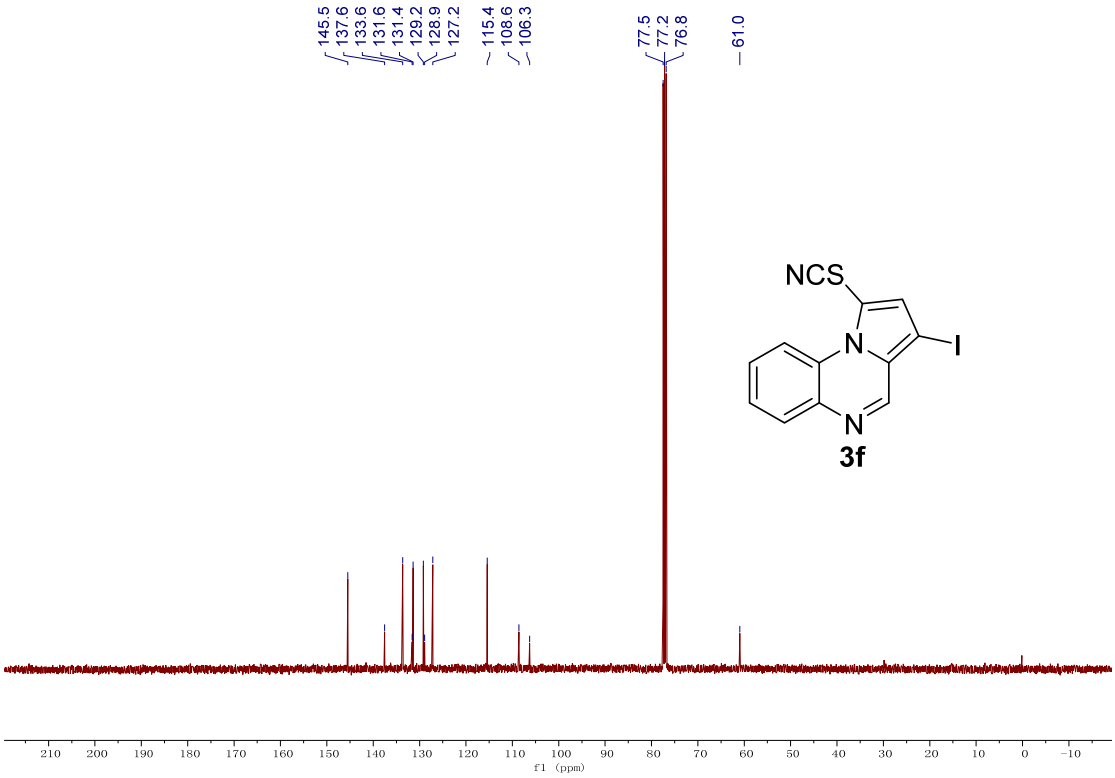
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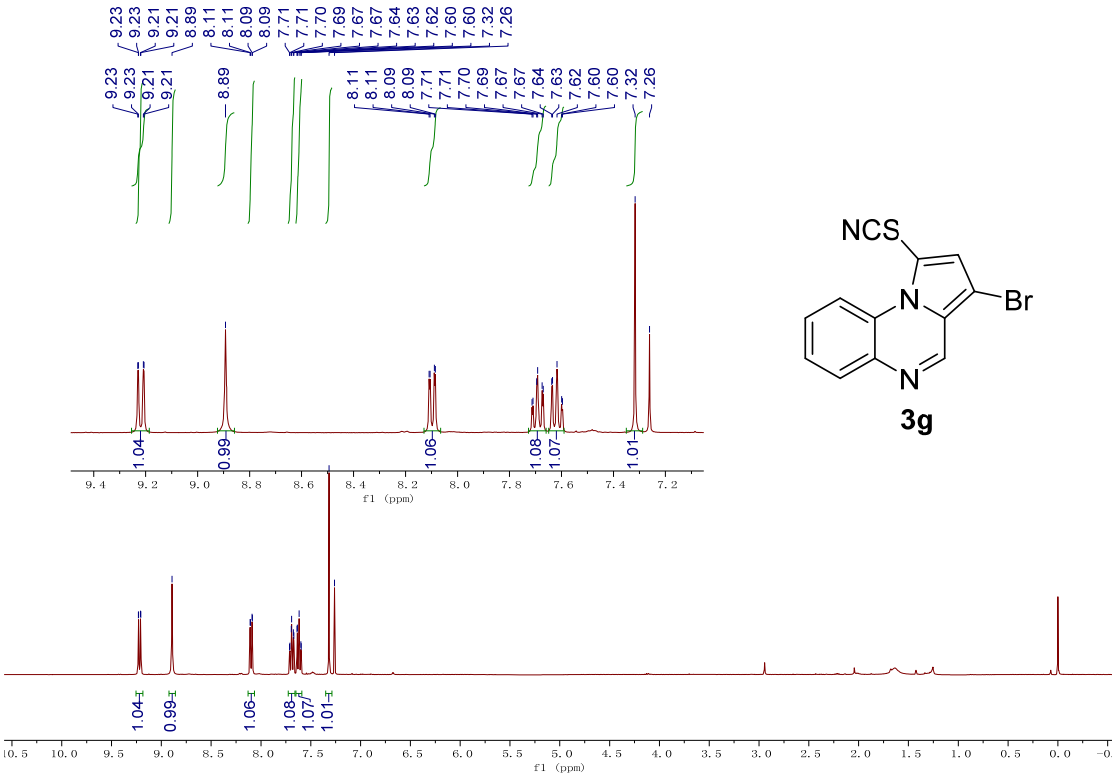
f1 (ppm)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7.67
7.67
7.64
7.63
7.62
7.60
7.60
7.32
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1.06
1.08
1.07
1.01
NCS
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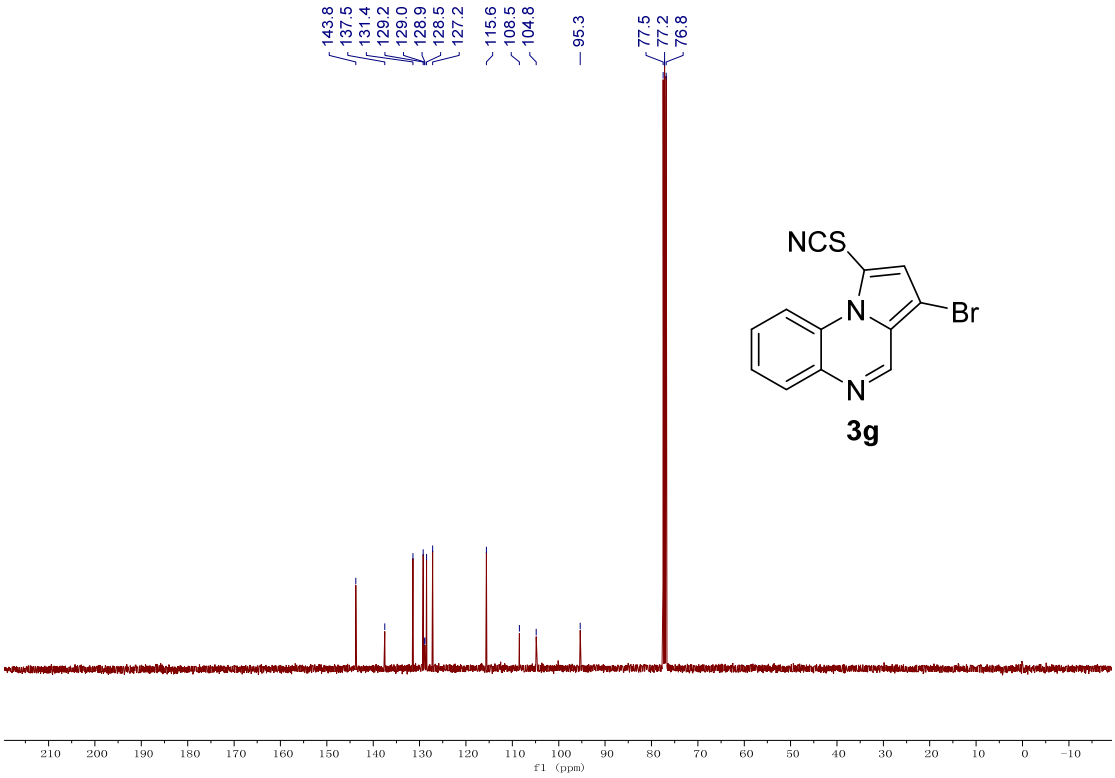
Br
N
3g
f1 (ppm)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129.0
128.9
128.5
127.2
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95.3
77.5
77.2
76.8
NCS
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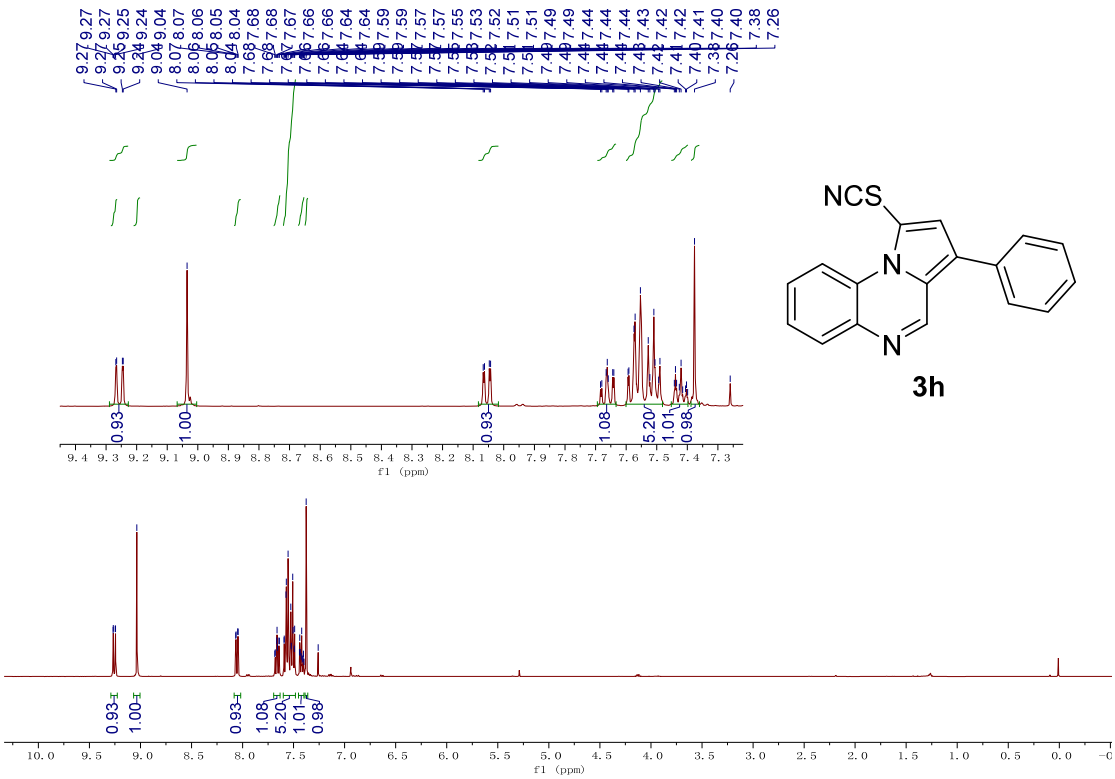
Br
N
3g
f1 (ppm)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8.04
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7.52
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7.44
7.43
7.42
7.41
7.40
7.38
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0.93
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1.01
0.98
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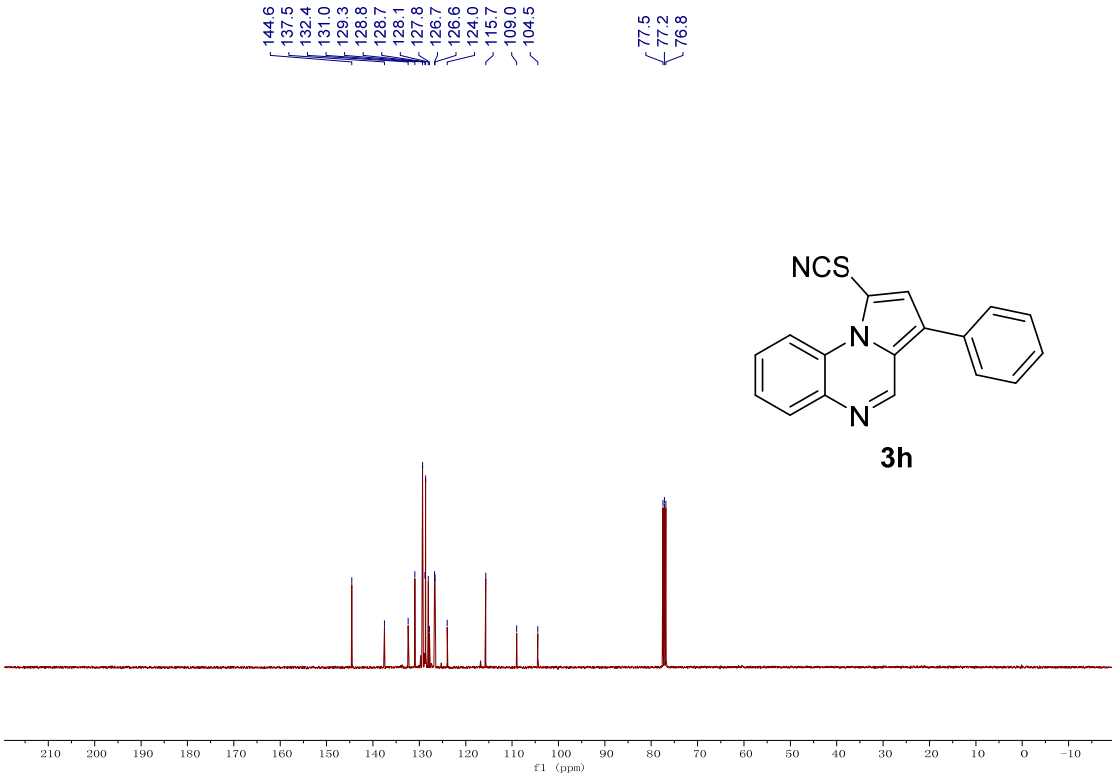
f1 (ppm)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109.0
104.5
77.5
77.2
76.8
NCS
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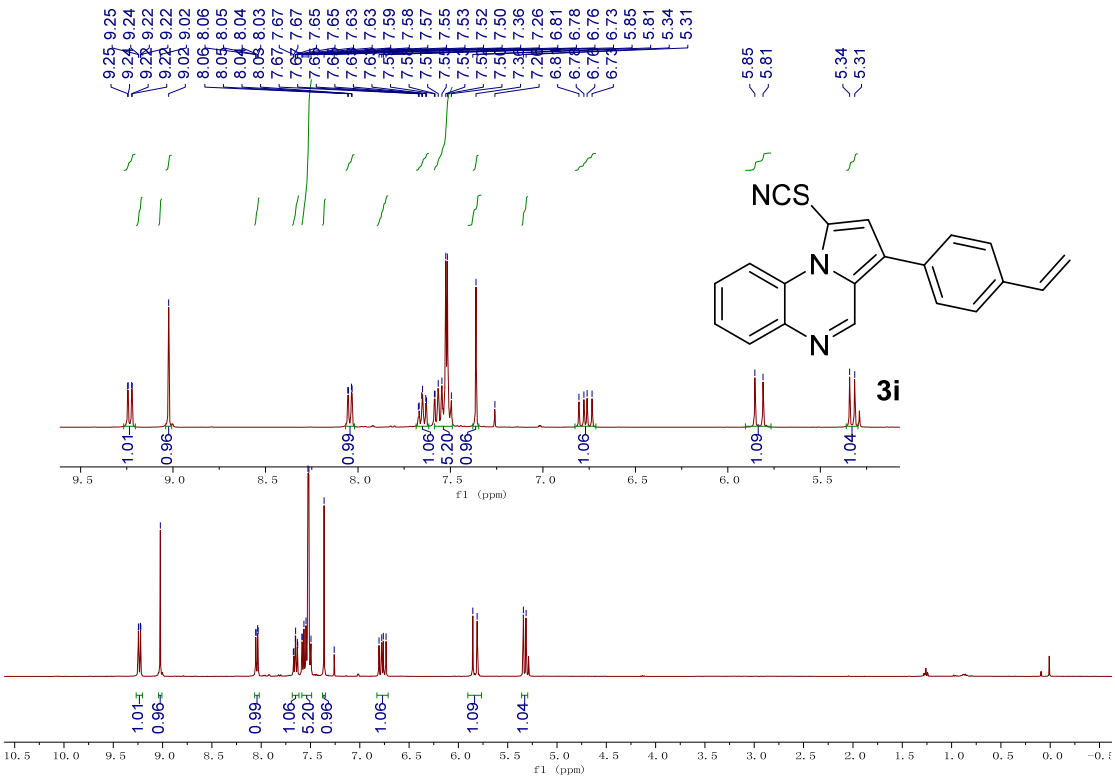
N
3h
f1 (ppm)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7.58
7.57
7.55
7.53
7.52
7.50
7.36
7.26
6.81
6.78
6.76
6.73
5.85
5.81
5.34
5.31
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1.06
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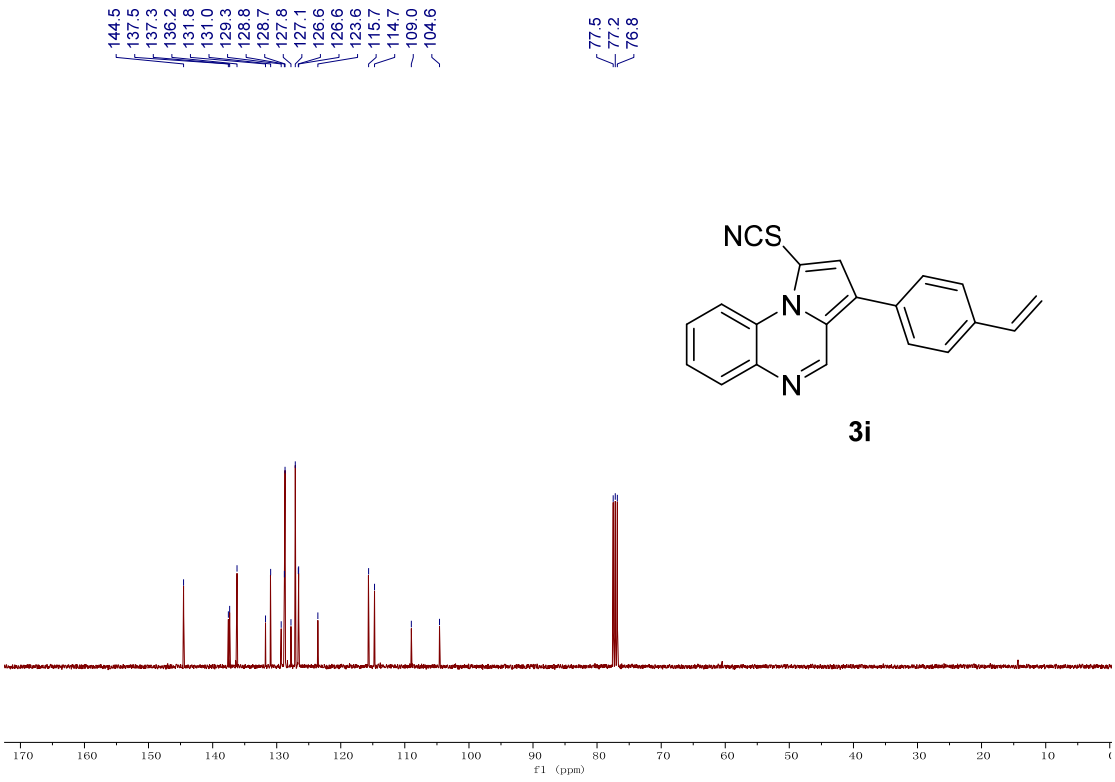
1.04
f1 (ppm)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126.6
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77.5
77.2
76.8
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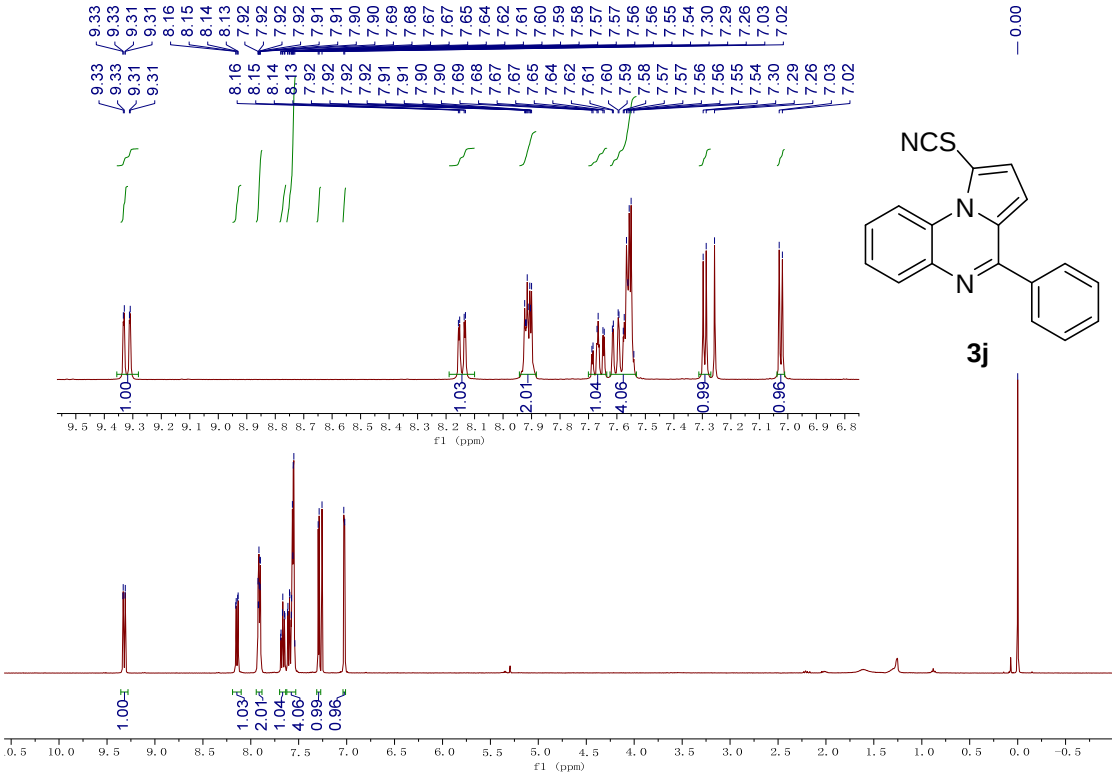
N
3i
f1 (ppm)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7.90
7.90
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7.68
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7.67
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7.56
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7.55
7.54
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7.29
7.26
7.03
7.02
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3j
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1.03
2.01
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4.06
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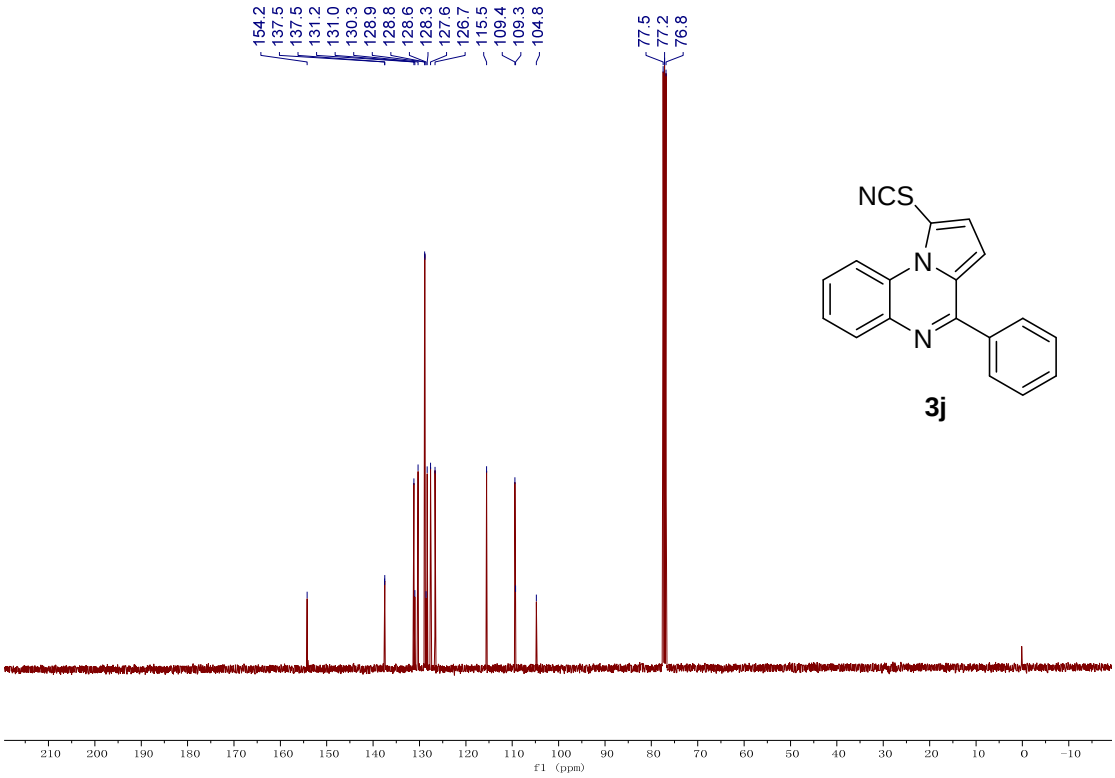
0.96
f1 (ppm)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128.3
127.6
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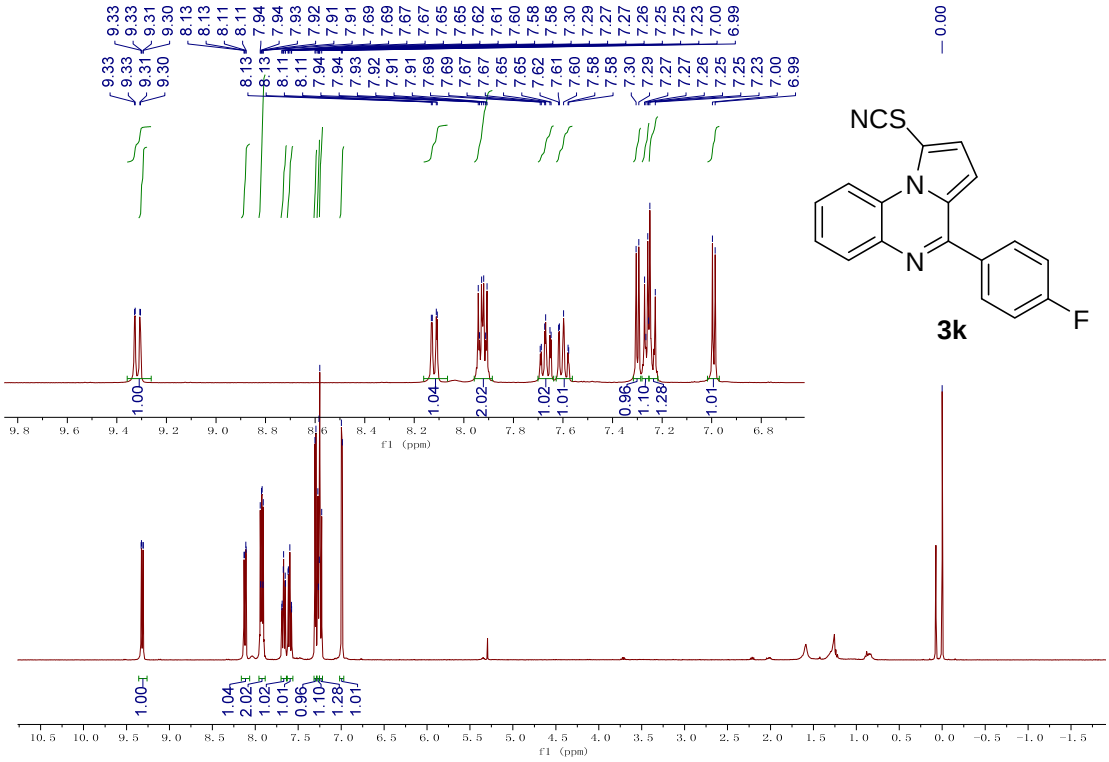
109.3
104.8
77.5
77.2
76.8
NCS
N
N
3j
f1 (ppm)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7.58
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7.26
7.25
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7.23
7.00
6.99
0.00
NCS
N
N
F
3k
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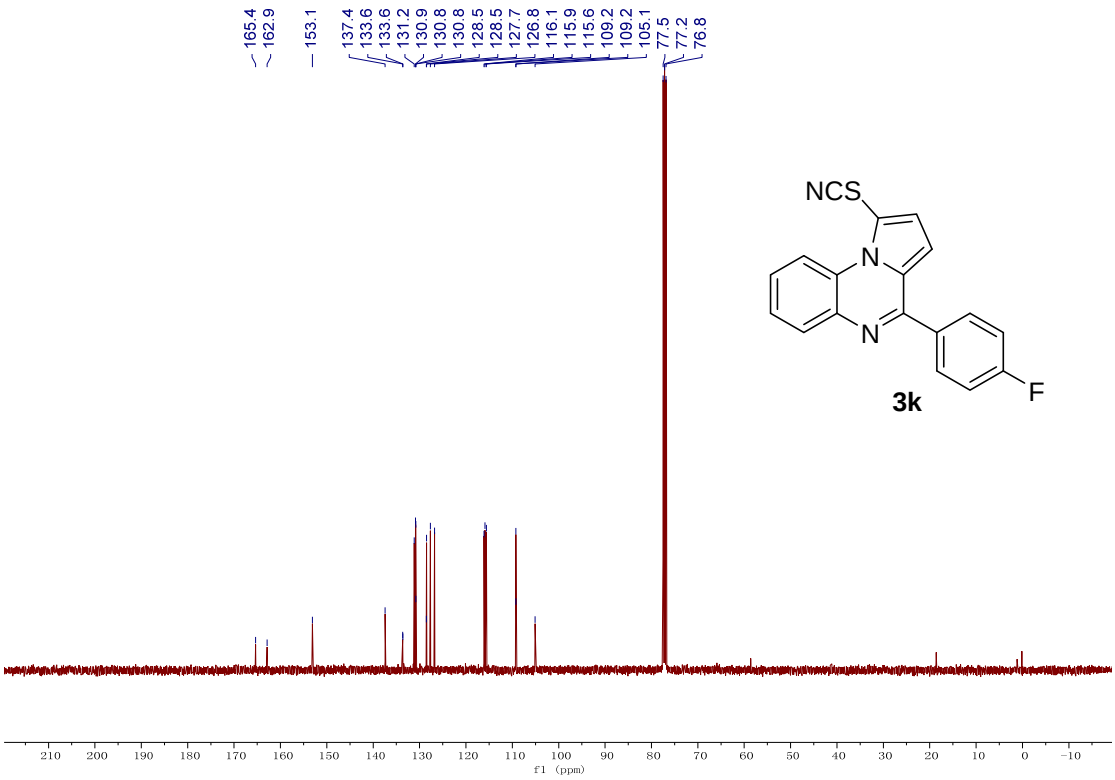
1.04
2.02
1.02
1.01
0.96
1.10
1.28
1.01
f1 (ppm)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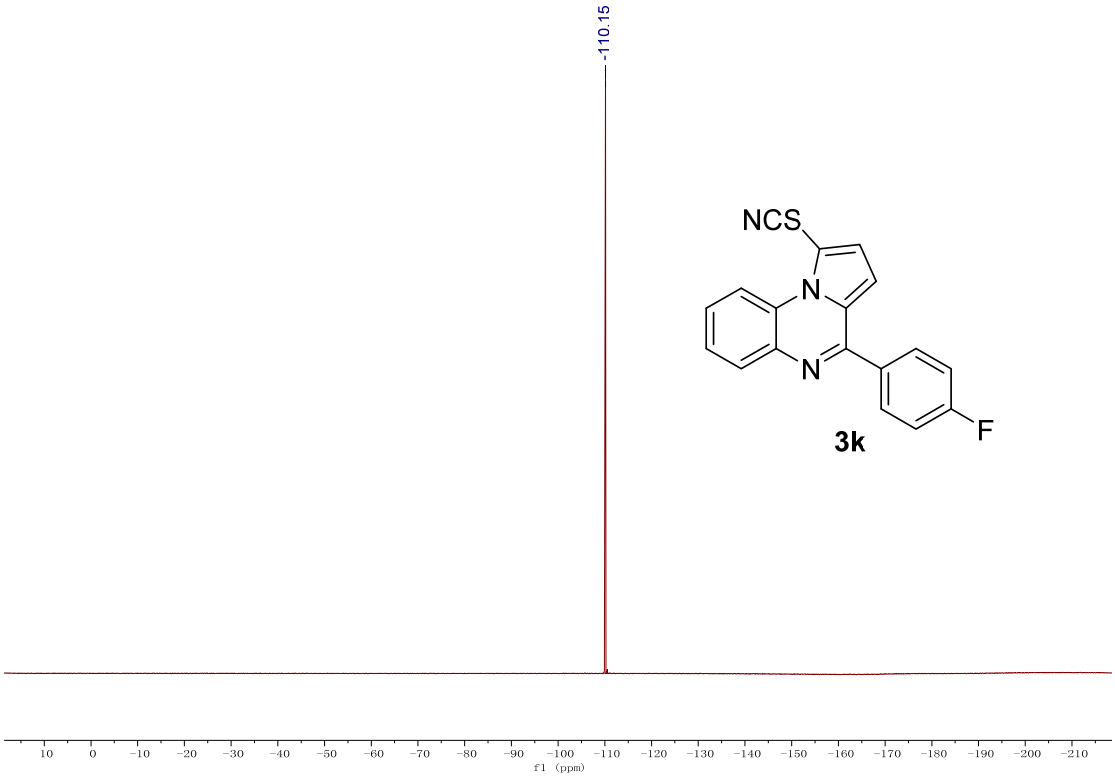
130.8
128.5
128.5
127.7
126.8
116.1
115.9
115.6
109.2
109.2
105.1
77.5
77.2
76.8
NCS
N
N
F
3k
f1 (ppm)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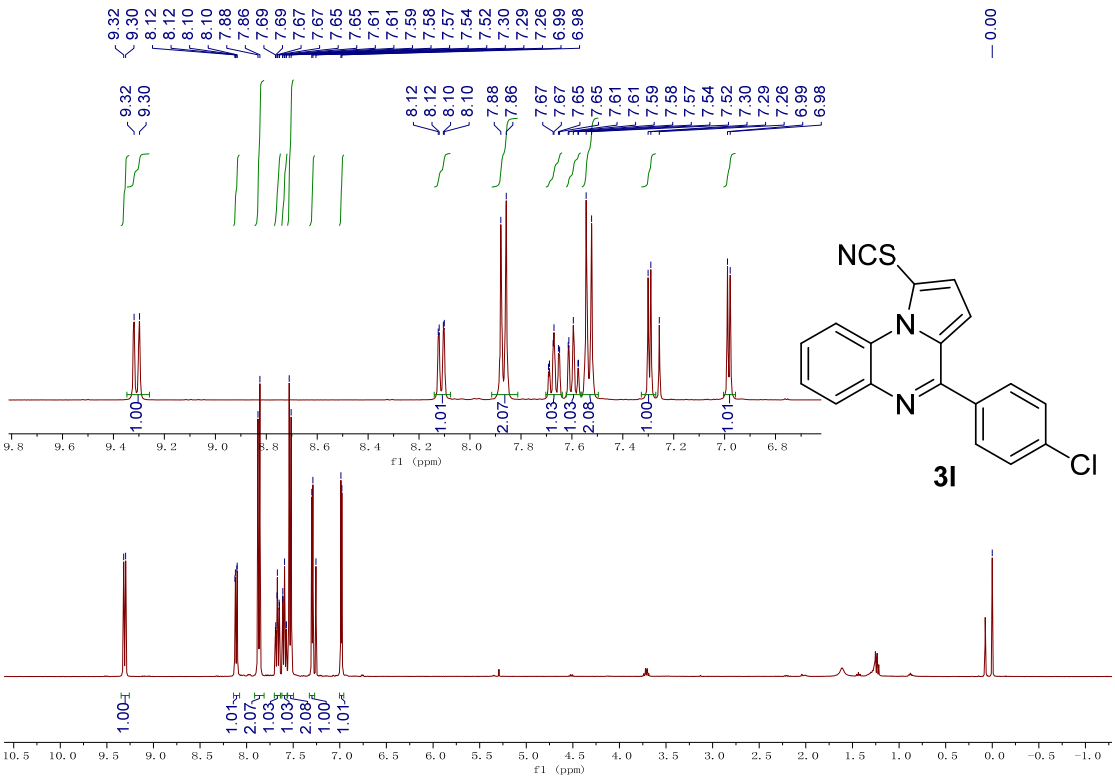
N
F
3k
f1 (ppm)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7.65
7.61
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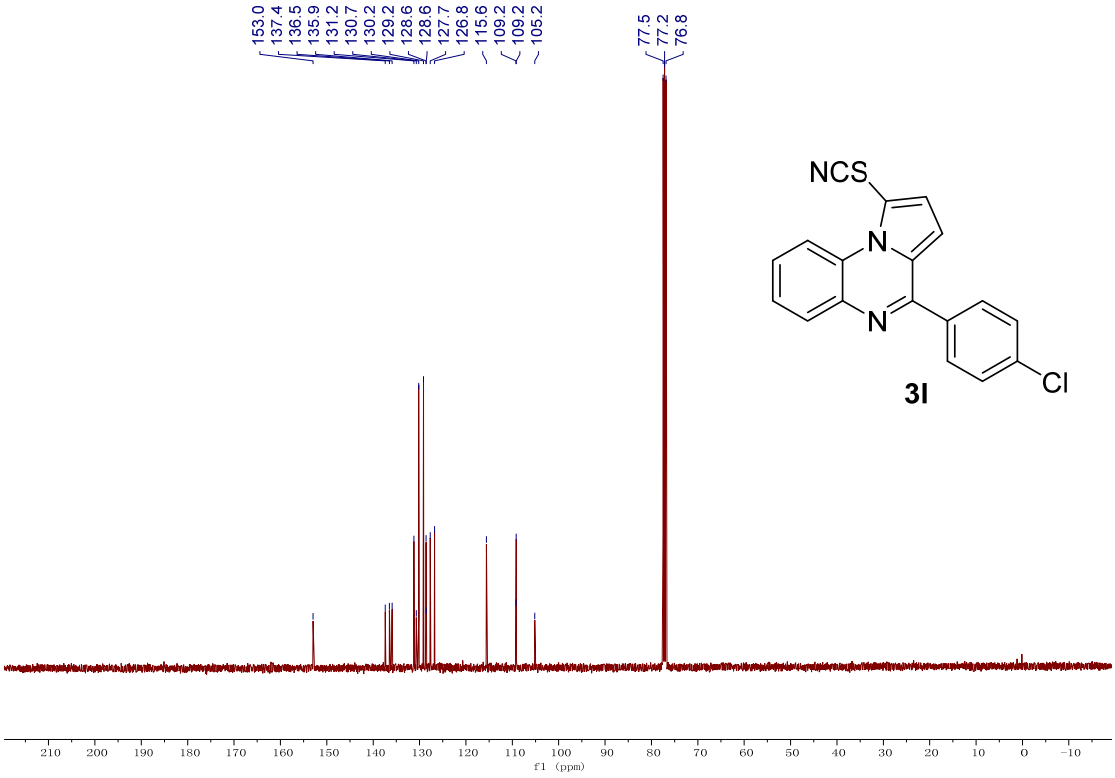
7.57
7.54
7.52
7.30
7.29
7.26
6.99
6.98
0.00
1.00
1.01
2.07
1.03
1.03
2.08
1.00
1.01
f1 (ppm)
NCS
N
N
Cl
3l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128.6
127.7
126.8
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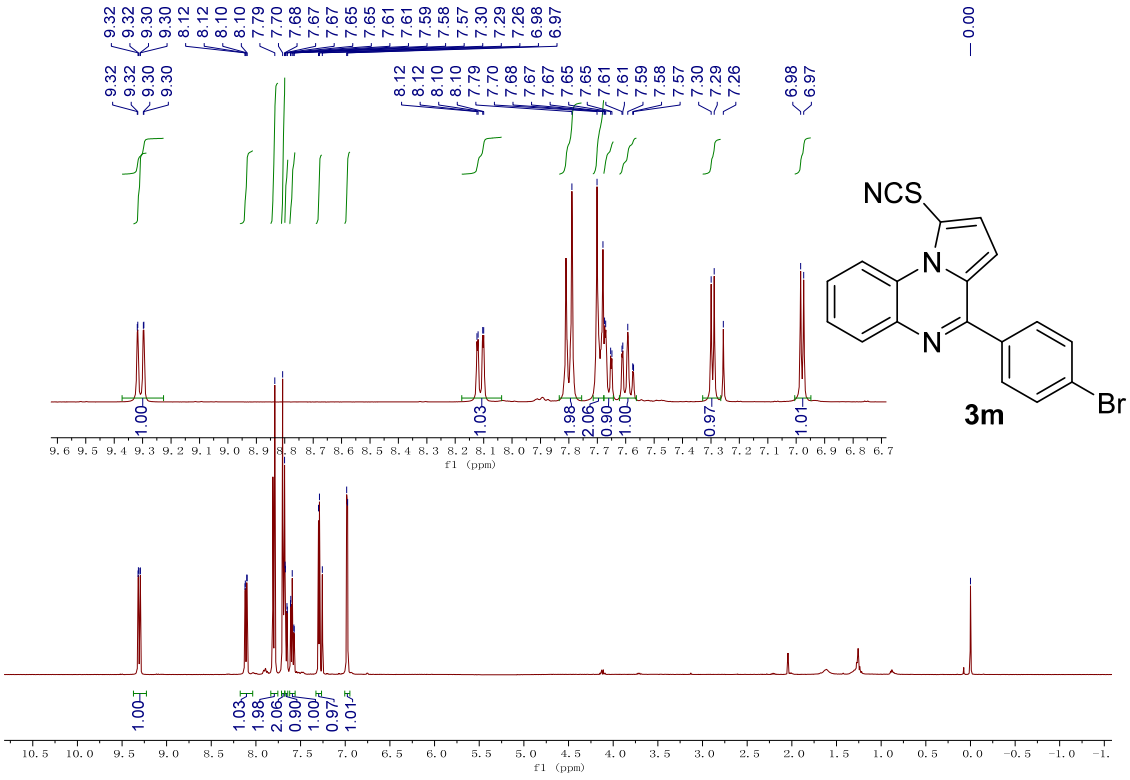
109.2
109.2
105.2
77.5
77.2
76.8
NCS
N
N
Cl
3l
f1 (ppm)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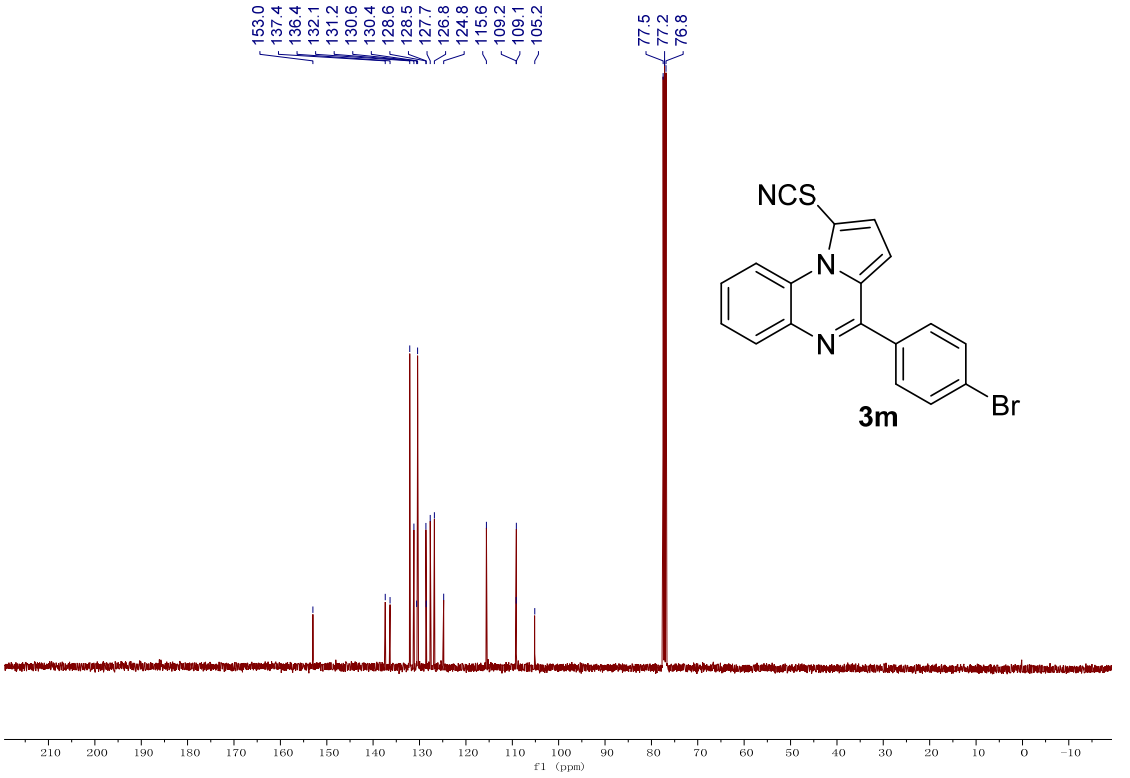
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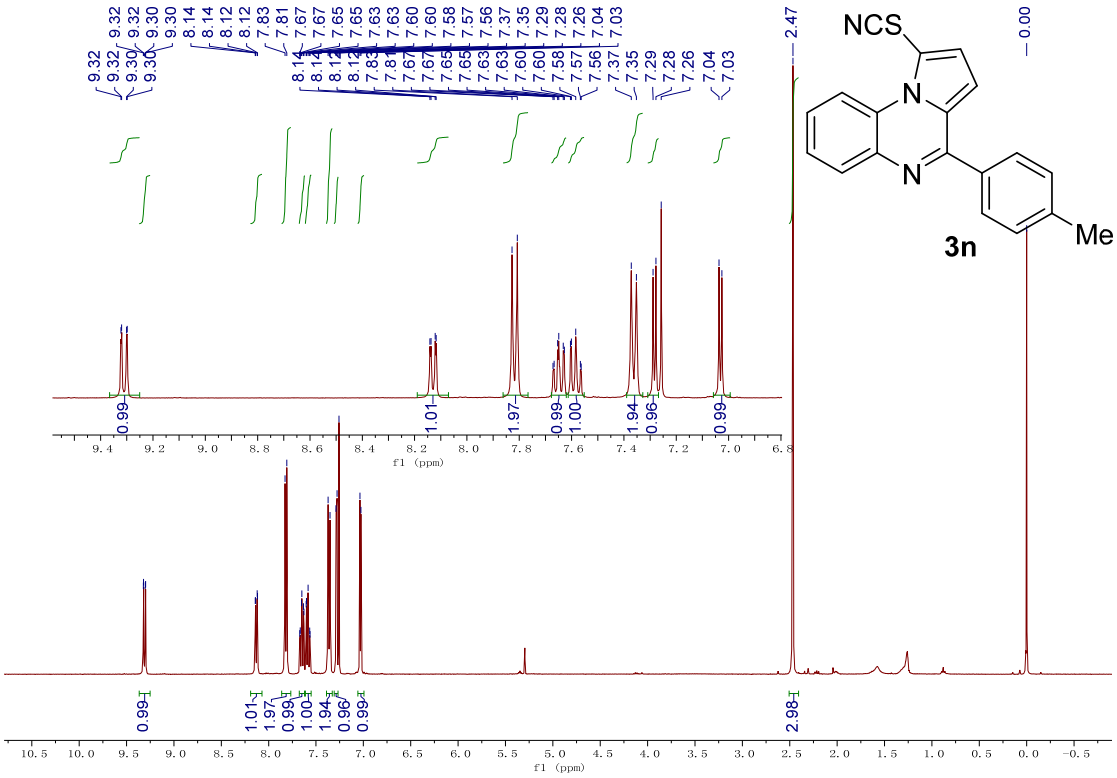
N
N
Br
3m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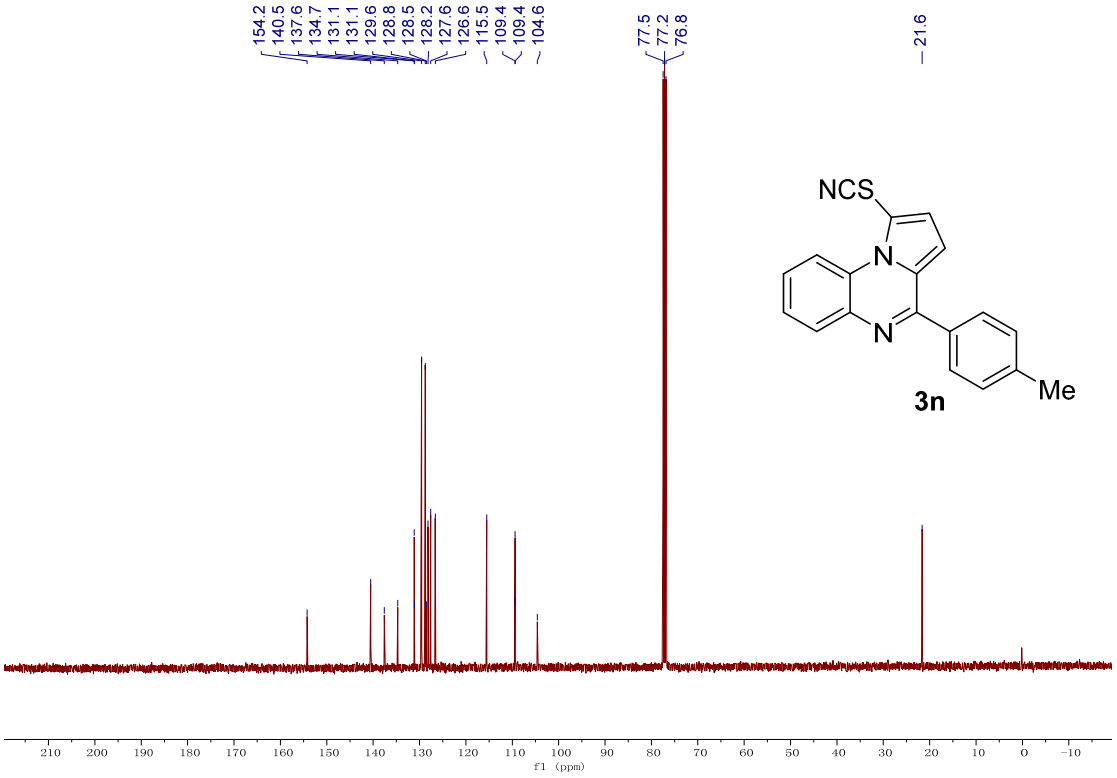
f1 (ppm)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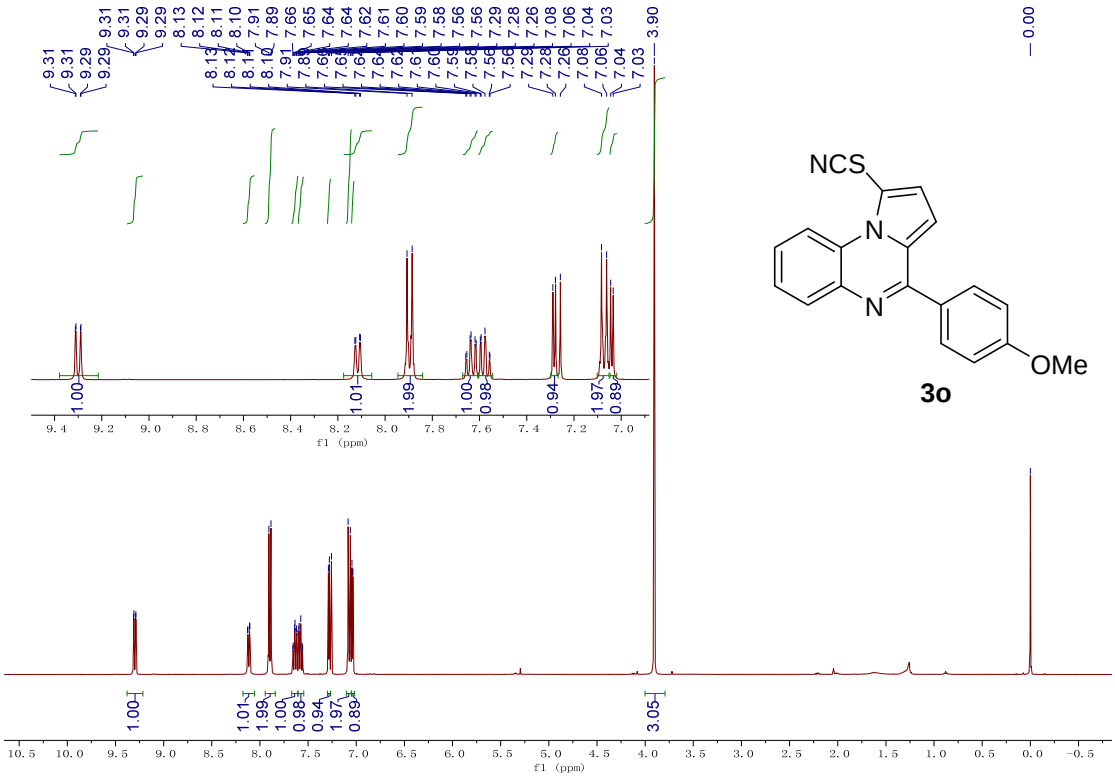
Me
3n
f1 (ppm)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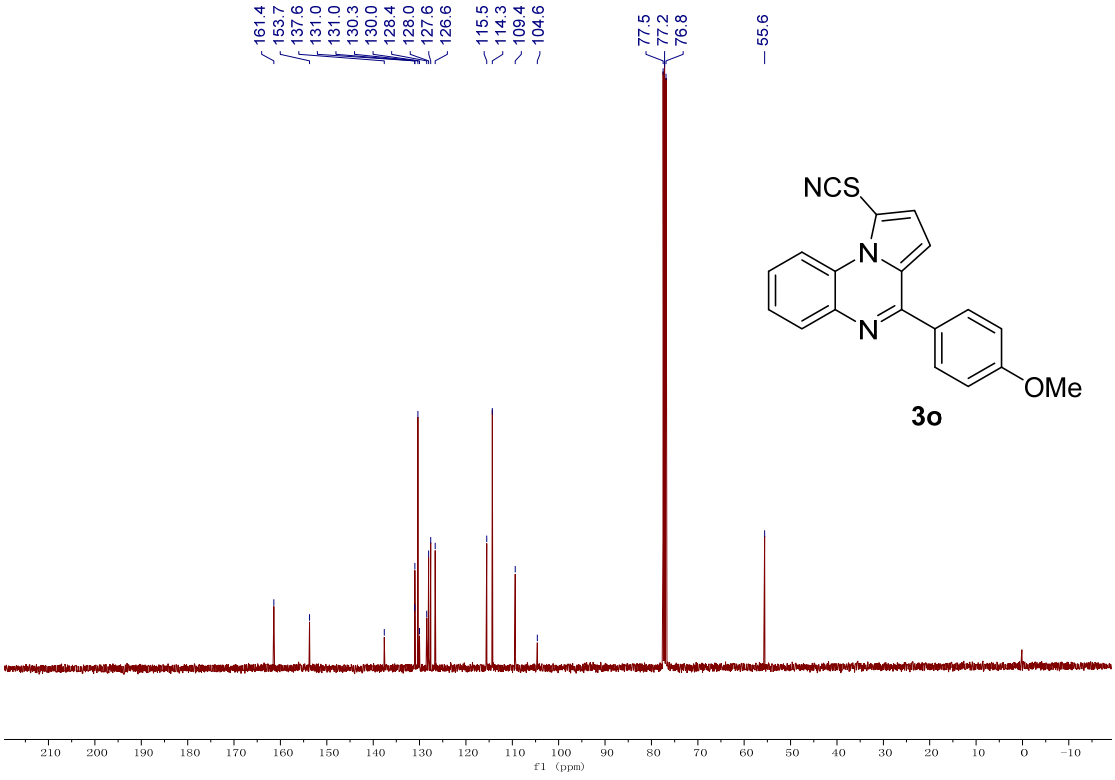
OMe
3o
f1 (ppm)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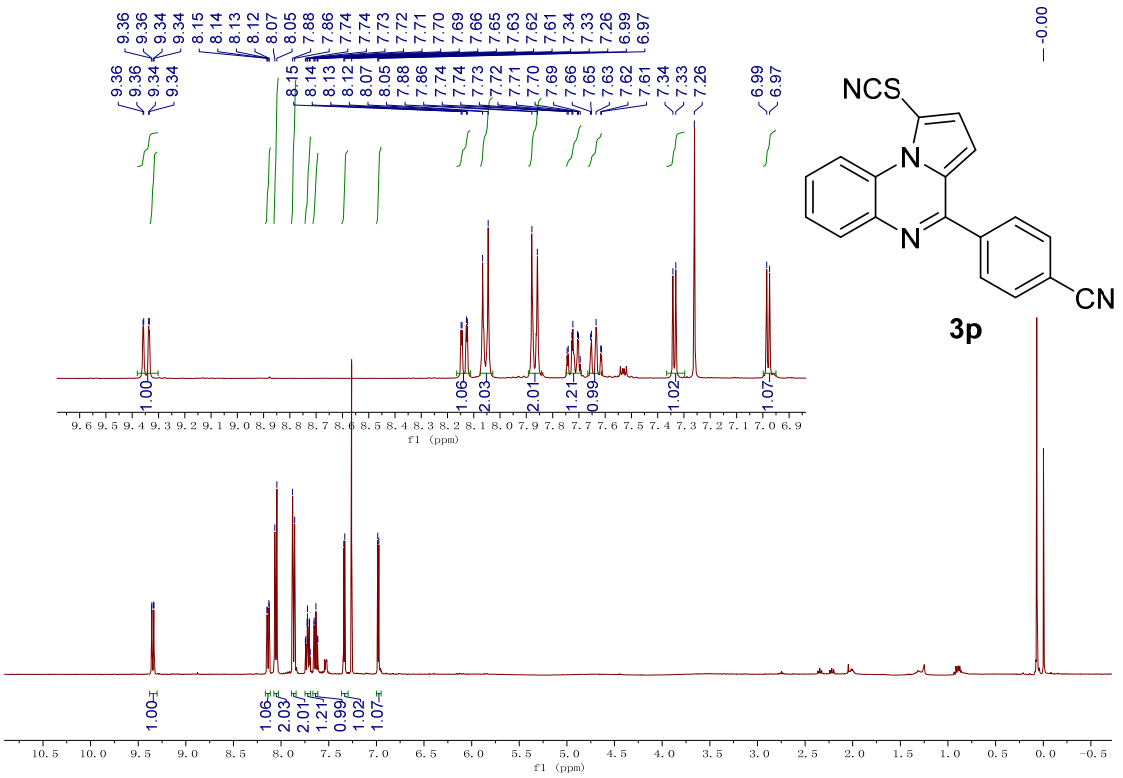
N
OMe
3o
f1 (ppm)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CN
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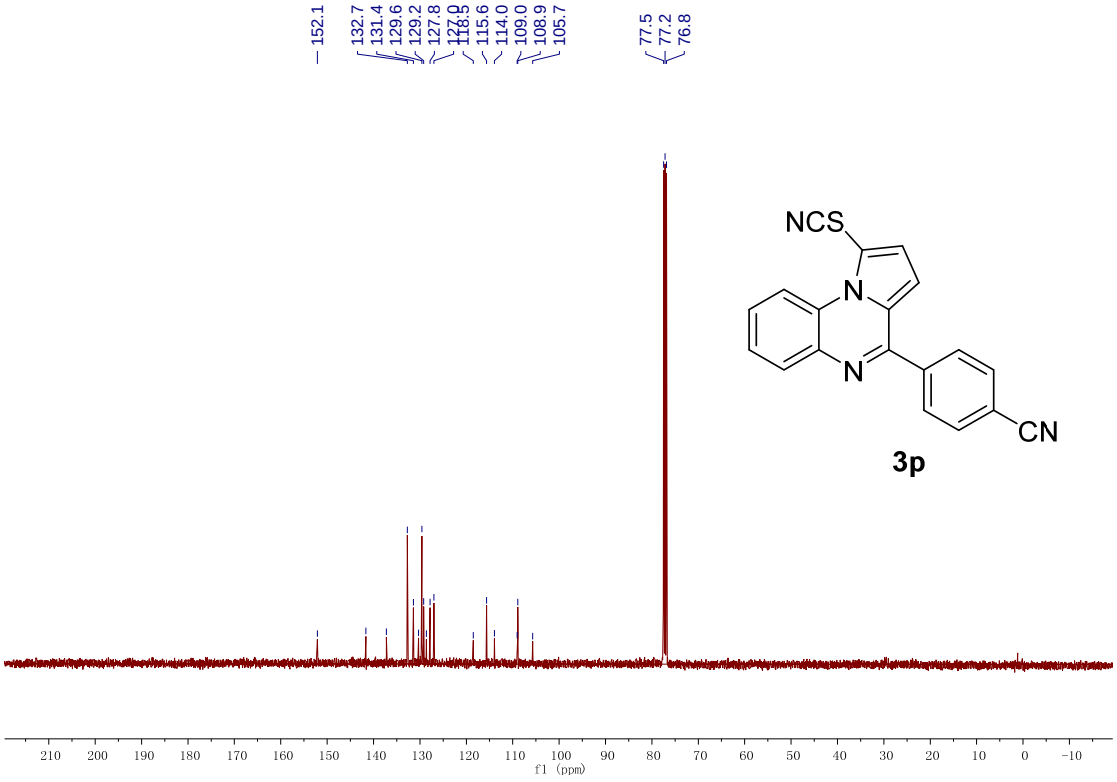
f1 (ppm)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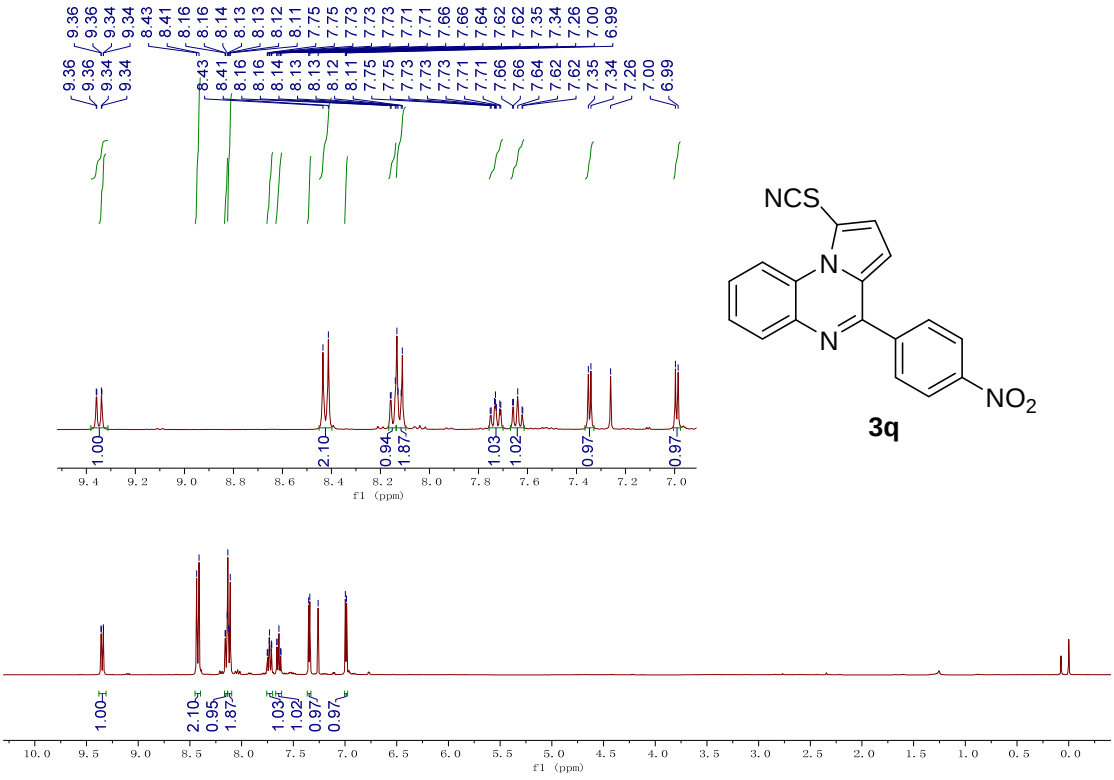
f1 (ppm)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8.11
7.75
7.73
7.71
7.66
7.64
7.62
7.35
7.34
7.26
7.00
6.99
1.00
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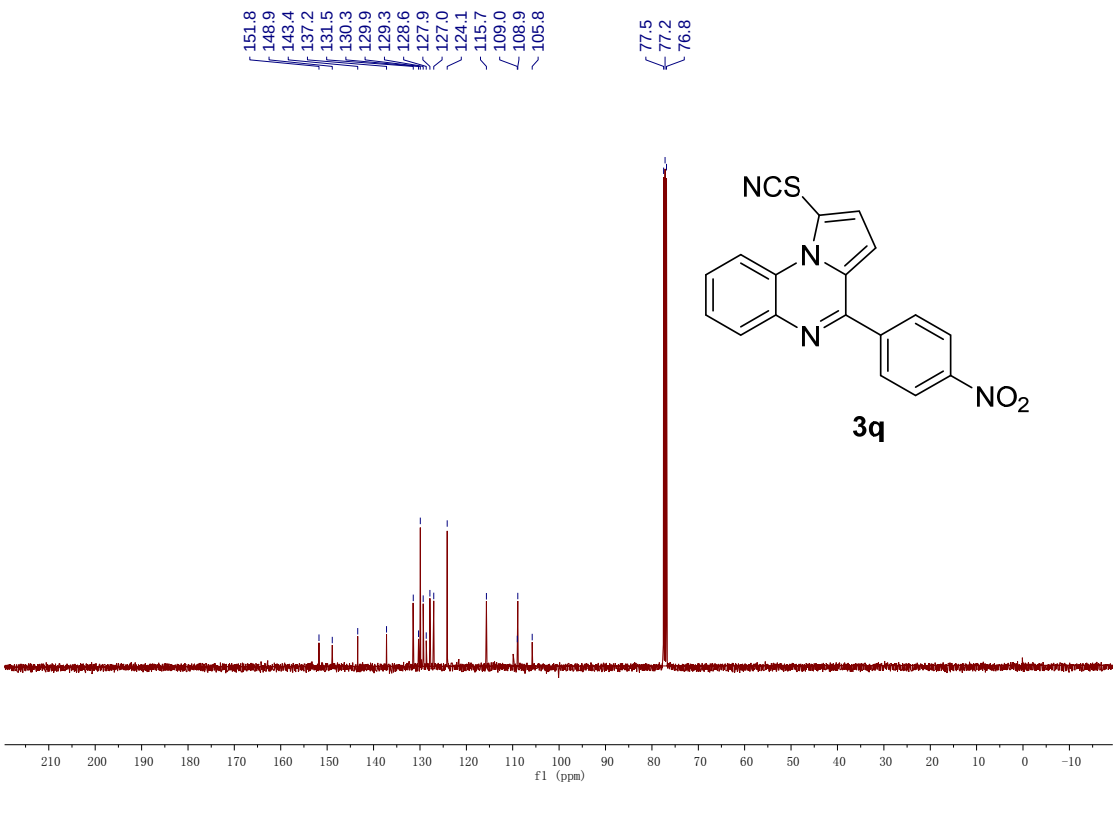
1.87
1.03
1.02
0.97
0.97
f1 (ppm)
NCS
N
N
NO2
3q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131.5
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129.9
129.3
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127.9
127.0
124.1
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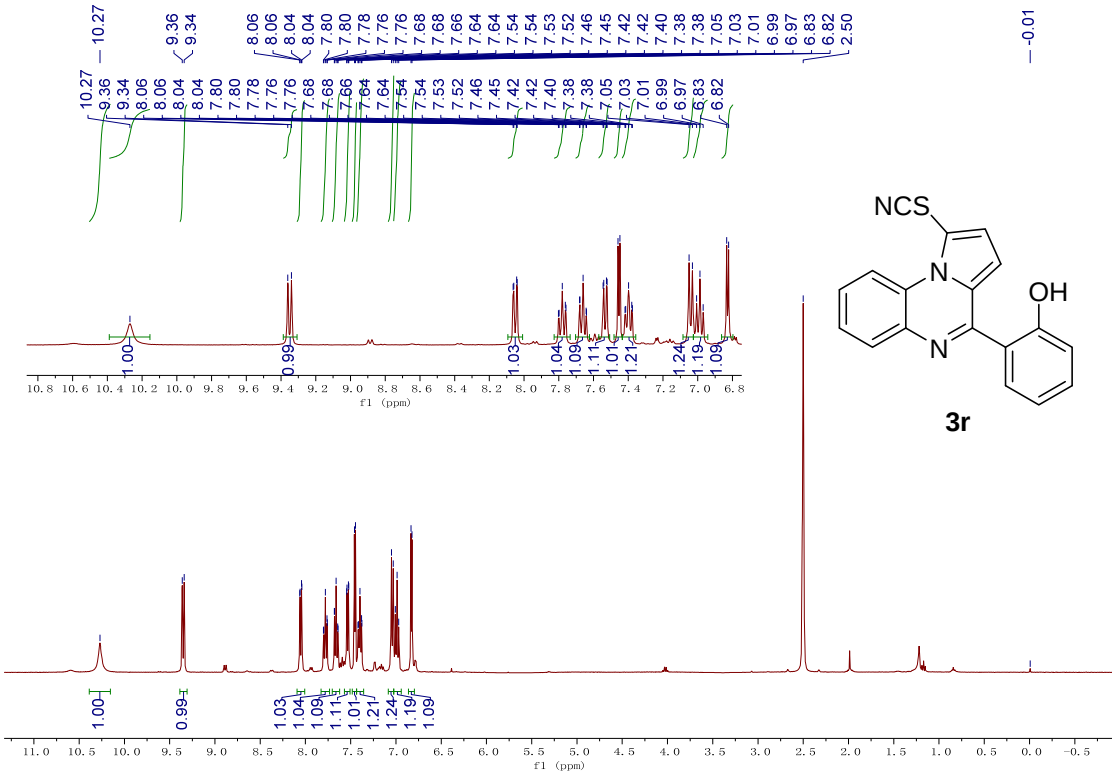
108.9
105.8
77.5
77.2
76.8
NCS
N
N
NO2
3q
f1 (ppm)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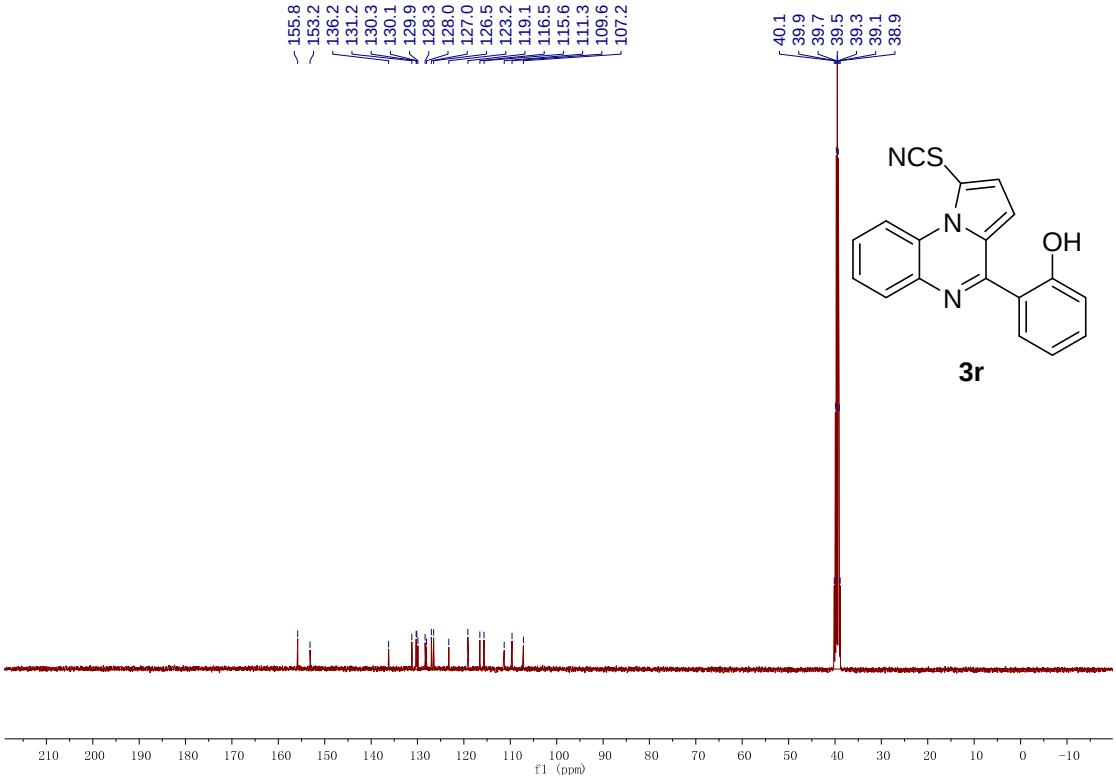
OH
3r
f1 (ppm)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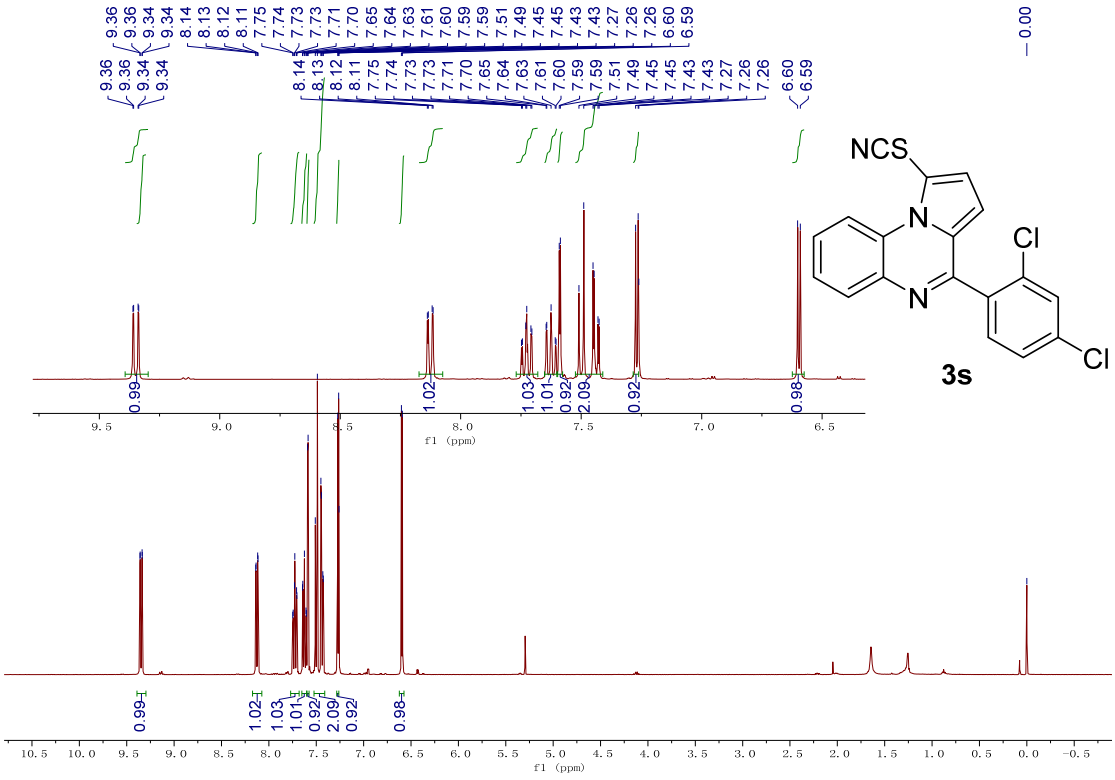
N
OH
3r
f1 (ppm)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Cl
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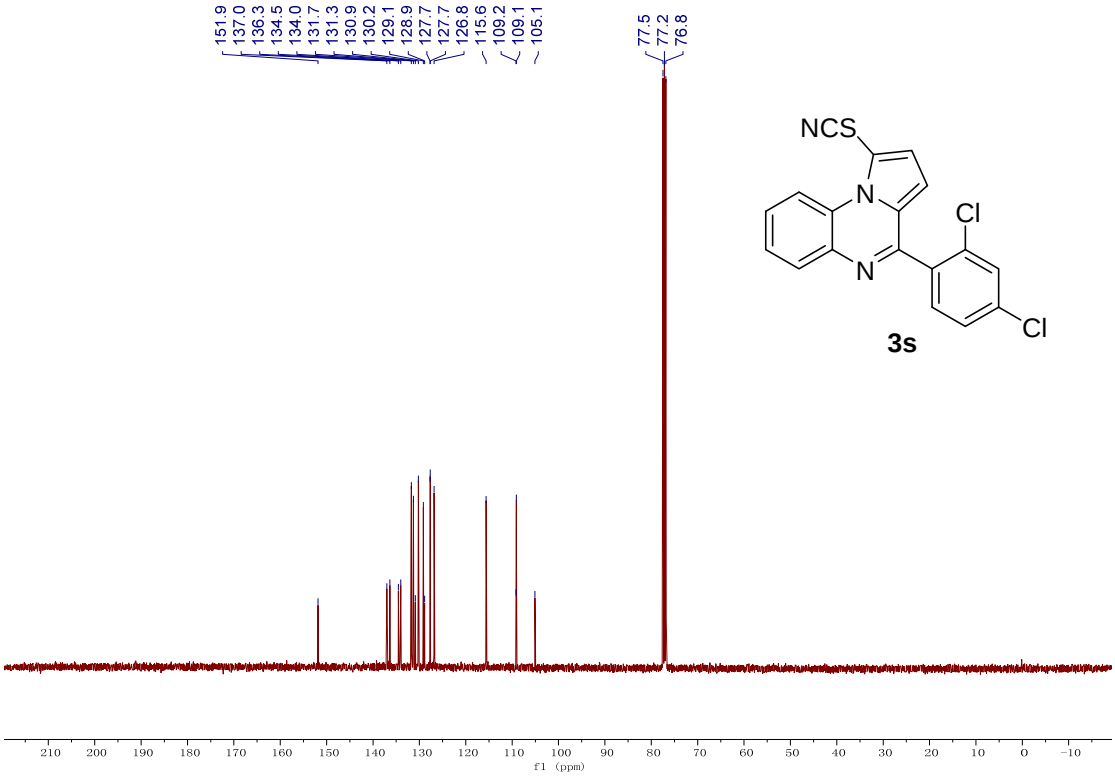
f1 (ppm)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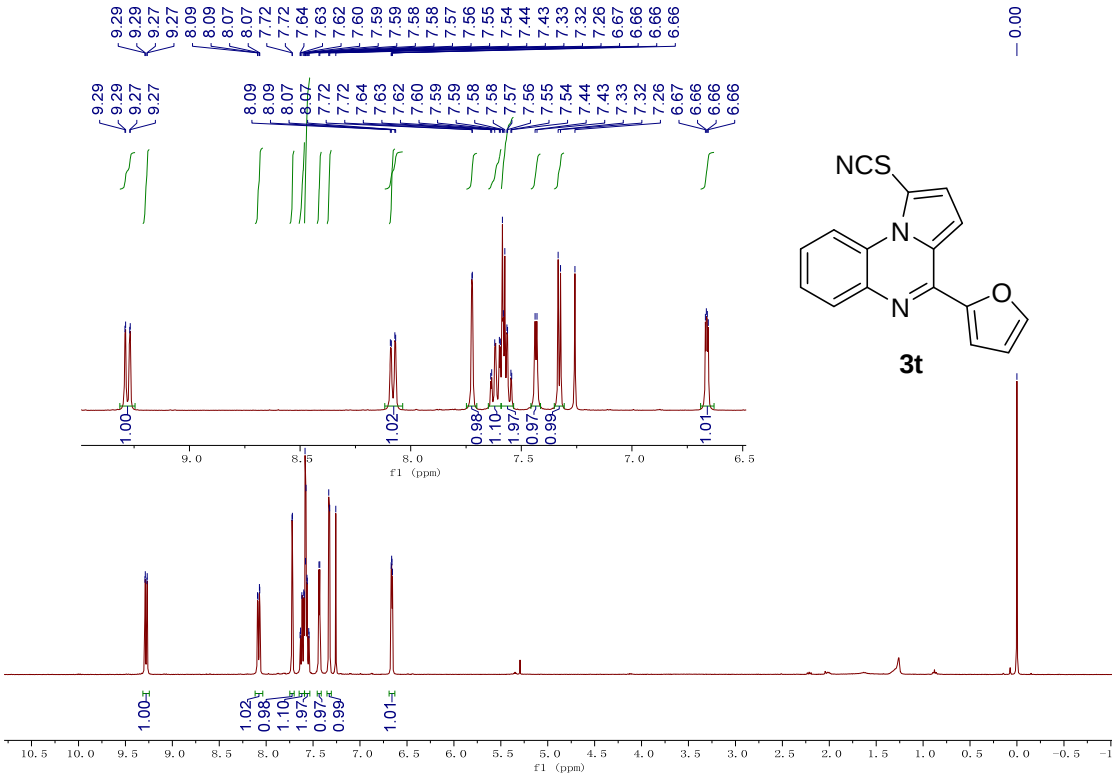
N
Cl
Cl
3s
f1 (ppm)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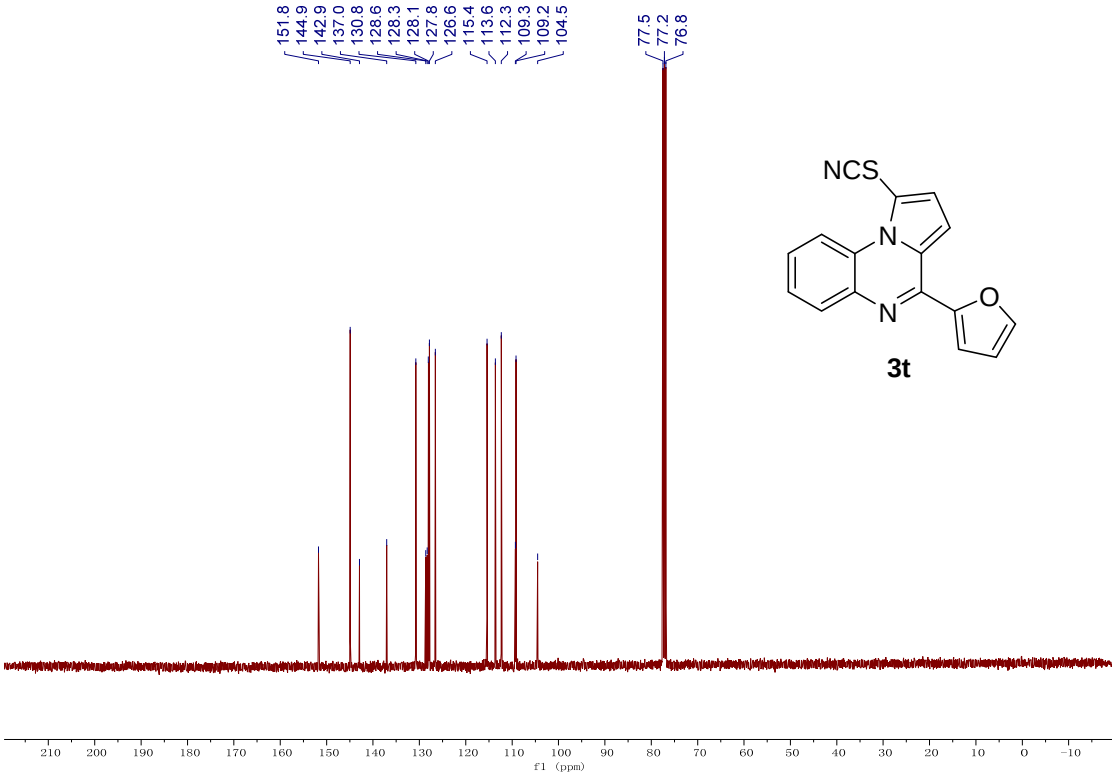
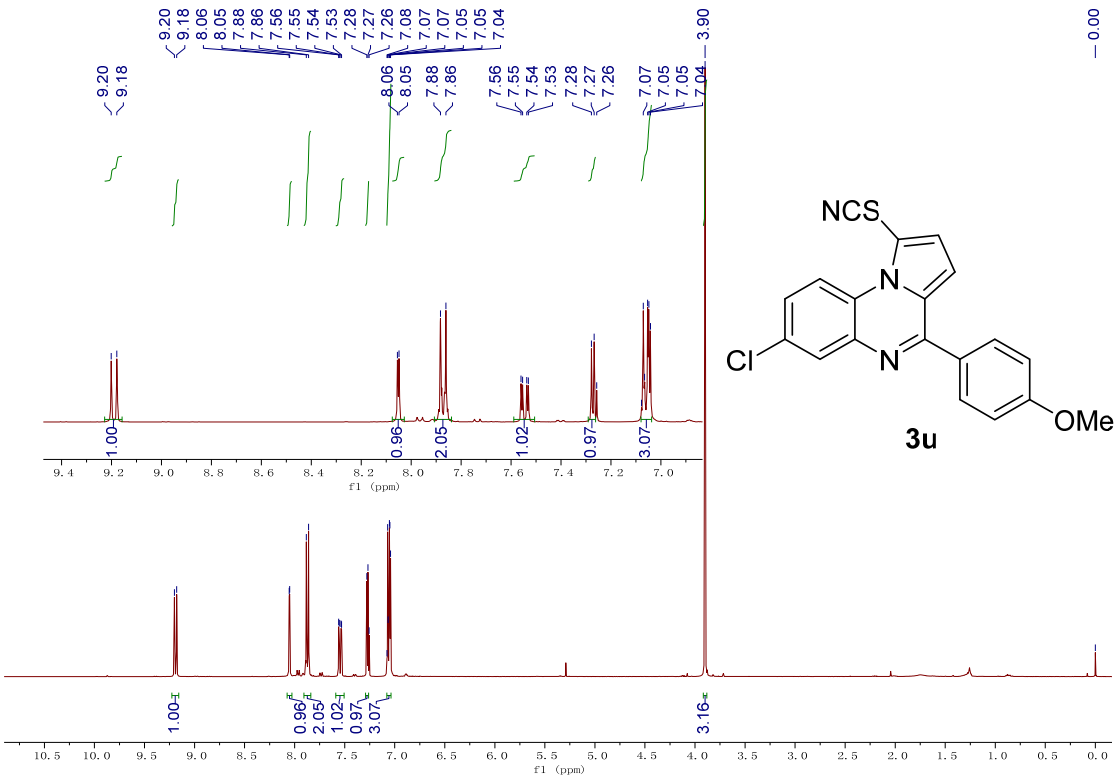
N
N
O
3t
1.00 1.02 0.98 1.10 1.97 0.97 0.99 1.01
f1 (ppm)


151.8 144.9 142.9 137.0 130.8 128.6 128.3 128.1 127.8 126.6 115.4 113.6 112.3 109.3 109.2 104.5
77.5 77.2 76.8
NCS
N
N
O
3t
f1 (ppm)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7.08
7.07
7.07
7.05
7.05
7.04
7.07
7.05
7.05
7.04
3.90
0.00
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Cl
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OMe
3u
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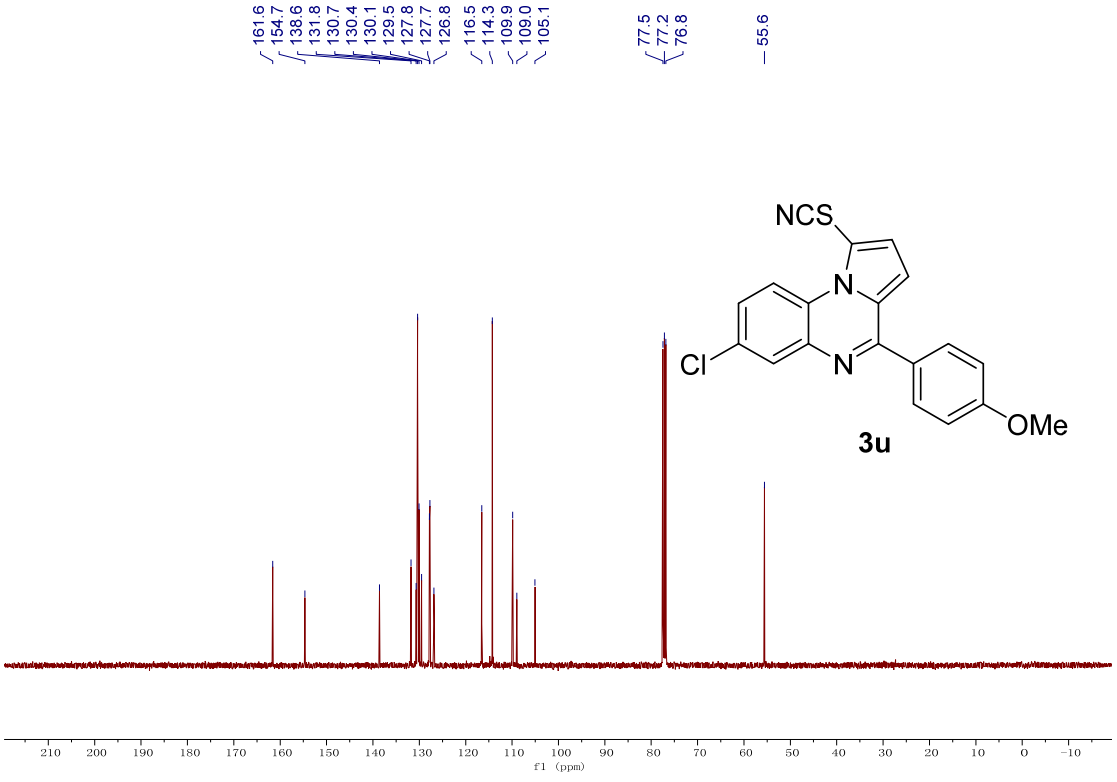
2.05
1.02
0.97
3.07
3.16
f1 (ppm)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131.8
130.7
130.4
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129.5
127.8
127.7
126.8
116.5
114.3
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109.0
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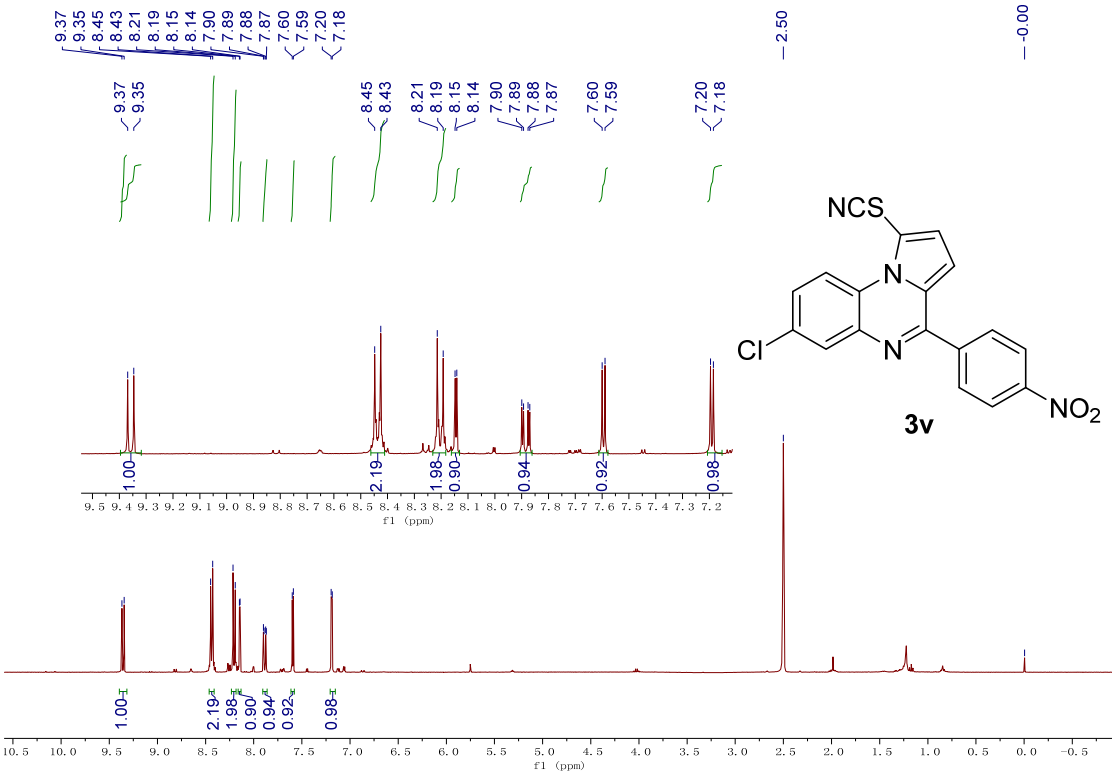
77.5
77.2
76.8
55.6
NCS
N
Cl
N
OMe
3u
f1 (ppm)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7.20
7.18
2.50
0.00
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Cl
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NO2
3v
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2.19
1.98
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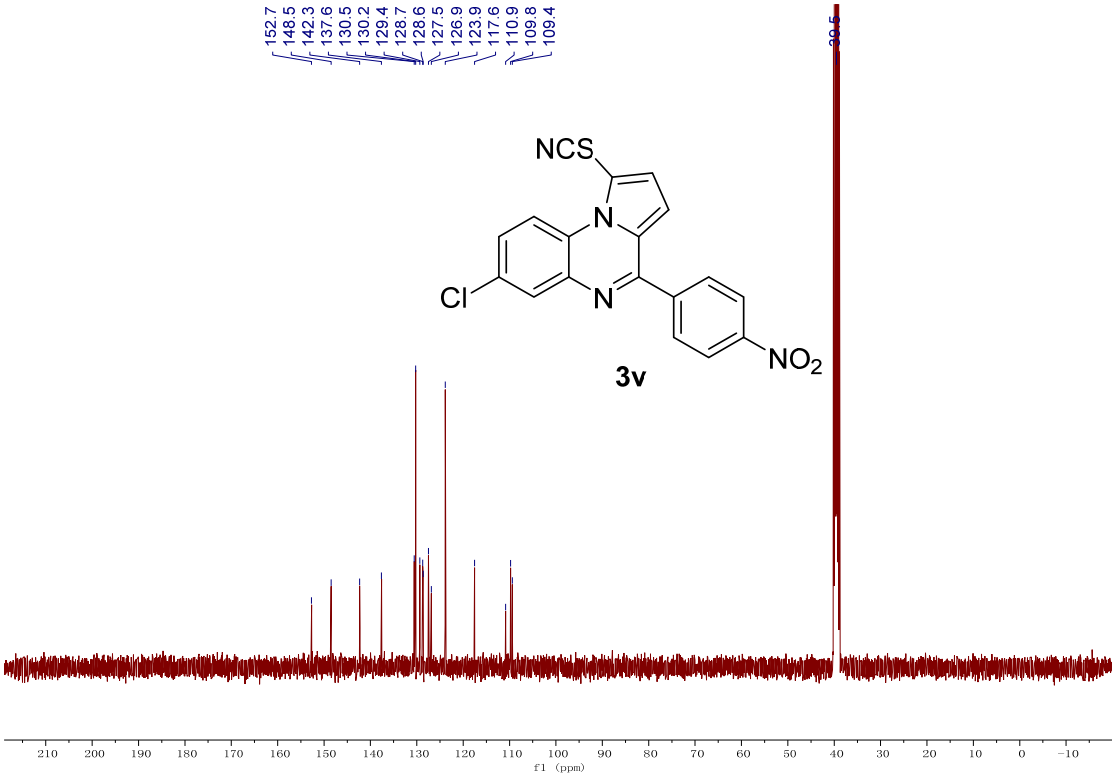
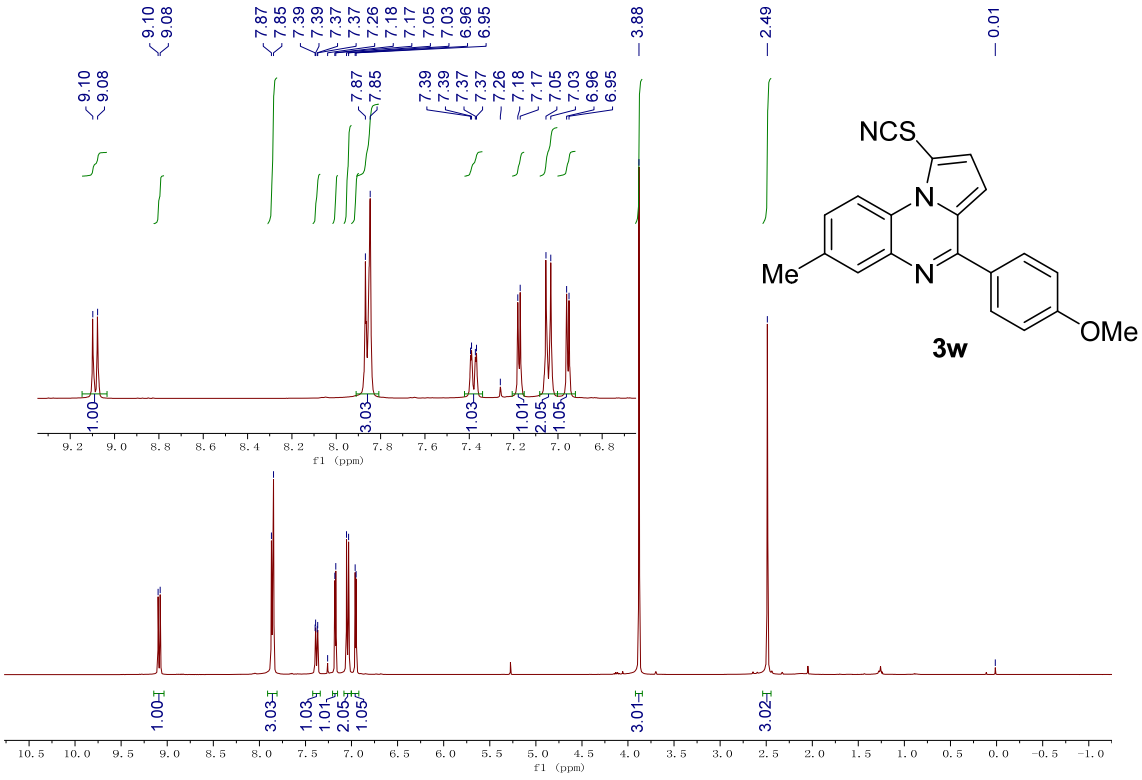
0.94
0.92
0.98
f1 (ppm)


152.7
148.5
142.3
137.6
130.5
130.2
129.4
128.7
128.6
127.5
126.9
123.9
117.6
110.9
109.8
109.4
39.5
NCS
N
Cl
N
NO2
3v
f1 (ppm)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6.95
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2.49
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1.05
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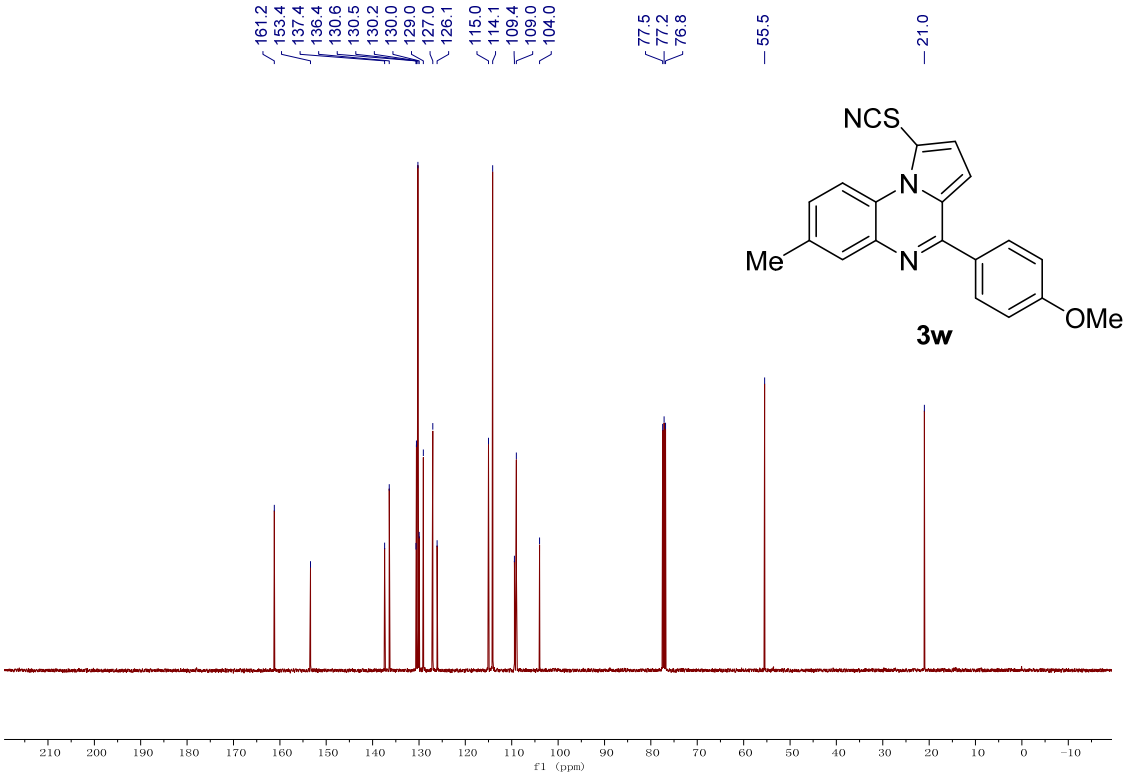
3.02
f1 (ppm)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127.0
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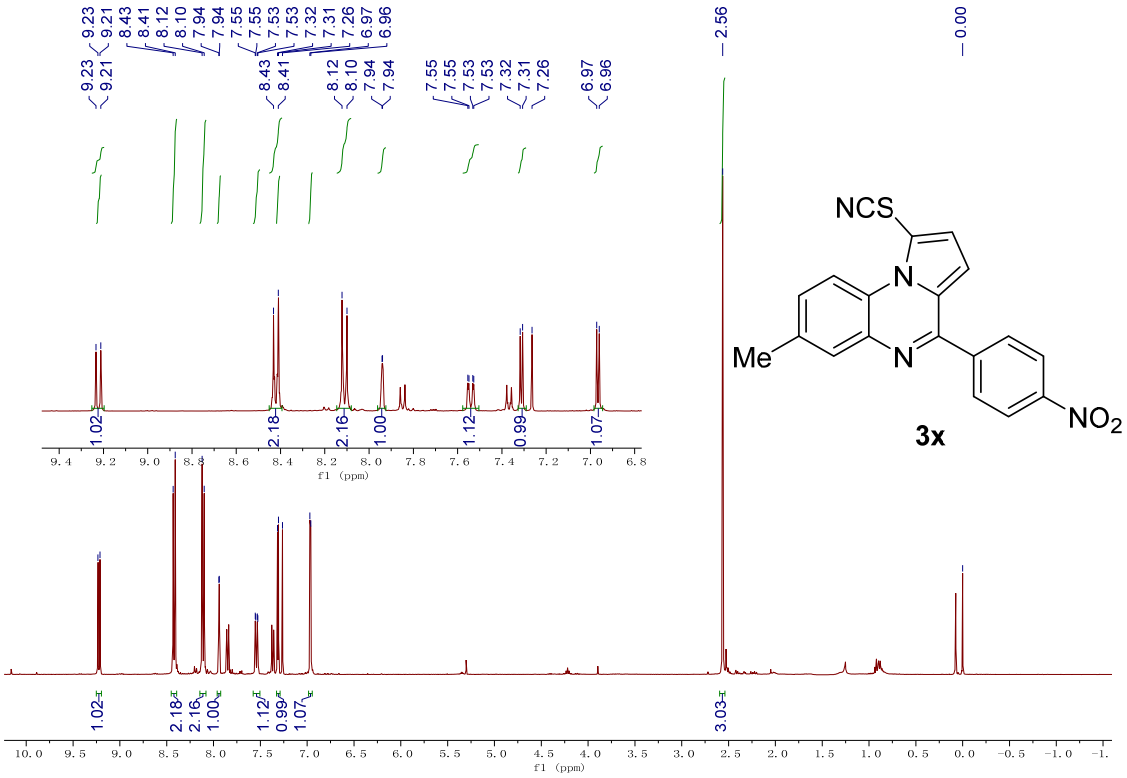
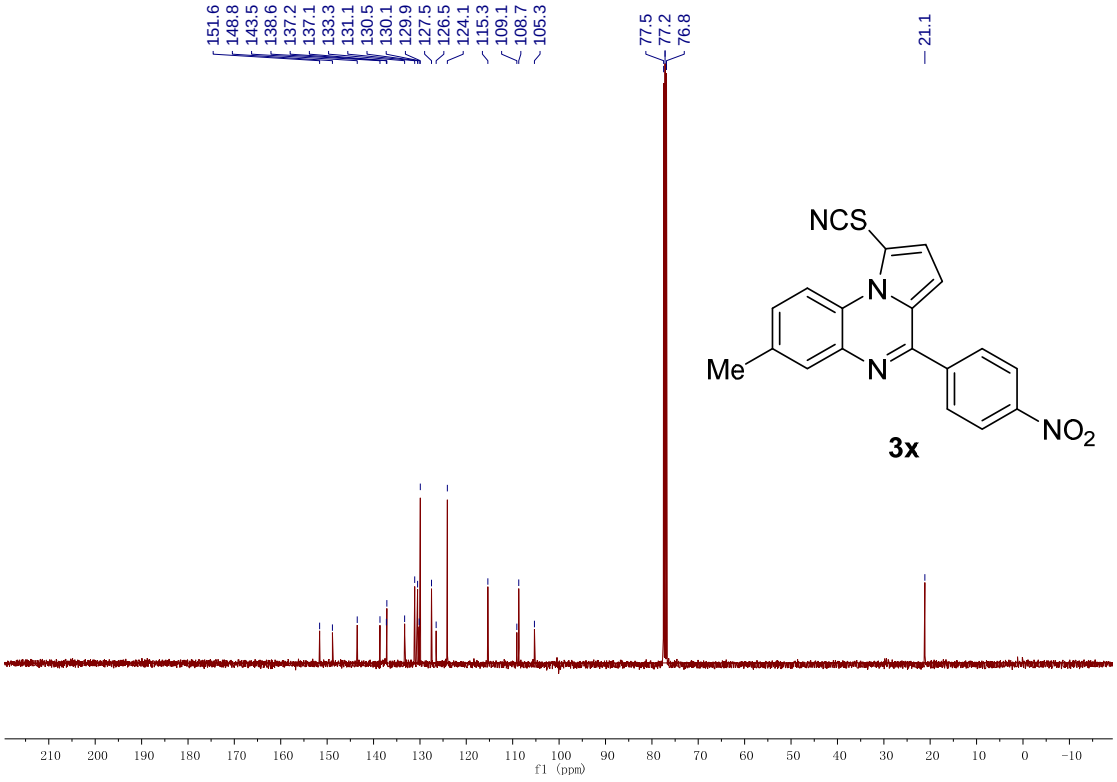
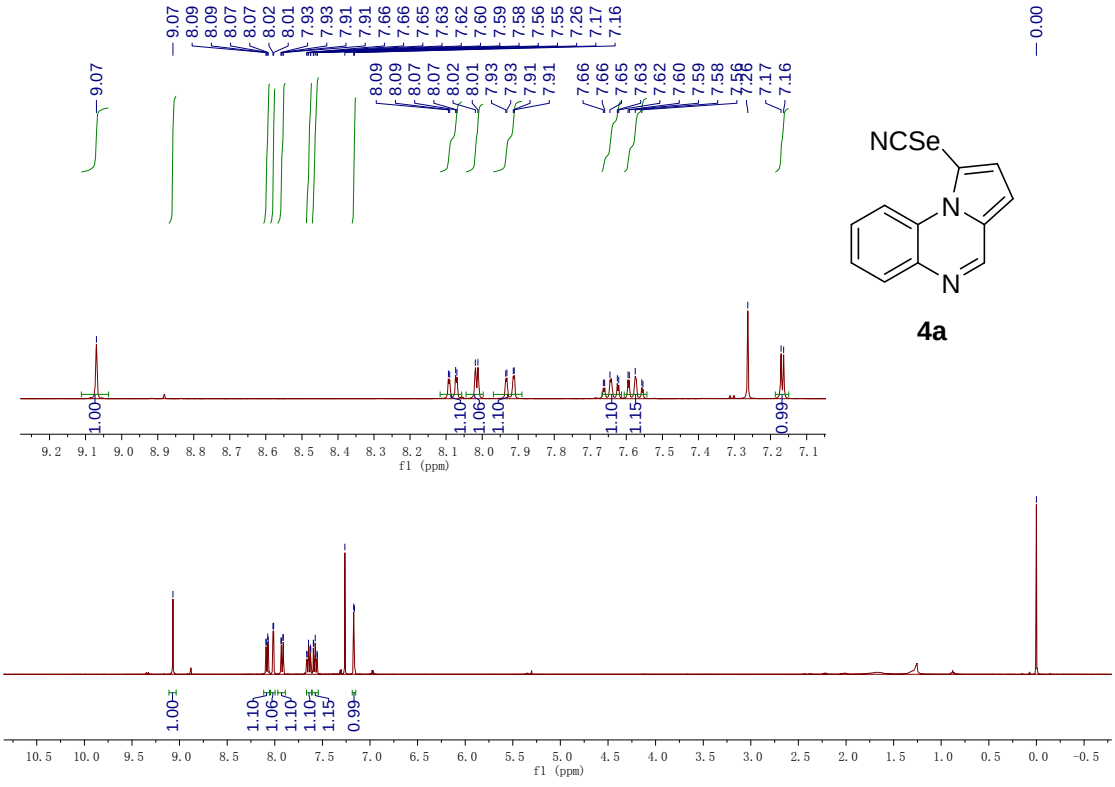
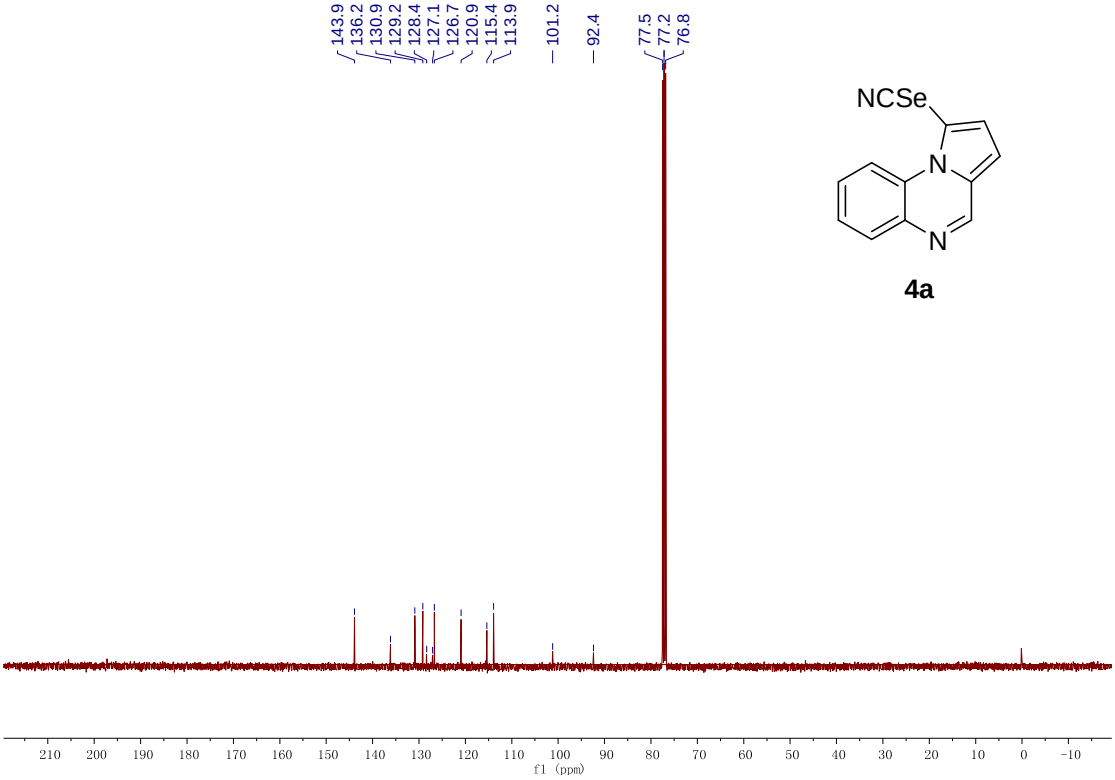
114.1
109.4
109.0
104.0
77.5
77.2
76.8
55.5
21.0
NCS
N
Me
N
OMe
3w
f1 (ppm)

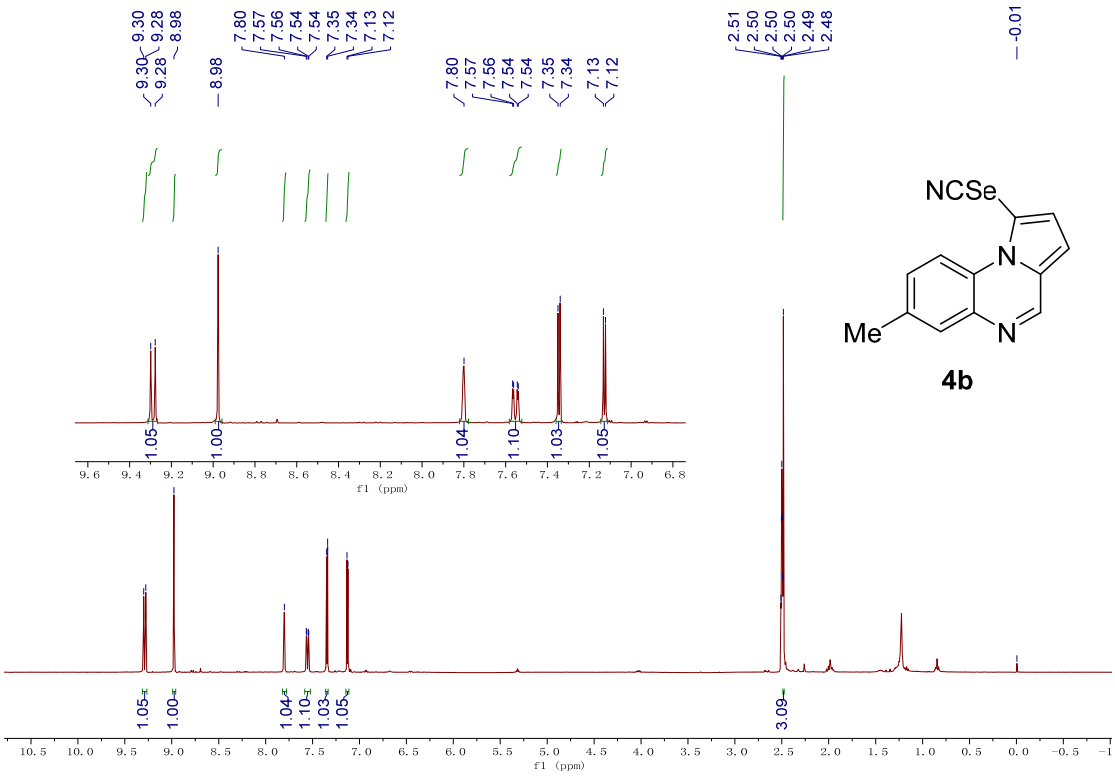

9.23
9.21
8.43
8.41
8.12
8.10
7.94
7.94
7.55
7.55
7.53
7.53
7.32
7.31
7.26
6.97
6.96
2.56
0.00
NCS
N
Me
N
NO2
3x
1.02
2.18
2.16
1.00
1.12
0.99
1.07
3.03
f1 (ppm)


151.6
148.8
143.5
138.6
137.2
137.1
133.3
131.1
130.5
130.1
129.9
127.5
126.5
124.1
115.3
109.1
108.7
105.3
77.5
77.2
76.8
21.1
NCS
N
Me
N
NO2
3x
f1 (ppm)

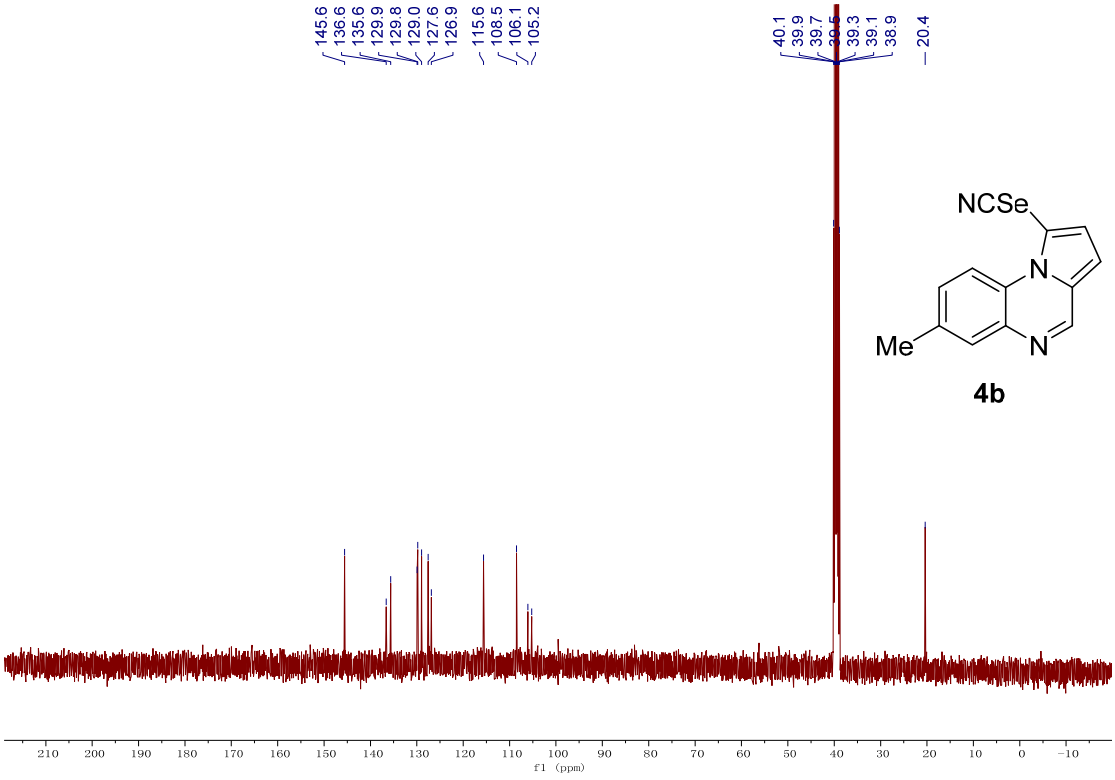

9.07
8.09
8.09
8.07
8.07
8.02
8.01
7.93
7.93
7.91
7.91
7.66
7.66
7.65
7.63
7.62
7.60
7.59
7.58
7.56
7.55
7.26
7.17
7.16
0.00
NCSe
N
N
4a
1.00
1.10
1.06
1.10
1.15
0.99
f1 (ppm)

1.00
1.10
1.06
1.10
1.10
1.15
0.99
f1 (ppm)

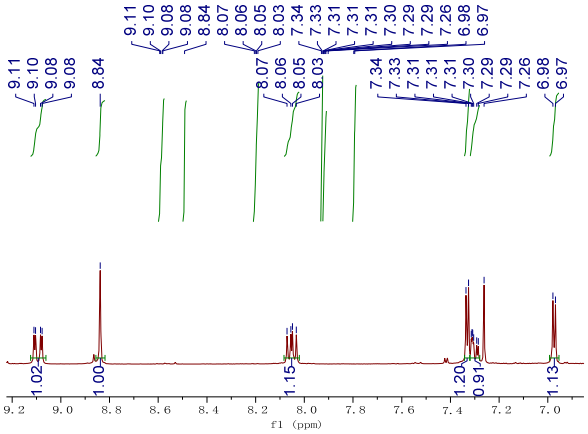

143.9
136.2
130.9
129.2
128.4
127.1
126.7
120.9
115.4
113.9
101.2
92.4
77.5
77.2
76.8
NCSe
N
N
4a
f1 (ppm)

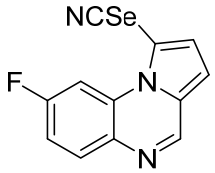

9.30
9.28
8.98
7.80
7.57
7.56
7.54
7.54
7.35
7.34
7.13
7.12
2.51
2.50
2.50
2.50
2.49
2.48
-0.01
1.05
1.00
1.04
1.10
1.03
1.05
3.09
f1 (ppm)
NCSe
N
Me
N

4b

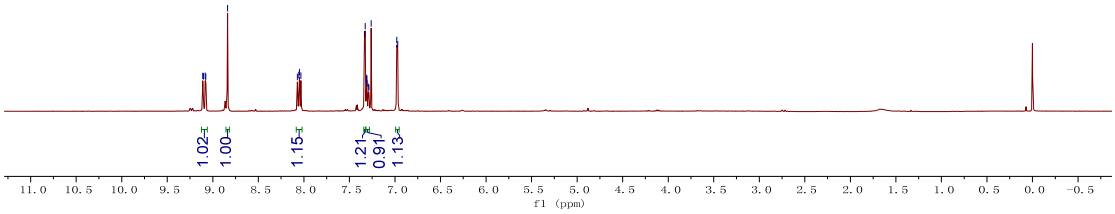

145.6
136.6
135.6
129.9
129.8
129.0
127.6
126.9
115.6
108.5
106.1
105.2
40.1
39.9
39.7
39.5
39.3
39.1
38.9
20.4
f1 (ppm)
NCSe
N
Me
N

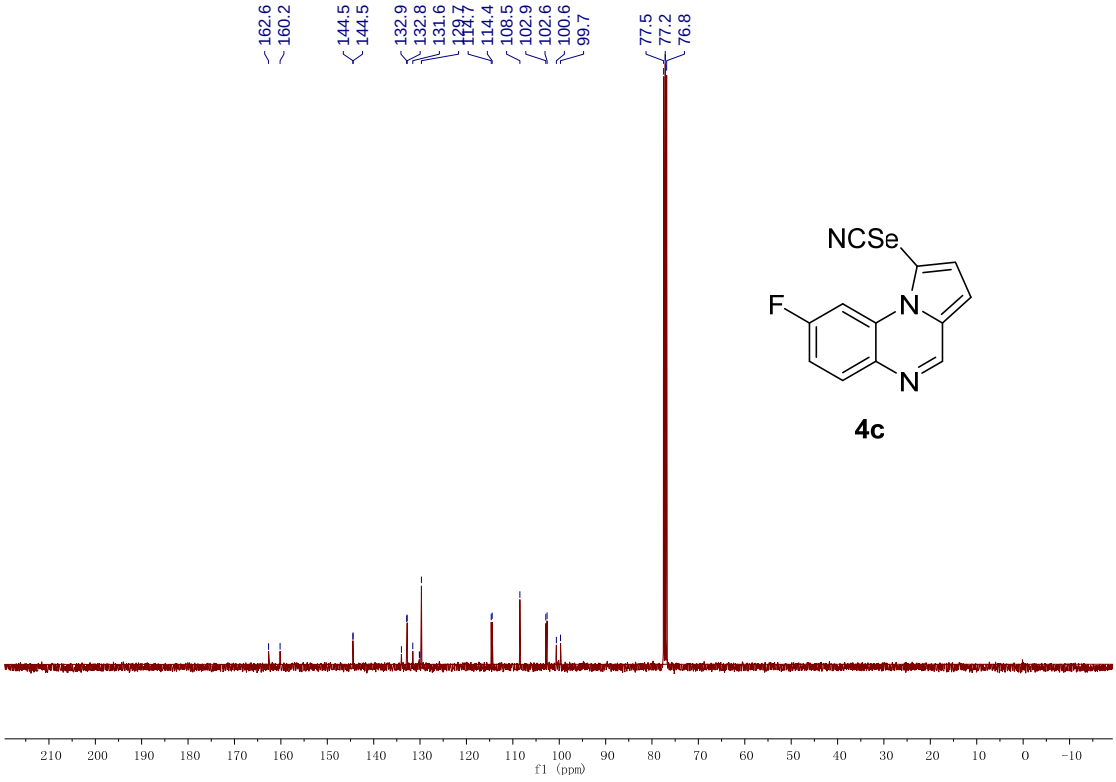
4b


9.11
9.10
9.08
9.08
8.84
8.07
8.06
8.05
8.03
7.34
7.33
7.31
7.31
7.30
7.29
7.26
6.98
6.97
1.02
1.00
1.15
1.20
0.91
1.13
f1 (ppm)


NCSe
F
N
N

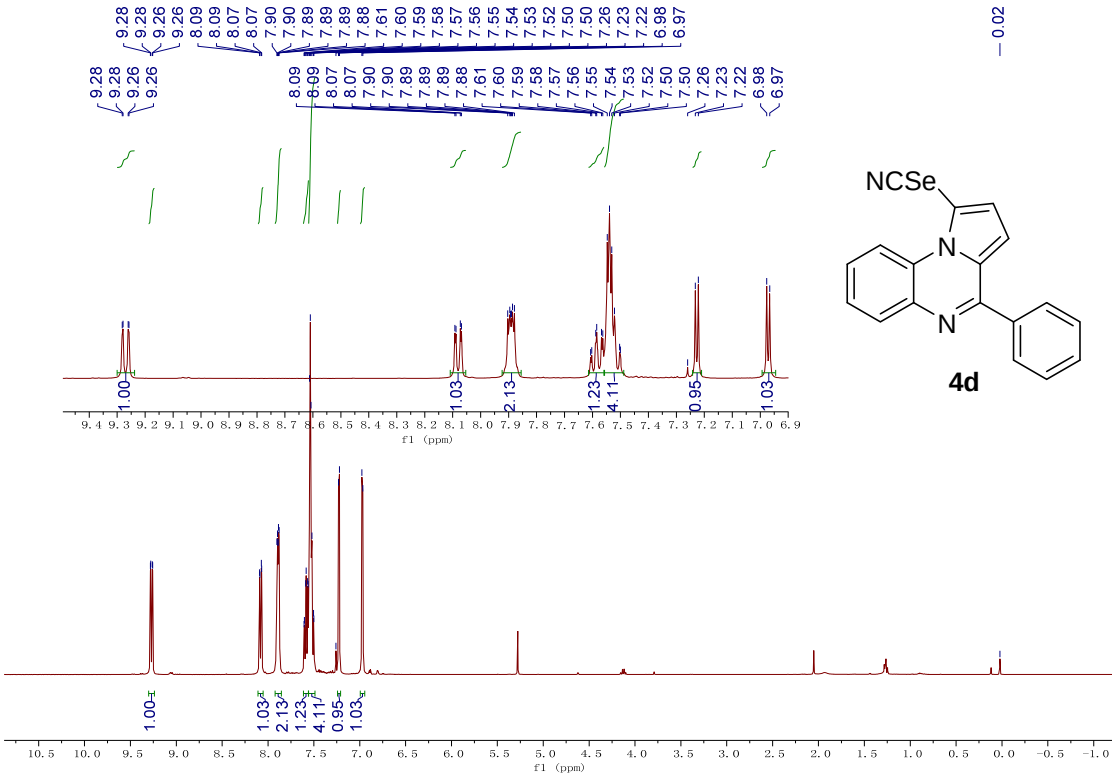
4c

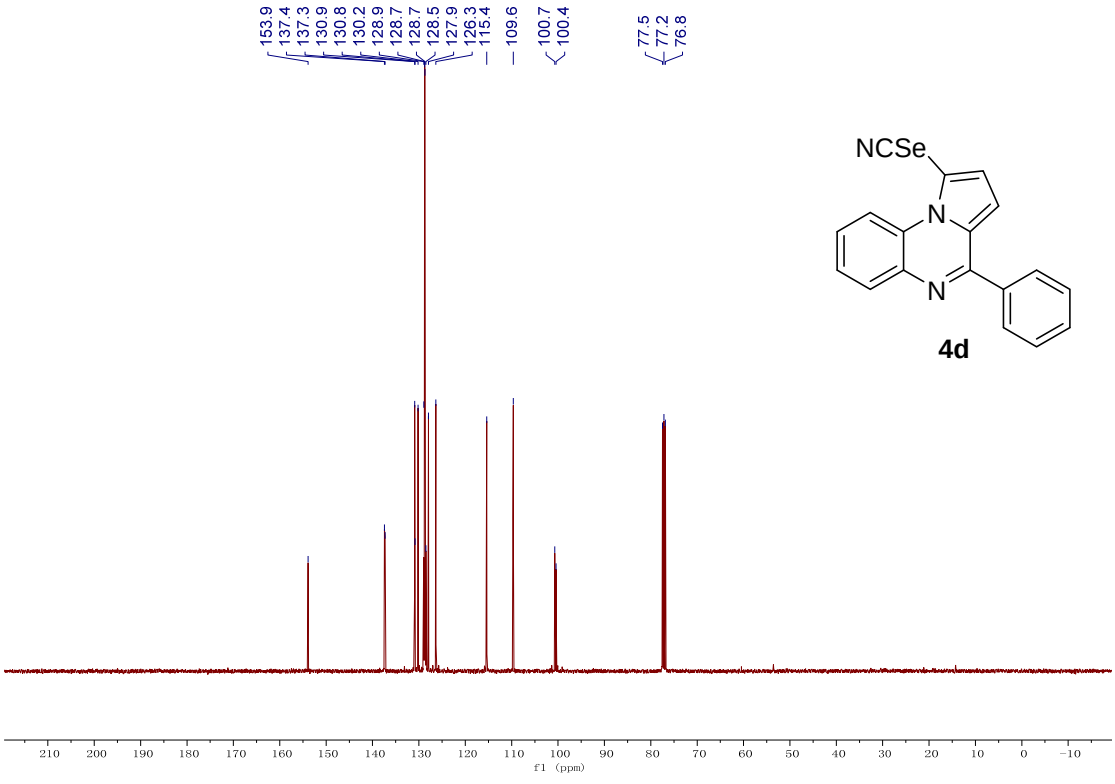

1.02
1.00
1.15
1.21
0.91
1.13
f1 (ppm)

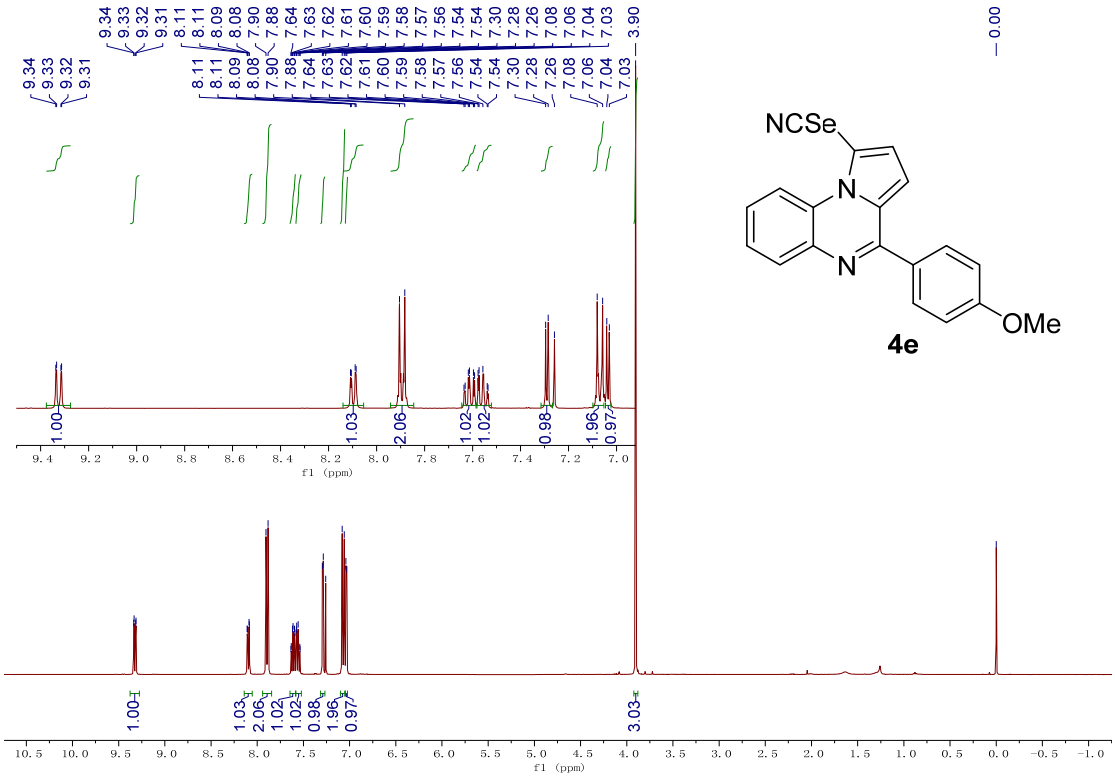

162.6
160.2
144.5
144.5
132.9
132.8
131.6
129.7
114.4
108.5
102.9
102.6
100.6
99.7
77.5
77.2
76.8
f1 (ppm)

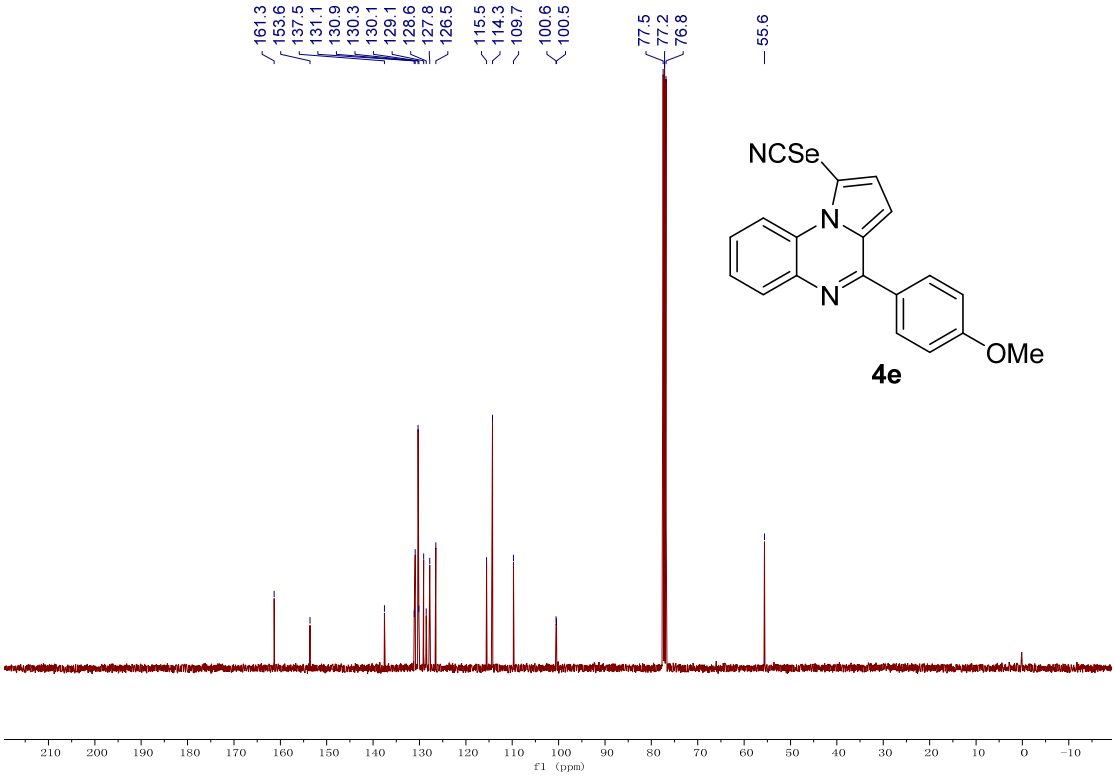
NCSe
F
N
N

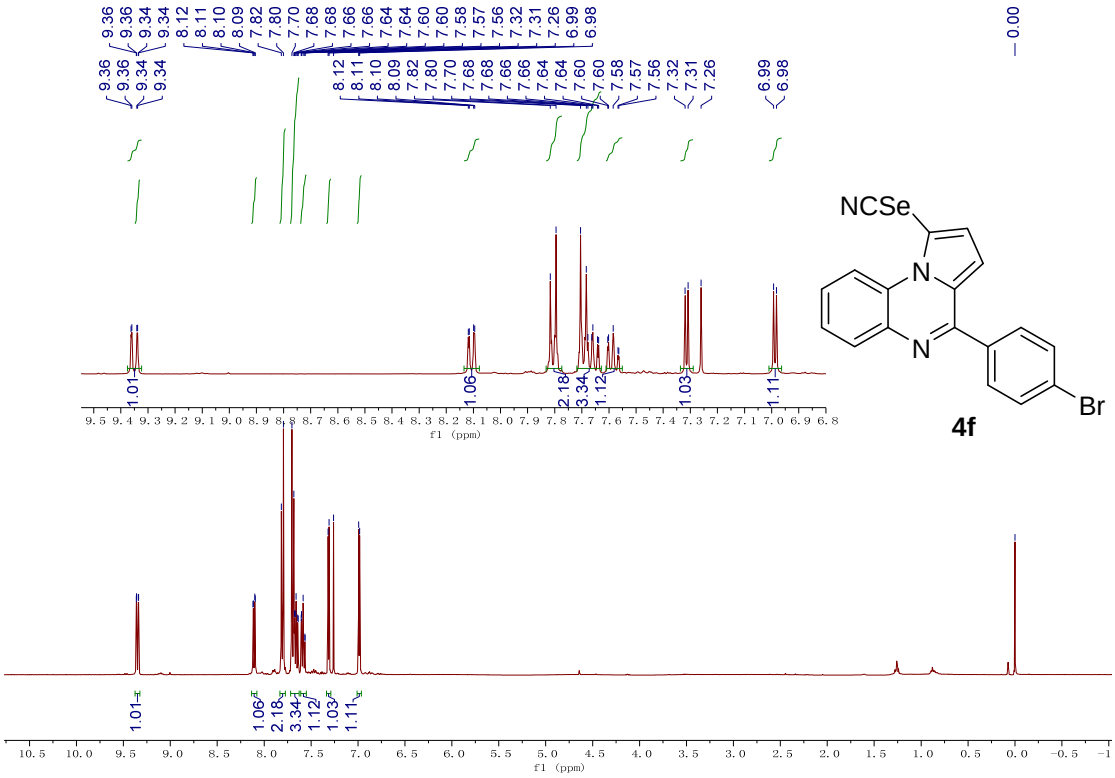
4c

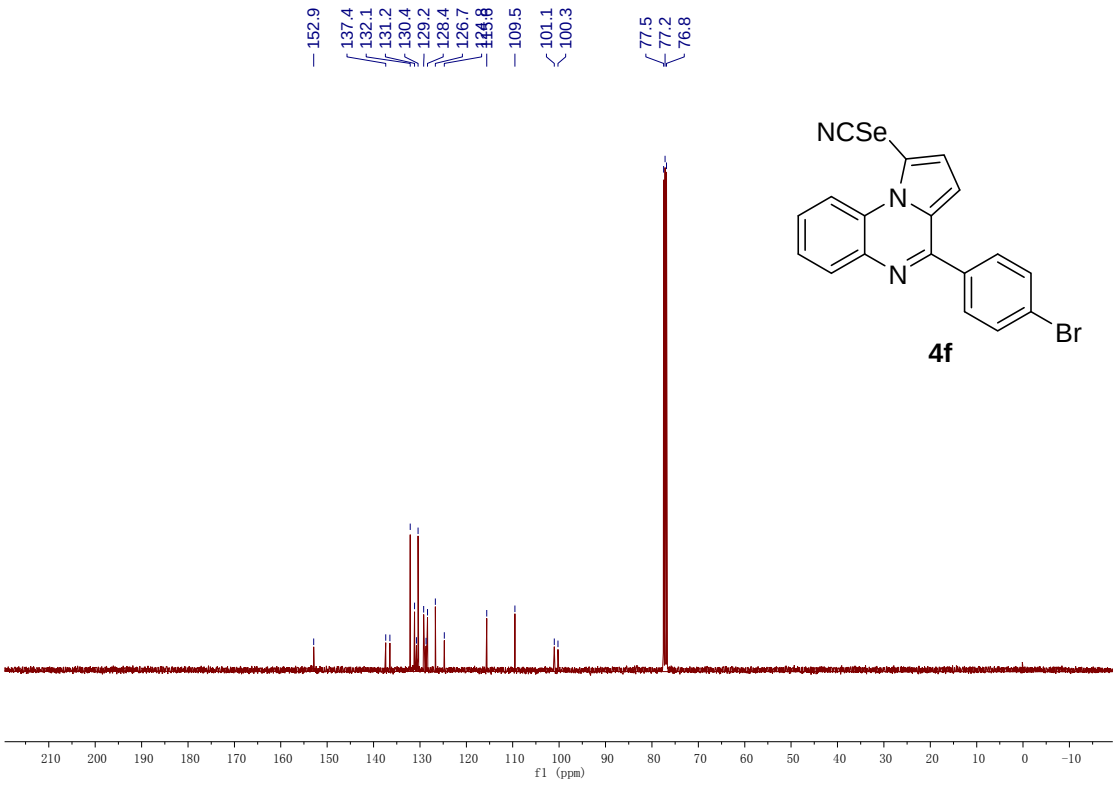

9.28
9.28
9.26
9.26
8.09
8.09
8.07
8.07
7.90
7.90
7.89
7.89
7.89
7.88
7.61
7.60
7.59
7.58
7.57
7.56
7.55
7.54
7.53
7.52
7.50
7.50
7.26
7.23
7.22
6.98
6.97
0.02
1.00
1.03
2.13
1.23
4.11
0.95
1.03
f1 (ppm)
NCSe
N
N
4d

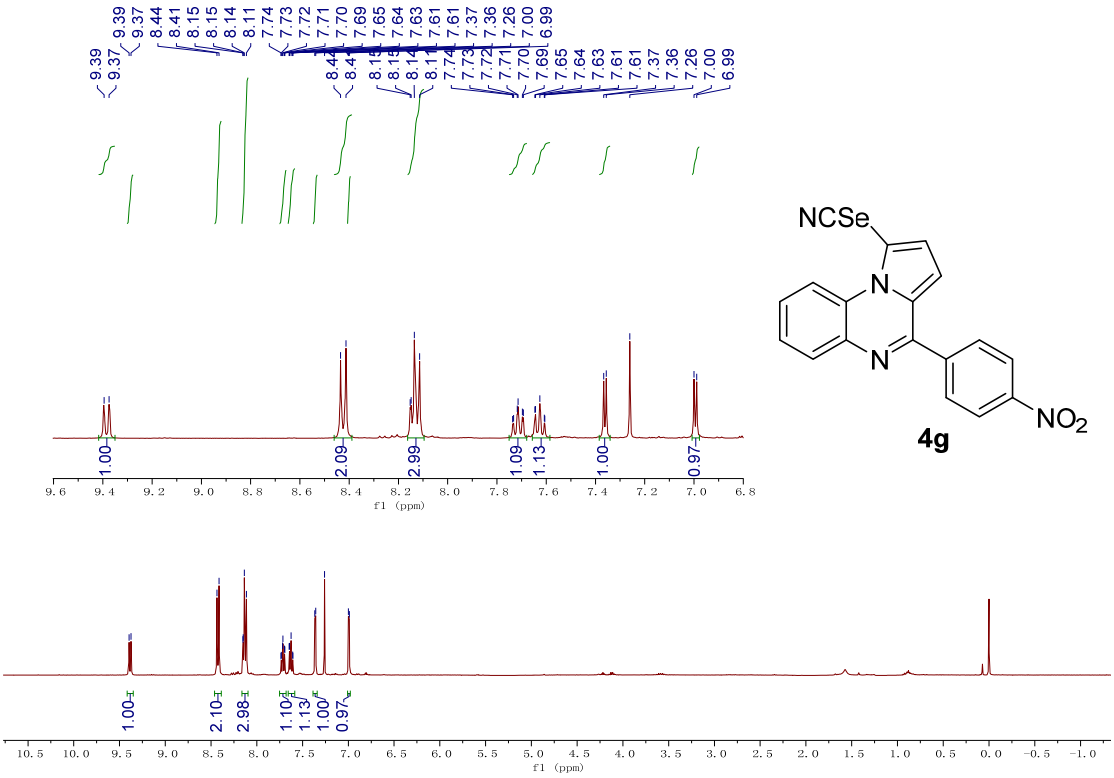

153.9
137.4
137.3
130.9
130.8
130.2
128.9
128.7
128.7
128.5
127.9
126.3
115.4
109.6
100.7
100.4
77.5
77.2
76.8
f1 (ppm)
NCSe
N
N
4d

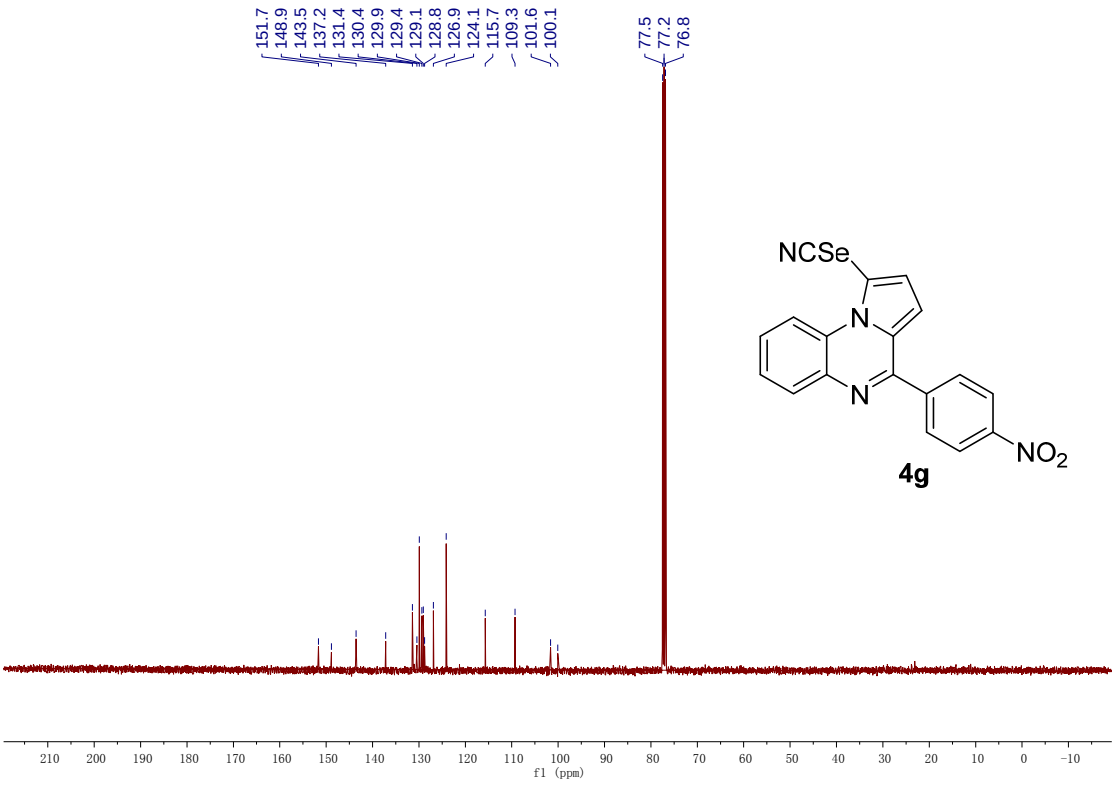

NCSe
N
N
OMe
4e
f1 (ppm)

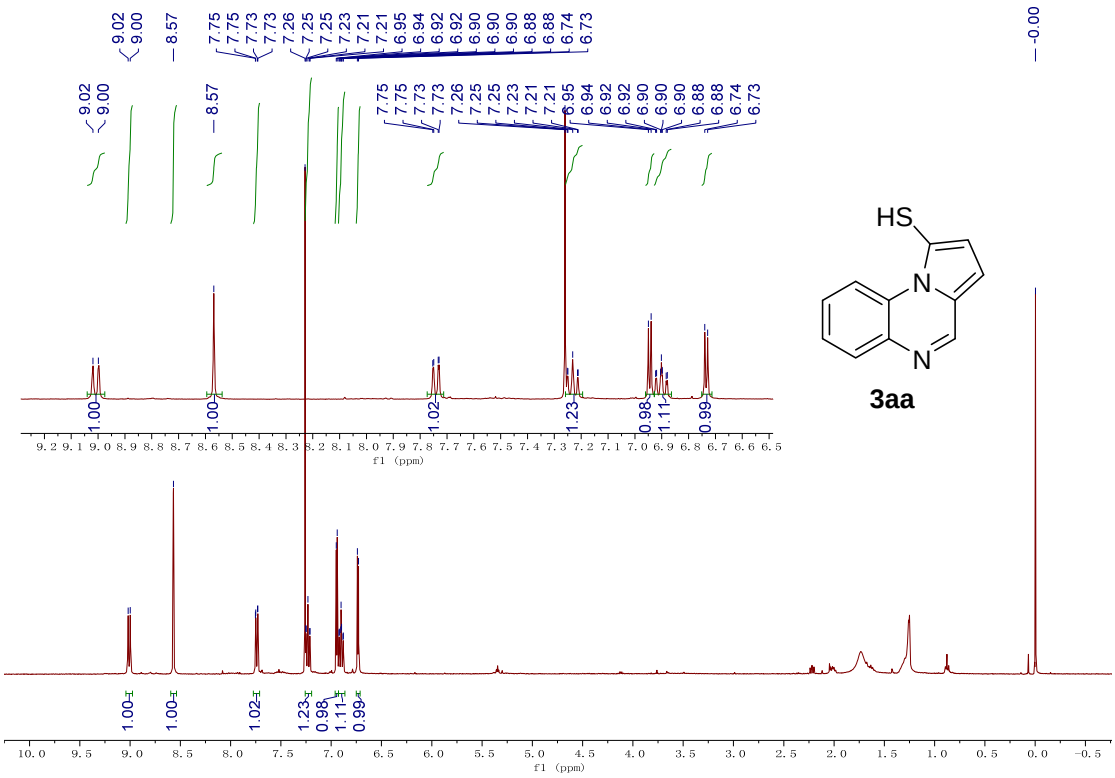

NCSe
N
N
OMe
4e
f1 (ppm)

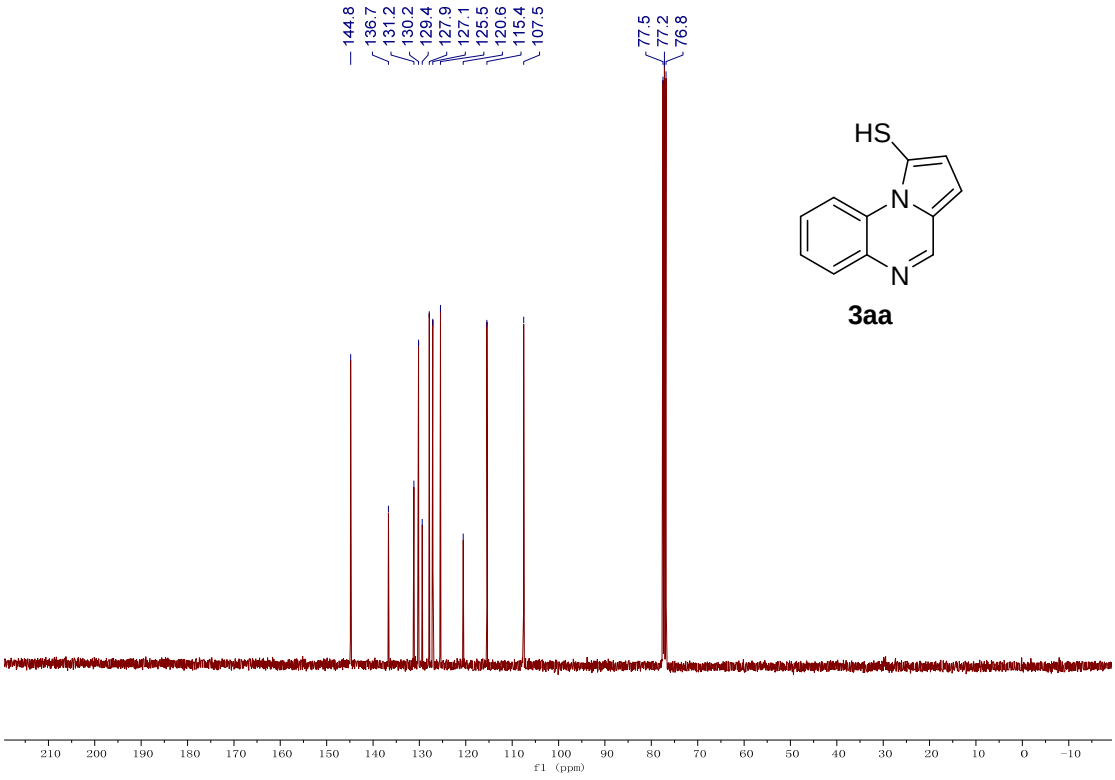

9.36
9.36
9.34
9.34
8.12
8.11
8.10
8.09
7.82
7.80
7.70
7.68
7.68
7.66
7.66
7.64
7.64
7.60
7.60
7.58
7.57
7.56
7.32
7.31
7.26
6.99
6.98
0.00
1.01
1.06
2.18
3.34
1.12
1.03
1.11
f1 (ppm)
NCSe
N
N
Br
4f

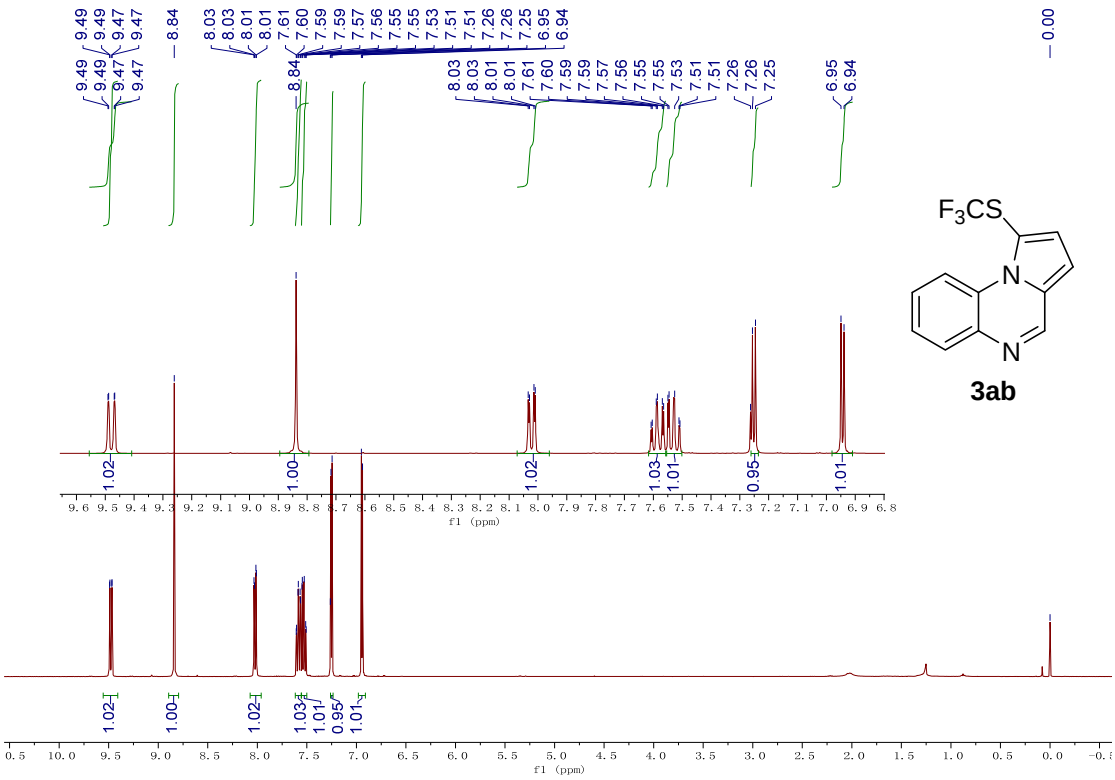

152.9
137.4
132.1
131.2
130.4
129.2
128.4
126.7
109.5
101.1
100.3
77.5
77.2
76.8
f1 (ppm)
NCSe
N
N
Br
4f


9.39
9.37
8.44
8.41
8.15
8.14
8.11
7.74
7.73
7.72
7.71
7.70
7.69
7.65
7.64
7.63
7.61
7.37
7.36
7.26
7.00
6.99
NCSe
N
N
NO2
4g
1.00
2.09
2.99
1.09
1.13
1.00
0.97
f1 (ppm)


151.7
148.9
143.5
137.2
131.4
130.4
129.9
129.4
129.1
128.8
126.9
124.1
115.7
109.3
101.6
100.1
77.5
77.2
76.8
NCSe
N
N
NO2
4g
f1 (ppm)

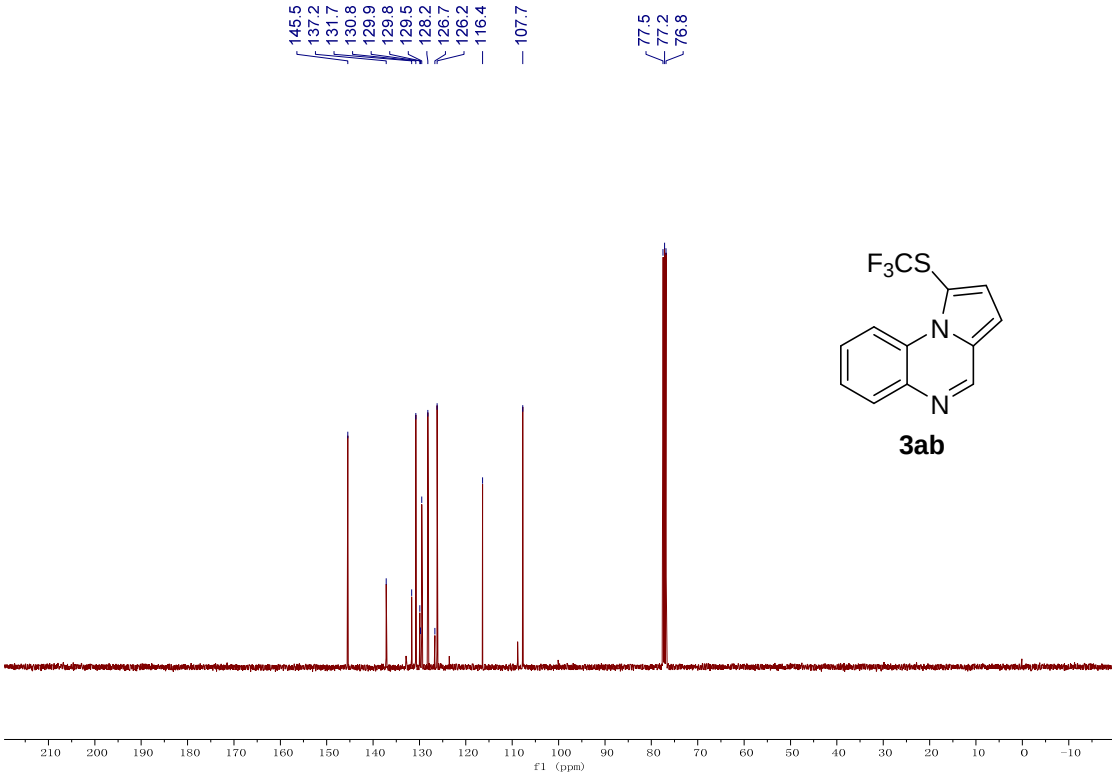

9.02
9.00
8.57
7.75
7.75
7.73
7.73
7.26
7.25
7.25
7.23
7.21
7.21
6.95
6.94
6.92
6.92
6.90
6.90
6.90
6.88
6.88
6.74
6.73
-0.00
1.00
1.00
1.02
1.23
0.98
1.11
0.99
f1 (ppm)
HS
N
N
3aa


144.8
136.7
131.2
130.2
129.4
127.9
127.1
125.5
120.6
115.4
107.5
77.5
77.2
76.8
f1 (ppm)
HS
N
N
3aa


9.49
9.49
9.47
9.47
8.84
8.03
8.03
8.01
8.01
7.61
7.60
7.59
7.59
7.57
7.56
7.55
7.55
7.53
7.51
7.51
7.26
7.26
7.25
6.95
6.94
0.00
1.02
1.00
1.02
1.03
1.01
0.95
1.01
f1 (ppm)

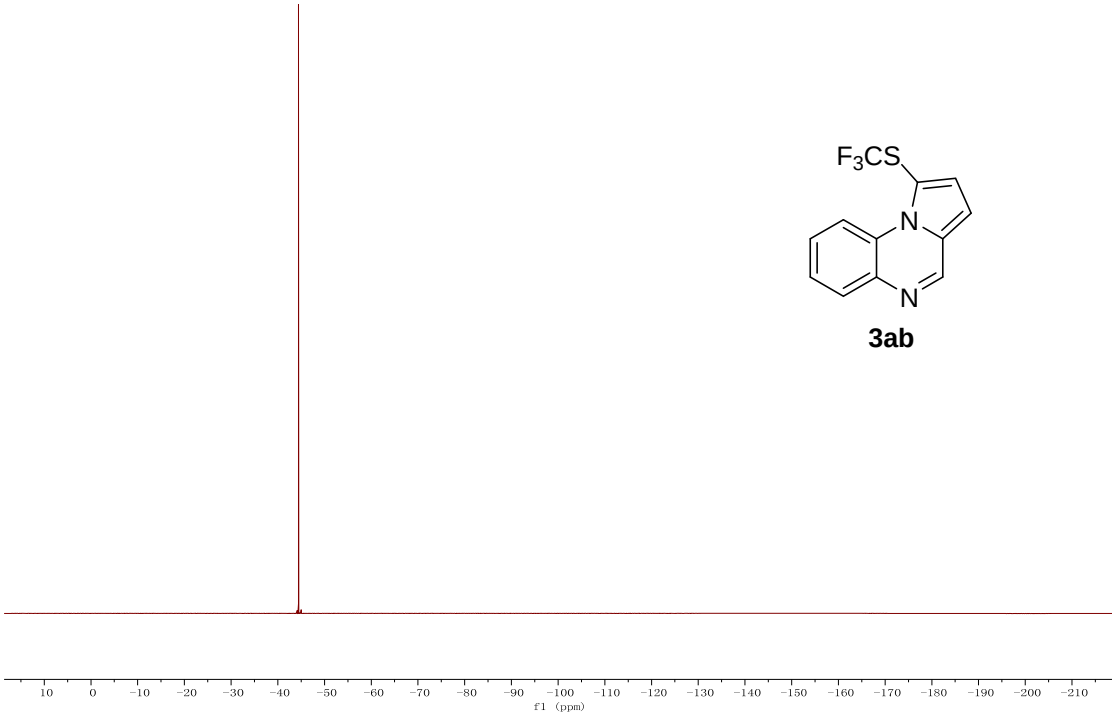
F3CS
N
N

3ab

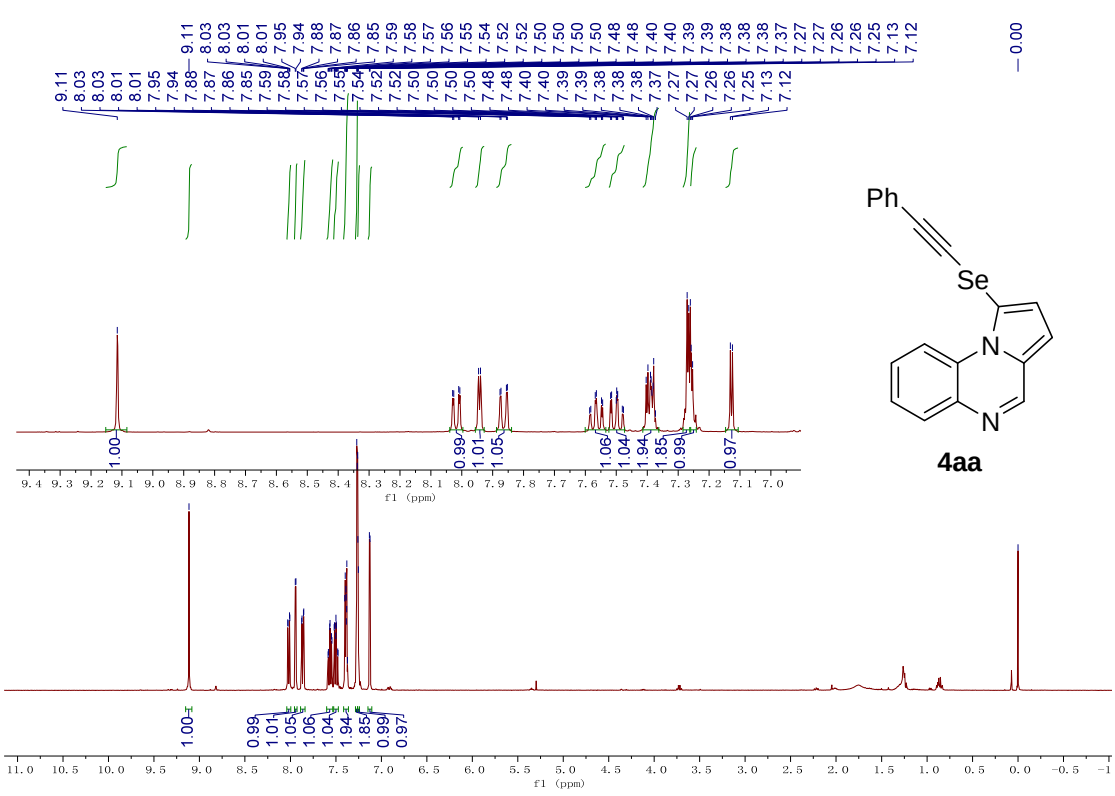

145.5
137.2
131.7
130.8
129.9
129.8
129.5
128.2
126.7
126.2
116.4
107.7
77.5
77.2
76.8
f1 (ppm)

F3CS
N
N

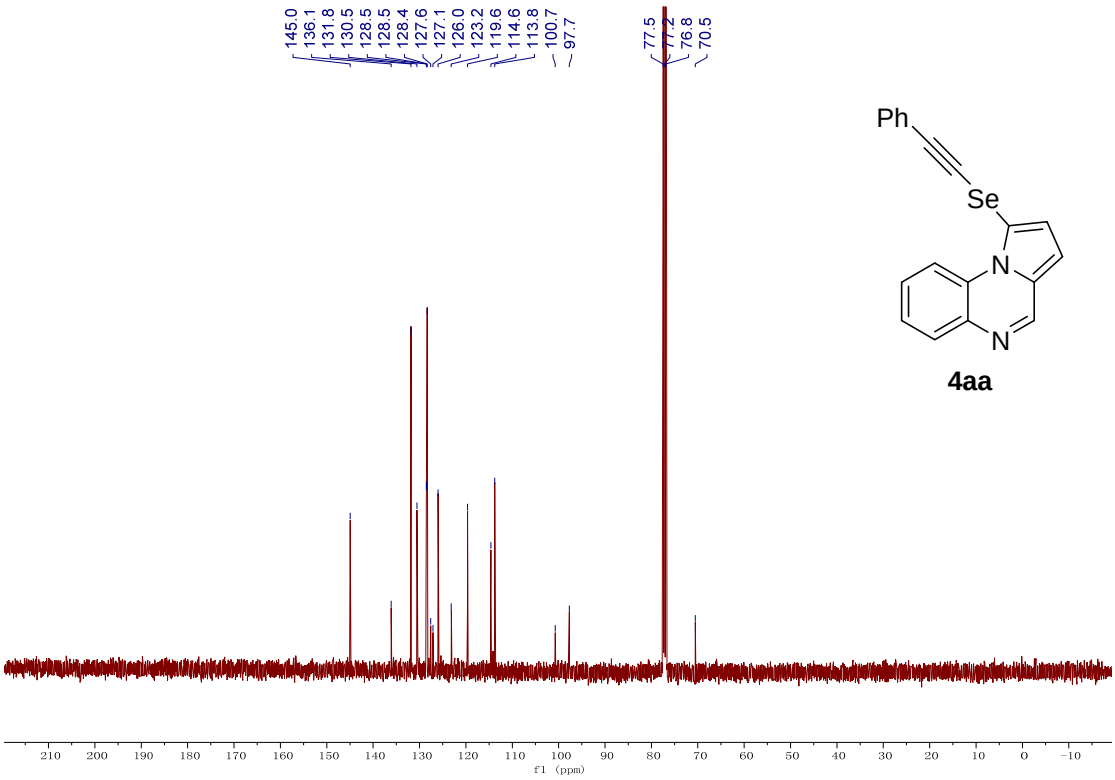
3ab



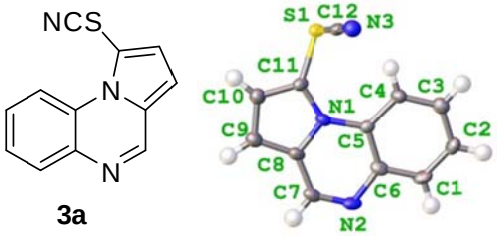
3ab



4aa


145.0
136.1
131.8
130.5
128.5
128.5
128.4
127.6
127.1
126.0
123.2
119.6
114.6
113.8
100.7
97.7
77.5
77.2
76.8
70.5
Ph
Se
N
N
4aa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

Single Crystal Data of 3a



3a

Structure of **3a** (CCDC: 1943642)

Table 1 Crystal data and structure refinement for 3a

Identification code	3a
Empirical formula	$C_{12}H_7N_3S$
Formula weight	225.27
Temperature/K	150.0
Crystal system	monoclinic
Space group	Pn
a/Å	16.2160(5)
b/Å	8.5645(2)
c/Å	16.5649(5)
α/°	90
β/°	117.9340(10)
γ/°	90
Volume/Å^3	2032.52(10)
Z	8
ρ_{calc}g/cm^3	1.472
μ/mm^{-1}	0.289
F(000)	928.0
Crystal size/mm^3	0.16 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.756 to 52.758
Index ranges	-20 ≤ h ≤ 20, -10 ≤ k ≤ 9, -20 ≤ l ≤ 20
Reflections collected	18145
Independent reflections	7628 [R_{int} = 0.0540, R_{sigma} = 0.0683]
Data/restraints/parameters	7628/2/577
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.0869
Final R indexes [all data]	R_1 = 0.0683, wR_2 = 0.0997
Largest diff. peak/hole / e Å^{-3}	0.28/-0.27
Flack parameter	0.09(7)