Electronic Supplementary Information for

$AgNO_2$-mediated direct nitration of quinoxaline tertiary benzylic C-H bond and direct conversion of 2-methyl quinoxalines into related nitriles

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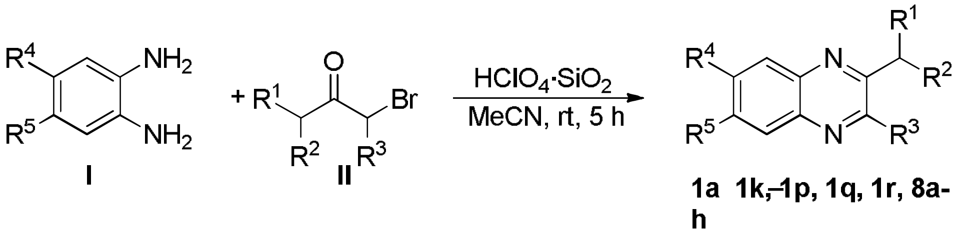
1. General Information

Melting points are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 500 at 25 °C in $CDCl_3$ at 500 MHz, 125 MHz, respectively, with TMS as internal standard. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. The IR spectra were recorded on an FT-IR spectrometer. GC-MS experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector with EI source, low and high resolution mass spectra (LRMS and HRMS) were obtained on a TOF MS instrument with EI or ESI source.

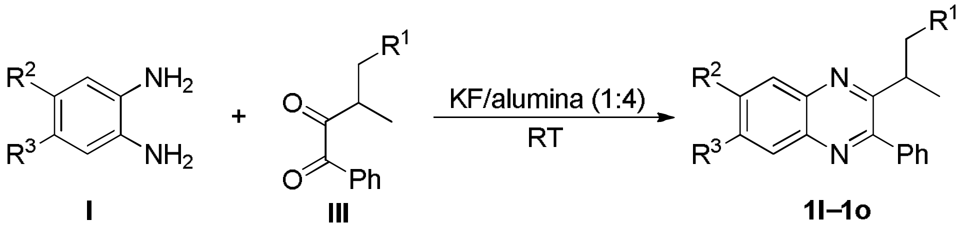
2. Preparation of Substituted Quinoxalines 1a–1k, 1p, 1q, 1r, 8a-h



Scheme S1

1a–1k, **1p**, **1q**, **1r**, **8a-h** were synthesized according to the literature procedure (Scheme S1).[1] General procedure: To a suspension of **II**[2] (2.0 mmol) and $HClO_4 \cdot SiO_2$[3] (0.2 g) in CH_3CN (10 mL) was added dropwise a solution of *o*-phenyldiamines **I** (2.4 mmol) in CH_3CN (2 mL) and the mixture was stirred at room temperature for 5 h. After completion (monitored by TLC), the reaction mixture was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was concentrated and the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc (6:1, V/V) as the eluent to obtain pure product.

3. Preparation of Substituted Quinoxalines 1l–1o



Scheme S2

1l–1o were synthesized according to the literature procedure (Scheme S2).[4] General procedure: A mixture of *o*-phenyldiamines **I** (1 mmol) and *α*-dicarbonyl compound **III** (1 mmol) was intimately mixed with pre-activated KF-alumina (1:4) (0.5 g) (Basic; Grade: Brockmann1, and activated by heating under vacuum at 150 ºC until bubbling ceases and then cooled to room temperature under vacuum) and stirred the solid mixture with a magnetic spin bar at room temperature for 1-2 hours. After the reaction was complete, the solid mixture washed with diethyl ether (3 × 10 mL) and the solid was filtered off. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc (6:1, V/V) as the eluent to obtain pure product.

4. Typical Experimental Procedure for the Synthesis of 2 via $AgNO_2$-Mediated Nitration of Quinoxaline Benzylic C-H Bond

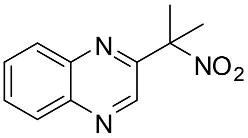
1 (0.3 mmol), $AgNO_2$ (55.4 mg, 0.36 mmol), $K_2S_2O_8$ (97.3 mg, 0.36 mmol), and anhydrous DCE (3.5 mL) were sequentially added to a 25-mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed and stirred at 110 or 130 ºC for 48 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent (10/1-3/1, V/V) to give pure product **2**.

5. Typical Experimental Procedure for the Conversion of 8 into 9

8 (0.3 mmol), $AgNO_2$ (101.6 mg, 0.66 mmol), $K_2S_2O_8$ (178.4 mg, 0.66 mmol), and DCE (4.0 mL) were sequentially added to a 25-mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the resultant mixture in the sealed tube was frozen by immersion of the flask in liquid N_2. When solvent was completely frozen, the flask was opened to the vacuum (high vacuum) and pumped for 2-3 minutes, with the flask still immersed in liquid N_2. The flask was then closed and warmed until solvent completely melted. This process was repeated three times and after the last cycle the flask was backfilled with an inert Ar gas. Then the flask was sealed and stirred at 130 ºC for 72 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent (6/1, V/V) to give pure product **9**.

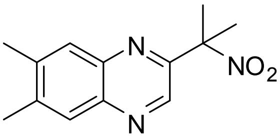
6. Characterization of all Products

2-(2-nitropropan-2-yl)quinoxaline (2a)



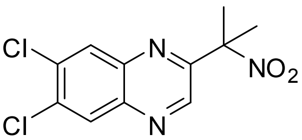
Brown oil; R_f = 0.5 (petroleum ether-EtOAc= 3:1); IR (neat): ν = 1524 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.97 (s, 1H), 8.16-8.10 (m, 2H), 7.84-7.82 (m, 2H), 2.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.7, 142.3, 142.0, 141.0, 130.8, 130.7, 129.7, 129.2, 90.7, 26.4; LRMS (ESI): 218.10 $[M+H]^+$; HRMS (ESI) for $C_{11}H_{12}N_3O_2$ $[M+H]^+$: calcd. 217.0930, found 217.0936.

6,7-dimethyl-2-(2-nitropropan-2-yl)quinoxaline (2b)



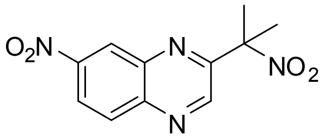
Yellow solid; R_f = 0.5 (petroleum ether-EtOAc= 3:1); mp 95-97 ºC; IR (KBr): ν = 1542 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.86 (s, 1H), 7.87 (s, 1H), 7.84 (s, 1H), 2.52 (s, 3H), 2.50 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 151.7, 141.5, 141.4, 141.1, 141.0, 140.0, 128.6, 128.1, 90.7, 26.3, 20.4, 20.3; LRMS (ESI): 246.24 $[M+H]^+$; HRMS (ESI) for $C_{13}H_{16}N_3O_2$ $[M+H]^+$: calcd. 246.1243, found 246.1237.

6,7-dichloro-2-(2-nitropropan-2-yl)quinoxaline (2c)



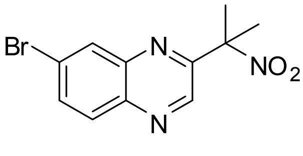
Yellow solid; R_f = 0.5 (petroleum ether-EtOAc= 6:1); mp 114-115 ºC; IR (KBr): ν = 1550 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.95 (s, 1H), 8.27 (s, 1H), 8.25 (s, 1H), 2.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.7, 143.4, 140.6, 139.7, 135.64, 135.60, 130.2, 129.8, 90.5, 26.2; LRMS (ESI): 285.89 $[M+H]^+$; HRMS (ESI) for $C_{11}H_{10}Cl_2N_3O_2$ $[M+H]^+$: calcd. 286.0150, found 286.0158.

7-nitro-2-(2-nitropropan-2-yl)quinoxaline (2d)



Brown solid; R_f = 0.6 (petroleum ether-EtOAc= 3:1); mp 127-129 ºC; IR (KBr): ν = 1544 (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.11 (s, 1H), 9.05 (d, J = 2.5 Hz, 1H), 8.60 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H), 8.28 (d, J = 9.0 Hz, 1H), 2.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.7, 148.4, 144.7, 143.3, 140.8, 131.4, 125.6, 124.1, 90.6, 26.2; LRMS (ESI): 285.37 $[M+Na]^+$; HRMS (ESI) for $C_{11}H_{10}N_4O_4Na$ $[M+Na]^+$: calcd. 285.0600, found 285.0607.

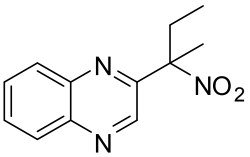
7-bromo-2-(2-nitropropan-2-yl)quinoxaline (2e)



Yellow solid; R_f = 0.3 (petroleum ether-EtOAc= 6:1); mp 122-123 ºC; IR (KBr): ν = 1598 (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.96 (s, 1H), 8.32 (d, J = 2.0 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.91 (dd, J_1 =9.0 Hz, J_2 = 2.0 Hz, 1H), 2.17 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.6, 142.6, 141.6, 140.8, 134.4, 132.0, 130.5, 124.9, 90.6, 26.3; LRMS (ESI): 296.21 $[M+H]^+$; HRMS (ESI) for $C_{11}H_{11}BrN_3O_2$ $[M+H]^+$: calcd. 296.0035, found

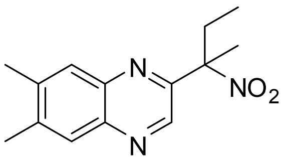
296.0028.

2-(2-nitrobutan-2-yl)quinoxaline (2f)



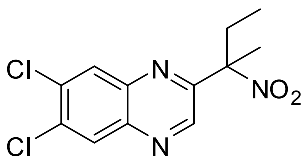
Brown oil; R_f = 0.5 (petroleum ether-EtOAc= 3:1); IR (neat): ν = 1524 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.93 (s, 1H), 8.15-8.09 (m, 2H), 7.83-7.81 (m, 2H), 2.74-2.70 (m, 1H), 2.61-2.57 (m, 1H), 2.11 (s, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.5, 142.5, 141.7, 141.1, 130.7, 130.6, 129.7, 129.1, 94.5, 31.8, 22.9, 8.6; LRMS (ESI): 231.96 $[M+H]^+$; HRMS (ESI) for $C_{12}H_{14}N_3O_2$ $[M+H]^+$: calcd. 232.1086, found 232.1081.

6,7-dimethyl-2-(2-nitrobutan-2-yl)quinoxaline (2g)



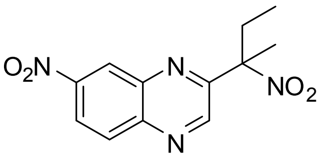
Brown solid; R_f = 0.5 (petroleum ether-EtOAc= 4:1); mp 59-60 ºC; IR (KBr): ν = 1542 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.84 (s, 1H), 7.89 (s, 1H), 7.86 (s, 1H), 2.72-2.55 (m, 2H), 2.52-2.51 (m, 6H), 2.01 (s, 3H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 151.6, 141.6, 141.4, 141.2, 140.7, 140.3, 128.7, 128.0, 94.5, 30.8, 22.8, 20.34, 20.25, 8.6; LRMS (ESI): 260.16; HRMS (ESI) for $C_{14}H_{18}N_3O_2$ $[M+H]^+$: calcd. 260.1399, found 260.1393.

6,7-dichloro-2-(2-nitrobutan-2-yl)quinoxaline (2h)



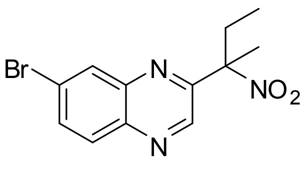
Brown solid; R_f = 0.5 (petroleum ether-EtOAc= 6:1); mp 80-82 ºC; IR (KBr): ν = 1550 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.91 (s, 1H), 8.27 (s, 1H), 8.25 (s, 1H), 2.73-2.66 (m, 1H), 2.60-2.53 (m, 1H), 2.09 (s, 3H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.6, 143.7, 140.5, 139.7, 135.6, 135.5, 130.2, 129.8, 94.3, 31.7, 22.9, 8.5; LRMS (ESI): 299.76 $[M+H]^+$; HRMS (ESI) for $C_{12}H_{12}Cl_2N_3O_2$ $[M+H]^+$: calcd. 300.0307, found 300.0312.

7-nitro-2-(2-nitrobutan-2-yl)quinoxaline (2i)



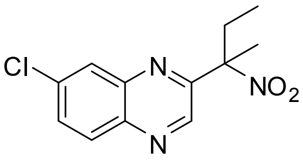
Brown solid; R_f = 0.4 (petroleum ether-EtOAc= 6:1); mp 80-82 ºC; IR (KBr): ν = 1550 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.07 (s, 1H), 9.04 (d, *J* = 2.5 Hz, 1H), 8.60 (dd, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 1H), 8.30 (d, *J* = 9.5 Hz, 1H), 2.78-2.70 (m, 1H), 2.64-2.57 (m, 1H), 2.14 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.8, 148.5, 145.9, 144.1, 140.0, 131.1, 126.0, 124.1, 94.4, 31.8, 23.0, 8.6; LRMS (ESI): 299.20 $[M+Na]^+$; HRMS (ESI) for $C_{12}H_{12}N_4O_4Na$ $[M+Na]^+$: calcd. 299.0756, found 299.0762.

7-bromo-2-(2-nitrobutan-2-yl)quinoxaline (2j)



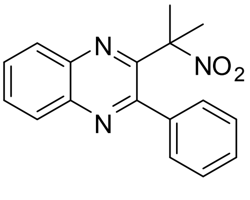
Yellow solid; $R_f = 0.5$ (petroleum ether-EtOAc= 4:1); mp 89-91 °C; IR (KBr): $\nu = 1541$ (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.92 (s, 1H), 8.31 (d, $J = 2.0$ Hz, 1H), 8.01 (d, $J = 9.0$ Hz, 1H), 7.90 (dd, $J_1 = 9.0$ Hz, $J_2 = 2.0$ Hz, 1H), 2.74-2.61 (m, 1H), 2.59-2.54 (m, 1H), 2.10 (s, 3H), 1.01 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.4, 142.9, 141.6, 140.6, 134.2, 132.0, 130.5, 124.8, 94.4, 31.8, 22.9, 8.6; LRMS (ESI): 309.85 $[M+H]^+$; HRMS (ESI) for $C_{12}H_{13}BrN_3O_2$ $[M+H]^+$: calcd. 310.0191, found 310.0185.

7-chloro-2-(2-nitrobutan-2-yl)quinoxaline (2k)



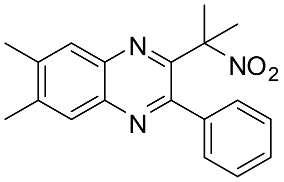
Yellow solid; $R_f = 0.3$ (petroleum ether-EtOAc= 6:1); mp 50-51 °C; IR (KBr): $\nu = 1550$ (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.93 (s, 1H), 8.14 (d, $J = 2.5$ Hz, 1H), 8.04 (d, $J = 9.0$ Hz, 1H), 7.76 (dd, $J_1 = 9.0$ Hz, $J_2 = 2.0$ Hz, 1H), 2.74-2.61 (m, 1H), 2.60-2.54 (m, 1H), 2.10 (s, 3H), 1.01 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.7, 143.5, 142.1, 139.6, 136.7, 131.7, 130.9, 128.1, 94.4, 31.8, 22.9, 8.6; LRMS (ESI): 265.91 $[M+H]^+$; HRMS (ESI) for $C_{12}H_{13}ClN_3O_2$ $[M+H]^+$: calcd. 266.0696, found 266.0691.

2-(2-nitropropan-2-yl)-3-phenylquinoxaline (2l)



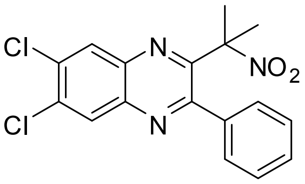
Yellow solid; R_f = 0.5 (petroleum ether-EtOAc= 6:1); mp 97-98 ºC; IR (KBr): ν = 1550 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.19-8.15 (m 2H), 7.86-7.84 (m 2H), 7.50-7.48 (m, 3H), 7.37-7.34 (m, 2H), 1.96 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.9, 151.1, 140.9, 140.0, 138.5, 131.0, 130.4, 129.4, 129.1, 129.0, 128.9, 128.5, 91.4, 27.7; LRMS (ESI): 293.94 $[M+H]^+$; HRMS (ESI) for $C_{17}H_{16}N_3O_2$ $[M+H]^+$: calcd. 294.1243, found 294.1243.

6,7-dimethyl-2-(2-nitropropan-2-yl)-3-phenylquinoxaline (2m)



Yellow solid; R_f = 0.4 (petroleum ether-EtOAc= 6:1); mp 121-123 ºC; IR (KBr): ν = 1543 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.92 (s, 1H), 7.89 (s, 1H), 7.48-7.45 (m, 3H), 7.34-7.32 (m, 2H), 2.55 (s, 3H), 2.53 (s, 3H), 1.93 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.9, 150.1, 141.8, 141.1, 139.8, 139.0, 138.8, 129.0, 128.9, 128.5, 128.4, 128.0, 91.5, 27.7, 20.5, 20.3; LRMS (ESI): 321.91 $[M+H]^+$; HRMS (ESI) for $C_{19}H_{20}N_3O_2$ $[M+H]^+$: calcd. 322.1556, found 322.1560.

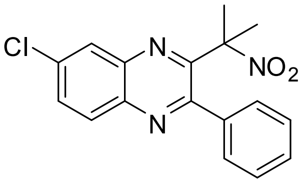
6,7-dichloro-2-(2-nitropropan-2-yl)-3-phenylquinoxaline (2n)



Yellow solid; R_f = 0.5 (petroleum ether-EtOAc= 10:1); mp 173-175 ºC; IR (KBr): ν =

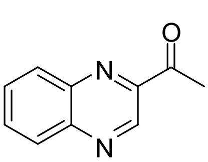
1549 (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.32 (s, 1H), 8.27 (s, 1H), 7.52-7.49 (m, 3H), 7.33-7.31 (m, 2H), 1.93 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.1, 152.3, 139.6, 138.7, 135.9, 135.3, 130.0, 129.7, 129.5, 128.8, 128.7, 91.3, 27.6; LRMS (ESI): 361.82 [M+H]$^+$; HRMS (ESI) for $C_{17}H_{14}Cl_2N_3O_2$ [M+H]$^+$: calcd. 362.0463, found 362.0457.

6-chloro-3-(2-nitropropan-2-yl)-2-phenylquinoxaline (2o)



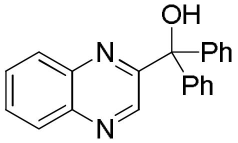
Yellow solid; R_f = 0.5 (petroleum ether-EtOAc= 6:1); mp 98-100 ºC; IR (KBr): ν = 1547 (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15-8.11 (m, 2H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.51-7.49 (m, 3H), 7.34-7.32 (m, 2H), 1.94 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.9, 151.3, 141.1, 138.4, 138.1, 137.0, 131.5, 130.6, 129.3, 128.8, 128.6, 127.9, 91.3, 27.6; LRMS (ESI): 327.88 [M+H]$^+$; HRMS (ESI) for $C_{17}H_{15}ClN_3O_2$: calcd. 328.0853, found 328.0859.

1-(quinoxalin-2-yl)ethanone (2q′)[5]



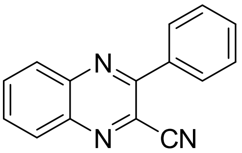
Yellow solid; R_f = 0.6 (petroleum ether-EtOAc= 6:1); mp 76-78 ºC (lit.[5] mp 77 ºC); IR (neat): ν = 1717 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.51 (s, 1H), 8.23-8.21 (m, 2H), 8.20-8.18 (m, 2H), 2.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 199.8, 146.6, 143.9, 143.1, 141.1, 132.2, 130.7, 130.5, 129.5, 25.5; GC-MS (EI, 70eV): *m/z* (%) = 172 (100) [M$^+$], 130 (97).

diphenyl(quinoxalin-2-yl)methanol (2r′)



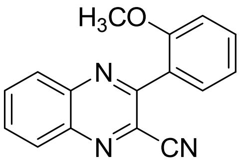
Yellow liquid, R$_f$ = 0.50 (petroleum ether-EtOAc = 6:1); m.p. 168-170 ºC; IR (neat): 3400 (O-H) cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.83 (s, 1H), 8.17–8.12 (m, 2H), 7.85–7.79 (m, 2H), 7.39–7.31 (m, 10H), 6.30 (br s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 157.4, 144.9, 144.6, 141.3, 139.7, 130.5, 130.0, 129.0, 128.7, 128.2, 128.0, 127.7, 80.1; GC-MS (EI, 70 eV): *m/z* (%) = 312 [M$^+$]; HRMS (EI) for $C_{21}H_{16}N_2O$: calcd. 312.1263, found 312.1267.

3-phenylquinoxaline-2-carbonitrile (9a)



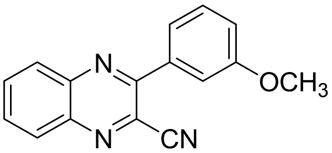
Pale yellow solid, R$_f$ = 0.48 (petroleum ether-EtOAc = 6:1); m.p. 168-170 ºC; IR (neat): 2251 (C≡N) cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.20 (t, *J* = 7.0 Hz, 2H), 8.08–8.06 (m, 2H), 7.97–7.94 (m, 1H), 7.89 (t, *J* = 8.5 Hz, 1H), 7.64–7.61 (m, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 154.2, 142.3, 140.6, 135.1, 133.5, 131.4, 130.8, 129.6, 129.5, 129.3, 129.0, 128.3, 116.6; GC-MS (EI, 70 eV): *m/z* (%) = 231 [M$^+$]; HRMS (EI) for $C_{15}H_9N_3$: calcd. 231.0796, found 231.0790.

3-(2-methoxyphenyl)quinoxaline-2-carbonitrile (9b)



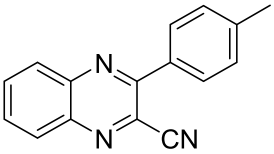
Pale yellow solid, R_f = 0.38 (petroleum ether-EtOAc = 6:1); m.p. 138-140 ºC; IR (neat): 2237(C≡N) cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.20–8.17 (m, 2H), 7.92–7.88 (m, 1H), 7.87–7.83 (m, 1H), 7.60–7.58 (m, 1H), 7.567–.53 (m, 1H), 7.19–7.16 (m, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 157.2, 153.4, 142.5, 140.2, 132.8, 132.2, 131.5, 131.2, 131.0, 129.44, 129.42, 124.9, 121.3, 116.3, 111.4, 55.3; GC-MS (EI, 70 eV): *m/z* (%) = 261 [M$^+$]; HRMS (EI) for $C_{16}H_{11}N_3O$: calcd. 261.0902, found 261.0906.

3-(3-methoxyphenyl)quinoxaline-2-carbonitrile (9c)



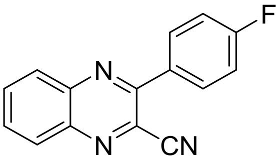
Pale yellow solid, R_f = 0.35 (petroleum ether-EtOAc = 6:1); m.p. 167-169 ºC; IR (neat): 2232 (C≡N) cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.22–8.19 (m, 2H), 7.98–7.94 (m, 1H), 7.9 –7. 88 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 2.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.16–7.14 (m, 1H), 3.94 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 159.7, 153.8, 142.1, 140.4, 136.1, 133.4, 131.2, 129.9, 129.4, 129.3, 128.2, 121.5, 116.9, 116.5, 114.1, 55.5; GC-MS (EI, 70 eV): *m/z* (%) = 261 [M$^+$]; HRMS (EI) for $C_{16}H_{11}N_3O$: calcd. 261.0902, found 261.0908.

3-*p*-tolylquinoxaline-2-carbonitrile (9d)



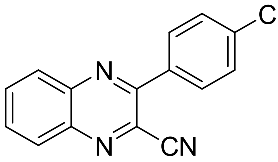
Pale yellow solid, R$_f$ = 0.45 (petroleum ether-EtOAc = 6:1); m.p. 185-186 ºC; IR (neat): 2240 (C≡N) cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.17 (t, J = 7.5 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.93–9.91 (m, 1H), 7.87–7.84 (m, 1H), 7.41 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 154.1, 142.4, 141.2, 140.4, 133.4, 132.3, 131.1, 129.6, 129.5, 129.4, 129.2, 128.3, 116.7, 21.4; GC-MS (EI, 70 eV): *m/z* (%) = 245 [M$^+$]; HRMS (EI) for $C_{16}H_{11}N_3$: calcd. 245.0953, found 245.0948.

3-(4-fluorophenyl)quinoxaline-2-carbonitrile (9e)



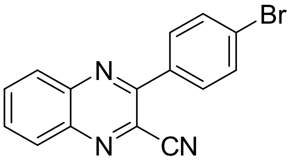
Pale yellow solid, R$_f$ = 0.43 (petroleum ether-EtOAc = 6:1); m.p. 176-178 ºC; IR (neat): 2228 (C≡N) cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.22–8.20 (m, 2H), 8.12–8.08 (m, 2H), 8.0–7.96 (m, 1H), 7.93–7.90 (m, 1H), 7.34–7.29 (m, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 164.5 (d, $J_{C\text{-}F}$ = 251.3 Hz), 153.2, 142.4, 140.7, 133.7, 131.51, 131.50 (d, $J_{C\text{-}F}$ = 8.8 Hz), 131.3 (d, $J_{C\text{-}F}$ = 2.5 Hz), 129.6 ($J_{C\text{-}F}$ = 1.3 Hz), 128.1, 116.6, 116.2 (d, $J_{C\text{-}F}$ = 22.5 Hz); GC-MS (EI, 70 eV): *m/z* (%) = 249 [M$^+$]; HRMS (EI) for $C_{15}H_8FN_3$: calcd. 249.0702, found 249.0707.

3-(4-chlorophenyl)quinoxaline-2-carbonitrile (9f)



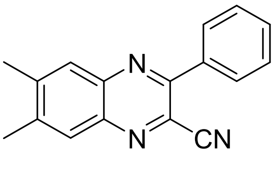
Pale yellow solid, R_f = 0.45 (petroleum ether-EtOAc = 6:1); m.p. 218-220 ºC; IR (neat): 2225 (C≡N) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.22–8.20 (m, 2H) 8.06–8.03 (m, 2H), 8.00–7.96 (m, 1H), 7.94–7.90 (m, 1H), 7.61–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.0, 142.4, 140.8, 137.4, 133.8, 133.6, 131.6, 130.7, 129.60, 129.58, 129.3, 128.1, 116.5; GC-MS (EI, 70 eV): *m/z* (%) = 265 [M^+]; HRMS (EI) for $C_{15}H_8ClN_3$: calcd. 265.0407, found 249.0401.

3-(4-bromophenyl)quinoxaline-2-carbonitrile (9g)



Pale yellow solid, R_f = 0.45 (petroleum ether-EtOAc = 6:1); m.p. 215-217 ºC; IR (neat): 2236 (C≡N) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.23–8.21 (m, 2H), 8.00–7.96 (m, 3H), 7.94–7.91 (m, 1H), 7.78–7.75 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.1, 142.4, 140.8, 134.0, 133.8, 132.4, 132.3, 131.7, 130.8, 129.6, 128.1,125.9, 116.5; GC-MS (EI, 70 eV): *m/z* (%) = 309 [M^+]; HRMS (EI) for $C_{15}H_8BrN_3$: calcd. 308.9902, found 308.9908.

6,7-dimethyl-3-phenylquinoxaline-2-carbonitrile (9h)

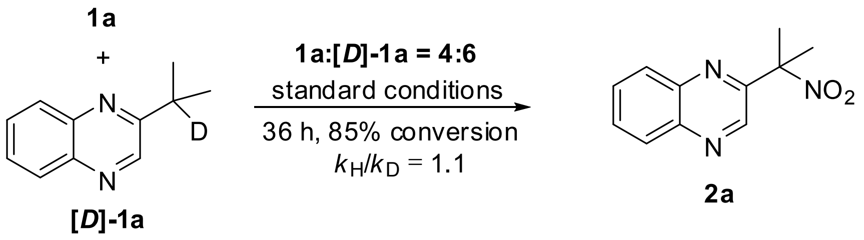


Pale yellow solid, R_f = 0.48 (petroleum ether-EtOAc = 6:1); m.p. 178-180 ºC; IR (neat):

2229 ($C\equiv N$) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05–8.03 (m, 2H), 7.96 (s, 1H), 7.93 (s, 1H), 7.63-7.58 (m, 3H), 2.574 (s, 3H), 2.566 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.7, 145.1, 142.5, 141.6, 139.9, 135.6, 130.5, 129.3, 128.9, 128.6, 128.3, 127.3, 117.0, 20.8, 20.4; GC-MS (EI, 70 eV): *m/z* (%) = 259 [M$^+$]; HRMS (EI) for $C_{17}H_{13}N_3$: calcd. 259.1109, found 259.1104.

7. Mechanistic Studies

7.1 Determination of Intermolecular Kinetic Isotope Effect between 1a and [*D*]-1a.



Preparation of **[*D*]-1a: [*D*]-1a** was prepared according to a modified procedure reported by Huang.[6] To a 25-mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal were sequentially added **1a** (51.7 mg, 0.3 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol% based on **1a**), 1,10-phenanthroline (2.7 mg, 0.015 mmol, 5 mol% based on **1a**), CD_3COOD (1.5 mmol, 5 equiv relative to **1a**), and anhydrous CH_2Cl_2 (3.5 mL). The flaske was sealed and heated to 120 °C for 24 h. After evaporation of the solvent of the resulting minxture under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc (4:1, V/V) as eluent. A mixture of **[*D*]-1a** and **1a** with a molar ratio of 6:4 was obtained (0.25 mmol, total yield: 83.3%) on the basis of ^1H NMR spectral analysis (Figure S1).

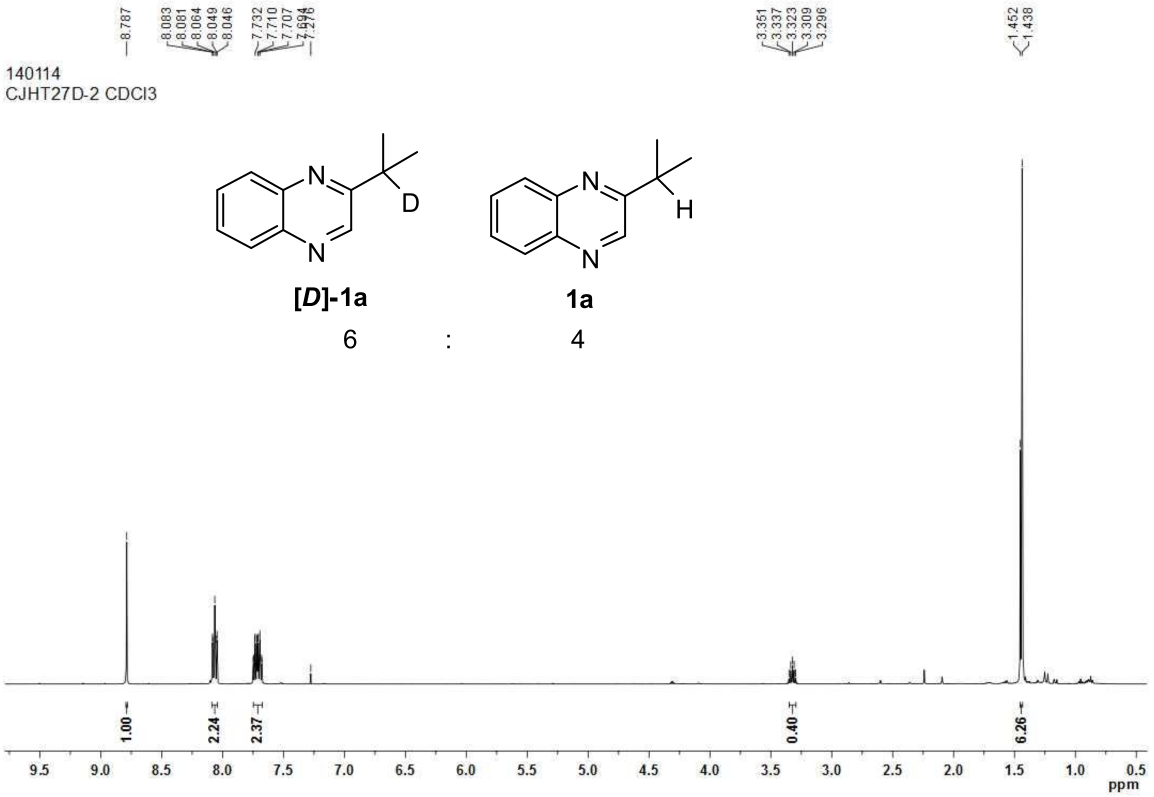


Figure S1. **^1H NMR Spectrum of [*D*]-1a and 1a (6:4) Mixture**

Determination of intermolecular kinetic isotope effect between **1a** and **[*D*]-1a**: To a 25-mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal were sequentially added a mixture of **1a** and **[*D*]-1a** (molar ratio 4:6, total 0.25 mmol), $AgNO_2$ (46.2 mg, 0.3 mmol), $K_2S_2O_8$ (81.1 mg, 0.3 mmol), and anhydrous DCE (3.5 mL). Then the flask was sealed and stirred at 110 for 36 h. GC-MS analysis showed that 85% of the starting substrates were consumed. The resulting mixture was then diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent (10/1, V/V) to recover the unreacted **1a** and **[*D*]-1a**. ^{1}H NMR spectral analysis showed that **1a** and **[*D*]-1a** have a molar ratio of 29:71 (Figure S2).

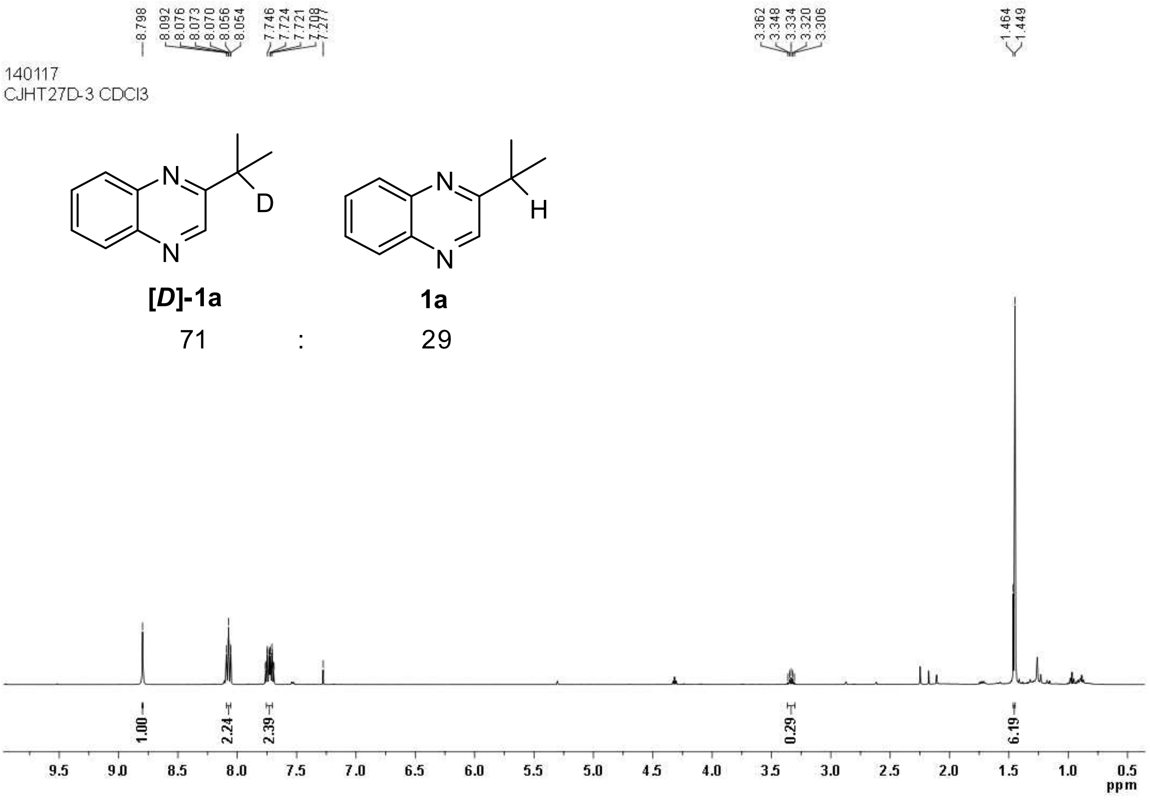


Figure S2. ^{1}**H NMR Spectrum of the Unreacted [*D*]-1a and 1a (71:29) Mixture**

Based on the above experimental data, the intermolecular kinetic isotope effect is calculated to be $k_H/k_D = [(0.25\times 0.4\text{-}0.25\times 0.15\times 0.29) \times 6/4]/(0.25\times 0.6\text{-}0.25\times 0.15\times 0.71) \approx 1.1$.

7.2 Effect of Radical Scavenger TEMPO on the Reaction.

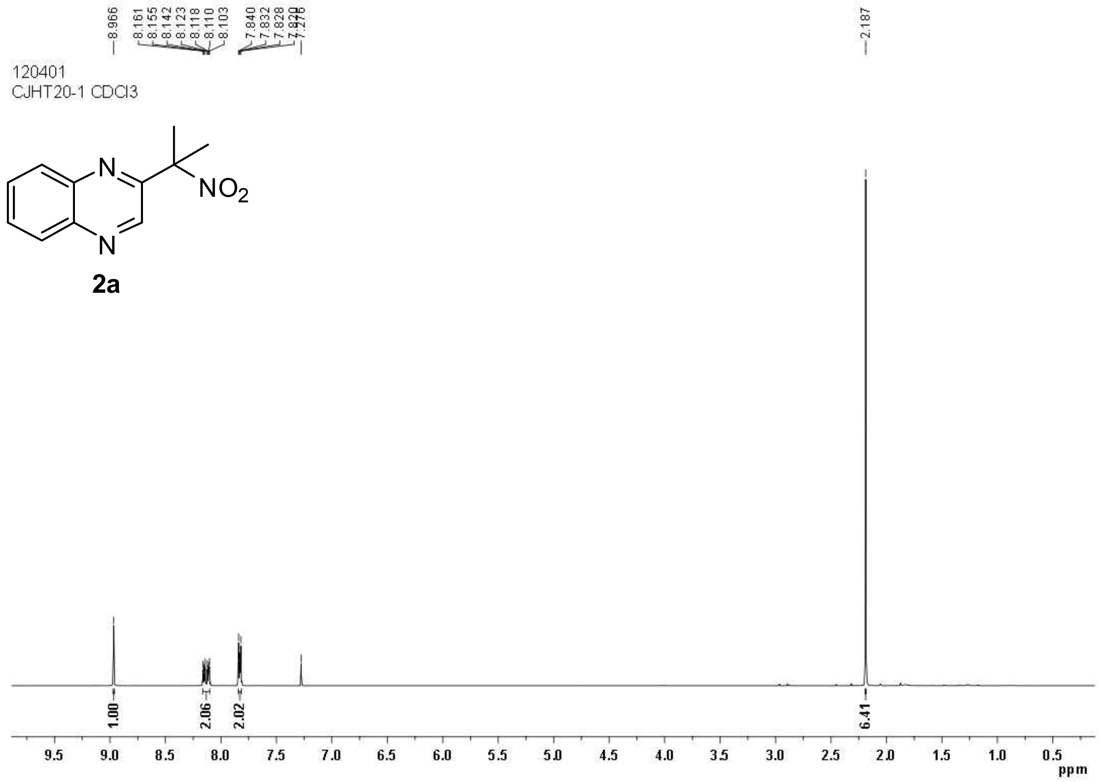
$$\mathbf{1a} \xrightarrow[\text{standard conditions}]{\text{TEMPO}} \mathbf{2a} \left\{ \begin{array}{l} \text{yield = 38\%, TEMPO: 0.5 equiv} \\ \text{yield: trace, TEMPO: 2.0 equiv} \end{array} \right\}$$

1a (51.7 mg, 0.3 mmol), $AgNO_2$ (55.4 mg, 0.36 mmol), $K_2S_2O_8$ (97.3 mg, 0.36 mmol), TEMPO (0.15 mmol or 0.6 mmol), phenanthrene (21.4 mg, 0.12 mmol, internal standard), and anhydrous DCE (3.5 mL) were sequentially added to a 25-mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed and stirred at 110 ºC for 48 h. Upon completion, the resulting mixture was analyzed by GC (38% of **2a**, TEMPO = 0.5 equiv; trace amount of **2a**, TEMPO = 2 equiv).

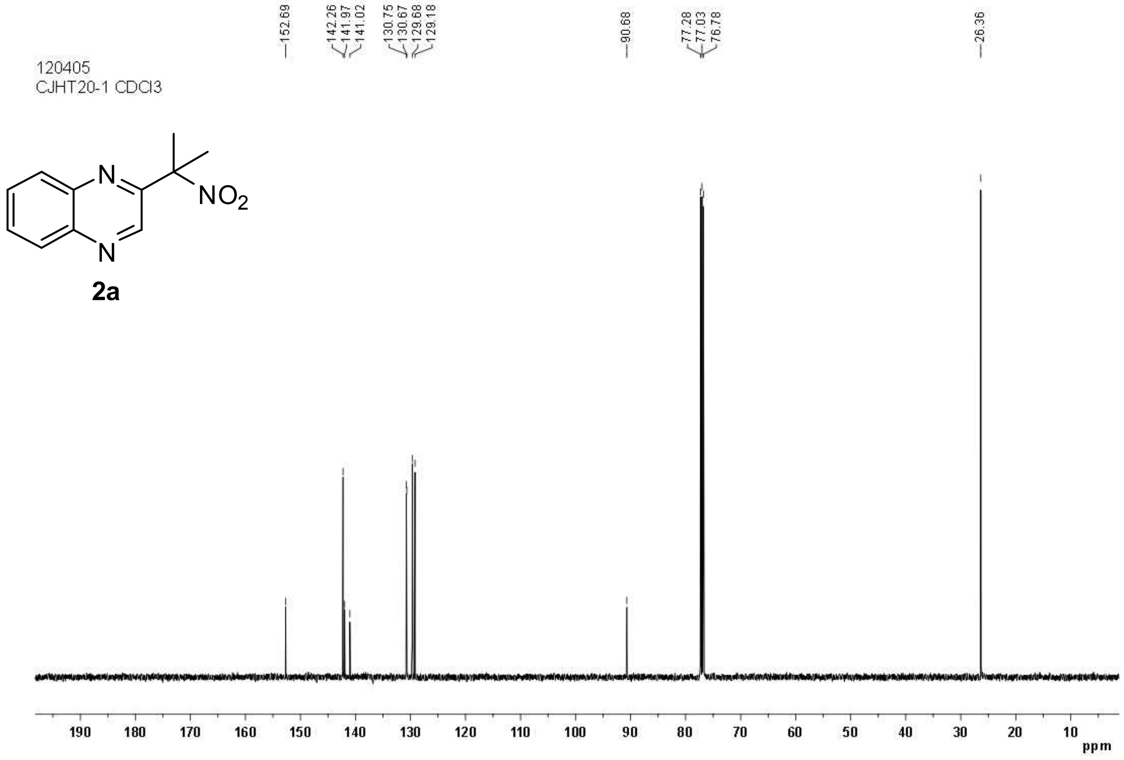
8. References

1. B. Das, K. Venkateswarlu, K. Suneel and A. Majhi, *Tetrahedron Lett.*, 2007, **48**, 5371.
2. S. Kajigaeshi, T. Kakinami, T. Okamoto and S. Fujsaki, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1159.
3. A. K. Chakraborti and R. Gulhane, *Chem. Commun.*, 2003, 1896.
4. S. Paul and B. Basu, *Tetrahedron Lett.*, 2011, **52**, 6597.
5. E. Hayashi, *Chem. Pharm. Bull.*, 1977, **25**, 579.
6. B. Qian, S. Guo, J. Shao, Q. Zhu, L. Yang, C. Xia and H. Huang, *J. Am. Chem. Soc.*, 2010, **132**, 3650.

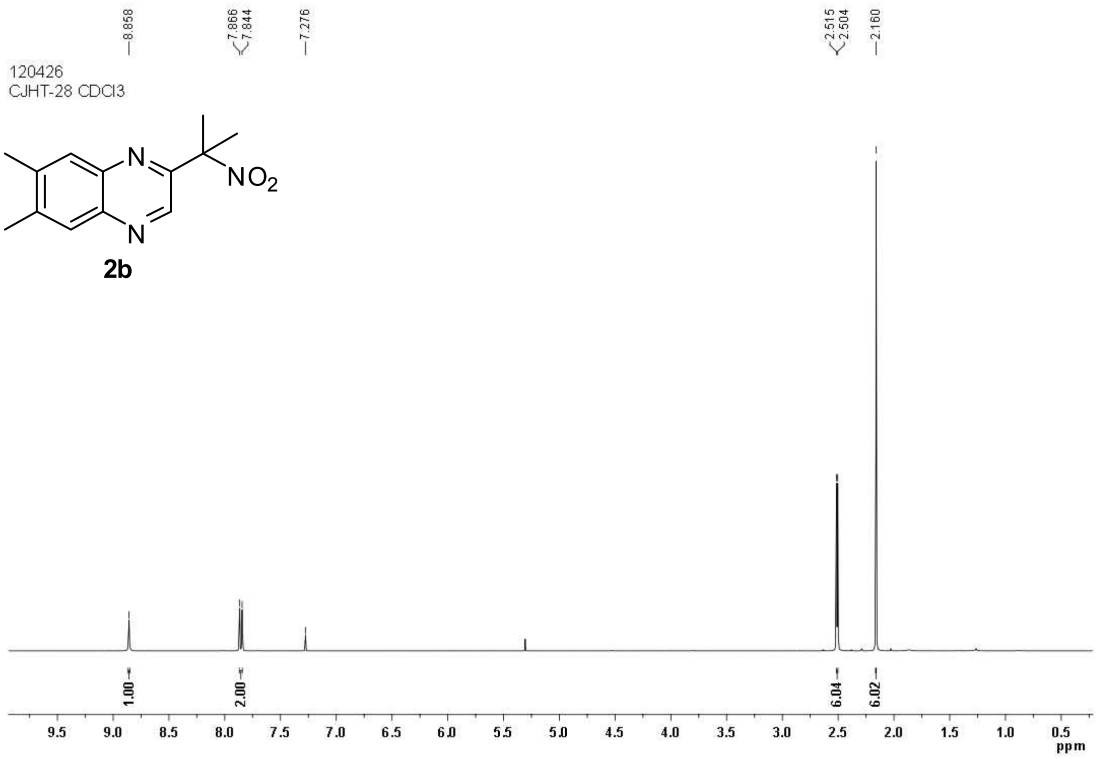
9. NMR Spectra of All Products



2a



2a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2.504
2.160
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N
NO2
1.00
2.00
6.04
6.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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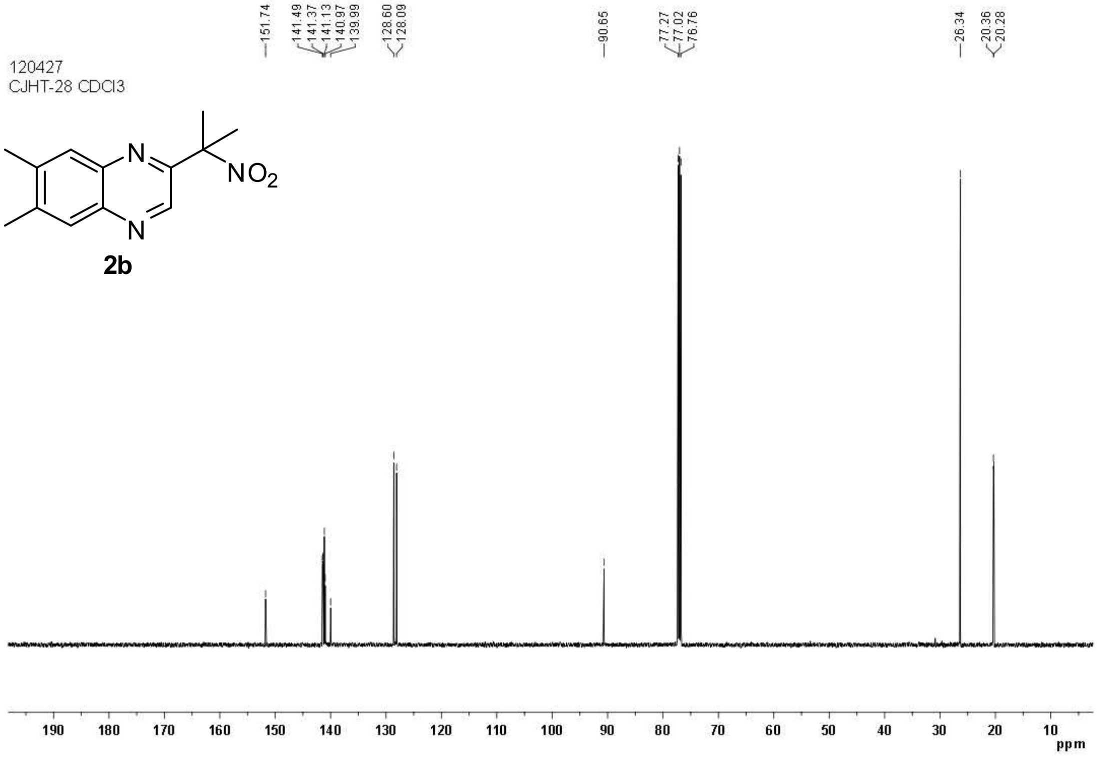
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

2b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139.99
128.60
128.09
90.65
77.27
77.02
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26.34
20.36
20.28
120427
CJHT-28 CDCl3
N
N
NO2
190
180
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140
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120
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60
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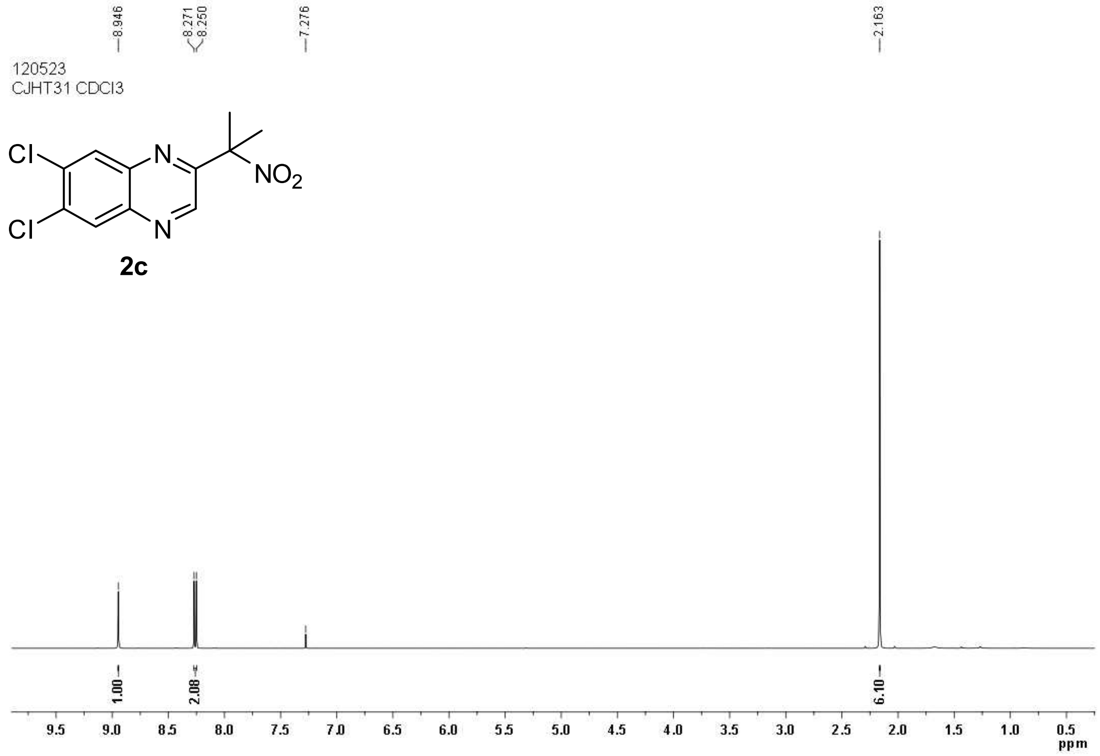
10
ppm

2b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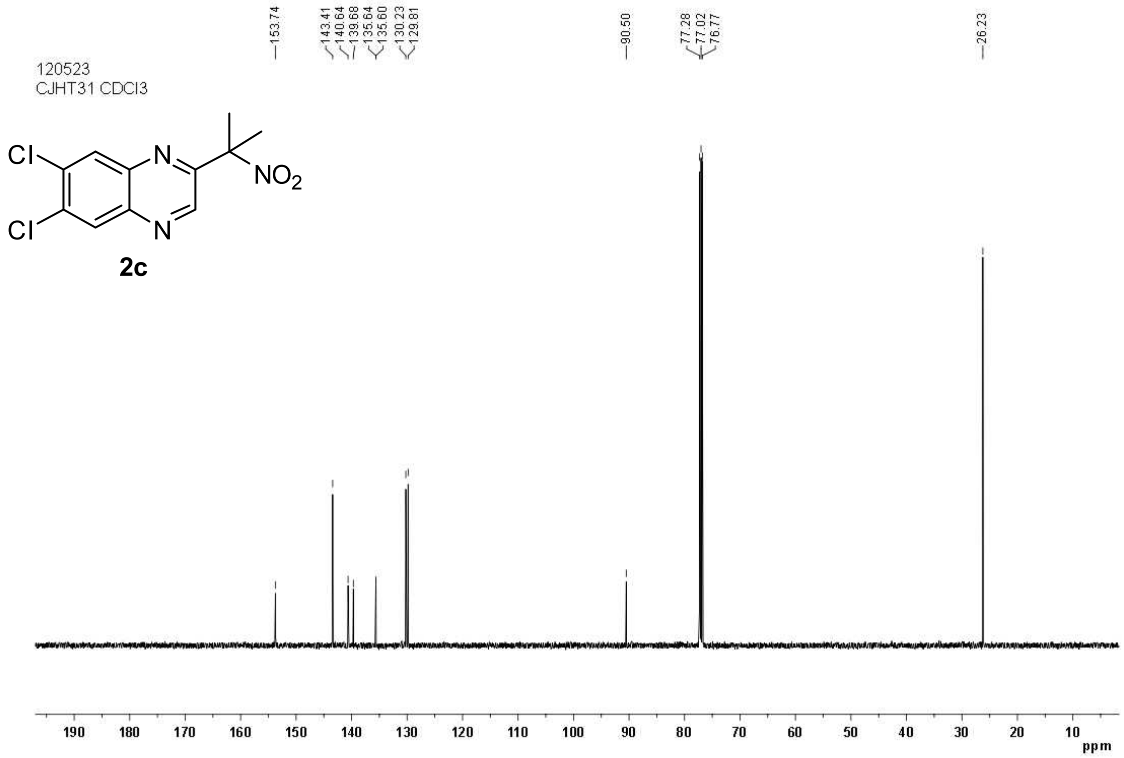
1.00
2.08
6.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm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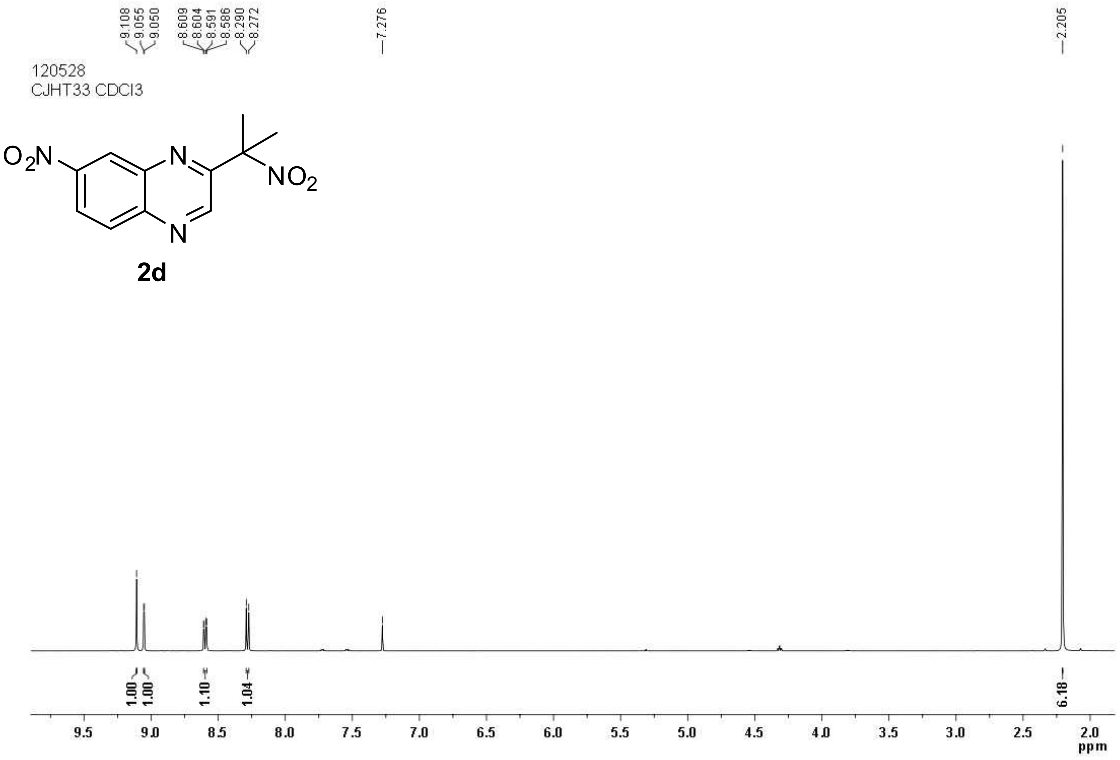
ppm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CJHT33 CDCl3
O_2N
N
N
NO_2
2d
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1.00
1.10
1.04
6.18
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9.0
8.5
8.0
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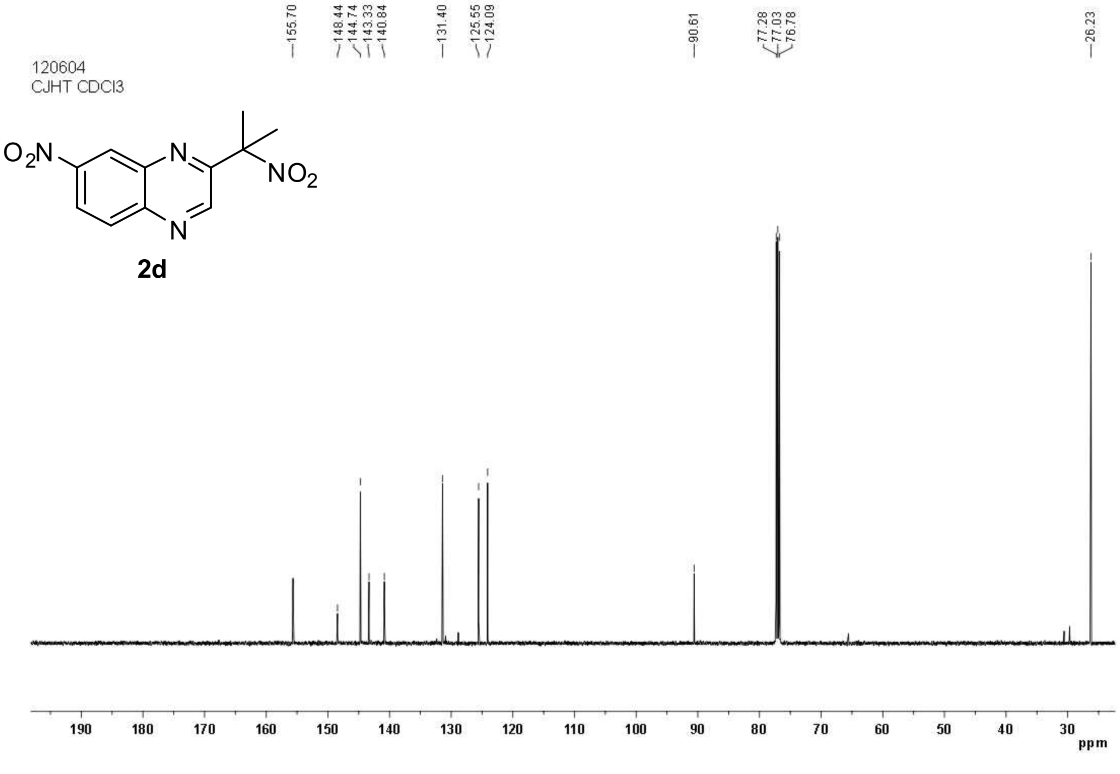
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26.23
120604
CJHT CDCl3
O_2N
N
N
NO_2
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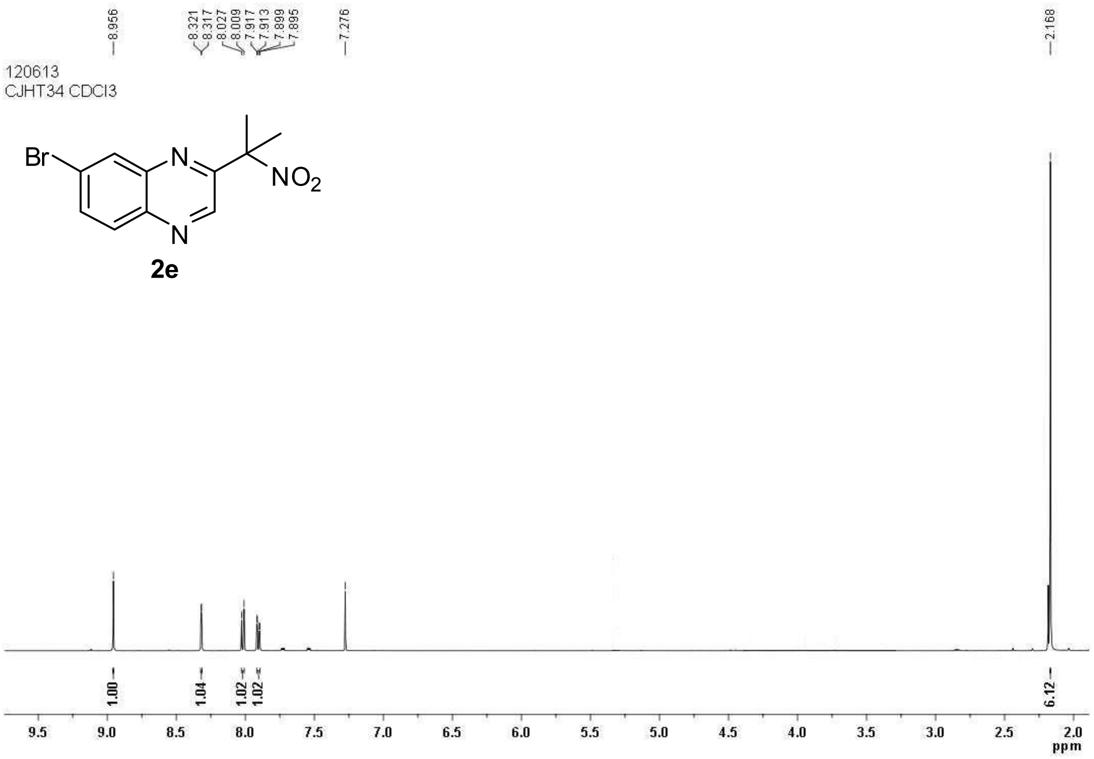
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CJHT34 CDCl3
Br
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N
NO2
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1.00
1.04
1.02
1.02
6.12
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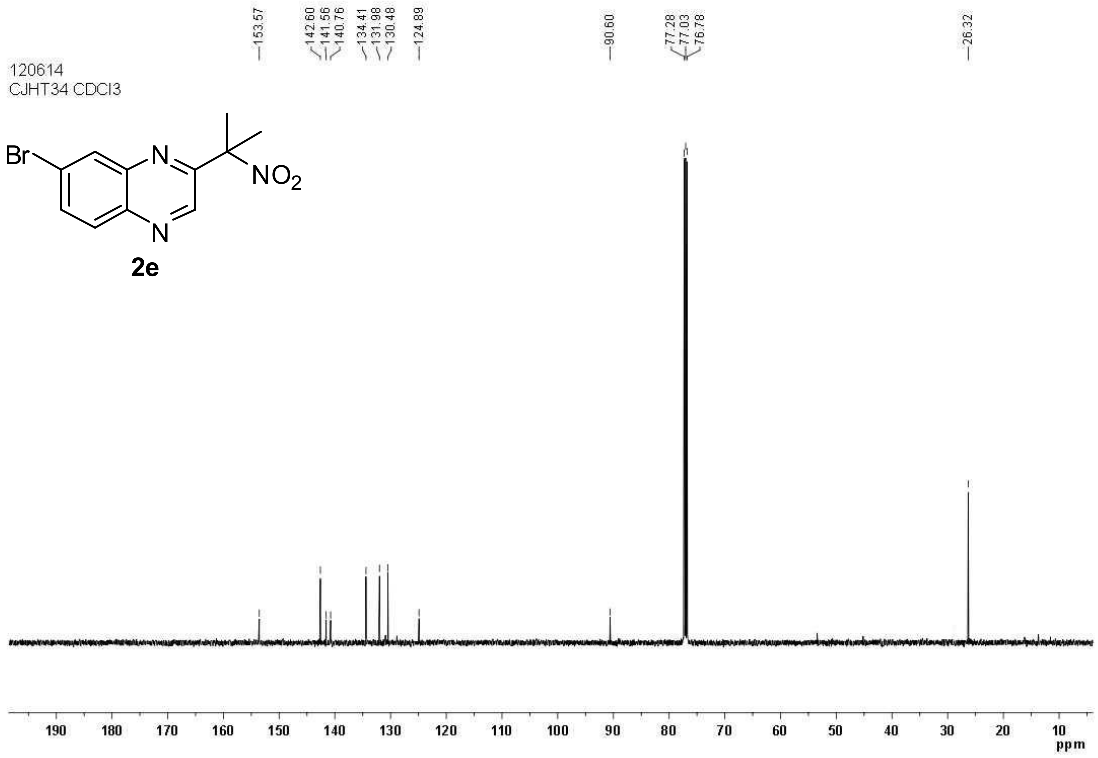
2.5
2.0
ppm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26.32
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CJHT34 CDCl3
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NO2
2e
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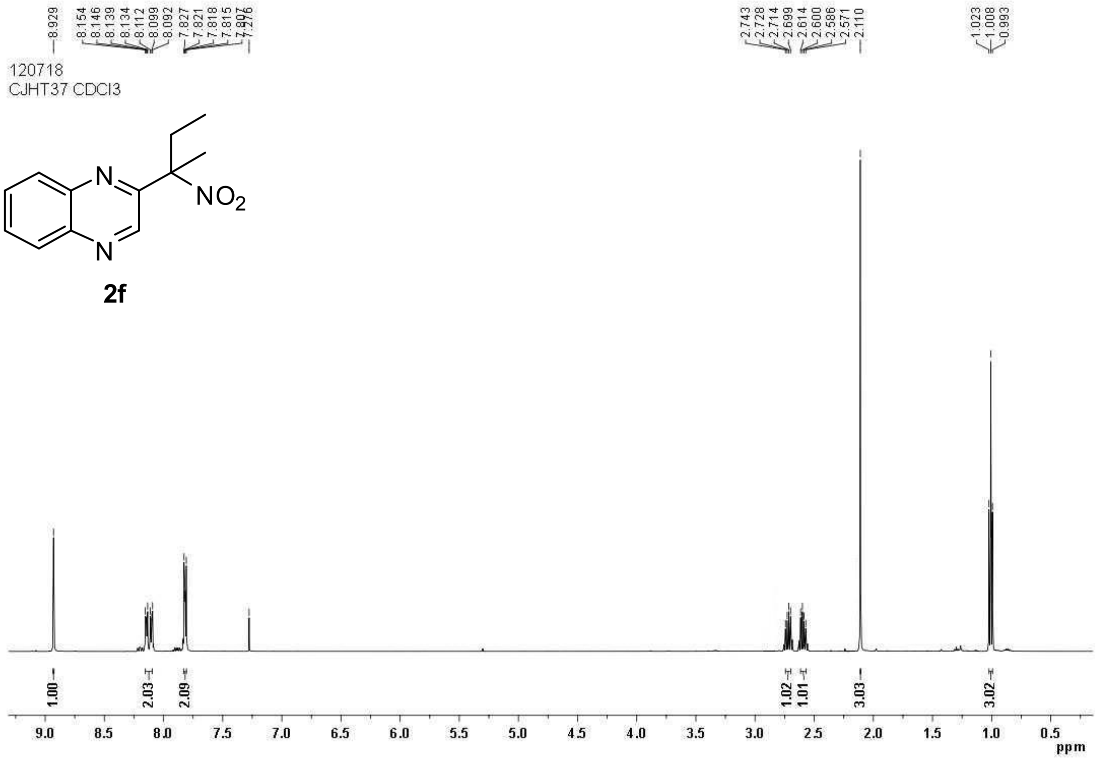
ppm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2.743
2.728
2.714
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2.614
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2.110
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1.008
0.993
120718
CJHT37 CDCl3
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N
NO2
2f
1.00
2.03
2.09
1.02
1.01
3.03
3.02
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8.0
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6.5
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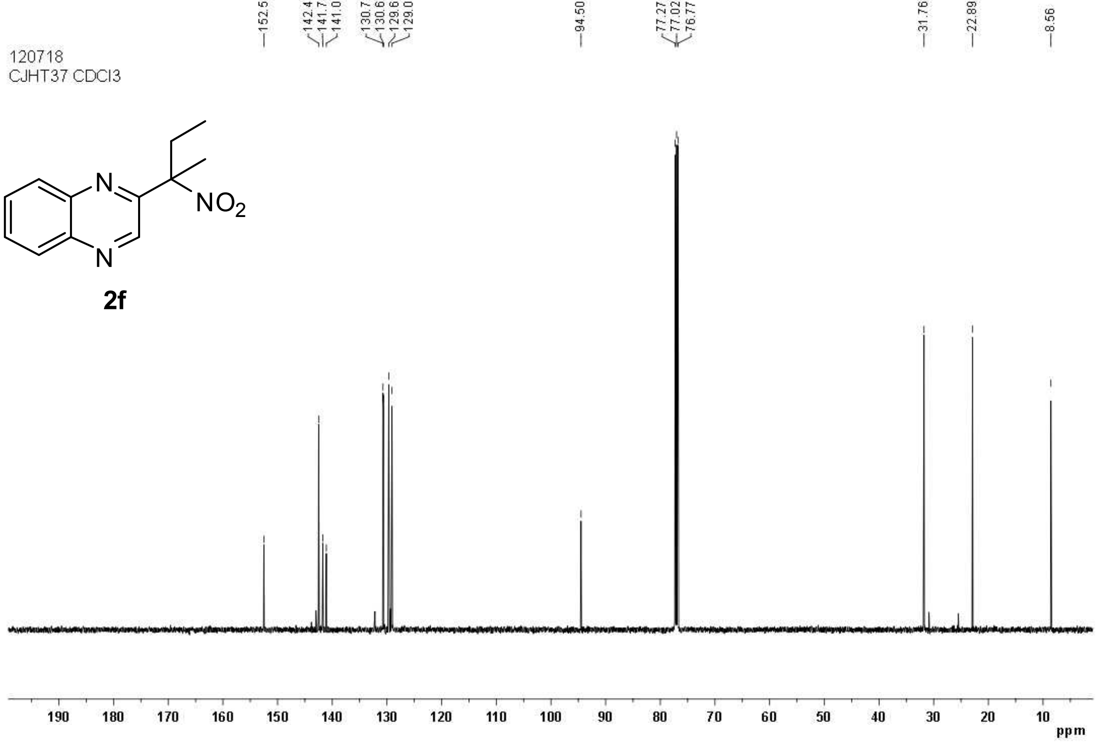
ppm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129.07
94.50
77.27
77.02
76.77
31.76
22.89
8.56
120718
CJHT37 CDCl3
N
N
NO2
2f
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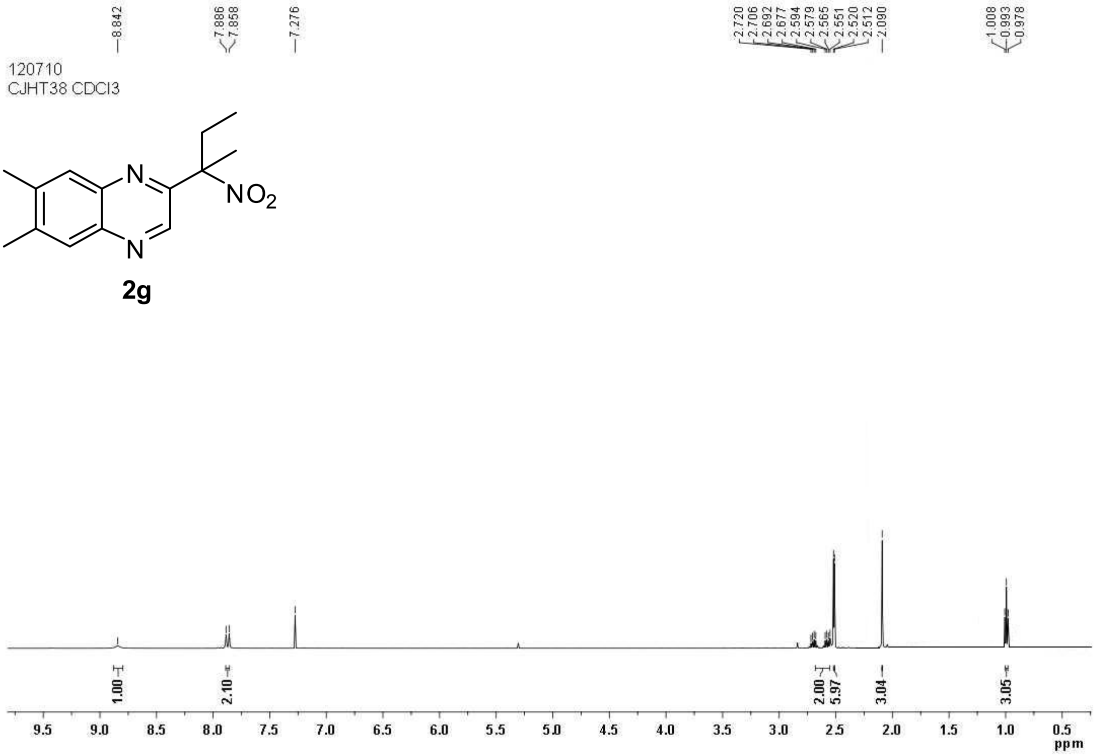
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2.520
2.512
2.090
1.008
0.993
0.978
120710
CJHT38 CDCl3
N
N
NO2
2g
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2.10
2.00
5.97
3.04
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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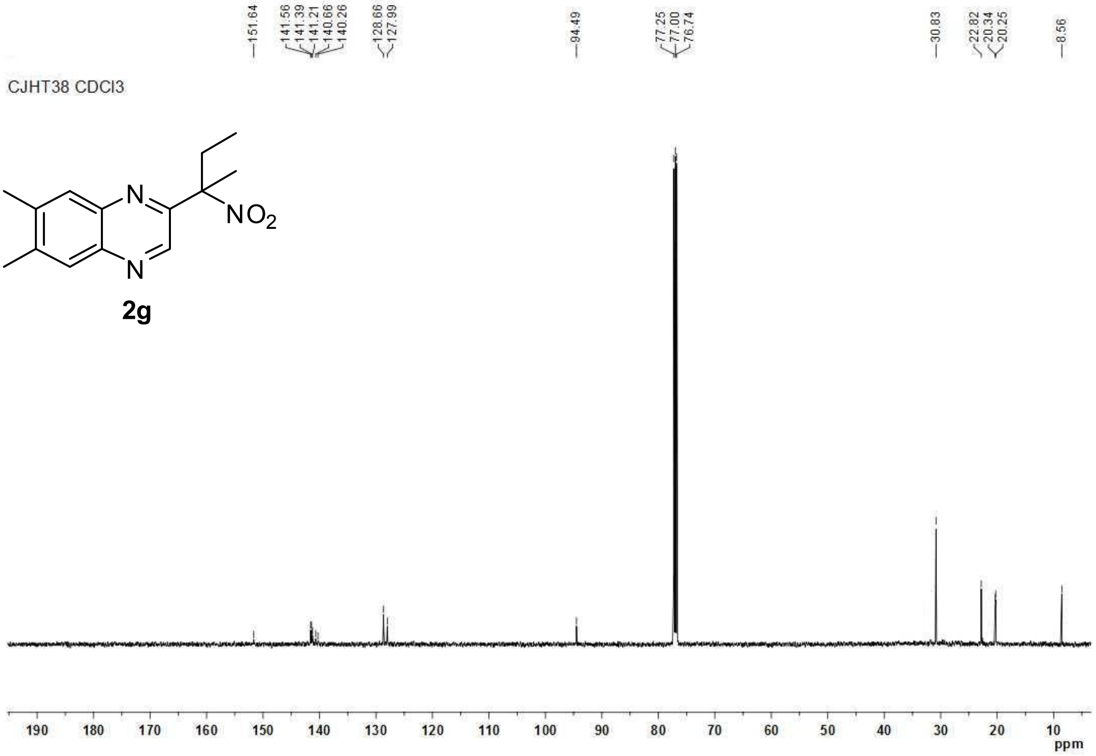
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127.99
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77.25
77.00
76.74
30.83
22.82
20.34
20.25
8.56
CJHT38 CDCl3
N
N
NO2
2g
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150
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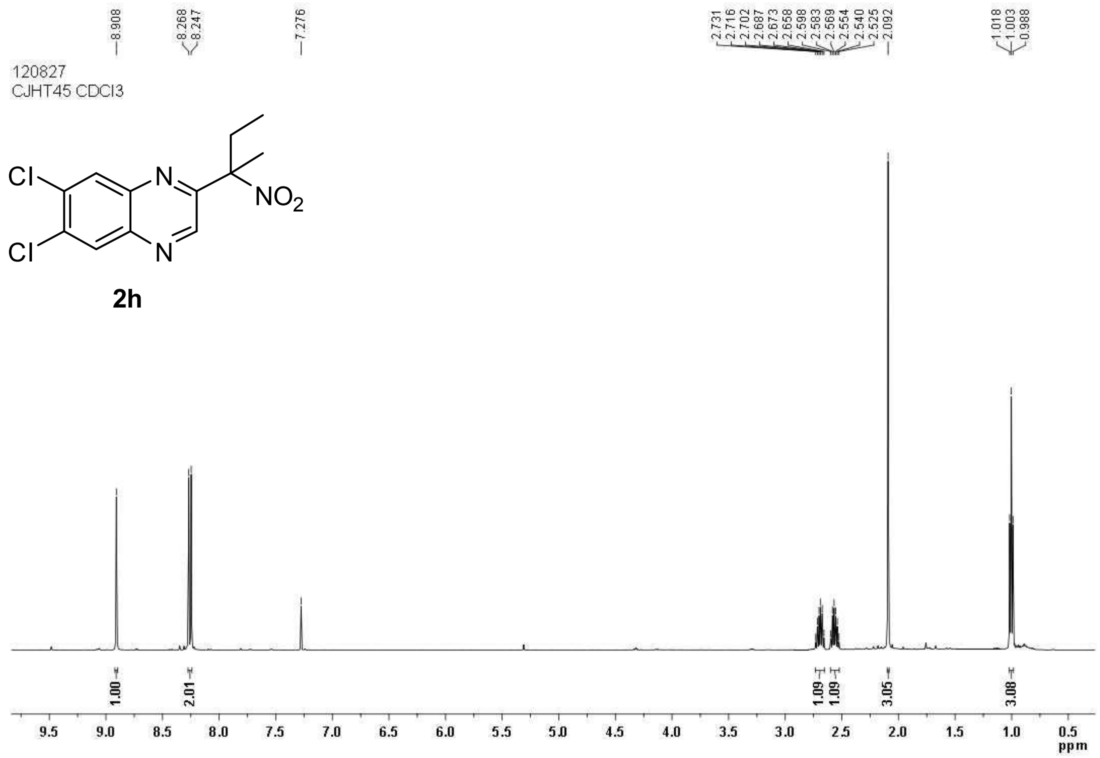
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2.687
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2.583
2.569
2.554
2.540
2.525
2.092
1.018
1.003
0.988
120827
CJHT45 CDCl3
Cl
Cl
N
N
NO2
2h
1.00
2.01
1.09
1.09
3.05
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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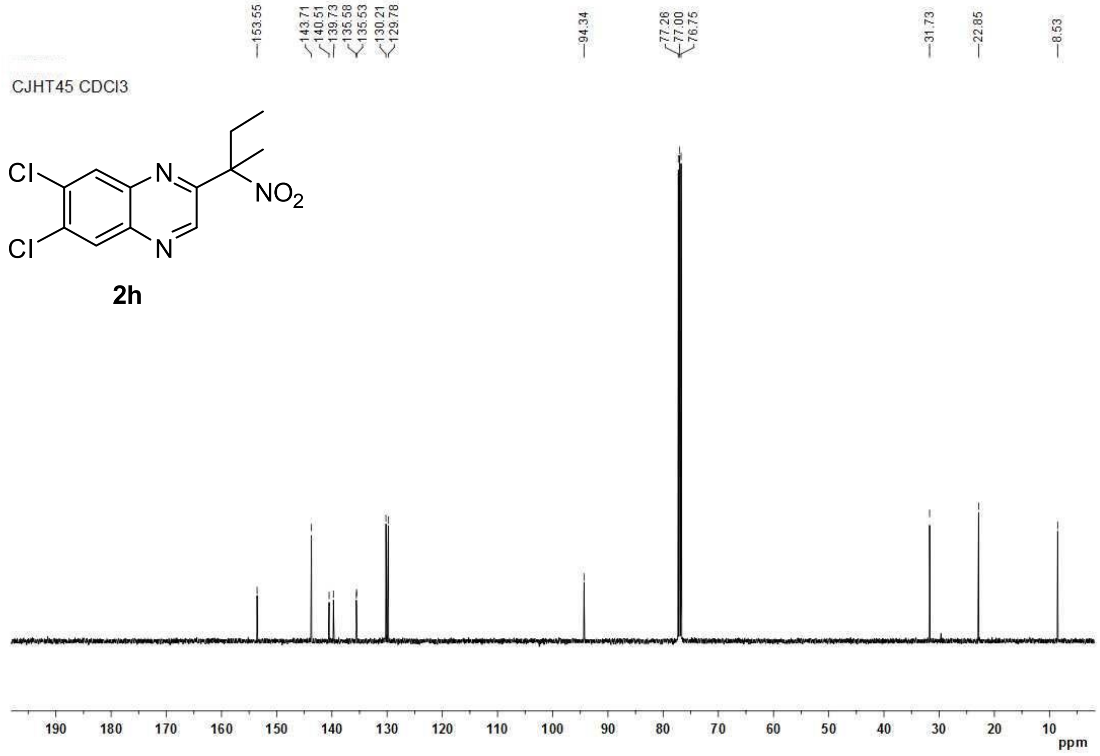
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31.73
22.85
8.53
CJHT45 CDCl3
Cl
Cl
N
N
NO2
2h
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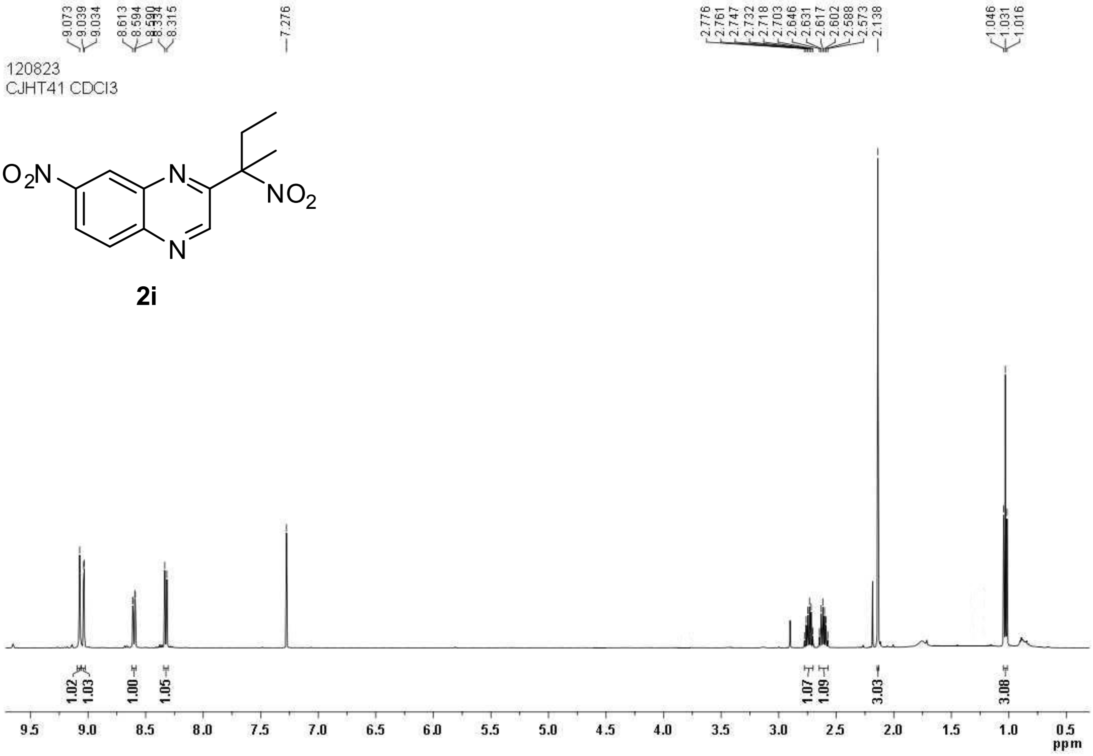
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8.315
7.276
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2.761
2.747
2.732
2.718
2.703
2.646
2.631
2.617
2.602
2.588
2.573
2.138
1.046
1.031
1.016
120823
CJHT41 CDCl3
O2N
N
N
NO2
1.02
1.03
1.00
1.05
1.07
1.09
3.03
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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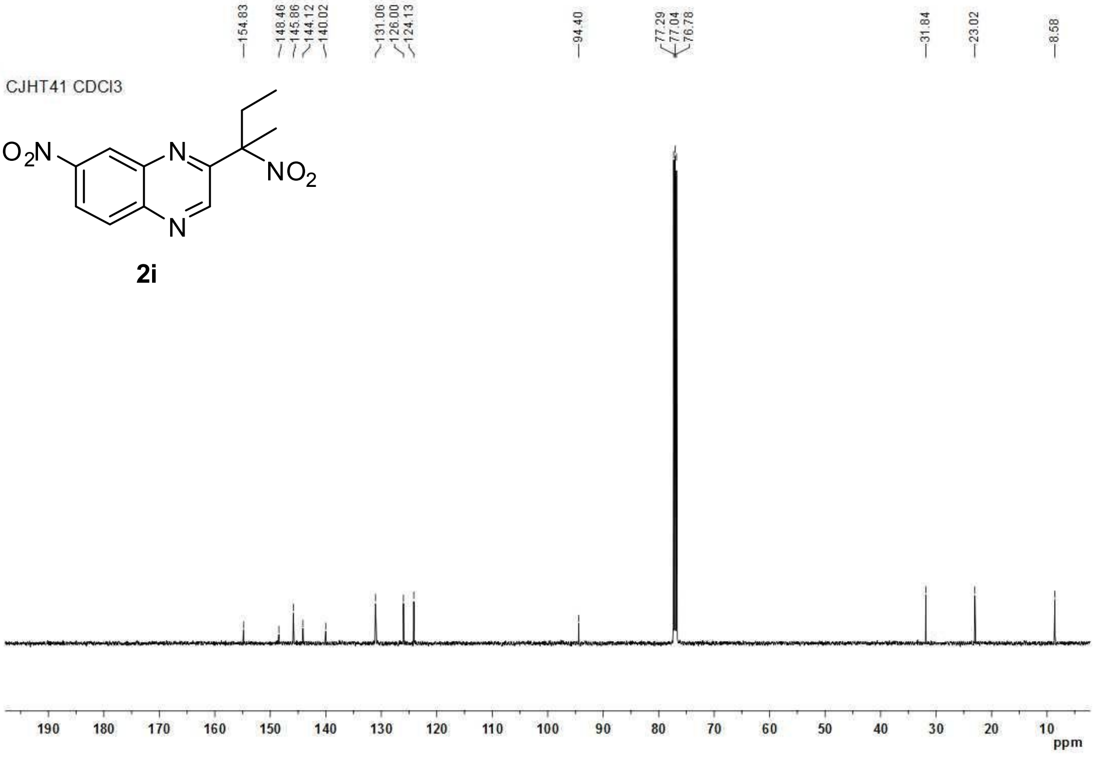
2i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148.46
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144.12
140.02
131.06
126.00
124.13
94.40
77.29
77.04
76.78
31.84
23.02
8.58
CJHT41 CDCl3
O2N
N
N
NO2
190
180
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100
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20
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ppm

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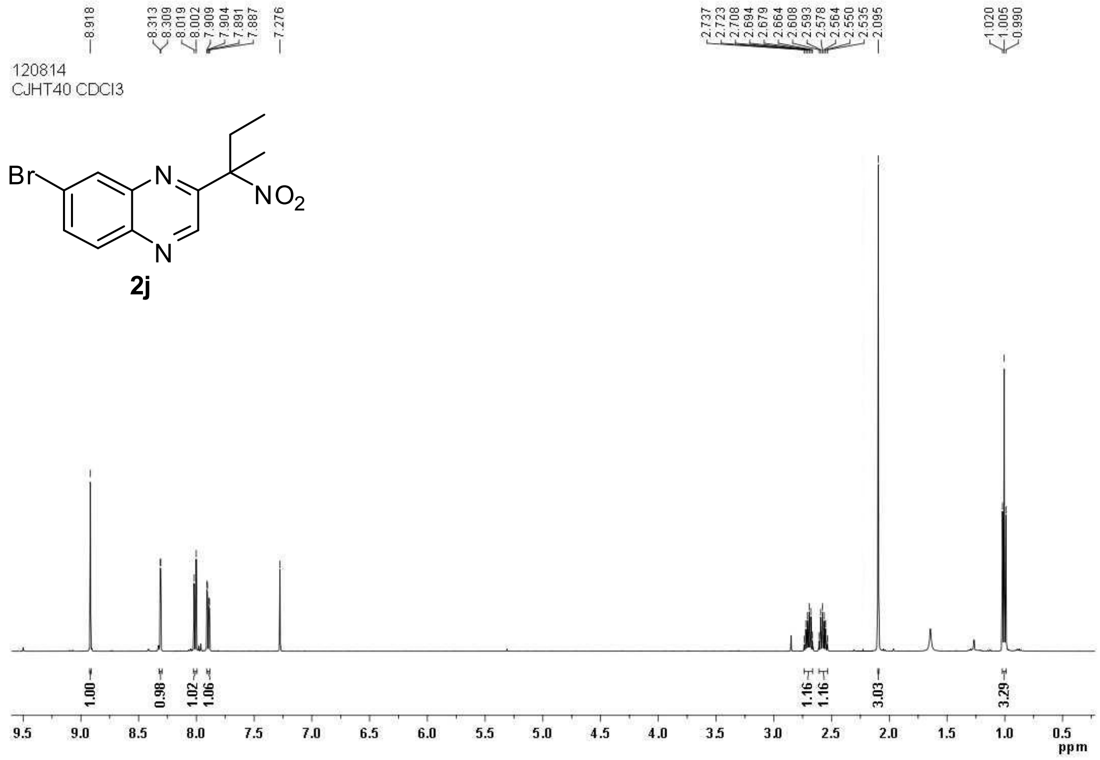

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7.276
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2.723
2.708
2.694
2.679
2.664
2.608
2.593
2.578
2.564
2.550
2.535
2.095
1.020
1.005
0.990
120814
CJHT40 CDCl3
Br
N
N
NO2
2j
1.00
0.98
1.02
1.06
1.16
1.16
3.03
3.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
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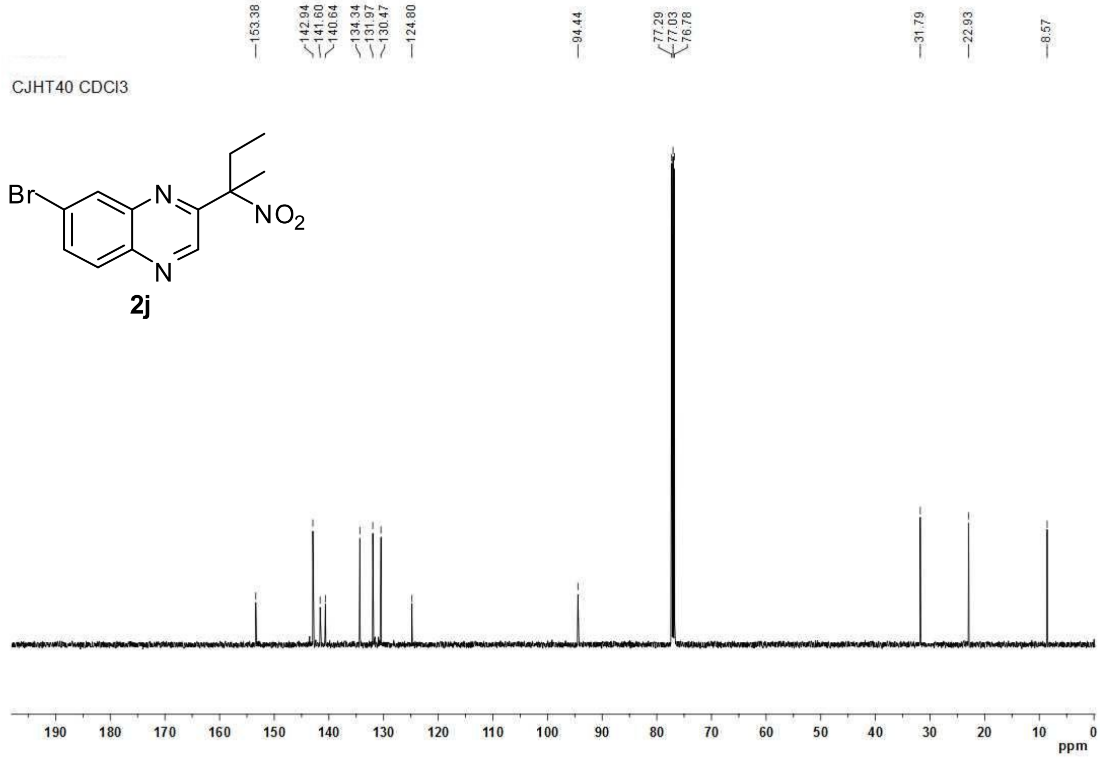
ppm



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131.97
130.47
124.80
94.44
77.29
77.03
76.78
31.79
22.93
8.57
CJHT40 CDCl3
Br
N
N
NO2
2j
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180
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140
130
120
110
100
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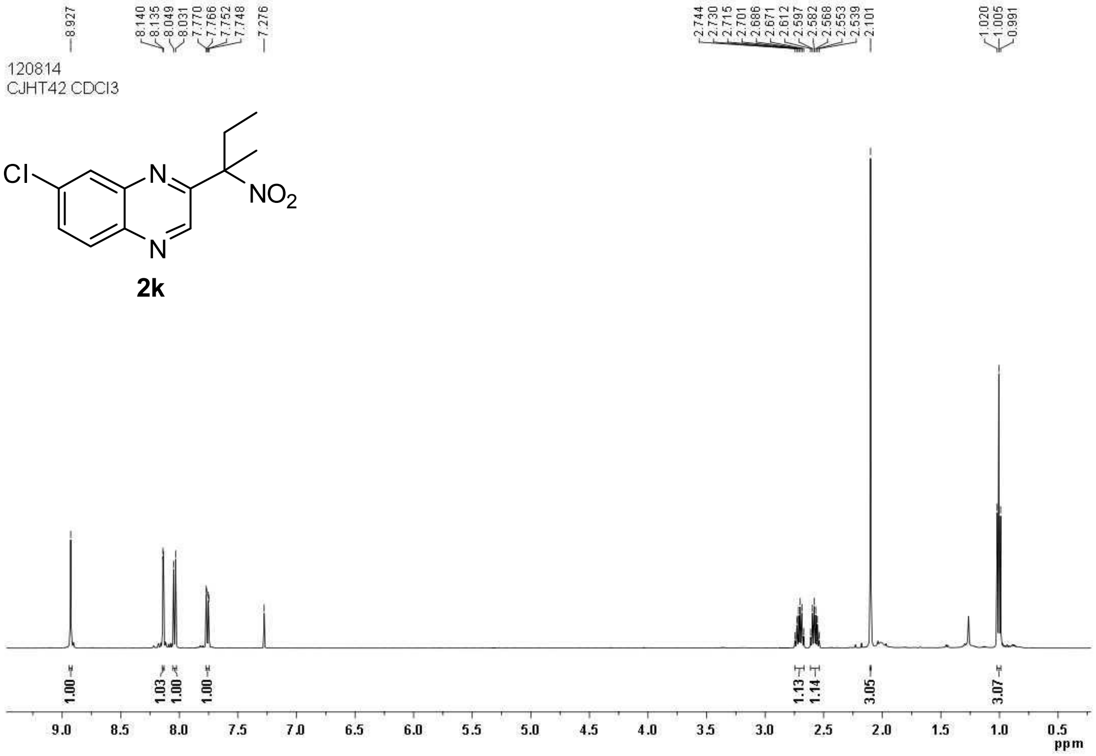
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7.752
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7.276
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2.701
2.686
2.671
2.612
2.597
2.582
2.568
2.553
2.539
2.101
1.020
1.005
0.991
120814
CJHT42 CDCl3
Cl
N
N
NO2
2k
1.00
1.03
1.00
1.00
1.13
1.14
3.05
3.07
9.0
8.5
8.0
7.5
7.0
6.5
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3.0
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2.0
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1.0
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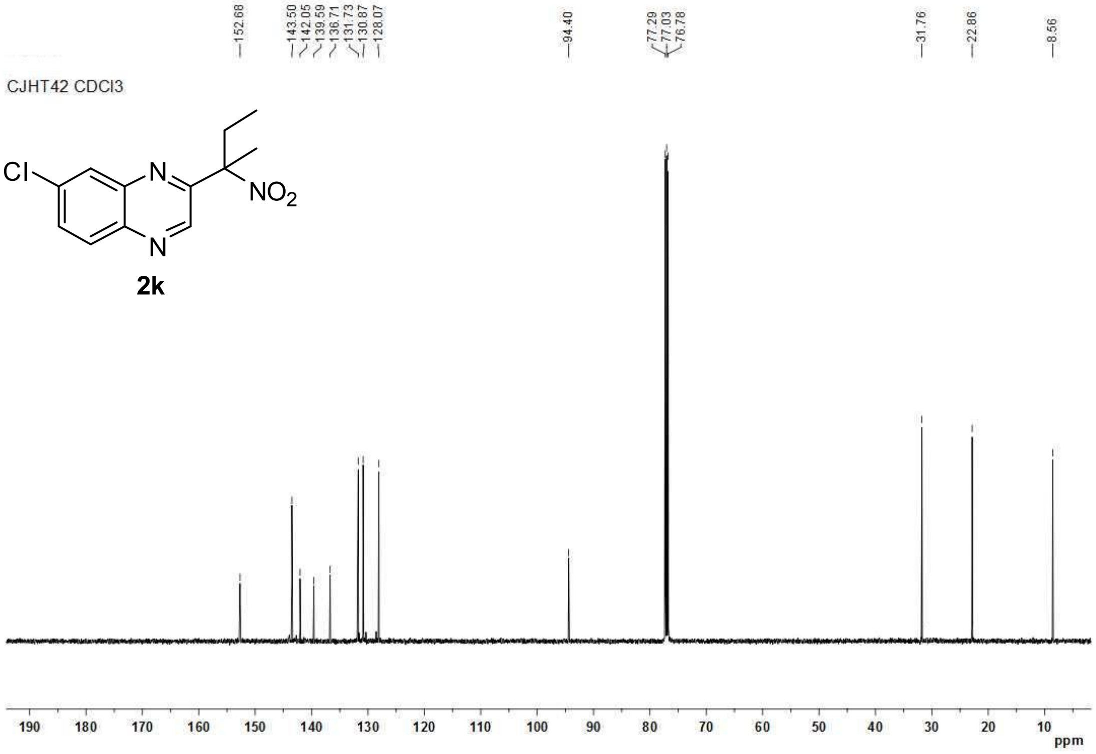
ppm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128.07
94.40
77.29
77.03
76.78
31.76
22.86
8.56
CJHT42 CDCl3
Cl
N
N
NO2
2k
190
180
170
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150
140
130
120
110
100
90
80
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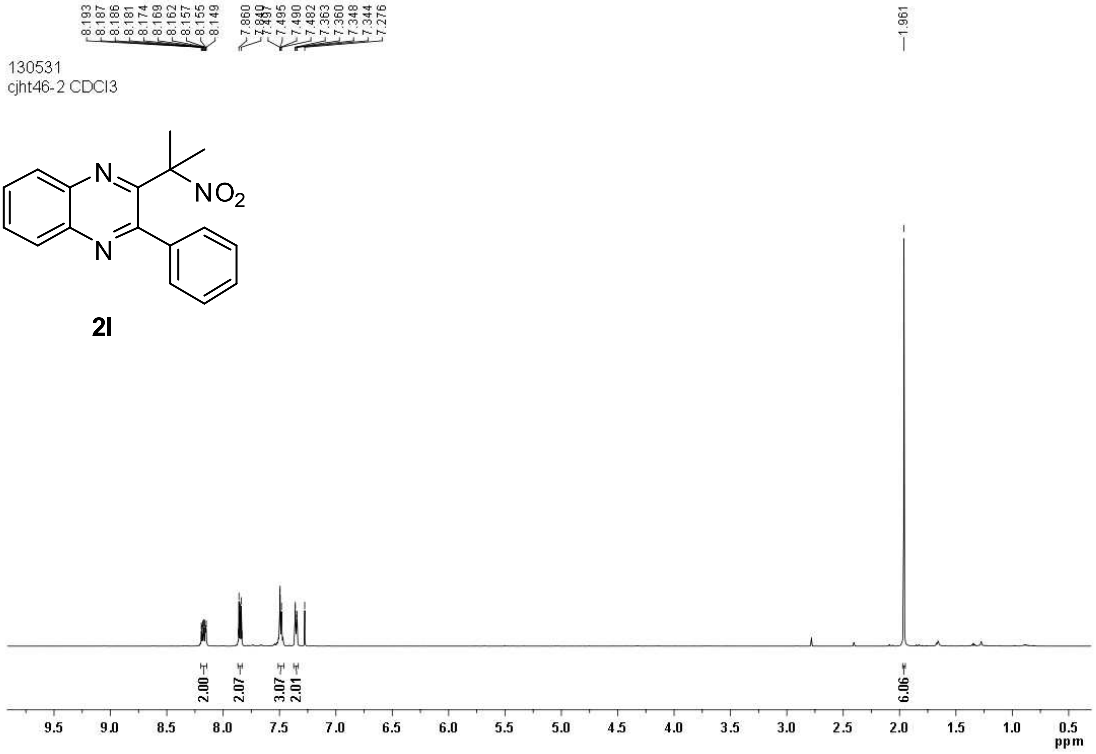
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8.169
8.162
8.157
8.155
8.149
7.860
7.849
7.497
7.495
7.490
7.482
7.363
7.360
7.348
7.344
7.276
1.961
130531
cjht46-2 CDCl3
N
N
NO2
2l
2.00
2.07
3.07
2.01
6.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
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2.0
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1.0
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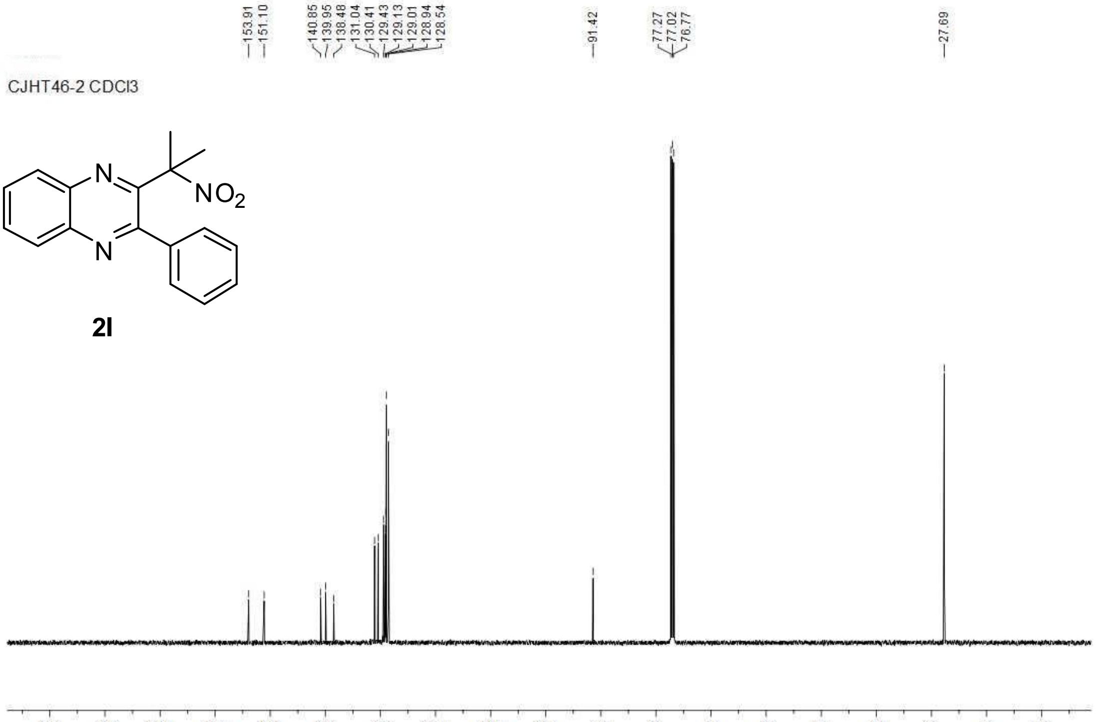
ppm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129.43
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129.01
128.94
128.54
91.42
77.27
77.02
76.77
27.69
CJHT46-2 CDCl3
N
N
NO2
2l
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180
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150
140
130
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70
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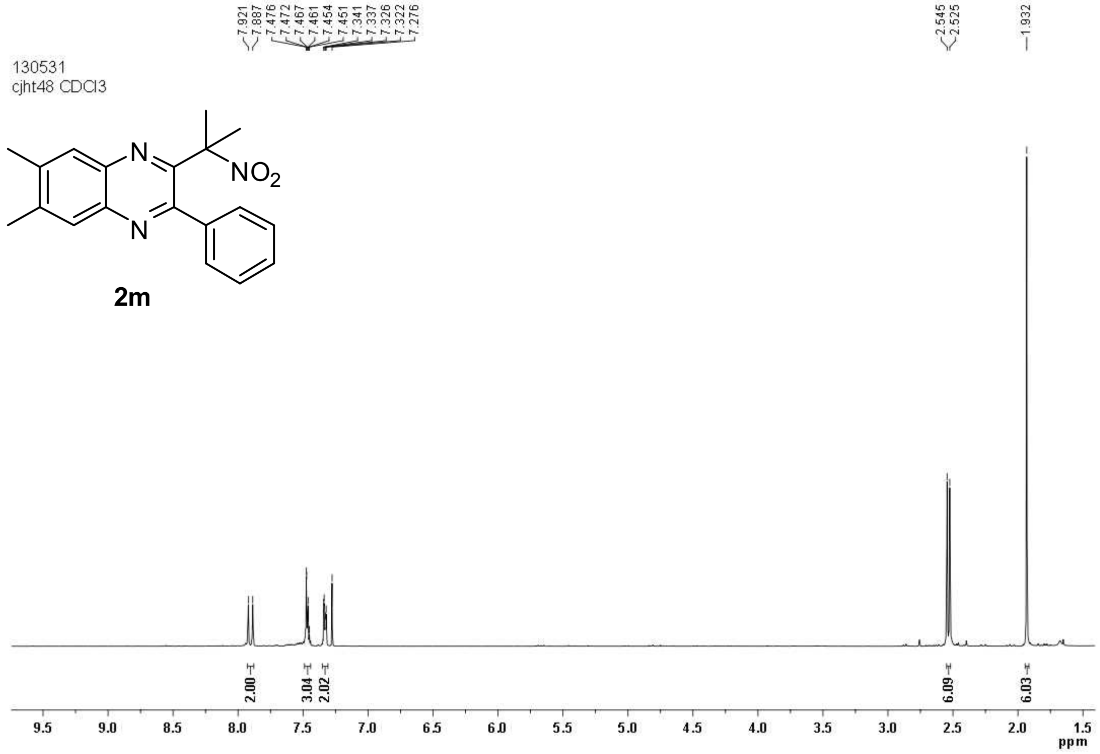
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7.337
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7.322
7.276
2.545
2.525
1.932
130531
cjht48 CDCl3
N
N
NO2
2m
2.00
3.04
2.02
6.09
6.03
9.5
9.0
8.5
8.0
7.5
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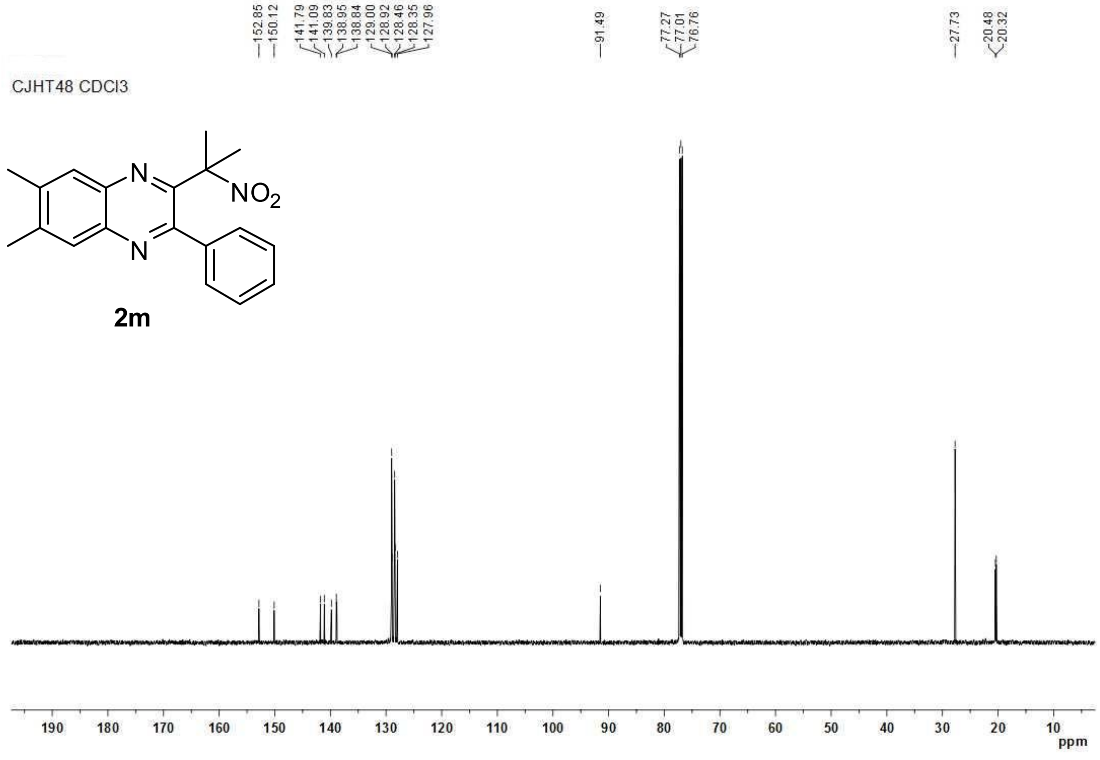
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129.00
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128.46
128.35
127.96
91.49
77.27
77.01
76.76
27.73
20.48
20.32
CJHT48 CDCl3
N
N
NO2
2m
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180
170
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150
140
130
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110
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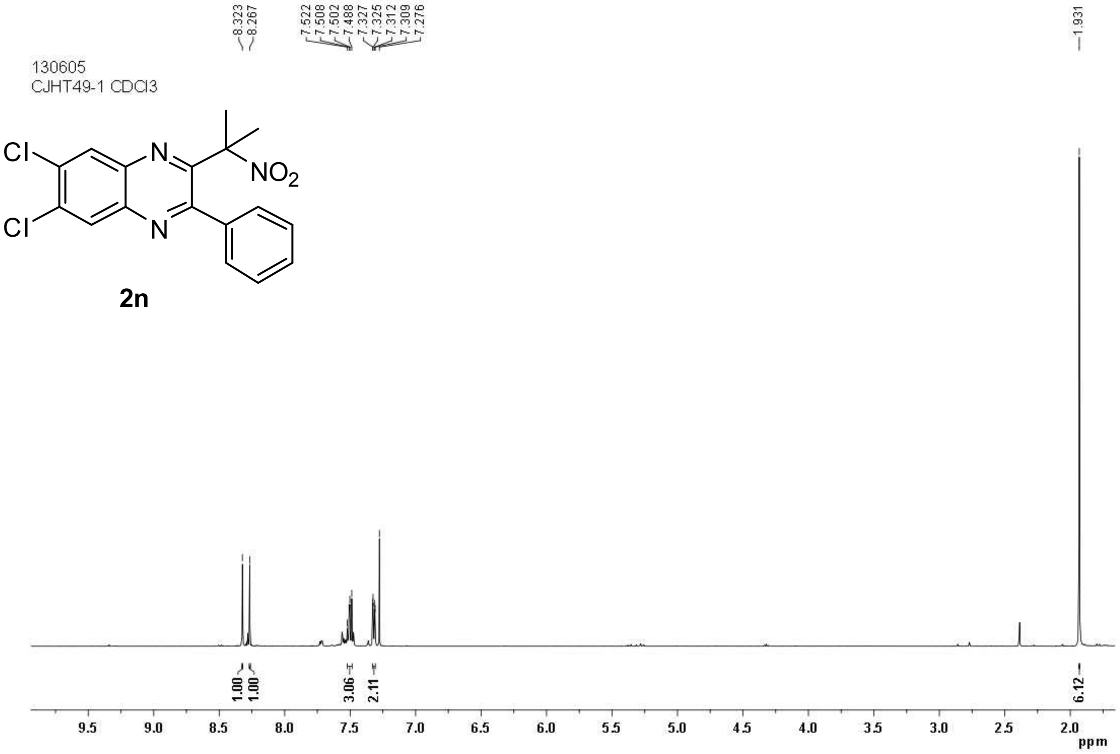
ppm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Cl
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7.488
7.327
7.325
7.312
7.309
7.276
1.931
1.00
1.00
3.06
2.11
6.12
9.5
9.0
8.5
8.0
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7.0
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6.0
5.5
5.0
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3.5
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2.5
2.0
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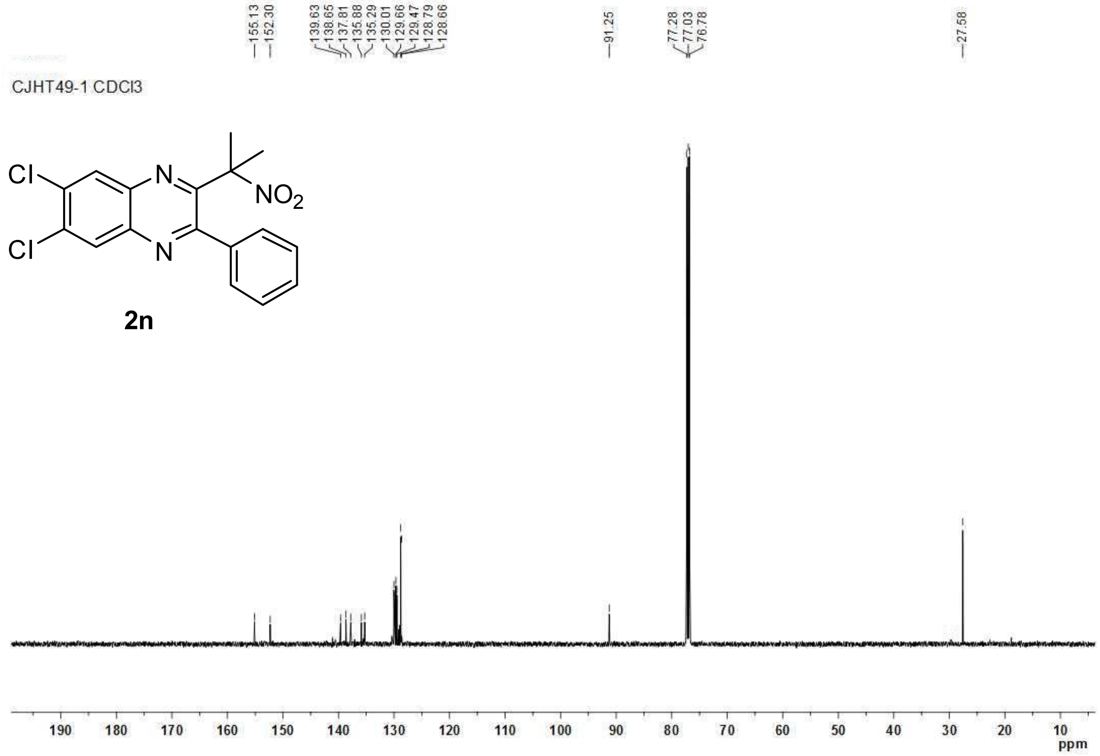
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Cl
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135.29
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129.66
129.47
128.79
128.66
91.25
77.28
77.03
76.78
27.58
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150
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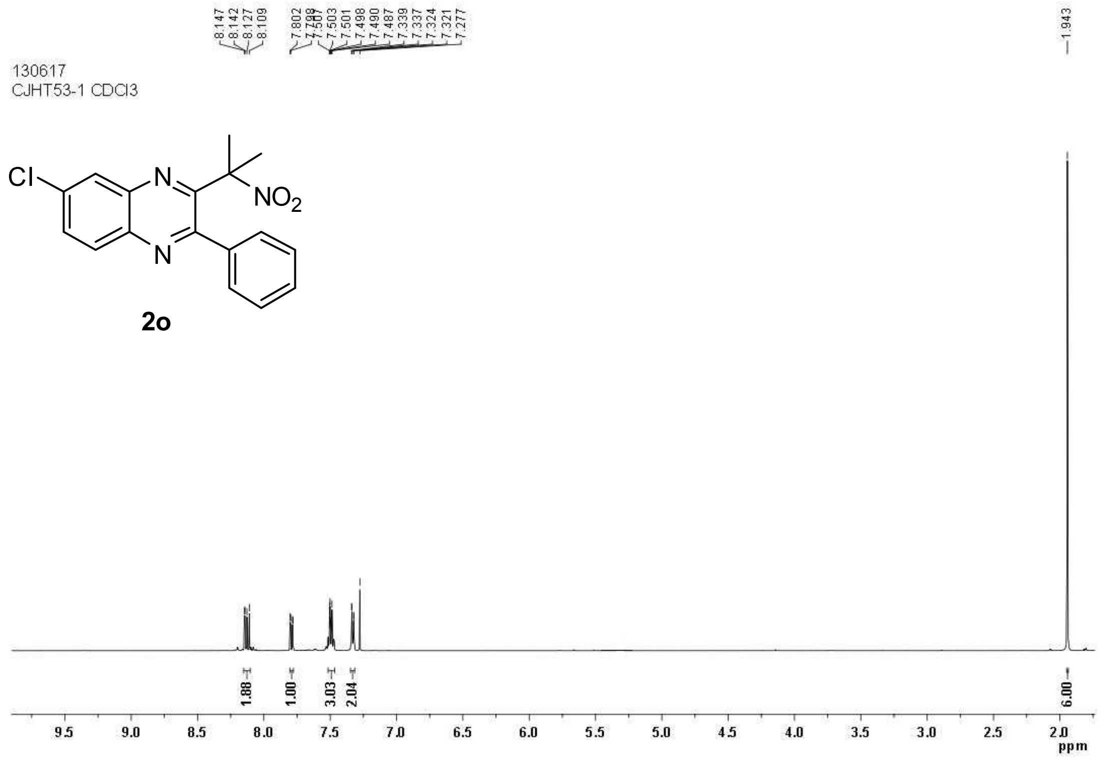
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7.501
7.498
7.490
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7.339
7.337
7.324
7.321
7.277
1.943
130617
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Cl
N
N
NO2
2o
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1.00
3.03
2.04
6.00
9.5
9.0
8.5
8.0
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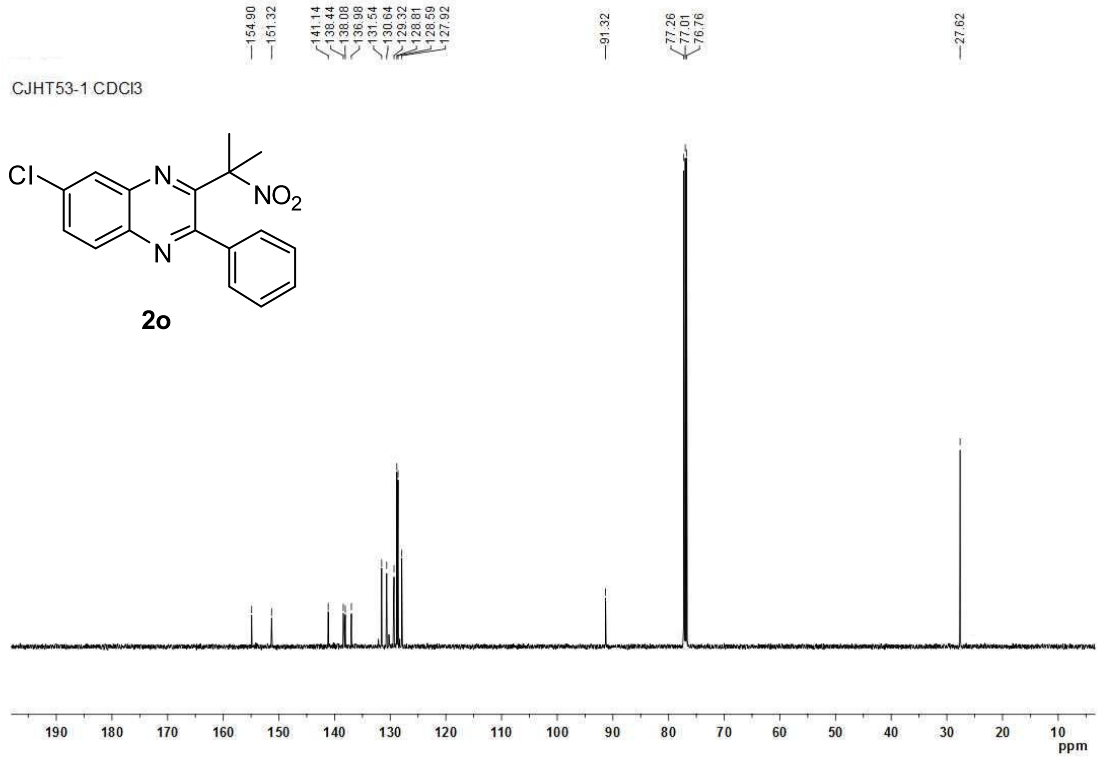
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130.64
129.32
128.81
128.59
127.92
91.32
77.26
77.01
76.76
27.62
CJHT53-1 CDCl3
Cl
N
N
NO2
2o
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140
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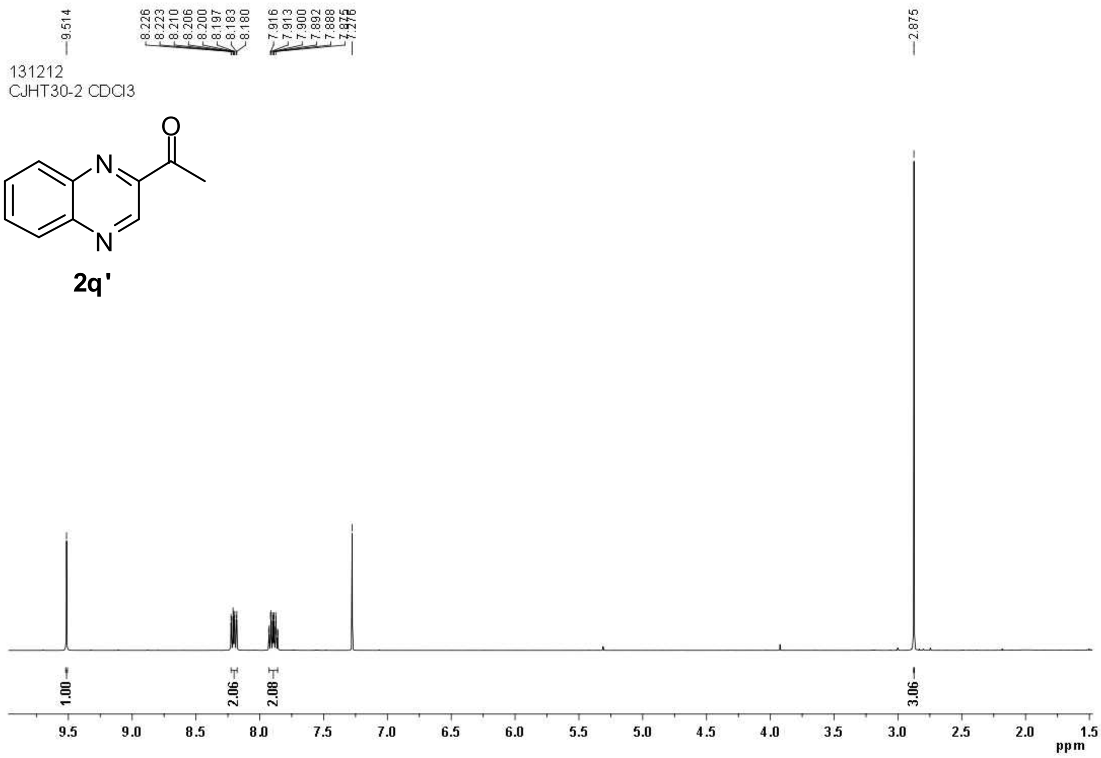
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8.200
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8.183
8.180
7.916
7.913
7.900
7.892
7.888
7.875
7.276
2.875
131212
CJHT30-2 CDCl3
O
N
N
1.00
2.06
2.08
3.06
9.5
9.0
8.5
8.0
7.5
7.0
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5.0
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2.5
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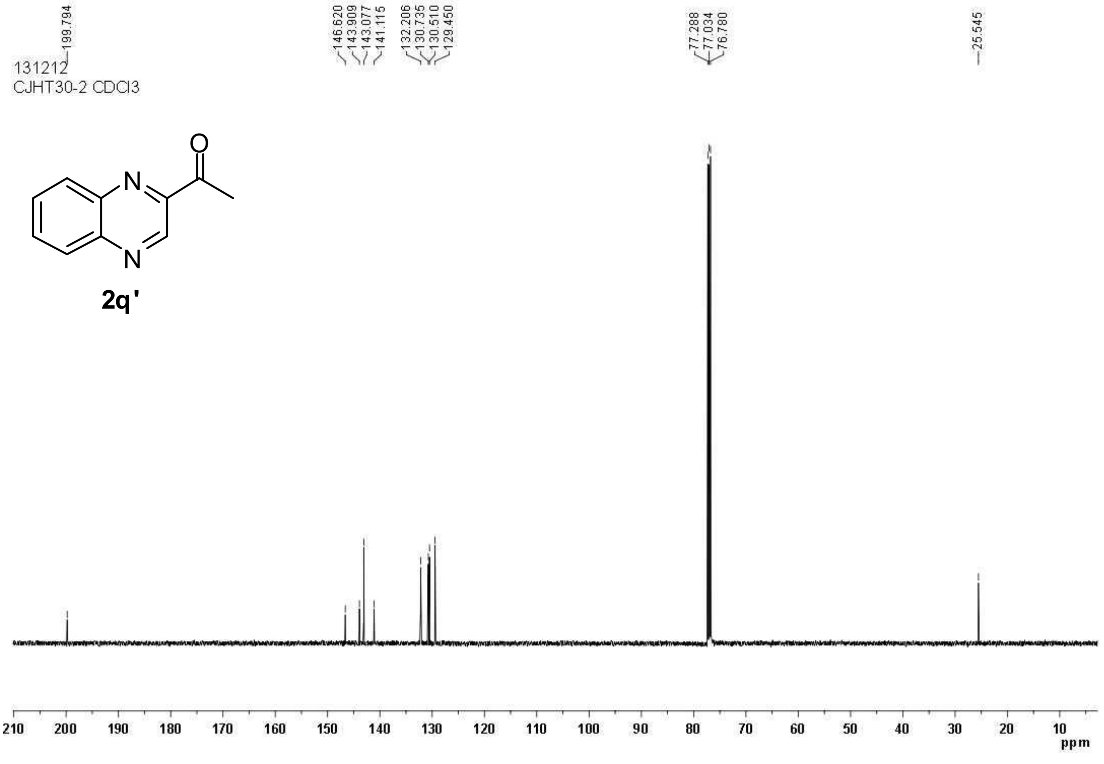
2q'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130.510
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77.034
76.780
25.545
131212
CJHT30-2 CDCl3
O
N
N
210
200
190
180
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120
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100
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50
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30
20
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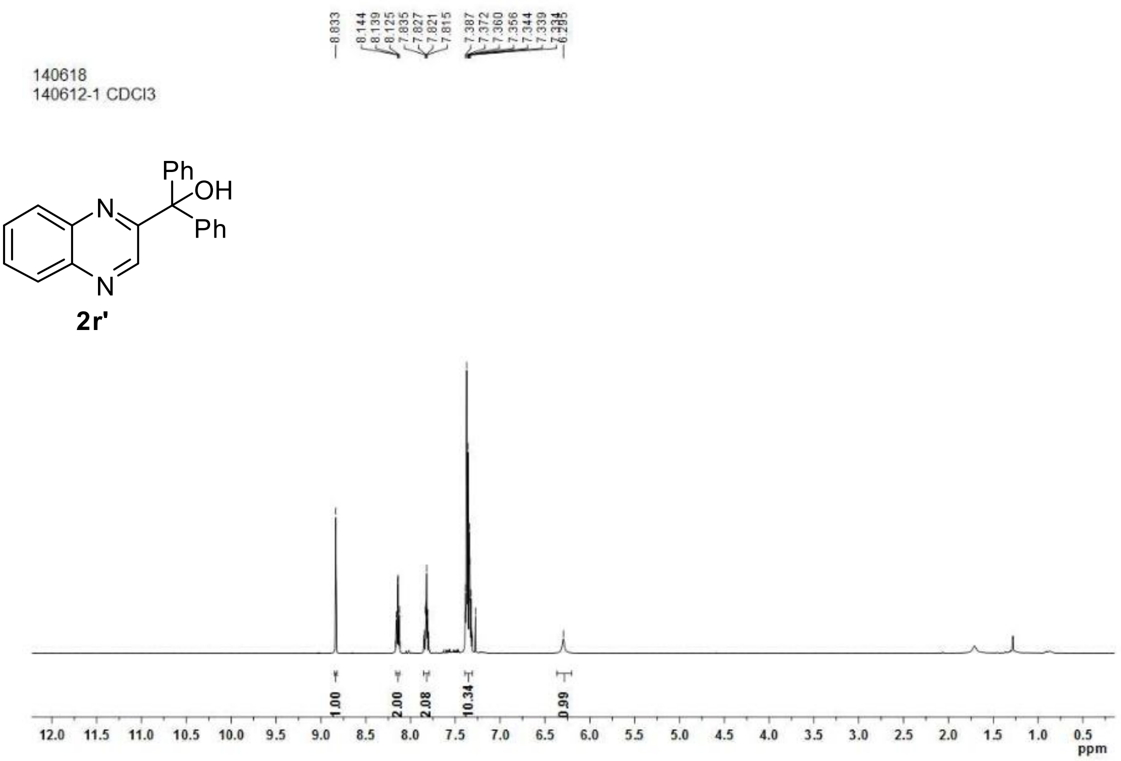
2q'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7.821
7.815
7.387
7.372
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7.356
7.344
7.339
7.334
6.295
140618
140612-1 CDCl3
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OH
Ph
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N
2r'
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2.00
2.08
10.34
0.99
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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4.5
4.0
3.5
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2.0
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1.0
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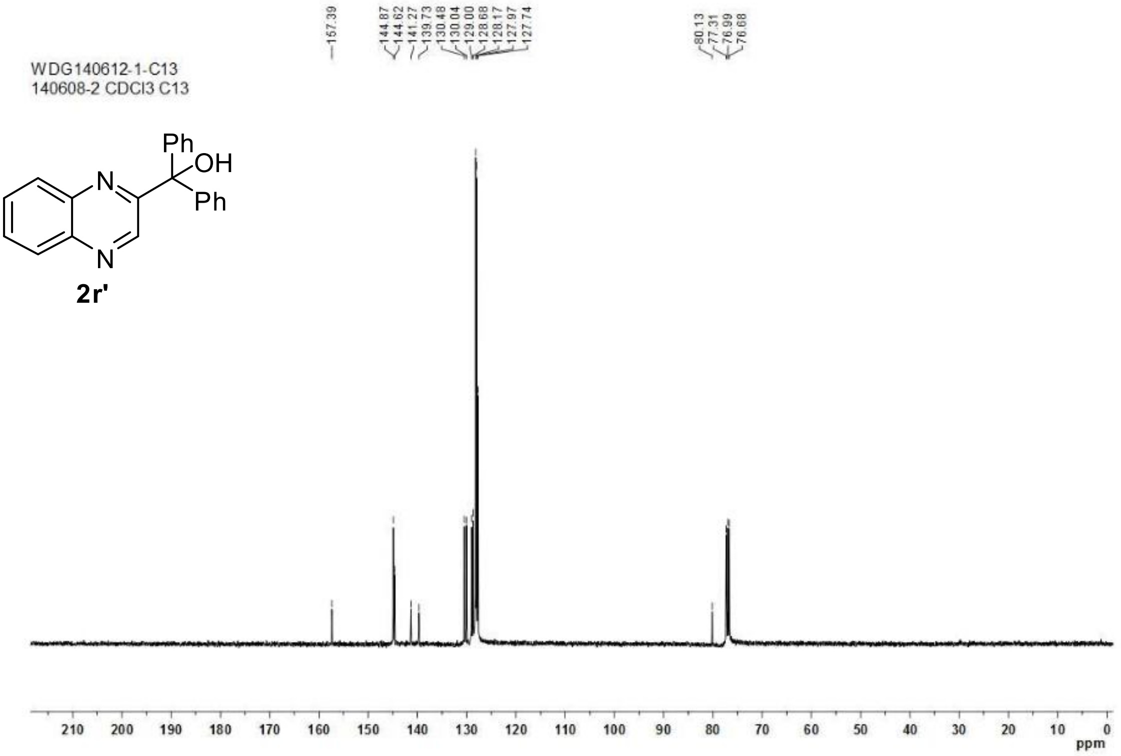
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129.00
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128.17
127.97
127.74
80.13
77.31
76.99
76.68
WDG140612-1-C13
140608-2 CDCl3 C13
Ph
OH
Ph
N
N
2r'
210
200
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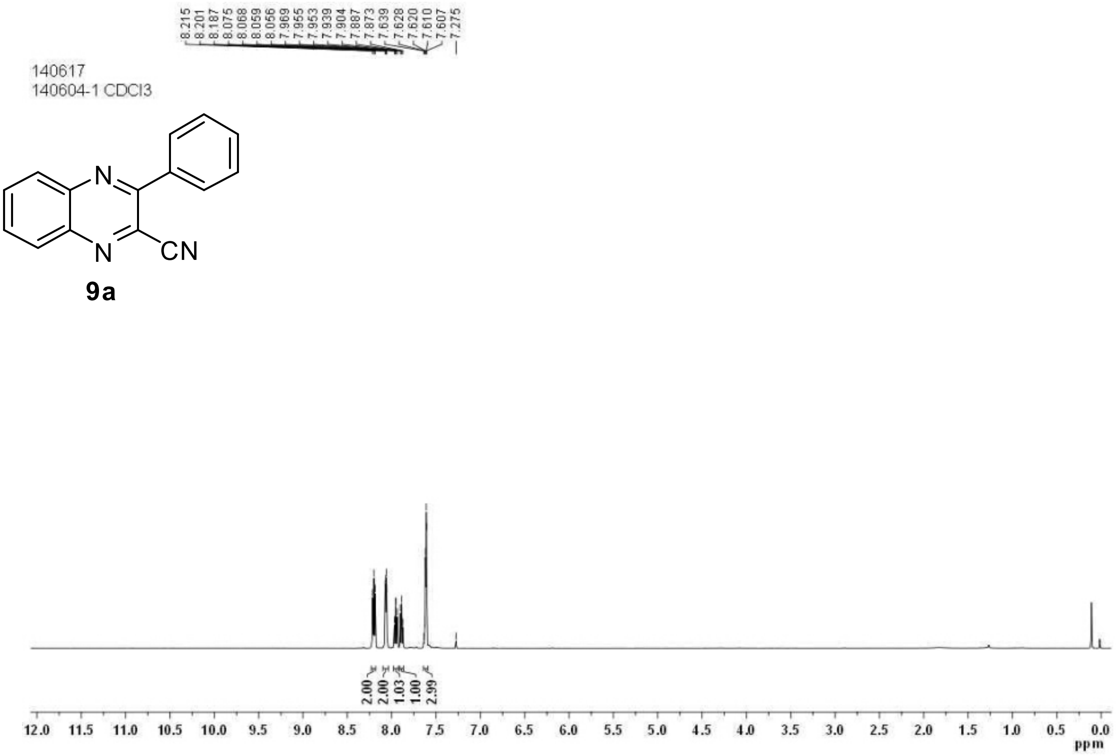
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7.939
7.904
7.887
7.873
7.639
7.628
7.620
7.610
7.607
7.275
140617
140604-1 CDCl3
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N
CN
9a
2.00
2.00
1.03
1.00
2.99
12.0
11.5
11.0
10.5
10.0
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7.0
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6.0
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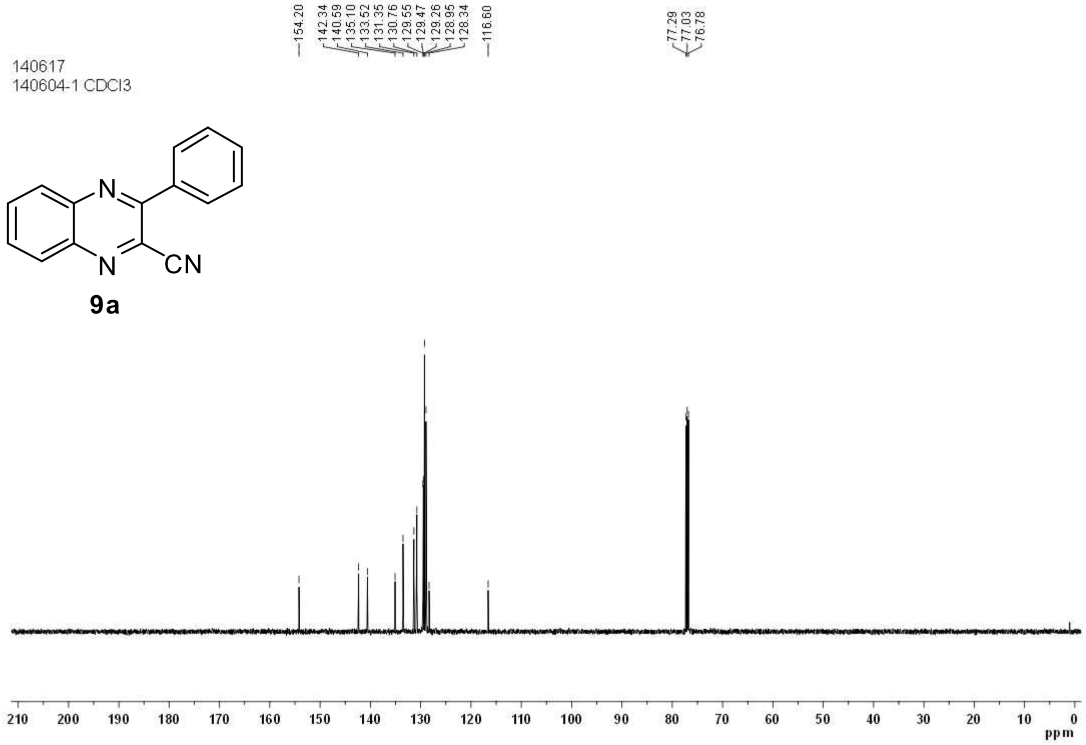
ppm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116.60
77.29
77.03
76.78
140617
140604-1 CDCl3
N
N
CN
9a
210
200
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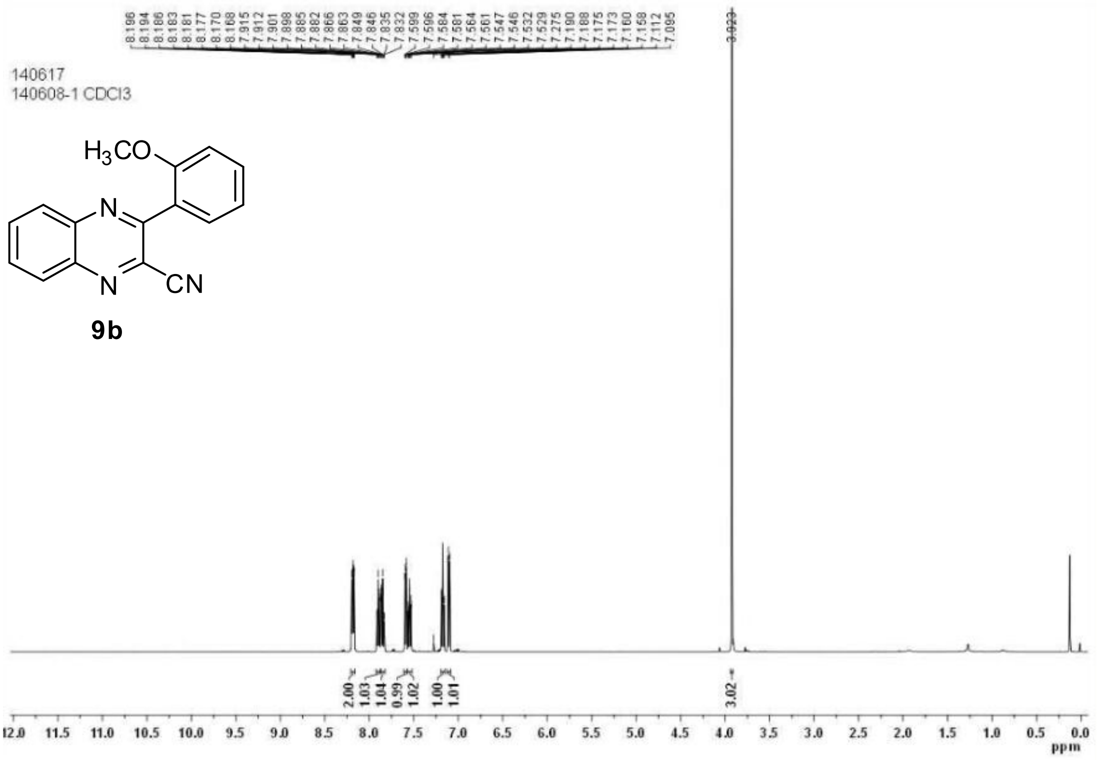
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H3CO
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8.170
8.168
7.915
7.912
7.901
7.898
7.885
7.882
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7.863
7.849
7.846
7.835
7.832
7.599
7.596
7.584
7.581
7.564
7.561
7.547
7.546
7.532
7.529
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7.190
7.188
7.175
7.173
7.160
7.158
7.112
7.095
3.923
2.00
1.03
1.04
0.99
1.02
1.00
1.01
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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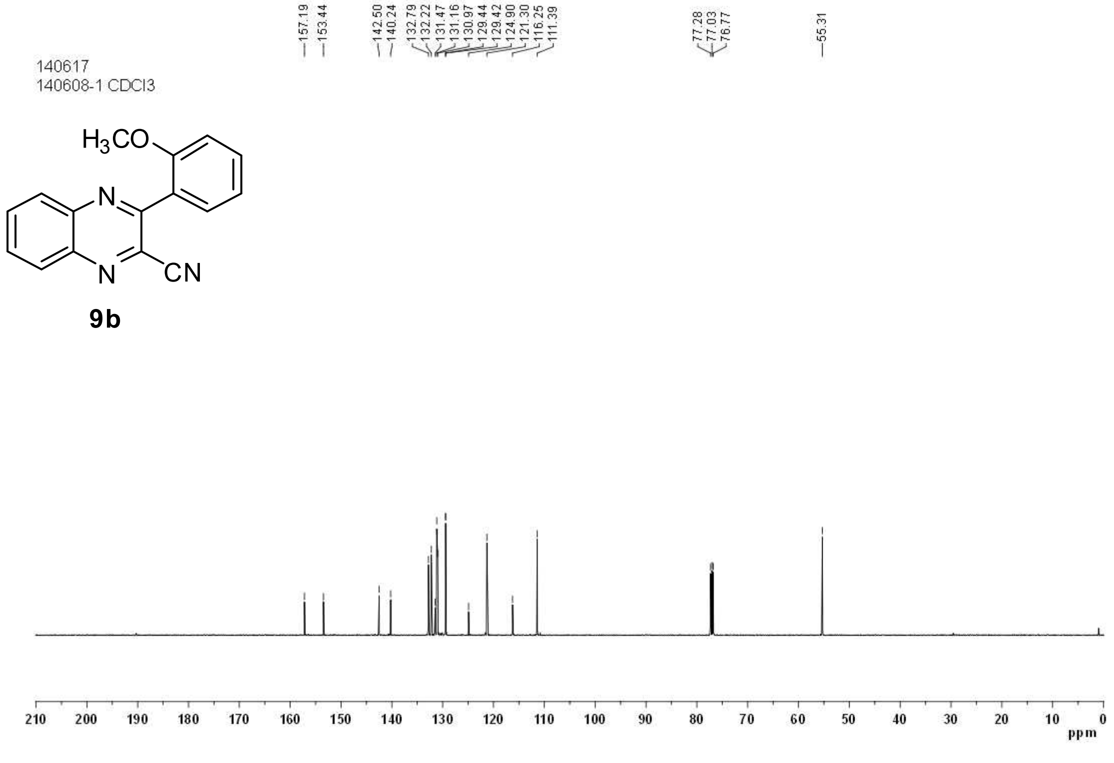
9b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CN
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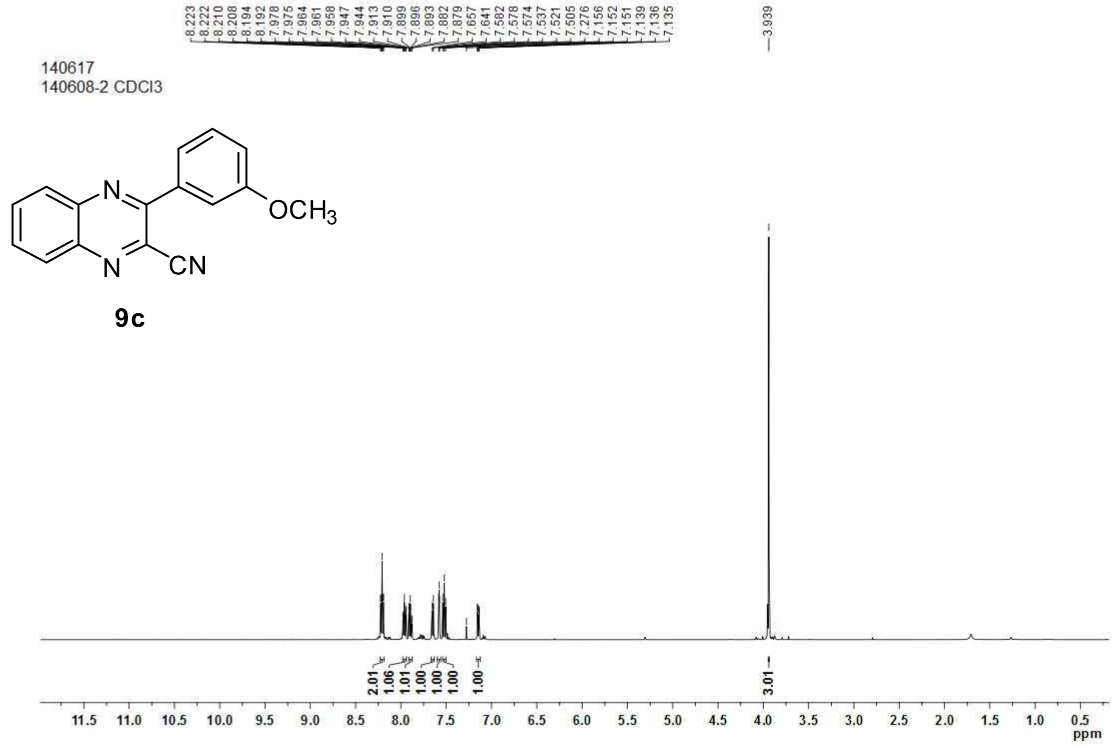
131.47
131.16
130.97
129.44
129.42
124.90
121.30
116.25
111.39
77.28
77.03
76.77
55.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

9b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7.961
7.958
7.947
7.944
7.913
7.910
7.899
7.896
7.893
7.882
7.879
7.657
7.641
7.582
7.578
7.574
7.537
7.521
7.505
7.276
7.156
7.152
7.151
7.139
7.136
7.135
3.939
140617
140608-2 CDCl3
N
N
OCH3
CN
9c
2.01
1.06
1.01
1.00
1.00
1.00
1.00
3.01
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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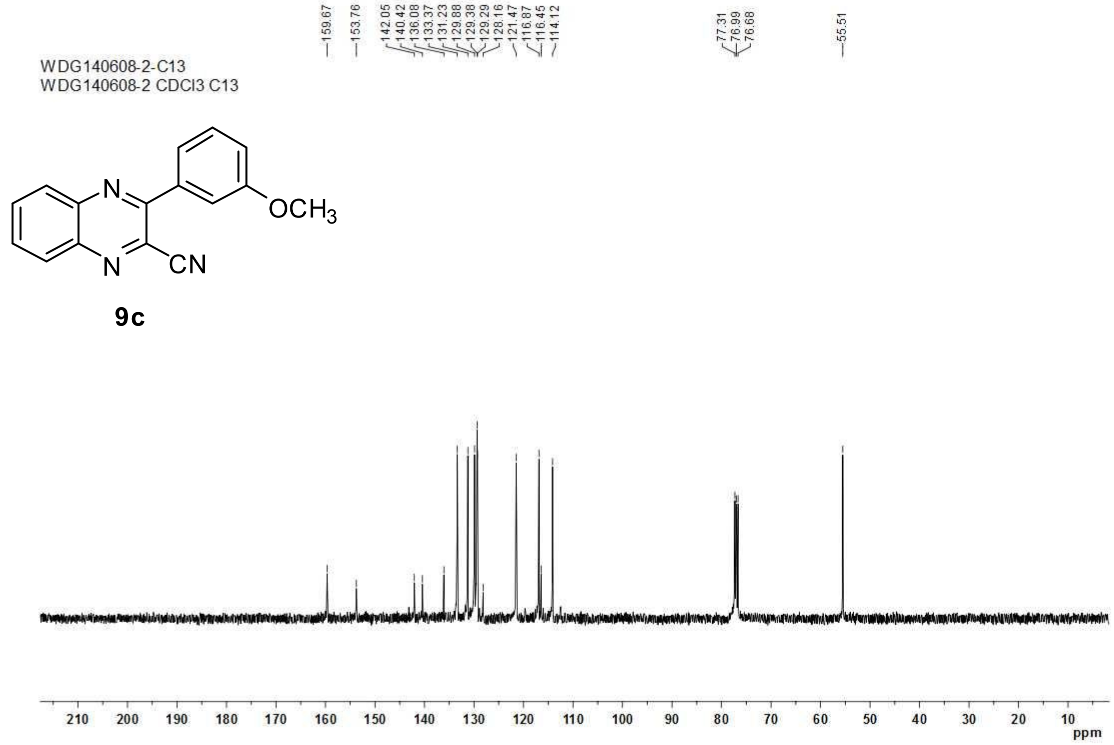
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133.37
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129.38
129.29
128.16
121.47
116.87
116.45
114.12
77.31
76.99
76.68
55.51
WDG140608-2-C13
WDG140608-2 CDCl3 C13
N
N
OCH3
CN
9c
210
200
190
180
170
160
150
140
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120
110
100
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30
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10
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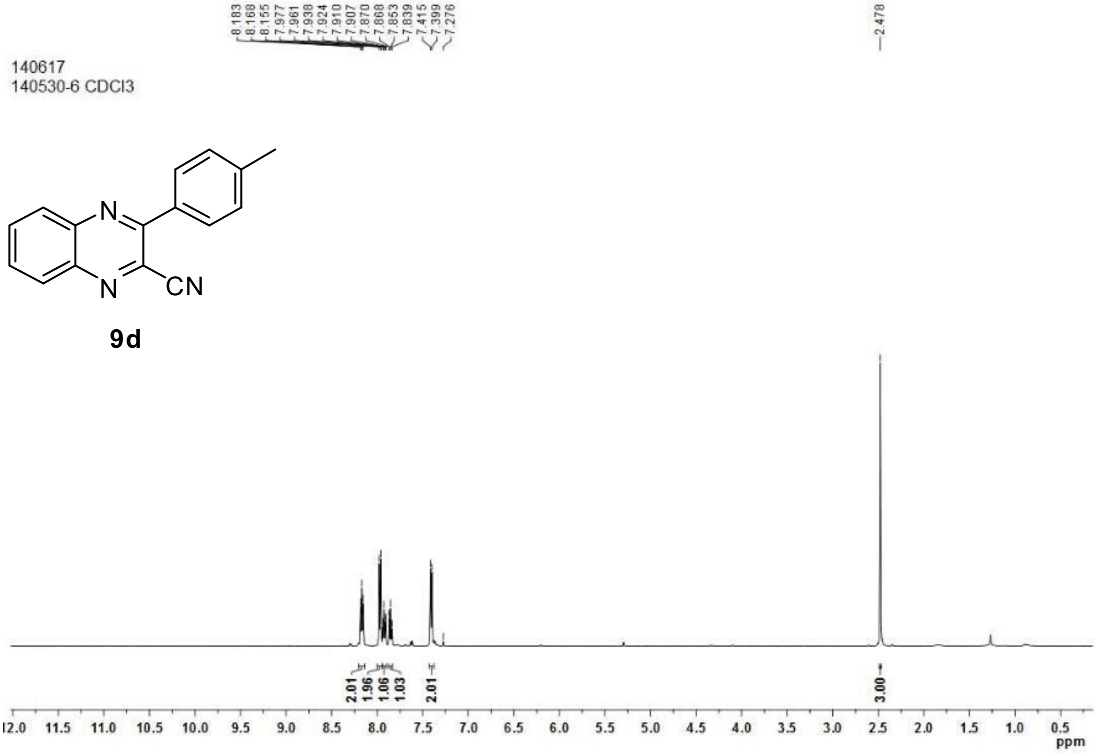
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7.938
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7.910
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7.870
7.868
7.853
7.839
7.415
7.399
7.276
2.478
140617
140530-6 CDCl3
N
N
CN
9d
2.01
1.96
1.06
1.03
2.01
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
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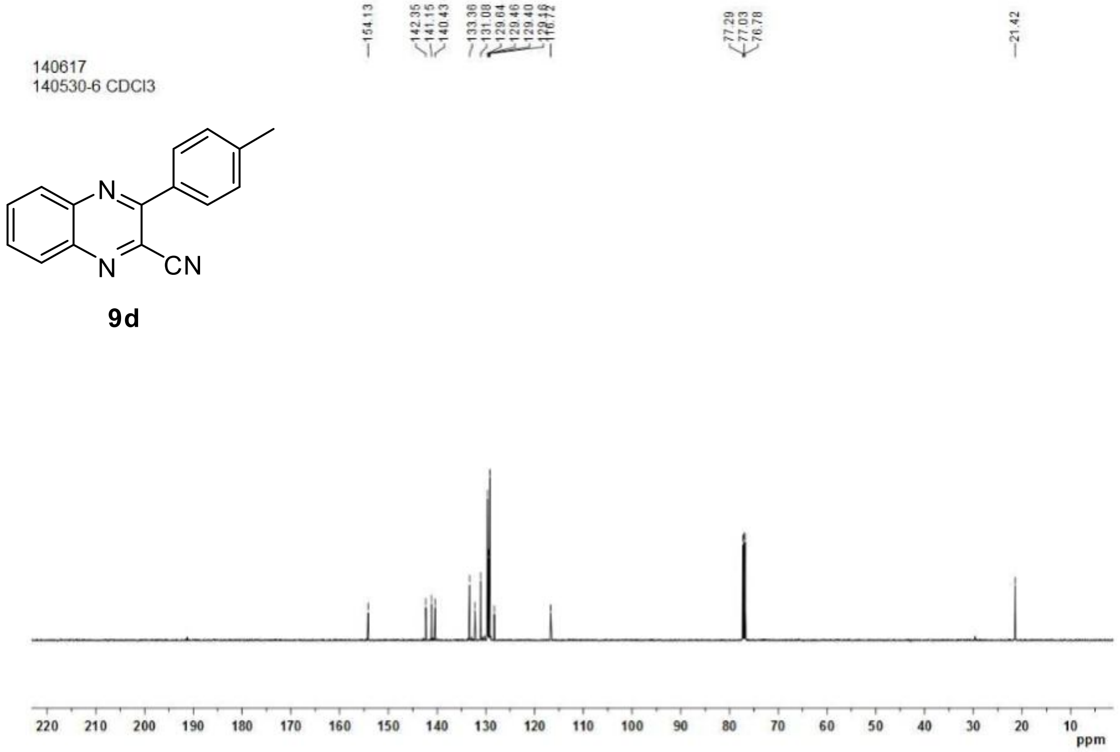
2.0
1.5
1.0
0.5
ppm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76.78
21.42
140617
140530-6 CDCl3
N
N
CN
9d
220
210
200
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150
140
130
120
110
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30
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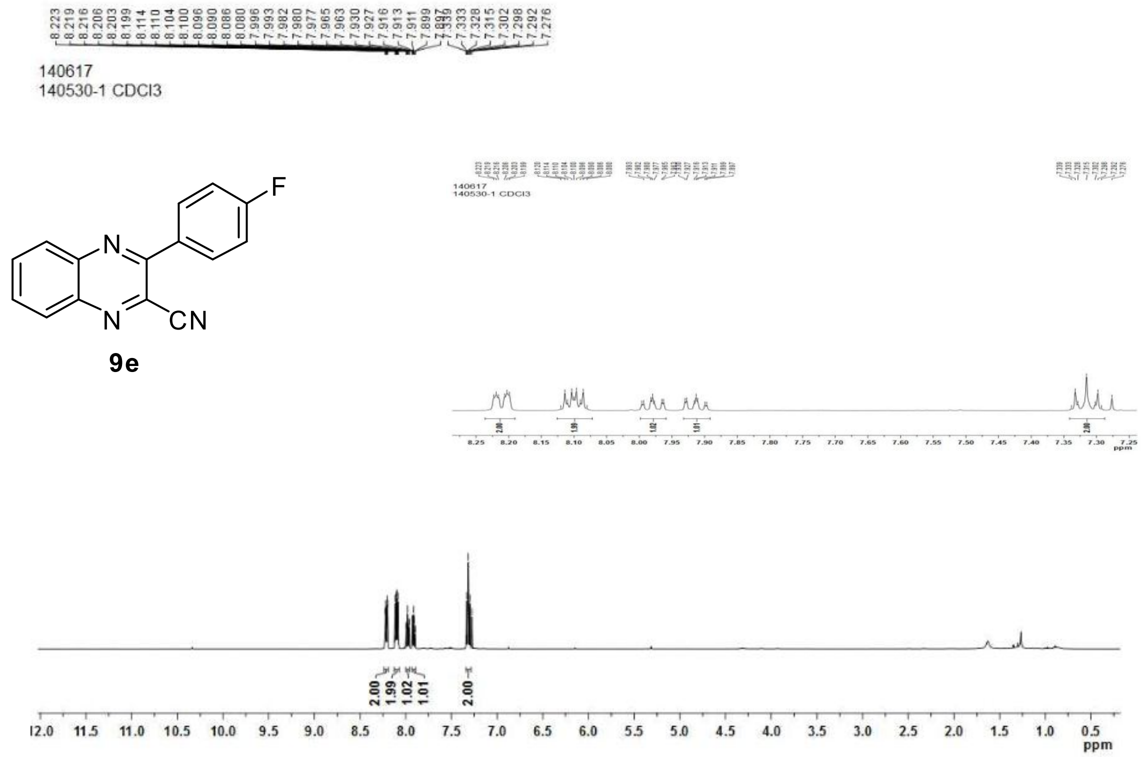
10
ppm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8.110
8.104
8.100
8.096
8.090
8.086
8.080
7.996
7.993
7.982
7.980
7.977
7.965
7.963
7.930
7.927
7.916
7.913
7.911
7.899
7.897
7.339
7.333
7.328
7.315
7.302
7.298
7.292
7.276
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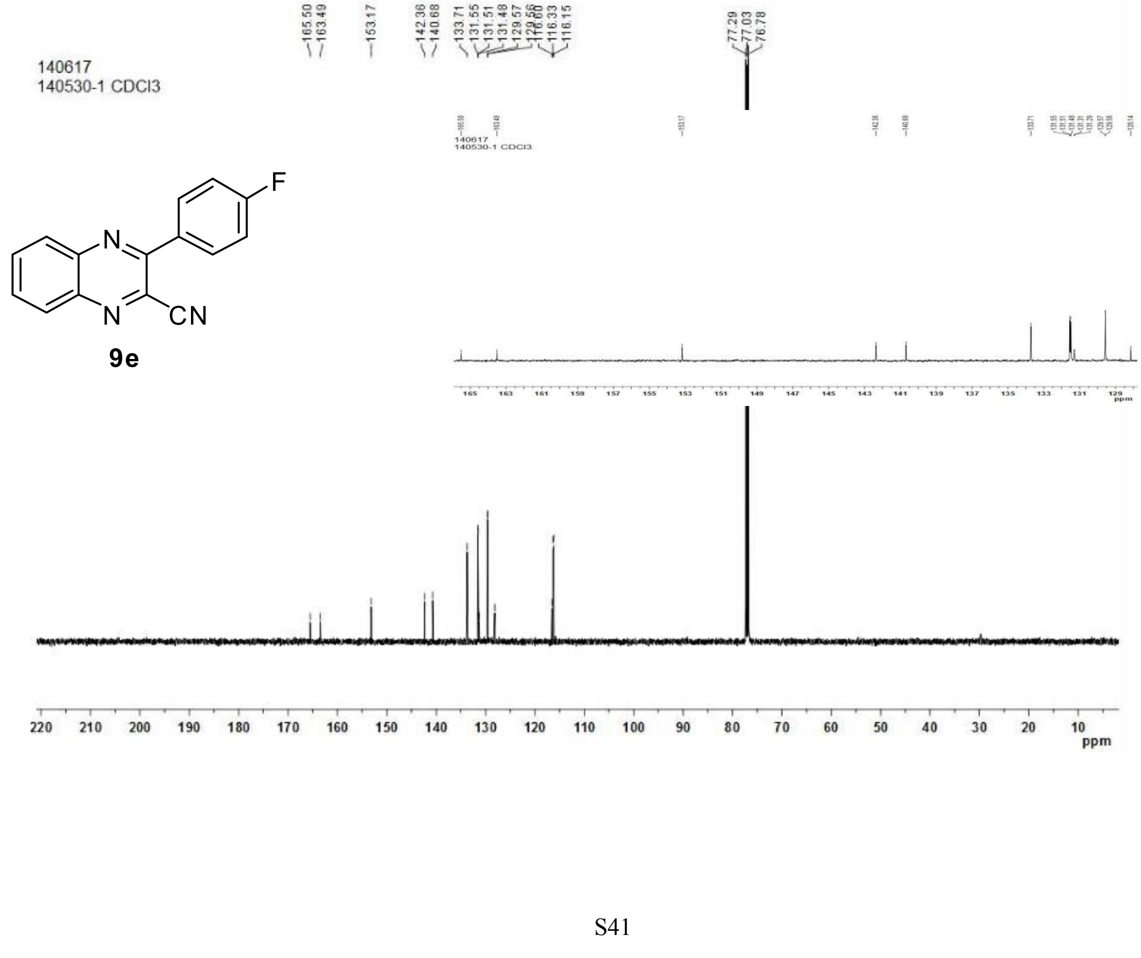
N
N
F
CN
2.00
1.99
1.02
1.01
2.00
ppm

9e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163.49
153.17
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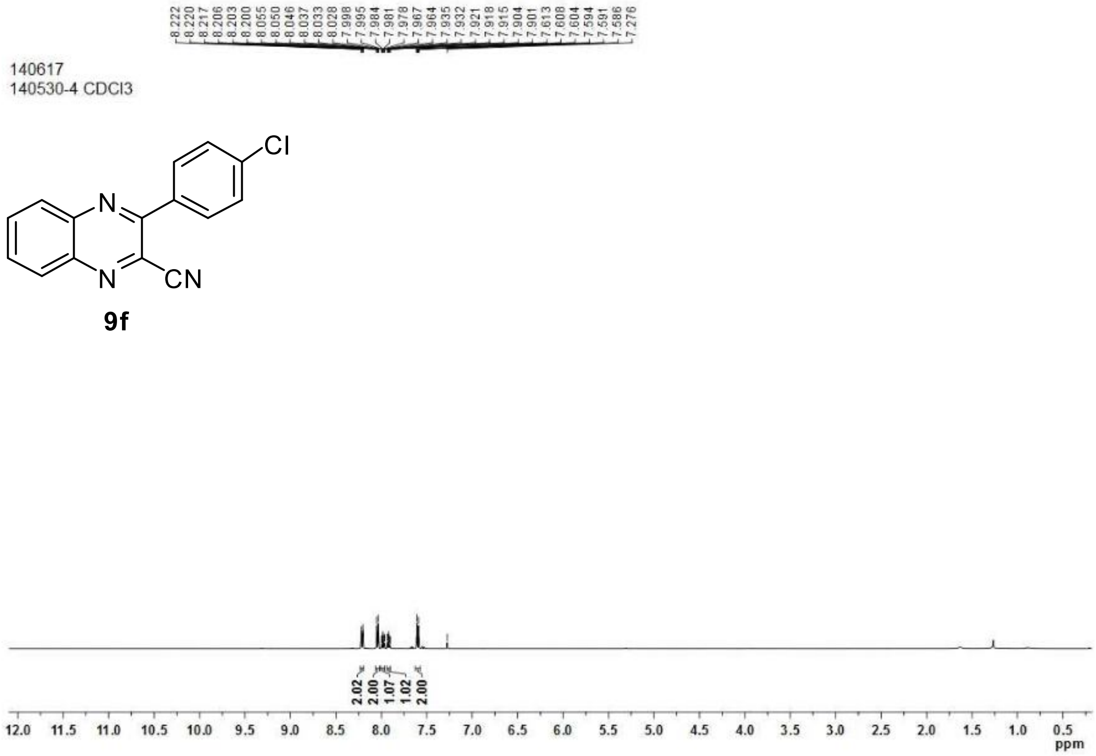
140.68
133.71
131.55
131.51
131.48
129.57
129.56
116.60
116.33
116.15
77.29
77.03
76.78
140617
140530-1 CDCl3
N
N
F
CN
ppm

9e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8.220
8.217
8.206
8.203
8.200
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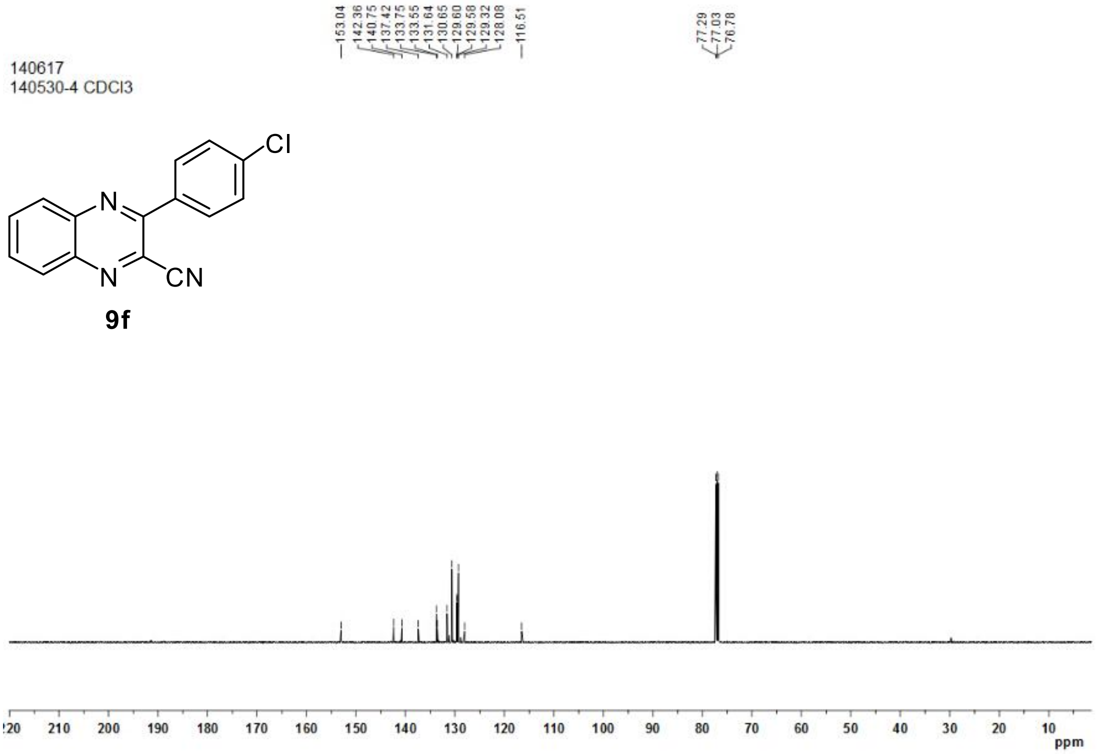
8.050
8.046
8.037
8.033
8.028
7.998
7.995
7.984
7.981
7.978
7.967
7.964
7.935
7.932
7.921
7.918
7.915
7.904
7.901
7.613
7.608
7.604
7.594
7.591
7.586
7.276
140617
140530-4 CDCl3
N
N
Cl
CN
9f
2.02
2.00
1.07
1.02
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm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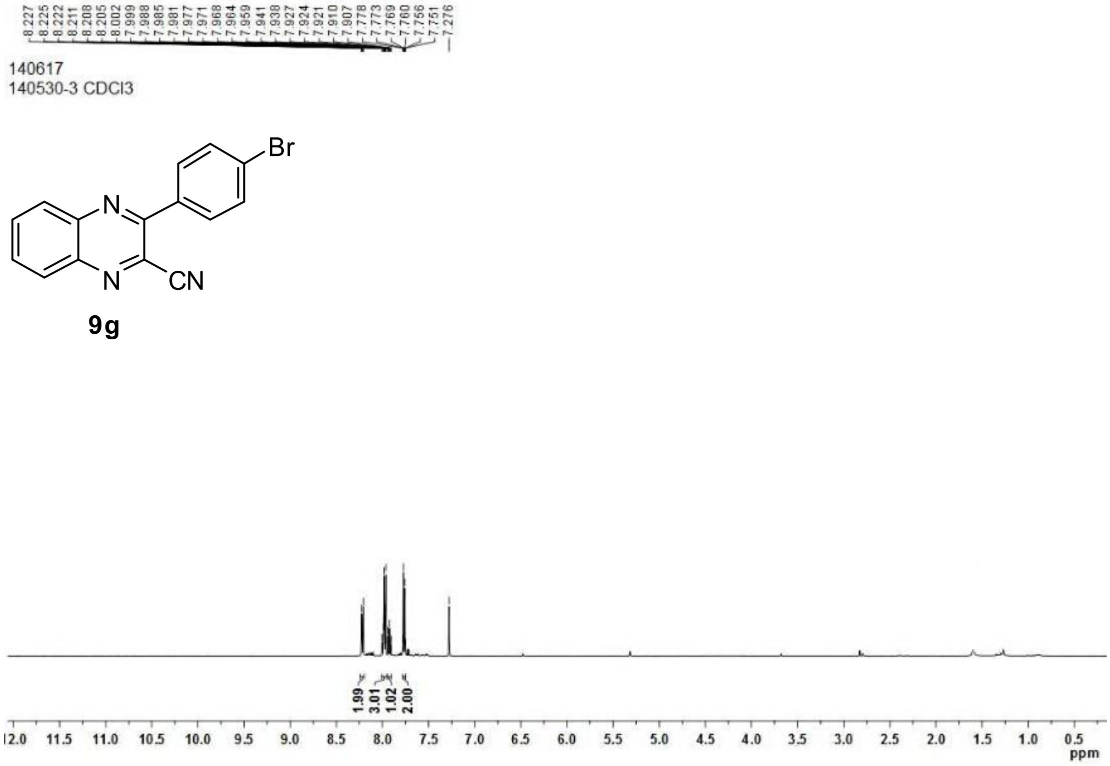
130.65
129.60
129.58
129.32
128.08
116.51
77.29
77.03
76.78
140617
140530-4 CDCl3
N
N
Cl
CN
9f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm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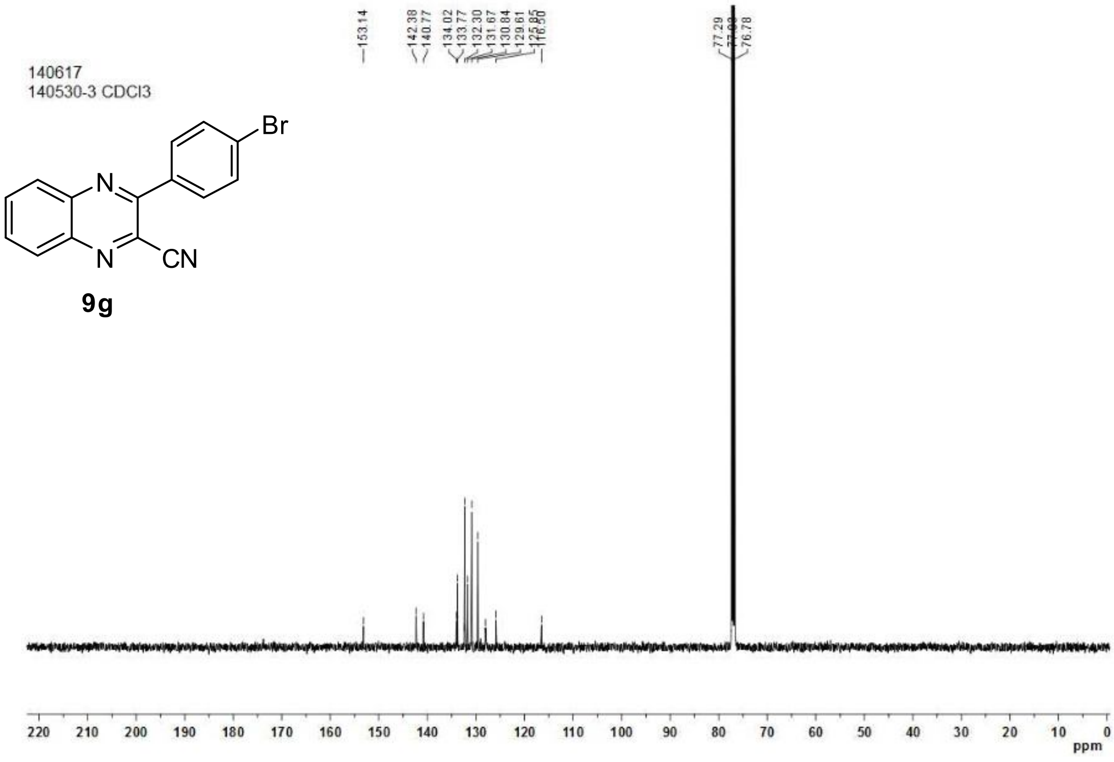
8.225
8.222
8.211
8.208
8.205
8.002
7.999
7.988
7.985
7.981
7.977
7.971
7.968
7.964
7.959
7.941
7.938
7.927
7.924
7.921
7.910
7.907
7.778
7.773
7.769
7.760
7.756
7.751
7.276
140617
140530-3 CDCl3
Br
N
N
CN
9g
1.99
3.01
1.02
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm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140.77
134.02
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132.30
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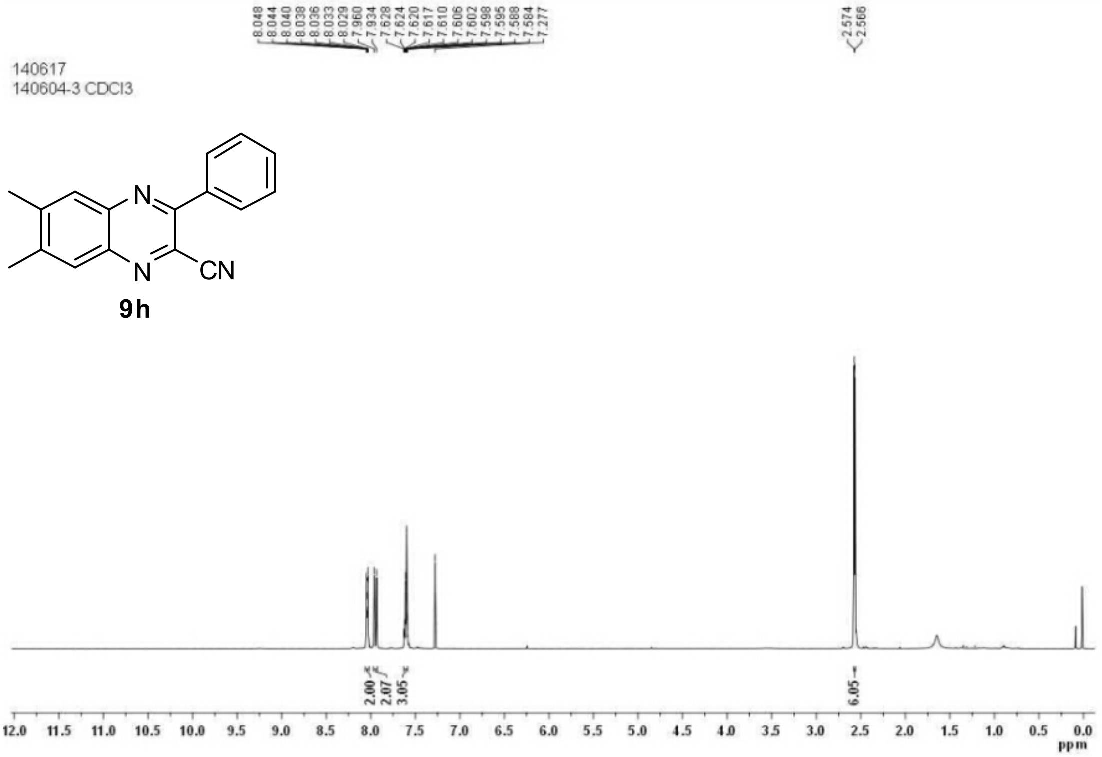
130.84
129.61
125.85
116.50
77.29
77.03
76.78
140617
140530-3 CDCl3
Br
N
N
CN
9g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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8.033
8.029
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7.628
7.624
7.620
7.617
7.610
7.606
7.602
7.598
7.595
7.588
7.584
7.277
2.574
2.566
140617
140604-3 CDCl3
N
N
CN
9h
2.00
2.07
3.05
6.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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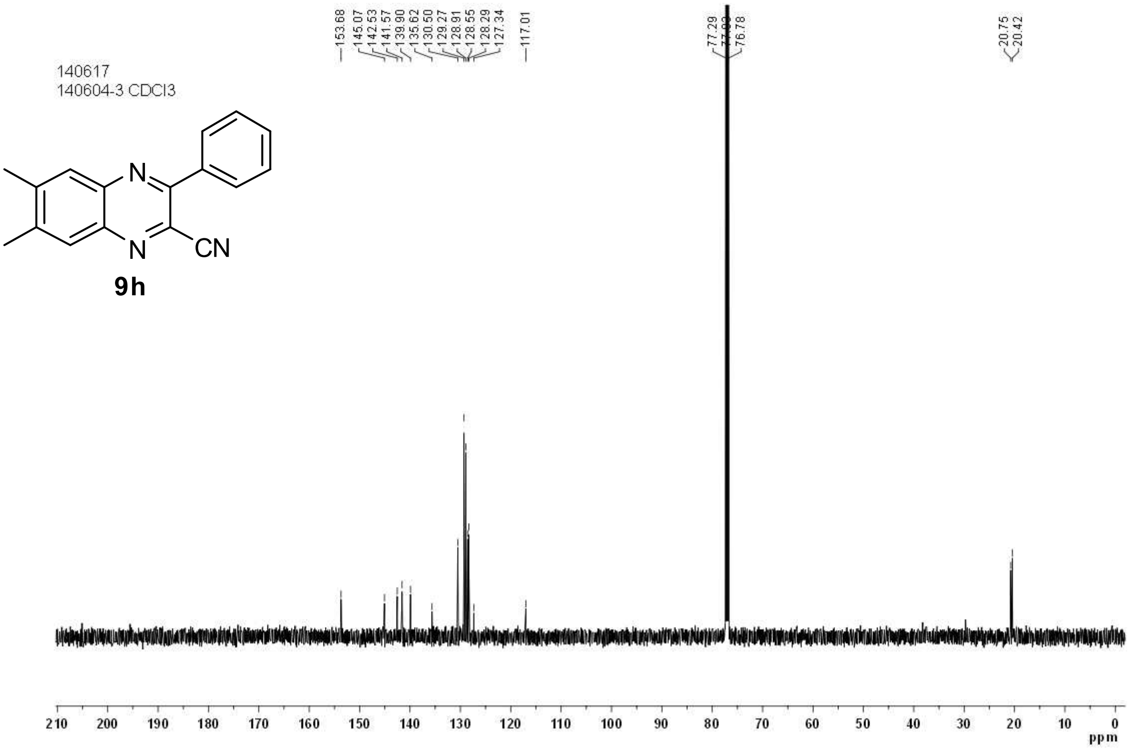
0.0
ppm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139.90
135.62
130.50
129.27
128.91
128.55
128.29
127.34
117.01
77.29
77.03
76.78
20.75
20.42
140617
140604-3 CDCl3
N
N
CN
9h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm