Construction of arylthio/arylamino methylene bonds by addition-elimination of nitroolefins with aromatic thiols and amines

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SUPPORTING INFORMATION

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General information:

Unless otherwise noted, chemicals were purchased from commercial suppliers at the highest purity grade available and were used without further purification. The isatin nitroolefin derivatives **2b, 2c, 2d** were synthesized by literature methods.[24] Thin layer chromatography was performed on pre-coated 0.25 mm silica gel plates (60F-254) using UV light as visualizing agent. Silica gel (100–200 mesh) was used for column chromatography. NMR spectra were recorded in $CDCl_3$ and/or DMSO-d_6 using TMS as an internal standard on 500 MHz and instrument. Chemical shifts (δ) were reported as parts per million (ppm) in δ scale downfield from TMS. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm, the middle peak). Coupling constants were expressed in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. High-resolution mass spectra (HRMS) were obtained on an Agilent 1290-6545XT LC QTOF instrument using ESI technique.

General procedures:

General procedure for the synthesis of 3a-3p:

Nitroolefin **2** (0.1 mmol) and thiophenol **1** (0.12 mmol) were taken in a 10 mL-RB. 1 mL of methanol was added in the reaction mixture and stirred until the completion of the reaction. Yellow solid was precipitated out within 1–10 minutes which is filtered and washed with a few drops of cold methanol and dried in vacuum.

General procedure for the synthesis of 5a-5v:

Nitroolefin **2** (0.1mmol) and aniline **4** (0.12 mmol) were taken in a 10 mL RB. 1 mL of methanol was added in the reaction mixture and stirred until the completion of the reaction. Yellow solid was precipitated out within 1-10 minutes which is filtered and washed with few drops of methanol and dried in vacuum.

Characterization data:

(*Z*)-2-(Nitromethylene)acenaphthylen-1(2*H*)-one (2a)

Yield: 13.7 gm (61%) as Yellow solid; MP: 132 –134 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.78 (d, J = 7.4 Hz, 1H), 8.20 (dd, J = 8.2, 0.7 Hz, 1H), 8.14–8.10 (m, 2H), 7.85 (s, 1H), 7.81 (ddd, J = 8.4, 7.2, 1.2 Hz, 2 H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.9, 144.2, 137.4, 135.2, 132.4, 130.8, 130.27, 130.23, 129.2, 129.1, 129.0, 128.4, 128.4, 127.9, 127.4, 123.1 ppm.

HRMS (ESI): *m/z* calcd for $C_{13}H_8NO_3$ $[M + H]^+$ 226.0499; found; 226.0509.

(*E*)-2-((Phenylthio)methylene)acenaphthylen-1(2*H*)-one (3a)

Yield: 25 mg (87%) as Yellow solid; MP: 130–132 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.76 (d, 2H, J = 7.4 Hz), 8.21–8.10 (m, 5H), 7.84 (s, 1H), 7.81 (ddd, 4H, J = 8.2, 7.3, 3.8 Hz) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.8, 144.1, 137.3, 135.1, 132.4, 130.8, 130.2, 130.2, 130.2, 130.2, 130.2, 130.1, 130.1, 129.0, 128.4, 127.8, 127.4, 123.0 ppm.

HRMS (ESI): *m/z* calcd for $C_{19}H_{13}OS$ $[M + H]^+$: 289.0682; found; 289.0686.

(*E*)-2-((*p*-Tolylthio)methylene)acenaphthylen-1(2*H*)-one (3b)

Yield: 28 mg (93%) as Yellow solid; MP: 119–121 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07 (d, 1H, *J* = 8.1 Hz), 8.01 (d, 1H, *J* = 7.0 Hz), 7.96 (d, 1H, *J* = 7.0 Hz), 7.9(s, 1H), 7.85 (d, 1H, *J* = 8.4 Hz), 7.71(dd, 2H, *J* = 15.3, 7.5 Hz), 7.62 (d, 1H, *J* = 7.6 Hz), 7.34–7.28 (m, 3H), 2.52 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 189.8, 139.8, 139.1, 138.4, 133.6, 133.1, 132.8, 132.7, 132.7, 132.7, 132.6, 131.3, 131.3, 131.3, 130.9, 130.8, 130.6, 130.4, 129.3, 128.5, 128.0, 127.3, 125.0, 121.8, 121.0, 21.0 ppm.

HRMS (ESI): *m/z* calcd for $C_{20}H_{15}OS$ $[M + H]^+$: 303.0844; found; 303.0850.

(*E*)-2-(((4-Chlorophenyl)thio)methylene)acenaphthylen-1(2*H*)-one (3c)

Yield: 30 mg (93%) as Yellow solid; MP: 193–195 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (d, 1H, *J* = 8.2 Hz), 8.02–8.00 (m, 1H), 7.92 (s, 1H), 7.87 (dd, 2H, *J* = 13.0, 7.6 Hz), 7.71 (ddd, 2H, *J* = 16.6, 8.2, 7.0 Hz), 7.55(d, 2H, *J* = 8.6 Hz), 7.42 (d, 2H, *J* = 8.6 Hz) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 193.9, 138.7, 135.4, 134.87, 134.80, 134.2, 131.1, 130.1, 129.8, 128.6, 128.3, 127.8, 122.7, 121.5, 117.1, 113.5, 109.7 ppm.

HRMS (ESI): *m/z* calcd for $C_{19}H_{12}ClOS$ $[M + H]^+$: 323.0297; found: 323.0255.

(*E*)-2-(((2-Chlorophenyl)thio)methylene)acenaphthylen-1(2*H*)-one (3d)

Yield: 30 mg (93%) as Yellow solid; MP: 130–132 ^{o}C.

IR (neat): 1705, 1587, 1498, 1437, 1305, 1254, 1174, 1106, 1032, 926, 841, 805, 730, 653, 567, 479 cm^{-1}

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.09 (d, 1H, *J* = 8.1 Hz), 8.02 (d, 1H, *J* = 7.0 Hz), 7.98 (d, 1H, *J* = 7.0 Hz), 7.93 (s, 1H), 7.87 (d, 1H, *J* = 8.4 Hz), 7.74–7.67 (m, 3H), 7.52-7.50 (m, 1H), 7.40–7.32 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 189.8, 139.4, 135.4, 135.1, 133.2, 132.9, 132.2, 131.7, 131.3, 130.4, 130.3, 129.8, 128.5, 128.1, 128.03, 128.02, 125.3, 121.9, 121.3 ppm.

HRMS (ESI): *m/z* calcd for $C_{19}H_{12}ClOS$ $[M + H]^+$: 323.0297; found : 323.0260.

(*E*)-2-((Naphthalen-2-ylthio)methylene)acenaphthylen-1(2*H*)-one (3e)

Yield: 30 mg (89%) as Yellow solid; MP: 142–144 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14 (s, 1H), 8.12–8.07 (m, 2H), 8.02 (dd, 1H, *J* = 7.0, 0.8 Hz), 7.96 (d, 1H, *J* = 7.1 Hz), 7.92 (d, 1H, *J* = 8.8 Hz), 7.88 (dd, 2H, *J* = 7.4, 2.9 Hz), 7.86 (s, 1H), 7.72 (dt, 2H, *J* = 8.6, 7.0 Hz), 7.66 (dd, 1H, *J* = 8.6, 2.1 Hz), 7.57–7.54 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 189.8, 139.1, 137.3, 133.6, 133.5, 133.0, 132.8, 131.2, 130.7, 130.3, 130.0, 129.5, 128.4, 128.0, 127.8, 127.7, 127.7, 127.1, 127.0, 125.0, 121.8, 120.9 ppm.

HRMS (ESI): *m/z* calcd for $C_{23}H_{15}OS$ $[M + H]^+$: 339.0844; found: 339.0810.

(*Z*)-3-((Phenylthio)methylene)indolin-2-one (3f)

Yield: 22 mg (87%) as Yellow solid; MP: 136–138 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.06 (s, 1H), 7.97 (s, 1H), 7.65 (d, 1H, *J* = 7.5 Hz), 7.59–7.57 (m, 2H), 7.42 (ddd, 3H, *J* = 8.9, 4.5, 2.9 Hz), 7.23 (td, 1H, *J* = 7.7, 1.1 Hz), 7.10 (td, 1H, *J* = 7.6, 0.9 Hz), 6.89 (d, 1H, *J* = 7.7 Hz) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 140.5, 140.0, 133.3, 131.1, 129.7, 128.9, 128.6, 124.0, 123.0, 122.7, 122.2, 109.7 ppm.

HRMS (ESI): *m/z* calcd for $C_{15}H_{12}NOS$ $[M + H]^+$: 254.0640; found: 254.0647.

(*Z*)-3-(((4-Chlorophenyl)thio)methylene)indolin-2-one (3g)

Yield: 27 mg (94%) as Yellow solid; MP: 179–181 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.44 (s, 1H), 7.87 (s, 1H), 7.63–7.60 (m, 1H), 7.53–7.49 (m, 2H), 7.40 (dt, 2H, *J* = 2.2, 1.6 Hz), 7.23 (dd, m, 1H, *J* = 7.8, 1.3 Hz), 7.09 (td, 1H, *J* = 7.7, 1.1 Hz), 6.91–6.89 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.6, 140.2, 139.2, 135.3, 132.4, 132.4, 132.4, 132.4, 132.4, 131.7, 130.0, 129.9, 129.9, 129.9, 129.9, 128.9, 124.0, 123.7, 122.5, 122.3, 109.8 ppm.

HRMS (ESI): *m/z* calcd for $C_{15}H_{11}NOClS$ $[M + H]^+$: 288.0250; found: 288.0234.

(*Z*)-3-(((2-Chlorophenyl)thio)methylene)indolin-2-one (3h)

Yield: 27 mg (94%) as Yellow solid; MP: 197–199 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15 (s, 1H), 7.87 (s, 1H), 7.71 (d, 1H, *J* = 8.1 Hz), 7.66–7.63 (m, 1H), 7.53–7.48 (m, 1H), 7.38–7.33 (m, 2H), 7.24 (dd, 1H, *J* = 7.8, 1.1 Hz), 7.14–7.08 (m, 1H), 6.90 (d, 1H, *J* = 8.1 Hz) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 140.1, 138.1, 135.5, 132.5, 132.4, 130.4, 130.1, 128.9, 128.1, 128.0, 124.3, 124.2, 122.5, 122.4, 109.8 ppm.

HRMS (ESI): *m/z* calcd for $C_{15}H_{11}ClNOS$ $[M + H]^+$: 288.0250; found: 288.0250.

(*Z*)-3-((Naphthalen-2-ylthio)methylene)indolin-2-one (3i)

Yield: 27 mg (89%) as Yellow solid; MP: 196–198 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.09 (s, 1H), 8.08–8.07 (m, 1H), 7.99–7.98 (m, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.86 (m, 1H), 7.80–7.77 (m, 1H), 7.74–7.69 (m, 1H), 7.63–7.60 (m, 1H), 7.57–7.54 (m, 2H), 7.46 (ddd, *J* = 6.8, 2.9, 1.3 Hz, 1H), 7.13 (td, *J* = 7.6, 1.1 Hz, 1H), 6.91–6.88 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): 167.5, 140.2, 140.0, 133.6, 132.9, 130.2, 129.6, 128.7, 127.9, 127.8, 127.7, 127.2, 127.2, 124.0, 123.2, 122.7, 122.3, 109.7 ppm.

HRMS (ESI): *m/z* calcd for $C_{19}H_{13}NOSK$ $[M + K]^+$: 342.0349; found: 342.0342.

(*Z*)-1-Benzyl-3-(((4-chlorophenyl)thio)methylene)indolin-2-one (3j)

Yield: 37 mg (98%) as Yellow solid; MP: 98–100 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (s, 1H), 7.76 (d, 1H, *J* = 7.2 Hz), 7.72–7.67 (m, 1H), 7.56–7.51 (m, 1H), 7.38 (m, 3H), 7.34 (d, 3H, *J* = 4.4 Hz), 7.28 (dd, 1H, *J* = 7.6, 5.0 Hz), 7.12 (ddd, 1H, *J* = 81.1, 58.0, 7.6, 0.8 Hz), 7.07 (m, 1H), 6.77 (t, 1H, *J* = 7.1 Hz), 5.02 (d, 2H, *J* = 16.9 Hz) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7, 166.1, 142.0, 139.1, 137.7, 136.1, 135.4, 132.3, 130.3, 129.9, 128.7, 128.0, 127.6, 127.5, 127.2, 124.0, 123.9, 122.3, 121.9, 121.8, 118.8, 109.1, 108.9, 43.7 ppm.

HRMS (ESI): *m/z* calcd for $C_{22}H_{17}ClNOS$ $[M + H]^+$: 378.0719; found: 378.0688.

(*Z*)-1-Benzyl-3-(((2-chlorophenyl)thio)methylene)indolin-2-one (3k)

Yield: 36 mg (95%) as Yellow solid; MP: 100–102 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (s, 1H), 7.74–7.72 (m, 1H), 7.67–7.65 (m, 1H), 7.52–7.49 (m, 1H), 7.36 (ddd, 3H, *J* = 7.2, 4.6, 1.9 Hz), 7.31 (d, 4H, *J* = 4.4 Hz), 7.19 (td, 1H, *J* = 7.8, 1.1 Hz), 7.11–7.07 (m, 1H), 6.74 (d, 1H, *J* = 7.8), 4.95 (s, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.2, 142.1, 137.8, 136.1, 133.6, 132.6, 132.4, 130.5, 130.3, 130.0, 129.0, 128.8, 128.0, 127.7, 127.6, 127.3, 124.0, 122.3, 122.0, 121.9, 118.8, 109.2, 109.0, 43.8 ppm.

HRMS (ESI): *m/z* calcd for $C_{22}H_{17}ClNOS$ $[M + H]^+$: 378.0719; found: 378.0686.

(*Z*)-1-Benzyl-3-((naphthalen-2-ylthio)methylene)indolin-2-one (3l)

Yield: 36 mg (92%) as Yellow solid; MP: 150–152 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16 (s, 1H), 8.09 (d, 1H, *J* = 1.7 Hz), 7.92– 7.85 (m, 4H), 7.72 (dd, 1H , *J* = 7.4, 0.5 Hz), 7.63 (dd, 1H , *J* = 8.6, 1.9 Hz), 7.55 (dd, 2H , *J* = 6.5, 3.0 Hz), 7.32-–7.31 (m, 4H), 7.18 (dd, 1H , *J* = 7.8, 1.2 Hz), 7.10 (td, 1H , *J* = 7.6, 1.0 Hz), 6.74 (s, 1H), 4.99 (s, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.3, 142.0, 139.8, 136.2, 133.6, 133.0, 130.5, 130.1, 129.6, 128.8, 128.5, 128.0, 127.9, 127.7, 127.7, 127.5, 127.3, 127.2, 127.1, 123.8, 123.0, 122.3, 122.2, 108.9, 43.7, 29.7 ppm.

HRMS (ESI): *m/z* calcd for $C_{26}H_{20}NOS$ $[M + H]^+$: 394.1260; found: 394.1257.

(*Z*)-3-(((4-Chlorophenyl)thio)methylene)-1-methylindolin-2-one (3m)

Yield: 29 mg (96%) as Yellow solid; MP: 140–142 ºC.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87 (s, 1H), 7.63 (ddd, 1H, *J* = 7.6, 1.2, 0.6 Hz), 7.50 (d, 2H, *J* = 8.8 Hz), 7.40 (d, 2H, *J* = 8.9 Hz), 7.30 (td, 1H, *J* = 7.7,1.3 Hz), 7.11 (td, 1H, *J* = 7.6, 1.1 Hz), 6.86–6.83 (m, 1H), 3.26 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.1, 143.0, 138.5, 132.37, 132.36, 132.3, 131.8, 129.9, 128.8, 123.7, 123.5, 122.2, 121.8, 108.0, 77.3, 77.1, 76.8, 26.2 ppm.

HRMS (ESI): *m/z* calcd for $C_{16}H_{13}NOSCl$ $[M + H]^+$: 302.0406; found: 302.0408.

(*Z*)-3-(((2-Chlorophenyl)thio)methylene)-1-methylindolin-2-one (3n)

Yield: 29 mg (96%) as Yellow solid; MP: 148–150 ºC.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.85 (s, 1H), 7.61 (ddd, 1H, *J* = 7.6, 1.2, 0.6 Hz), 7.50–7.47 (m, 2H), 7.40–7.37 (m, 2H), 7.28 (td, 1H, *J* = 7.7, 1.3 Hz), 7.09 (td, 1H, *J* = 7.6, 1.1 Hz), 6.84–6.81 (m, 1H), 3.24 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.1, 141.8, 140.2, 136.3, 136.23, 129.1, 129.0, 128.7, 128.1, 128.1, 127.5, 127.3, 123.7, 122.1, 108.7, 43.6, 40.1 ppm.

HRMS (ESI): *m/z* calcd for $C_{16}H_{13}NO\,ClS$ [M + H]: 302.0406; found: 302.0408.

(*Z*)-1-Benzyl-3-((cyclohexylthio)methylene)indolin-2-one (3o)

Yield: 32 mg (92%) as Yellow solid; MP: 126–128 ºC.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.01 (s, 1H), 7.60–7.56 (m, 1H), 7.39–7.37 (m, 4H), 7.24–7.21 (m, 1H), 7.12 (ddd, 1H, *J* = 7.9, 5.3, 1.40 Hz), 7.05–6.95 (m, 1H), 6.74–6.68 (m, 1H), 4.96 (s, 2H), 3.25–3.02 (m, 1H), 2.21–2.10 (m, 1H), 1.86 (ddd, 2H, *J* = 13.6, 7.9, 3.8 Hz), 1.71–1.55 (m, 3H), 1.48–1.24 (m, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.3, 141.6, 140.4, 140.2, 136.4, 128.8, 128.8, 128.8, 128.8, 128.7, 128.7, 127.8, 127.6, 127.5, 127.3, 123.5, 122.7, 122.0, 121.7, 121.6, 118.1, 108.9, 108.6, 48.7, 48.5, 43.6, 33.8, 33.7, 25.8, 25.3 ppm.

HRMS (ESI): *m/z* calcd for $C_{22}H_{24}NSO$ $[M + H]^+$: 350.1579; found: 350.1611.

(*Z*)-1-Benzyl-3-((benzylthio)methylene)indolin-2-one (3p)

Yield: 33 mg (92%) as Yellow solid; MP: 180–182 ºC.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92 (s, 1H), 7.55 (dd, 1H, *J* = 7.5, 0.6 Hz), 7.42–7.36 (m, 5H), 7.33–7.30 (m, 2H), 7.29–7.27 (m, 3H), 7.12 (m, 1H), 7.01 (td, 1H, *J* = 7.6, 1.0 Hz), 6.69 (d, 1H, *J* = 7.7 Hz), 4.94 (s, 2H), 4.26 (s, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.1, 141.8, 140.2, 136.29, 136.23, 129.2, 129.1, 129.05, 129.02, 128.8, 128.78, 128.74, 128.1, 128.1, 127.5, 127.3, 123.7, 122.5, 122.4, 122.1, 108.7, 44.3, 40.1 ppm.

HRMS (ESI): *m/z* calcd for $C_{23}H_{20}NOS$ $[M + H]^+$: 358.1266; found: 358.1270.

(*E*)-2-((Phenylamino)methylene)acenaphthylen-1(2*H*)-one (5a)

Yield: 24 mg (89%) as Yellow solid; MP: 120–122 °C

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 11.14 (d, J = 13.4 Hz, 1H), 8.03–7.99 (m, 3H), 7.72–7.66 (m, 2H), 7.54 (dd, J = 8.3, 7.0 Hz, 1H), 7.44 (d, J = 5.6 Hz, 1H), 7.42–7.38 (m, 2H), 7.21 (dd, J = 8.8, 1.0 Hz, 2H), 7.11 (tt, J = 7.6, 1.1 Hz, 1H) ppm.

^{13}C NMR, ($CDCl_3$, 125 MHz): δ 193.8, 140.1, 136.1, 135.3, 134.6, 134.5, 131.1, 130.2, 130.0, 129.9, 129.9, 129.9, 128.4, 127.8, 123.7, 122.5, 121.5, 116.1, 113.4, 109.2 ppm.

HRMS (ESI): *m/z* calcd for $C_{19}H_{14}NO$ $[M + H]^+$: 272.1075; found: 272.1073.

(*E*)-2-((*p*-Tolylamino)methylene)acenaphthylen-1(2*H*)-one (5b)

Yield: 28 mg (98%) as Yellow solid; MP: 134–136 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ: 11.15 (d, 1H, J =12.2 Hz), 8.04 (d, 1H, J = 3.2 Hz), 8.03 (d, 1H, J = 2.0 Hz), 8.00 (d, 1H, J = 12.5 Hz), 7.73–7.67 (m, 2H), 7.56 (dd, 1H, J = 8.3, 7.0 Hz), 7.45 (d, 1H, J = 6.8 Hz), 7.22 (d, 2H, J = 8.1 Hz), 7.13 (d, 2H, J = 8.4 Hz), 2.38 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.6, 137.6, 136.4, 135.4, 134.5, 134.3, 133.4, 130.9, 130.3, 130.1, 128.3, 127.7, 122.3, 121.3, 116.1, 114.9, 113.2, 108.7 ppm.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO$ $[M + H]^+$: 286.1232; found: 286.1208.

(*E*)-2-(((4-Methoxyphenyl)amino)methylene)acenaphthylen-1(2*H*)-one (5c)

Yield: 29 mg (96%) as Yellow solid; MP: 112–114 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.12 (s, 1H), 8.01 (d, 1H, J = 1.6 Hz), 8.00 (s, 1H), 7.91 (d, 1H, J = 12.5 Hz), 7.68 (d, 1H, J = 7.7 Hz), 7.64 (d, 1H, J = 8.3 Hz), 7.54–7.50 (m, 1H), 7.40 (d, 1H, J = 6.9 Hz), 7.16–7.13 (m, 2H), 6.96–6.92 (m, 2H), 3.83 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 193.5, 156.5, 137.2, 135.6, 134.6, 134.2, 133.7, 130.9, 130.1, 128.3, 127.8, 122.3, 121.4, 121.4, 121.3, 117.8, 117.8, 117.8, 117.7, 117.7, 115.3, 115.2, 115.2, 115.2, 115.2, 115.2, 115.2, 113.12, 108.5, 55.7 ppm.

HRMS (ESI): *m/z* calcd for $C_{20}H_{16}NO_2$ $[M + H]^+$: 302.1181; found: 302.1186.

(*E*)-2-(((4-Chlorophenyl)amino)methylene)acenaphthylen-1(2*H*)-one (5d)

Yield: 29 mg (95%) as Yellow solid; MP: 155–157 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.13 (d, 1H, J = 12.1 Hz), 8.05–8.01 (m, 2H), 7.93 (d, 1H, J = 12.3 Hz), 7.73–7.68 (m, 2H), 7.55 (dd, 1H, J = 8.3, 6.9 Hz), 7.45 (dd, 1H, J = 6.9, 0.5 Hz), 7.37–7.34 (m, 2H), 7.15–7.12 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.0, 138.8, 135.5, 134.9, 134.8, 134.3, 131.2, 130.2, 129.9, 128.6, 128.4, 127.9, 122.8, 121.6, 117.2, 113.6, 109.8 ppm.

HRMS (ESI): *m/z* calcd for $C_{19}H_{13}NOCl$ $[M + H]^+$: 306.0686; found: 306.0651.

(*E*)-2-(((4-Bromophenyl)amino)methylene)acenaphthylen-1(2*H*)-one (5e)

Yield: 33 mg (95%) as Yellow solid; MP: 135–137 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.11 (d, 1H, J = 12.1 Hz), 8.16 (dd, 1H, J = 34.7, 8.3 Hz), 8.04–8.00 (m, 1H), 7.93–7.80 (m, 2H), 7.71–7.67 (m, 1H), 7.56–7.43 (m, 4H), 7.07 (d, 2H, J = 8.9 Hz) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.0, 139.3, 135.3, 135.0, 134.9, 134.3, 132.9, 132.8, 132.4, 131.2, 130.2, 130.1, 129.0, 128.41, 128.40, 128.3, 127.9, 127.8, 123.0, 122.8, 121.6, 117.5, 116.0, 113.7, 113.6, 109.9 ppm.

HRMS (ESI): *m/z* calcd for $C_{19}H_{13}BrNO$ $[M + H]^+$: 350.0181; found: 350.0142.

(*E*)-2-(((4-Iodophenyl)amino)methylene)acenaphthylen-1(2*H*)-one (5f)

Yield: 38 mg (96%) as Yellow solid; MP: 198–200 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.06 (d, 1H, J = 11.6 Hz), 7.99 (dd, 2H, J = 11.7, 7.5 Hz), 7.86 (d, 1H, J = 12.2 Hz), 7.70–7.62 (m, 4H), 7.55–7.51 (m, 1H), 7.42 (s, 1H), 6.95–6.90 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.0, 139.8, 138.6, 134.9, 134.87, 134.80, 134.2, 131.1, 130.1, 128.3, 127.8, 122.7, 121.5, 117.7, 113.6, 109.9, 86.0 ppm.

HRMS (ESI): *m/z* calcd for $C_{19}H_{12}INO$ $[M]^+$: 396.9964; found: 396.9929.

(*E*)-2-(((3,5-Bis(trifluoromethyl)phenyl)amino)methylene)acenaphthylen-1(2*H*)-one (5g)

Yield: 34 mg (84%) as Yellow solid; MP: 232–234 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.28 (d, 1H, J = 11.7 Hz), 8.04 (dd, 2H, J = 9.0, 7.7 Hz), 7.89 (d, 1H, J = 11.8 Hz), 7.74–7.68 (m, 2H), 7.61–7.57 (m, 1H), 7.55 (s, 1H), 7.53 (d, 3H, J = 4.0 Hz) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.4, 141.6, 135.6, 133.8, 133.7, 133.4, 133.2, 131.5, 130.2, 128.3, 127.9,

124.1, 123.4, 121.9, 121.8, 116.0, 115.2, 114.3, 111.7 ppm.

HRMS (ESI): *m/z* calcd for $C_{21}H_{12}NOF_6$ $[M + H]^+$: 408.0823; found: 408.0782.

(*E*)-2-(((3-Chloro-4-methoxyphenyl)amino)methylene)acenaphthylen-1(2*H*)-one (5h)

Yield: 31 mg (93%) as Yellow solid; MP: 182–184 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.09 (d, 1H, J = 12.2 Hz), 8.03 (t, 2H, J = 7.0 Hz), 7.87 (d, 1H, J = 12.3 Hz), 7.74–7.67 (m, 2H), 7.58–7.54 (m, 1H), 7.45 (d, 1H, J = 6.9 Hz), 7.29 (s, 1H), 7.06 (dd, 1H, J = 8.8, 2.7 Hz), 6.96 (d, 1H, J = 8.8 Hz), 3.93 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 193.7, 151.6, 136.2, 135.0, 134.5, 134.3, 134.2, 131.0, 130.1, 128.3, 127.7, 123.8, 122.5, 121.4, 118.1, 115.8, 113.4, 113.3, 109.2, 56.5 ppm.

HRMS (ESI): *m/z* calcd for $C_{20}H_{15}NO_2Cl$ $[M + H]^+$: 336.0791; found: 336.0781.

(*Z*)-3-((p-Tolylamino)methylene)indolin-2-one (5i)

Yield: 24 mg (96%) as Yellow solid; MP: 117–119 °C.

^{1}H NMR ($CDCl_3$ + DMSO, 500 MHz): δ 10.30 (d, 1H, J = 12.5 Hz), 9.63 (s, 1H), 7.71 (d, 1H, J = 12.5 Hz), 6.99–6.97 (m, 1H), 6.74 (d, 2H, J = 8.1 Hz), 6.69–6.66 (m, 2H), 6.59 (dt, 1H, J = 7.6, 3.8 Hz), 6.52 (dd, 1H, J = 7.5, 1.1 Hz), 6.49 (dd, 1H, J = 8.2, 4.4 Hz), 1.90 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$ + DMSO, 125 MHz): δ 170.7, 137.6, 137.3, 137.0, 132.9, 130.3, 124.3, 124.0, 120.7, 116.3, 115.9, 109.7, 99.6, 20.8 ppm.

HRMS (ESI): *m/z* calcd for $C_{16}H_{15}N_2O$ $[M + H]^+$: 251.1184; found: 251.1201.

(*Z*)-3-(((4-Chlorophenyl)amino)methylene)indolin-2-one (5j)

Yield: 26 mg (96%) as Yellow solid; MP: 282–284 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.66 (dd, 1H, J = 13.6, 6.05 Hz), 7.95 (dd, 1H, J = 22.8, 13.2 Hz), 7.60–7.65 (m, 1H), 7.37 (dd, 1H, J = 1.4, 0.7 Hz), 7.36–7.35 (m, 1H), 7.35 (s, 1H), 7.33 (d, 1H, J = 2.4 Hz), 7.12 (dd, 1H, J = 6.6, 1.0 Hz), 7.10–7.09 (m, 1H), 7.09–7.07 (m, 1H), 7.05–7.01 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$ + DMSO, 125 MHz): δ 171.0, 140.5, 138.3, 138.2, 133.3, 125.3, 125.1, 121.4, 118.8, 118.2, 115.5, 110.2, 101.5, 80.2, 80.0, 79.7, 41.0, 40.8, 40.6, 40.5, 40.3 ppm.

HRMS (ESI): *m/z* calcd for $C_{15}H_{12}ClN_2O$ $[M + H]^+$: 271.0638; found : 271.0635.

(*Z*)-3-(((3,5-Dimethylphenyl)amino)methylene)indolin-2-one (5k)

Yield: 26 mg (98%) as Yellow solid; MP: 238–240 °C.

^{1}H NMR ($CDCl_3$ + DMSO, 500 MHz): δ 10.52 (s, 1H), 9.23 (s, 1H), 7.94–7.88 (m, 1H), 7.29 (s, 1H), 7.25 (d, 1H, *J* = 9.1 Hz), 6.94 (ddd, 1H, *J* = 12.8, 7.6, 6.4 Hz), 6.86 (ddd, 1H, *J* = 7.5, 4.2, 1.1 Hz), 6.84–6.80 (m, 1H), 6.67 (d, 1H, *J* = 14.7 Hz), 6.63–6.58 (m, 1H), 2.23 (s, 3H), 2.20 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$ + DMSO, 125 MHz): δ 170.7, 170.66, 139.8, 139.7, 139.6, 139.6, 137.0, 136.9, 136.7, 136.6, 125.4, 125.3, 124.3, 124.3, 124.1, 124.1, 120.9, 120.8, 116.1, 116.0, 113.8, 113.7, 109.7, 109.7, 99.6, 21.4 ppm.

HRMS (ESI): *m/z* calcd for $C_{17}H_{17}N_2O$ $[M + H]^+$: 265.1341; found: 265.1351.

(Z)-3-(((4-Bromophenyl)amino)methylene)indolin-2-one (5l)

Yield: 30 mg (95%) as Yellow solid; MP: 289–291 °C.

^{1}H NMR ($CDCl_3$ + DMSO, 500 MHz): δ 10.68 (d, *J* = 12.4 Hz, 1H), 10.42 (s, 1H), 8.47 (d, *J* = 12.3 Hz, 1H), 7.52–7.49 (m, 1H), 7.46–7.44 (m, 2H), 7.31–7.29 (m, 2H), 6.95 (td, *J* = 7.6, 1.2 Hz, 1H), 6.86 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (dd, *J* = 4.6, 4.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$ + DMSO, 125 MHz): δ 170.4, 139.9, 137.7, 137.6, 132.6, 132.5, 124.6, 124.5, 120.8, 119.1, 118.3, 118.2, 118.2, 117.6, 114.9, 109.6, 100.9 ppm.

HRMS (ESI): *m/z* calcd for $C_{15}H_{12}BrN_2O$ $[M + H]^+$: 315.0133; found: 315.0115.

(*Z*)-3-(((3,5-Bis(trifluoromethyl)phenyl)amino)methylene)indolin-2-one (5m)

Yield: 31 mg (83%) as Yellow solid; MP: 270–272 °C.

^{1}H NMR ($CDCl_3$ + DMSO, 500 MHz: δ 10.16 (s, 1H), 8.43 (s, 1H), 8.00 (dd, 1H, *J* = 21.3, 7.5 Hz), 7.80 (s, 1H), 7.65–7.59 (m, 2H), 7.21 (t, 1H, *J* = 7.6 Hz), 7.12–7.04 (m, 3H) ppm.

^{13}C NMR ($CDCl_3$ + DMSO, 125 MHz): δ 175.6, 157.7, 146.7, 142.7, 137.8, 137.5, 130.2, 128.3, 125.8, 122.3, 120.2, 116.0, 114.7, 108.1, 34.3 ppm.

HRMS (ESI): *m/z* calcd for $C_{17}H_{11}N_2OF_6$ $[M + H]^+$: 373.0770; found: 373.0772.

(*Z*)-3-(((4-Methoxyphenyl)amino)methylene)indolin-2-one (5n)

Yield: 25 mg (94%) as Yellow solid; MP: 124–126 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.62 (d, 1H, 12.6 Hz), 8.19 (s, 1H, *J* =12.6 Hz), 7.92 (d, 1H, *J* =12.7 Hz), 7.35 (d, 1H, *J* = 7.4 Hz), 7.13–7.09 (m, 2H), 7.07 (dd, 1H, *J* = 7.6, 1.1 Hz), 7.02 (td, 1H, *J* = 7.5, 0.9 Hz), 6.96–6.91 (m, 3H), 3.78 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$ + DMSO, 125 MHz): δ 170.7, 137.6, 137.3, 137.0, 132.9, 130.3, 124.3, 124.0, 120.7,

116.3, 115.9, 109.7, 99.6, 41.8 ppm.

HRMS (ESI): *m/z* calcd for $C_{16}H_{15}N_2O_2$ $[M + H]^+$: 267.1128; found: 267.1128.

(*Z*)-3-(((3,4-Dimethoxyphenyl)amino)methylene)-1-methylindolin-2-one (5o)

Yield: 29 mg (93%) as Yellow solid; MP: 157–159 ºC.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.86 (d, 1H, *J* = 12.9), 7.96 (d, 1H, *J* = 12.9 Hz), 7.38–7.35 (m, 1H), 7.13 (ddd, 2H, *J* = 8.8,9.0, 3.2 Hz), 7.03 (dt, 1H, *J* = 7.5, 3.8 Hz), 6.89 (d, 1H, *J* = 7.7 Hz), 6.55–6.50 (m, 2H), 3.94 (s, 3H), 3.81 (s, 3H), 3.36 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.9, 156.6, 149.7, 138.5, 136.2, 123.8, 123.4, 121.1, 115.6, 113.7, 107.8, 104.4, 99.4, 98.8, 56.0, 55.7, 25.6 ppm.

HRMS (ESI): *m/z* calcd for $C_{18}H_{19}N_2O_3$ $[M + H]^+$: 311.1396; found: 311.1306.

(*Z*)-3-(((3,5-Bis(trifluoromethyl)phenyl)amino)methylene)-1-methylindolin-2-one (5p)

Yield: 33 mg (85%) as Yellow solid; MP: 217–219 ºC.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.01 (s, 1H), 7.93 (d, 1H, *J* = 11.9 Hz), 7.52 (d, 3H, *J* = 5.0 Hz), 7.46–7.44 (m, 1H), 7.23–7.20 (m, 1H), 7.10–7.06 (m, 1H), 6.91 (d, 1H, *J* = 7.8 Hz), 3.35 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.0, 141.5, 139.6, 133.9, 133.5, 133.2, 125.8, 124.1, 122.4, 122.0, 121.8, 117.0, 116.0, 116.0, 115.3, 115.2, 108.3, 102.8, 25.8 ppm.

HRMS (ESI): *m/z* calcd for $C_{18}H_{13}N_2OF_6$ $[M + H]^+$: 387.0929; found: 387.0929.

(*Z*)-1-Benzyl-3-(((4-methoxyphenyl)amino)methylene)indolin-2-one (5q)

Yield: 34 mg (95%) as Yellow solid; MP: 127–129 ºC.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.73 (d, 1H, *J* = 12.7 Hz), 7.98 (d, 1H, *J* = 12.7 Hz), 7.42–7.38 (m, 1H), 7.34 (s, 2H), 7.33 (d, 2H, *J* = 2.2 Hz), 7.27 (dd, 1H, *J* = 3.4, 2.5 Hz), 7.15–7.12 (m, 2H), 7.05 (td, 2H, *J* = 7.3, 1.3 Hz), 6.97–6.94 (m, 2H), 6.84 (dd, 1H, *J* = 6.9, 1.5 Hz), 5.09 (s, 2H), 3.84 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.9, 156.4, 137.8, 137.6, 136.8, 133.5, 128.6, 127.3, 127.2, 123.9, 123.7, 121.2, 117.7, 115.7, 115.1, 108.7, 98.3, 55.6, 43.2 ppm.

HRMS (ESI): *m/z* calcd for $C_{23}H_{21}N_2O_2$ $[M + H]^+$: 357.1603; found: 357.1607.

(*Z*)-1-Benzyl-3-(((4-chlorophenyl)amino)methylene)indolin-2-one (5r)

Yield: 35 mg (97%) as Yellow solid; MP: 184–186 ºC.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.76 (d, 1H, *J* = 12.4 Hz), 7.95 (d, 1H, *J* = 12.4 Hz), 7.39 (m, 1H), 7.34 (d, 1H, *J* = 2.1 Hz), 7.32 (s, 1H), 7.30 (s, 3H), 7.25 (m, 1H), 7.09 (d, 1H, *J* = 2.4 Hz), 7.07 (dd, 2H, *J* = 3.1, 1.8 Hz), 7.03 (ddd, 2H, *J* = 14.8, 7.6, 1.3 Hz), 6.81 (m, 1H), 5.01 (s, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.0, 138.6, 138.1, 136.6, 136.2, 130.0, 130.1, 129.9, 128.8, 128.8, 128.81, 128.6, 127.5, 127.3, 127.3, 127.2, 124.7, 121.6, 117.1, 116.3, 109.0, 100.0, 43.3 ppm.

HRMS (ESI): *m/z* calcd for $C_{22}H_{18}ClN_2O$ $[M + H]^+$: 361.1102; found: 361.1105.

(*Z*)-1-Benzyl-3-(((3,5-dimethylphenyl)amino)methylene)indolin-2-one (5s)

Yield: 34 mg (96%) as Yellow solid; MP: 176–178 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.62 (d, 1H, *J* = 12.6 Hz), 7.97 (d, 1H, *J* = 12.6 Hz), 7.36–7.34 (m, 1H), 7.27 (s, 1H), 7.25 (d, 2H, *J* = 3.6 Hz), 7.20–7.17 (m, 1H), 7.01-6.94 (m, 3H), 6.76–6.73 (m, 3H), 6.69 (s, 1H), 5.00 (s, 2H), 2.28 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.9, 139.8, 139.6, 137.8, 136.9, 136.8, 128.7, 127.3, 127.2, 125.5, 124.1, 123.7, 121.3, 115.9, 113.9, 108.7, 98.9, 43.2, 21.4 ppm.

HRMS (ESI): *m/z* calcd for $C_{24}H_{23}N_2O$ $[M + H]^+$: 355.1805; found: 355.1805.

(*Z*)-1-Benzyl-3-(((3,4-dimethoxyphenyl)amino)methylene)indolin-2-one (5t)

Yield: 37 mg (96%) as Yellow solid; MP: 138–140 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.89 (d, 1H, *J* = 12.9 Hz), 8.03 (d, 1H, *J* = 13.0 Hz), 7.41 (dd, 1H, *J* = 5.9, 2.5 Hz), 7.34–7.30 (m, 4H), 7.27–7.23 (m, 1H), 7.20 (d, 1H, *J* = 8.6 Hz), 7.06–7.00 (m, 2H), 6.80 (dd, 1H, *J* = 6.1, 2.4 Hz), 6.59–6.53 (m, 2H), 5.12 (s, 2H), 3.97 (s, 3H), 3.85 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.8, 156.7, 149.7, 137.6, 136.9, 136.4, 128.6, 127.2, 127.1, 123.9, 123.7, 123.4, 121.1, 115.6, 113.8, 108.7, 104.4, 99.4, 98.6, 55.9, 55.6, 43.1 ppm.

HRMS (ESI): *m/z* calcd for $C_{24}H_{23}N_2O_3$ $[M + H]^+$: 387.1709; found: 387.1730.

(*Z*)-1-Benzyl-3-((naphthalen-2-ylamino)methylene)indolin-2-one (5u)

Yield: 35 mg (93%) as Yellow solid; MP: 185–187 ^{o}C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.70 (s, 1H), 8.25 (d, 2H, *J* = 2.1 Hz), 7.89 (d, 1H, *J* = 8.1 Hz), 7.66–7.59 (m, 3H), 7.58–7.54 (m, 1H), 7.52–7.54 (m, 1H), 7.47–7.44 (m, 1H), 7.37 (dd, 2H, *J* = 9.2, 4.6 Hz), 7.35–7.31 (m, 2H), 7.28–7.27 (m, 1H), 7.10–7.04 (m, 2H), 6.85–6.83 (m, 1H), 5.14 (s, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.4, 138.0, 137.8, 136.7, 136.0, 134.4, 128.9, 128.8, 128.6, 127.5, 127.2, 126.8, 126.7, 125.8, 124.8, 124.5, 124.1, 123.5, 121.5, 120.8, 116.3, 110.4, 109.0, 100.4, 43.3 ppm.

HRMS (ESI): *m/z* calcd for $C_{26}H_{21}N_2O$ $[M + H]^+$: 377.1654; found: 377.1627.

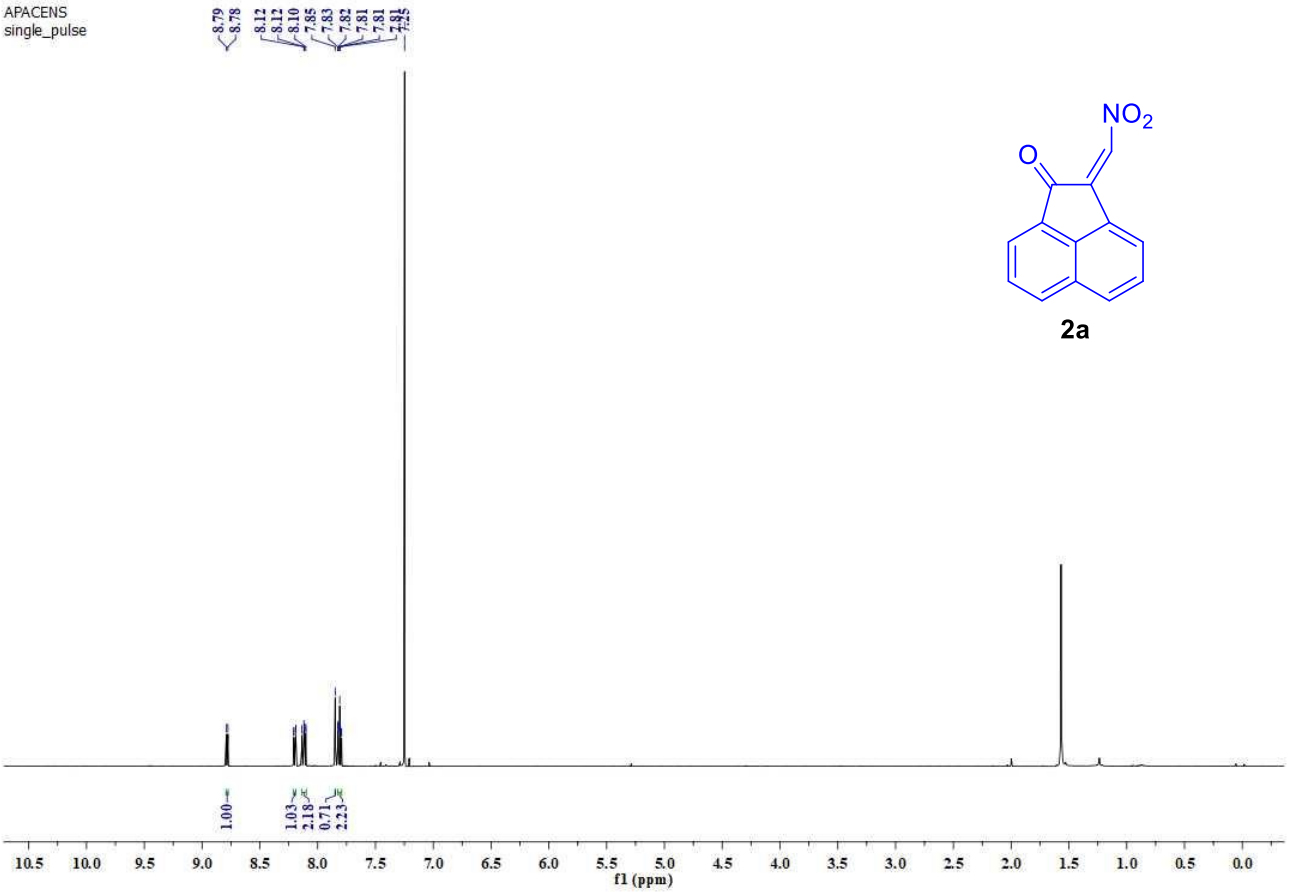
(*Z*)-1-Benzyl-3-(((3,5-bis(trifluoromethyl)phenyl)amino)methylene)indolin-2-one (5v)

Yield: 40 mg (87%) as Yellow solid; MP: 170–172 ^oC.

^1H NMR ($CDCl_3$, 500 MHz): δ 11.03 (d, 1H, *J* = 11.9 Hz), 7.93 (d, 1H, *J* = 11.9 Hz), 7.48 (s, 3H), 7.41 (d, 1H, *J* = 7.3 Hz), 7.27 (s, 2H), 7.23 (m, 1H), 7.21 (s, 2H), 7.07 (td, 1H, *J* = 7.7, 1.1 Hz), 7.01 (dt, 1H, *J* = 7.5, 3.8 Hz), 6.78 (d, 1H, *J* = 7.7 Hz), 4.99 (s, 2H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.0, 141.4, 138.7, 136.2, 134.2, 133.5, 133.2, 128.8, 128.7, 127.6, 127.5, 127.2, 127.0, 125.7, 122.5, 121.8, 117.0, 116.1, 115.2, 115.0, 109.2, 109.1, 102.5, 43.4 ppm.

HRMS (ESI): *m/z* calcd for $C_{24}H_{17}N_2OF_6$ $[M + H]^+$: 463.1245; found: 463.1309.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7.81
1.00
1.03
2.18
0.71
2.23
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
f1 (ppm)

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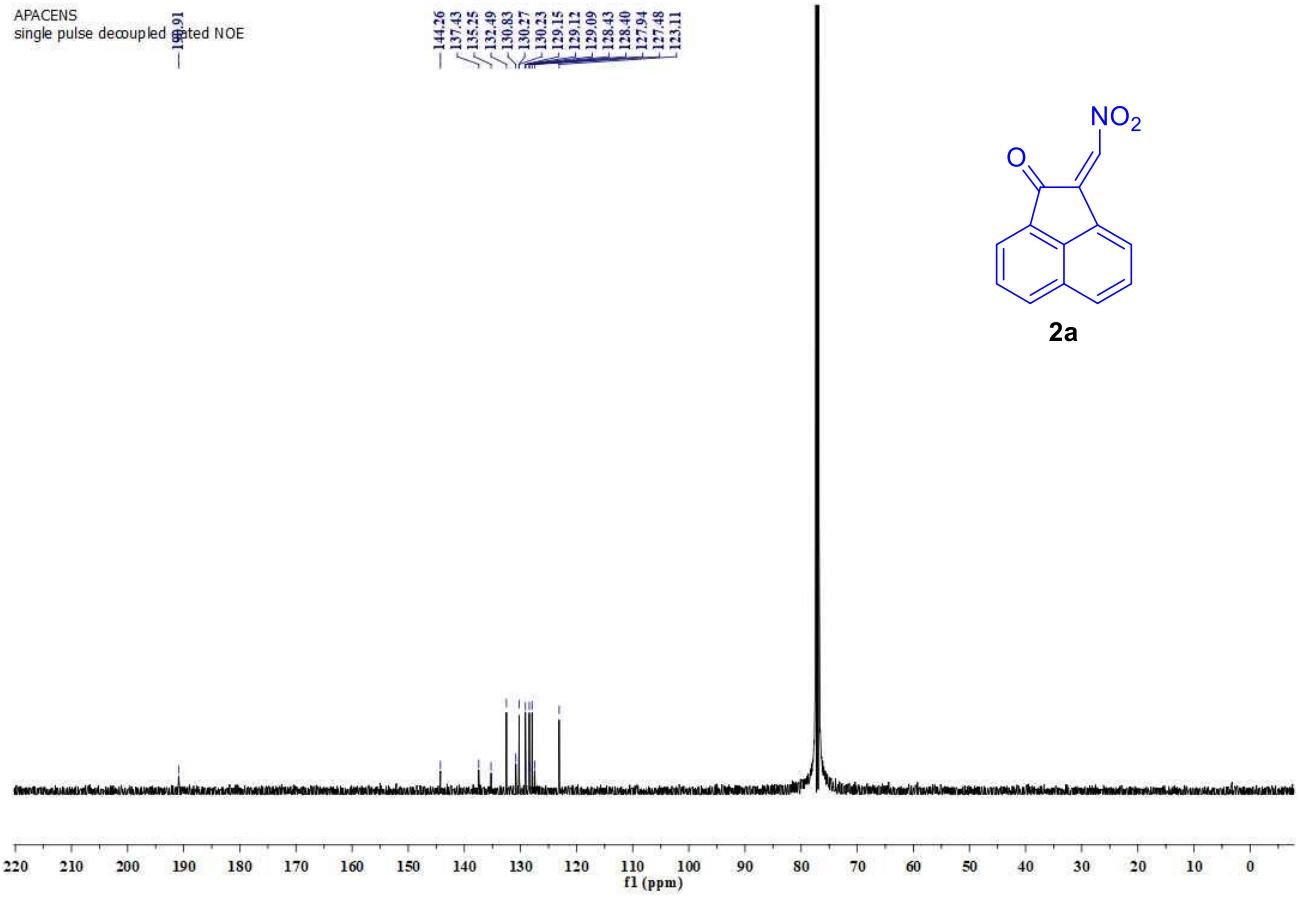
O

2a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128.43
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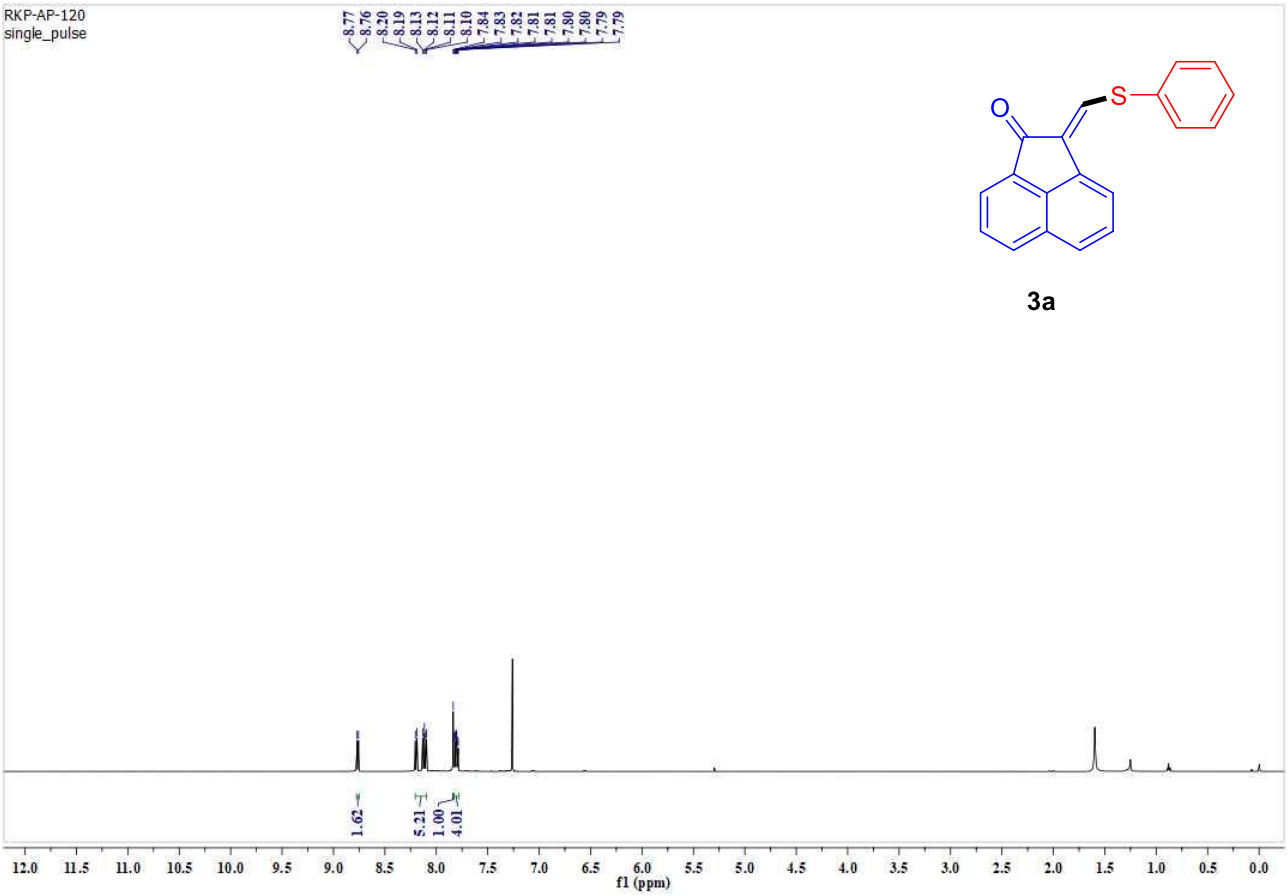
f1 (ppm)

NO2
O

2a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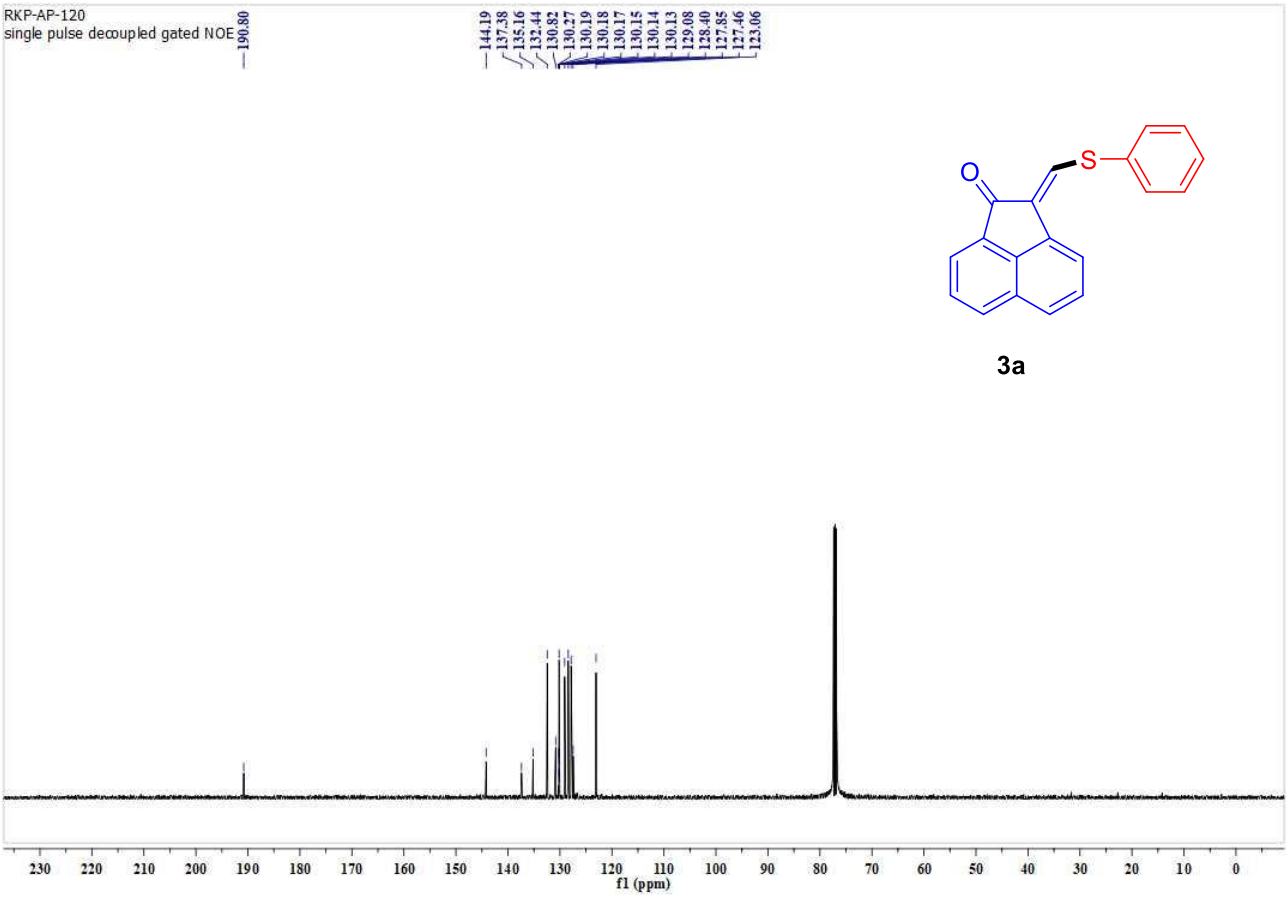
f1 (ppm)

3a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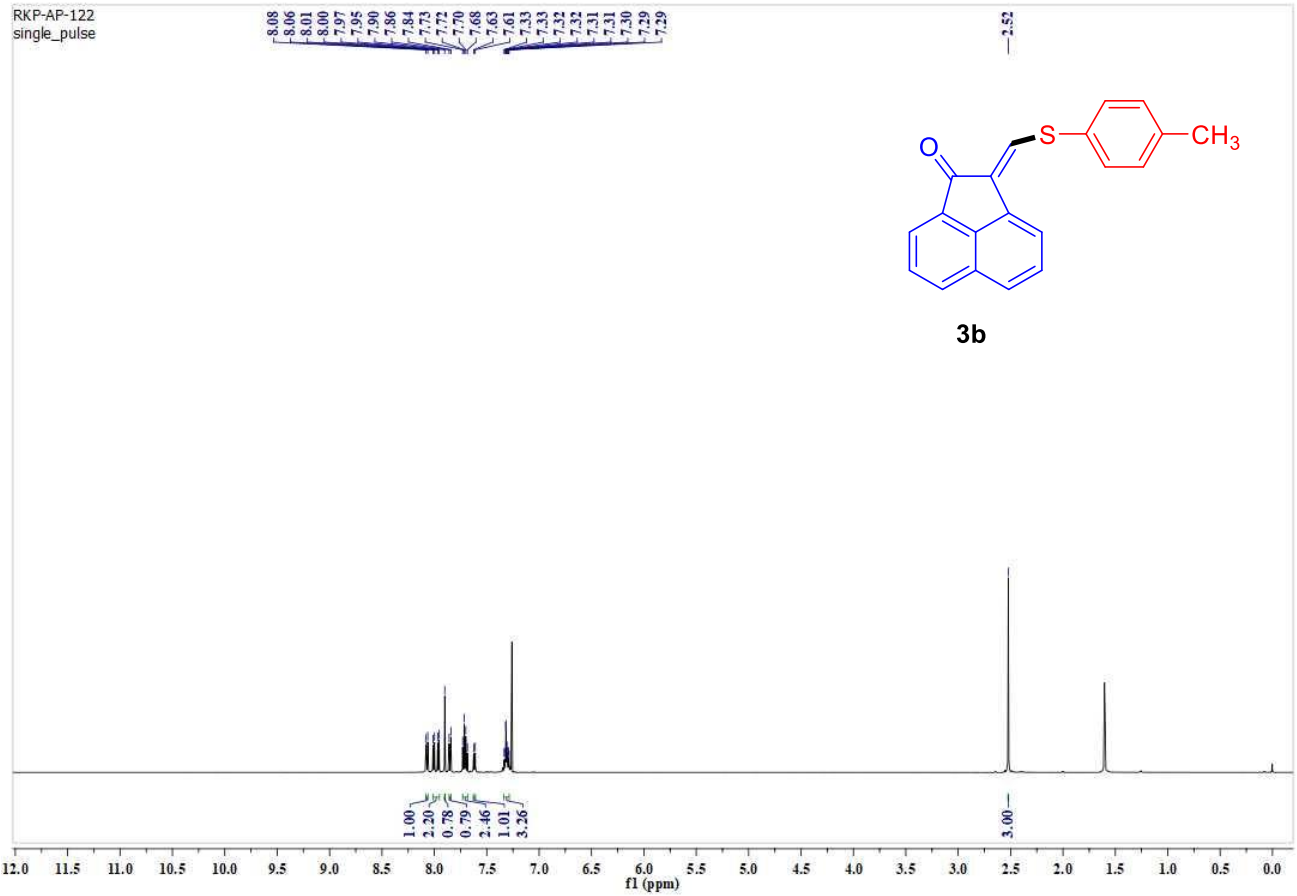
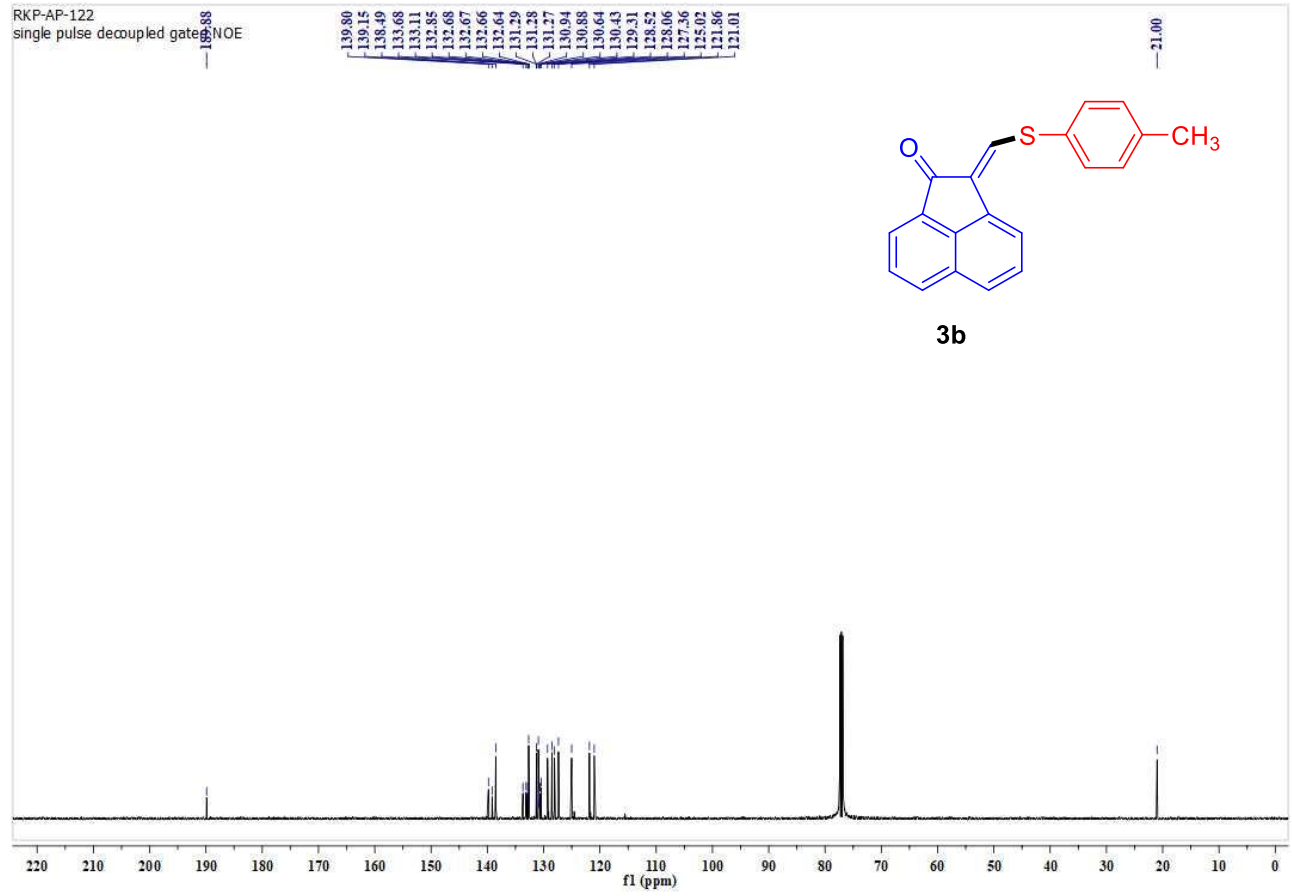
130.17
130.15
130.14
130.13
129.08
128.40
127.85
127.46
123.06
O
S
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

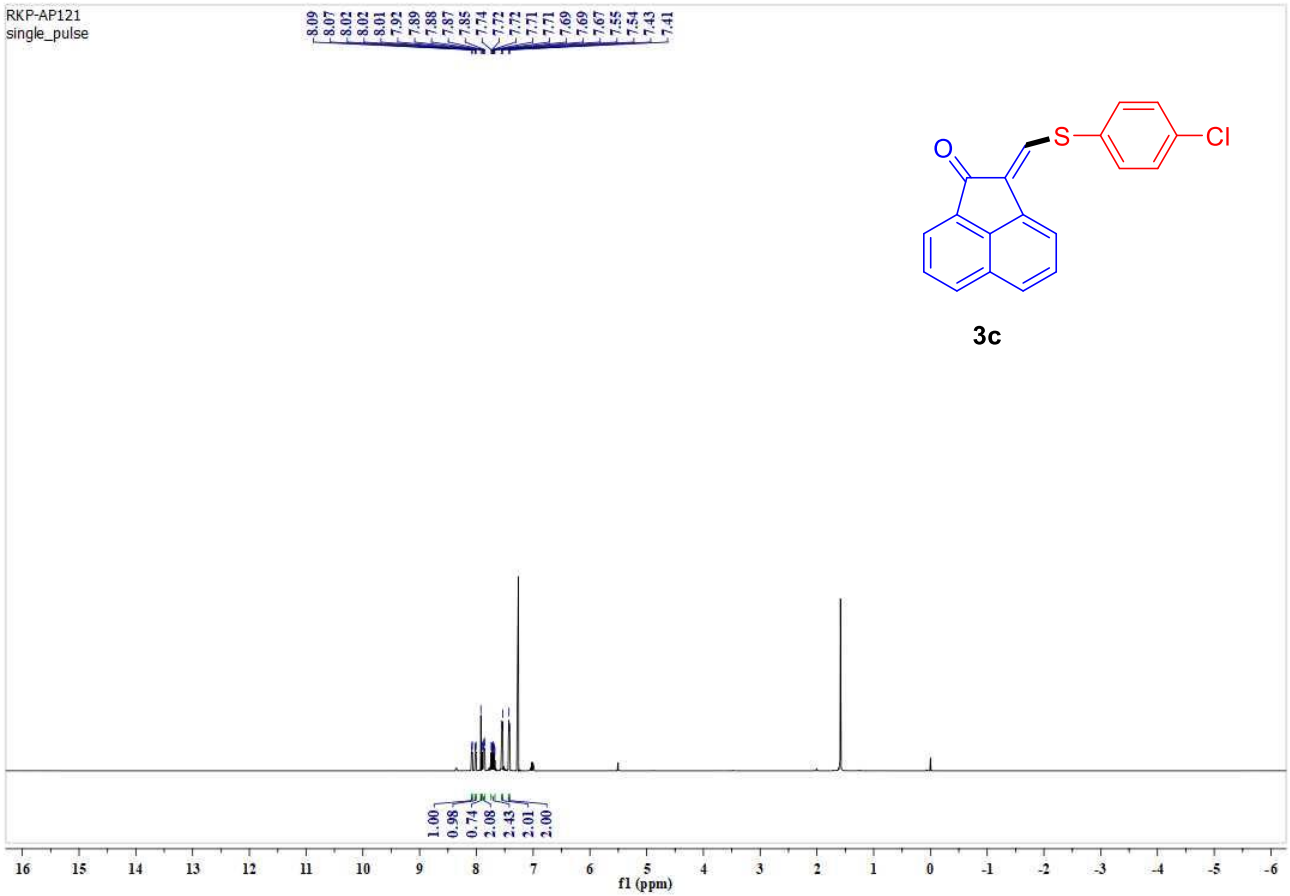
3a


RKP-AP-122
single_pulse
8.08
8.06
8.01
8.00
7.97
7.95
7.90
7.86
7.84
7.73
7.72
7.70
7.68
7.63
7.61
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
2.52
O
S
CH3
1.00
2.20
0.78
0.79
2.46
1.01
3.26
3.00
f1 (ppm)

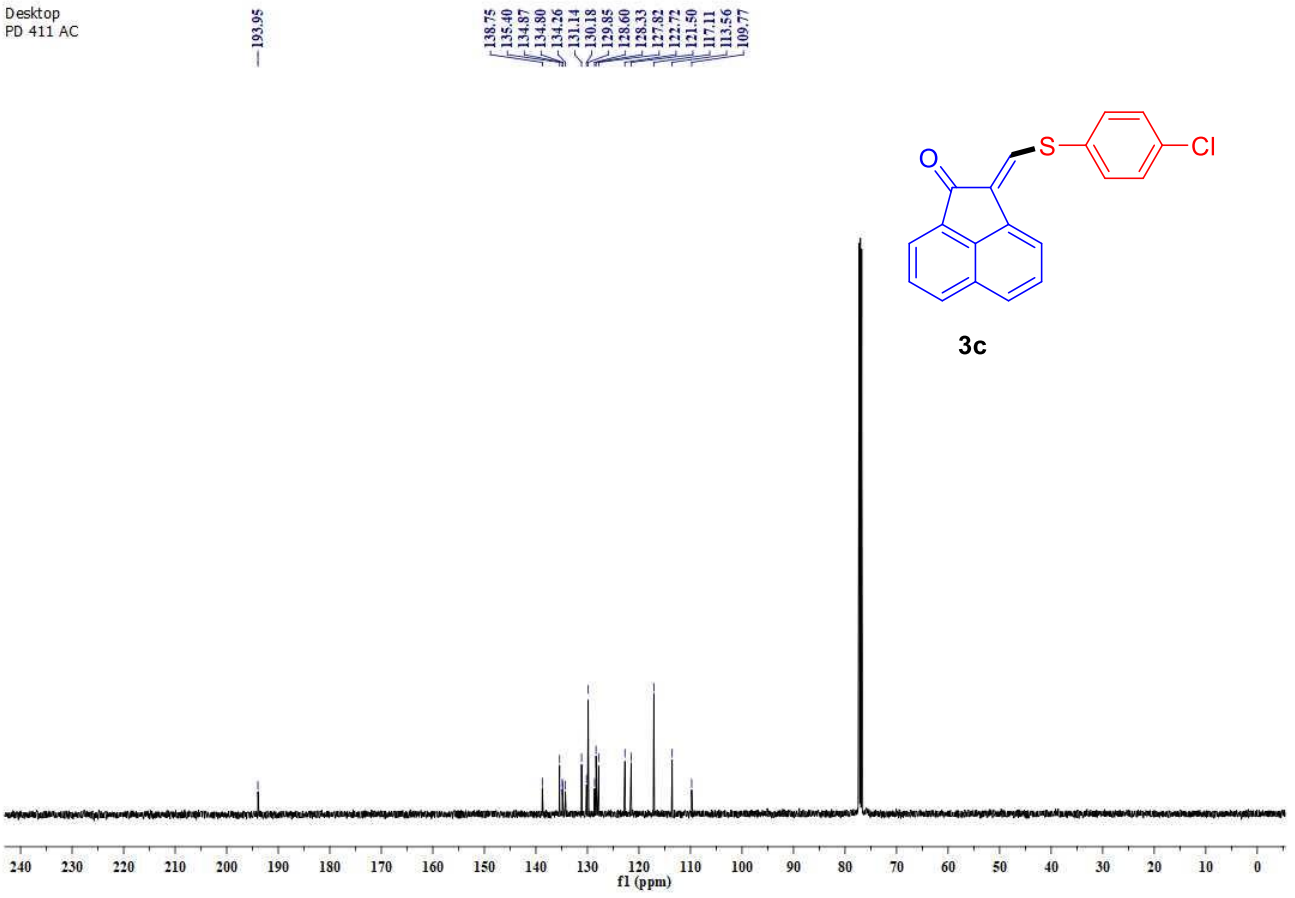
3b


RKP-AP-122
single pulse decoupled gated NOE
189.88
139.80
139.15
138.49
133.68
133.11
132.85
132.68
132.67
132.66
132.64
131.29
131.28
131.27
130.94
130.88
130.64
130.43
129.31
128.52
128.06
127.36
125.02
121.86
121.01
21.00
O
S
CH3
f1 (ppm)

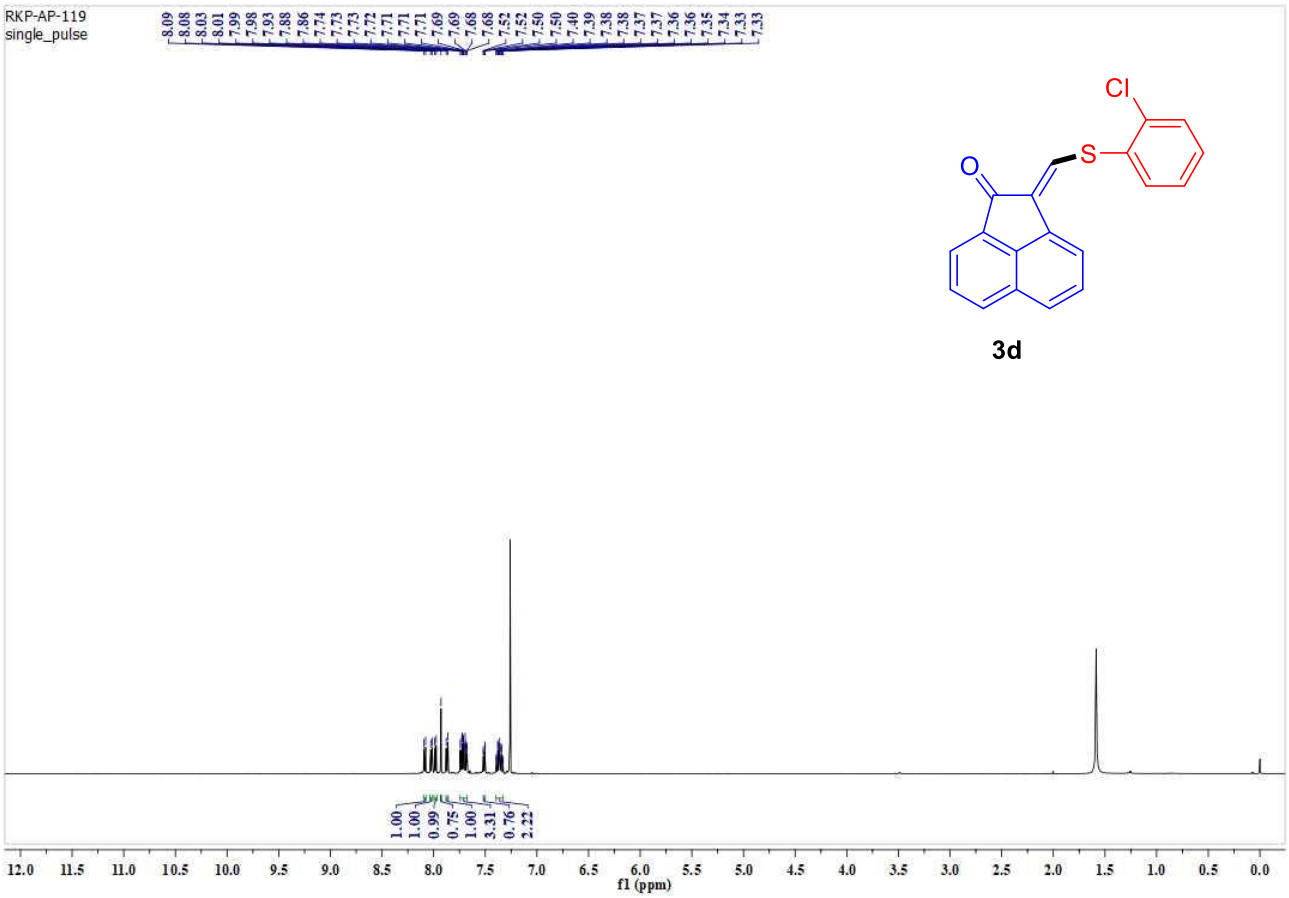
3b

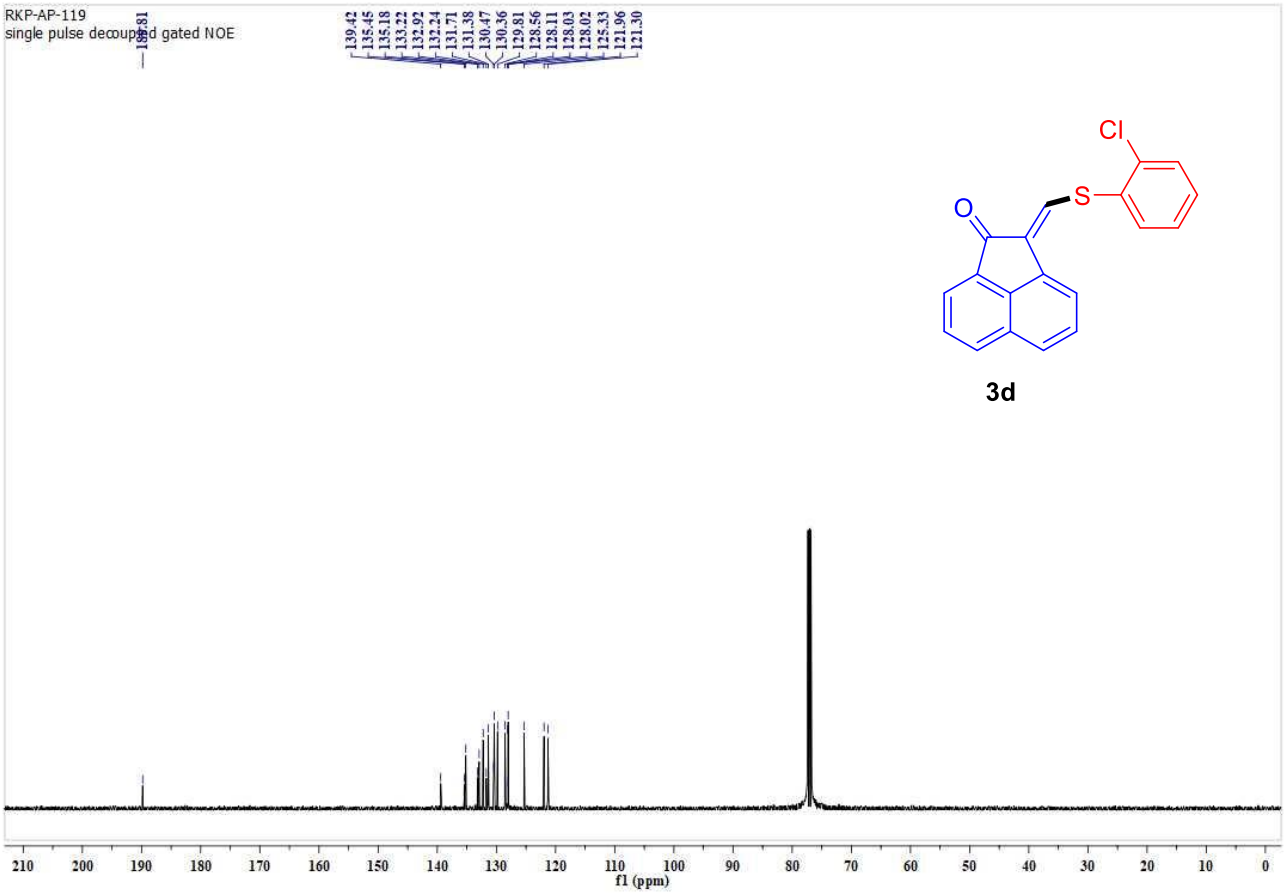

RKP-AP121
single_pulse
8.09
8.07
8.02
8.02
8.01
7.92
7.89
7.88
7.87
7.85
7.74
7.72
7.72
7.71
7.71
7.69
7.69
7.67
7.55
7.54
7.43
7.41
O
S
Cl
1.00
0.98
0.74
2.08
2.43
2.01
2.00
f1 (ppm)

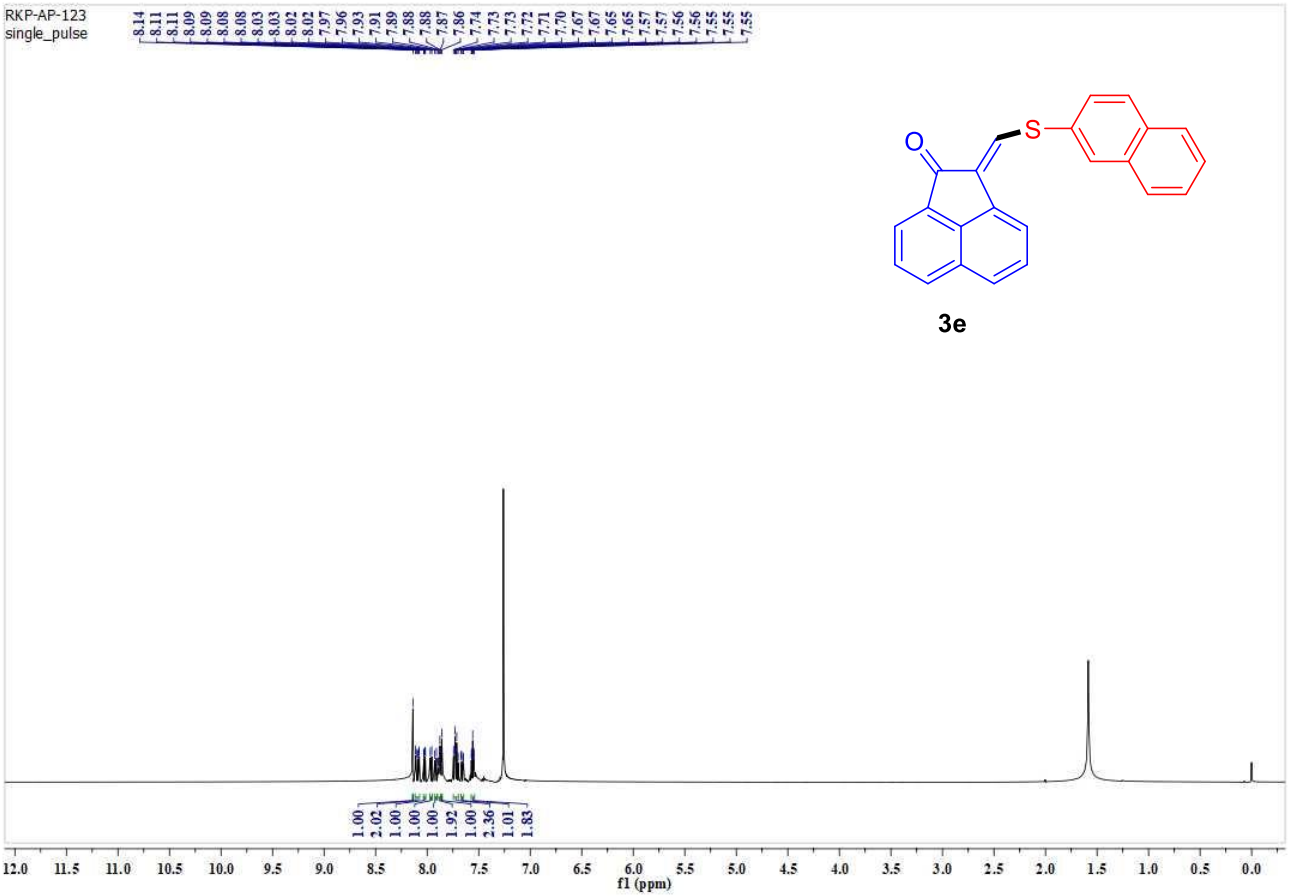
3c


Desktop
PD 411 AC
193.95
138.75
135.40
134.87
134.80
134.26
131.14
130.18
129.85
128.60
128.33
127.82
122.72
121.50
117.11
113.56
109.77
O
S
Cl
f1 (ppm)

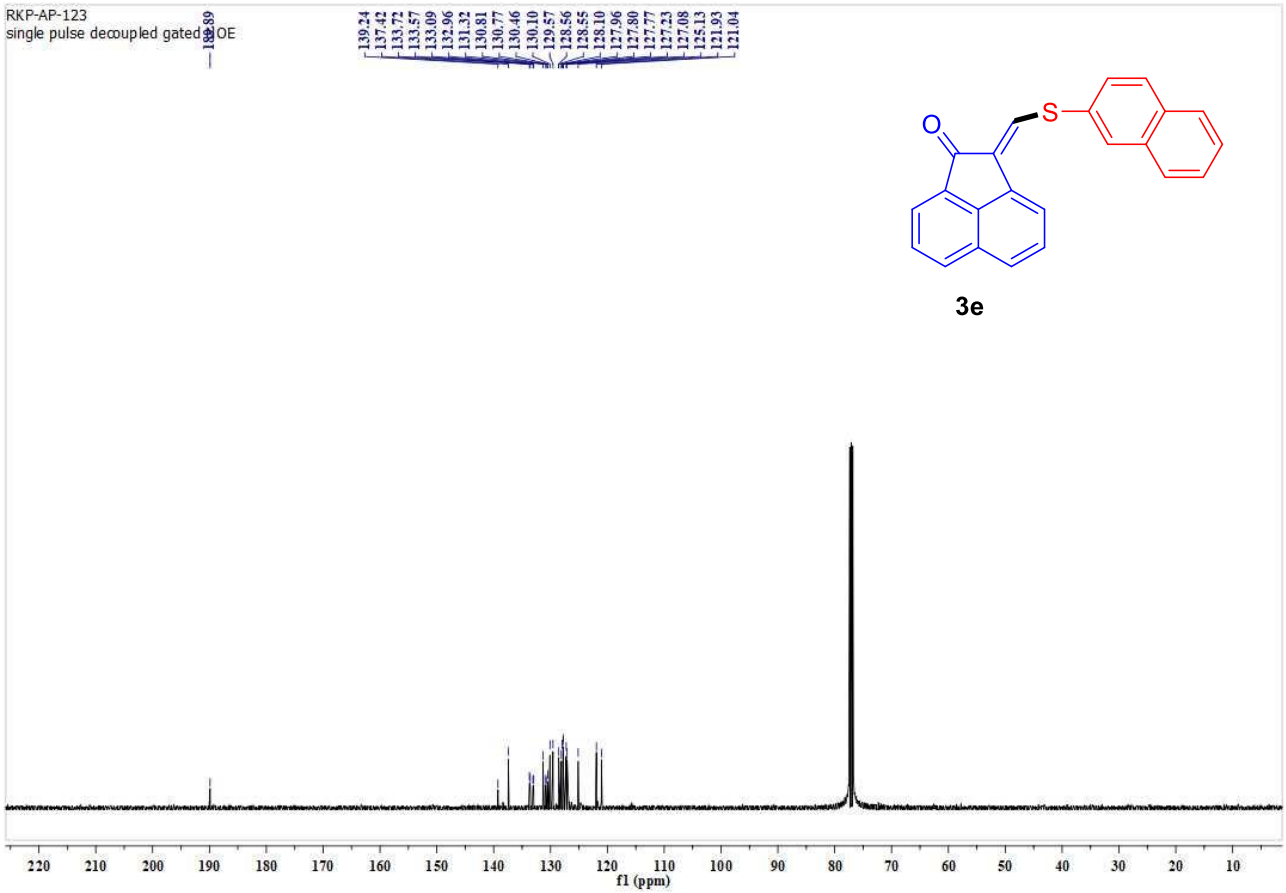
3c


RKP-AP-119
single_pulse
Cl
S
O
3d
f1 (ppm)

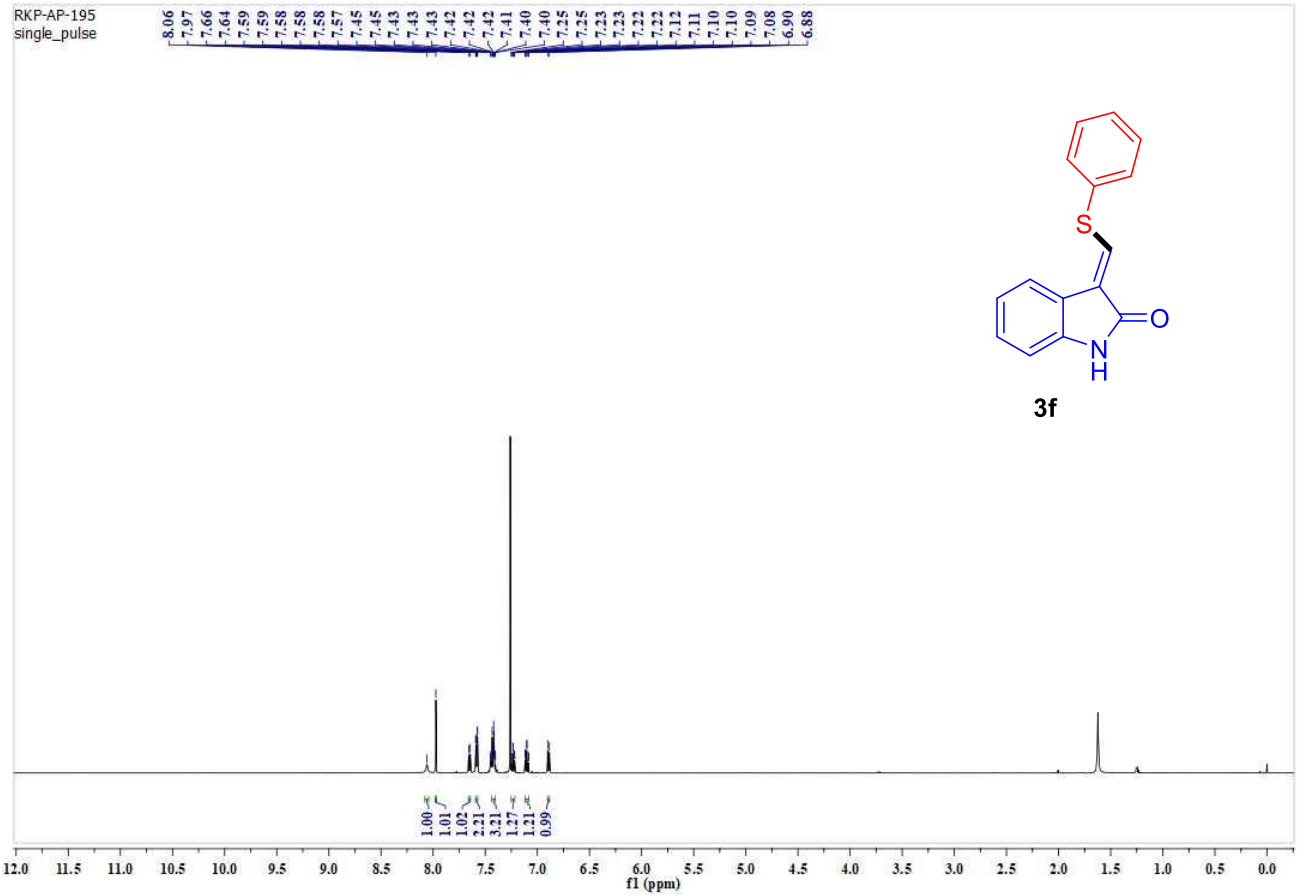

RKP-AP-119
single pulse decoupled gated NOE
Cl
S
O
3d
f1 (ppm)

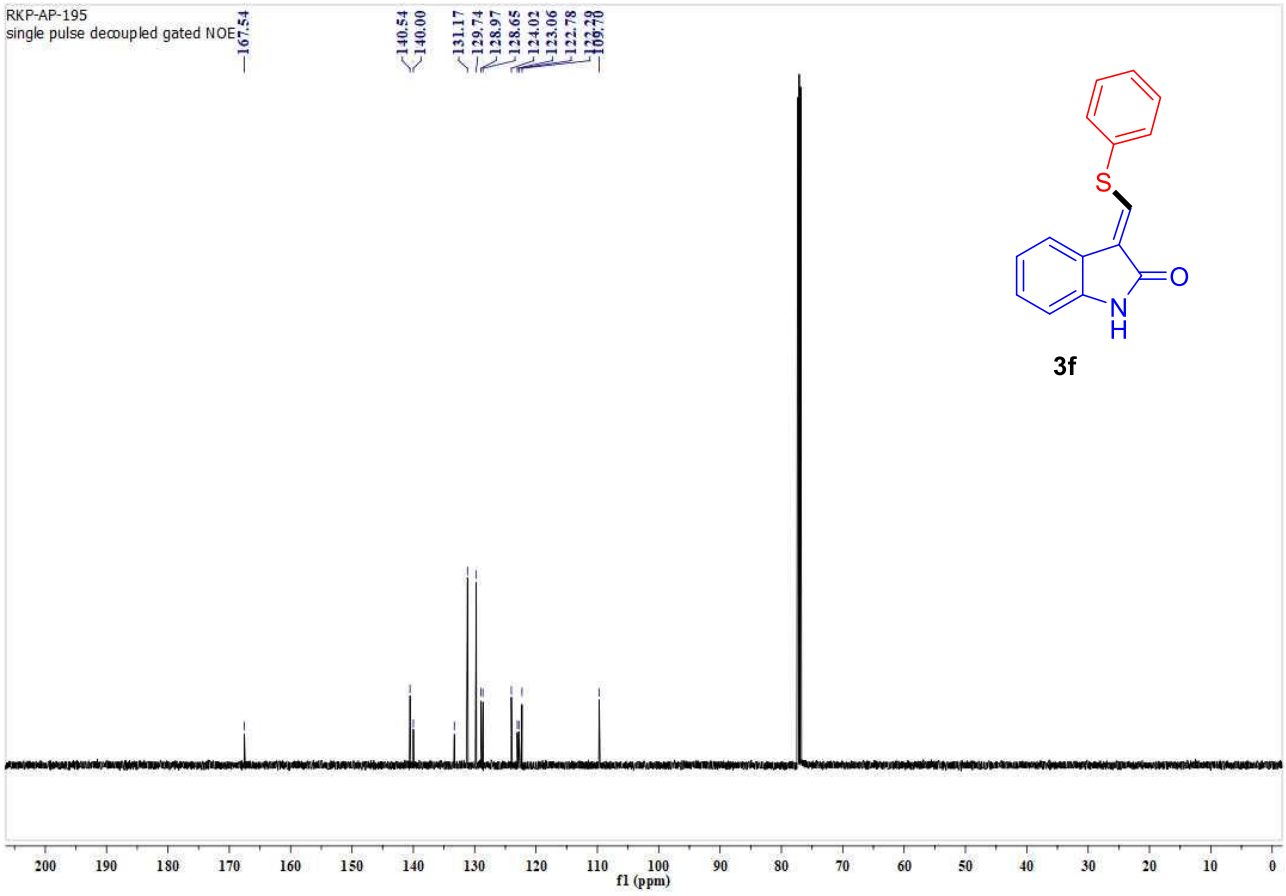

RKP-AP-123
single_pulse
8.14 8.11 8.11 8.09 8.09 8.08 8.08 8.03 8.03 8.02 8.02 7.97 7.96 7.93 7.91 7.89 7.88 7.88 7.87 7.86 7.74 7.73 7.73 7.72 7.71 7.70 7.67 7.67 7.65 7.57 7.57 7.56 7.56 7.55 7.55 7.55
O
S
1.00 2.02 1.00 1.00 1.00 1.92 1.00 2.36 1.01 1.83
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 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
f1 (ppm)

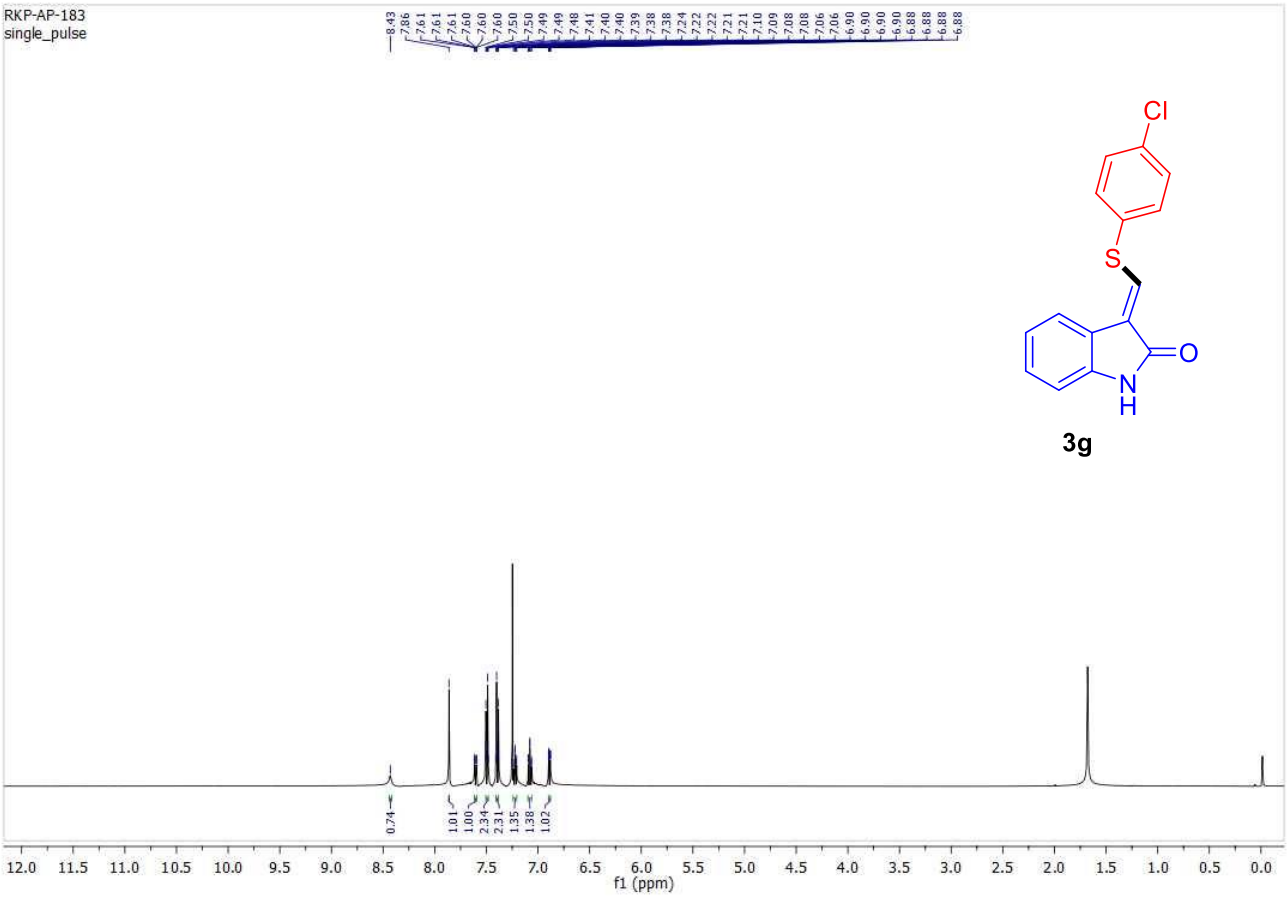
3e

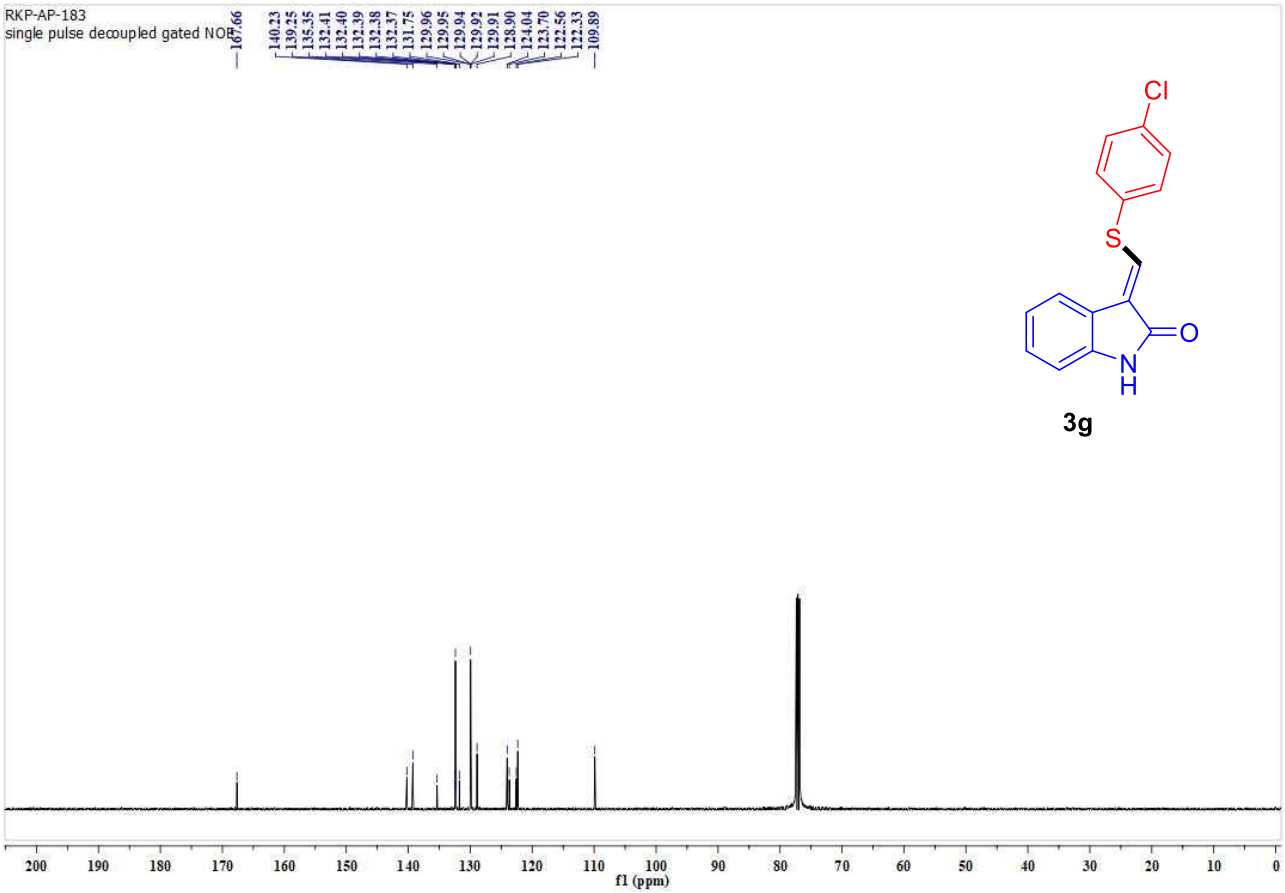

RKP-AP-123
single pulse decoupled gated NOE
139.24 137.42 133.72 133.57 133.09 132.96 131.32 130.81 130.77 130.46 130.10 129.57 128.56 128.55 128.10 127.96 127.80 127.77 127.23 127.08 125.13 121.93 121.04
O
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

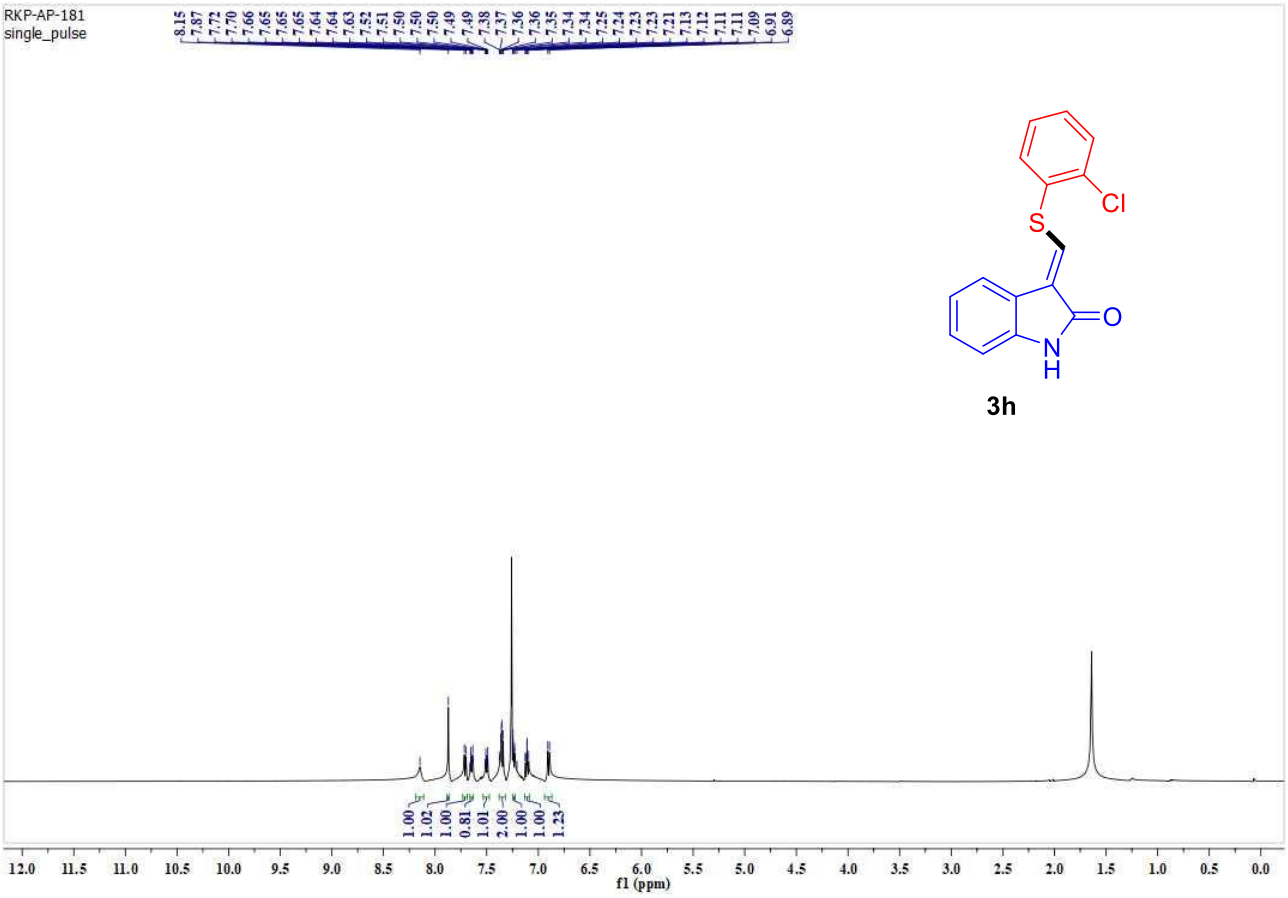
3e

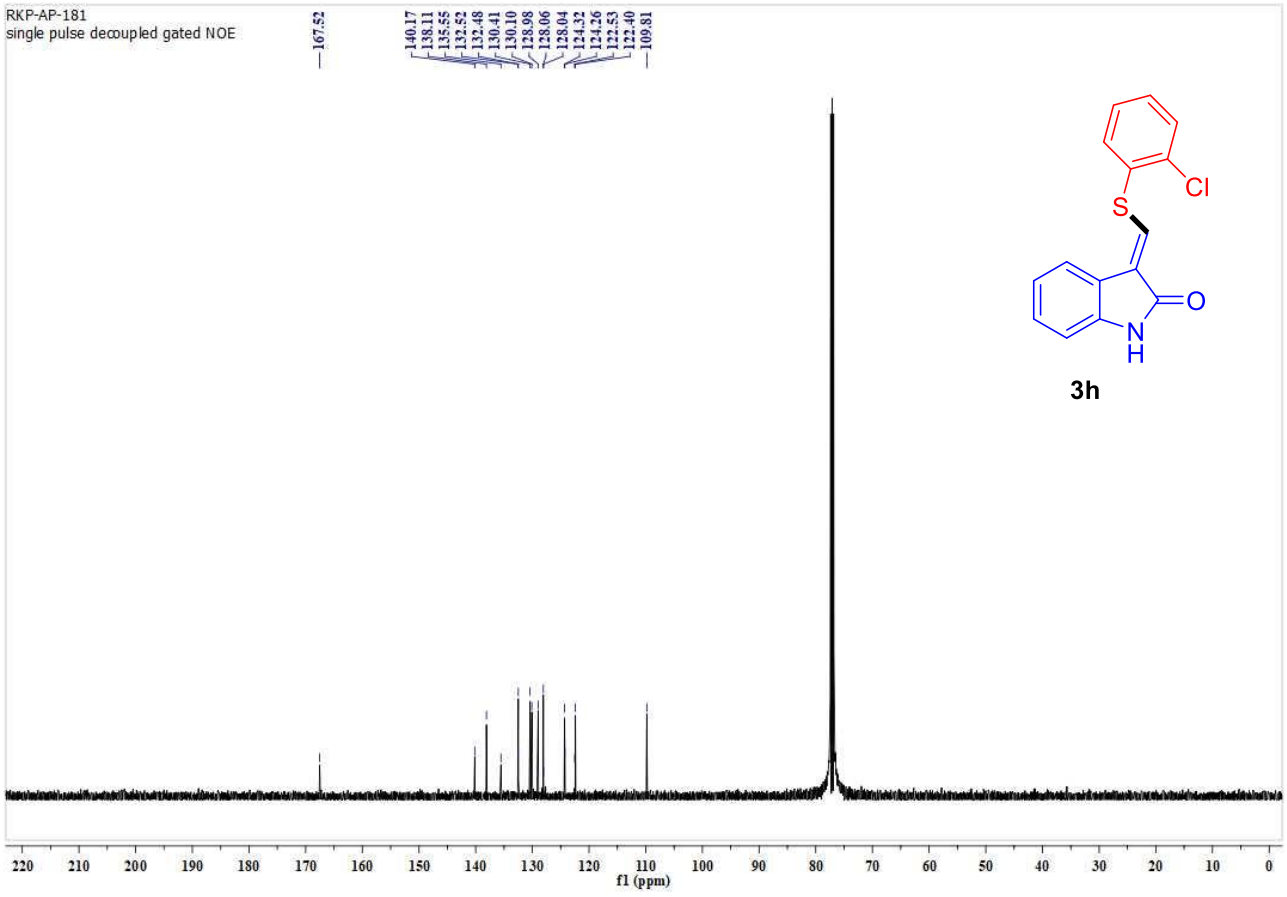

RKP-AP-195
single_pulse
8.06 7.97 7.66 7.64 7.59 7.59 7.58 7.58 7.58 7.57 7.45 7.45 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.40 7.40 7.25 7.25 7.23 7.23 7.22 7.22 7.12 7.11 7.10 7.10 7.09 7.08 6.90 6.88
1.00 1.01 1.02 2.21 3.21 1.27 1.21 0.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
S
O
N
H
3f

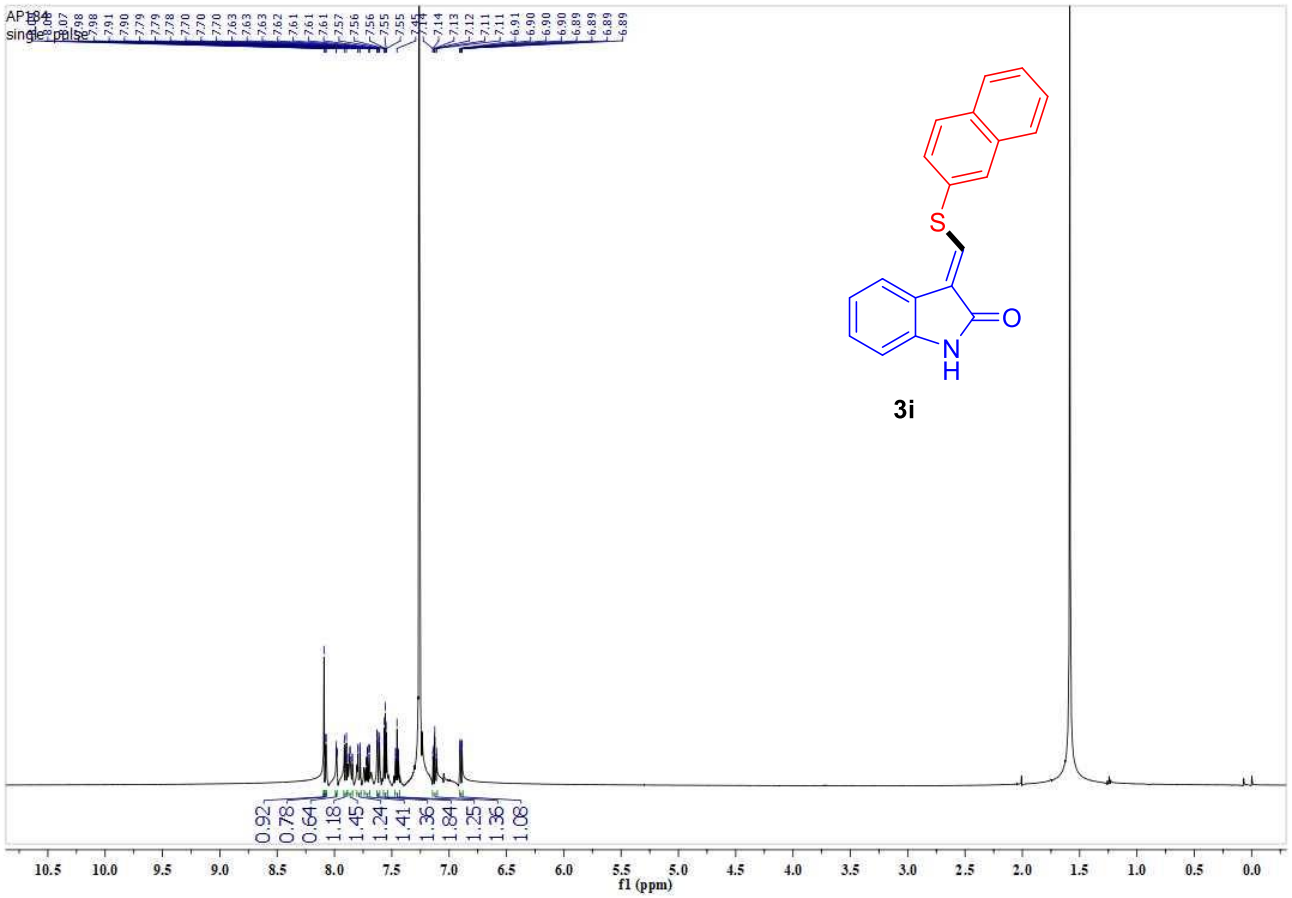

RKP-AP-195
single pulse decoupled gated NOE
167.54
140.54 140.00 131.17 129.74 128.97 128.65 124.02 123.06 122.78 122.29 109.70
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
S
O
N
H
3f


RKP-AP-183
single_pulse
Cl
S
O
N
H
3g
f1 (ppm)

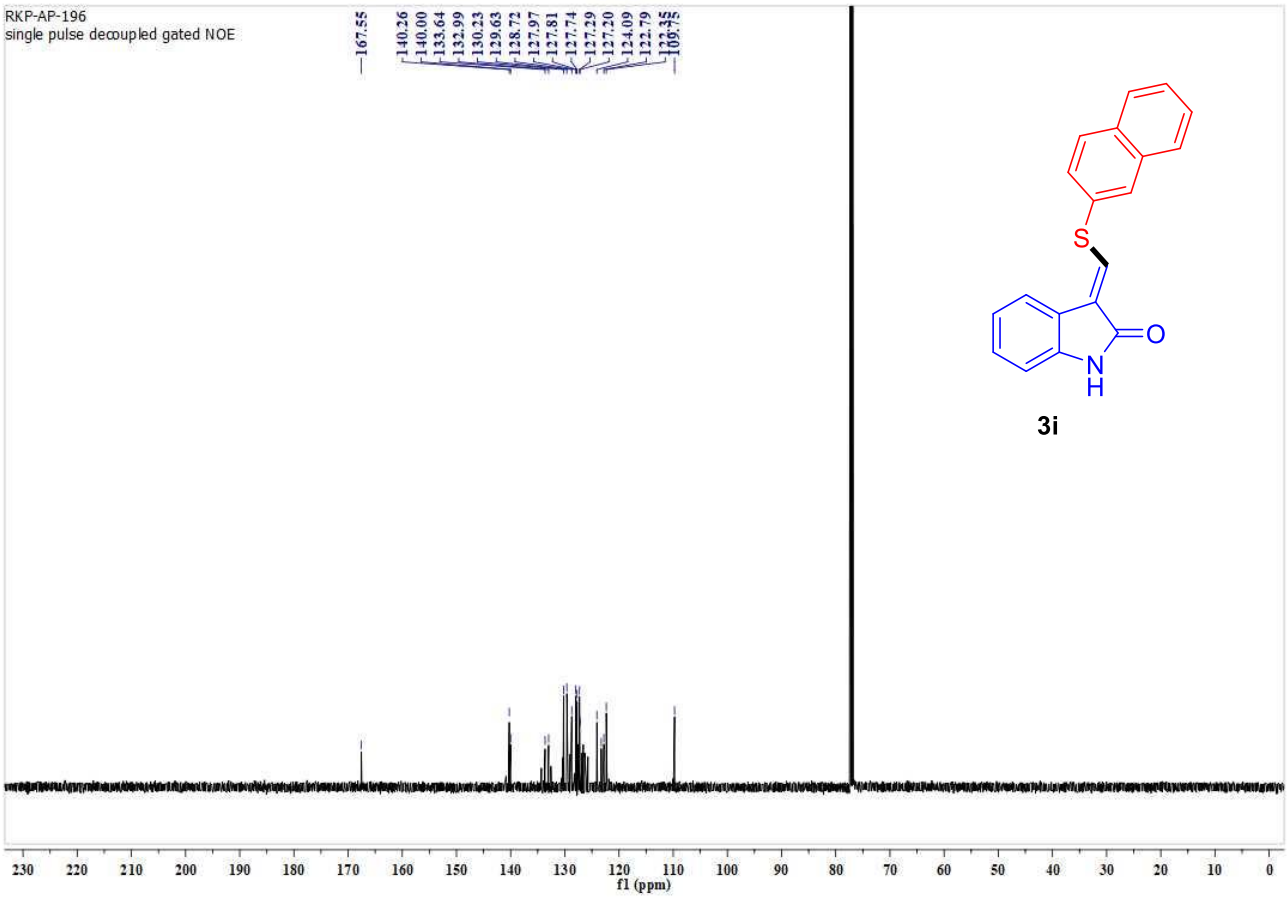

RKP-AP-183
single pulse decoupled gated NOE
Cl
S
O
N
H
3g
f1 (ppm)


RKP-AP-181
single_pulse
8.15
7.87
7.72
7.70
7.66
7.65
7.65
7.65
7.64
7.64
7.63
7.52
7.51
7.50
7.50
7.50
7.49
7.49
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.25
7.24
7.23
7.23
7.21
7.13
7.12
7.11
7.11
7.09
6.91
6.89
Cl
S
O
N
H
3h
1.00
1.02
1.00
0.81
1.01
2.00
1.00
1.00
1.23
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
f1 (ppm)

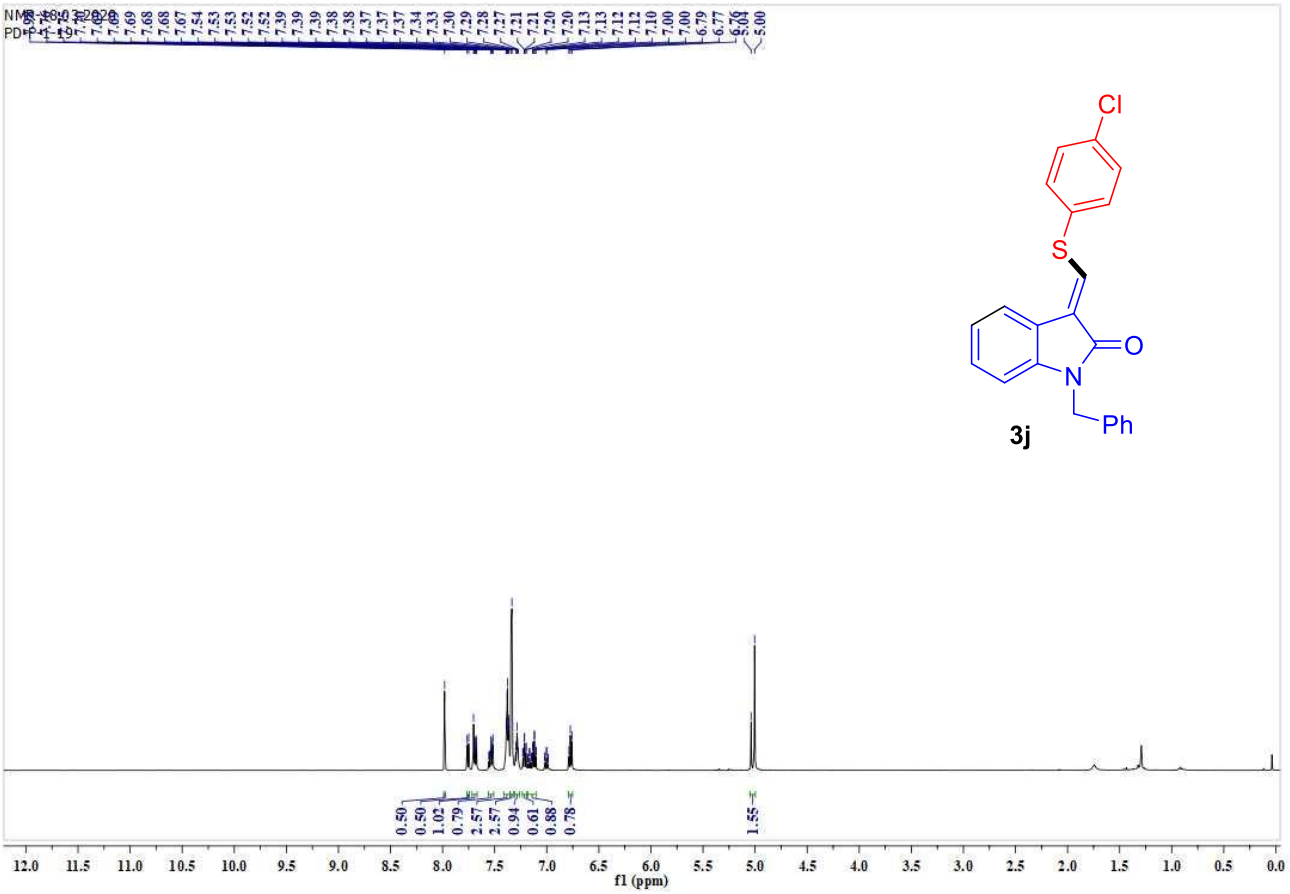

RKP-AP-181
single pulse decoupled gated NOE
167.52
140.17
138.11
135.55
132.52
132.48
130.41
130.10
128.98
128.06
128.04
124.32
124.26
122.53
122.40
109.81
Cl
S
O
N
H
3h
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

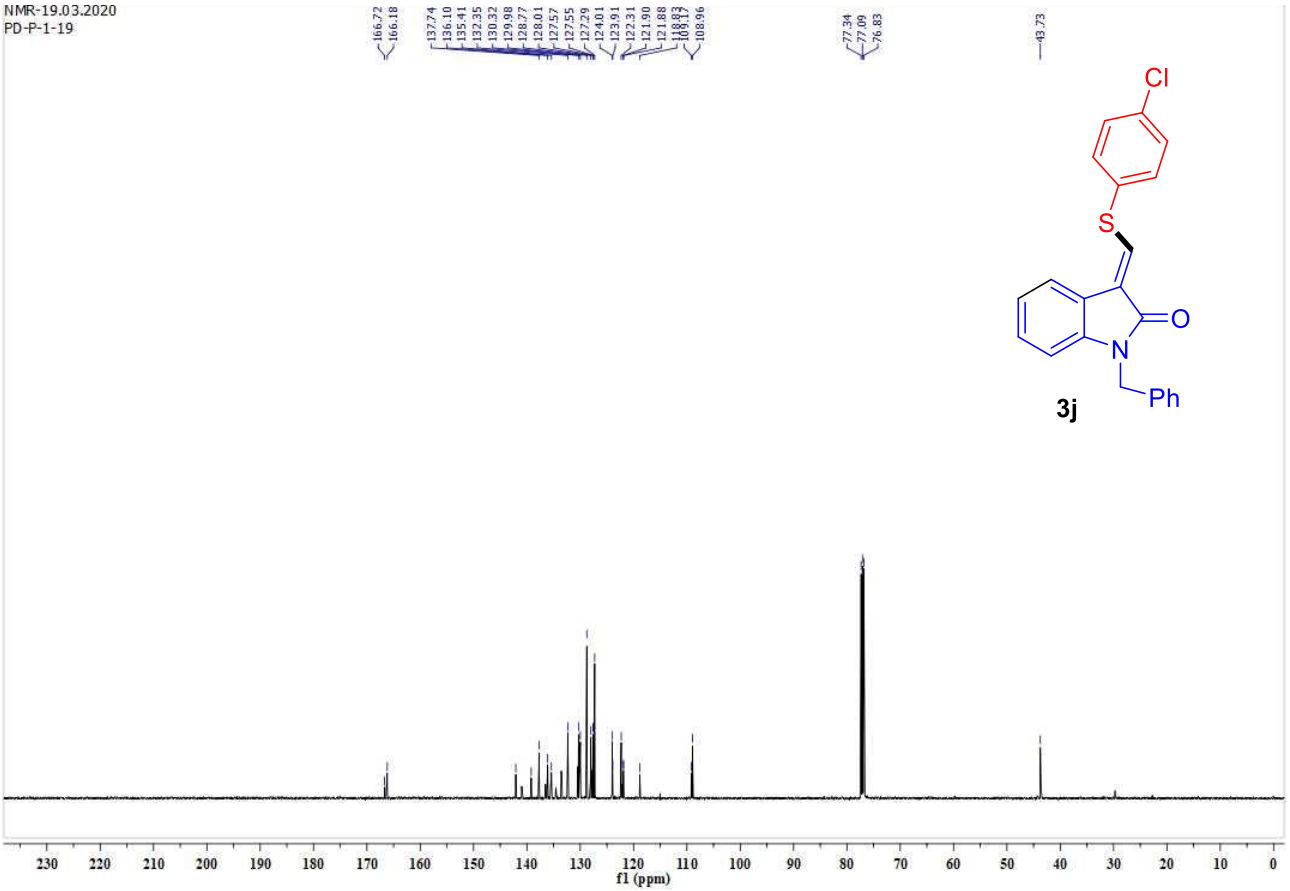

AP184
single pulse
0.92
0.78
0.64
1.18
1.45
1.24
1.41
1.36
1.84
1.25
1.36
1.08
f1 (ppm)

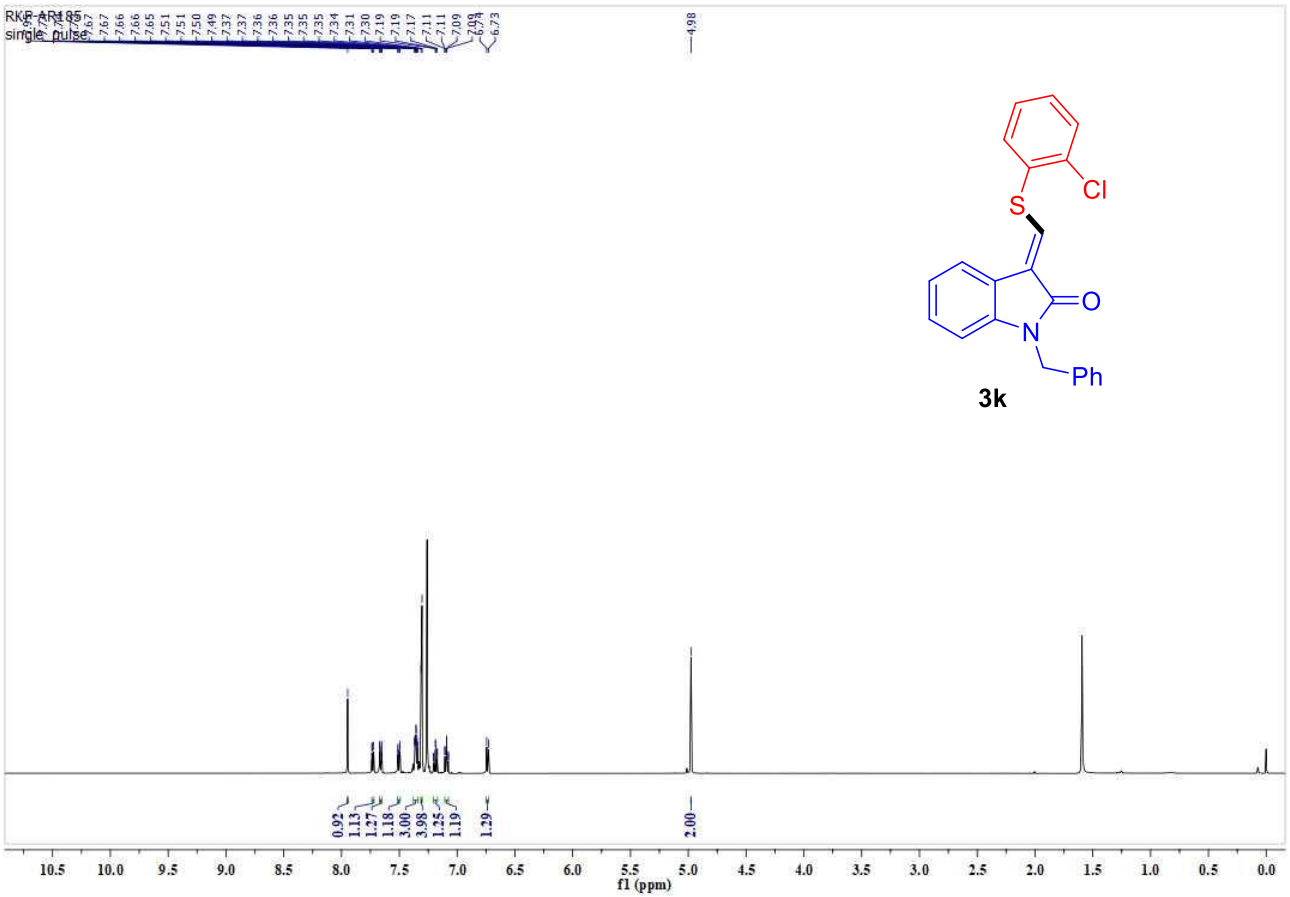
3i

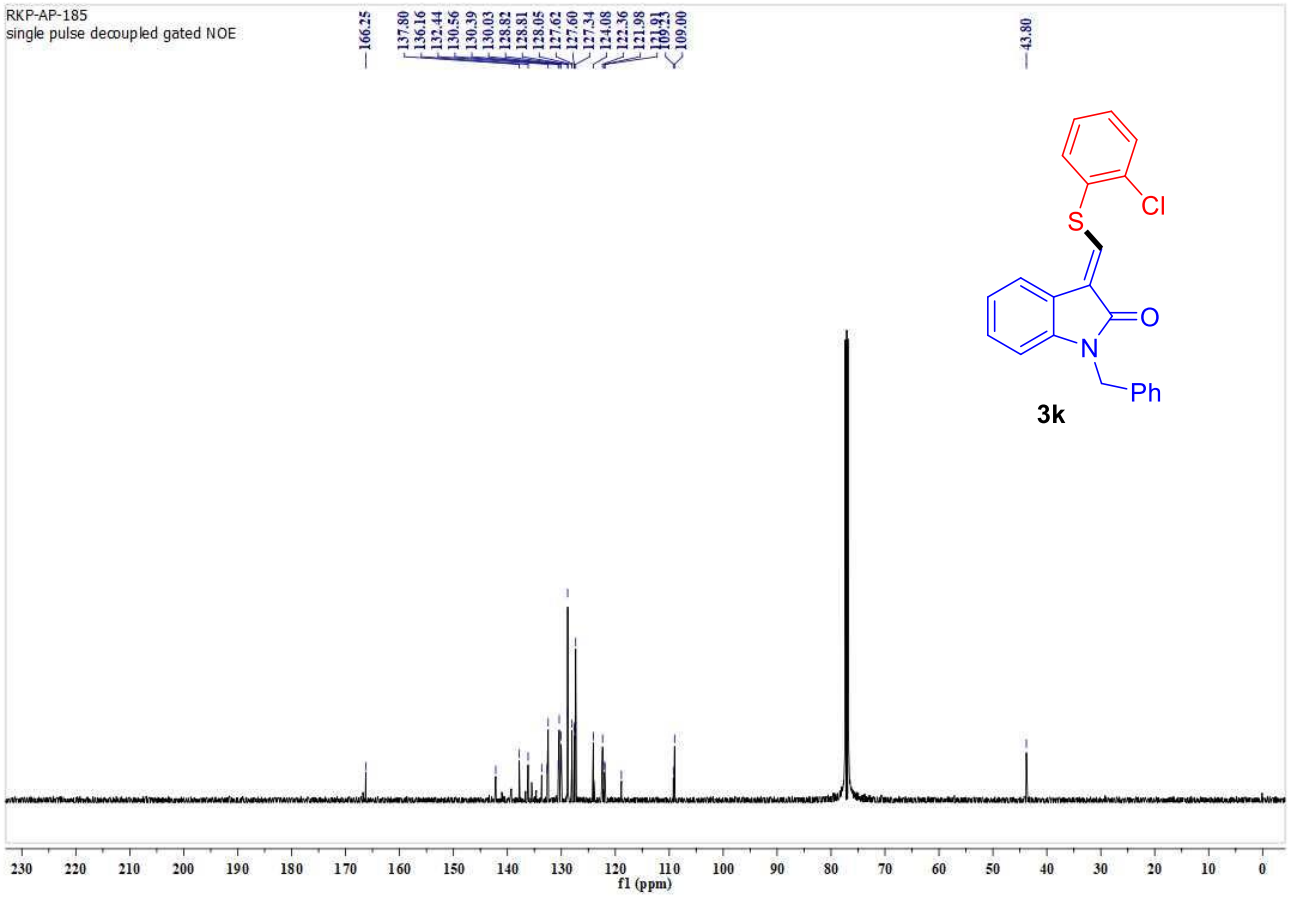

RKP-AP-196
single pulse decoupled gated NOE
167.55
140.26
140.00
133.64
132.99
130.23
129.63
128.72
127.97
127.81
127.74
127.29
127.20
124.09
122.79
f1 (ppm)

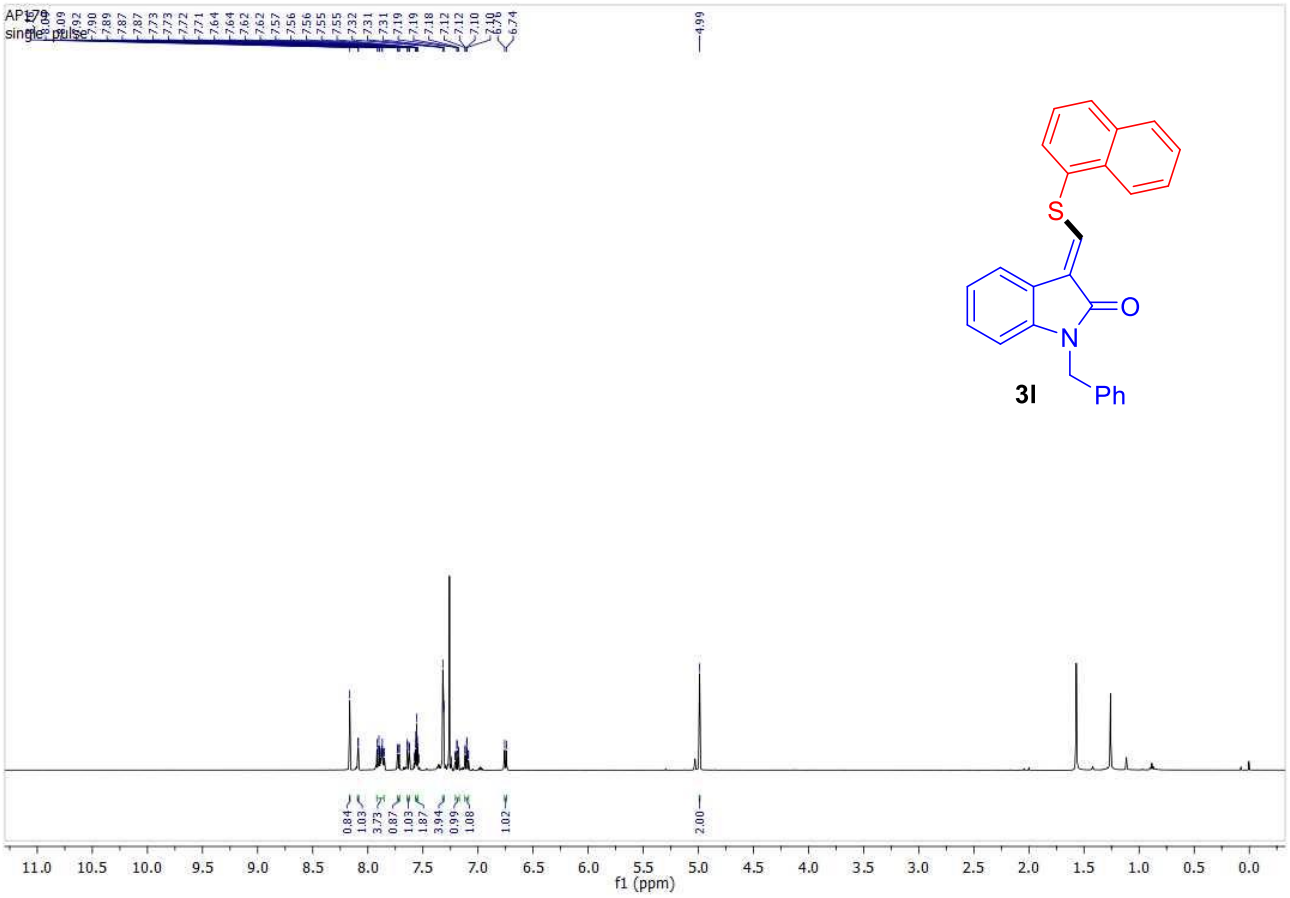
3i

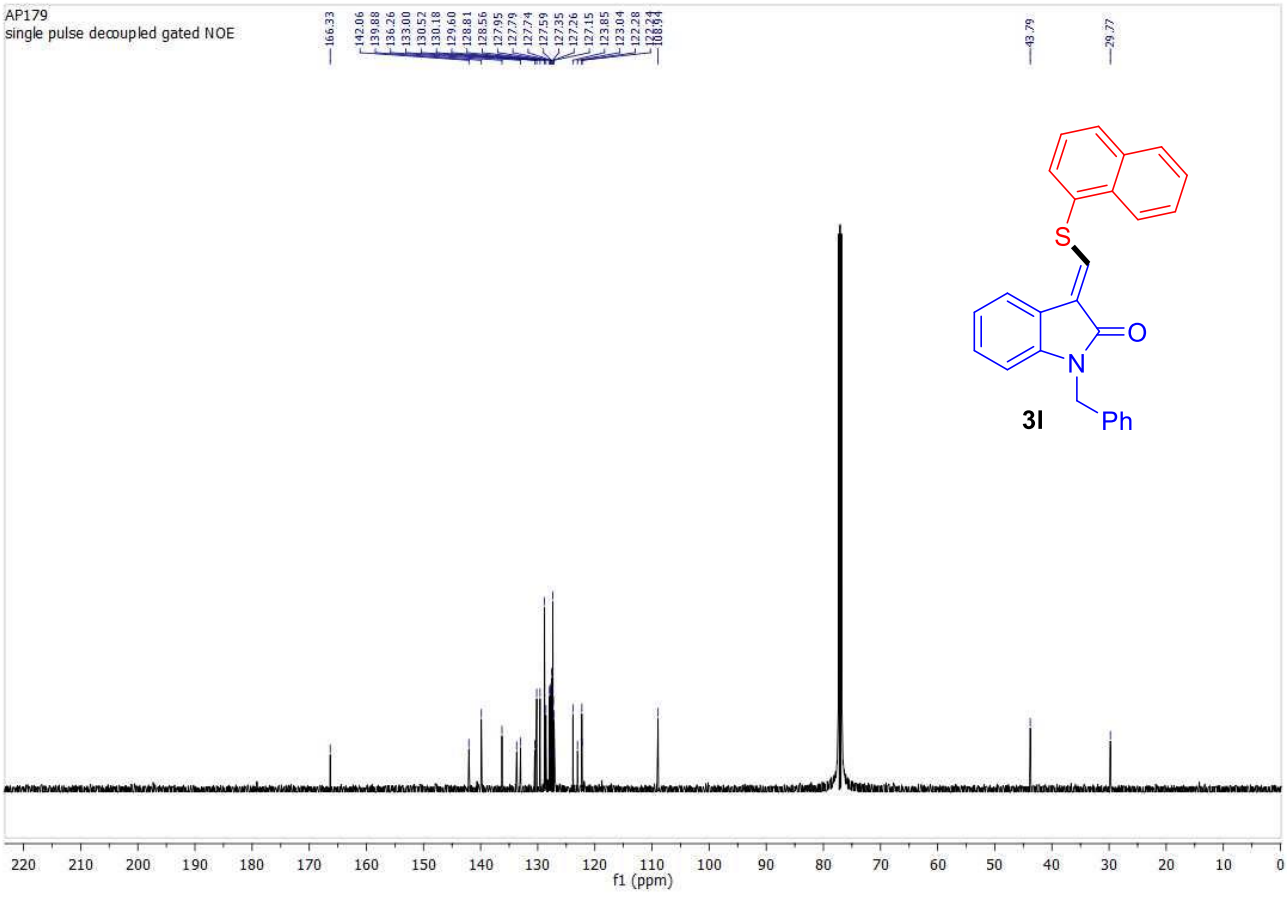

Cl
S
O
N
Ph
3j
0.50
0.50
1.02
0.79
2.57
2.57
0.94
0.61
0.88
0.78
1.55
f1 (ppm)

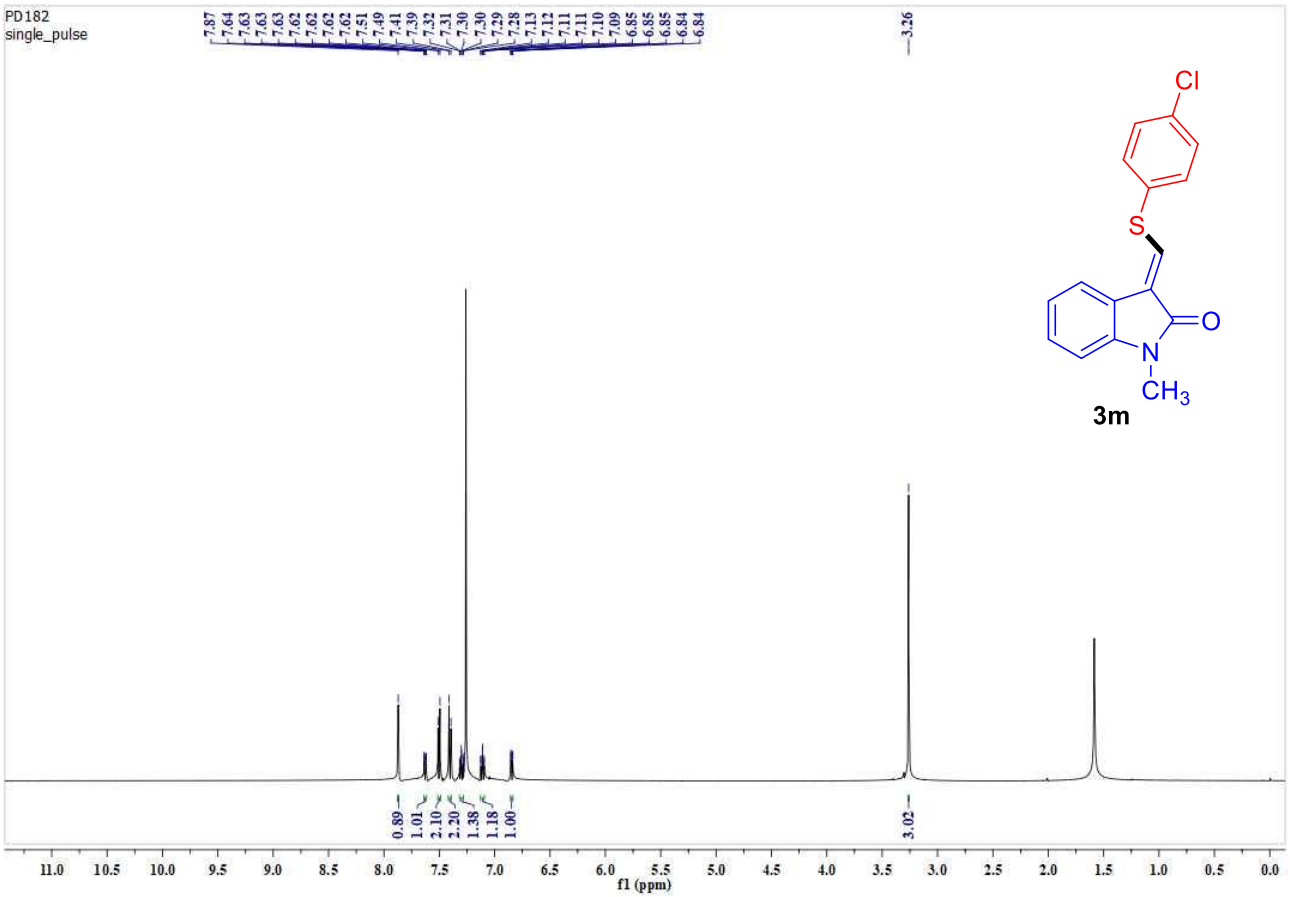

NMR-19.03.2020
PD-P-1-19
Cl
S
O
N
Ph
3j
f1 (ppm)

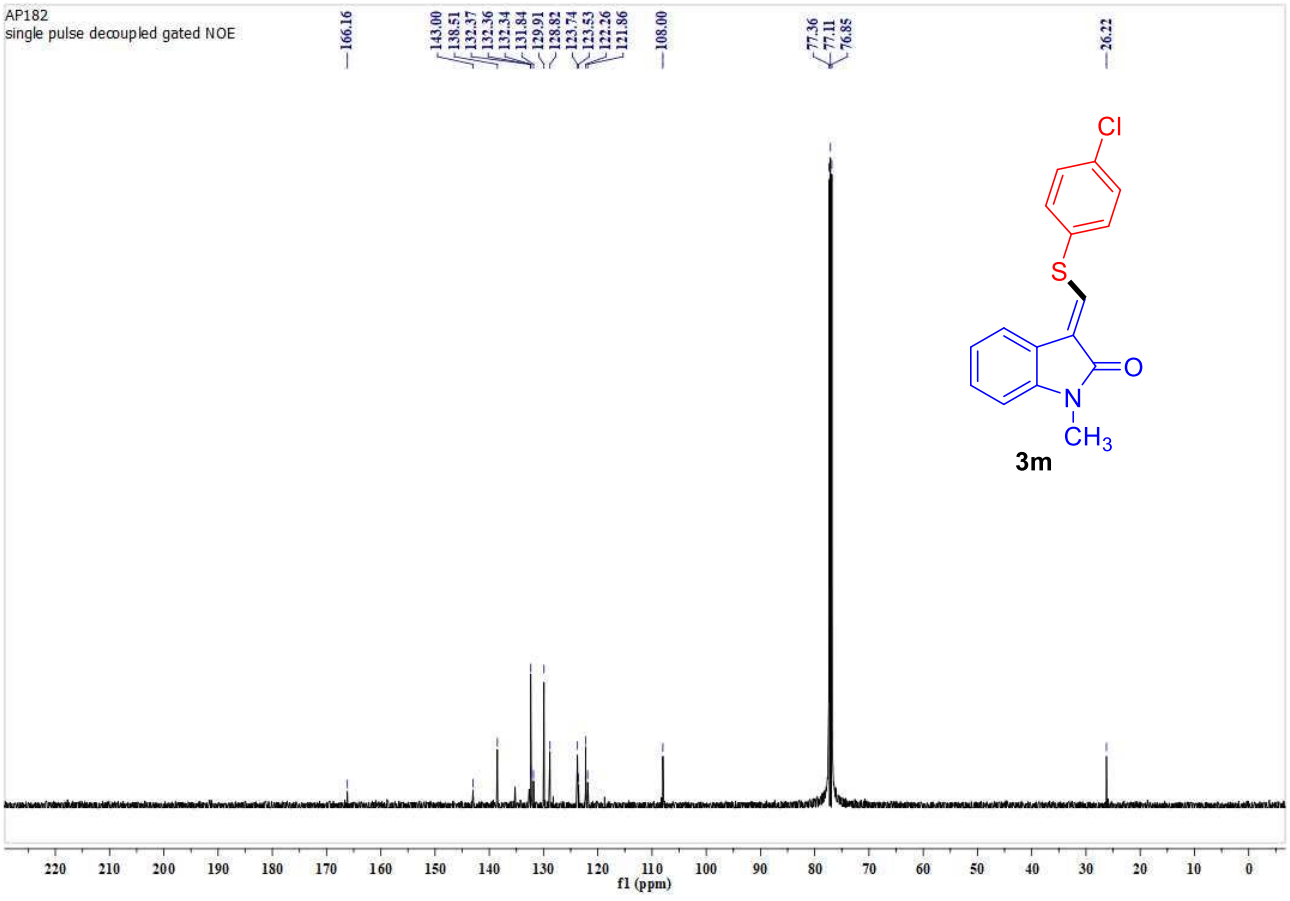

RKP-AP-185
single pulse
4.98
0.92
1.13
1.27
1.18
3.00
3.98
1.25
1.19
1.29
2.00
f1 (ppm)
Cl
S
O
N
Ph
3k

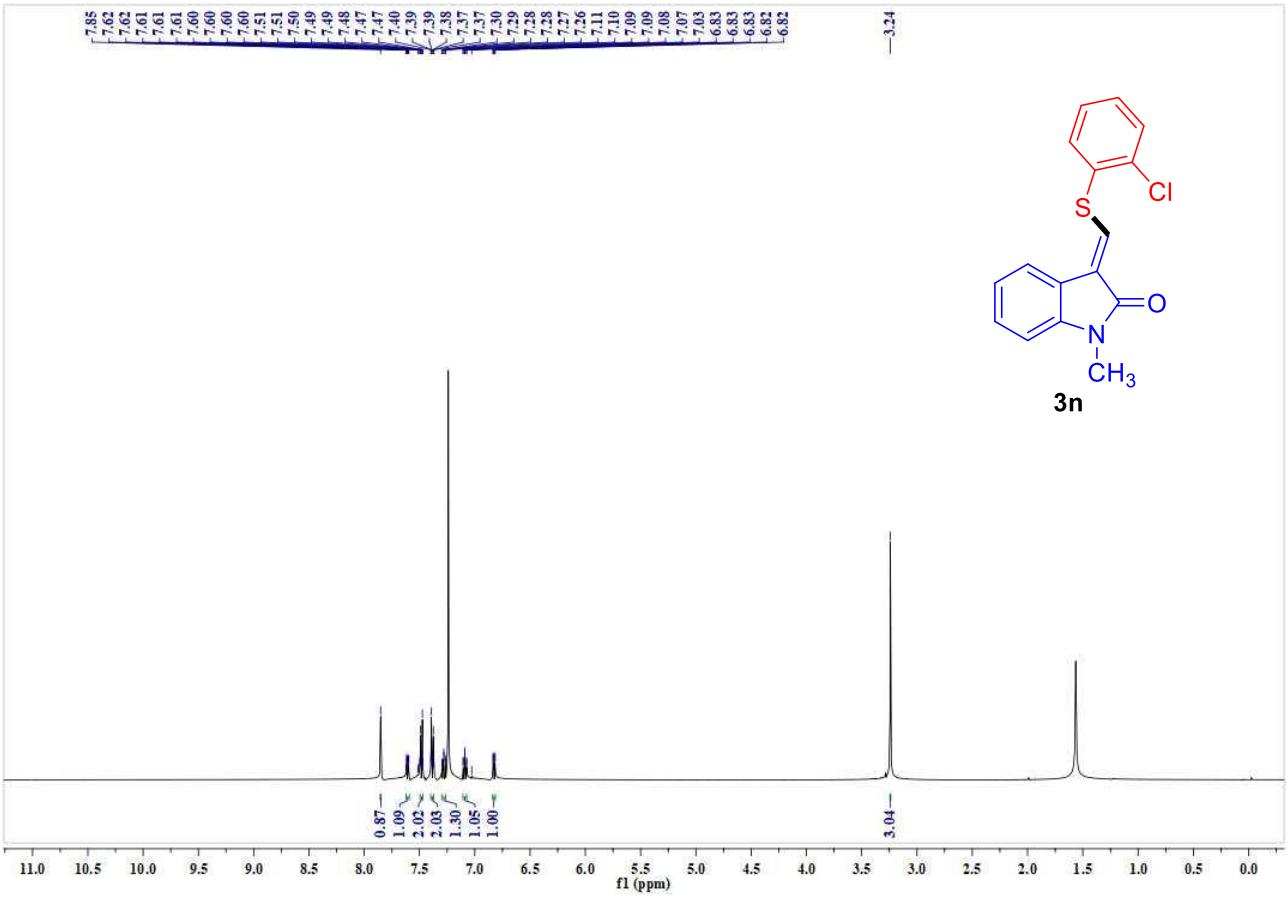

RKP-AP-185
single pulse decoupled gated NOE
166.25
137.80
136.16
132.44
130.56
130.39
130.03
128.82
128.81
128.05
127.62
127.60
127.34
124.08
122.36
121.98
109.21
109.00
43.80
f1 (ppm)
Cl
S
O
N
Ph
3k

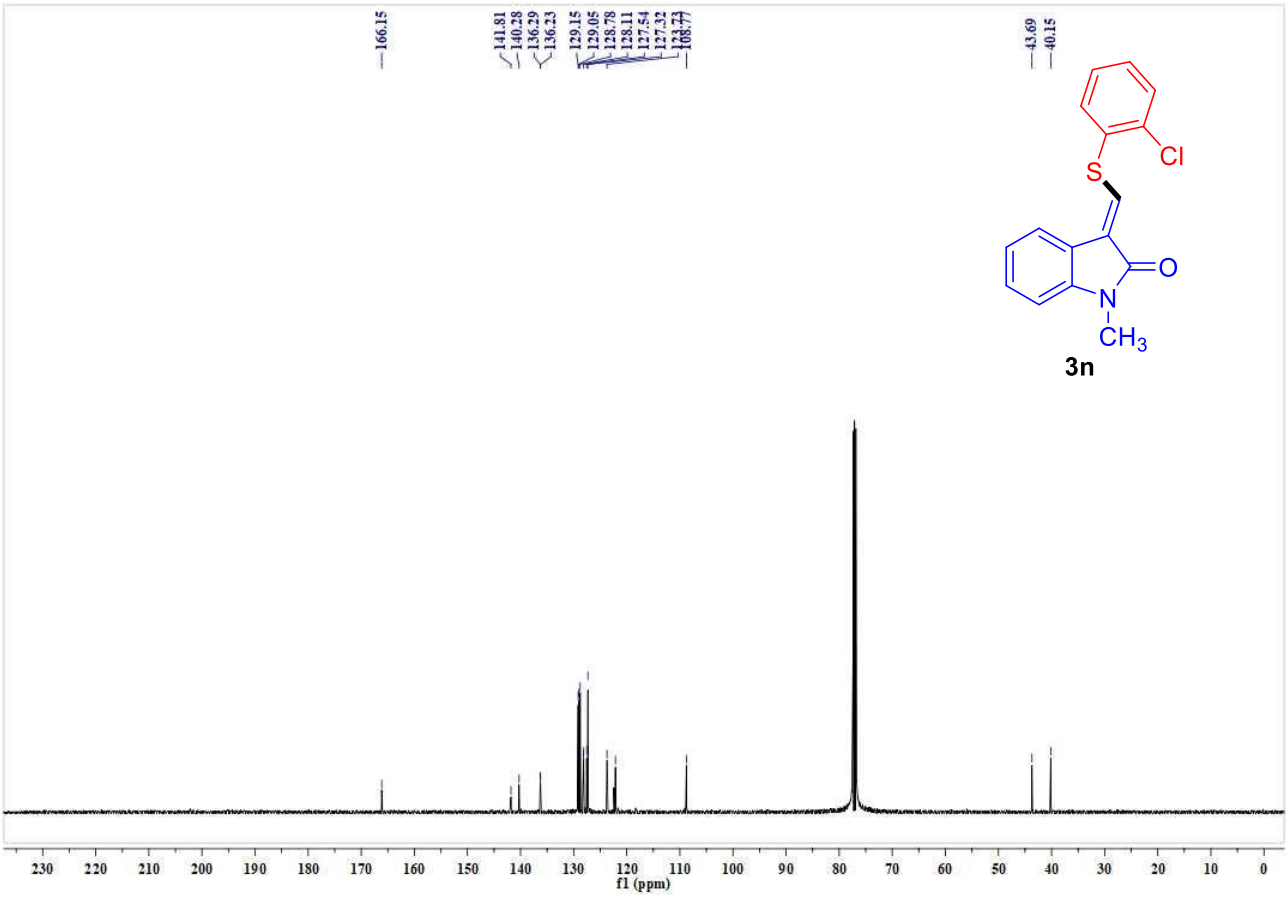

AP179
single pulse
8.09
8.09
7.92
7.90
7.89
7.87
7.87
7.73
7.73
7.72
7.71
7.64
7.64
7.62
7.62
7.57
7.56
7.56
7.55
7.55
7.32
7.31
7.31
7.19
7.19
7.18
7.12
7.12
7.10
7.10
6.74
4.99
0.84
1.03
3.73
0.87
1.03
1.87
3.94
0.99
1.08
1.02
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
S
O
N
Ph
3l

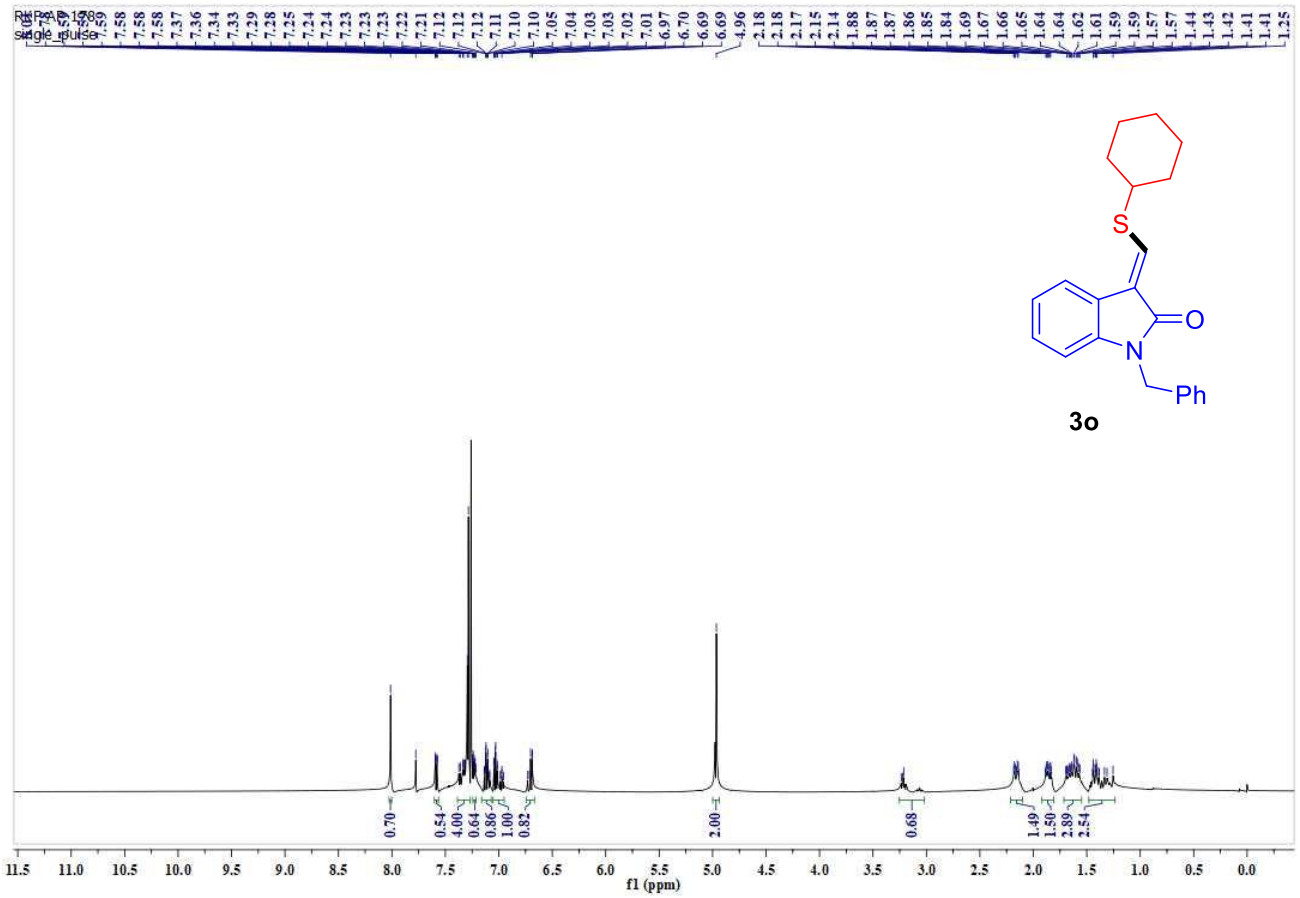

AP179
single pulse decoupled gated NOE
166.33
142.06
139.88
136.26
133.00
130.52
130.18
129.60
128.81
128.56
127.95
127.79
127.74
127.59
127.35
127.26
127.15
123.85
123.04
122.28
108.94
43.79
29.77
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
S
O
N
Ph
3l

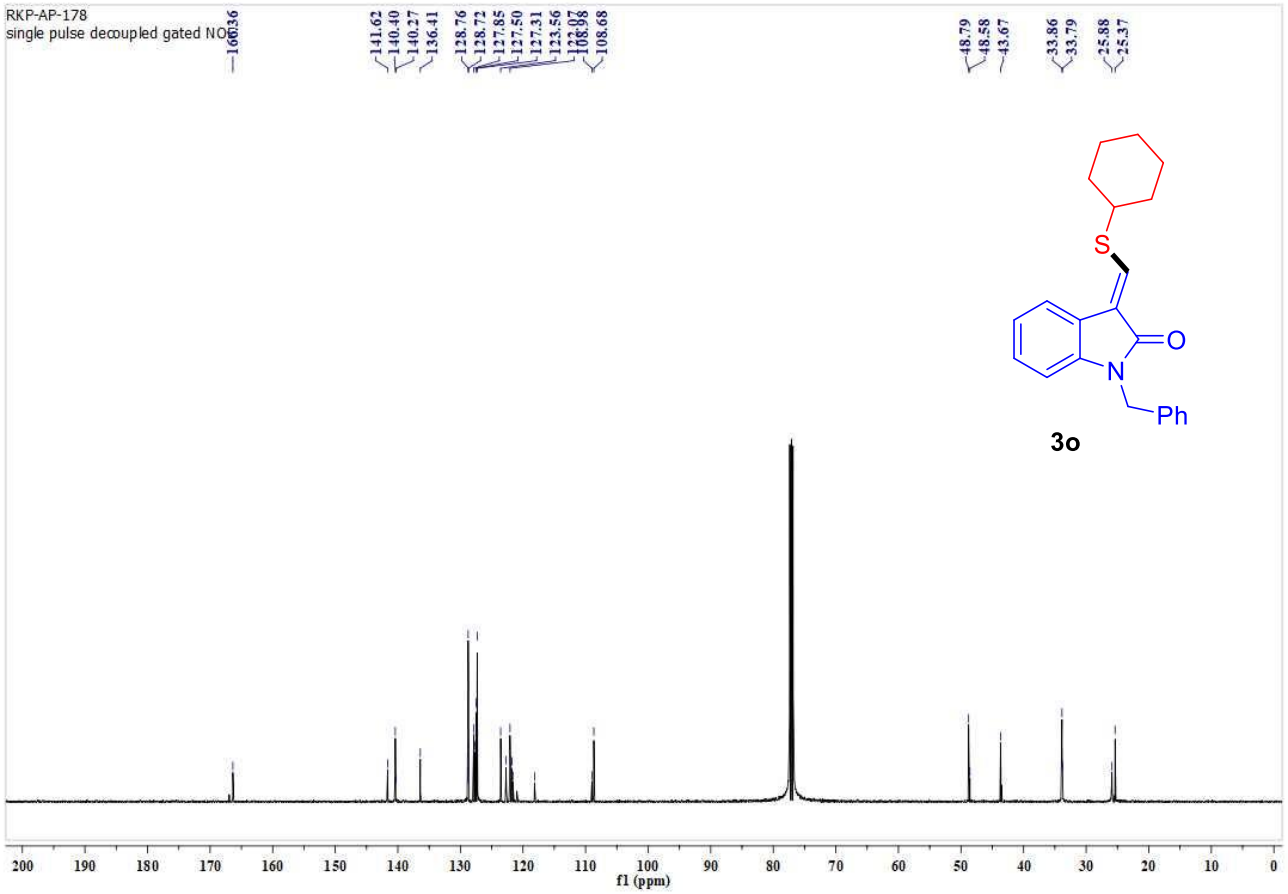

PD182
single_pulse
7.87
7.64
7.63
7.63
7.63
7.62
7.62
7.62
7.62
7.51
7.49
7.41
7.39
7.32
7.31
7.30
7.30
7.29
7.28
7.13
7.12
7.11
7.11
7.10
7.09
6.85
6.85
6.84
6.84
3.26
Cl
S
O
N
CH3
3m
0.89
1.01
2.10
2.20
1.38
1.18
1.00
3.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

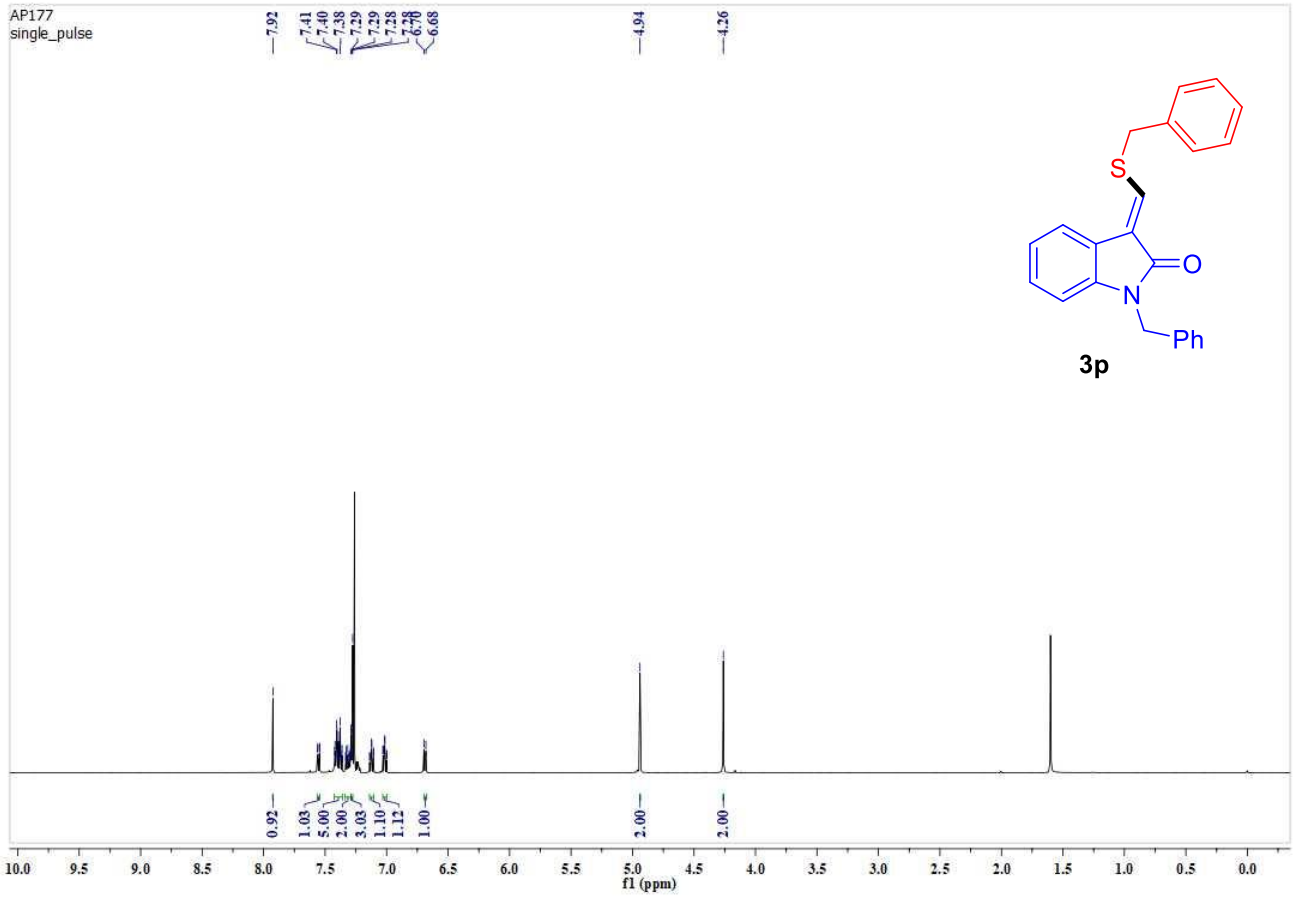

AP182
single pulse decoupled gated NOE
166.16
143.00
138.51
132.37
132.36
132.34
131.84
129.91
128.82
123.74
123.53
122.26
121.86
108.00
77.36
77.11
76.85
26.22
Cl
S
O
N
CH3
3m
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

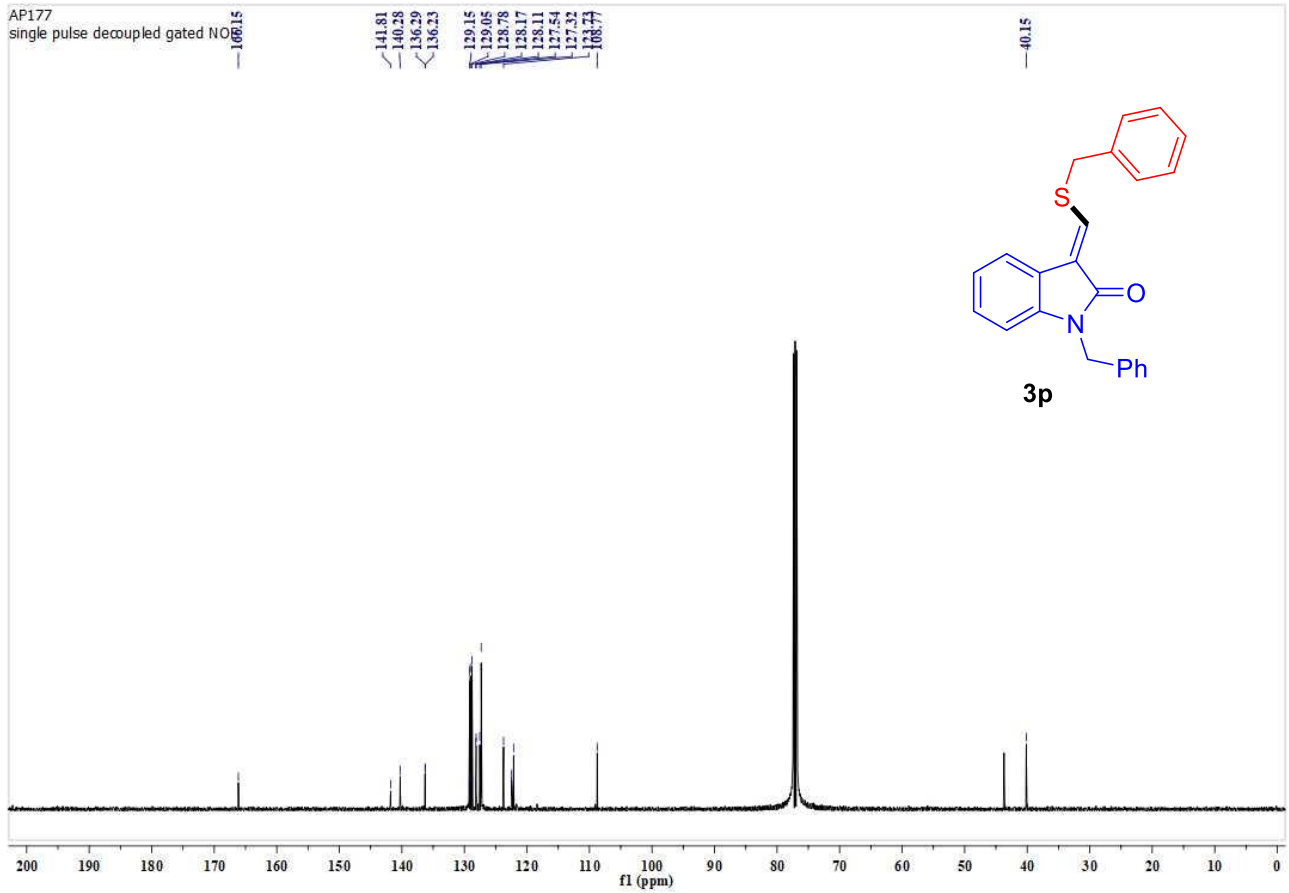

7.85 7.62 7.62 7.61 7.61 7.61 7.60 7.60 7.60 7.60 7.60 7.51 7.51 7.50 7.49 7.49 7.48 7.47 7.47 7.40 7.39 7.39 7.38 7.37 7.37 7.30 7.29 7.28 7.28 7.27 7.26 7.11 7.10 7.09 7.09 7.08 7.07 7.03 6.83 6.83 6.83 6.82 6.82
3.24
Cl
S
O
N
CH3
3n
0.87 1.09 2.02 2.03 1.30 1.05 1.00
3.04
11.0 10.5 10.0 9.5 9.0 8.5 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
f1 (ppm)

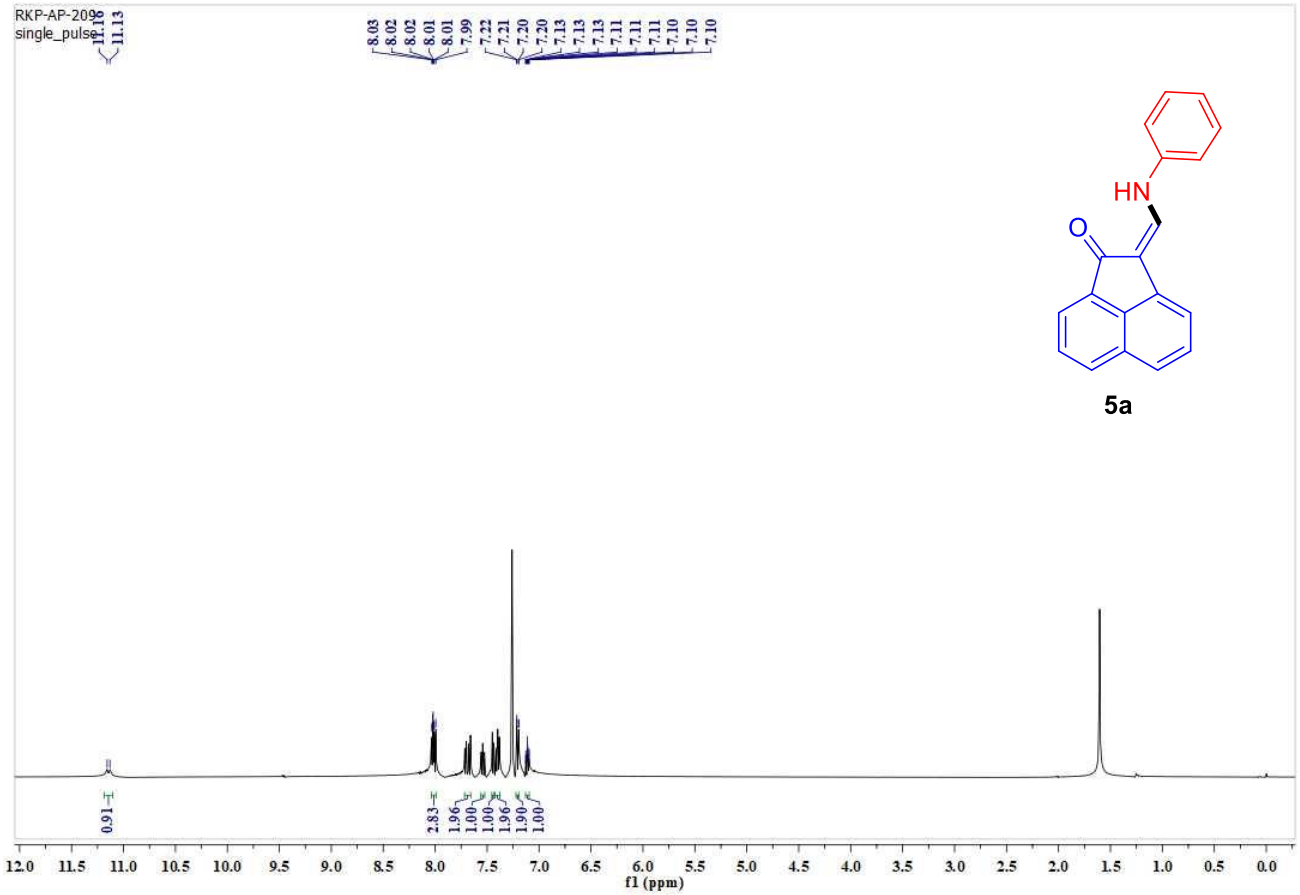

166.15
141.81 140.28 136.29 136.23 129.15 129.05 128.78 128.11 127.54 127.32 123.72 108.77
43.69 40.15
Cl
S
O
N
CH3
3n
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


RKP-AP-178
single_pulse
S
O
N
Ph
3o
0.70
0.54
4.00
0.64
0.86
1.00
0.82
2.00
0.68
1.49
1.50
2.89
2.54
f1 (ppm)

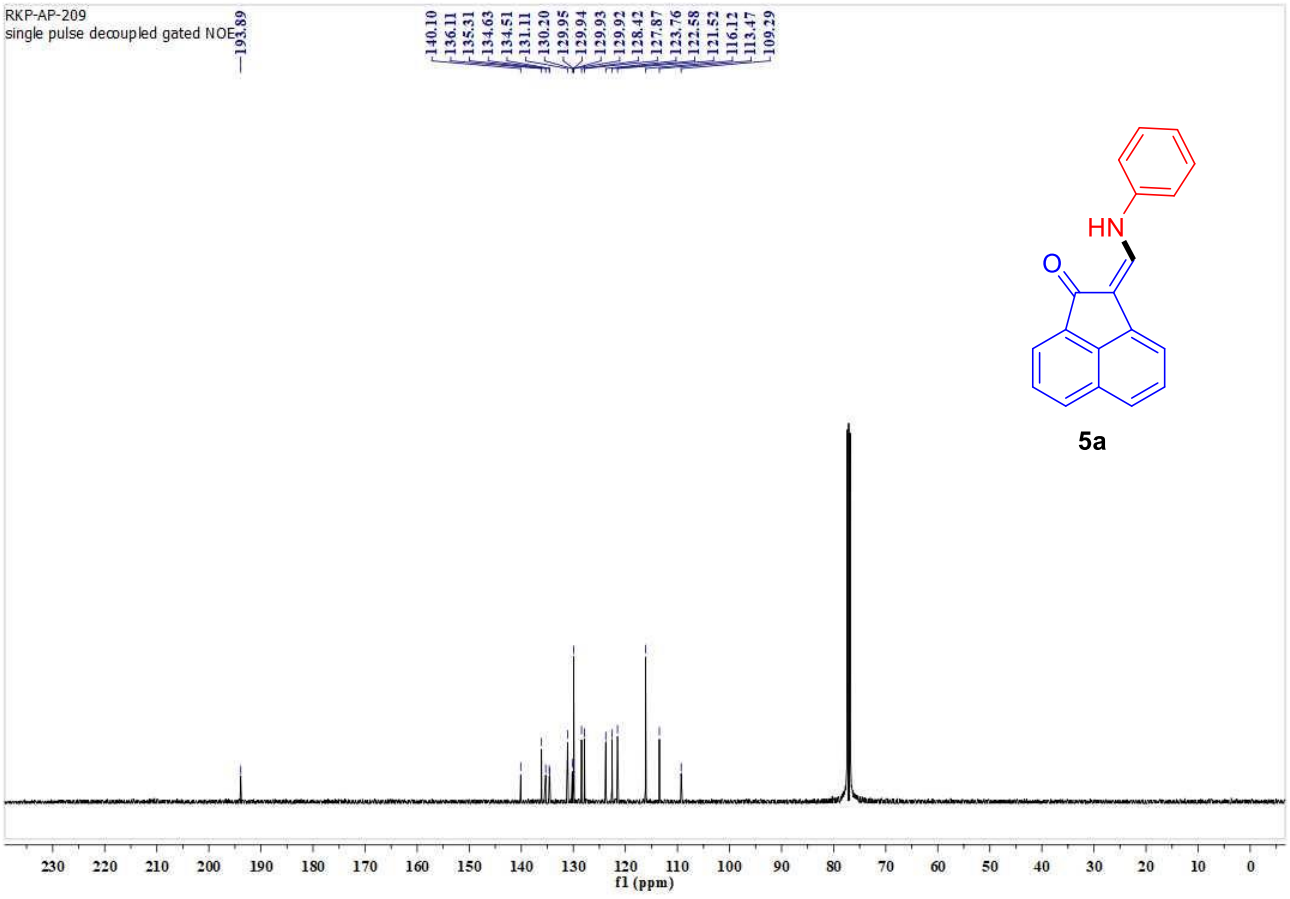

RKP-AP-178
single pulse decoupled gated NOE
166.36
141.62
140.40
140.27
136.41
128.76
128.72
127.85
127.50
127.31
123.56
123.07
108.98
108.68
48.79
48.58
43.67
33.86
33.79
25.88
25.37
S
O
N
Ph
3o
f1 (ppm)


AP177
single_pulse
7.92
7.41
7.40
7.38
7.29
7.29
7.28
7.28
6.70
6.68
4.94
4.26
S
O
N
Ph
3p
0.92
1.03
5.00
2.00
3.03
1.10
1.12
1.00
2.00
2.00
f1 (ppm)

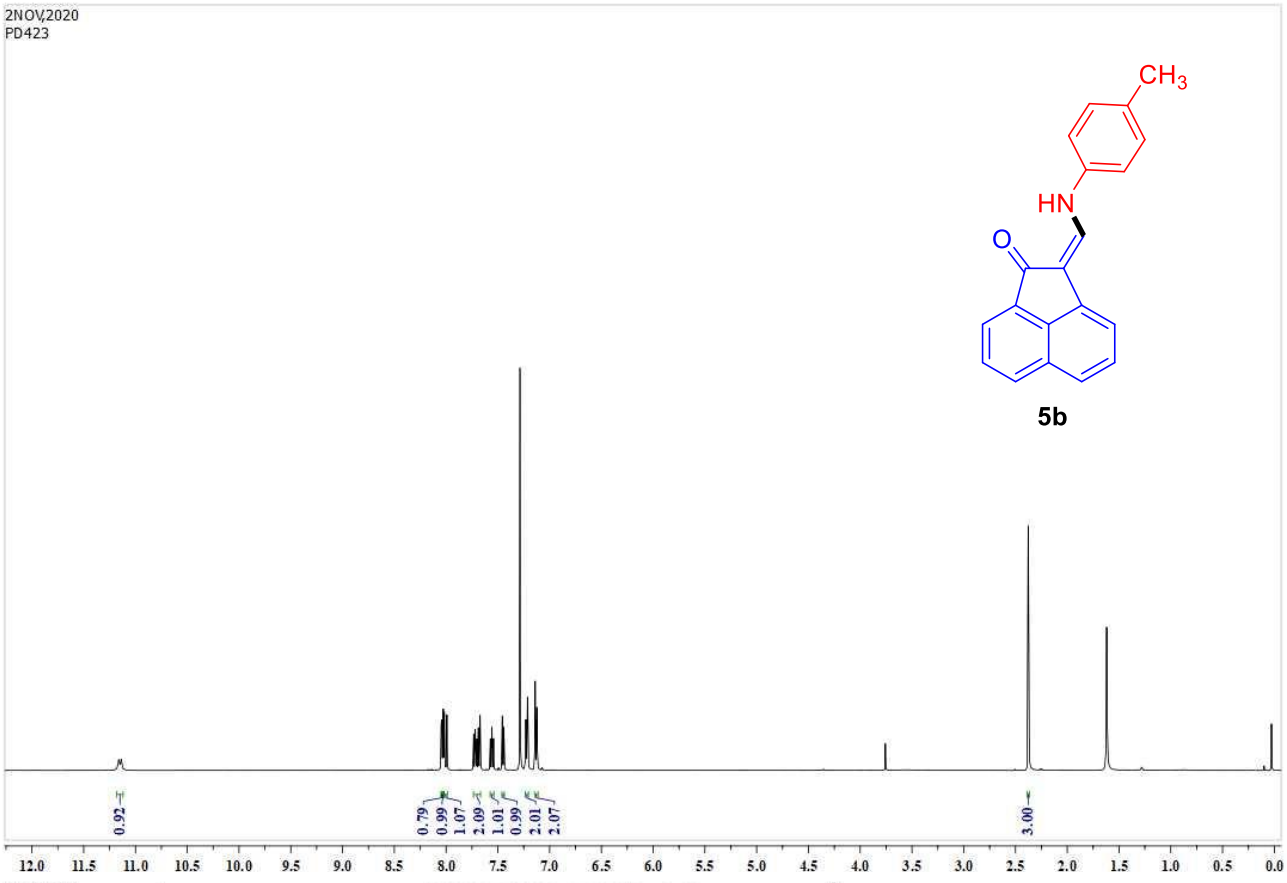

AP177
single pulse decoupled gated NOE
166.15
141.81
140.28
136.29
136.23
129.15
129.05
128.78
128.17
128.11
127.54
127.32
40.15
S
O
N
Ph
3p
f1 (ppm)

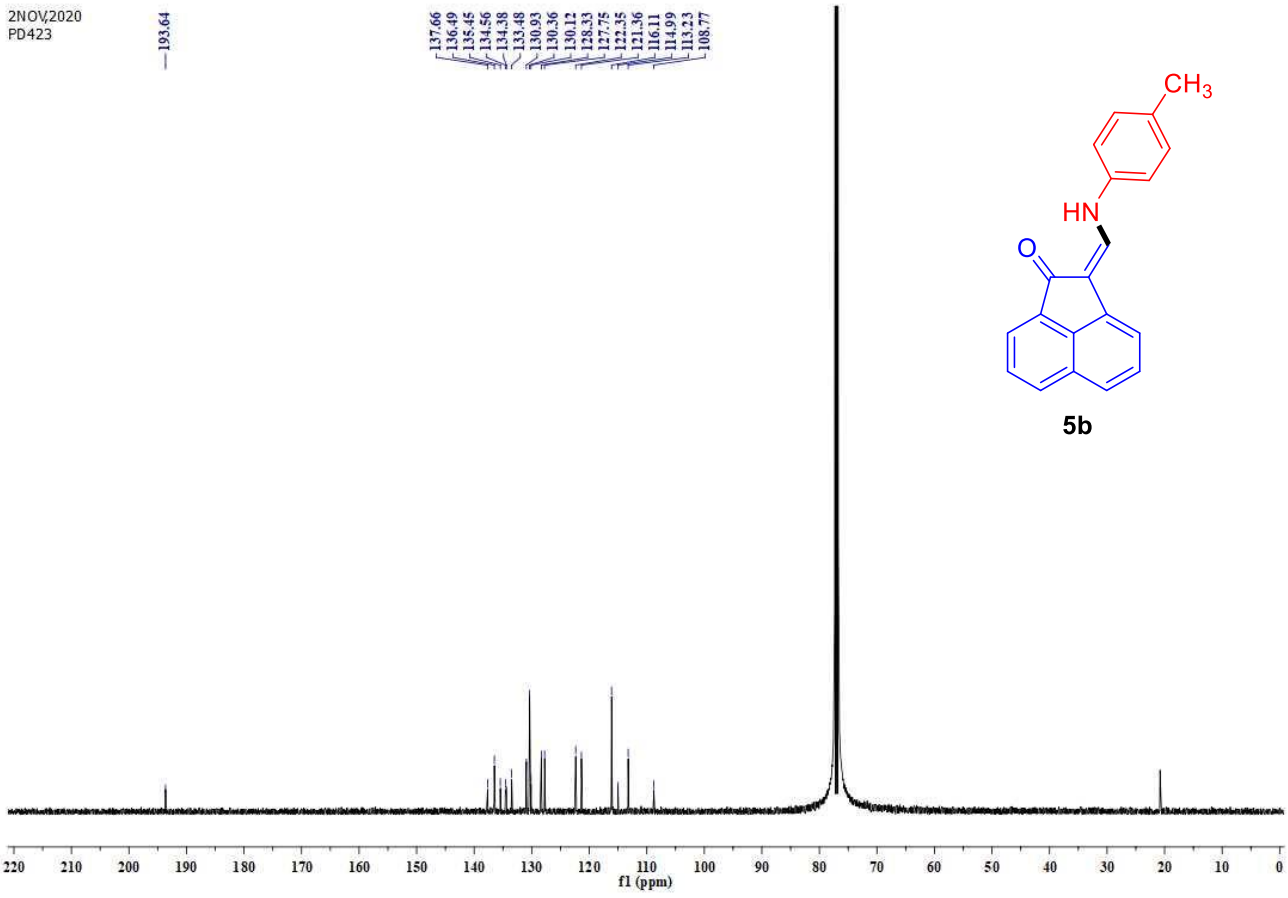

RKP-AP-209
single_pulse
11.16
11.13
8.03
8.02
8.02
8.01
8.01
7.99
7.22
7.21
7.20
7.20
7.13
7.13
7.13
7.11
7.11
7.11
7.10
7.10
7.10
HN
O
0.91
2.83
1.96
1.00
1.00
1.96
1.90
1.00
f1 (ppm)

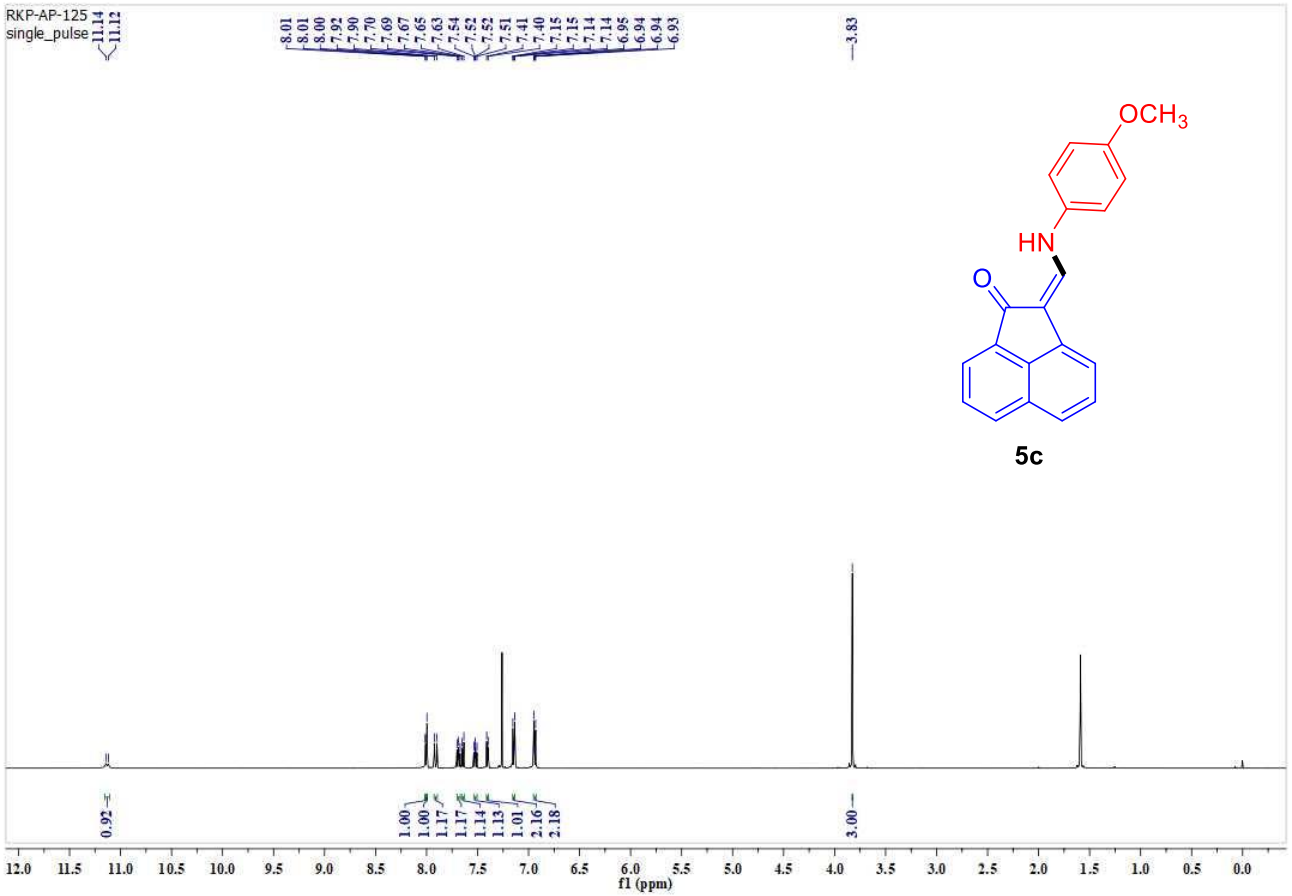
5a

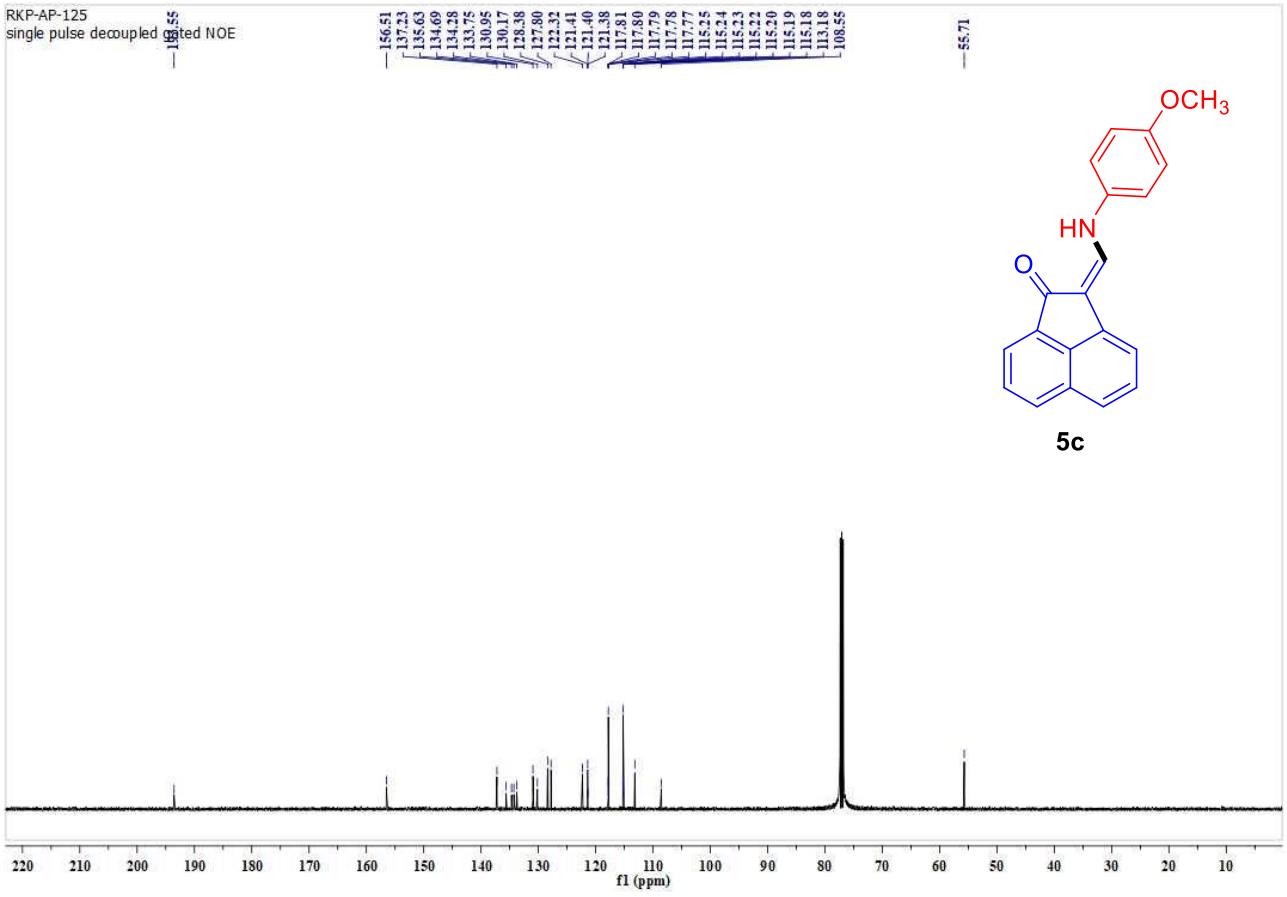

RKP-AP-209
single pulse decoupled gated NOE
193.89
140.10
136.11
135.31
134.63
134.51
131.11
130.20
129.95
129.94
129.93
129.92
128.42
127.87
123.76
122.58
121.52
116.12
113.47
109.29
HN
O
f1 (ppm)

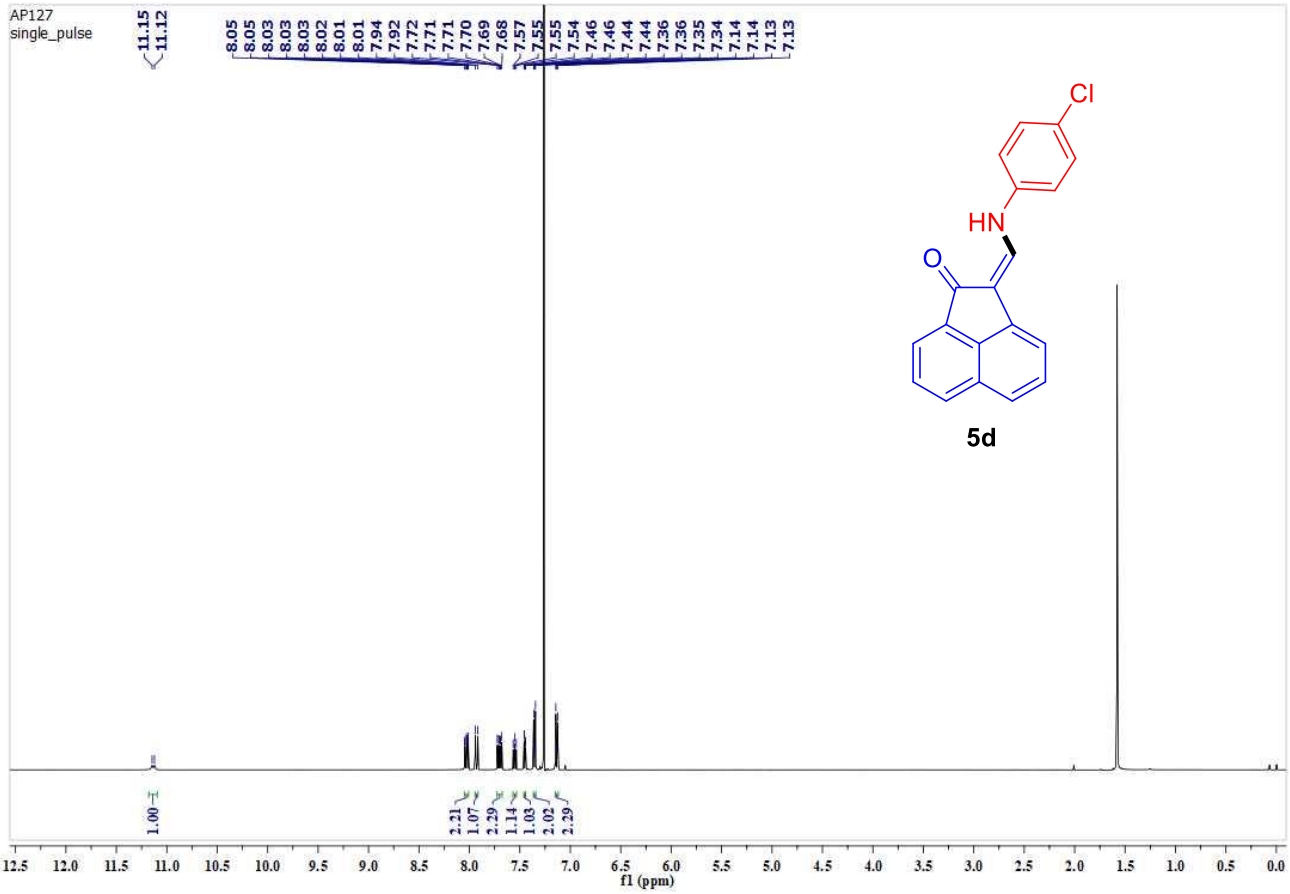
5a

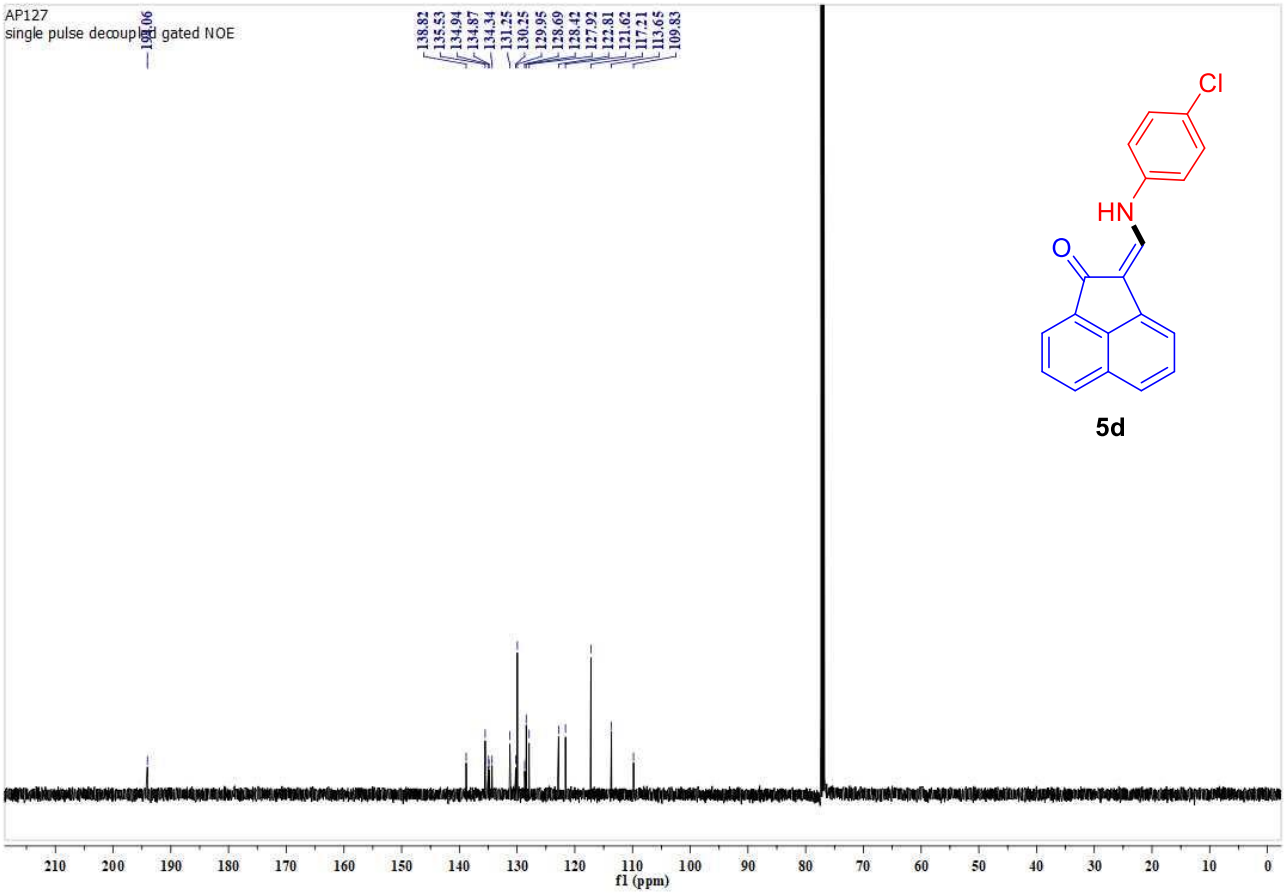

2NOV,2020
PD423
CH3
HN
O
5b
0.92
0.79
0.99
1.07
2.09
1.01
0.99
2.01
2.07
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

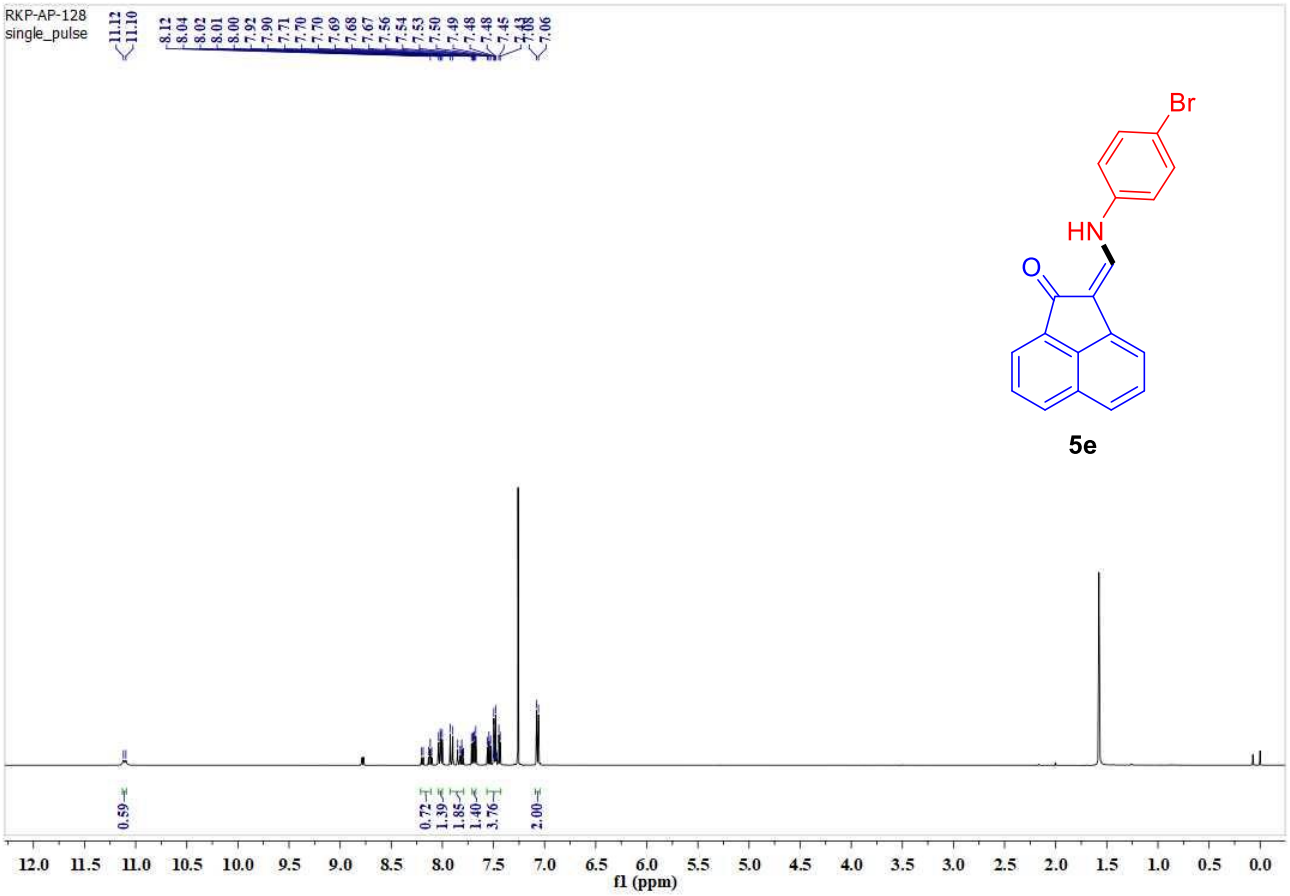

2NOV,2020
PD423
193.64
137.66
136.49
135.45
134.56
134.38
133.48
130.93
130.36
130.12
128.33
127.75
122.35
121.36
116.11
114.99
113.23
108.77
CH3
HN
O
5b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

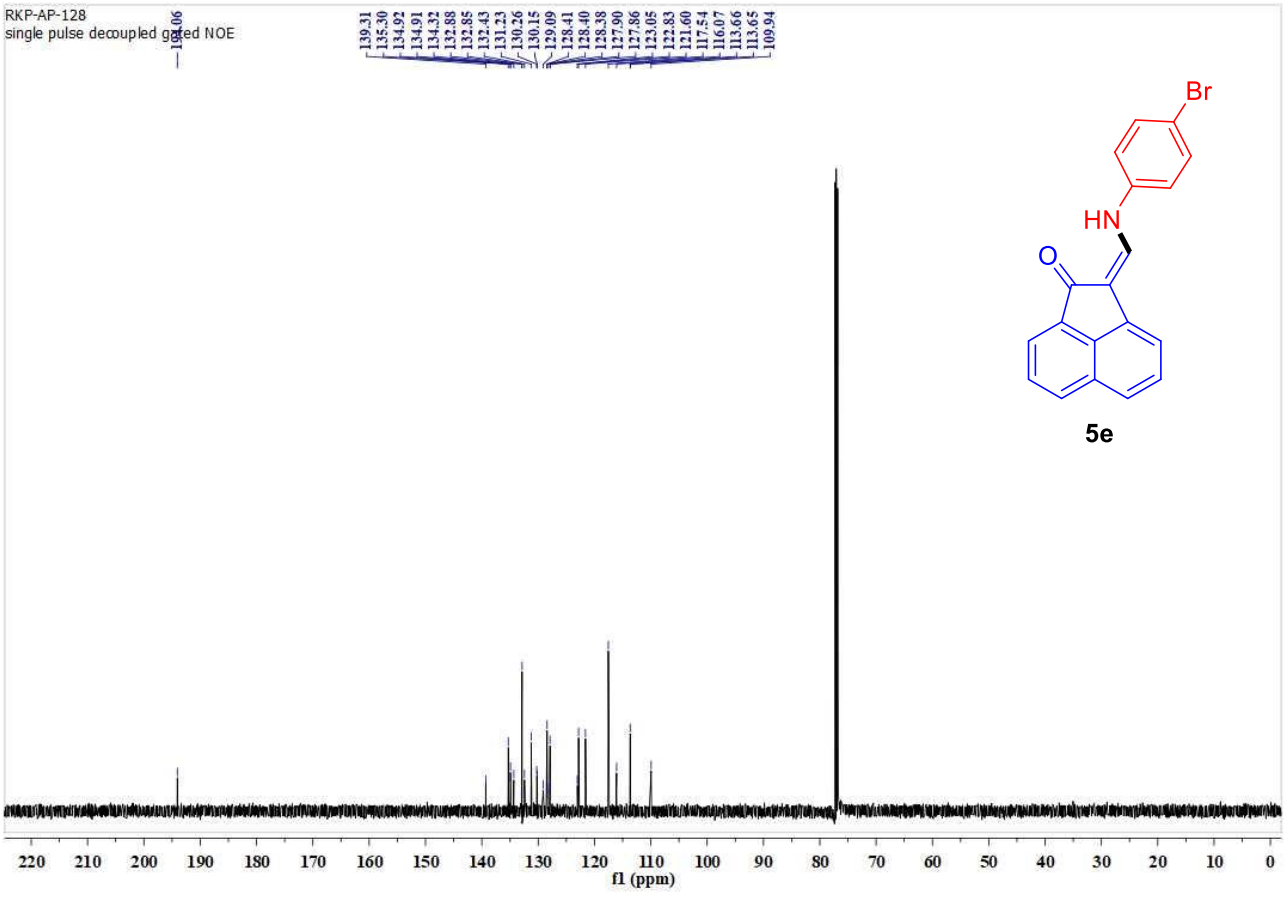

RKP-AP-125
single_pulse
11.14
11.12
8.01
8.01
8.00
7.92
7.90
7.70
7.69
7.67
7.65
7.63
7.54
7.52
7.52
7.51
7.41
7.40
7.15
7.15
7.14
7.14
6.95
6.94
6.94
6.93
3.83
OCH3
HN
O
5c
0.92
1.00
1.00
1.17
1.17
1.14
1.13
1.01
2.16
2.18
3.00
f1 (ppm)

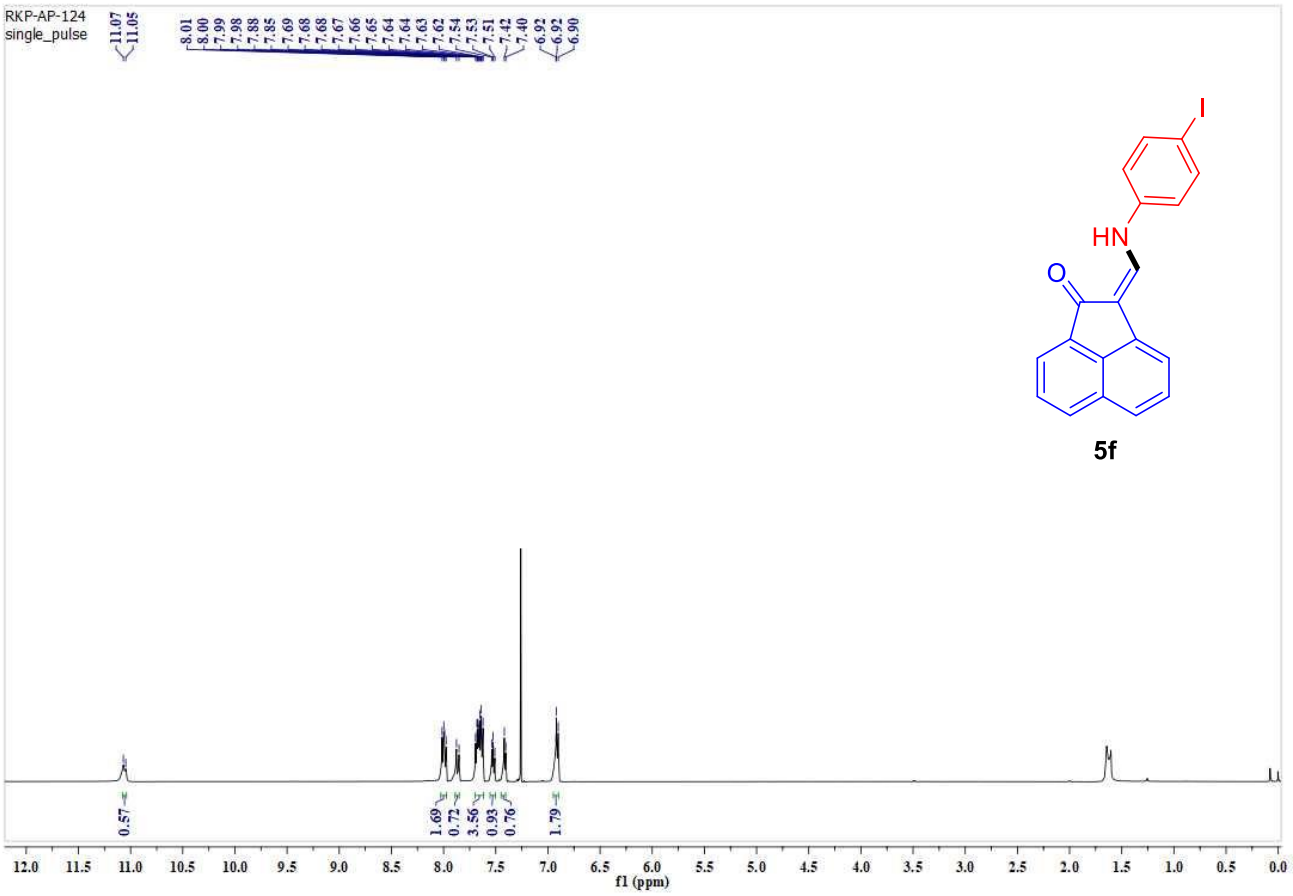

RKP-AP-125
single pulse decoupled gated NOE
156.51
137.23
135.63
134.69
134.28
133.75
130.95
130.17
128.38
127.80
122.32
121.41
121.40
121.38
117.81
117.80
117.79
117.78
117.77
115.25
115.24
115.23
115.22
115.20
115.19
115.18
113.18
108.55
55.71
OCH3
HN
O
5c
f1 (ppm)


AP127
single_pulse
11.15
11.12
8.05
8.05
8.03
8.03
8.03
8.02
8.01
8.01
7.94
7.92
7.72
7.71
7.71
7.70
7.69
7.68
7.57
7.55
7.55
7.54
7.46
7.46
7.44
7.44
7.36
7.35
7.34
7.14
7.14
7.13
7.13
Cl
HN
O
5d
1.00
2.21
1.07
2.29
1.14
1.03
2.02
2.29
f1 (ppm)

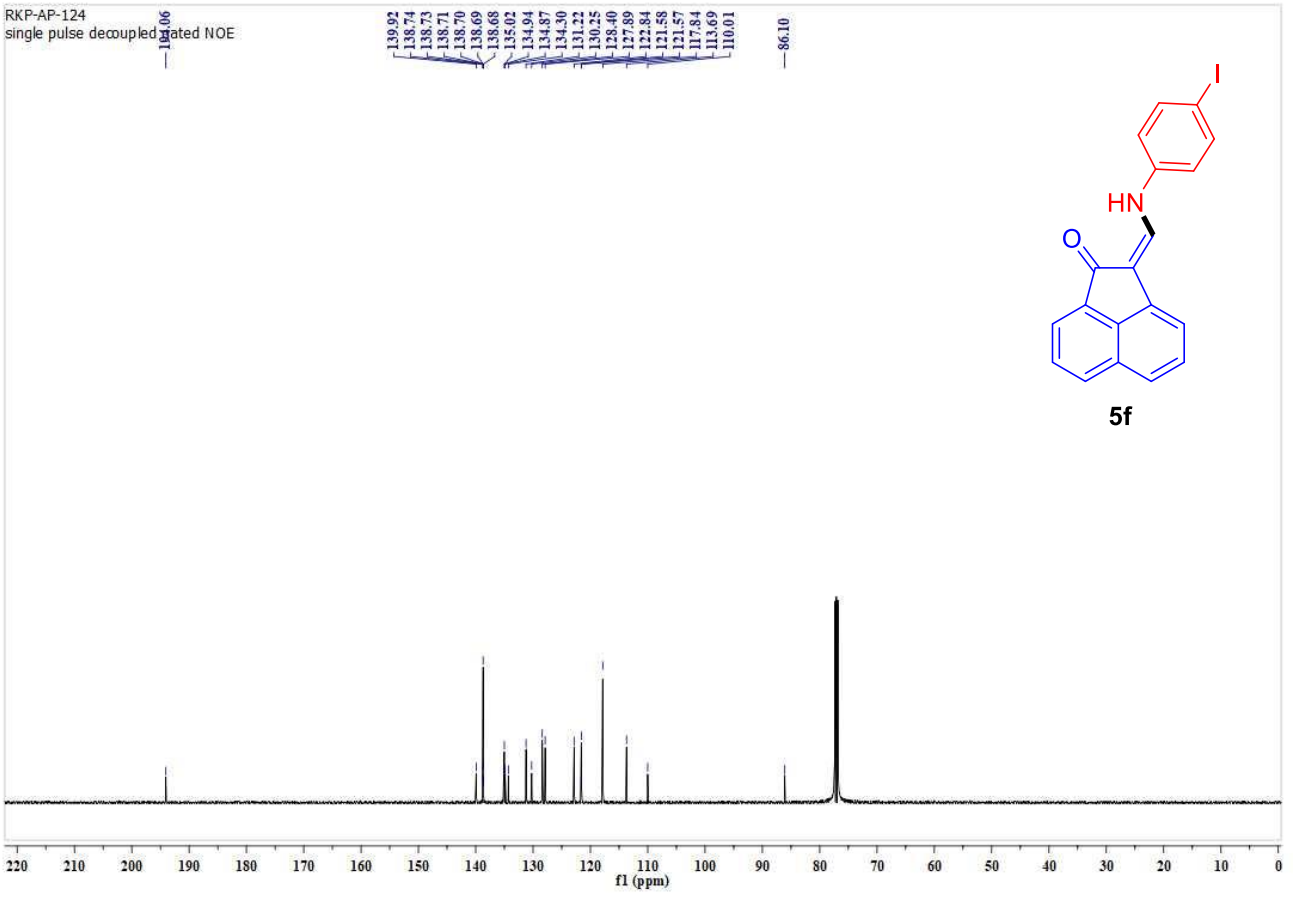

AP127
single pulse decoupled gated NOE
138.82
135.53
134.94
134.87
134.34
131.25
130.25
129.95
128.69
128.42
127.92
122.81
121.62
117.21
113.65
109.83
Cl
HN
O
5d
f1 (ppm)


RKP-AP-128
single_pulse
11.12
11.10
8.12
8.04
8.02
8.01
8.00
7.92
7.90
7.71
7.70
7.70
7.69
7.68
7.67
7.56
7.54
7.53
7.50
7.49
7.48
7.48
7.45
7.08
7.06
Br
HN
O
5e
0.59
0.72
1.39
1.85
1.40
3.76
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 0.0
f1 (ppm)

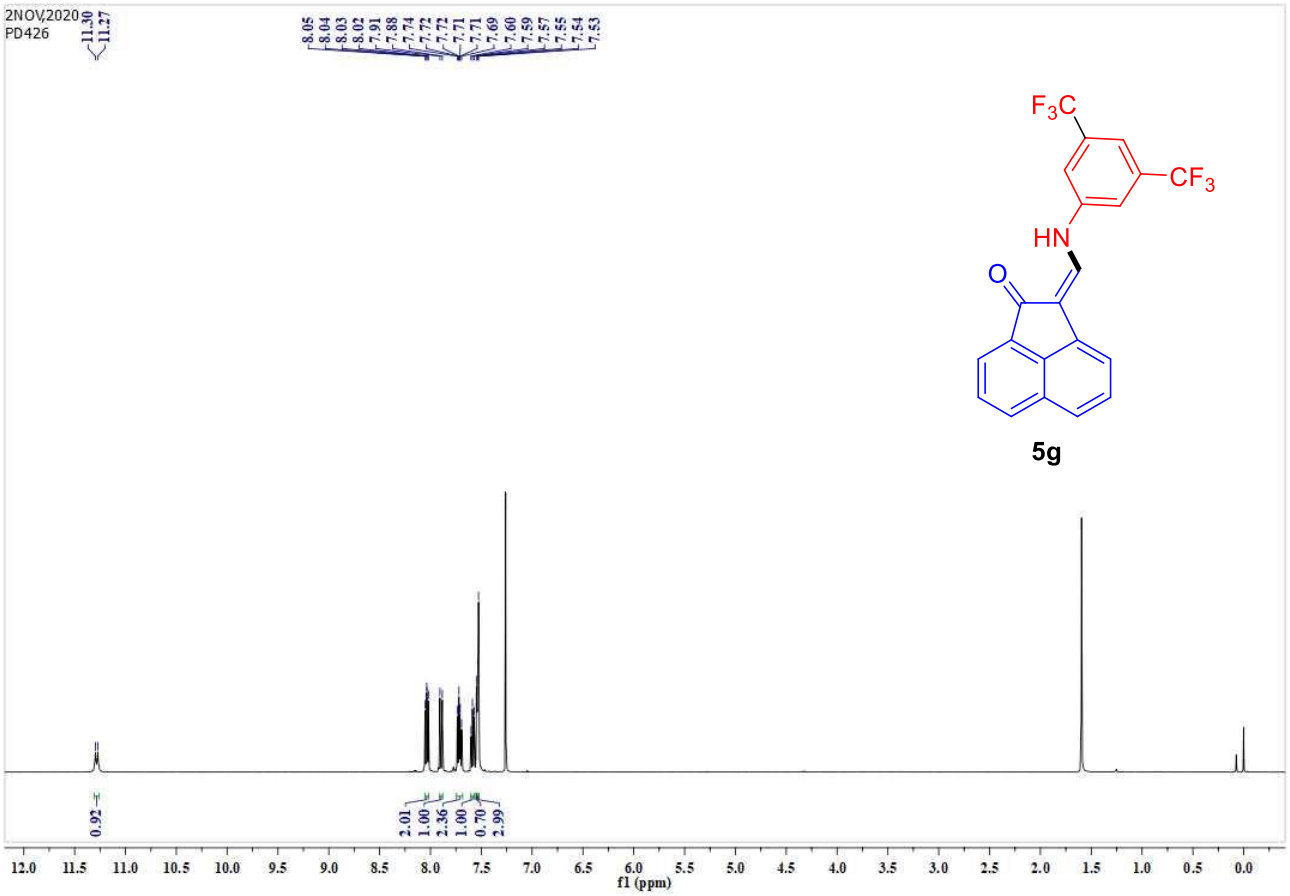

RKP-AP-128
single pulse decoupled gated NOE
194.06
139.31
135.30
134.92
134.91
134.32
132.88
132.85
132.43
131.23
130.26
130.15
129.09
128.41
128.40
128.38
127.90
127.86
123.05
122.83
121.60
117.54
116.07
113.66
113.65
109.94
Br
HN
O
5e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

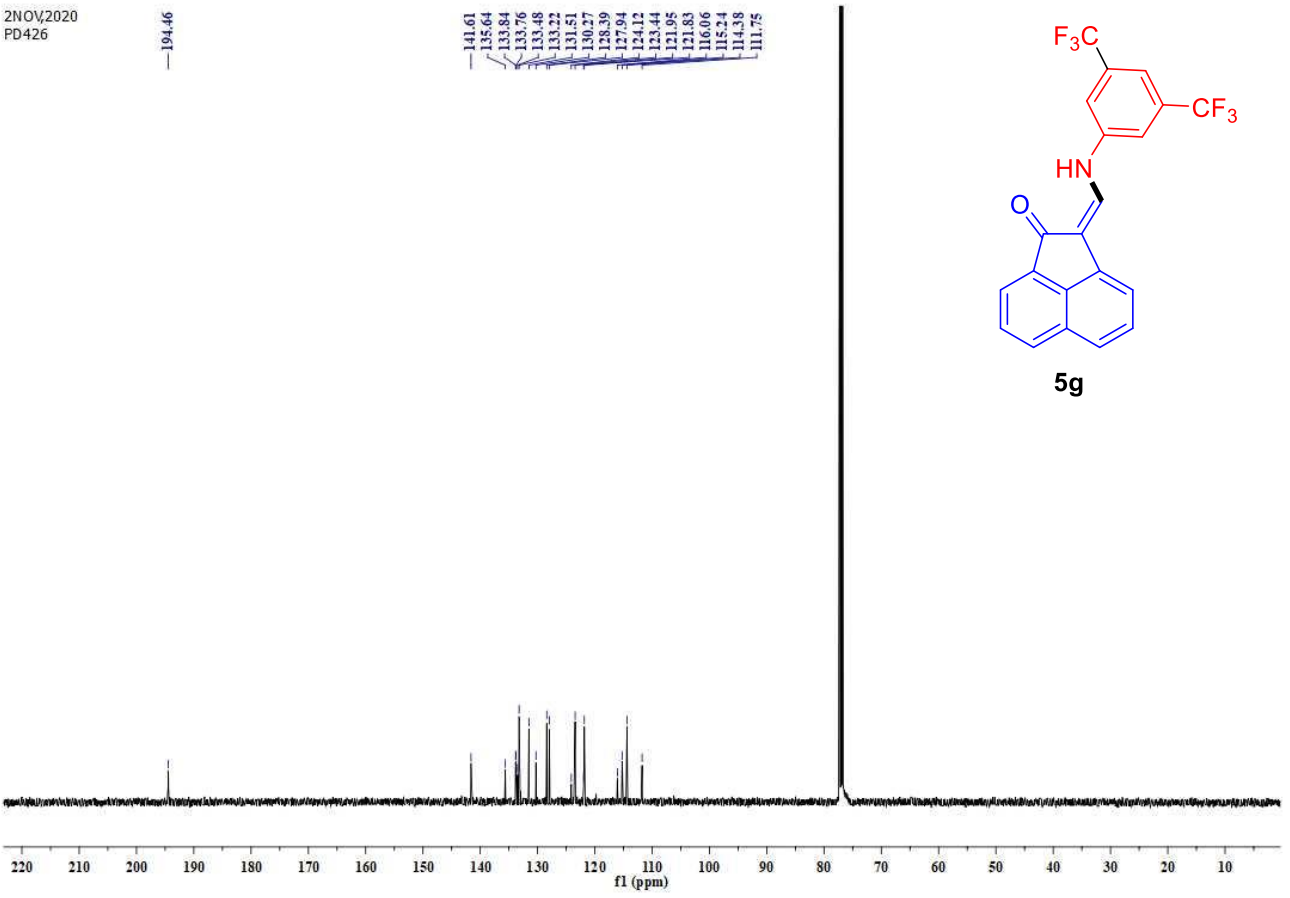

RKP-AP-124
single_pulse
11.07
11.05
8.01
8.00
7.99
7.98
7.88
7.85
7.69
7.68
7.68
7.67
7.66
7.65
7.64
7.64
7.63
7.62
7.54
7.53
7.51
7.42
7.40
6.92
6.92
6.90
I
HN
O
0.57
1.69
0.72
3.56
0.93
0.76
1.79
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

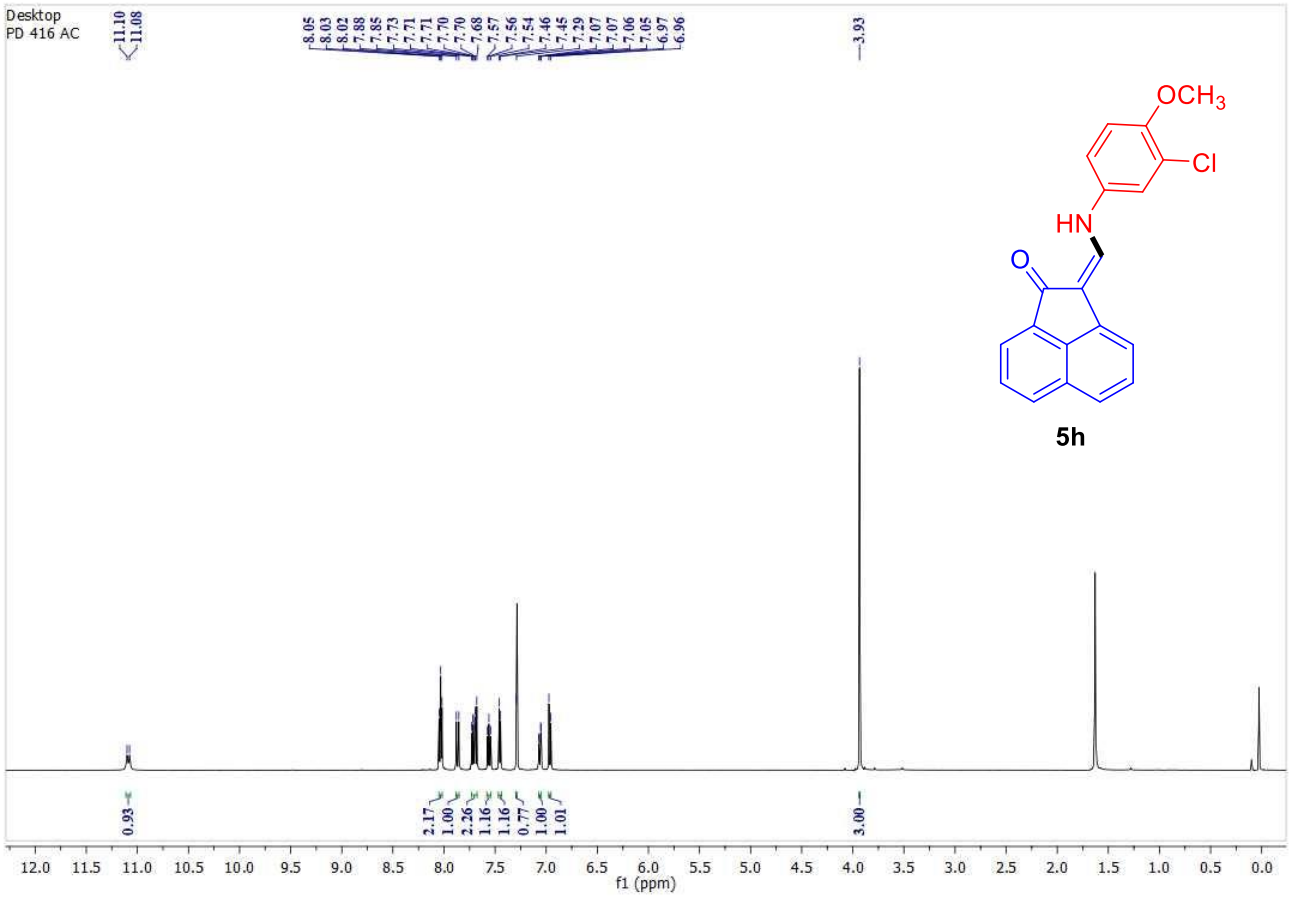
5f

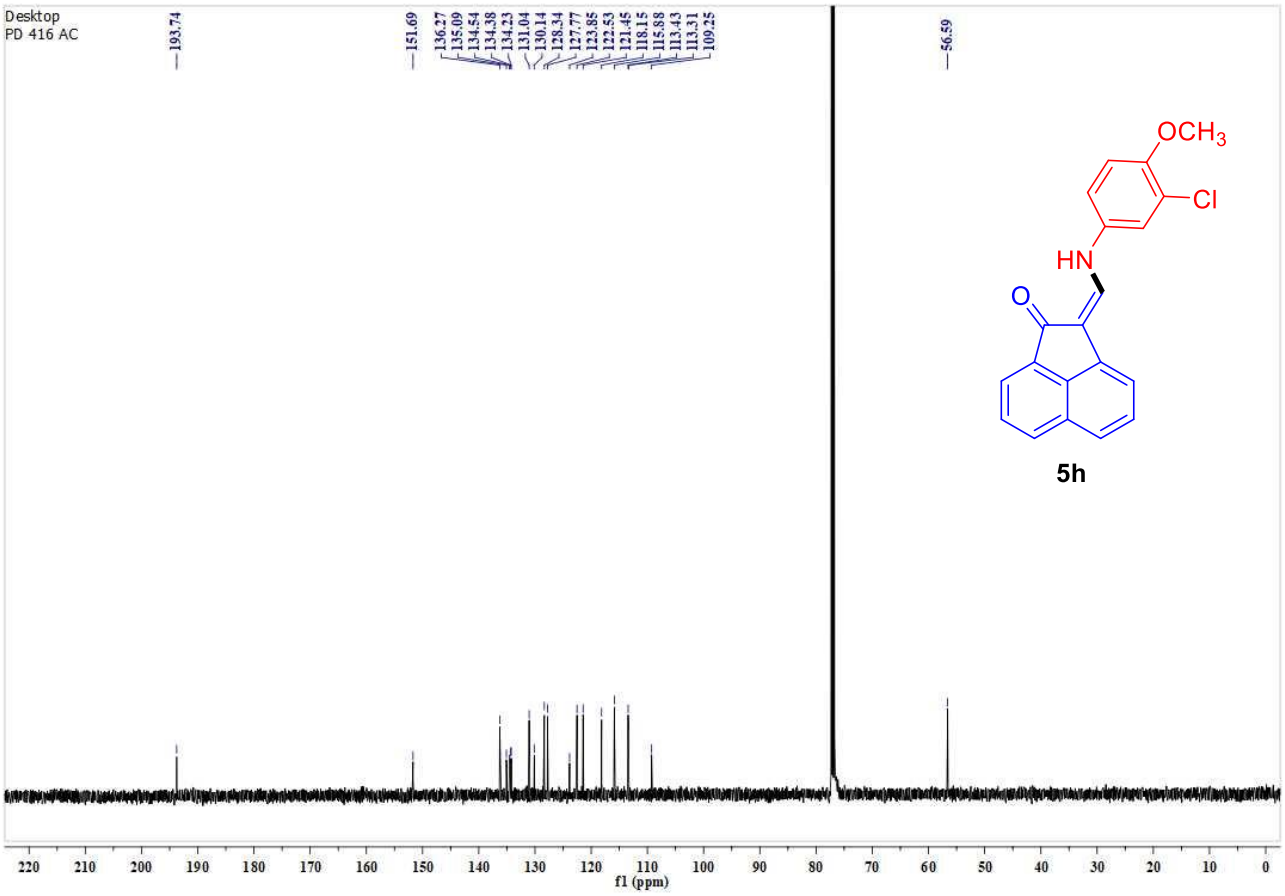

RKP-AP-124
single pulse decoupled gated NOE
194.06
139.92
138.74
138.73
138.71
138.70
138.69
138.68
135.02
134.94
134.87
134.30
131.22
130.25
128.40
127.89
122.84
121.58
121.57
117.84
113.69
110.01
86.10
I
HN
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

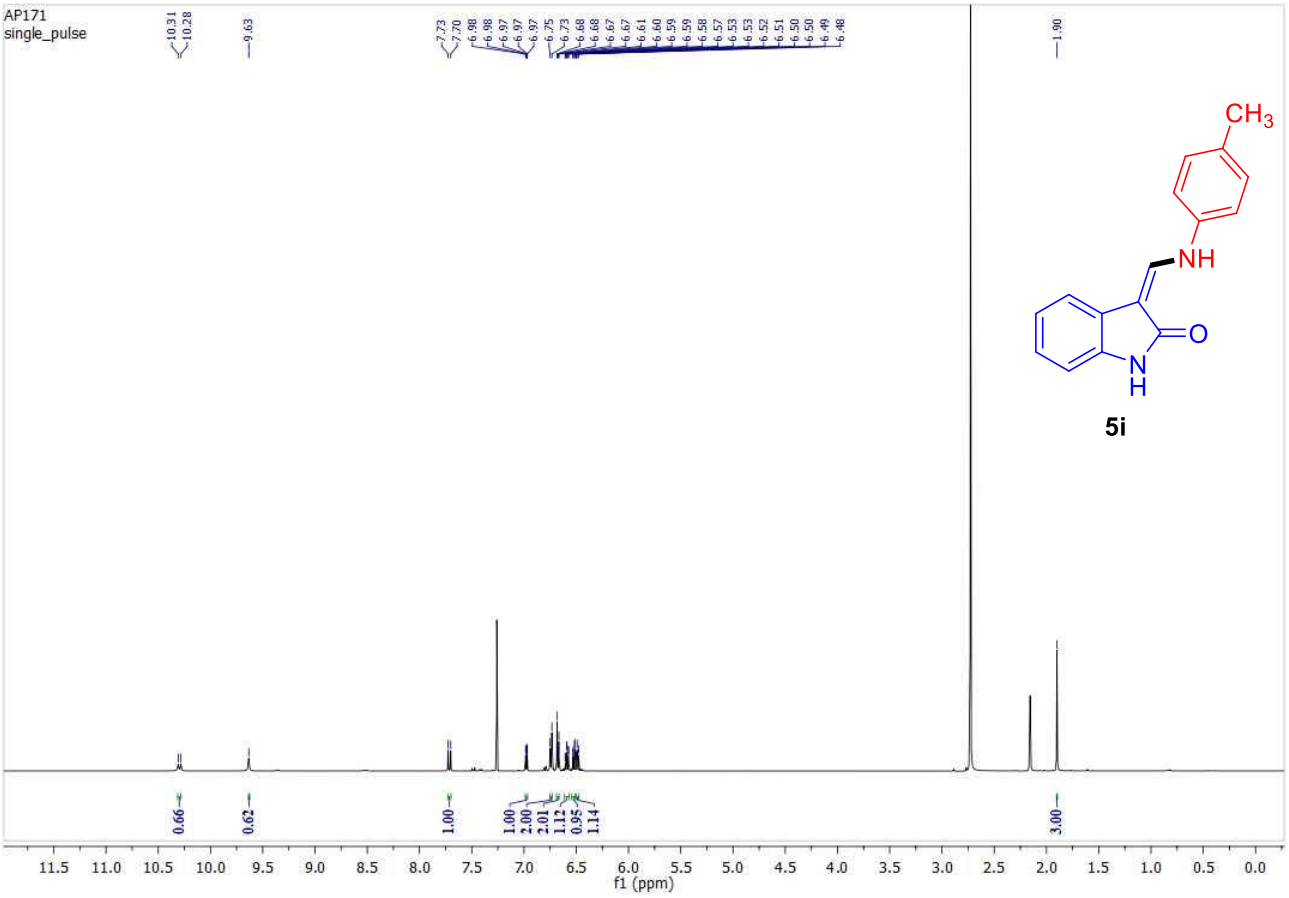
5f


2NOV,2020
PD426
11.30
11.27
8.05
8.04
8.03
8.02
7.91
7.88
7.74
7.72
7.72
7.71
7.71
7.69
7.60
7.59
7.57
7.55
7.54
7.53
F3C
CF3
HN
O
5g
0.92
2.01
1.00
2.36
1.00
0.70
2.99
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
f1 (ppm)

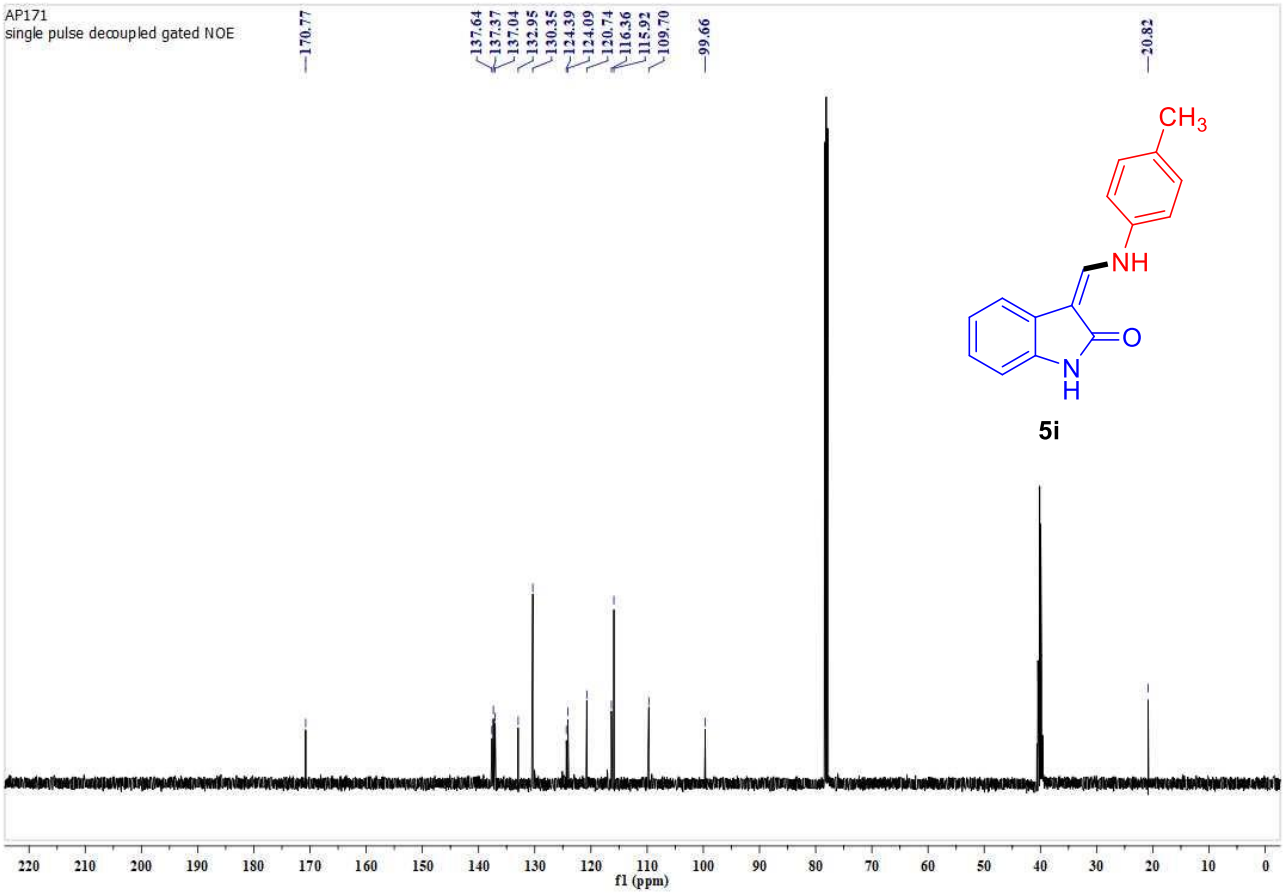

2NOV,2020
PD426
194.46
141.61
135.64
133.84
133.76
133.48
133.22
131.51
130.27
128.39
127.94
124.12
123.44
121.95
121.83
116.06
115.24
114.38
111.75
F3C
CF3
HN
O
5g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Desktop
PD 416 AC
11.10
11.08
8.05
8.03
8.02
7.88
7.85
7.73
7.71
7.71
7.70
7.70
7.68
7.57
7.56
7.54
7.46
7.45
7.29
7.07
7.07
7.06
7.05
6.97
6.96
3.93
0.93
2.17
1.00
2.26
1.16
1.16
0.77
1.00
1.01
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 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
OCH3
Cl
HN
O
5h

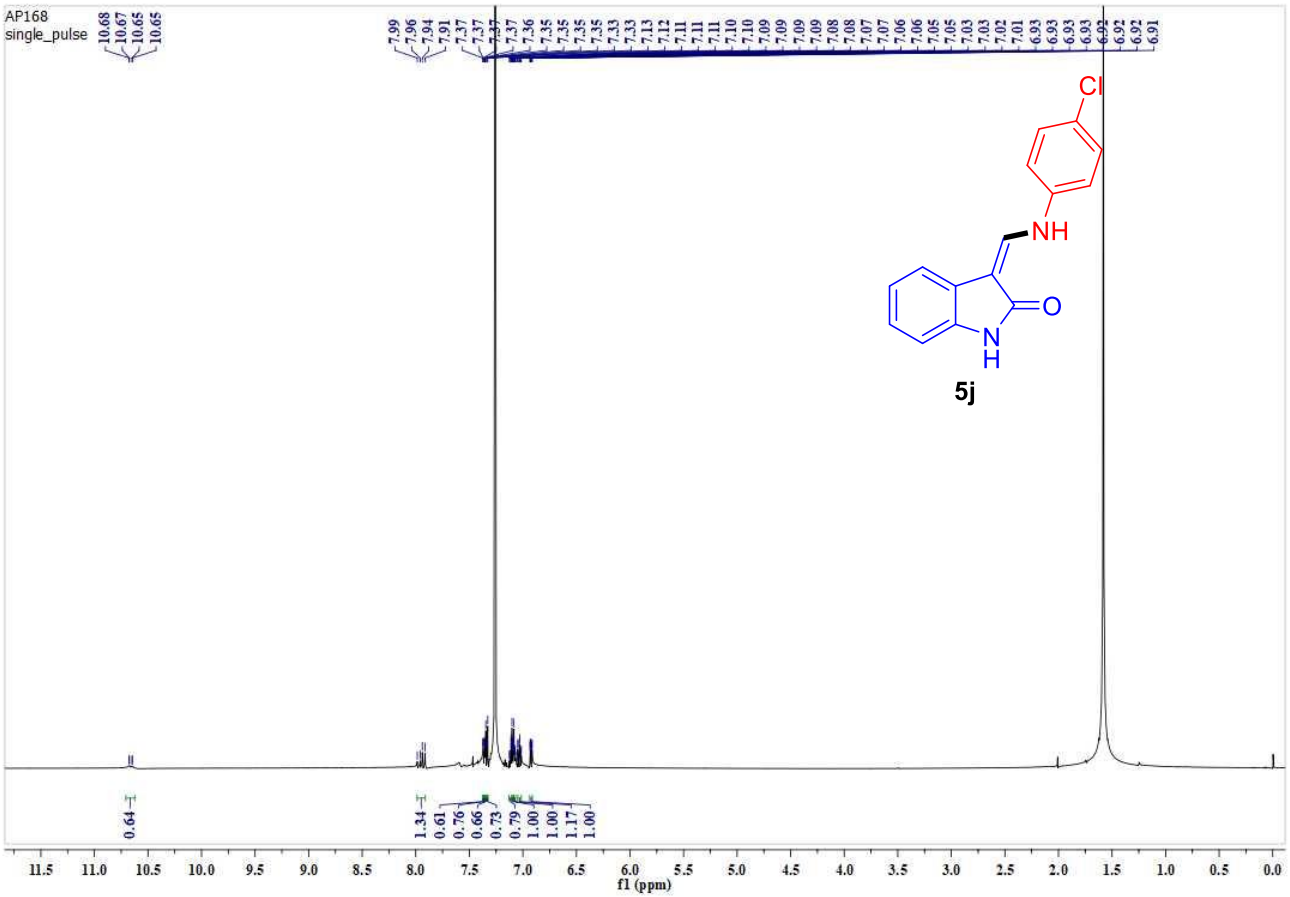

Desktop
PD 416 AC
193.74
151.69
136.27
135.09
134.54
134.38
134.23
131.04
130.14
128.34
127.77
123.85
122.53
121.45
118.15
115.88
113.43
113.31
109.25
56.59
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
OCH3
Cl
HN
O
5h

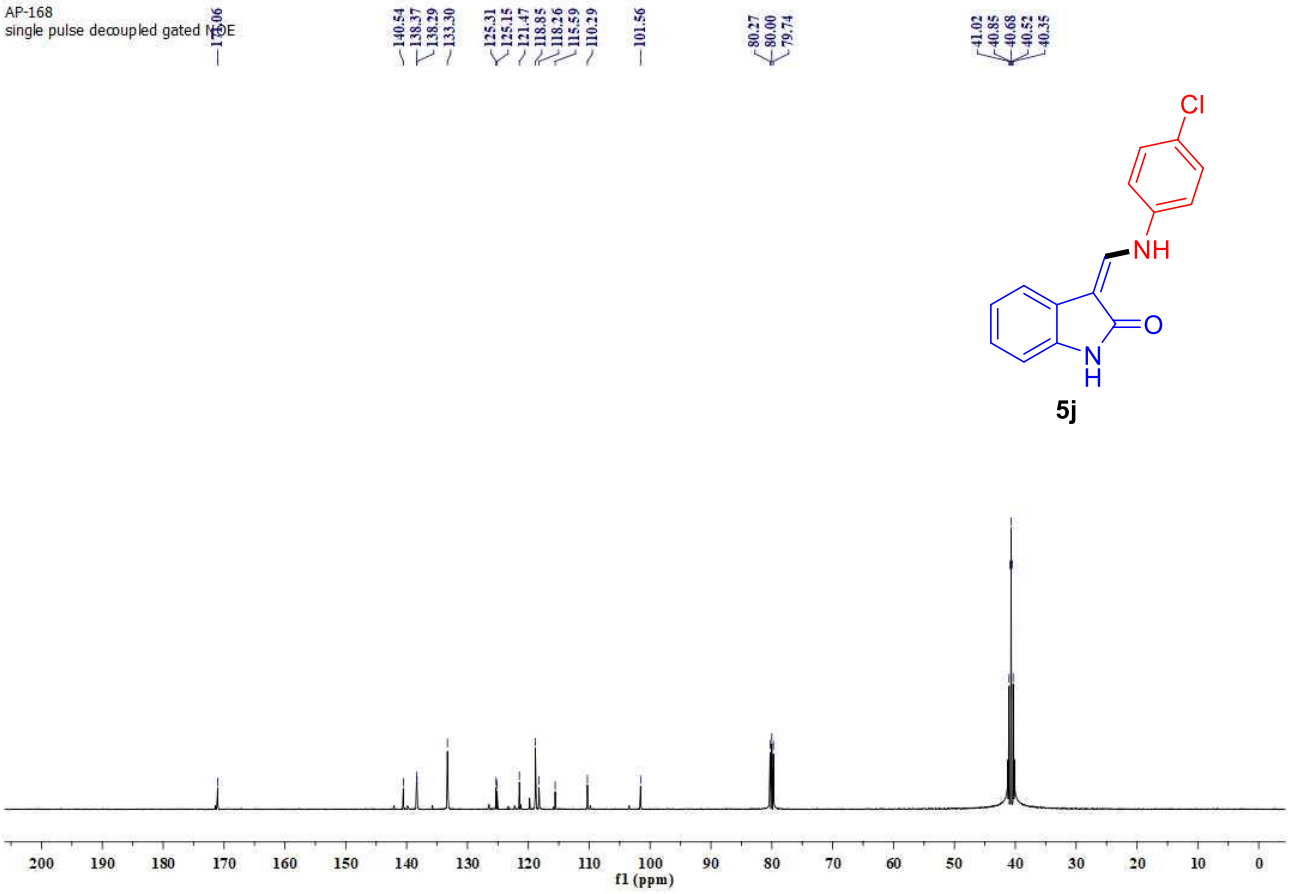

AP171
single_pulse
10.31
10.28
9.63
7.73
7.70
6.98
6.98
6.97
6.97
6.97
6.75
6.73
6.68
6.68
6.67
6.67
6.61
6.60
6.59
6.59
6.58
6.57
6.53
6.53
6.52
6.51
6.50
6.50
6.49
6.48
1.90
0.66
0.62
1.00
1.00
2.00
2.01
1.12
0.95
1.14
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
CH3
NH
O
N
H

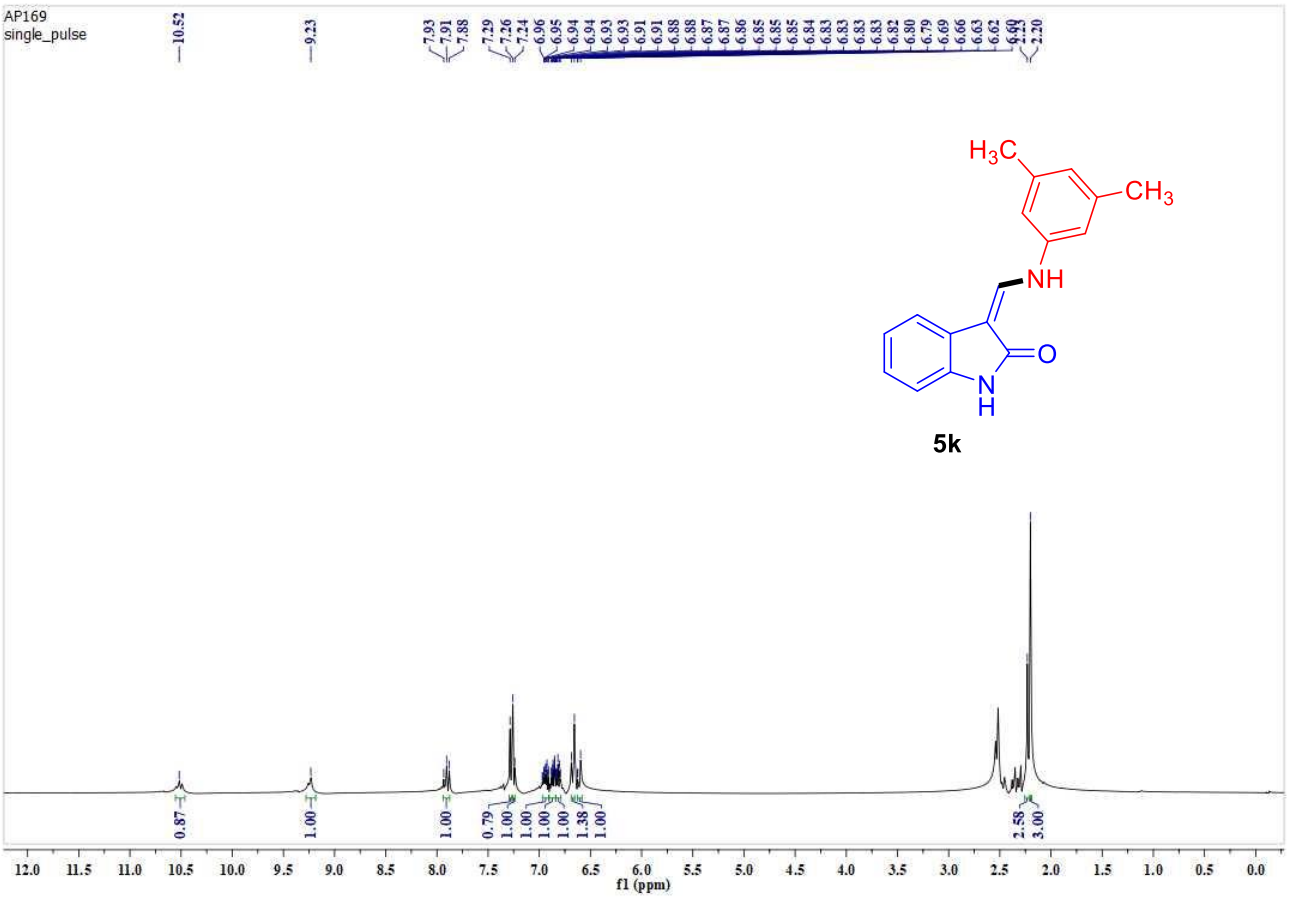
5i

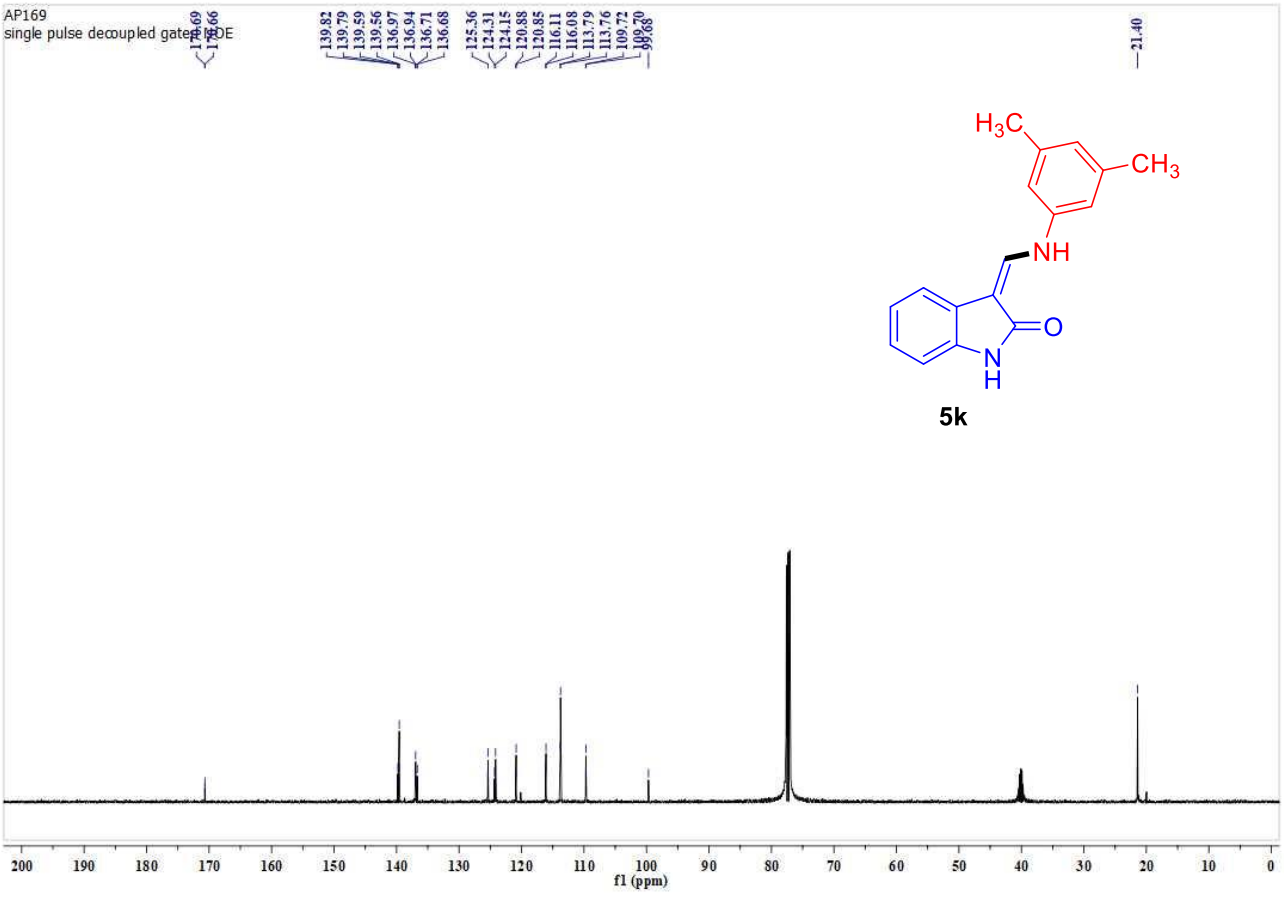

AP171
single pulse decoupled gated NOE
170.77
137.64
137.37
137.04
132.95
130.35
124.39
124.09
120.74
116.36
115.92
109.70
99.66
20.82
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
CH3
NH
O
N
H

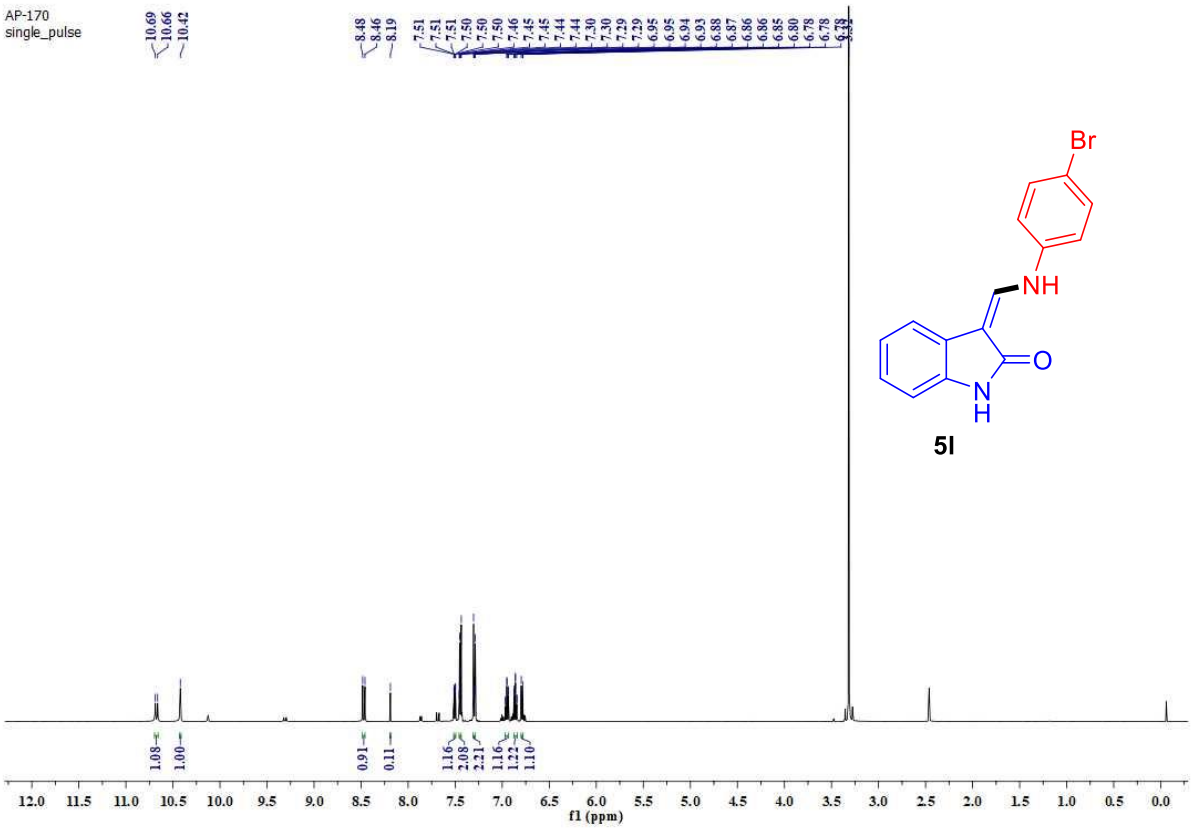
5i


AP168
single_pulse
Cl
NH
O
N
H
5j
f1 (ppm)

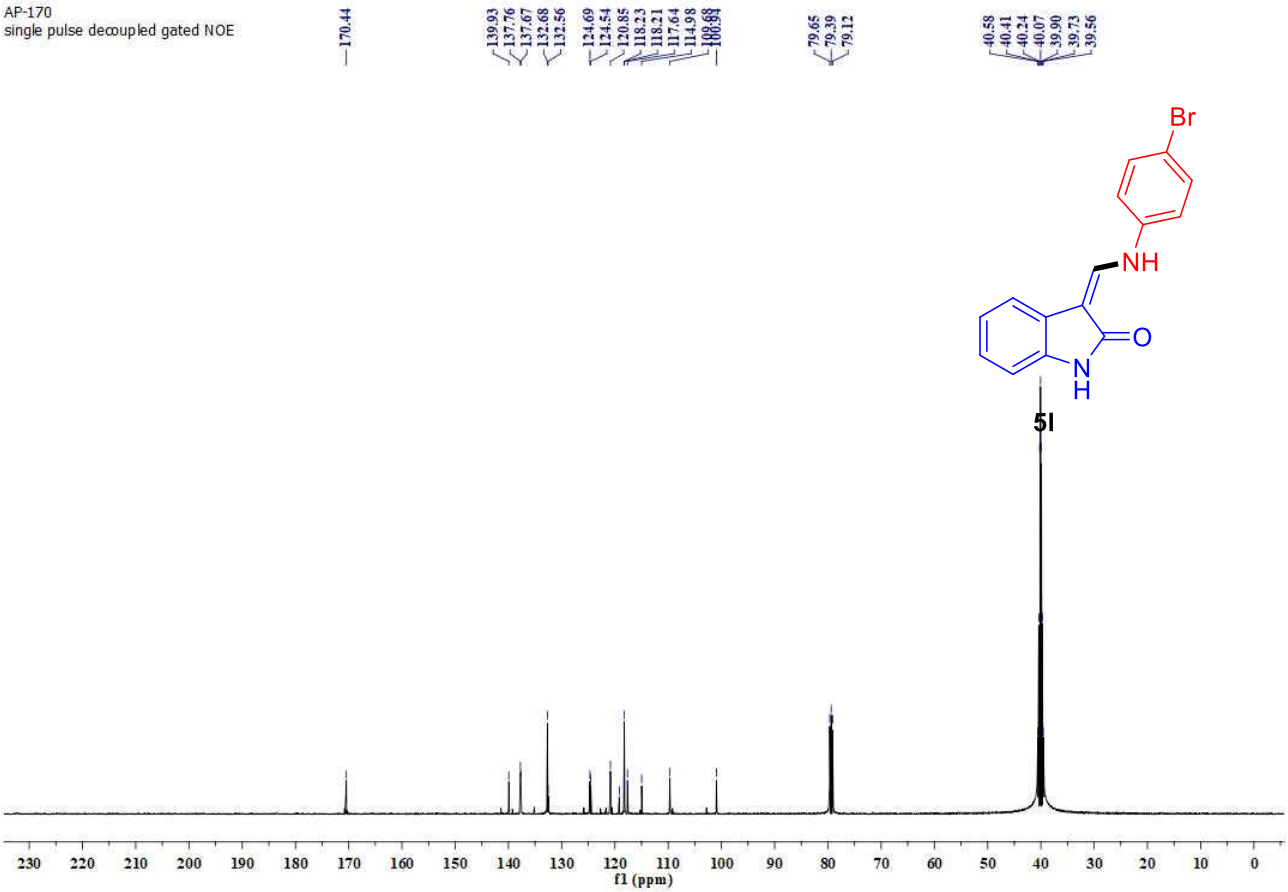

AP-168
single pulse decoupled gated NOE
Cl
NH
O
N
H
5j
f1 (ppm)


AP169
single_pulse
10.52
9.23
7.93
7.91
7.88
7.29
7.26
7.24
6.96
6.95
6.94
6.94
6.93
6.93
6.91
6.91
6.88
6.88
6.87
6.87
6.86
6.85
6.85
6.85
6.84
6.83
6.83
6.83
6.82
6.80
6.79
6.69
6.66
6.63
6.62
2.20
H3C
CH3
NH
O
N
H
5k
0.87
1.00
1.00
0.79
1.00
1.00
1.00
1.00
1.38
1.00
2.58
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
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

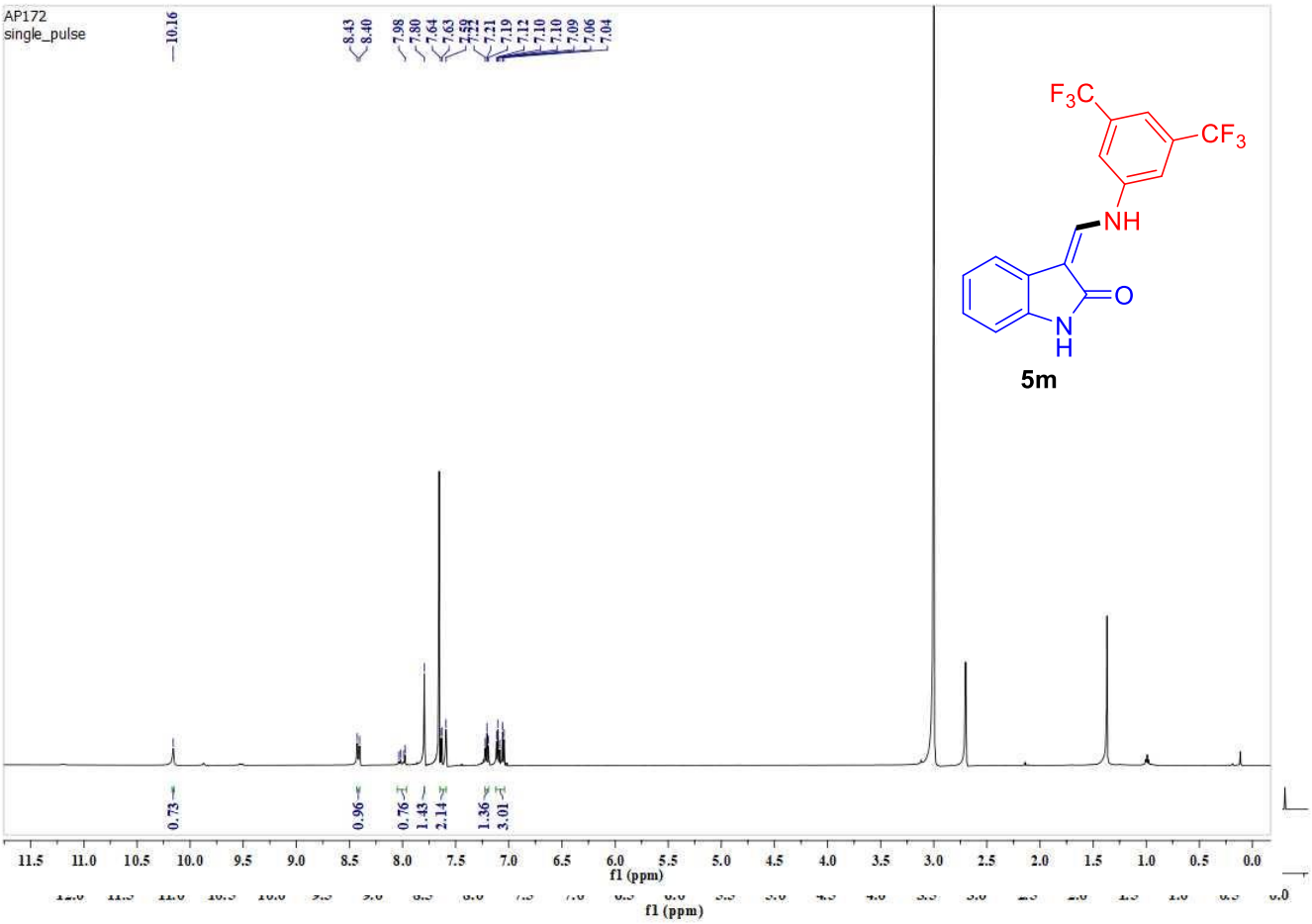

AP169
single pulse decoupled gated NOE
139.82
139.79
139.59
139.56
136.97
136.94
136.71
136.68
125.36
124.31
124.15
120.88
120.85
116.11
116.08
113.79
113.76
109.72
109.70
99.68
21.40
H3C
CH3
NH
O
N
H
5k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

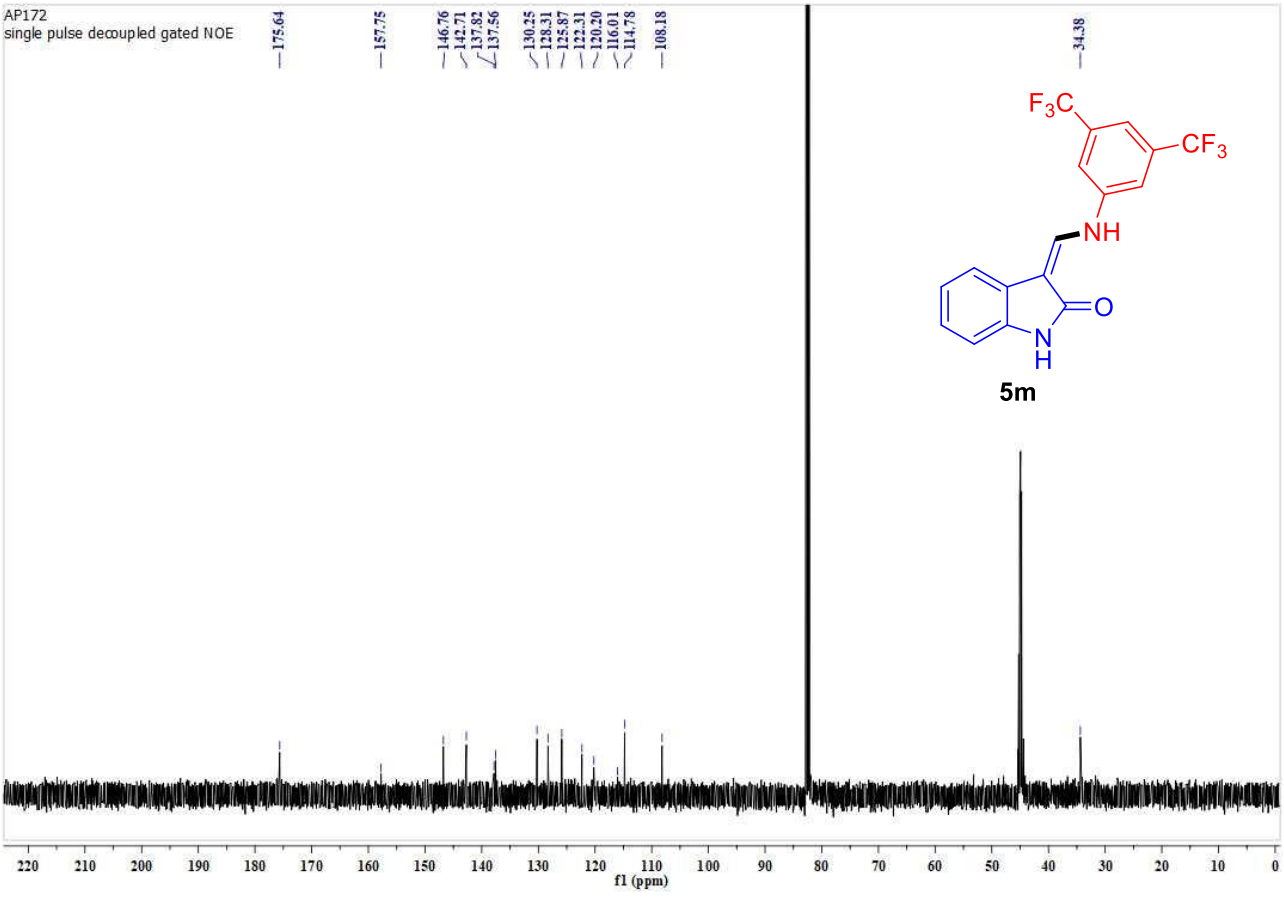

AP-170
single_pulse
10.69
10.66
10.42
8.48
8.46
8.19
7.51
7.51
7.51
7.50
7.50
7.50
7.46
7.45
7.45
7.44
7.44
7.30
7.30
7.29
7.29
6.95
6.95
6.94
6.93
6.88
6.87
6.86
6.86
6.85
6.80
6.78
6.78
6.33
1.08
1.00
0.91
0.11
1.16
2.08
2.21
1.16
1.22
1.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Br
NH
O
N
H

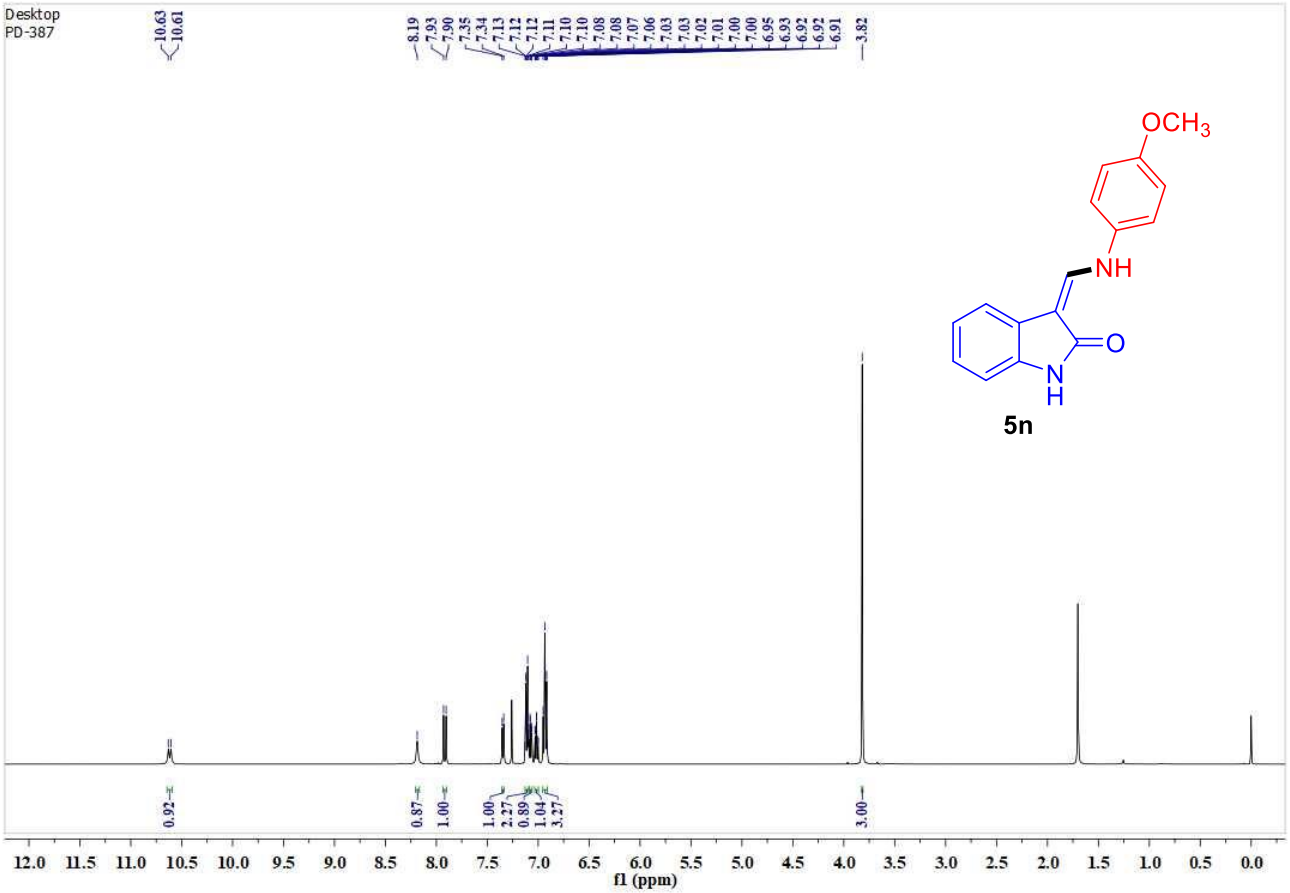
5l

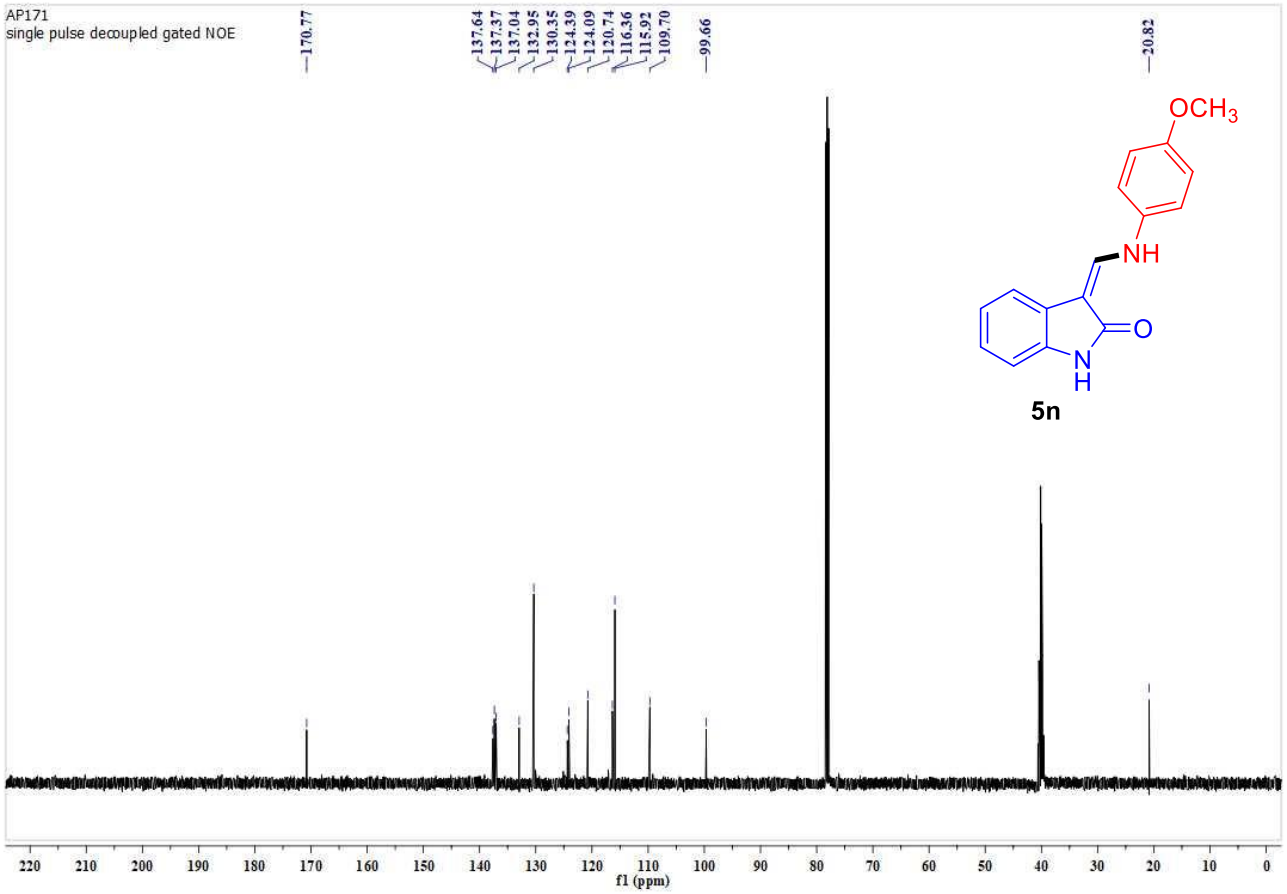

AP-170
single pulse decoupled gated NOE
170.44
139.93
137.76
137.67
132.68
132.56
124.69
124.54
120.85
118.23
118.21
117.64
114.98
79.65
79.39
79.12
40.58
40.41
40.24
40.07
39.90
39.73
39.56
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Br
NH
O
N
H

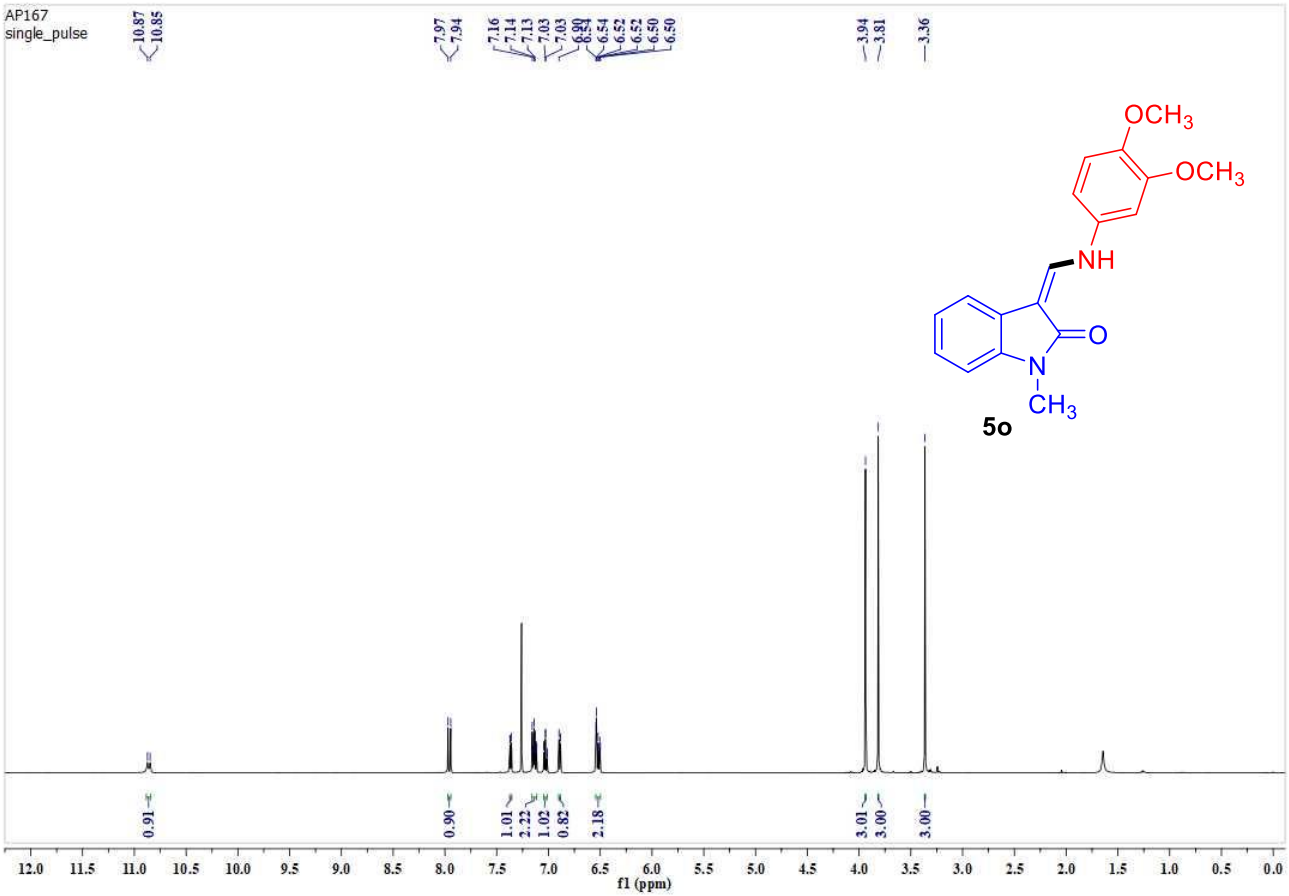
5l

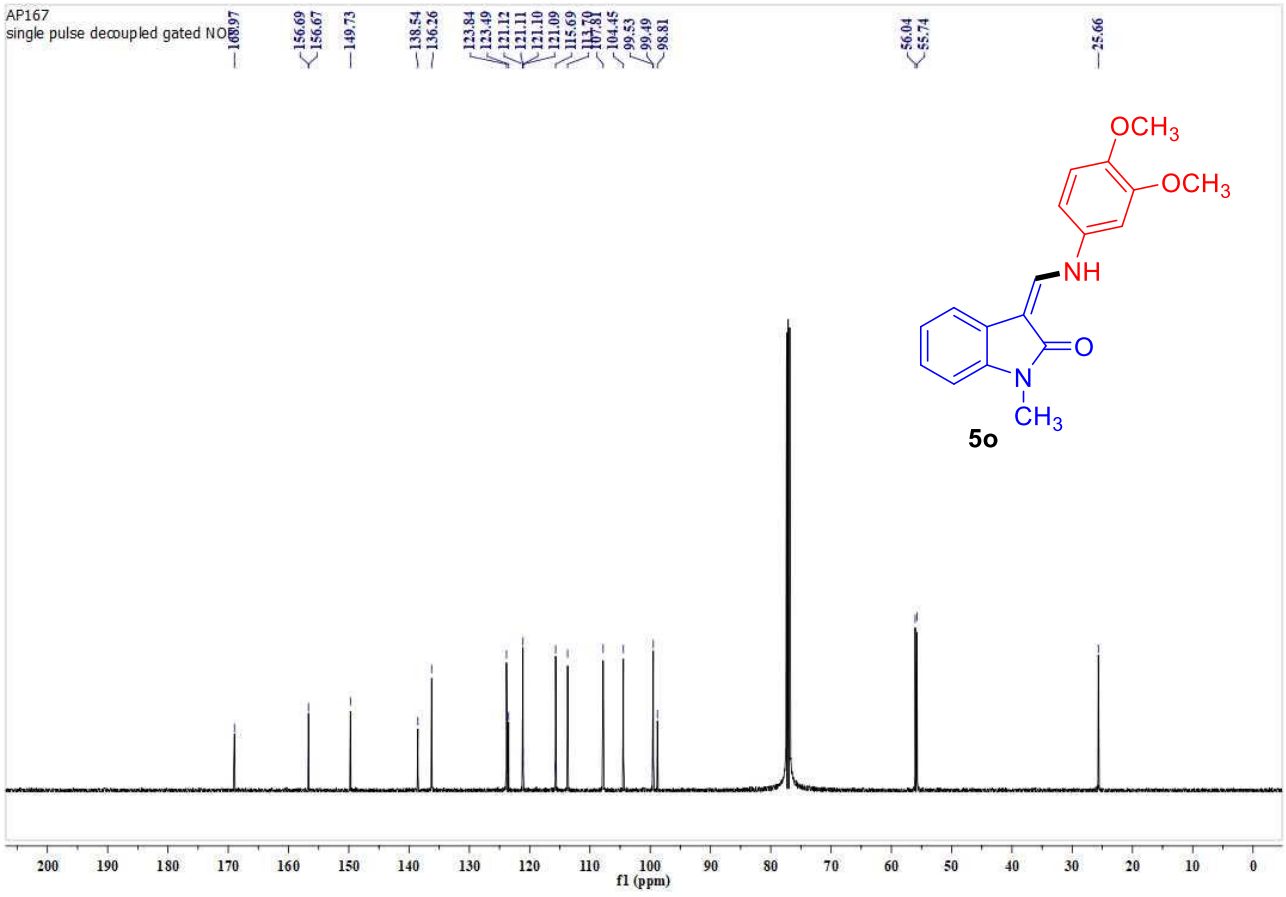

AP172
single_pulse
10.16
8.43
8.40
7.98
7.80
7.64
7.63
7.21
7.19
7.12
7.10
7.10
7.09
7.06
7.04
0.73
0.96
0.76
1.43
2.14
1.36
3.01
f1 (ppm)
F3C
CF3
NH
O
N
H
5m

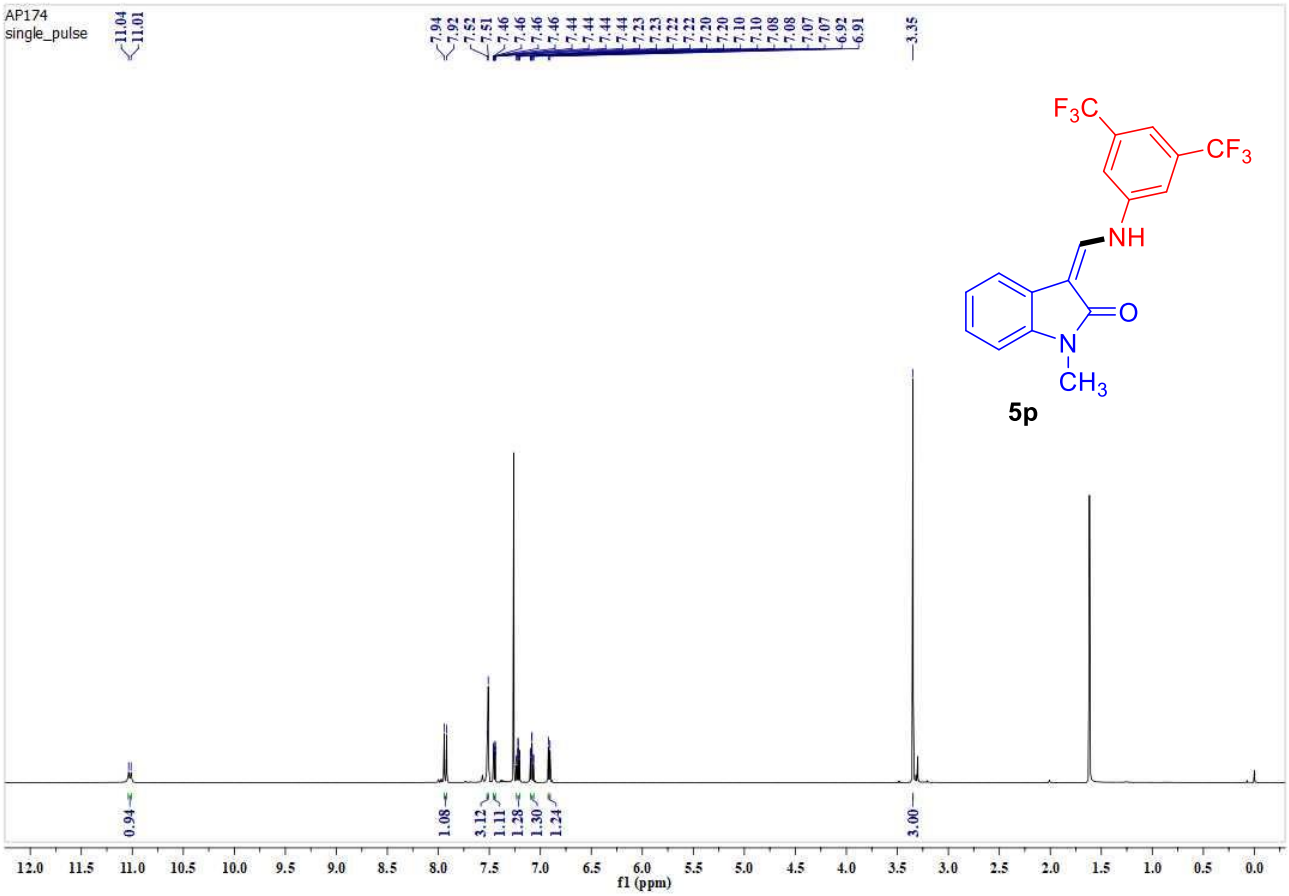

AP172
single pulse decoupled gated NOE
175.64
157.75
146.76
142.71
137.82
137.56
130.25
128.31
125.87
122.31
120.20
116.01
114.78
108.18
34.38
f1 (ppm)
F3C
CF3
NH
O
N
H
5m

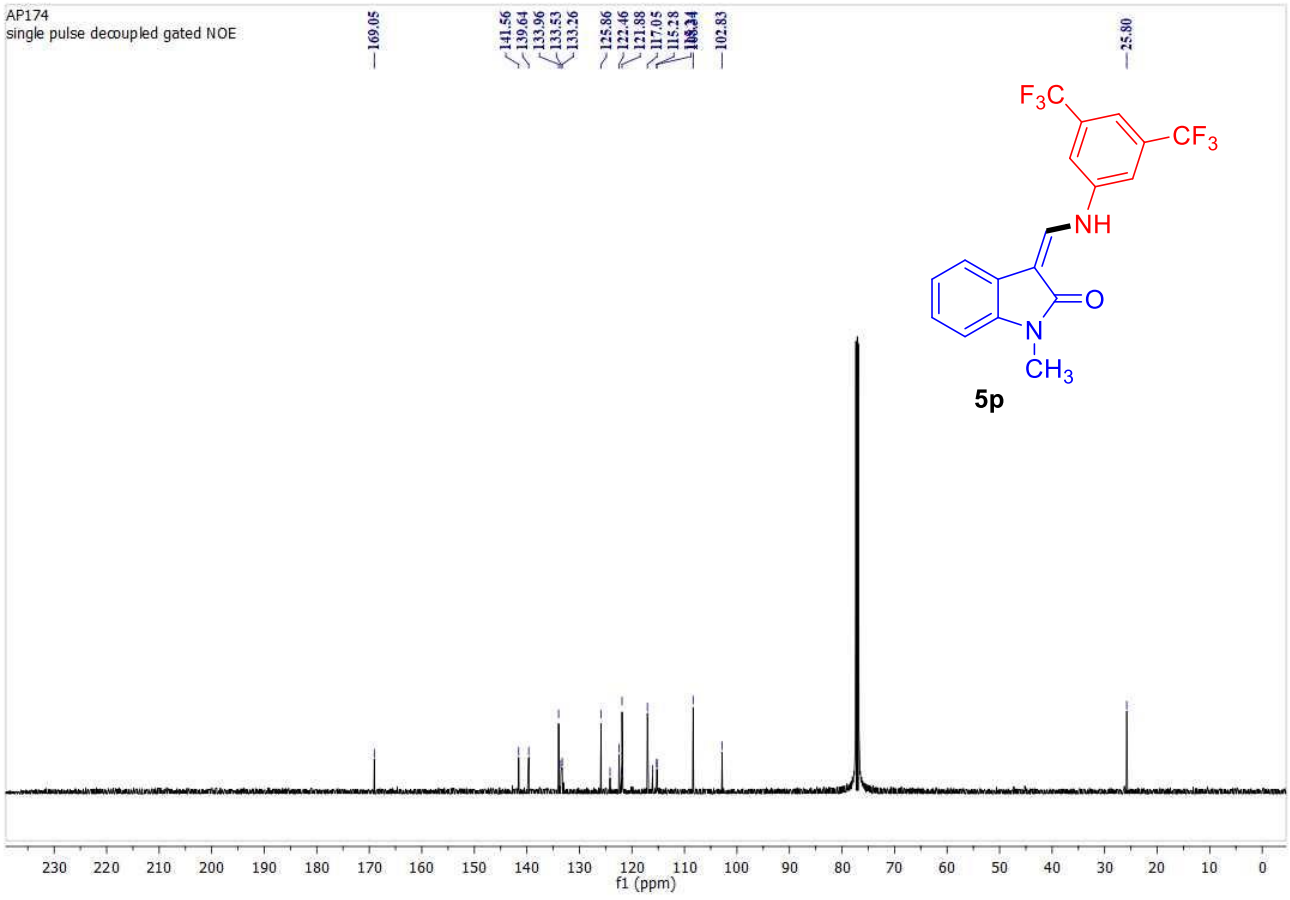

Desktop
PD-387
10.63
10.61
8.19
7.93
7.90
7.35
7.34
7.13
7.12
7.12
7.11
7.10
7.10
7.08
7.08
7.07
7.06
7.03
7.03
7.02
7.01
7.00
7.00
6.95
6.93
6.92
6.92
6.91
3.82
0.92
0.87
1.00
1.00
2.27
0.89
1.04
3.27
3.00
OCH3
NH
O
N
H
5n
f1 (ppm)

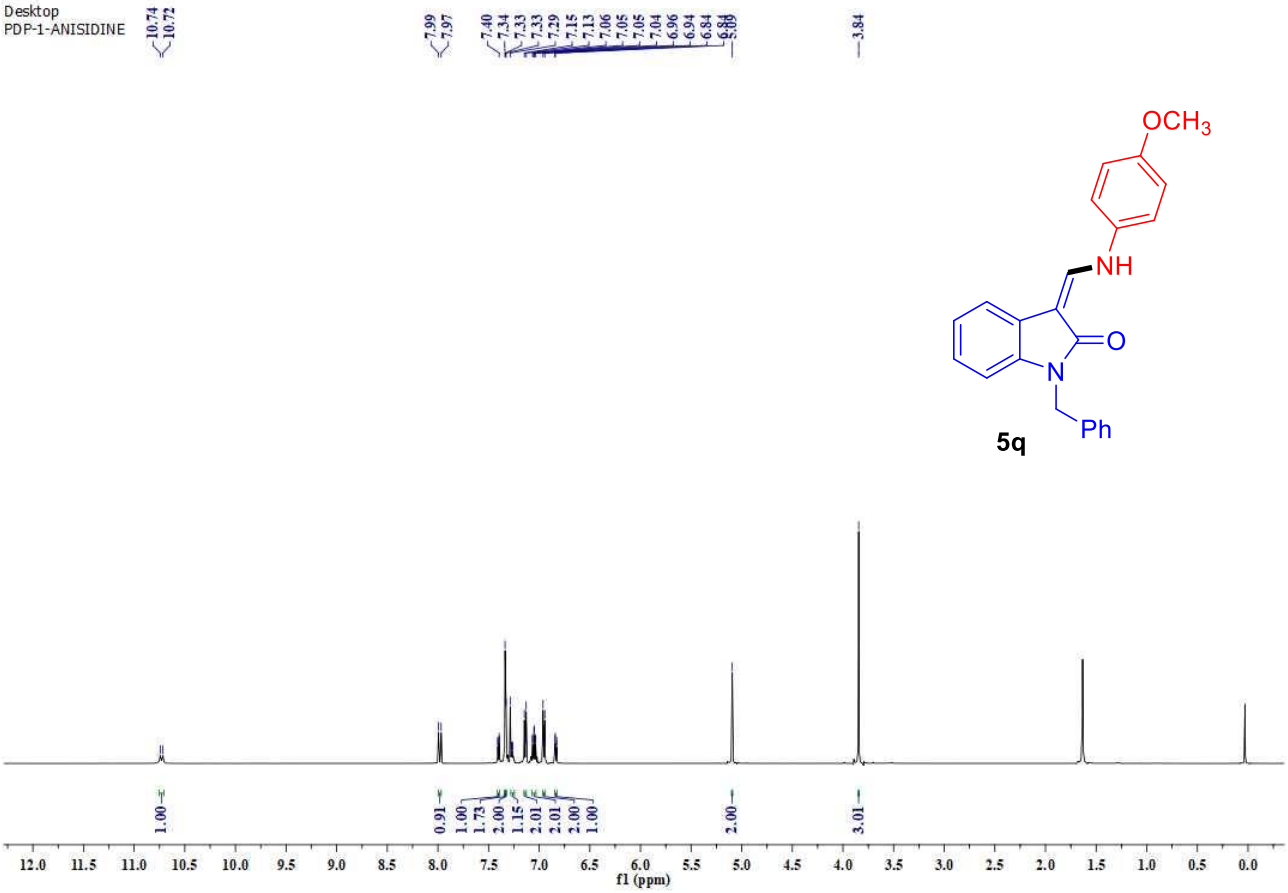

AP171
single pulse decoupled gated NOE
170.77
137.64
137.37
137.04
132.95
130.35
124.39
124.09
120.74
116.36
115.92
109.70
99.66
20.82
OCH3
NH
O
N
H
5n
f1 (ppm)

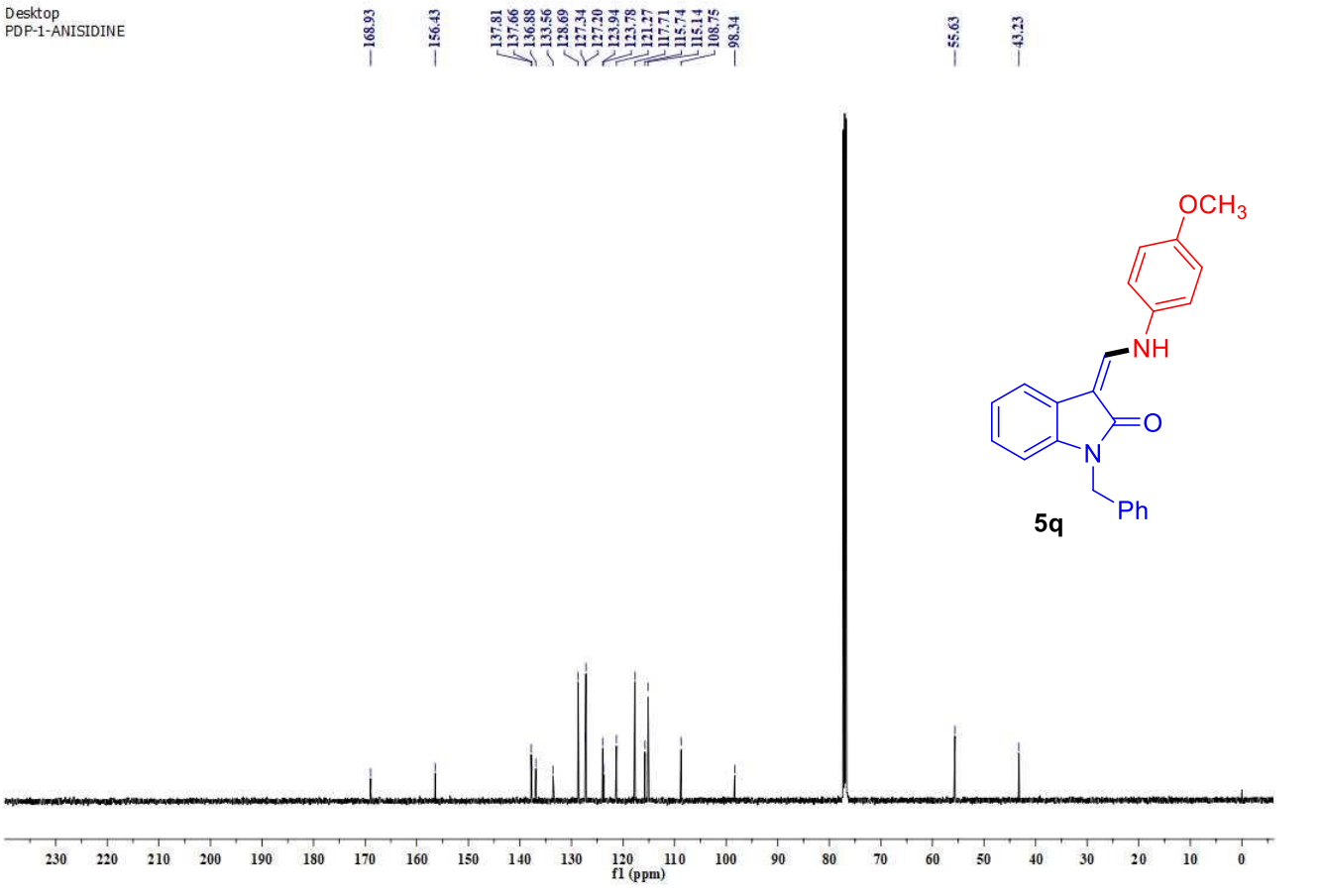

AP167
single_pulse
10.87
10.85
7.97
7.94
7.16
7.14
7.13
7.03
7.03
6.54
6.52
6.52
6.50
6.50
3.94
3.81
3.36
OCH3
OCH3
NH
O
N
CH3
5o
0.91
0.90
1.01
2.22
1.02
0.82
2.18
3.01
3.00
3.00
f1 (ppm)

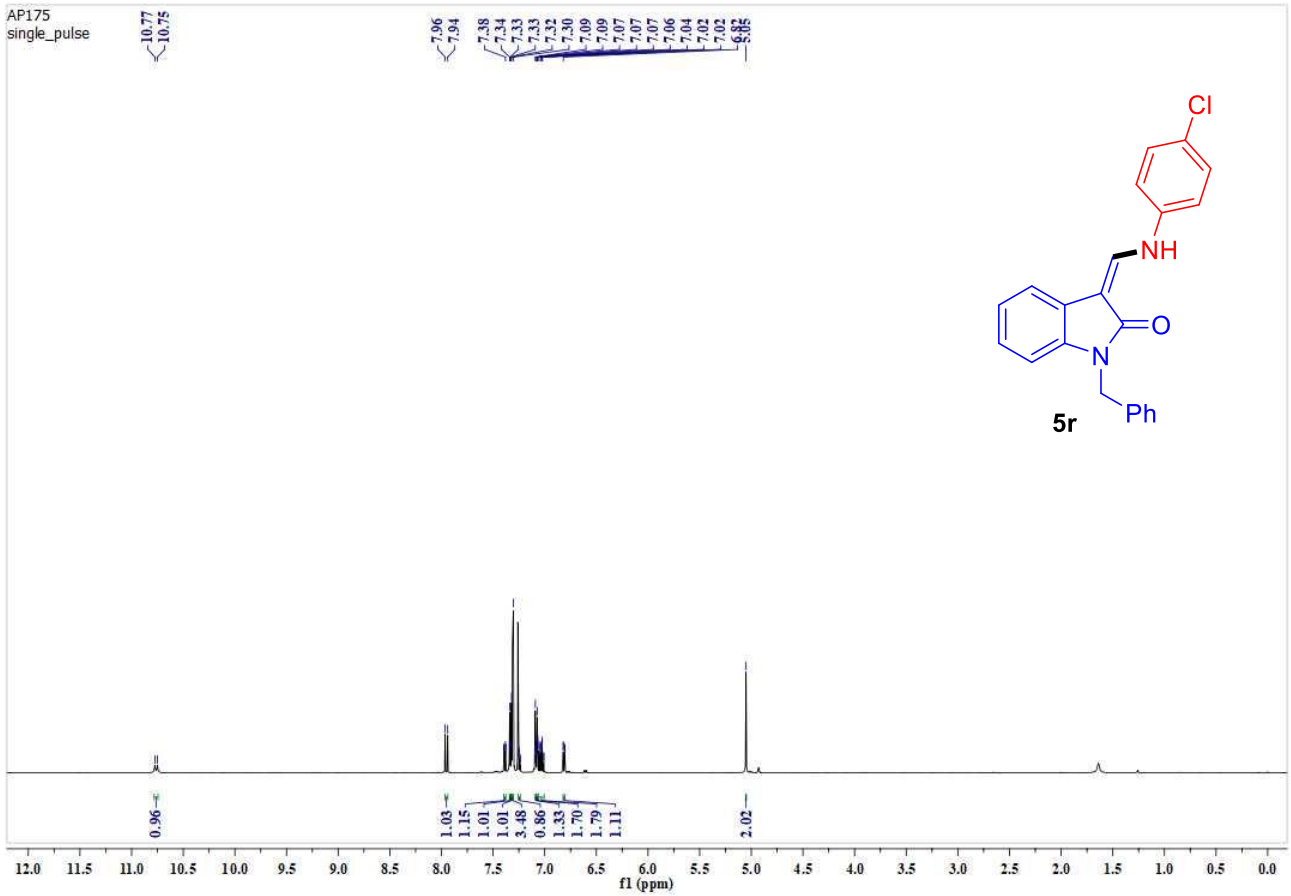

AP167
single pulse decoupled gated NOE
168.97
156.69
156.67
149.73
138.54
136.26
123.84
123.49
121.12
121.11
121.10
121.09
115.69
107.81
104.45
99.53
99.49
98.81
56.04
55.74
25.66
OCH3
OCH3
NH
O
N
CH3
5o
f1 (ppm)

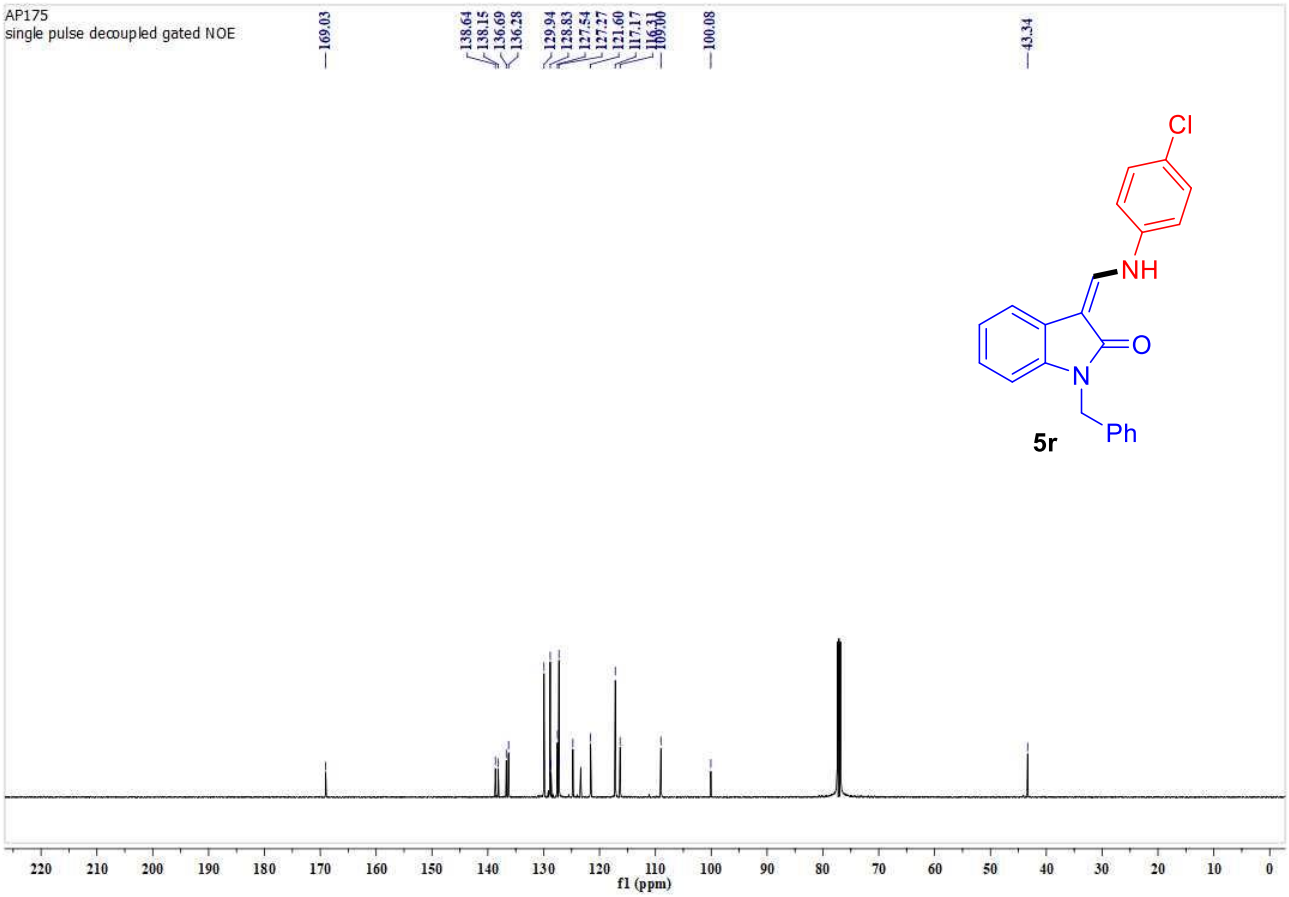

AP174
single_pulse
11.04
11.01
7.94
7.92
7.52
7.51
7.46
7.46
7.46
7.46
7.44
7.44
7.44
7.44
7.23
7.23
7.22
7.22
7.20
7.20
7.10
7.10
7.08
7.08
7.07
7.07
6.92
6.91
3.35
F3C
CF3
NH
O
N
CH3
5p
0.94
1.08
3.12
1.11
1.28
1.30
1.24
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

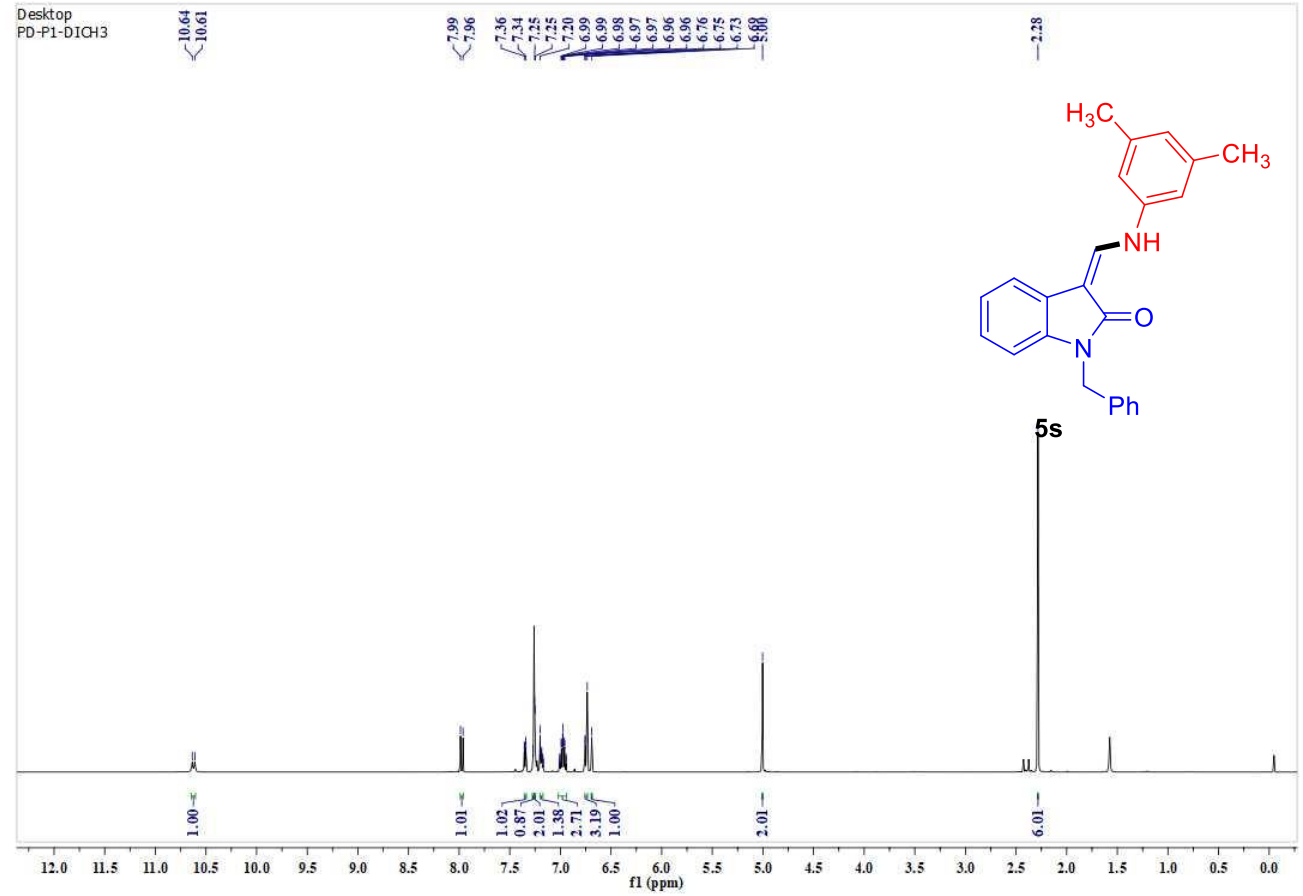

AP174
single pulse decoupled gated NOE
169.05
141.56
139.64
133.96
133.53
133.26
125.86
122.46
121.88
117.05
115.28
102.83
25.80
F3C
CF3
NH
O
N
CH3
5p
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

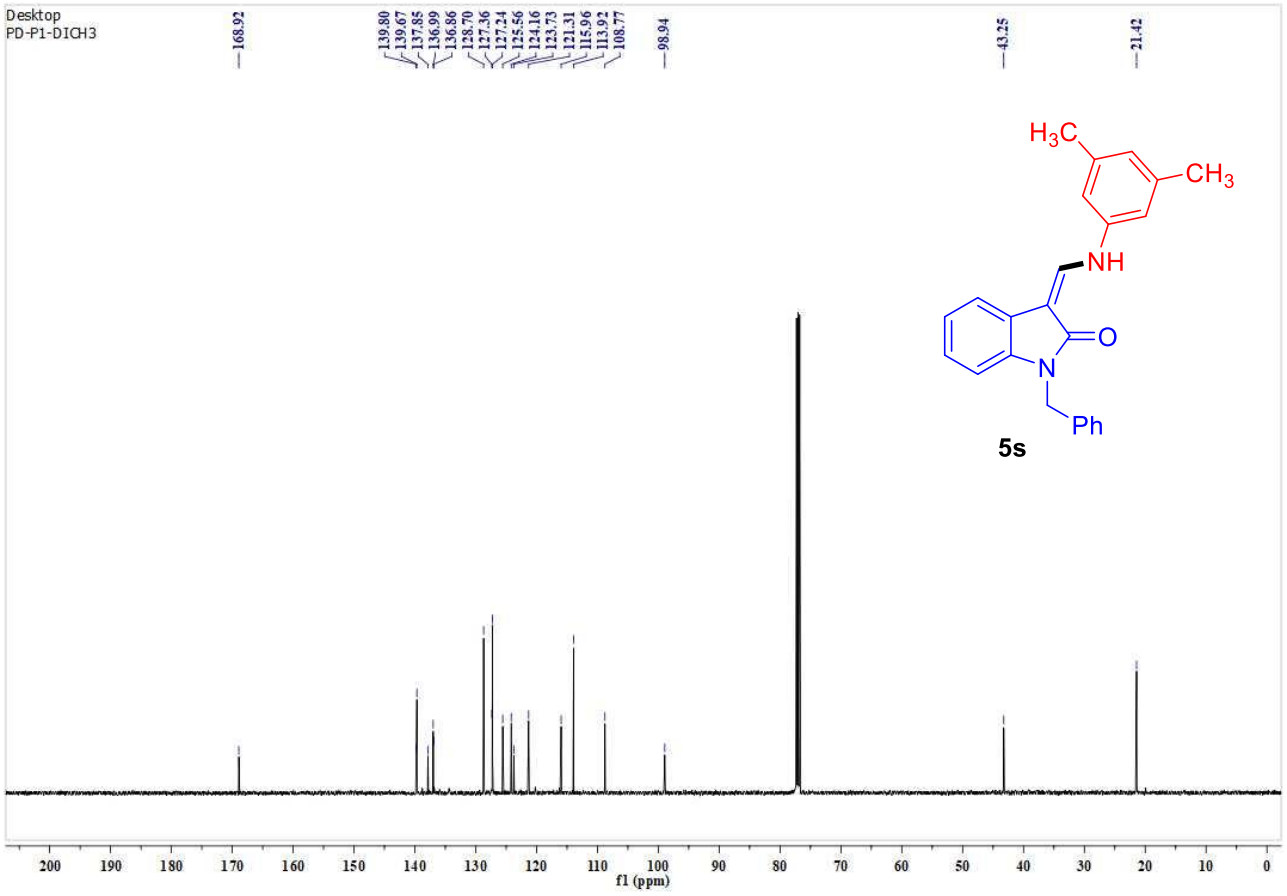

Desktop
PDP-1-ANISIDINE
10.74
10.72
7.99
7.97
7.40
7.34
7.33
7.33
7.29
7.15
7.13
7.06
7.05
7.05
7.04
6.96
6.94
6.84
3.84
OCH3
NH
O
N
Ph
5q
1.00
0.91
1.00
1.73
2.00
1.15
2.01
2.01
2.00
1.00
2.00
3.01
f1 (ppm)

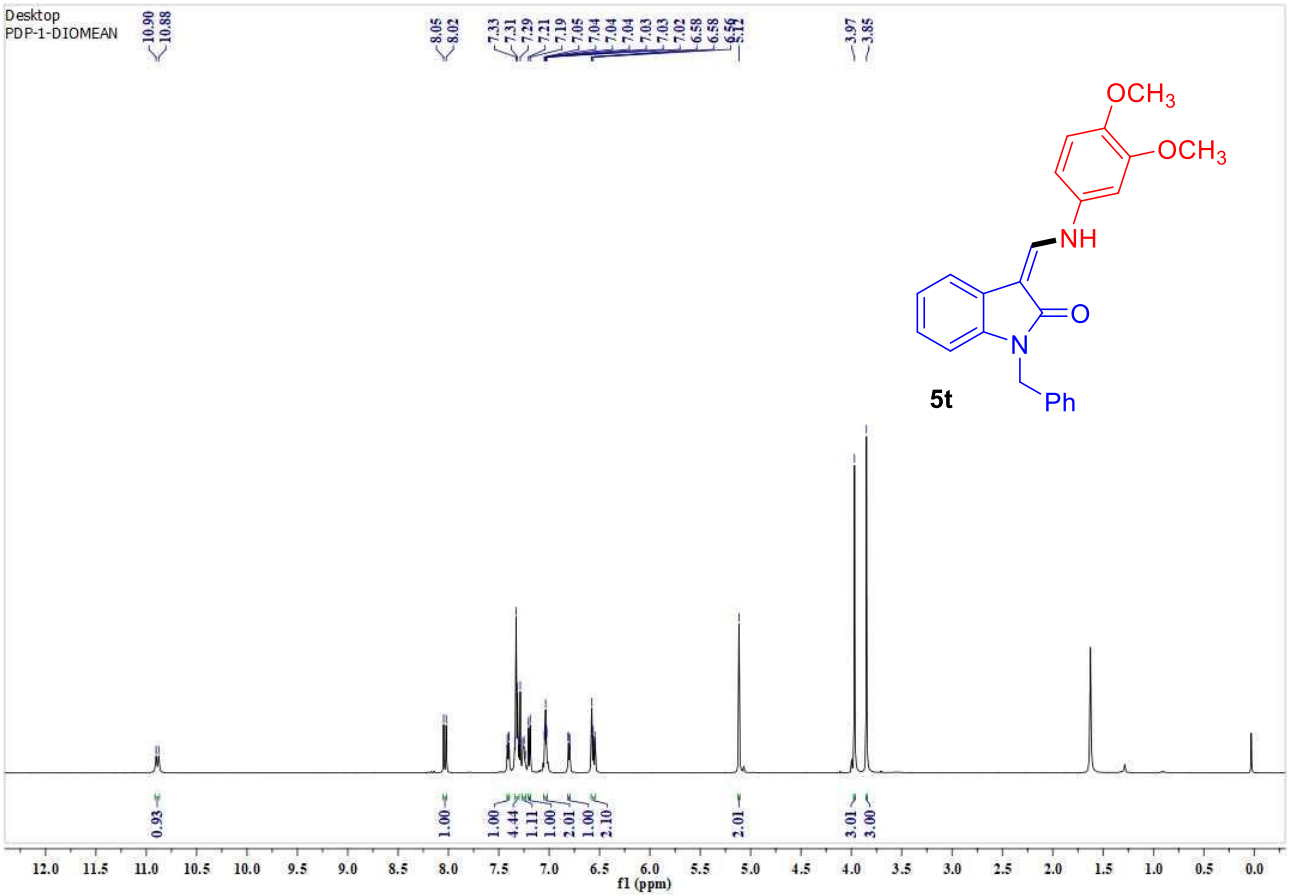

Desktop
PDP-1-ANISIDINE
168.93
156.43
137.81
137.66
136.88
133.56
128.69
127.34
127.20
123.94
123.78
121.27
117.71
115.74
115.14
108.75
98.34
55.63
43.23
OCH3
NH
O
N
Ph
5q
f1 (ppm)

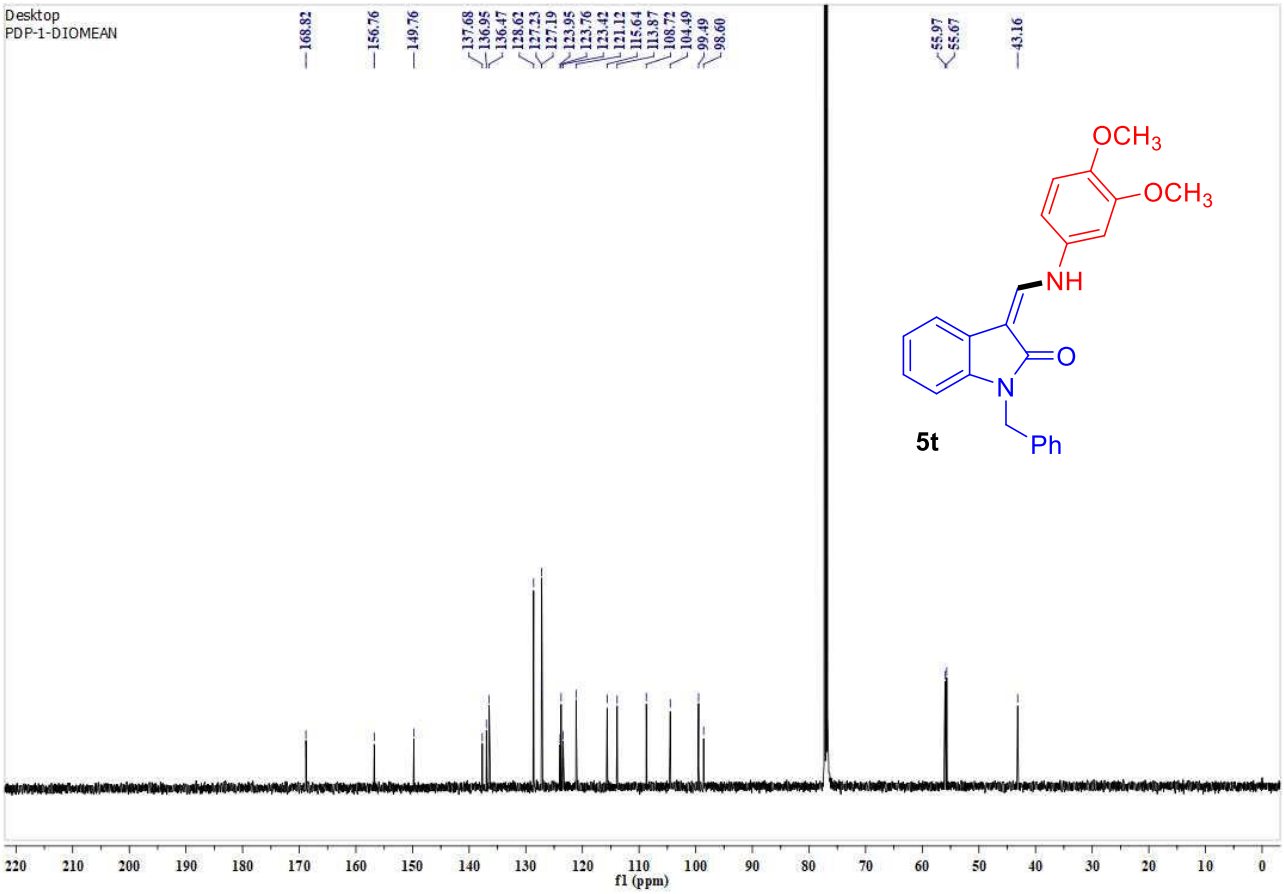

AP175
single_pulse
10.77
10.75
7.96
7.94
7.38
7.34
7.33
7.33
7.32
7.30
7.09
7.09
7.07
7.07
7.07
7.06
7.04
7.02
7.02
6.92
6.92
Cl
NH
O
N
Ph
5r
0.96
1.03
1.15
1.01
1.01
3.48
0.86
1.33
1.70
1.79
1.11
2.02
f1 (ppm)

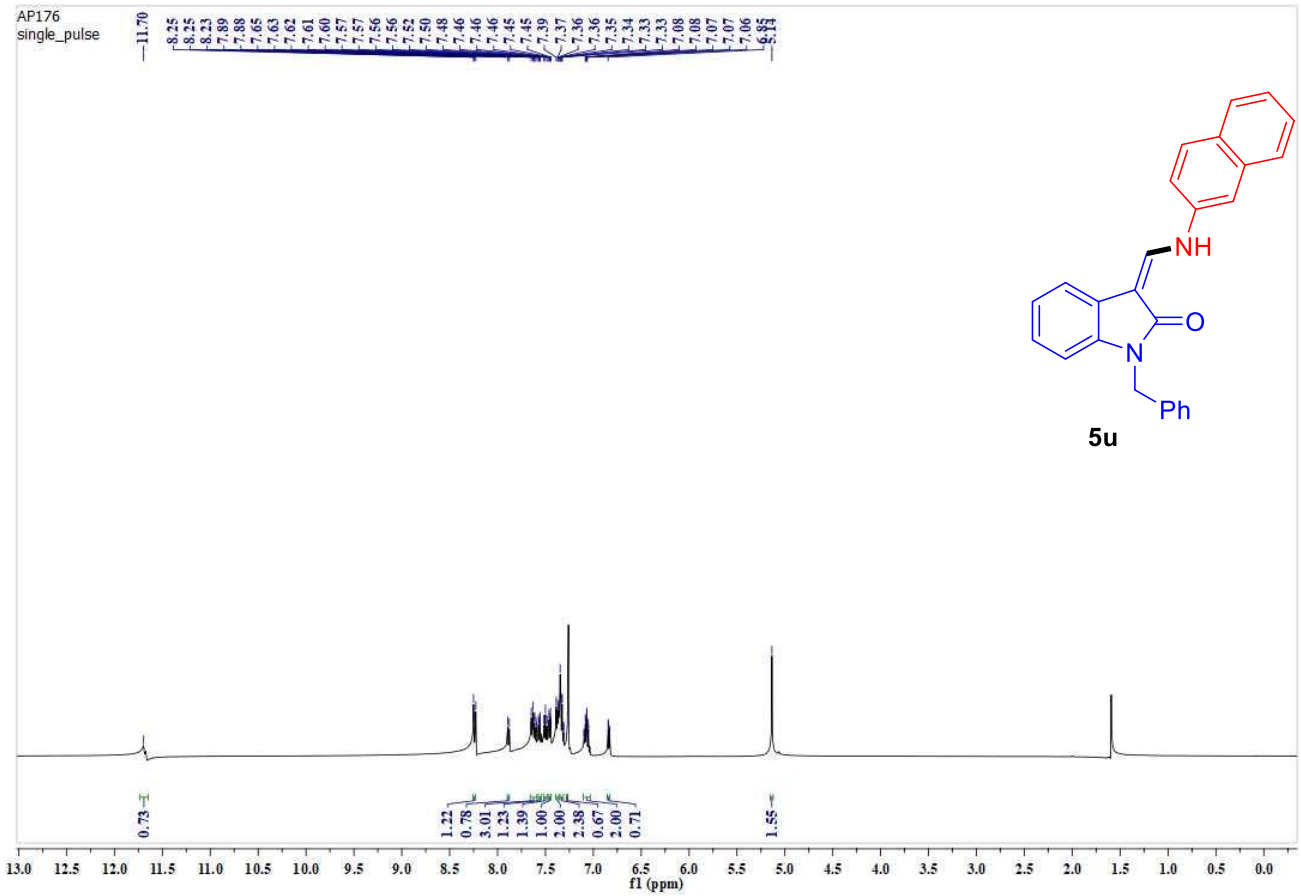

AP175
single pulse decoupled gated NOE
169.03
138.64
138.15
136.69
136.28
129.94
128.83
127.54
127.27
121.60
117.17
116.31
109.00
100.08
43.34
Cl
NH
O
N
Ph
5r
f1 (ppm)

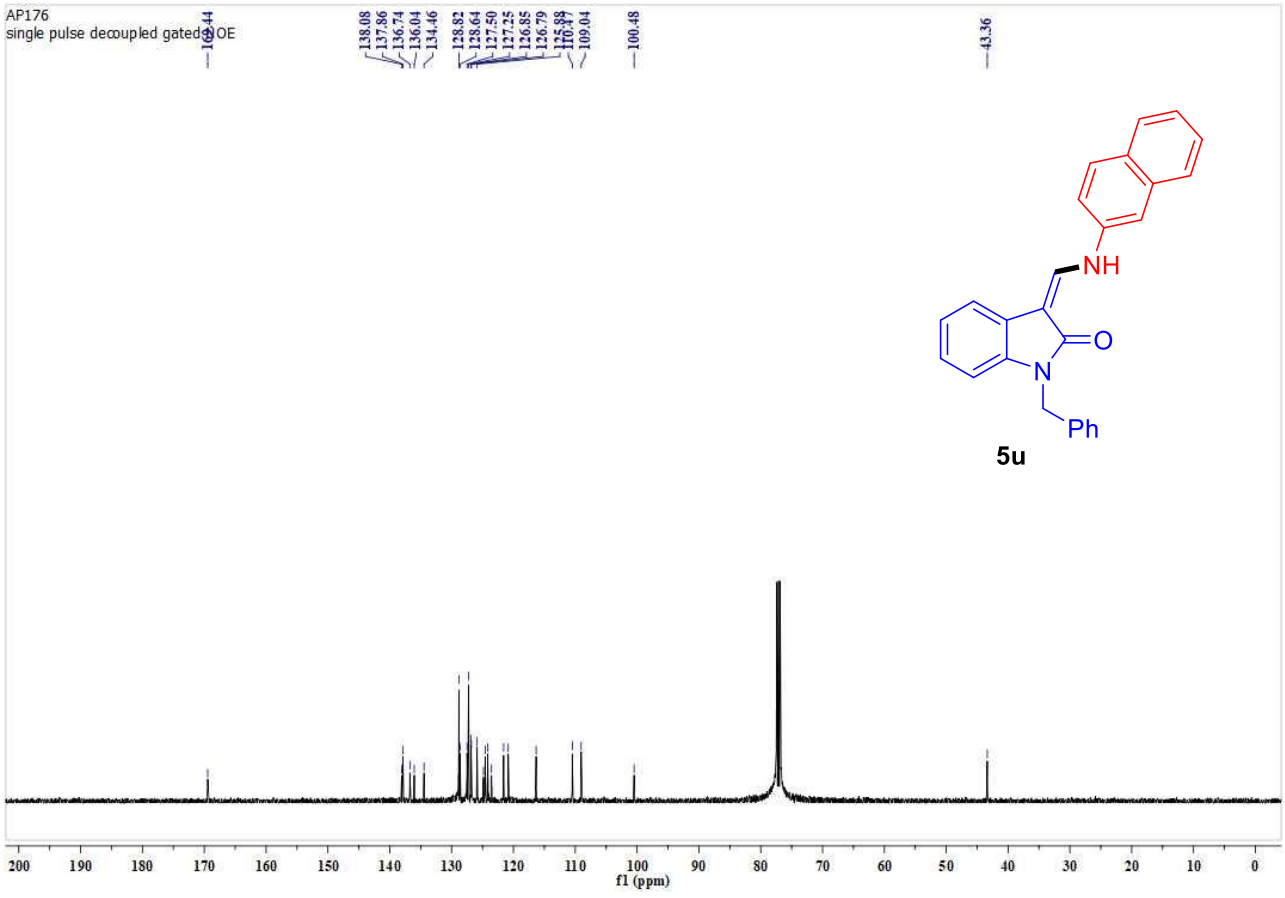

Desktop
PD-P1-DICH3
10.64
10.61
7.99
7.96
7.36
7.34
7.25
7.25
7.20
6.99
6.99
6.98
6.97
6.97
6.96
6.96
6.76
6.75
6.73
6.68
5.00
2.28
1.00
1.01
1.02
0.87
2.01
1.38
2.71
3.19
1.00
2.01
6.01
f1 (ppm)
H3C
CH3
NH
O
N
Ph
5s

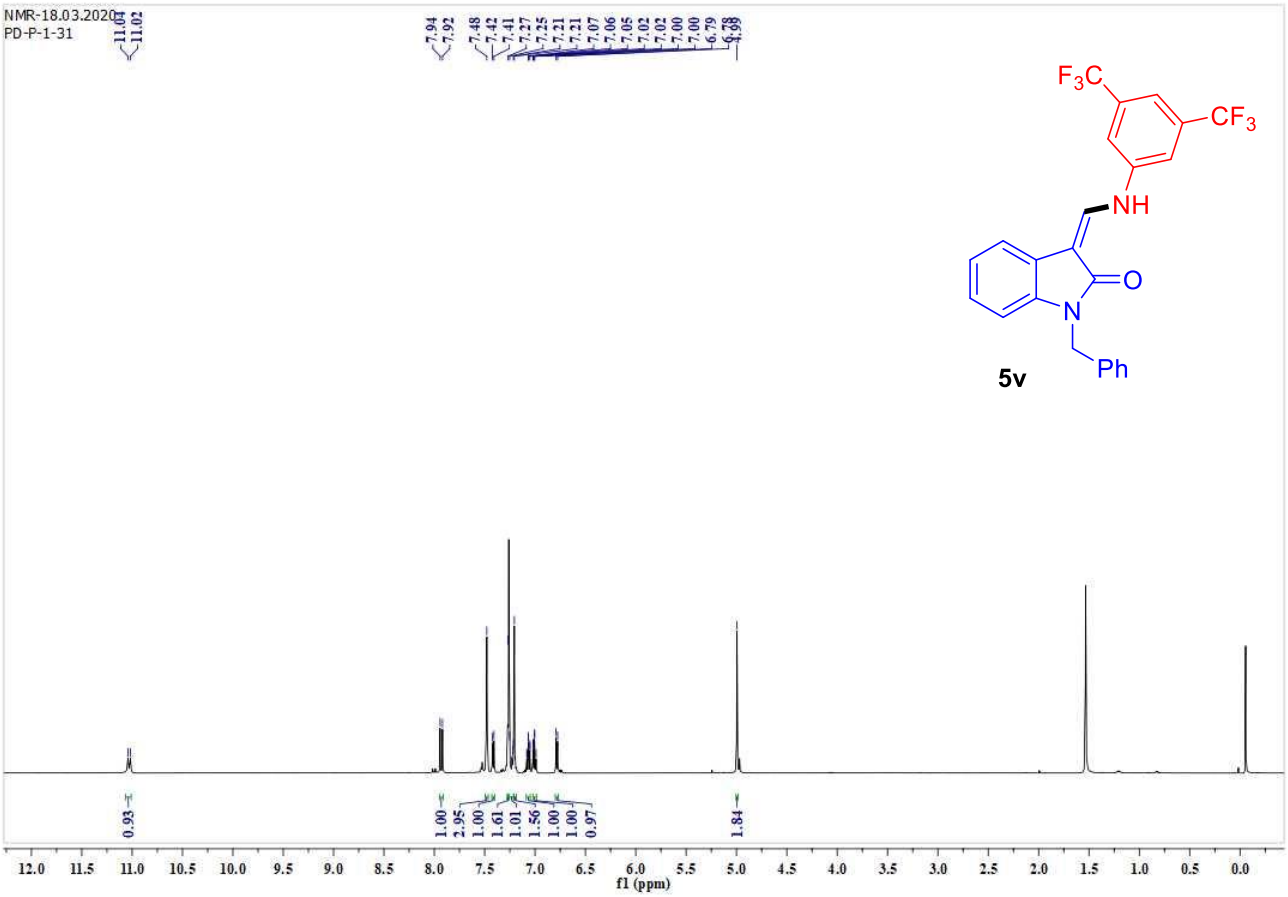

Desktop
PD-P1-DICH3
168.92
139.80
139.67
137.85
136.99
136.86
128.70
127.36
127.24
125.56
124.16
123.73
121.31
115.96
113.92
108.77
98.94
43.25
21.42
f1 (ppm)
H3C
CH3
NH
O
N
Ph
5s

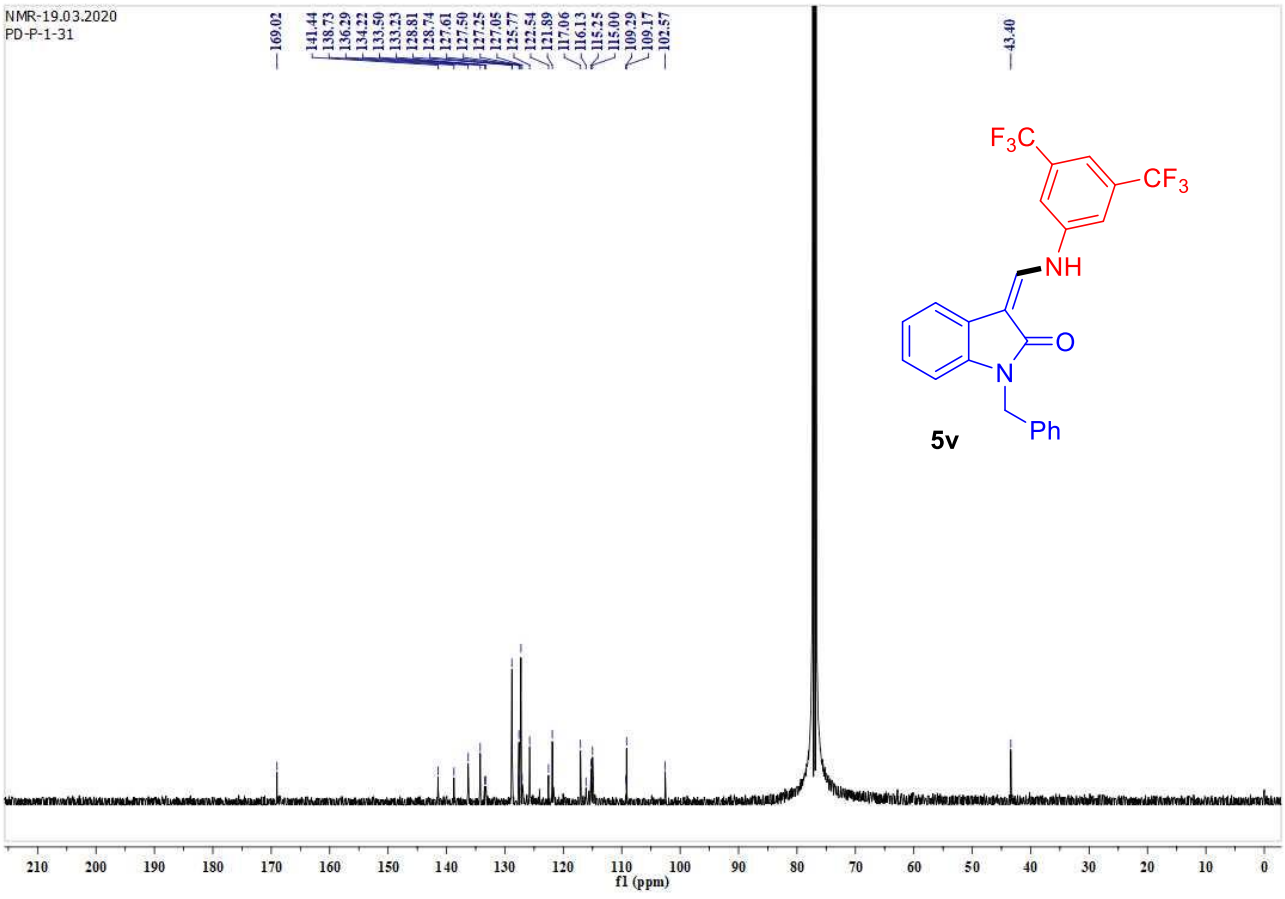

Desktop
PDP-1-DIOMEAN
10.90
10.88
8.05
8.02
7.33
7.31
7.29
7.21
7.19
7.05
7.04
7.04
7.04
7.03
7.03
7.02
6.58
6.56
5.11
3.97
3.85
OCH3
OCH3
NH
O
N
Ph
5t
0.93
1.00
1.00
4.44
1.11
1.00
2.01
1.00
2.10
2.01
3.01
3.00
f1 (ppm)

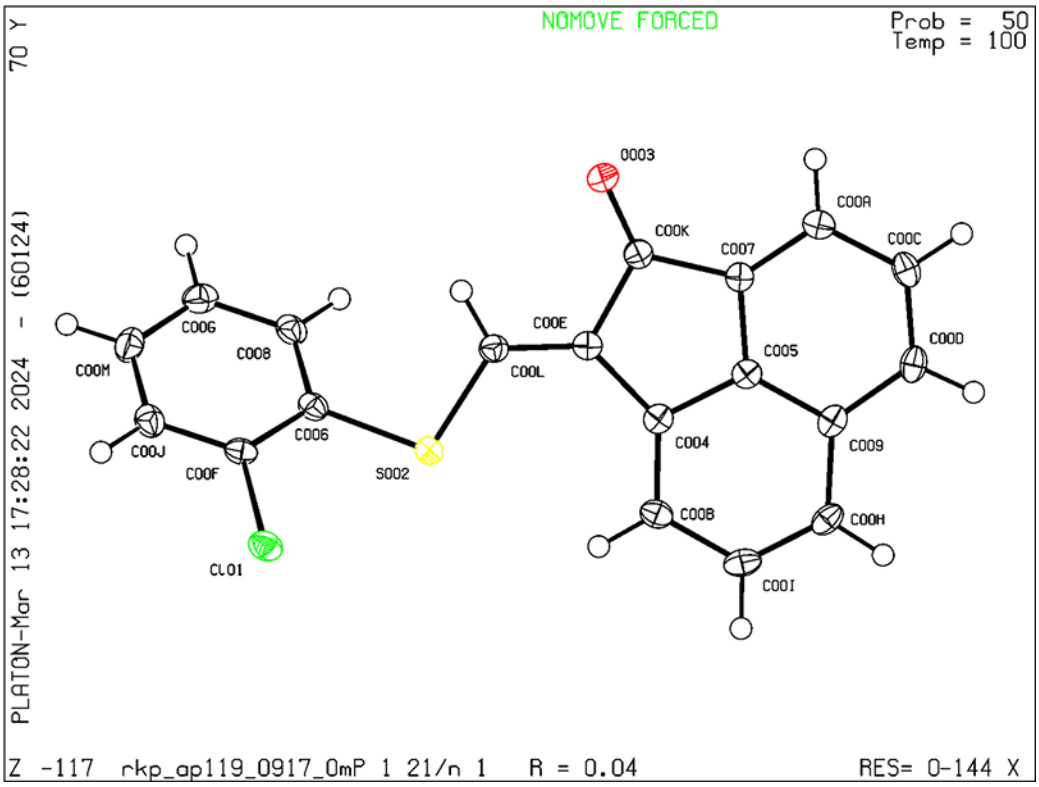

Desktop
PDP-1-DIOMEAN
168.82
156.76
149.76
137.68
136.95
136.47
128.62
127.23
127.19
123.95
123.76
123.42
121.12
115.64
113.87
108.72
104.49
99.49
98.60
55.97
55.67
43.16
OCH3
OCH3
NH
O
N
Ph
5t
f1 (ppm)


AP176
single_pulse
11.70
8.25
8.25
8.23
7.89
7.88
7.65
7.63
7.62
7.61
7.60
7.57
7.57
7.56
7.56
7.52
7.50
7.48
7.46
7.46
7.46
7.45
7.45
7.39
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.08
7.08
7.07
7.07
7.06
6.85
5.14
NH
O
N
Ph
5u
0.73
1.22
0.78
3.01
1.23
1.39
1.00
2.00
2.38
0.67
2.00
0.71
1.55
f1 (ppm)


AP176
single pulse decoupled gated NOE
170.44
138.08
137.86
136.74
136.04
134.46
128.82
128.64
127.50
127.25
126.85
126.79
125.88
110.47
109.04
100.48
43.36
NH
O
N
Ph
5u
f1 (ppm)

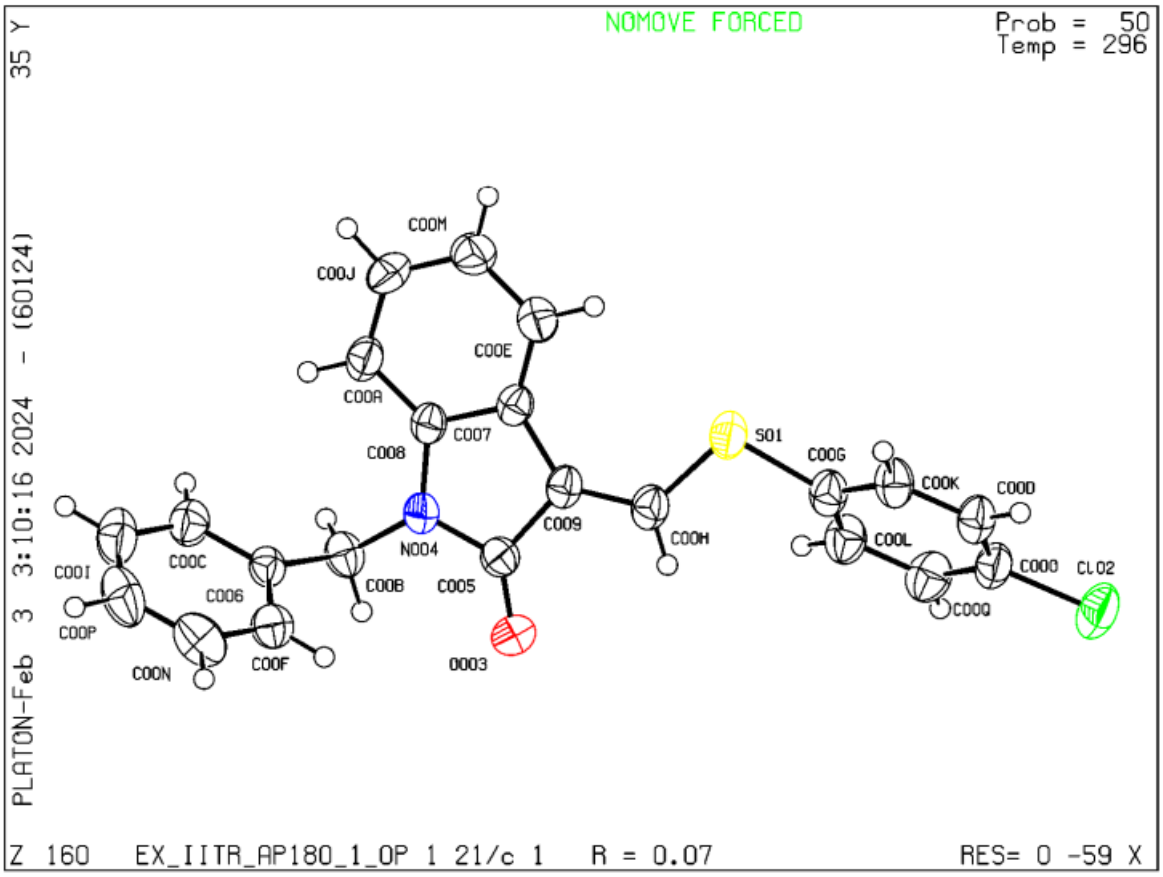

NMR-18.03.2020
PD-P-1-31
11.04
11.02
7.94
7.92
7.48
7.42
7.41
7.27
7.25
7.21
7.21
7.07
7.06
7.05
7.02
7.02
7.00
7.00
6.79
6.78
4.99
F3C
CF3
NH
O
N
Ph
5v
0.93
1.00
2.95
1.00
1.61
1.01
1.56
1.00
1.00
0.97
1.84
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


NMR-19.03.2020
PD-P-1-31
169.02
141.44
138.73
136.29
134.22
133.50
133.23
128.81
128.74
127.61
127.50
127.25
127.05
125.77
122.54
121.89
117.06
116.13
115.25
115.00
109.29
109.17
102.57
43.40
F3C
CF3
NH
O
N
Ph
5v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



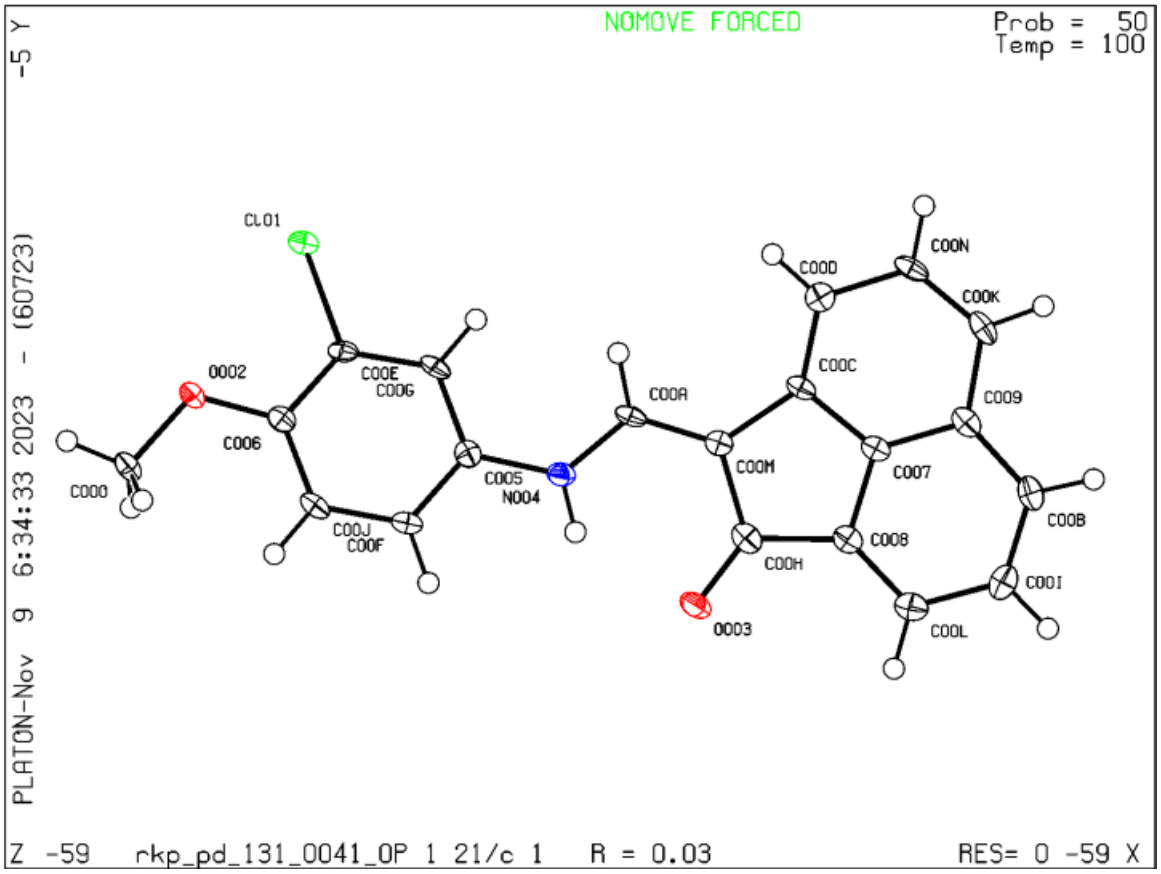
Formula	$C_{19}H_{11}ClOS$
Formula Wt.	322.79
Crystal color	yellow
Crystal system	Needle shape
Space group	P 1 21/n 1
a(Å)	3.8430(2)
b(Å)	14.0193(7)
c(Å)	26.2392(12)
α(deg)	90
β(deg)	92.820(1)
c(deg)	90
V(Å^3)	1411.96(12)

Figure S1: ORTEP plot of the crystal structure of **3d**.



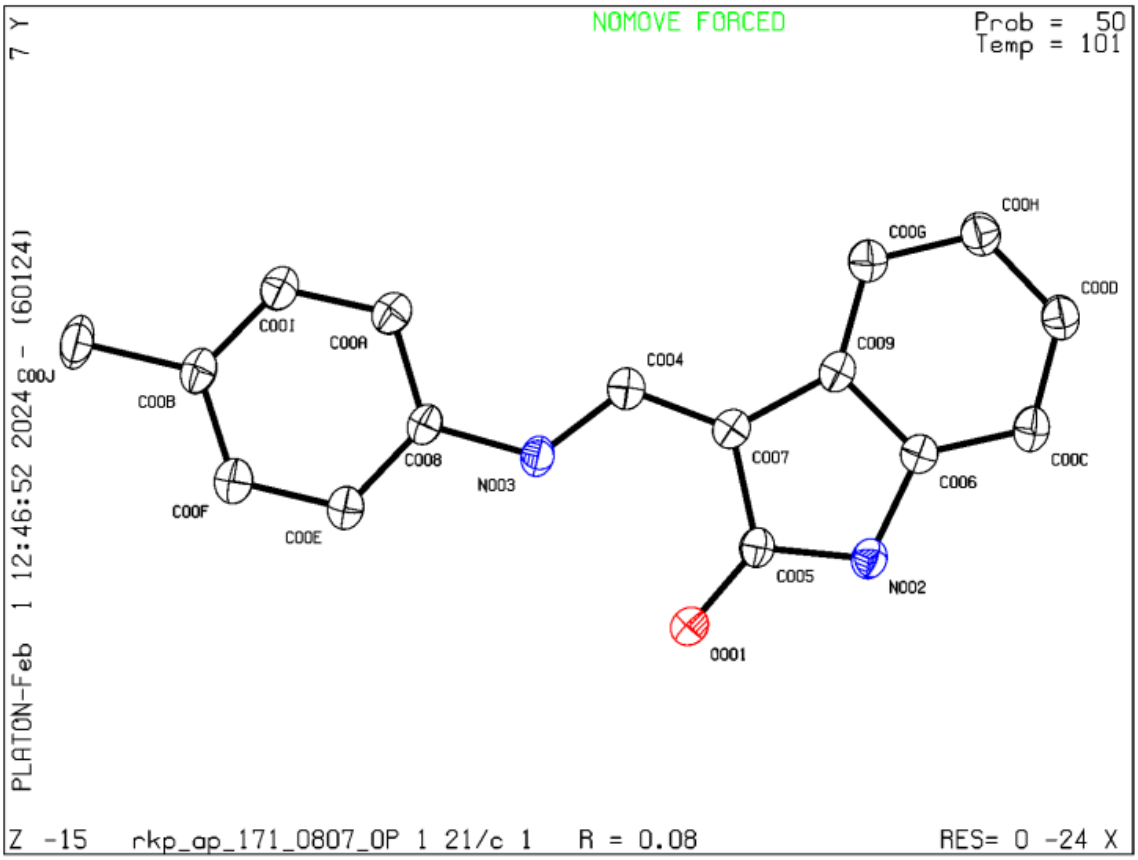
Formula	$C_{22}H_{16}ClNOS$
Formula Wt.	377.90
Crystal color	yellow
Crystal system	Needle shape
Space group	P21/c
a(Å)	20.066(4)
b(Å)	5.963(2)
c(Å)	16.542(3)
α(deg)	90.25(3)
β(deg)	112.50(3)
c(deg)	90.04(3)
V(Å^3)	1828.6(9)

Figure S2: ORTEP plot of the crystal structure of **3j**.



Formula	$C_{20}H_{14}ClNO_2$
Formula Wt.	335.77
Crystal color	yellow
Crystal system	Needle shape
Space group	P21/c
a(Å)	14.6971 (12)
b(Å)	3.9784 (3)
c(Å)	25.694 (2)
α(deg)	90
β(deg)	94.365 (2)
c(deg)	90
V(Å^3)	1498.0 (2)

Figure S3: ORTEP plot of the crystal structure of **5h**.



Formula	$C_{16}H_{14}N_2O$
Formula Wt.	250.29
Crystal color	yellow
Crystal system	Needle shape
Space group	P21/c
a(Å)	14.0955(6)
b(Å)	6.0166(3)
c(Å)	15.1711(7)
α(deg)	90
β(deg)	103.195(1)
c(deg)	90
V(Å^3)	1252.65(10)

Figure S4: ORTEP plot of the crystal structure of **5i**.

Computational Studies:

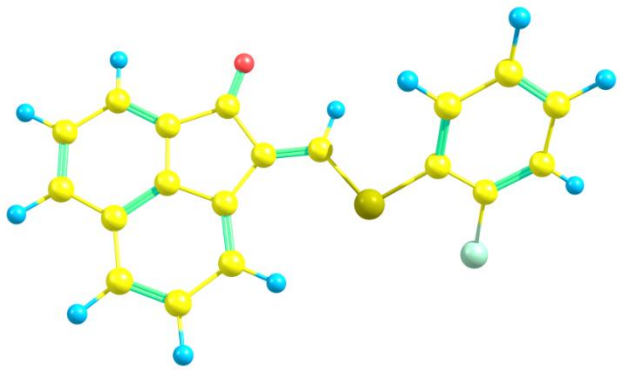
All the computational studies were done using density functional theory (DFT) method in ORCA program. Density functional theory has been performed to study the optimized energies of the molecule. The molecular properties of the compounds had been computed by DFT using the standard def2-SVP basis sets. The geometry optimization was performed at the B3LYP hybrid density functional with the same basis set with a dispersion correction D3BJ at 298 K temperature.

The structures and energies of configurations of arylthio/arylamino methylene derivatives were calculated on this basis set in ORCA program. Gibbs free energy for each *E* and *Z* structure, as well as optimized structures with single-point energies and relative frequencies, are provided by the DFT calculation. In order to investigate the effect of solvent on the isomeric composition, the structures were optimized in the solvent phase at B3LYP/def2-SVP level of theory using solvation model Conductor-like Polarizable Continuum Model (CPCM) with methanol solvent. Also, we have computed the solvent effect on energies by optimizing the structures and were used CPCM for the calculation of single point energies of methanol solvent.

In this investigation, theoretical calculation of molecules had been performed to have an idea about the lowest energy structures of the species *i.e.*, more stable structure. From the theoretical values obtained in this work, we can find that the optimized bond lengths and angles for molecule are in good agreement with the experimental values from single crystal XRD analysis.

Coordinates of 3d (*E*-Isomer)

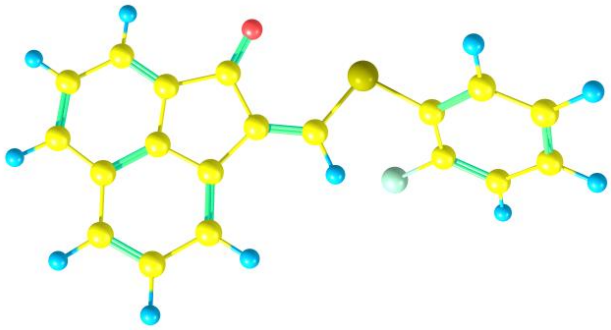
C	0.937047000	0.720554000	-3.911536000
C	-0.224548000	0.421695000	-3.227324000
C	2.155183000	0.747302000	-3.180749000
C	-1.653927000	0.304626000	-3.655202000
H	3.082983000	0.984225000	-3.707659000
C	-0.176888000	0.153123000	-1.841637000
C	2.203059000	0.481413000	-1.817268000
H	3.161422000	0.511030000	-1.291410000
C	1.017510000	0.169697000	-1.092174000



H	0.918837000	0.930914000	-4.983392000
C	-1.461498000	-0.134797000	-1.291918000
C	-2.426345000	-0.055916000	-2.396648000
C	-1.542393000	-0.414482000	0.061325000
C	0.896463000	-0.127062000	0.297472000
H	-2.495091000	-0.640477000	0.543195000
H	1.786396000	-0.130746000	0.932214000
C	-0.347677000	-0.408075000	0.838460000
H	-0.423429000	-0.632186000	1.905604000
O	-2.118671000	0.451160000	-4.766832000
S	-4.790782000	-0.581816000	-1.099115000
C	-3.761752000	-0.253749000	-2.463197000
H	-4.239693000	-0.138665000	-3.442129000
C	-7.387825000	-2.443925000	-3.658203000
C	-8.615746000	-2.253669000	-3.018901000
C	-6.215628000	-1.947847000	-3.087209000
H	-9.535659000	-2.645264000	-3.458715000
H	-5.256753000	-2.128361000	-3.575559000
C	-8.668431000	-1.566587000	-1.805218000
C	-6.254315000	-1.230042000	-1.881050000
H	-9.615016000	-1.411279000	-1.285165000
C	-7.496447000	-1.058076000	-1.240939000

Cl	-7.591981000	-0.205842000	0.279677000
H	-7.335592000	-2.993516000	-4.60068500

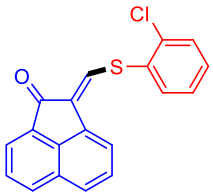
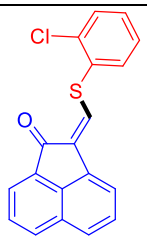
Coordinates of 3d (*Z*-Isomer)



C	0.692812000	1.492260000	-2.059514000
C	-0.321542000	0.655181000	-1.638956000
C	1.802087000	1.685525000	-1.192652000
C	-1.611561000	0.220386000	-2.260625000
H	2.612708000	2.345862000	-1.511342000
C	-0.233267000	0.021975000	-0.378772000
C	1.888110000	1.063199000	0.047513000
H	2.759124000	1.240359000	0.684559000
C	0.853930000	0.195917000	0.502244000
H	0.643794000	1.991711000	-3.029883000
C	-1.361829000	-0.803065000	-0.102148000
C	-2.259269000	-0.702971000	-1.264625000
C	-1.395900000	-1.474531000	1.105437000
C	0.786206000	-0.512434000	1.738145000
H	-2.234133000	-2.120888000	1.377969000
H	1.597420000	-0.418853000	2.464761000
C	-0.309307000	-1.315414000	2.014012000
H	-0.347390000	-1.850492000	2.966518000

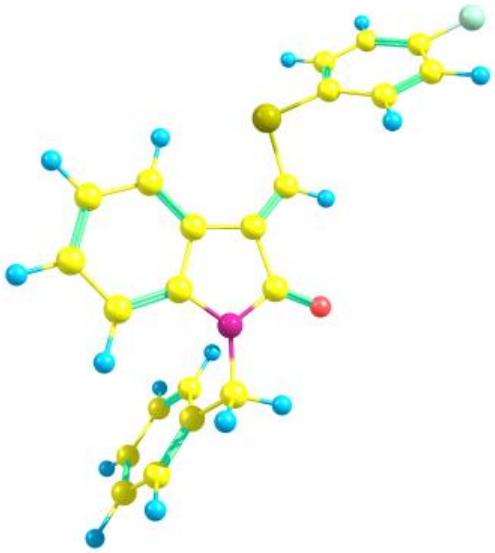
O	-2.071126000	0.526530000	-3.345878000
S	-4.428013000	-1.076948000	-2.905959000
C	-3.458052000	-1.296696000	-1.467505000
H	-3.883969000	-1.958953000	-0.709837000
C	-7.310890000	-3.924419000	-3.124946000
C	-8.148486000	-3.643207000	-2.042485000
C	-6.169297000	-3.150284000	-3.336259000
H	-9.041713000	-4.246267000	-1.863288000
H	-5.498985000	-3.367979000	-4.170688000
C	-7.849040000	-2.585417000	-1.182624000
C	-5.848165000	-2.083172000	-2.482962000
H	-8.496353000	-2.348141000	-0.336858000
C	-6.714306000	-1.800511000	-1.409172000
Cl	-6.399631000	-0.470777000	-0.322539000
H	-7.540272000	-4.750673000	-3.801506000

For both the isomers of **3d**, we have performed theoretical calculations. Optimizing the coordinates revealed that *E*-isomer possesses less optimized energy and less Gibbs free energy, so is more stable than *Z*-isomer as data shown in below table:

S.No.	Isomer	Compound (3d)	E(a.u.)	GFE(a.u.)	Esolvent(a.u.)
1	*E*		-1662.913655744	-1662.71579355	-1662.9256569453
2	*Z*		-1662.911814293	-1662.71349097	-1662.9253050682

Coordinates of 3j (*E*-Isomer)

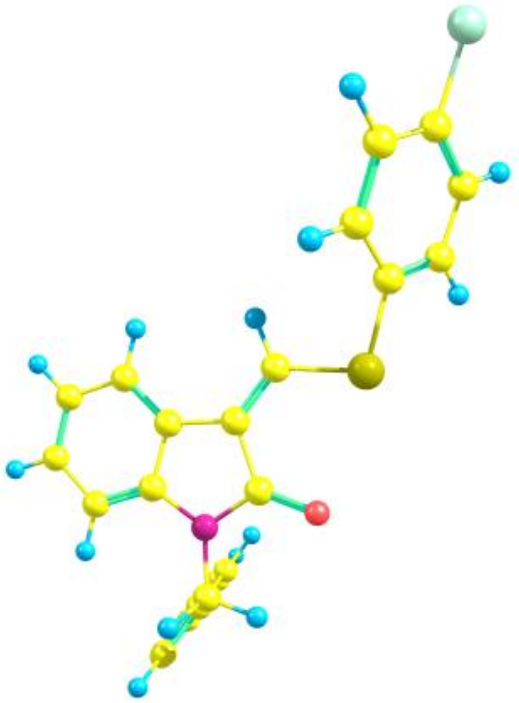
C	-0.895682000	-0.480389000	-7.118570000
C	-0.453305000	-0.534044000	-5.796046000
C	-1.027512000	0.331923000	-4.828404000
C	-2.029473000	1.237270000	-5.160384000
C	-2.457435000	1.277848000	-6.497104000
C	-1.900524000	0.435172000	-7.464604000
C	0.550721000	-1.334215000	-5.102742000
C	0.533645000	-0.898806000	-3.665008000
N	-0.429543000	0.107389000	-3.583831000
H	-0.467747000	-1.138818000	-7.876592000
H	-2.478361000	1.884820000	-4.406626000
H	-3.245577000	1.979615000	-6.781185000
H	-2.253937000	0.485588000	-8.496861000
O	1.204865000	-1.307584000	-2.737090000
C	1.415558000	-2.294234000	-5.502965000
S	1.530057000	-2.934425000	-7.117319000
C	-2.161929000	0.526237000	-1.864021000
C	-2.963080000	1.569220000	-1.384022000
C	-2.678221000	-0.777171000	-1.873164000
H	-2.572002000	2.591178000	-1.380755000
H	-2.061520000	-1.596483000	-2.251064000



C	-4.256046000	1.317756000	-0.914367000
C	-3.969597000	-1.030893000	-1.408218000
H	-4.870314000	2.142728000	-0.544569000
H	-4.360101000	-2.051678000	-1.421357000
C	-4.762960000	0.016230000	-0.926793000
H	-5.775032000	-0.182751000	-0.565528000
C	-0.753377000	0.797640000	-2.355224000
H	-0.013899000	0.446067000	-1.618029000
H	-0.604612000	1.883040000	-2.486871000
C	3.042491000	-3.876268000	-7.031990000
C	4.249043000	-5.888998000	-7.648231000
H	4.192031000	-2.382561000	-5.958775000
C	5.367893000	-4.133634000	-6.393776000
H	2.174402000	-5.532353000	-8.121642000
C	3.075409000	-5.134568000	-7.649304000
H	4.280221000	-6.870572000	-8.123550000
C	4.198678000	-3.373475000	-6.416981000
C	5.388550000	-5.387432000	-7.012641000
H	6.268341000	-3.752179000	-5.909857000
Cl	6.853172000	-6.335173000	-6.992567000
H	2.080833000	-2.728102000	-4.748893000

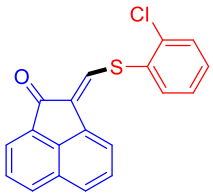
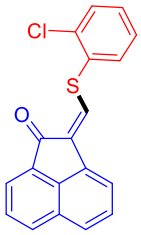
Coordinates of 3j (*Z*-Isomer)

C	-1.473767000	0.340430000	-7.370436000
C	-0.942654000	-0.096317000	-6.157935000
C	-1.251805000	0.602856000	-4.963044000
C	-2.085053000	1.717391000	-4.963120000
C	-2.608525000	2.141776000	-6.194207000
C	-2.308749000	1.466322000	-7.383288000
C	-0.060954000	-1.201202000	-5.785683000
C	0.126995000	-1.118156000	-4.308377000
N	-0.603250000	-0.009367000	-3.883713000
H	-1.244887000	-0.187680000	-8.299813000
H	-2.334358000	2.236508000	-4.036990000
H	-3.266310000	3.014057000	-6.219721000
H	-2.731123000	1.816908000	-8.327653000
O	0.777887000	-1.859612000	-3.592665000
C	0.511329000	-2.156885000	-6.556603000
S	1.527468000	-3.438323000	-5.946446000
C	-2.067891000	0.269282000	-1.904168000
C	-2.592343000	1.276549000	-1.085090000
C	-2.838578000	-0.875777000	-2.149466000
H	-2.001912000	2.177960000	-0.894957000
H	-2.440468000	-1.664516000	-2.792823000



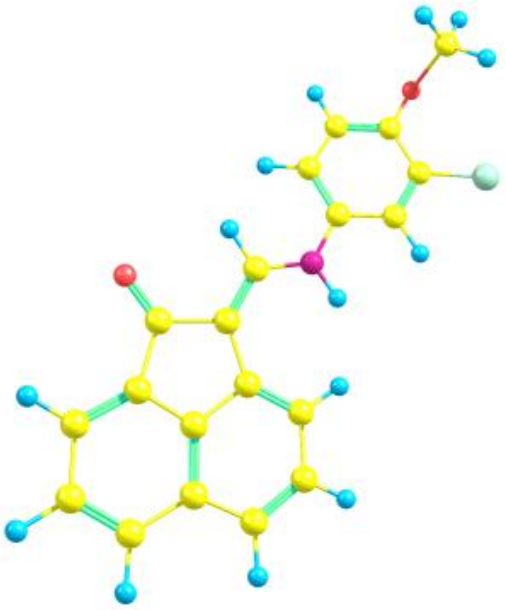
C	-3.861019000	1.142604000	-0.512702000
C	-4.106909000	-1.010695000	-1.582308000
H	-4.257182000	1.938037000	0.123736000
H	-4.697885000	-1.908350000	-1.781481000
C	-4.622148000	-0.002029000	-0.761081000
H	-5.616059000	-0.107646000	-0.319070000
C	-0.680923000	0.406953000	-2.501646000
H	0.034803000	-0.233702000	-1.961686000
H	-0.333714000	1.449854000	-2.405655000
C	2.030490000	-4.206792000	-7.481675000
C	2.393587000	-6.258882000	-8.729384000
H	2.668429000	-2.385789000	-8.469549000
C	2.994712000	-4.117278000	-9.708374000
H	1.528222000	-6.180038000	-6.753986000
C	1.950708000	-5.603149000	-7.579811000
H	2.329518000	-7.345031000	-8.811071000
C	2.568712000	-3.470584000	-8.548113000
C	2.909017000	-5.510731000	-9.791378000
H	3.410469000	-3.549233000	-10.542107000
Cl	3.457115000	-6.323809000	-11.235408000
H	0.334396000	-2.169695000	-7.635883000

Structure optimization of both *E* and *Z* isomers of **3j** compound concluded that *E*-isomer of **3j** is more favorable which was also confirmed by its crystal structure.

S.No.	Isomer	Compound (3j)	E (a.u.)	GFE (a.u.)	$E_{solvent}$ (a.u.)
1	*E*		-1834.798960279	-1834.52584765	-1834.8140728130
2	*Z*		-1834.796965032	-1834.52496011	-1834.8132684436

Coordinates of 5h (*E*-Isomer)

C	1.215155000	0.284250000	-2.457349000
C	-0.070408000	0.054769000	-2.009221000
C	2.236951000	0.475753000	-1.488893000
C	-1.368638000	-0.187170000	-2.721163000
H	3.259948000	0.658339000	-1.827886000
C	-0.335665000	0.013493000	-0.623730000
C	1.975079000	0.439501000	-0.124387000
H	2.788785000	0.594660000	0.589565000
C	0.656290000	0.203811000	0.359147000
H	1.438811000	0.318071000	-3.526203000
C	-1.714553000	-0.237179000	-0.341098000
C	-2.391903000	-0.373036000	-1.636508000
C	-2.091206000	-0.285977000	0.991235000
C	0.226577000	0.138820000	1.718322000
H	-3.124322000	-0.455752000	1.306262000
H	0.948989000	0.278471000	2.526509000
C	-1.106596000	-0.097395000	2.005503000
H	-1.426031000	-0.140569000	3.050018000
O	-1.561754000	-0.227934000	-3.922416000
C	-7.919361000	-1.133596000	-2.983043000
C	-8.800241000	-1.535526000	-1.972223000



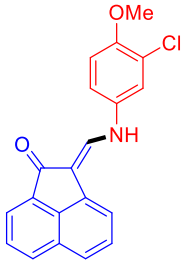
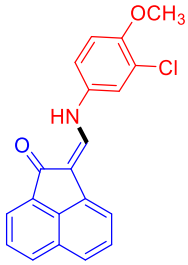
C	-6.569613000	-0.895830000	-2.731955000
H	-5.927003000	-0.561030000	-3.545911000
C	-8.278528000	-1.702713000	-0.676558000
C	-6.057914000	-1.076199000	-1.435457000
Cl	-9.335261000	-2.180846000	0.626328000
C	-6.929186000	-1.479732000	-0.410023000
H	-6.560685000	-1.624348000	0.607704000
H	-8.329022000	-0.990065000	-3.985182000
O	-10.122616000	-1.709590000	-2.247524000
C	-10.543032000	-3.053281000	-2.442254000
H	-10.018142000	-3.513975000	-3.298925000
H	-10.370231000	-3.666677000	-1.541874000
H	-11.620725000	-3.022330000	-2.653773000
N	-4.712740000	-0.861708000	-1.113182000
C	-3.686535000	-0.627263000	-1.970803000
H	-3.918353000	-0.660873000	-3.038634000
H	-4.484857000	-0.918721000	-0.127761000

Coordinates of 5h (*Z*-Isomer)

C	0.447093000	0.637860000	-2.515159000
C	-0.569644000	0.200442000	-1.688583000
C	1.721608000	0.878205000	-1.934869000
C	-2.003649000	-0.148519000	-1.926795000
H	2.537000000	1.224175000	-2.575245000
C	-0.320253000	0.006779000	-0.311229000
C	1.964289000	0.687740000	-0.578893000
H	2.960538000	0.885299000	-0.173296000
C	0.931151000	0.238152000	0.292227000
H	0.277184000	0.794768000	-3.582877000
C	-1.478800000	-0.444871000	0.387542000
C	-2.553665000	-0.554158000	-0.605969000
C	-1.364078000	-0.668407000	1.747444000
C	1.013072000	-0.003844000	1.696384000
H	-2.211216000	-1.013010000	2.346235000
H	1.956519000	0.157134000	2.224108000
C	-0.107511000	-0.441390000	2.383290000
H	-0.032206000	-0.622251000	3.458864000
O	-2.618779000	-0.112073000	-2.992972000
C	-8.157683000	-1.623805000	-2.671592000
C	-8.811237000	-2.087279000	-1.523217000

C	-6.814623000	-1.260862000	-2.645569000
H	-6.327998000	-0.894125000	-3.552510000
C	-8.062037000	-2.181507000	-0.336561000
C	-6.073067000	-1.362476000	-1.454298000
Cl	-8.836429000	-2.742600000	1.124539000
C	-6.713714000	-1.828460000	-0.293901000
H	-6.186786000	-1.924900000	0.654245000
H	-8.739773000	-1.542964000	-3.592032000
O	-10.138312000	-2.391751000	-1.568345000
C	-10.453650000	-3.772597000	-1.684985000
H	-10.030714000	-4.200023000	-2.612408000
H	-10.081069000	-4.348014000	-0.820786000
H	-11.549298000	-3.847242000	-1.719977000
N	-4.729826000	-0.988943000	-1.475968000
C	-3.856599000	-0.947136000	-0.444561000
H	-4.231082000	-1.240734000	0.539455000
H	-4.316874000	-0.692794000	-2.370557000

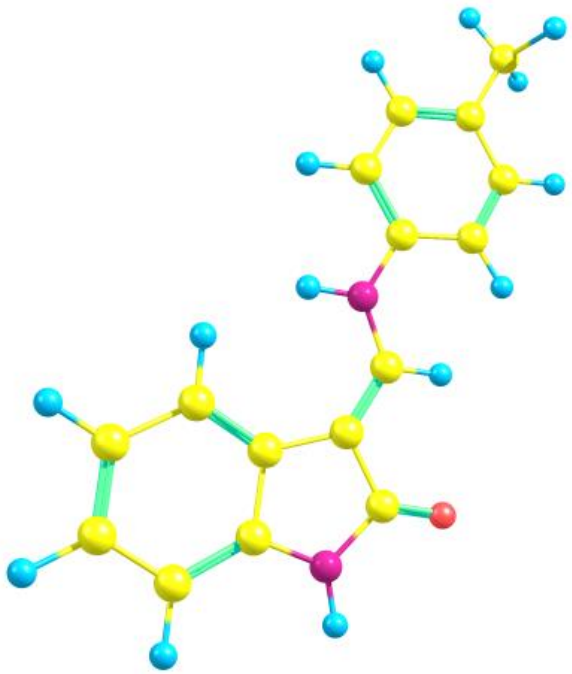
By optimizing both the *E* and *Z* isomers of **5h** compound, *Z*-isomer of **5h** was found to be more favorable according to optimized energy, Gibb's free energy and also by crystal structure analysis.

S.No.	Isomer	Compound (5h)	E (a.u.)	GFE (a.u.)	$E_{solvent}$ (a.u.)
1	*E*		-1434.5680019	-1434.3246832	-1434.5874193
2	*Z*		-1434.5769975	-1434.3331589	-1434.5920011

The DFT calculations and single crystal XRD studies reveal hydrogen bonding between carbonyl oxygen and N–H of enamine leading to *Z*-isomer predominantly.

Coordinates of 5i (*E*-isomer)

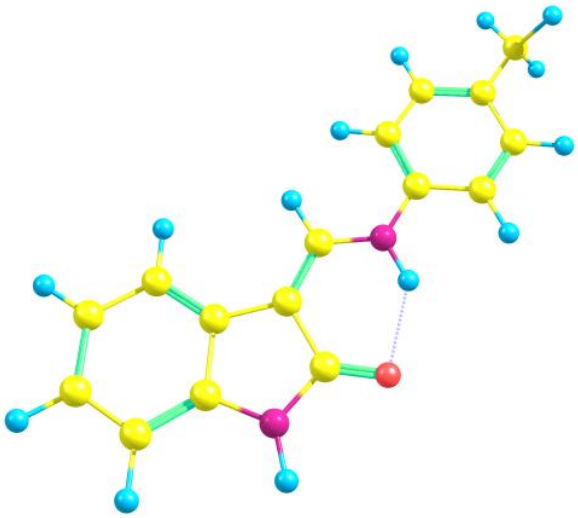
C	-0.770457000	-0.872742000	-7.167731000
C	-0.233653000	-0.672754000	-5.892915000
C	-0.916678000	0.191187000	-4.989189000
C	-2.101602000	0.829949000	-5.338413000
C	-2.621794000	0.606793000	-6.622619000
C	-1.965358000	-0.232438000	-7.528045000
C	0.952463000	-1.152668000	-5.192353000
C	0.952015000	-0.532524000	-3.837343000
N	-0.202438000	0.252085000	-3.797455000
H	-0.276093000	-1.514415000	-7.902037000
H	-2.612949000	1.489288000	-4.633173000
H	-3.551924000	1.099559000	-6.916145000
H	-2.383119000	-0.389797000	-8.524970000
O	1.756656000	-0.655059000	-2.932392000
C	1.960704000	-2.005538000	-5.531465000
N	2.094596000	-2.677103000	-6.699577000
C	3.138950000	-3.532108000	-7.079868000
C	4.047187000	-5.075734000	-8.723394000
H	4.410238000	-3.211074000	-5.343180000
C	5.286805000	-4.597724000	-6.728865000
H	2.146152000	-4.073743000	-8.924682000
C	3.034024000	-4.215657000	-8.301295000
H	3.938101000	-5.595956000	-9.678944000
C	4.286630000	-3.731419000	-6.293278000
C	5.195694000	-5.287703000	-7.948615000



H	6.170122000	-4.737690000	-6.099052000
H	2.734016000	-2.167888000	-4.776484000
H	-0.457854000	0.795470000	-2.982909000
H	1.349387000	-2.574843000	-7.378416000
C	6.301368000	-6.207195000	-8.401812000
H	6.546330000	-6.953591000	-7.628117000
H	6.025386000	-6.749538000	-9.318315000
H	7.228152000	-5.646242000	-8.612455000

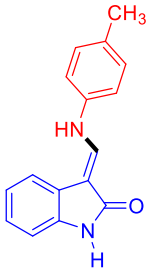
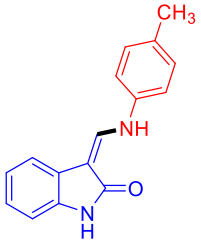
Coordinates of 5i (*Z*- isomer)

C	0.822874000	0.774364000	-3.474313000
C	1.840526000	-0.181155000	-3.506607000
C	2.799252000	-0.209533000	-2.457147000
C	2.753681000	0.689405000	-1.397053000
C	1.723085000	1.641326000	-1.384851000
C	0.769476000	1.683757000	-2.409449000
C	2.198027000	-1.250763000	-4.428190000
C	3.401382000	-1.911894000	-3.885295000
N	3.705947000	-1.241862000	-2.710411000
H	0.074054000	0.815384000	-4.269906000
H	3.497651000	0.656921000	-0.597494000 aw2
H	1.666952000	2.357835000	-0.561789000
H	-0.024636000	2.433460000	-2.378664000
O	4.029847000	-2.861469000	-4.355032000
C	1.619762000	-1.658487000	-5.603636000
N	2.111569000	-2.682148000	-6.331985000



C	1.625119000	-3.192683000	-7.538712000
C	0.007047000	-3.309495000	-9.342690000
H	3.306385000	-4.539536000	-7.736231000
C	1.937090000	-4.730446000	-9.394376000
H	-0.189773000	-1.998983000	-7.651803000
C	0.428121000	-2.759714000	-8.130776000
H	-0.929556000	-2.956830000	-9.783796000
C	2.373530000	-4.191741000	-8.188121000
C	0.745934000	-4.300668000	-10.002852000
H	2.539145000	-5.505286000	-9.877835000
H	0.734359000	-1.148752000	-5.990806000
H	4.494670000	-1.493850000	-2.128313000
H	2.955346000	-3.107061000	-5.923445000
C	0.294165000	-4.882164000	-11.318431000
H	0.263508000	-5.983823000	-11.282608000
H	-0.709481000	-4.525228000	-11.593445000
H	0.982353000	-4.606117000	-12.136083000

By optimizing both the *E* and *Z* isomers of **5i** compound, *Z*-isomer of **5i** was found to be more favorable according to optimized energy, Gibb's free energy and also by crystal structure analysis.

S.No.	Isomer	Compound 5i	E (a.u.)	GFE (a.u.)	$E_{solvent}$ (a.u.)
1	E		-801.9040699	-801.6810268	-801.92397833
2	Z		-801.9126937	-801.6881056	-801.9282757

The DFT calculations and single crystal XRD studies reveal hydrogen bonding between carbonyl oxygen and N–H of enamine leading to *Z*-isomer predominantly.