Palladium catalyzed carbonylative annulation of *C*(sp^2)-*H* bond of *N*,1-diaryl-1*H*-tetrazol-5-amines and *N*,4-diaryl-4*H*-triazol-3-amines to quinazolinones

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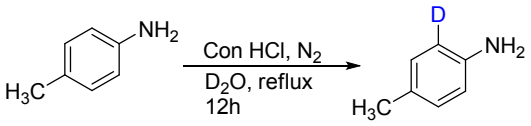
Supporting information:

Synthesis of 2-deutero-*p*-toluidine (*p*-toluidine-d_1)[1]:



To the suspension of *p*-toluidine (4.7 mmol, 503 mg) in D_2O (5 mL) in 10 mL round bottom flask, was added 11.6 M HCl (1.1 equiv). The reaction mixture was degassed with N_2 for 10 min and stirred at 135^{o}C under inert atmosphere. After 12h, reaction mixture was cooled to room temperature and 3M NaOH solution was added (up to pH 10). It was extracted with EtOAc and washed with brine solution. Organic layer was dried over Na_2SO_4, concentrated under reduced pressure to get 2-deutero-*p*-toluidineas a brownish solid (93%, 472 mg).

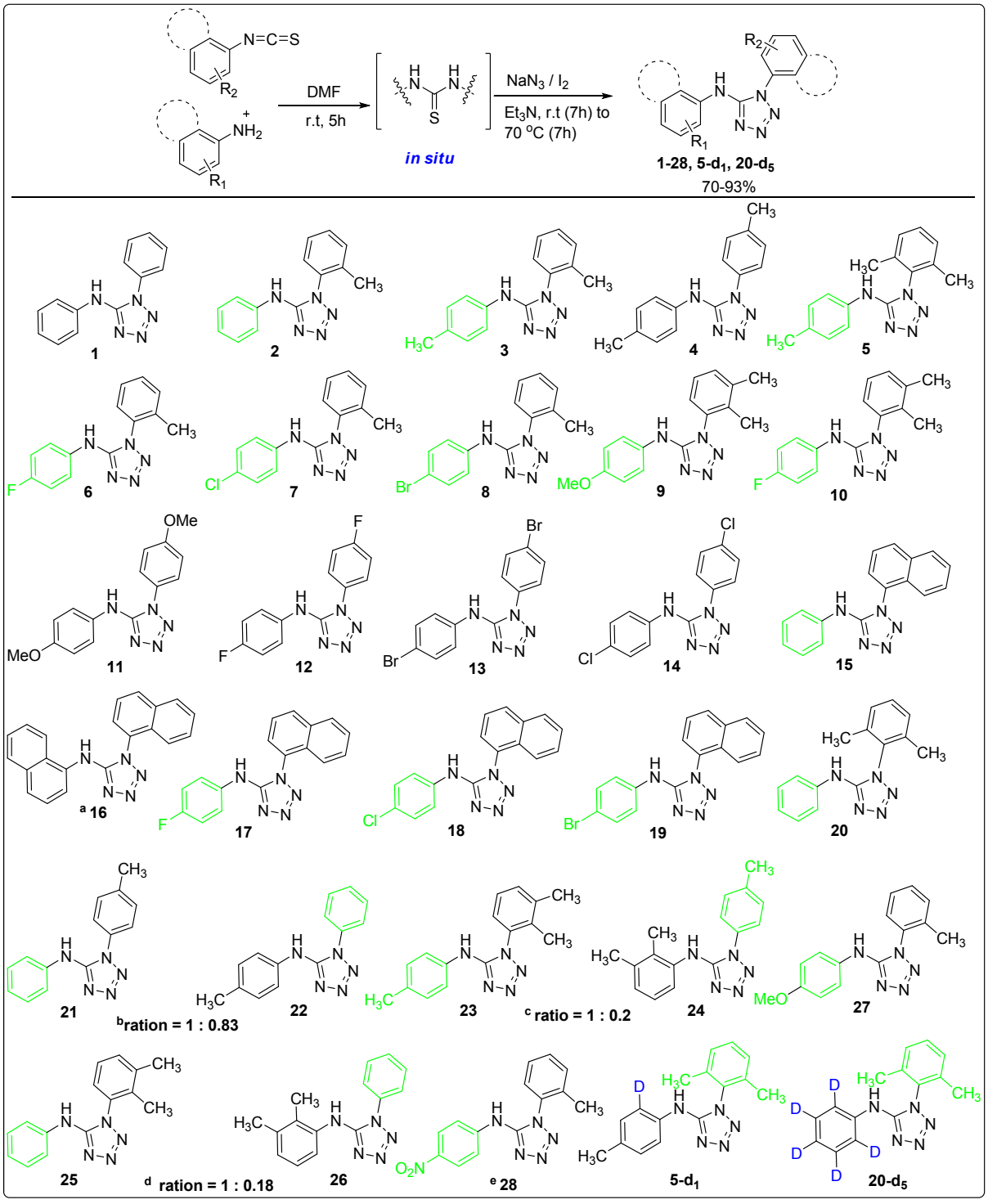
Spectral data:

p-toluidine-d_1: Yellow solid, Mp: 110 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00-6.98 (m, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 3.54 (s, 2H), 2.26 (s, 3H);

Synthesis of *N*,1-diaryl-1*H*-tetrazol-5-amines (1-28, 5-d_1& 20-d_5):

N,1-diaryl-1*H*-tetrazol-5-amines were synthesized as follows according to reported procedure[2] with minor changes. To a solution of aryl isothiocyanate (2.2 mmol) in DMF (10 mL) was added aniline (1 equiv.) and stirred for 5h at room temperature. Formation of thiourea was confirmed by TLC. NaN_3 (3 eqiv.) was added to the reaction mixture followed by I_2 (1.1 equiv.) in two portions in 15 min. Then Et_3N (3 eqiv.) was added drop wise and stirred at room temperature for 7h and 7h at 70^{o}C for complete conversion. Reaction was monitored by TLC. Reaction mixture was cooled to r.t and treated with sodium thiosulfate solution followed by extraction with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4. The crude product was obtained upon concentration under reduced pressure and was purified by flash column chromatography.

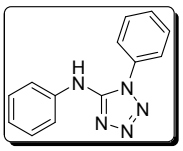
Table SI.1. Synthesis of *N*,1-diaryl-1*H*-tetrazol-5-amines:



Note: Green colored part comes from arylisothiocyanate,[a]**16** was isolated in 52% yield, [b]ratio(by NMR) of **21**&**22**, [c]ratio (by NMR) of **23**&**24**, ,[d]ratio (by NMR) of **25**&**26**, [e]**28** was isolated in 65% yield.

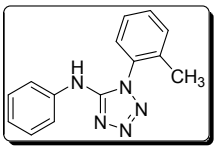
Spectral data for *N*,1-diaryl-1*H*-tetrazol-5-amines :

***N*,1-Diphenyl-1*H*-tetrazol-5-amine (1)[2]:**



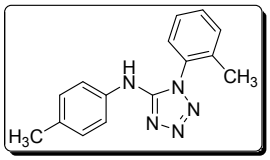
1: White solid, Mp: 156-158 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65-7.60 (m, 3H), 7.55-7.52 (m, 4H), 7.36-7.33 (m, 2H), 7.10-7.08 (m, 1H), 6.47 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 138.1, 132.7, 130.7, 129.5, 124.9, 123.6, 118.2; HRMS (ESI, m/z) Calcd for $C_{13}H_{11}N_5Na$ 260.0912 (M+Na), found 260.0913.

***N*-Phenyl-1-*o*-tolyl-1*H*-tetrazol-5-amine (2):**



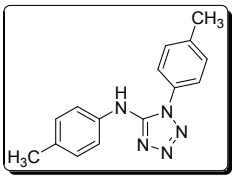
2: White solid, Mp: 179-181 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.53 (m, 3H), 7.49-7.43 (m, 2H), 7.37-7.33 (m, 3H), 7.10-7.06 (m, 1H), 6.09 (s, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 138.1, 136.5, 132.4, 131.6, 131.0, 129.4, 127.9, 127.4, 123.5, 118.0, 17.5; HRMS (ESI, m/z) Calcd for $C_{14}H_{13}N_5Na$ 274.1069 (M+Na), found 274.1053.

1-*o*-Tolyl-*N*-*p*-tolyl -1*H*-tetrazol-5-amine (3):



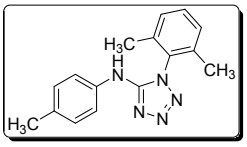
3: White solid, Mp: 154-156 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.50 (m, 1H), 7.47-7.41 (m, 4H), 7.34-7.32 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.08 (s, 1H), 2.31 (s, 3H), 2.16 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 136.5, 135.6, 133.1, 132.3, 131.5, 129.9, 127.9, 127.4, 124.4, 118.2, 20.8, 17.5; HRMS (ESI, m/z) Calcd for $C_{15}H_{15}N_5Na$ 288.1225 (M+Na), found 288.1225.

***N*,1-Bis(*p*-tolyl) -1*H*-tetrazol-5-amine (4)[3]:**



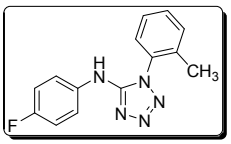
4: White solid, Mp: 156-158 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.37 (m, 6H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 2.47 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ151.9, 141.1, 135.6, 133.1, 131.2, 130.1, 129.9, 124.9, 118.3, 21.4, 20.8; HRMS (ESI, m/z) Calcd for $C_{15}H_{15}N_5Na$ 288.1225 (M+Na), found 288.1222.

1-(2,6-Dimethylphenyl)-*N*-*p*-tolyl -1*H*-tetrazol-5-amine (5)[1]:



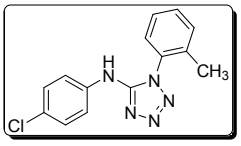
5: White solid, Mp: 182-184 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 744-7.39 (m, 3H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.89 (s, 1H), 2.31 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 137.2, 135.6, 133.2, 131.5, 129.99, 129.95, 129.4, 118.2, 20.8, 17.6; HRMS (ESI, m/z) Calcd for $C_{16}H_{18}N_5$ 280.1562 (M+H), found 280.1570.

***N*-(4-Fluorophenyl)-1-*o*-tolyl- 1*H*-tetrazol-5-amine (6):**



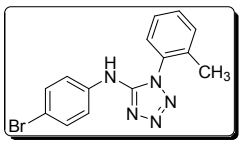
6: White solid, Mp: 149-151 °C: 110 °C, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.27 (s, 1H), 7.68-7.64 (m, 2H), 7.59-7.44 (m, 4H), 7.19-7.13(m, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.7, 156.3, 152.9, 136.1, 135.6, 131.6, 131.4, 130.9, 128.0, 127.4, 120.0, 119.9, 115.4, 115.2, 16.9; HRMS (ESI, m/z) Calcd for $C_{14}H_{12}N_5FNa$ 292.0974 (M+Na), found 292.0997.

***N*-(4-Chlorophenyl)-1-*o*-tolyl- 1*H*-tetrazol-5-amine (7):**



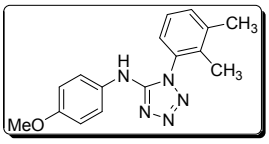
7: White solid, Mp: 166-168 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.50 (m, 3H), 7.49-7.43(m, 2H), 7.35-7.33 (m, 1H), 7.30 (AA^{l}BB^l pattern *J* = 9.0 Hz, 2H), 6.17 (s, 1H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 136.7, 136.5, 132.4, 131.7, 130.9, 129.4, 128.5, 128.0, 127.4, 119.3, 17.5; HRMS (ESI, m/z) Calcd for $C_{14}H_{13}N_5Cl$ 286.0859 (M+H), found 286.0870.

***N*-(4-Bromophenyl)-1-*o*-tolyl- 1*H*-tetrazol-5-amine (8):**



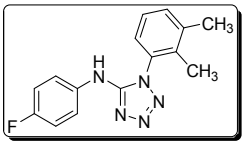
8: White solid, Mp: 174-176 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 1H),7.48-7.43 (m, 6H), 7.34-7.32 (m, 1H), 6.20 (s, 1H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 137.2, 136.6, 132.4, 132.3, 131.8. 130.8, 128.0, 127.4, 119.6, 116.0, 17.5; HRMS (ESI, m/z) Calcd for $C_{14}H_{13}N_5Br$ 330.0354 (M+H), found 330.0367.

1-(2,3-Dimethylphenyl)-*N*--(4-methoxyphenyl)-1*H*-tetrazol-5-amine (9):



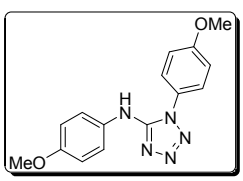
9: Pale yellow solid, Mp: 164-166 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.39 (m, 3H), 7.31 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 6.86 (d, J = 9.2 Hz, 2H), 5.97 (s, 1H), 3.78 (s, 3H), 2.39 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ156.0, 153.0, 140.0, 135.1, 132.8, 131.4, 131.1, 127.2, 125.1, 120.3, 114.6, 55.7, 20.5, 14.2; HRMS (ESI, m/z) Calcd for $C_{16}H_{18}N_5O$ 296.1511 (M+H), found 296.1517.

1-(2,3-Dimethylphenyl)-*N*--(4-fluorophenyl)-1*H*-tetrazol-5-amine (10):



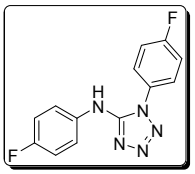
10: White solid, Mp: 144-146 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.49 (m, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.34-7.30 (m, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.04-7.00 (m, 2H), 6.14 (s, 1H), 2.39 (s,3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 140.1, 135.1, 134.2, 133.0, 130.9, 127.3, 125.0, 119.98,119.90, 116.2, 115.9, 20.5, 14.2; HRMS (ESI, m/z) Calcd for $C_{15}H_{14}N_5FNa$ 306.1131 (M+Na), found 306.1114.

***N*,1-Bis(4-methoxyphenyl)-1*H*-tetrazol-5-amine (11)[4]:**



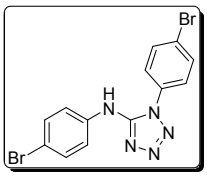
11: White solid, Mp: 156-158 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.40 (m, 4H), 7.09 (AA^lBB^l pattern, J = 8.8 Hz, 2H), 6.87 (AA^lBB^l pattern,J = 8.8 Hz, 2H), 6.18 (s, 1H), 3.89 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 156.1, 152.5, 131.4, 126.8, 125.2, 120.4, 115.7, 114.6, 55.8, 55.7; HRMS (ESI, m/z) Calcd for $C_{15}H_{15}N_5O_2Na$ 320.1123 (M+Na), found 320.1110.

***N*,1-Bis(4-fluorophenyl)-1*H*-tetrazol-5-amine (12) [4]:**



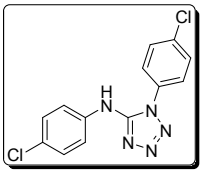
12: White solid, Mp: 176-178 °C, ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.32 (s, 1H), 7.77-7.73 (m, 2H), 7.66-7.62 (m, 2H), 7.51 (t, J = 8.8 Hz, 2H), 7.17 (t, J = 8.8 Hz, 2H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.0, 161.5, 158.8, 156.4, 152.6, 136.1, 129.34, 129.31, 128.7, 128.6, 120.2, 120.1, 117.0, 116.8, 115.5, 115.3; HRMS (ESI, m/z) Calcd for $C_{13}H_9N_5F_2Na$ 296.0724 (M+Na), found 296.0728.

***N*,1-Bis(4-bromophenyl)-1*H*-tetrazol-5-amine (13):**



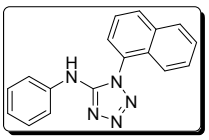
13: White solid, Mp: 189-191 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H), 7.45-7.41 (m, 6H), 6.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 137.0, 134.0, 132.4, 131.5, 126.5, 125.1, 120.0, 116.4; ; HRMS (ESI, m/z) Calcd for $C_{13}H_{10}N_5Br_2$ 393.9303 (M+H), found 393.9301.

***N*,1-Bis(4-chlorophenyl)-1*H*-tetrazol-5-amine (14) [4]:**



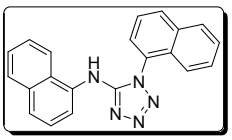
14: White solid, Mp: 156-158 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.4 Hz, 2H), 7.51-7.47 (m, 4H), 7.31 (d, J = 8.8 Hz, 2H), 6.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 137.0, 136.5, 131.0, 129.5, 128.9, 126.3, 119.7; HRMS (ESI, m/z) Calcd for $C_{13}H_{10}N_5Cl_2$ 306.0313 (M+H), found 306.0311.

1-(1-Naphthyl)-*N*--phenyl-1*H*-tetrazol-5-amine (15)[3]:



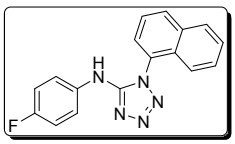
15: Pale grey solid, Mp: 199-202 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.04(d, *J* = 8.8 Hz, 1H), 7.70-7.58 (m, 4H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.4Hz, 1H), 7.34-7.30 (m, 2H), 7.08-7.04 (m, 1H), 6.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 138.0, 134.7, 132.1, 129.46, 129.42, 129.1, 128.8, 128.3, 127.9, 125.9, 125.6, 123.5, 121.9, 118.1; HRMS (ESI, m/z) Calcd for $C_{17}H_{13}N_5Na$310.1069 (M+ Na), found 310.1057.

***N*,1-bis(1-naphthyl)-1*H*-tetrazol-5-amine (16):**



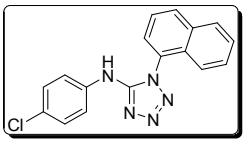
16: Grey solid, Mp: 161-163 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.09 (m, 2H), 8.04-8.02 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.68-7.59 (m, 5H), 7.56-7.54 (m, 1H), 7.45-7.41 (m, 2H), 7.34-7.32 (m, 2H), 6.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 134.6, 134.1, 132.8, 131.9, 128.9, 128.8, 128.7, 128.5, 127.8, 126.4, 126.2, 126.0, 125.9, 125.6, 125.5, 125.2, 121.9, 119.7, 117.9; HRMS (ESI, m/z) Calcd for $C_{21}H_{15}N_5Na$360.1225(M+ Na), found 360.1211.

***N*-(4-Fluorophenyl)-1-(1-naphthyl)-1*H*-tetrazol-5-amine (17):**



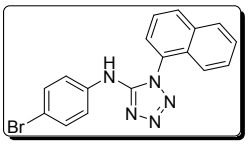
17: Pale grey solid, Mp: 151-153 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.69-7.58 (m, 4H), 7.47-7.39 (m, 3H), 7.02-6.97 (m, 2H), 6.15 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 157.8, 153.1, 134.6, 134.1, 132.0, 129.1, 128.83, 128.80, 128.2, 127.8, 125.8, 125.6, 121.8, 120.18, 120.10, 116.1, 115.9; HRMS (ESI, m/z) Calcd for $C_{17}H_{13}N_5F$ 306.1155(M+ H), found 306.1154.

***N*-(4-Chlorophenyl)-1-(1-naphthyl)-1*H*-tetrazol-5-amine (18):**



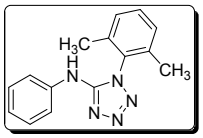
18: Pale yellow, Mp: 204-206 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.71-7.58 (m, 4H), 7.47 ($AA^{l}BB^{l}$ pattern,*J* = 9.2 Hz, 2H), 7.41-7.39 (m, 1H), 7.27 ($AA^{l}BB^{l}$ pattern,*J* = 9.2 Hz, 2H), 6.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 136.6, 134.7, 132.2, 129.4, 129.1, 128.94, 128.90, 128.5, 128.1, 127.9, 125.9, 125.6, 121.8, 119.4; HRMS (ESI, m/z) Calcd for $C_{17}H_{12}N_5ClNa$ 344.0679(M+ Na), found 344.0667.

***N*-(4-Bromophenyl)-1-(1-naphthyl)-1*H*-tetrazol-5-amine (19):**



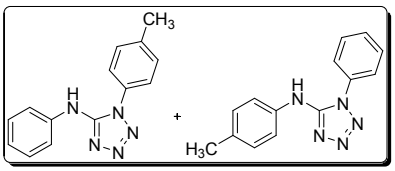
19: Half white solid, Mp: 211-213 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.70-7.58 (m, 4H), 7.45-7.38 (m, 5H), 6.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 137.1,134.7, 132.3, 132.2, 129.1, 128.9, 128.8, 128.1, 127.9, 125.9, 125.6, 121.8, 119.7, 116.0; HRMS (ESI, m/z) Calcd for $C_{17}H_{13}N_5Br$ 366.0354(M+ H), found 366.0366.

1-(2,6-Dimethylphenyl)-*N*-phenyl-1*H*-tetrazol-5-amine (20)[5]:



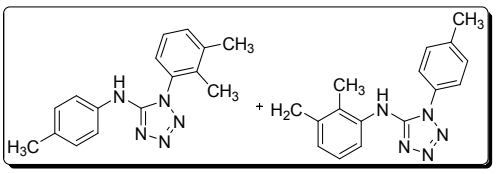
20: White solid, Mp: 196-200 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.36-7.32 (m, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.09-7.06 (m, 1H), 6.02 (s, 1H), 2.06 (s, 6H);^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 135.1, 137.2, 131.5, 129.9, 129.5, 129.4, 123.5, 118.1, 17.6; HRMS (ESI, m/z) Calcd for $C_{15}H_{15}N_5Na$ 288.1225 (M+Na), found 288.1230.

1-Phenyl-*N*-*p*-tolyl-1*H*-tetrazol-5-amine (21) &*N*-phenyl-1-*p*-tolyl-1*H*-tetrazol-5-amine(22)[2]:



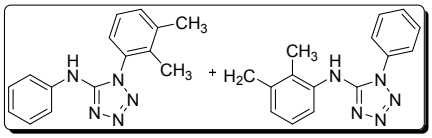
21 and 22 (in the ratio 1 : 0.83): White solid, Mp: 156-158 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.58 (m, 2.48H), 7.55-7.51 (m, 3.89H), 7.43-7.38 (m, 5.75H), 7.36-7.32 (m, 2.16H), 7.14 (d, *J* = 8.4 Hz, 1.68H), 7.09-7.05 (m, 1H), 6.40 (s, 1.74H), 2.47 (s, 3H), 2.31 (s, 2.49H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 151.7, 141.2, 138.1, 135.6, 133.3, 132.8, 131.2, 130.6, 130.5, 130.0, 129.9, 129.4, 124.9, 123.4, 118.5, 118.1, 21.4, 20.8; HRMS (ESI, m/z) Calcd for $C_{14}H_{13}N_5Na$ 274.1069(M+ Na), found 274.1062.

1-(2,3-Dimethylphenyl)-*N*-*p*-tolyl -1*H*-tetrazol-5-amine (23) & N-(2,3-dimethylphenyl)-1-*p*-tolyl -1*H*-tetrazol-5-amine (24):



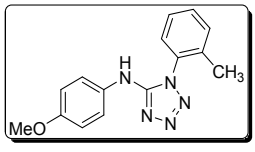
23 and 24 (in the ratio 1 : 0.2): White solid, Mp: 184-186 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 0.23H), 7.44-7.40 (m, 4.03H), 7.31(t, *J* = 7.6 Hz, 1H), 7.17-7.10 (m, 3.42H), 6.97-6.95 (m, 0.39H), 6.23 (s, 0.25H), 6.06 (s, 0.77H), 2.47 (s, 0.73H), 2.39 (s, 3.04H), 2.30 (s, 3.18H), 2.28 (s, 0.74H), 2.08 (s, 0.61H), 2.00 (s, 3.00H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 140.0, 135.7, 135.1, 133.0, 132.9, 131.1, 131.0, 129.95, 129.91, 129.88, 129.85, 127.2, 126.5, 125.0, 124.4, 118.6, 118.24, 118.20, 118.1, 21.4, 20.8, 20.7, 20.5, 14.2, 13.5; HRMS (ESI, m/z) Calcd for $C_{16}H_{18}N_5$280.1562(M+ H), found 280.1555.

1-(2,3-Dimethylphenyl)-*N*-phenyl-1*H*-tetrazol-5-amine (25)&N-(2,3-dimethylphenyl)-1-phenyl-1*H*-tetrazol-5-amine (26):



25 and 26 (1:0.18): White solid, Mp: 172-174 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.60 (m, 0.71H), 7.56-7.54 (m, 2.49H), 7.41 (d, *J* = 7.6 Hz, 1.03H), 7.35-7.30 (m, 3.16H), 7.18-7.16 (m, 1.26H), 7.08-7.05 (m, 1.08H), 6.96 (d, *J* = 7.2 Hz, 0.23H), 6.29 (s, 0.20H), 6.15 (s, 0.88H), 2.39 (s, 3.00H), 2.28 (s, 0.56H), 2.091 (s, 0.50H), 2.00 (s, 2.99H);^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 140.1, 138.2, 135.1, 132.9, 130.9, 130.6, 130.4, 129.48, 129.45, 129.41, 129.35, 127.30, 126.7, 126.5, 125.0, 124.4, 123.4, 118.9, 118.06, 118.02, 117.9, 20.7, 20.5, 14.2, 13.5;

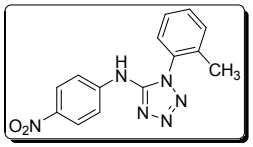
N-(4-Methoxyphenyl)-1-*o*-tolyl-1*H*-tetrazol-5-amine (27):



27: Pale yellow solid, Mp: 146-148 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.49 (m, 1H), 7.46-7.40 (m, 4H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.86 ($AA^{l}BB^{l}$ pattern, *J* = 9.2 Hz, 2H), 6.03 (s, 1H), 3.78, (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 152.8, 136.5, 132.3, 131.5, 131.3, 131.1, 127.9,

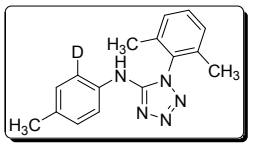
127.4, 120.4, 114.6, 55.6, 17.6; HRMS (ESI, m/z) Calcd for $C_{15}H_{15}N_5ONa$ 304.1174 (M+ Na), found 304.1201.

N-(4-Nitrophenyl)-1-*o*-tolyl-1*H*-tetrazol-5-amine (28):



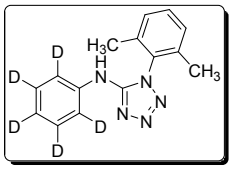
28: Brownish orange solid, Mp: 194196-158 °C, ^{1}H NMR (500 MHz, DMSO-d_6):δ 10.09 (s, 1H), 8.24 (AA^{1}BB^1 pattern,*J* = 9.0 Hz, 2H), 7.89 (AA^{1}BB^1 pattern,*J* = 9.0 Hz, 2H), 7.61-7.58 (m, 1H), 7.56-7.54 (m, 2H), 7.49-7.46 (m, 1H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 152.0, 146.0, 141.2, 135.6, 131.5, 131.4, 131.2, 128.0, 127.5, 125.2, 117.5, 16.9, HRMS (ESI, m/z) Calcd for $C_{14}H_{13}N_6O_2$ 297.1100 (M+ H), found 297.1088.

1-(2,6-Dimethylphenyl)-*N*-(*o*-deutero-*p*-tolyl)-1*H*-tetrazol-5-amine (5-d_1)[1]:



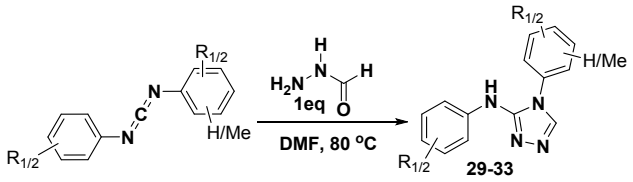
5-d_1: White solid, Mp: 187-190 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.15-7.14 (m, 2H), 5.85 (s, 1H), 2.31 (s, 3H), 2.06(s, 6H);^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 137.2, 135.62 (t, 135.68, 135.62, 135.5), 133.2, 131.5, 129.9, 129.8, 129.4, 118.2, 20.8, 17.6; HRMS (ESI, m/z) Calcd for $C_{16}H_{17}DN_5$ 281.1619(M+ H), found 281.1615;

1-(2,6-Dimethylphenyl)-*N*-(phenyl-d_5)-1*H*-tetrazol-5-amine (20-d_5):



5-d_1: White solid, Mp: 197-200 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 6.00 (s, 1H), 2.06 (s, 6H);^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 138.0, 137.1, 131.5, 129.9, 129.4, 128.9 (t, 129.1, 128.9, 128.6), 122.9 (t, 123.1, 122.9, 122.7), 117.7 (t, 117.9, 117.7, 117.4), 17.6; HRMS (ESI, m/z) Calcd for $C_{15}H_{11}D_5N_5$ 270.1641(M+ H), found 270.1645;

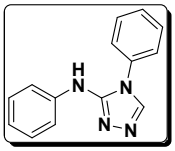
Synthesis of *N*,4-diaryl-4*H*-1,2,4-triazol-3-amines[4]:



N,N'-diphenylmethanediimine (1.6 mmol) and formichydrazide (1.2 equiv, 1.9 mmol) were suspended in DMF (8 mL) and stirred at 80°C for 5-7 h. Reaction was monitored by TLC . After complete consumption of starting material, reaction mixture was cooled to room temperature and diluted with EtOAc (15 mL). Resulted Organic mixture was extracted with water for two times. Organic layer was concentrated and crude product was purified by column chromatography.

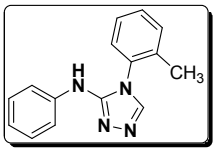
Spectral data for *N*,4-diaryl-4*H*-1,2,4-triazol-3-amines:

***N*,4-Diphenyl-4*H*-1,2,4-triazol-3-amine (29) [4]:**



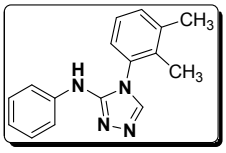
29: White solid,yield 73% (275 mg), Mp: 156-158 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.61-7.53 (m, 3H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.41-7.39 (m, 2H), 7.31-7.27 (m, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.07 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 140.0, 139.5, 132.7, 130.7, 130.0, 129.2, 125.7, 122.2, 117.4; HRMS (ESI, m/z) Calcd for $C_{14}H_{13}N_4$ 237.1140(M+ H), found 237.1167;

***N*-Phenyl-4-*o*-tolyl-4*H*-1,2,4-triazol-3-amine (30):**



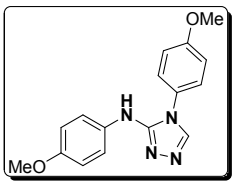
30: White solid,yield 45% (180 mg), Mp: 250-252 °C, ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.35 (s, 1H), 8.32 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 2H), 7.39-7.35 (m, 2H), 7.23-7.19 (m, 2H), 6.84 (t, *J* = 7.6 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.6, 141.5, 141.1, 135.4, 132.0, 131.3, 129.7, 128.6, 128.1, 127.2, 120.3, 116.7, 17.1; HRMS (ESI, m/z) Calcd for $C_{15}H_{14}N_4Na$ 273.1116(M+ Na), found 273.1102;

4-(2,3-Dimethylphenyl)-*N*-phenyl-4*H*-1,2,4-triazol-3-amine (31):



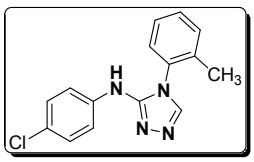
31: White solid,yield 61% (257 mg), Mp: 220-223 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.54-7.51 (m, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.30-7.26 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 5.78 (s, 1H), 2.38 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 140.0, 139.9, 139.3, 134.9, 132.2, 131.0, 129.2, 127.3, 125.5, 122.1, 117.3, 20.5, 14.2; HRMS (ESI, m/z) Calcd for $C_{16}H_{16}N_4Na$ 287.1273(M+ Na), found 287.1263;

***N*,4-Bis(4-methoxyphenyl)-4*H*-1,2,4-triazol-3-amine (32)[4]:**



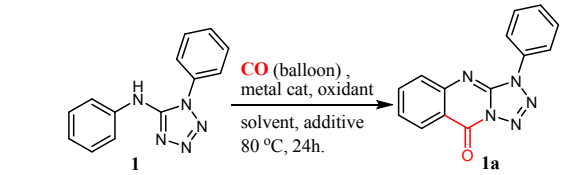
32: White solid,yield 52% (246 mg), Mp: 156-158 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.41 ($AA^{l}BB^{l}$ pattern,*J* = 7.2 Hz, 2H), 7.29 ($AA^{l}BB^{l}$ pattern,*J* = 7.2 Hz, 2H), 7.05 ($AA^{l}BB^{l}$ pattern,*J* = 7.2 Hz, 2H), 6.83 ($AA^{l}BB^{l}$ pattern,*J* = 7.2 Hz, 2H), 5.86 (s, 1H), 3.87 (s, 3H), 3.76 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$): δ 160.6, 155.1, 151.1, 140.2, 132.8, 127.4, 125.0, 119.3, 115.7, 114.5, 55.8, 55.6; HRMS (ESI, m/z) Calcd for $C_{16}H_{17}N_4O_2$ 297.1352(M+ H), found 297.1980;

***N*-(4-Chlorophenyl)-4-*o*-tolyl-4*H*-1,2,4-triazol-3-amine (33):**



33: White solid, yield 70% (318 mg), Mp: 210-213 °C,^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.52-7.48 (m, 3H), 7.45-7.39 (m, 2H), 7.29-7.27(m, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 5.84 (s, 1H), 2.15 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 139.8, 137.9, 136.3, 132.3, 131.0, 130.9, 129.1, 128.1, 127.9, 127.0, 118.6, 17.6; HRMS (ESI, m/z) Calcd for $C_{15}H_{14}N_4Cl$285.0907(M+ H), found 285.0910.

Optimizatio of reaction conditions of scheme 9



Entry	Metal cat.	Solvent	Additive	Oxidant	Yield (%)[a]
1	$Pd(OAc)_2$	1,4 Dioxane	-	$Cu(OAc)_2$	Trace
2	$Pd(OAc)_2$	1,4 Dioxane	TFA	$Cu(OAc)_2$	15
3	$Pd(OCOCF_3)_2$	1,4 Dioxane	"	$Cu(OAc)_2$	22
4	$Pd(OCOCF_3)_2$	CH_3CN	"	$Cu(OAc)_2$	25
5	$Pd(OCOCF_3)_2$	Toluene	"	$Cu(OAc)_2$	36
6	$Pd(OCOCF_3)_2$	CH_3CN	"	$K_2S_2O_8$	11
7	$Pd(OCOCF_3)_2$	Toluene	"	$K_2S_2O_8$	17
8[b]	$Pd(OCOCF_3)_2$	CH_3CN	"	$K_2S_2O_8$	15
9[b]	$Pd(OCOCF_3)_2$	Toluene	"	$K_2S_2O_8$	17
10[c]	$Pd(OCOCF_3)_2$	Toluene	"	$Cu(OAc)_2 + O_2$	47
11[d]	$Pd(OCOCF_3)_2$	Toluene	"	$Cu(OAc)_2$	44
12[d]	$Pd(OCOCF_3)_2$	Toluene	"	AgOAc	67

Reaction conditions: Pd cat. (10 mol%), Oxidant (1 equiv.), additive (1 equiv), solvent (4 mL),[a] = isolated yields, [b] = PPh_3 used as ligand, [c] = CO/O_2 (1:1), [d] = 3 equiv. of oxidant used.

References:

1. P. Sadhu, S. K. Alla, T. Punniyamurthy, *J. Org. Chem.***2013**, *78*, 6104.
2. R. Yella, N. Khatun, S. K. Rout, B. K. Patel, *Org. Biomol. Chem*. **2011**, *9*, 3235.
3. Y. Xie, D. Guo, X. Jiang, X. Pan, W. Wang, T. Jin, Z. Mi, *Tetrahedron Letters*. **2015**, *56*, 2533.
4. S. Guin, S. K. Rout, A. Gogoi, S. Nandi, K. K. Ghara, B. K. Patel, *Adv. Synth. Catal.***2012**, *354*, 2757.
5. P. Sadhu, S.K. Alla, T. Punniyamurthy, *J. Org. Chem.***2015**, *80*, 8245.

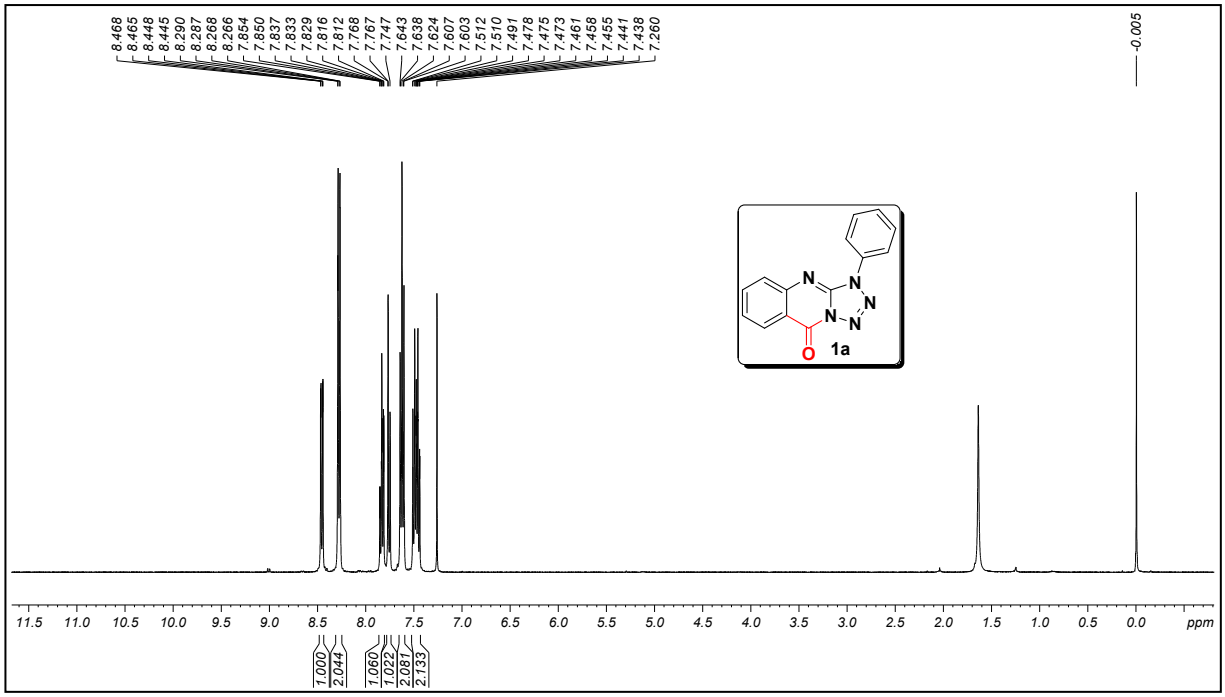


Figure S1. 400 MHz ^{1}H NMR spectrum of **1a** in $CDCl_3$

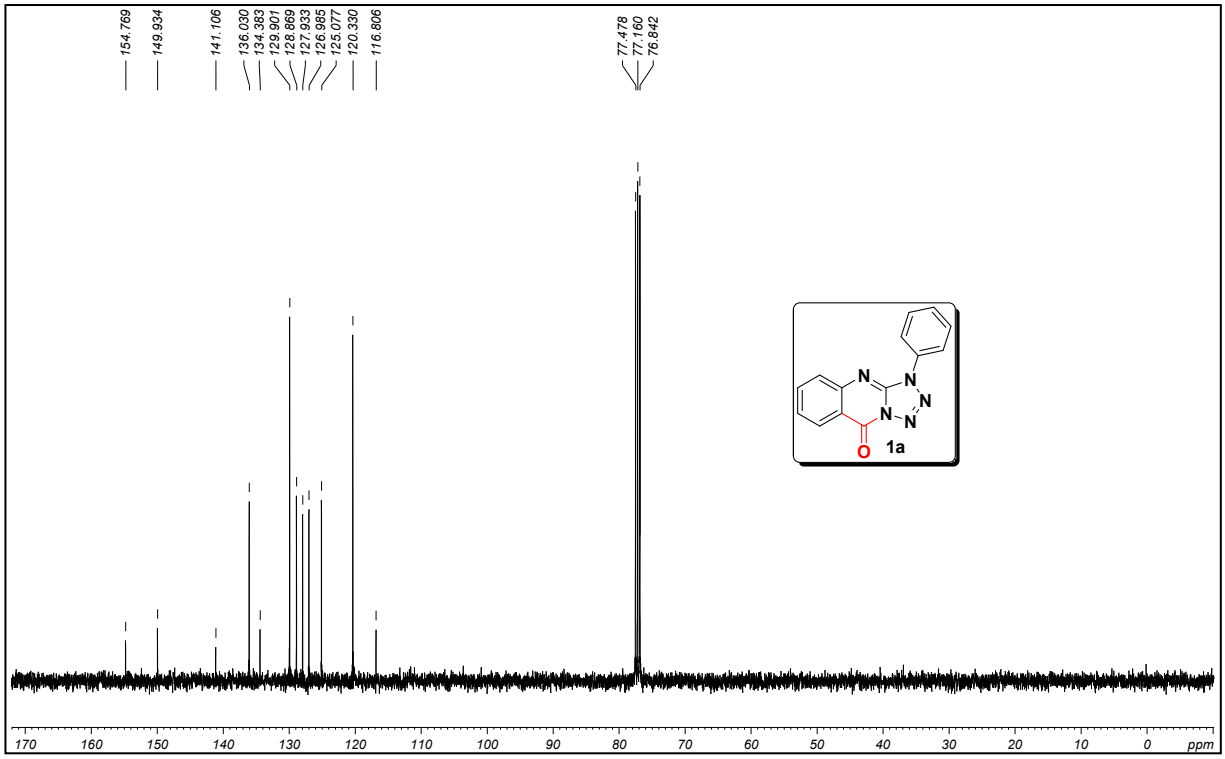


Figure S2. 100 MHz ^{13}C NMR spectrum of **1a** in $CDCl_3$

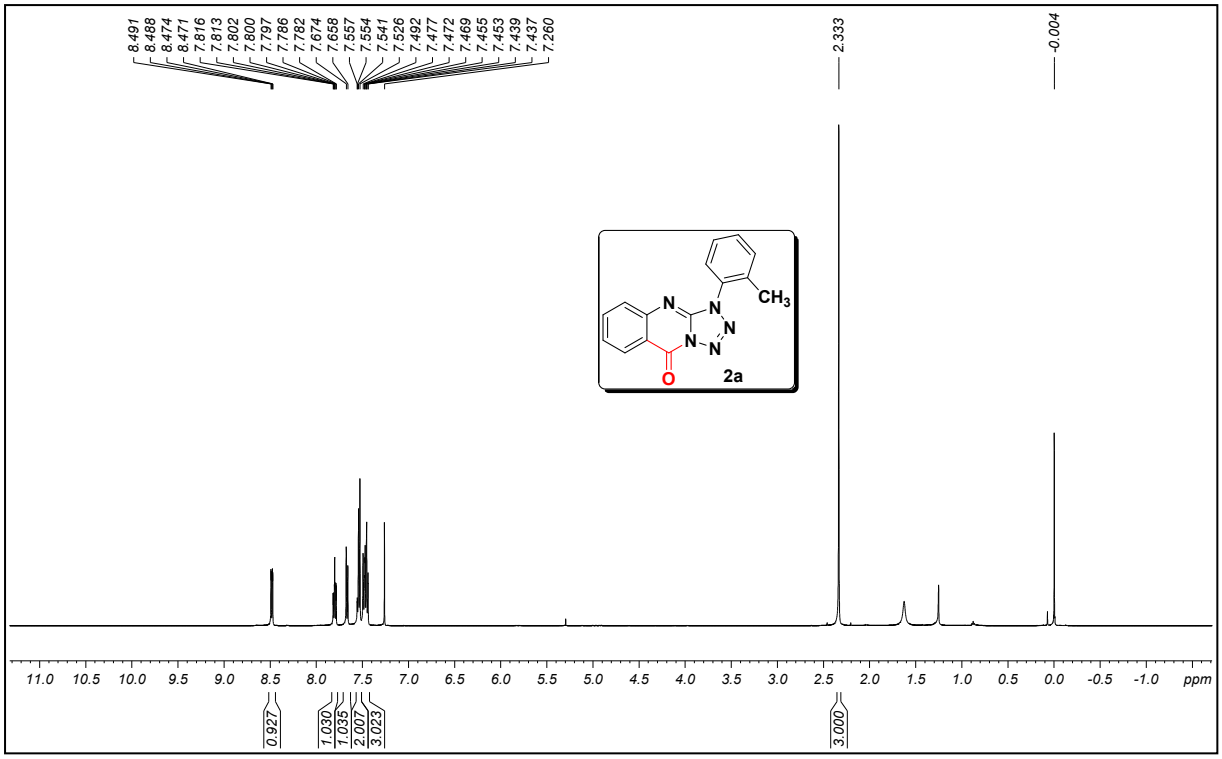


Figure S3. 500 MHz ^{1}H NMR spectrum of **2a** in $CDCl_3$

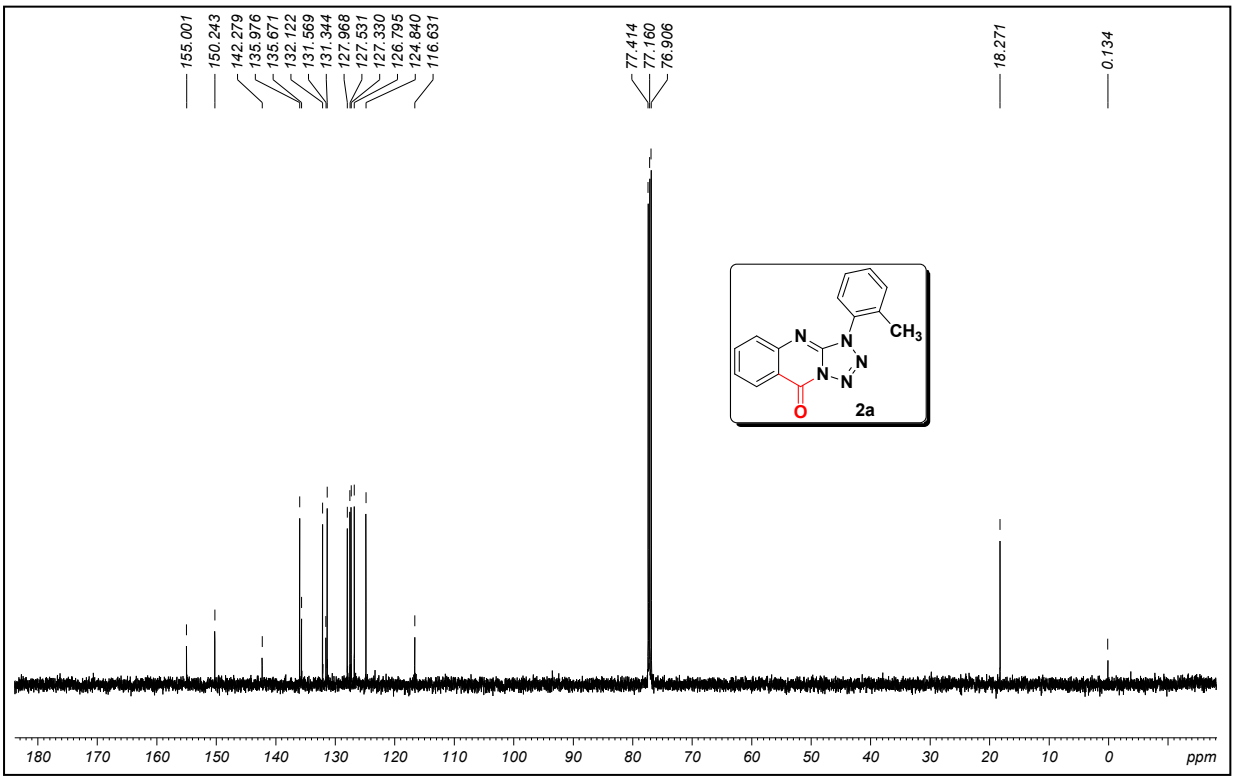


Figure S4. 125 MHz ^{13}C NMR spectrum of **2a** in $CDCl_3$

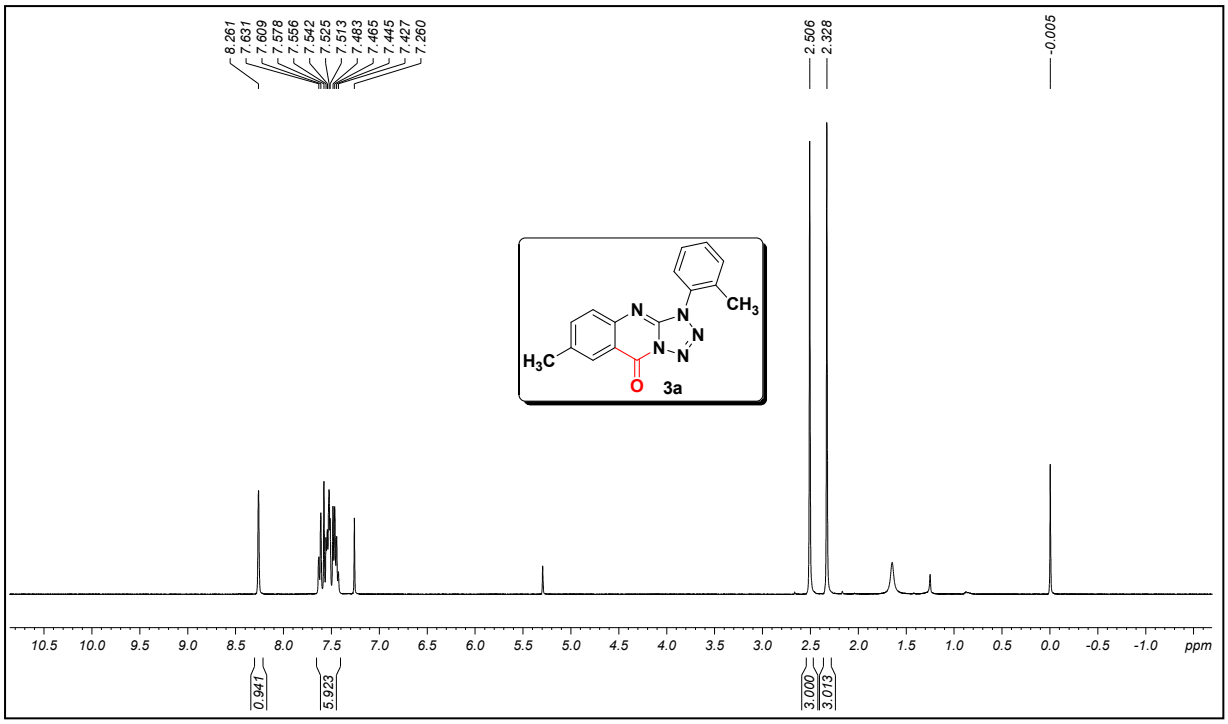


Figure S5. 400 MHz ^{1}H NMR spectrum of **3a** in $CDCl_3$

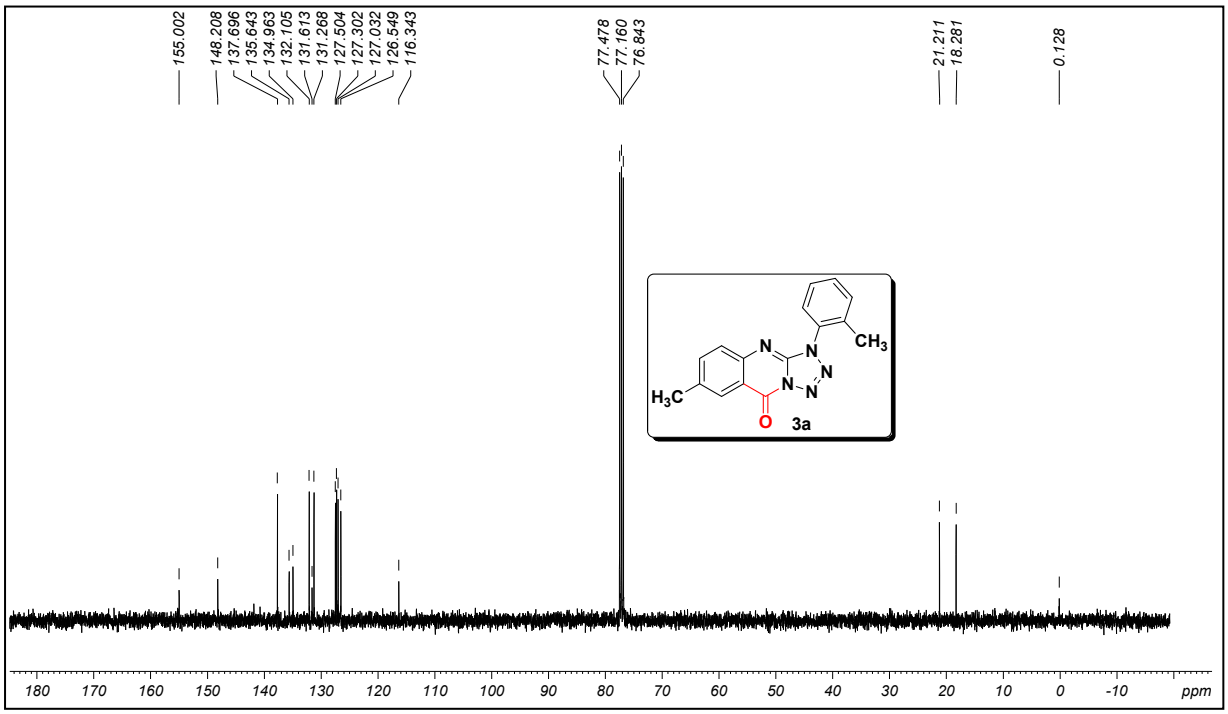
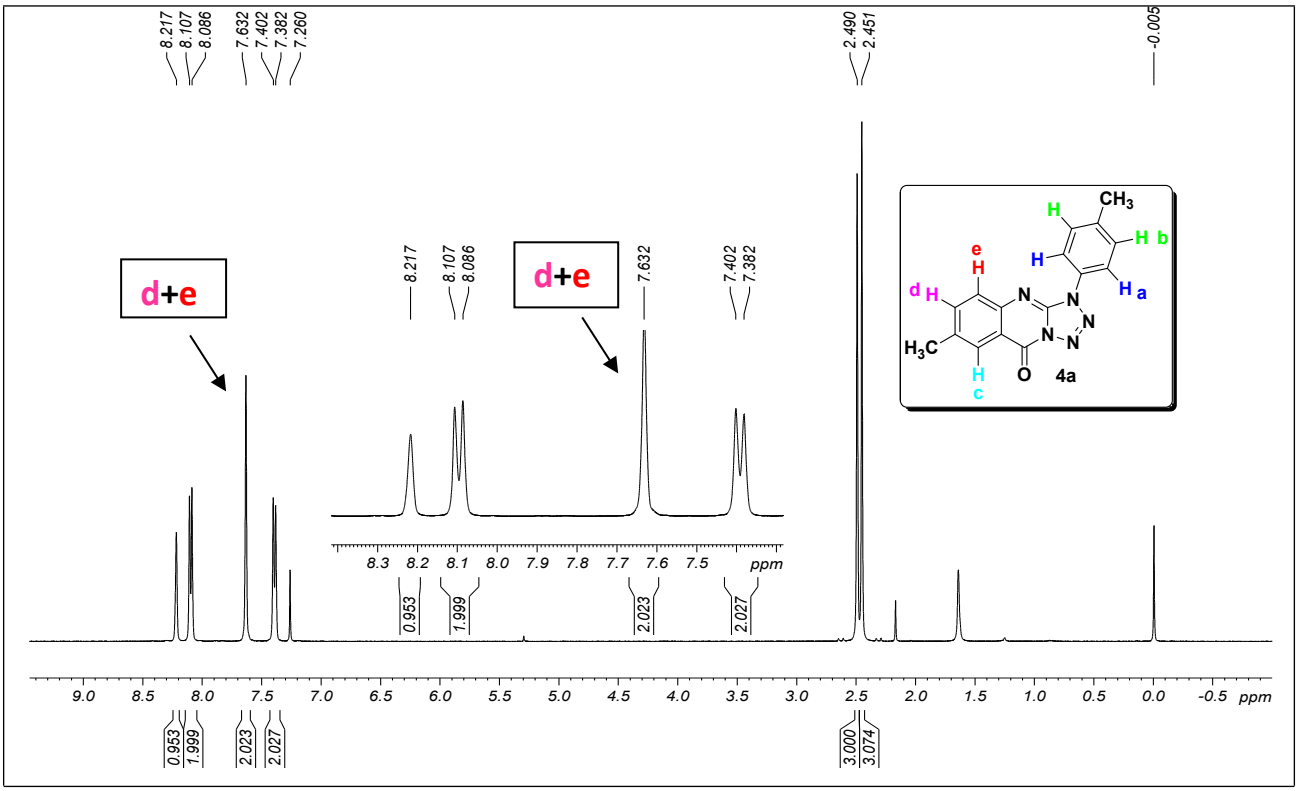


Figure S6. 100 MHz ^{13}C NMR spectrum of **3a** in $CDCl_3$

^{1}H NMR Spectrum of compound 4a in $CDCl_3$



^{1}H NMR spectrum of compound 4a with shift reagent in $CDCl_3$

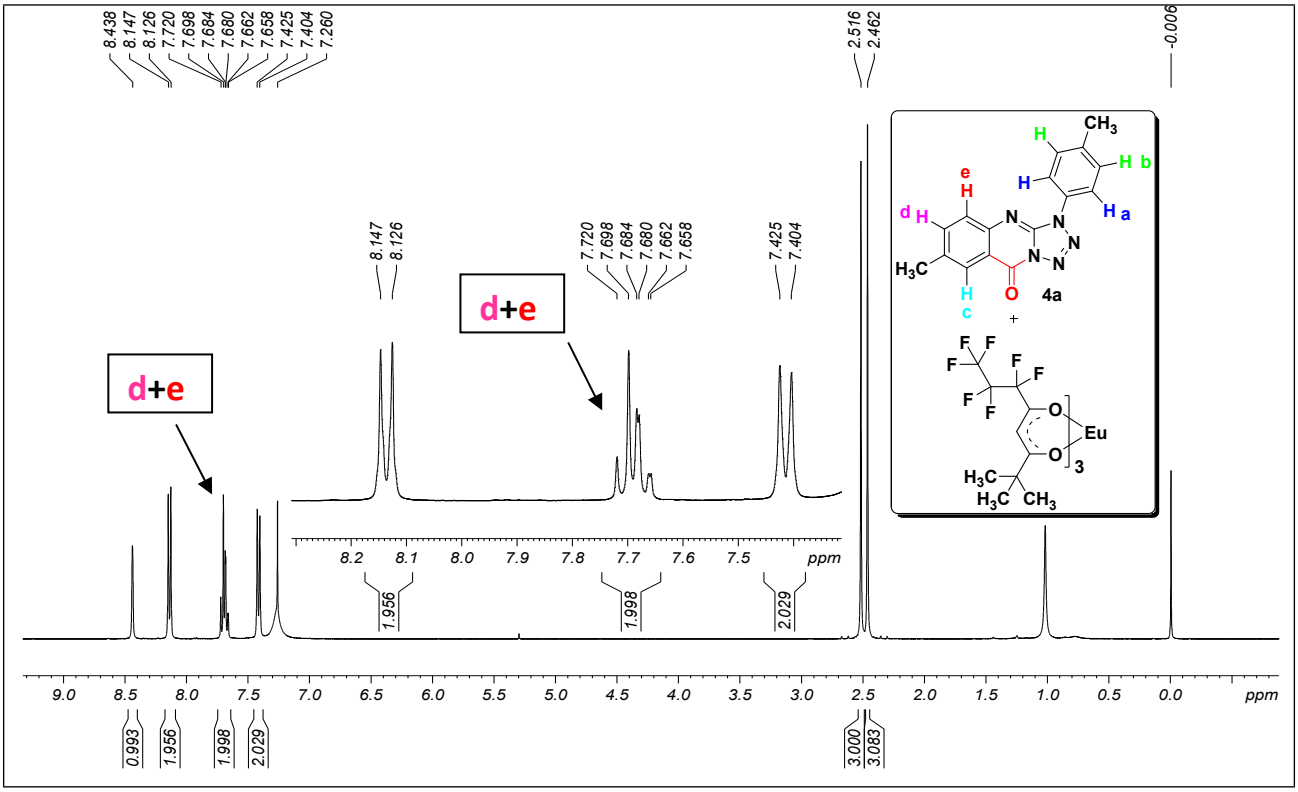


Figure S7. 400 MHz ^{1}H NMR spectrum of compound **4a** with and without shift reagent in CDCl3

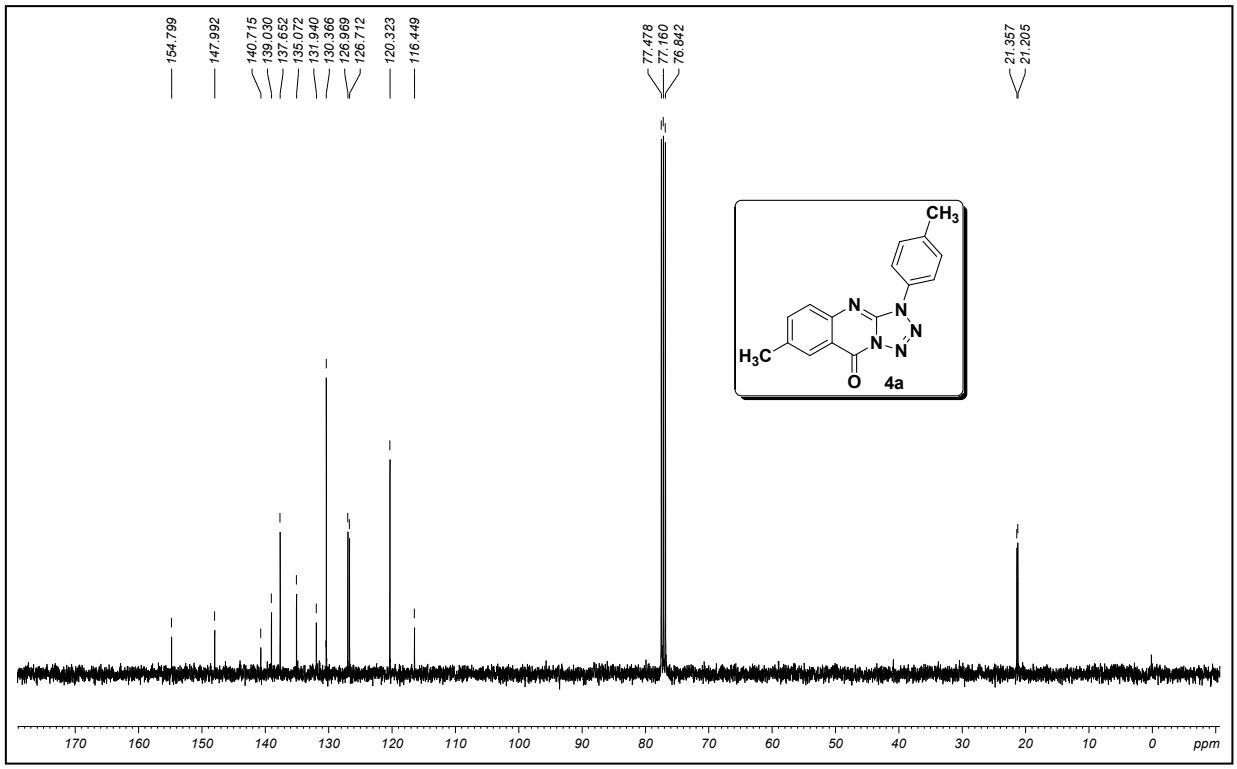


Figure S8. 100 MHz ^{13}C NMR spectrum of **4a** in $CDCl_3$

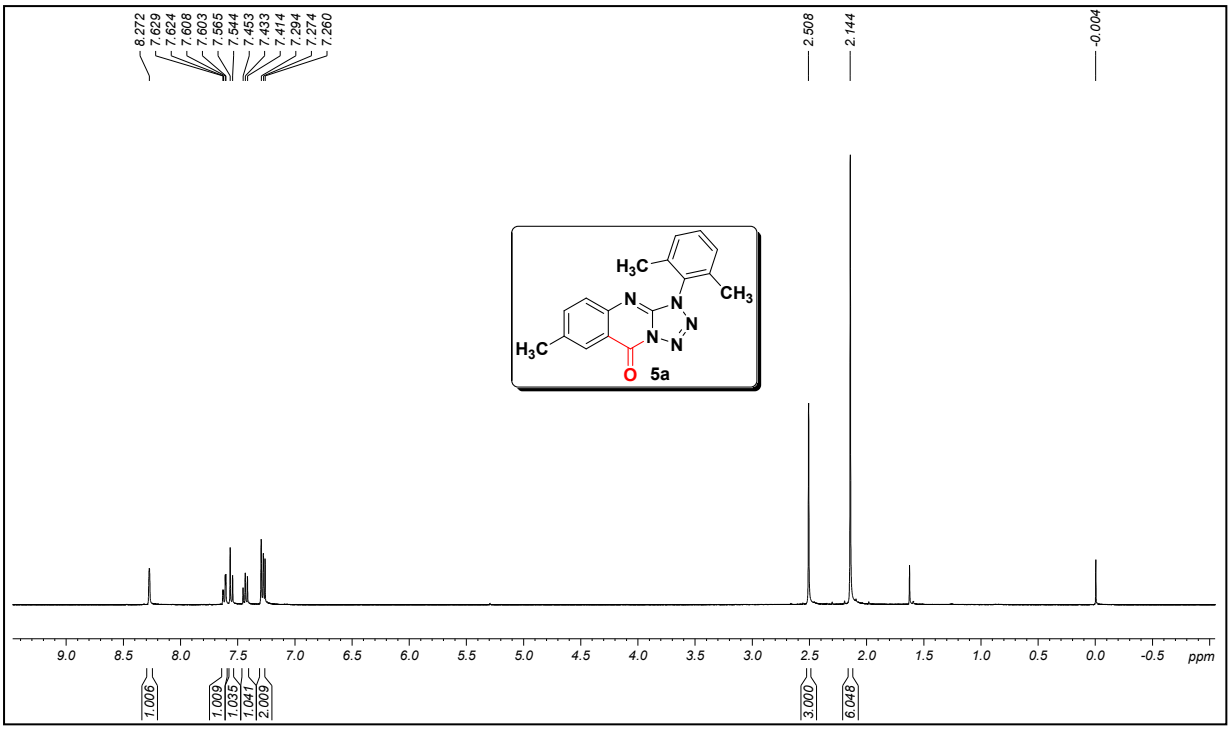


Figure S9. 400 MHz ^{1}H NMR spectrum of **5a** in $CDCl_3$

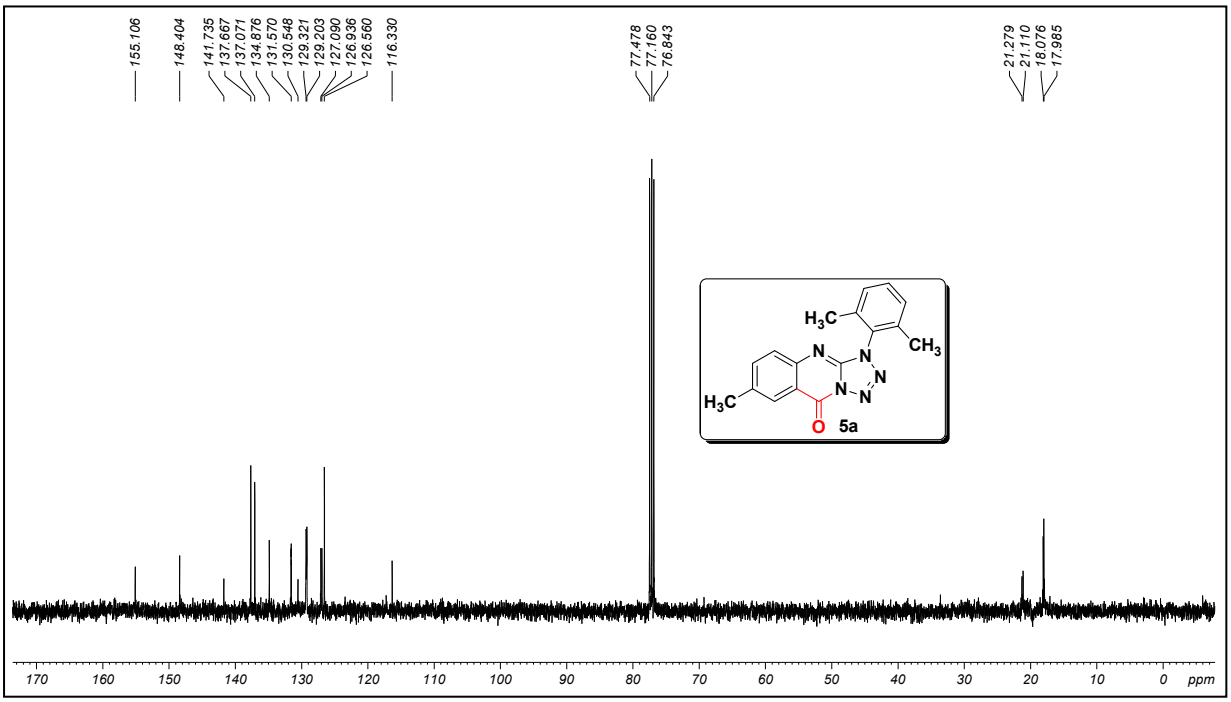


Figure S10. 100 MHz ^{13}C NMR spectrum of **5a** in $CDCl_3$

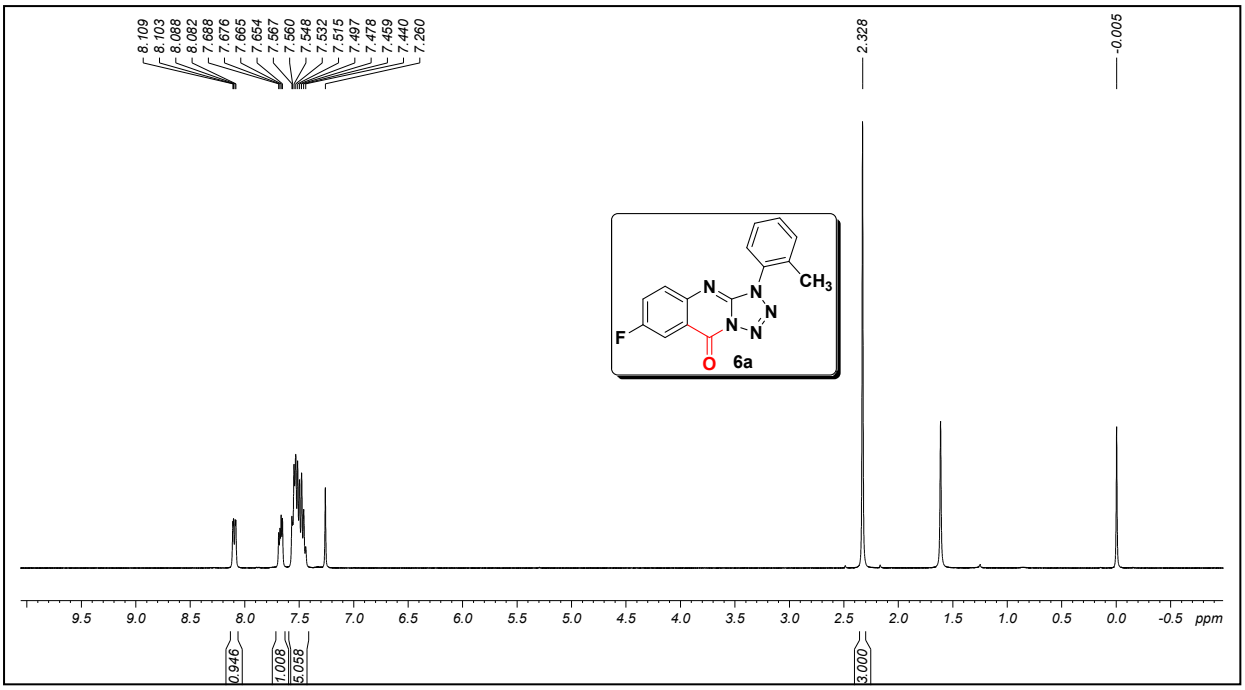


Figure S11. 400 MHz ^{1}H NMR spectrum of **6a** in $CDCl_3$

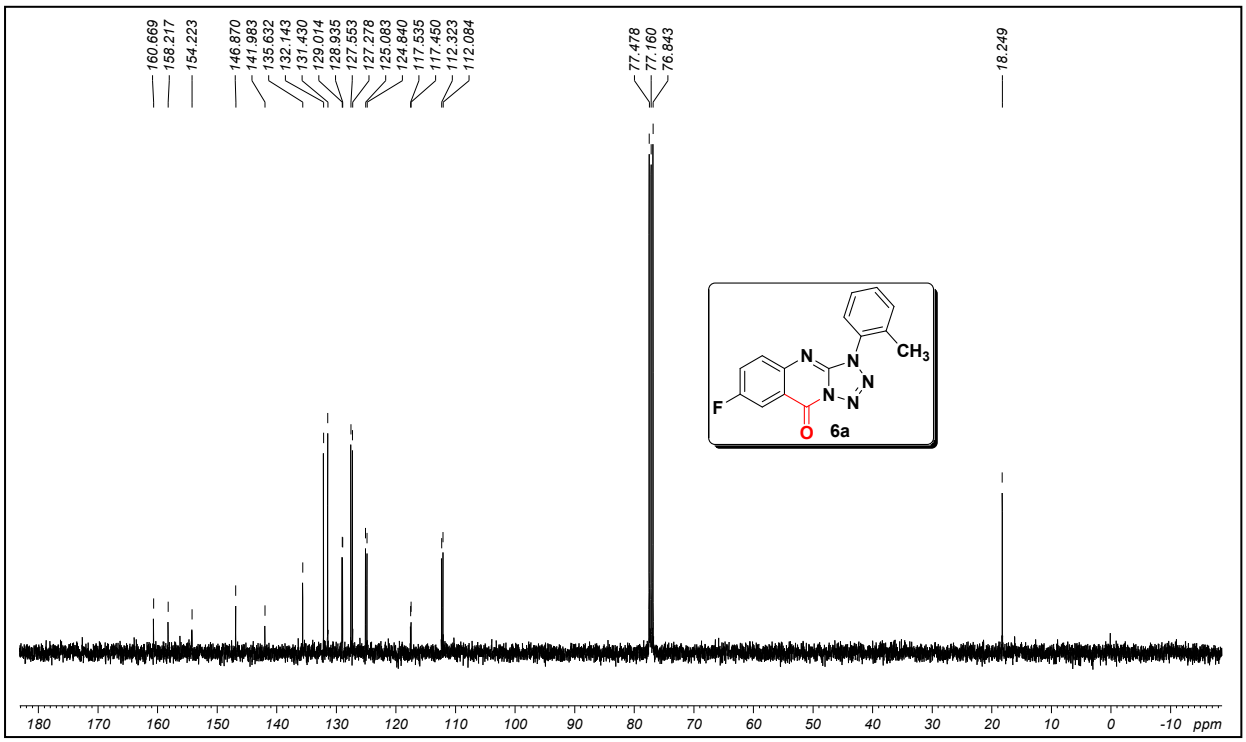


Figure S12. 100 MHz ^{13}C NMR spectrum of **6a** in $CDCl_3$

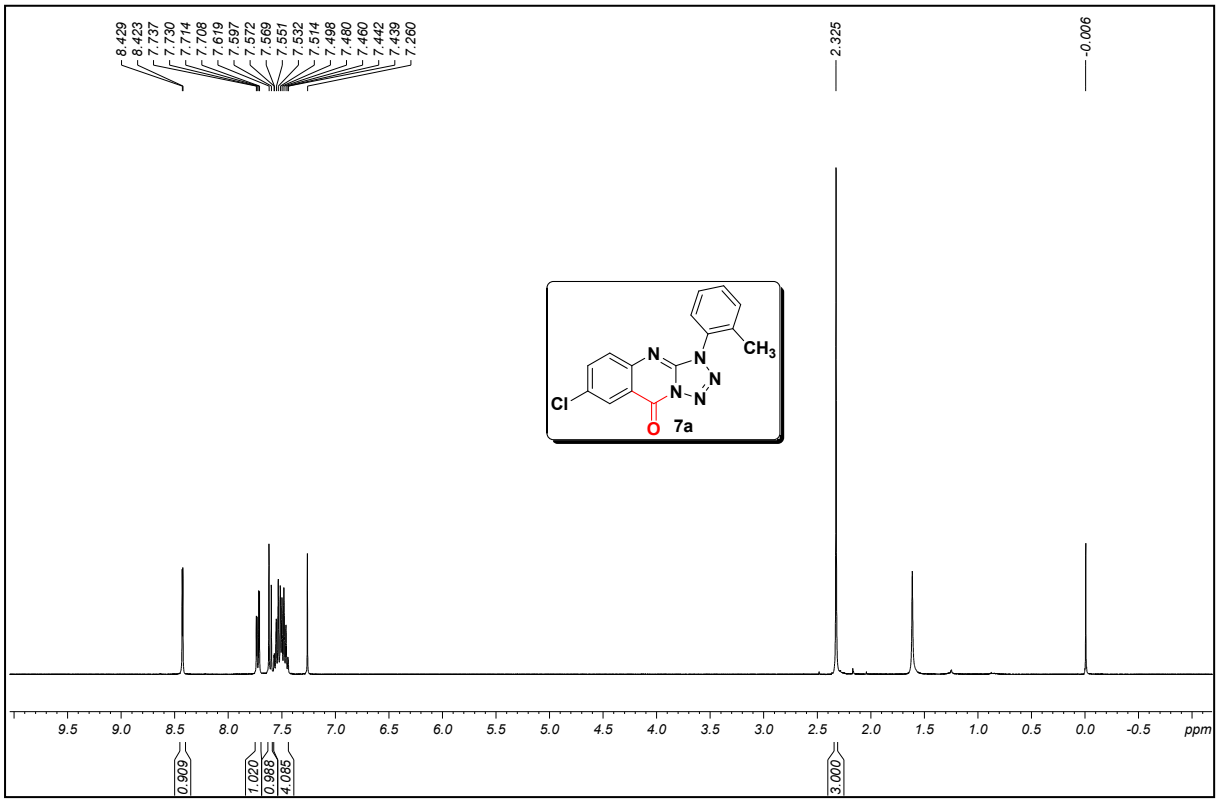


Figure S13. 400 MHz ^{1}H NMR spectrum of **7a** in $CDCl_3$

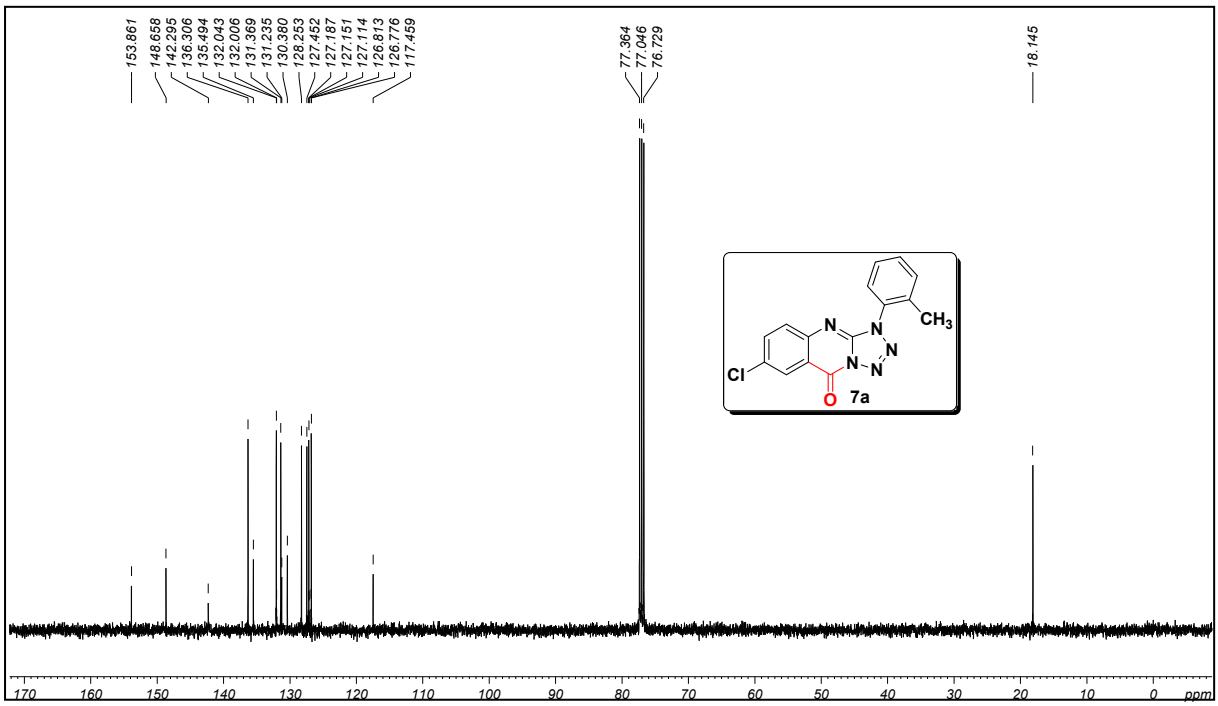


Figure S14. 100 MHz ^{13}C NMR spectrum of **7a** in $CDCl_3$

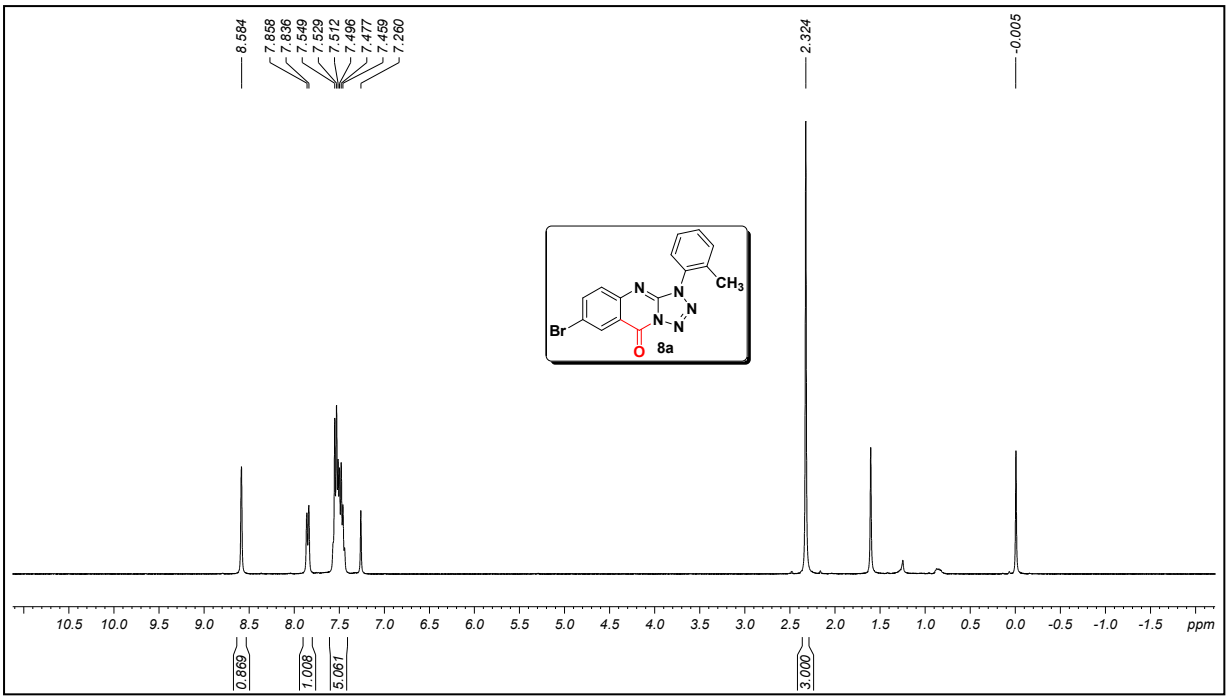


Figure S15. 400 MHz ^{1}H NMR spectrum of **8a** in $CDCl_3$

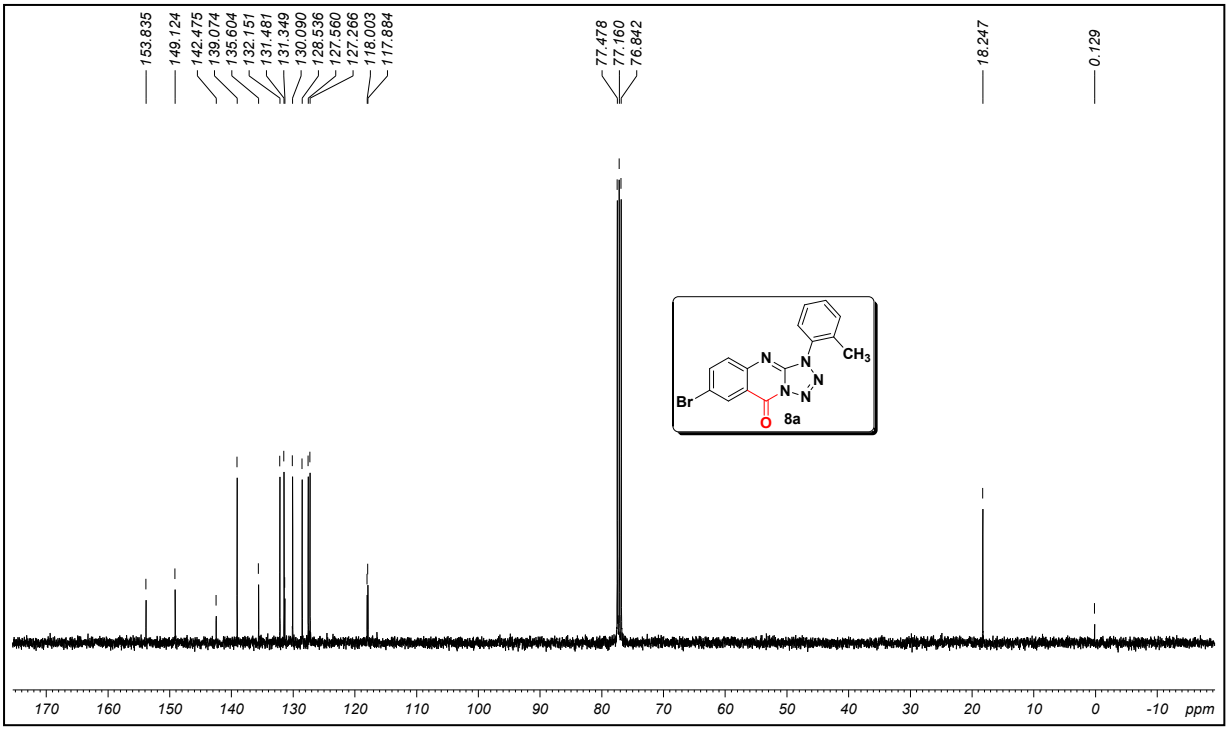


Figure S16. 100 MHz ^{13}C NMR spectrum of **8a** in $CDCl_3$

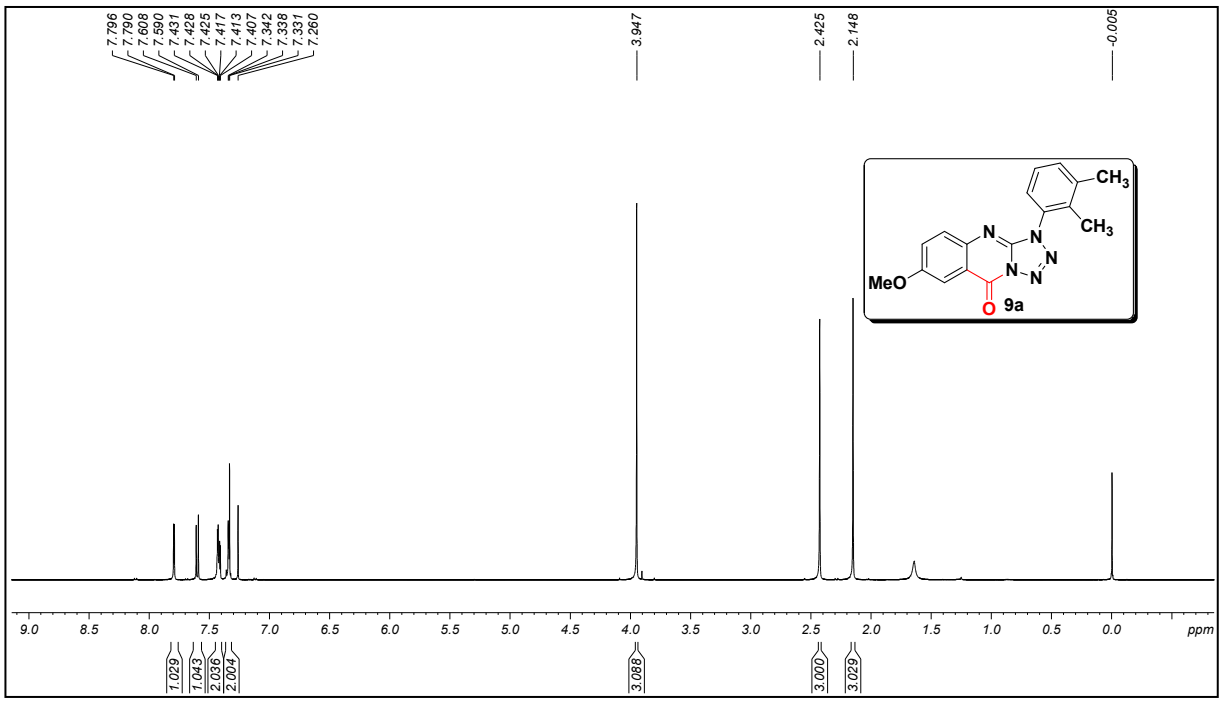


Figure S17. 500 MHz ^{1}H NMR spectrum of **9a** in $CDCl_3$

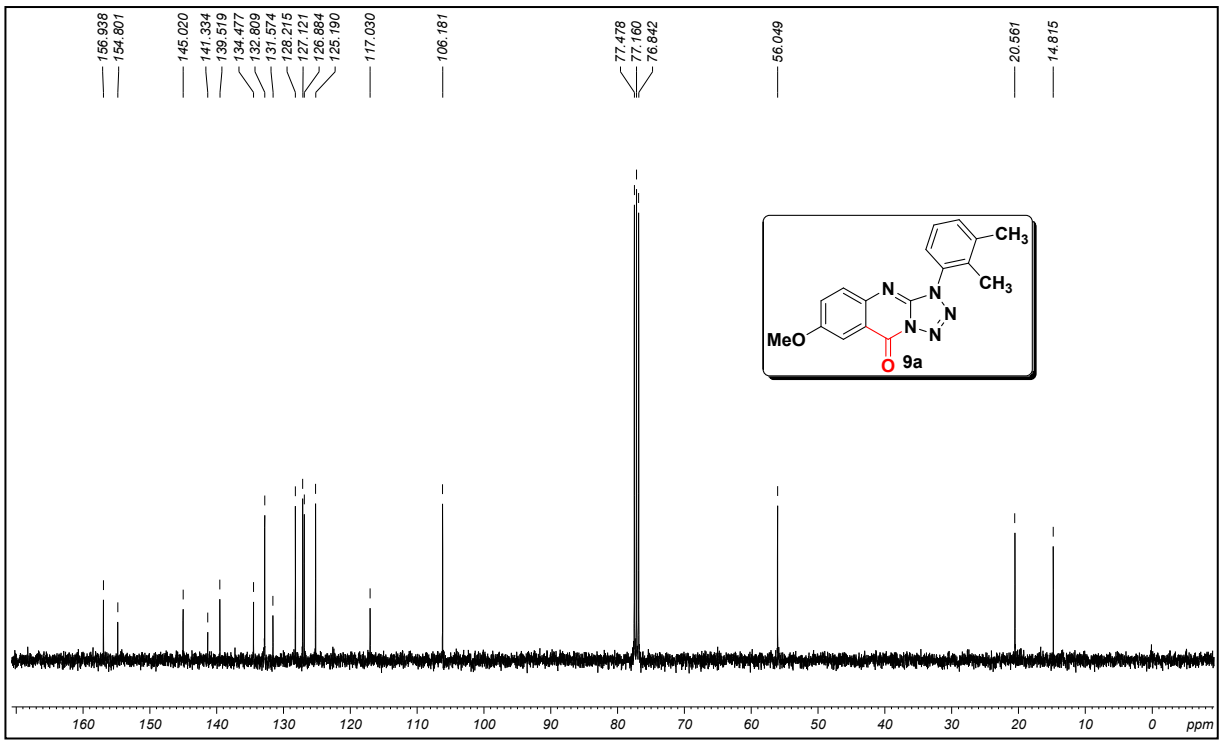


Figure S18. 100 MHz ^{13}C NMR spectrum of **9a** in $CDCl_3$

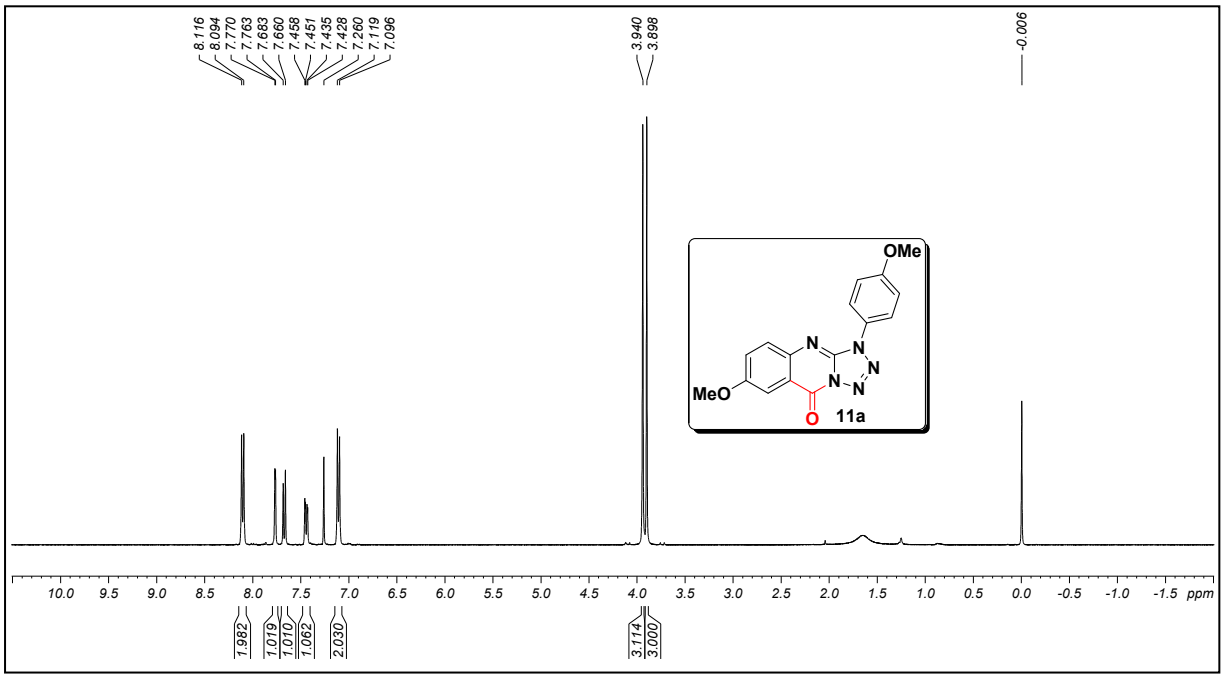


Figure S19. 400 MHz ^{1}H NMR spectrum of **11a** in $CDCl_3$

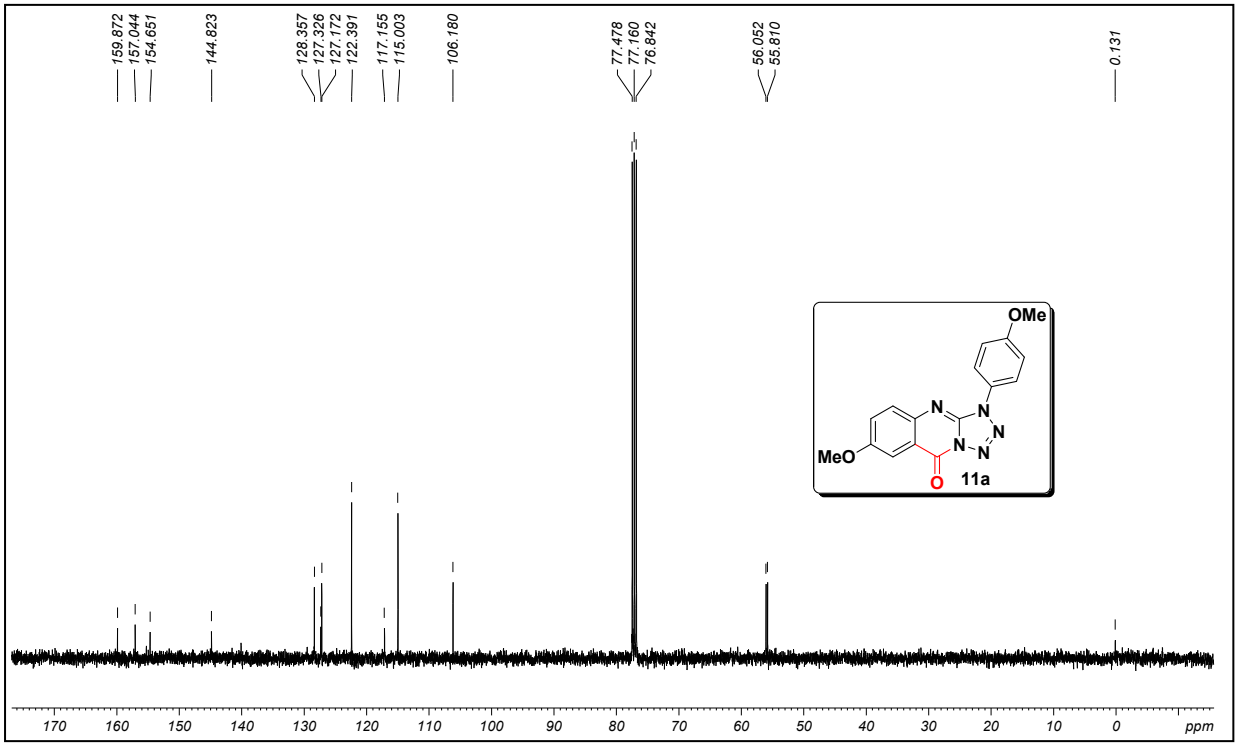


Figure S20. 100 MHz ^{13}C NMR spectrum of **11a** in $CDCl_3$

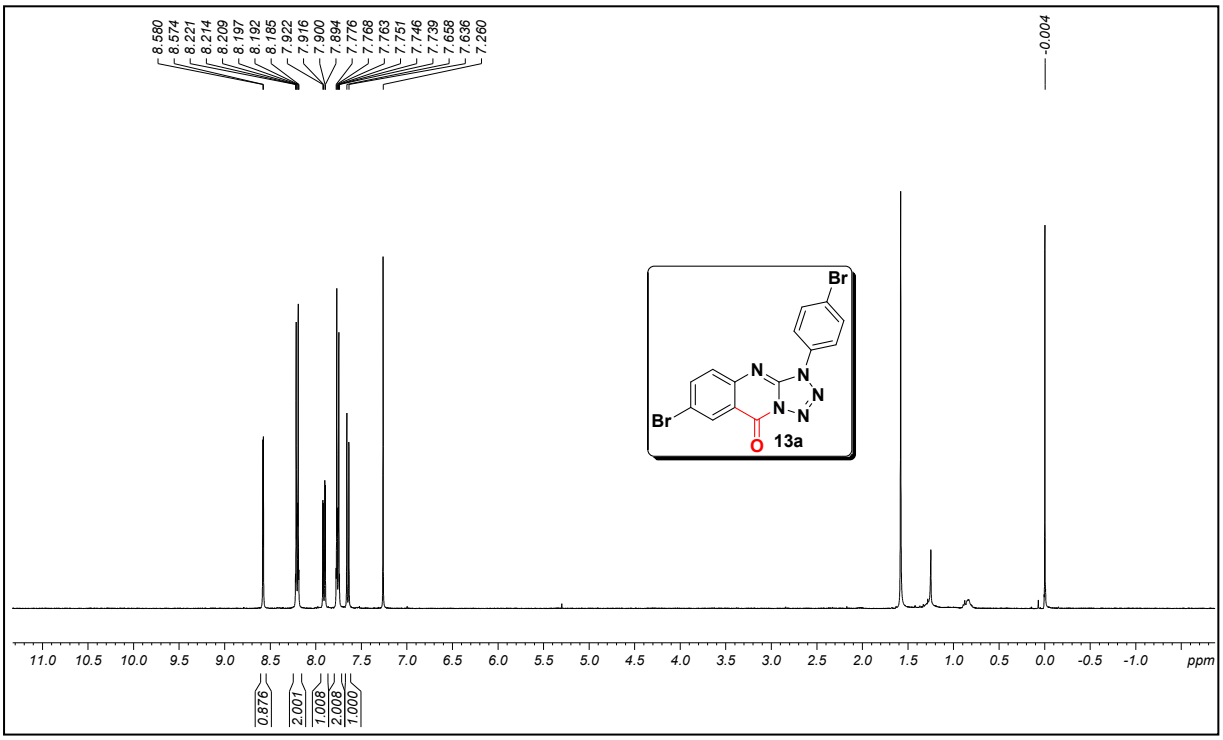


Figure S21. 400 MHz ^{1}H NMR spectrum of **13a** in $CDCl_3$

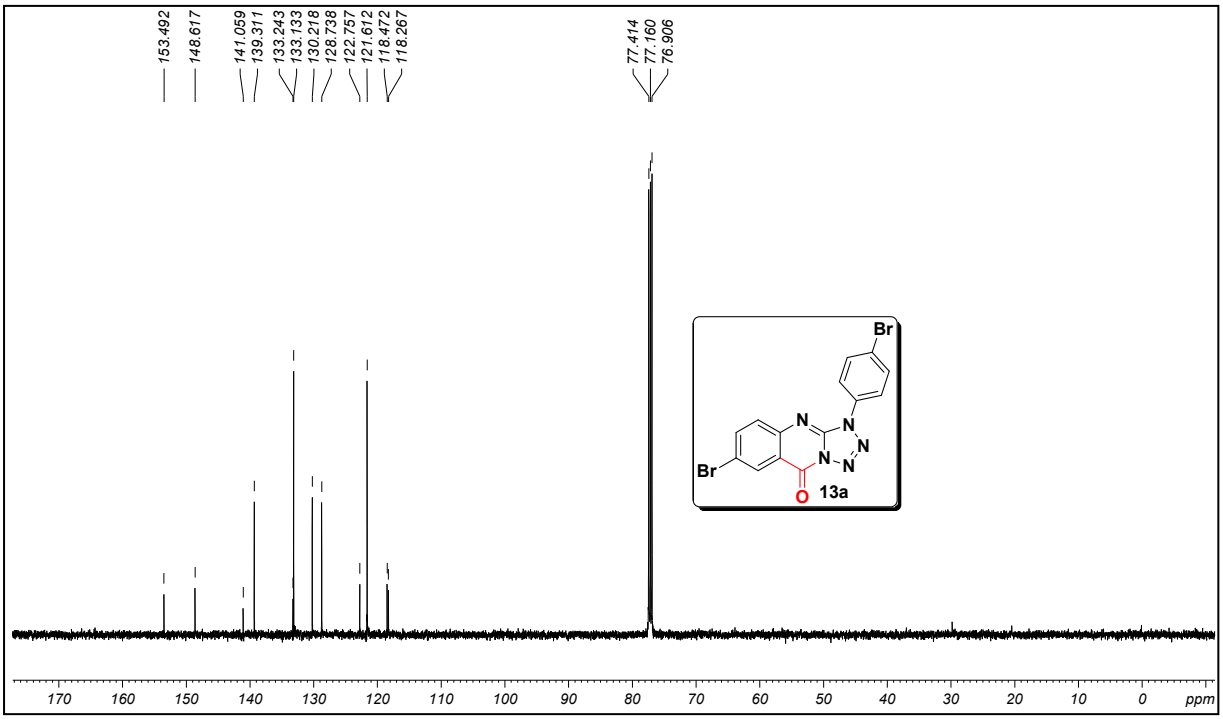


Figure S22. 125 MHz ^{13}C NMR spectrum of **13a** in $CDCl_3$

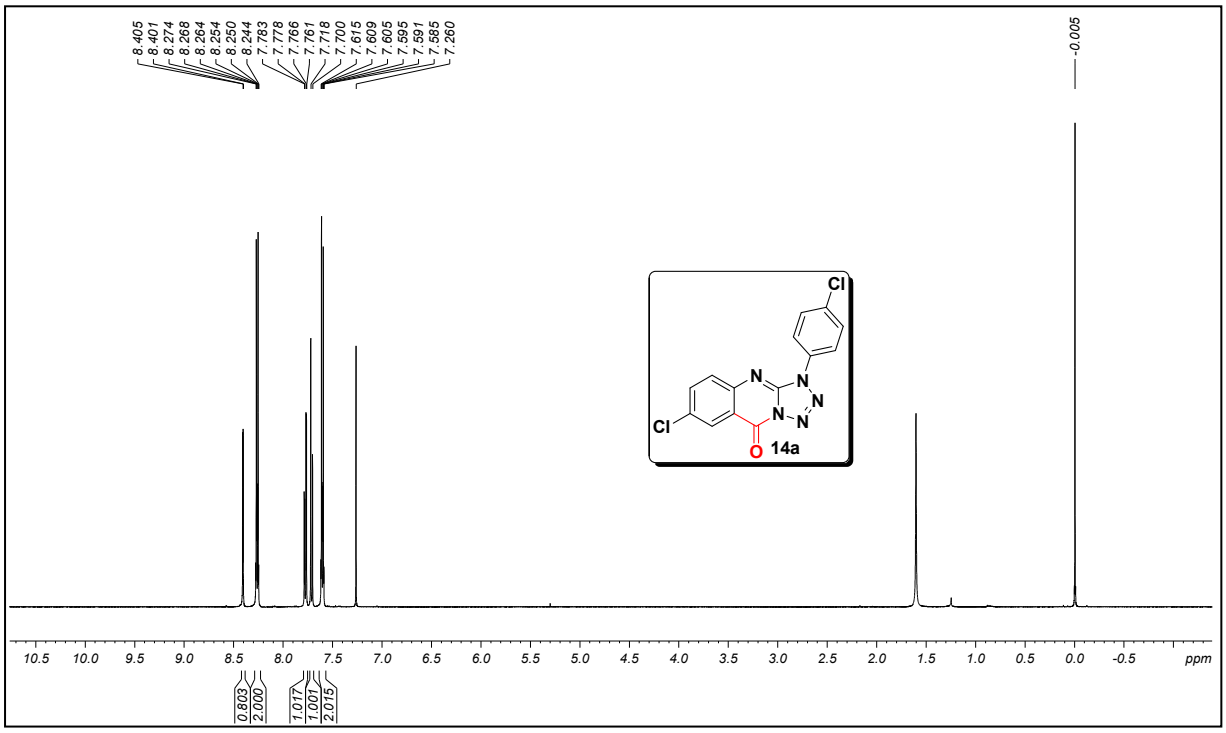


Figure S23. 500 MHz ^{1}H NMR spectrum of **14a** in $CDCl_3$

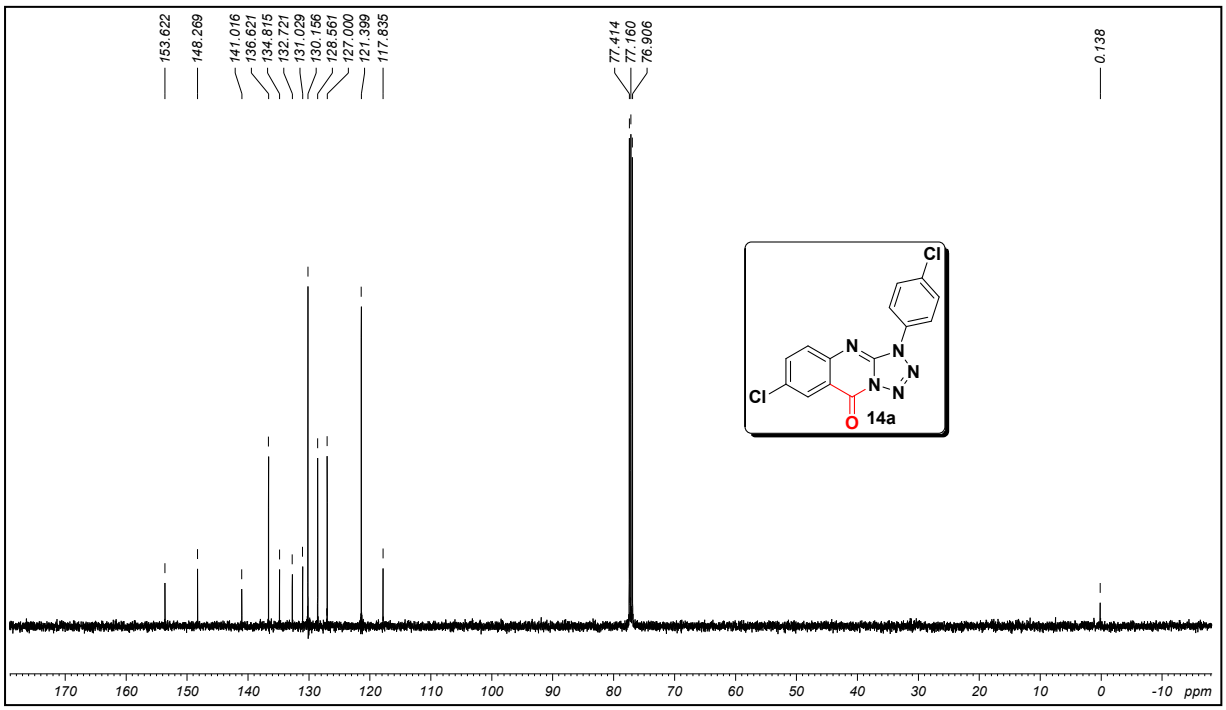


Figure S24. 125 MHz ^{13}C NMR spectrum of **14a** in $CDCl_3$

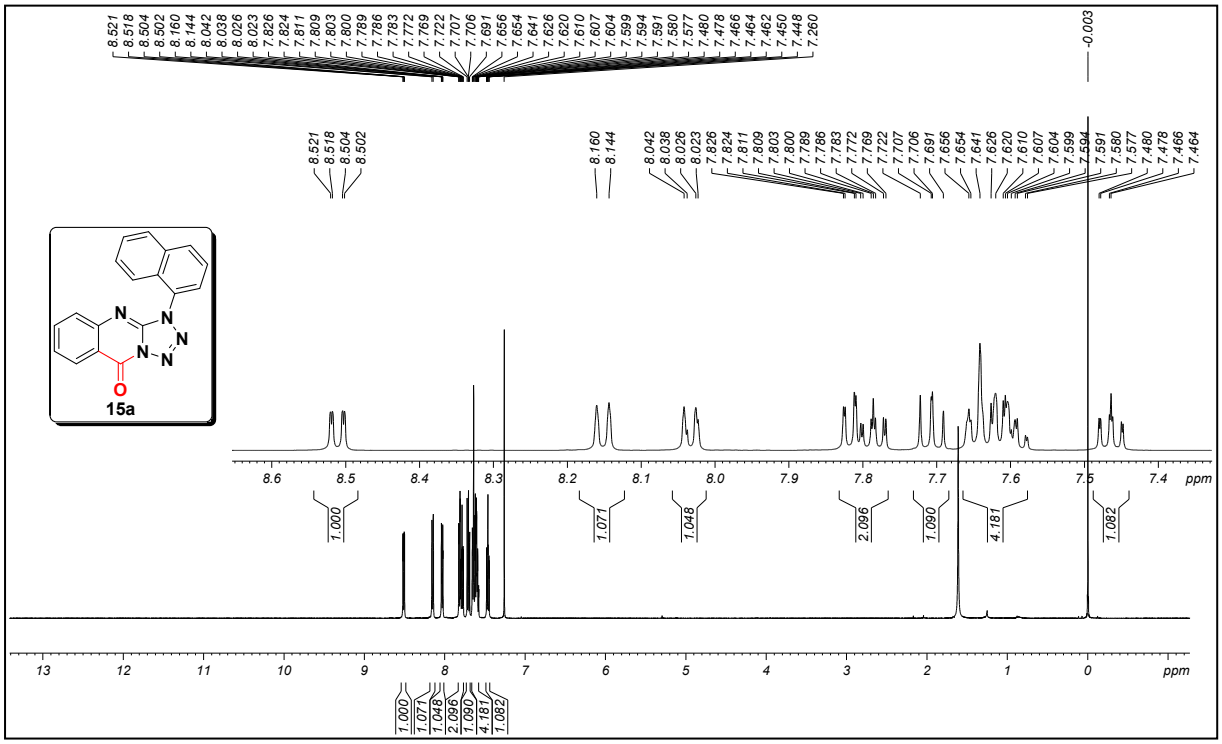


Figure S25. 500 MHz ^{1}H NMR spectrum of **15a** in $CDCl_3$

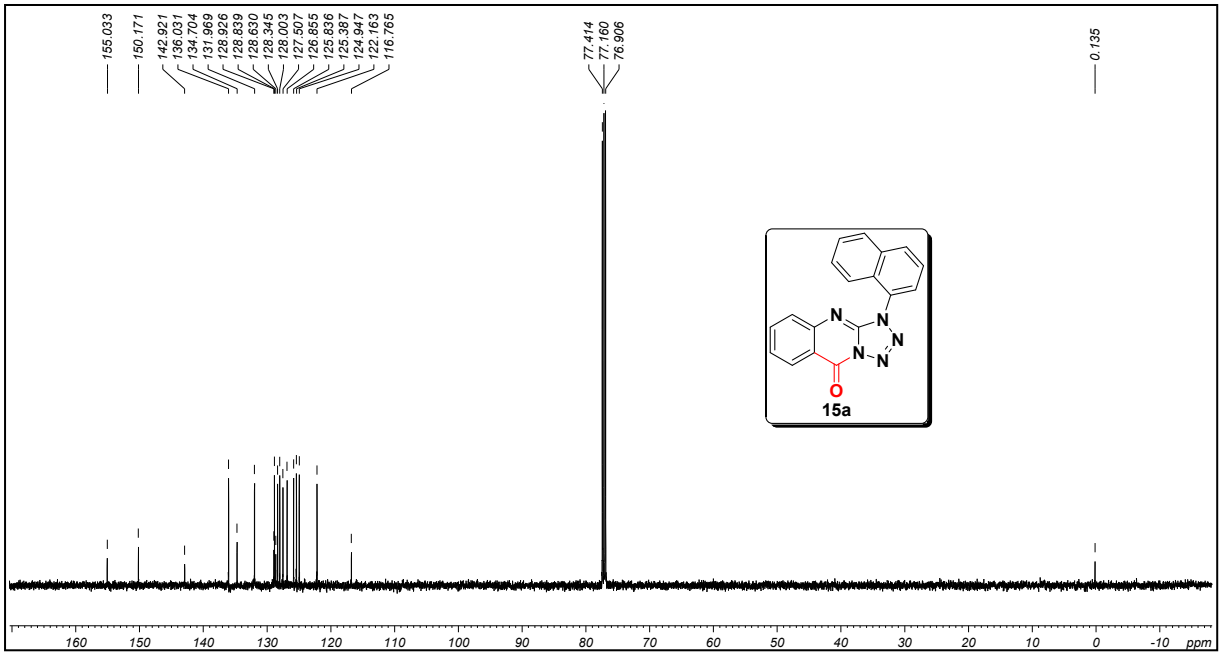


Figure S26. 125 MHz ^{13}C NMR spectrum of **15a** in $CDCl_3$

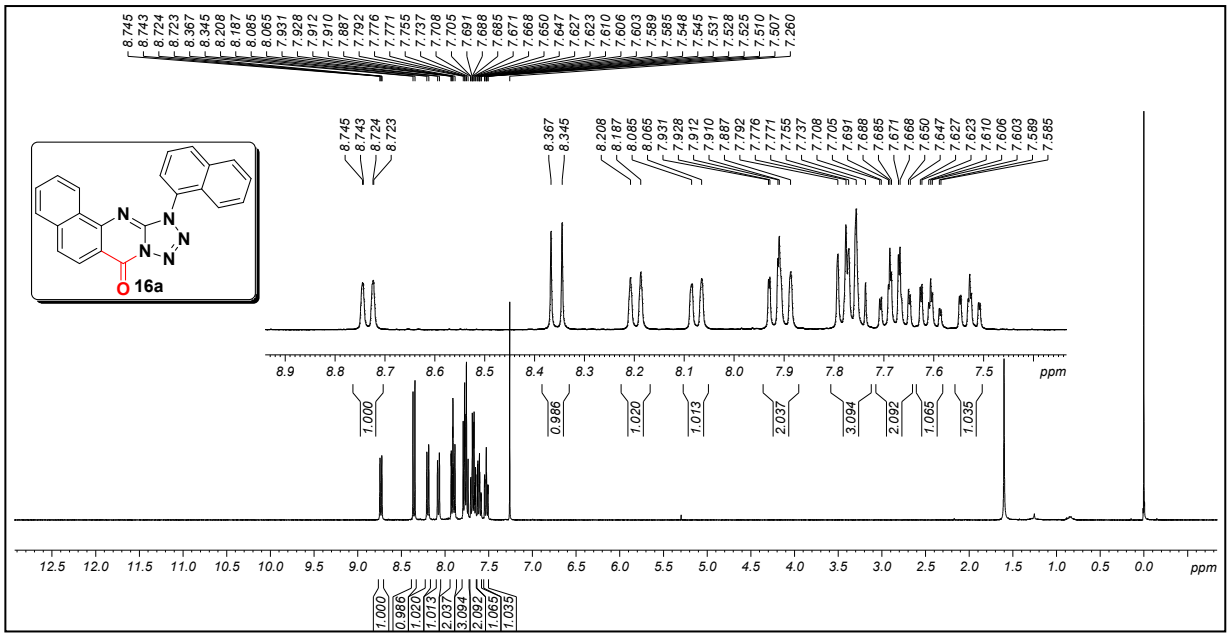


Figure S27. 400 MHz ^{1}H NMR spectrum of **16a** in $CDCl_3$

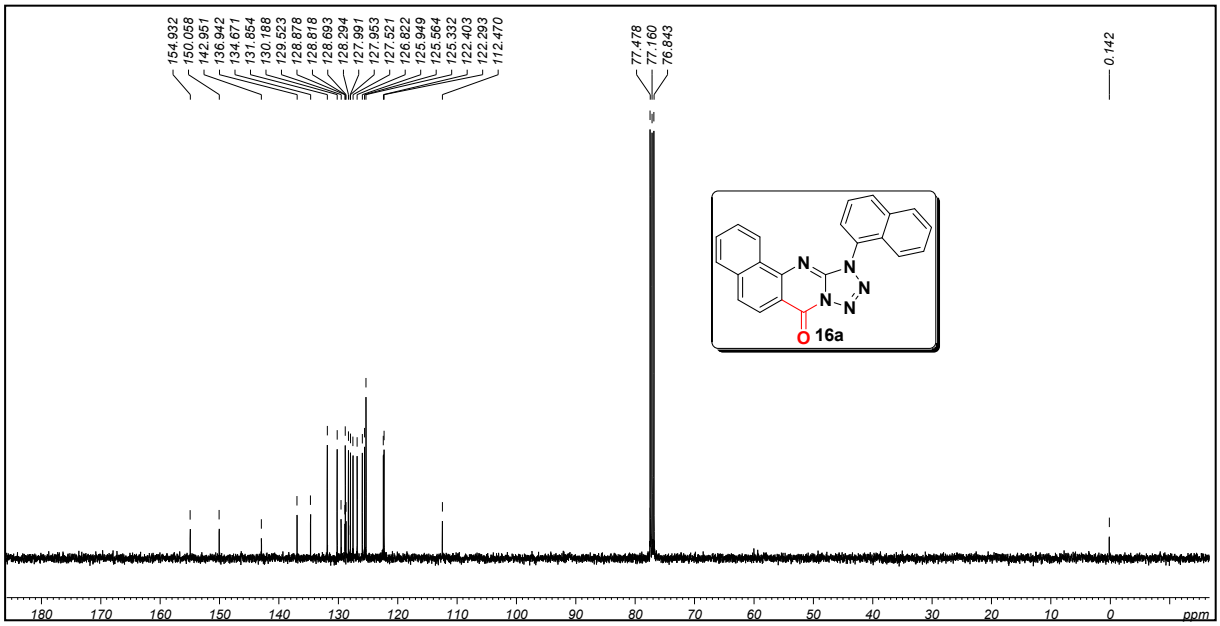


Figure S28. 100 MHz ^{13}C NMR spectrum of **16a** in $CDCl_3$

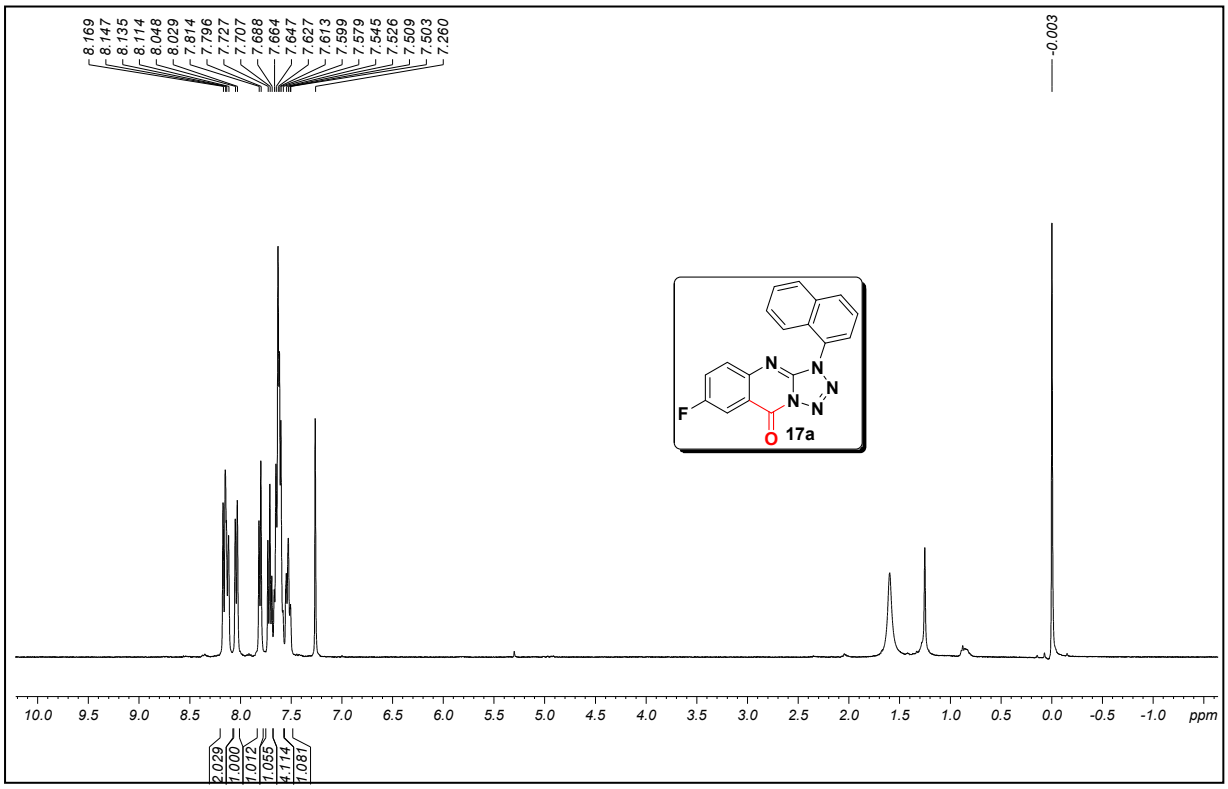


Figure S29. 400 MHz ^{1}H NMR spectrum of **17a** in $CDCl_3$

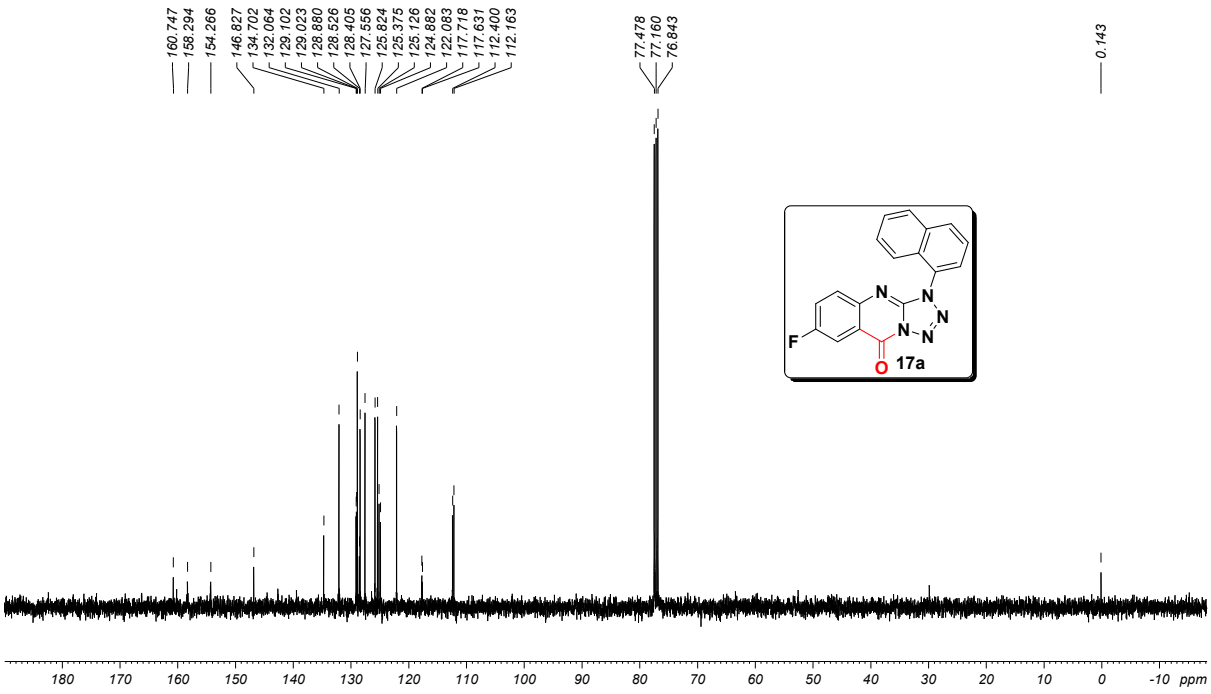


Figure S30. 100 MHz ^{13}C NMR spectrum of **17a** in $CDCl_3$

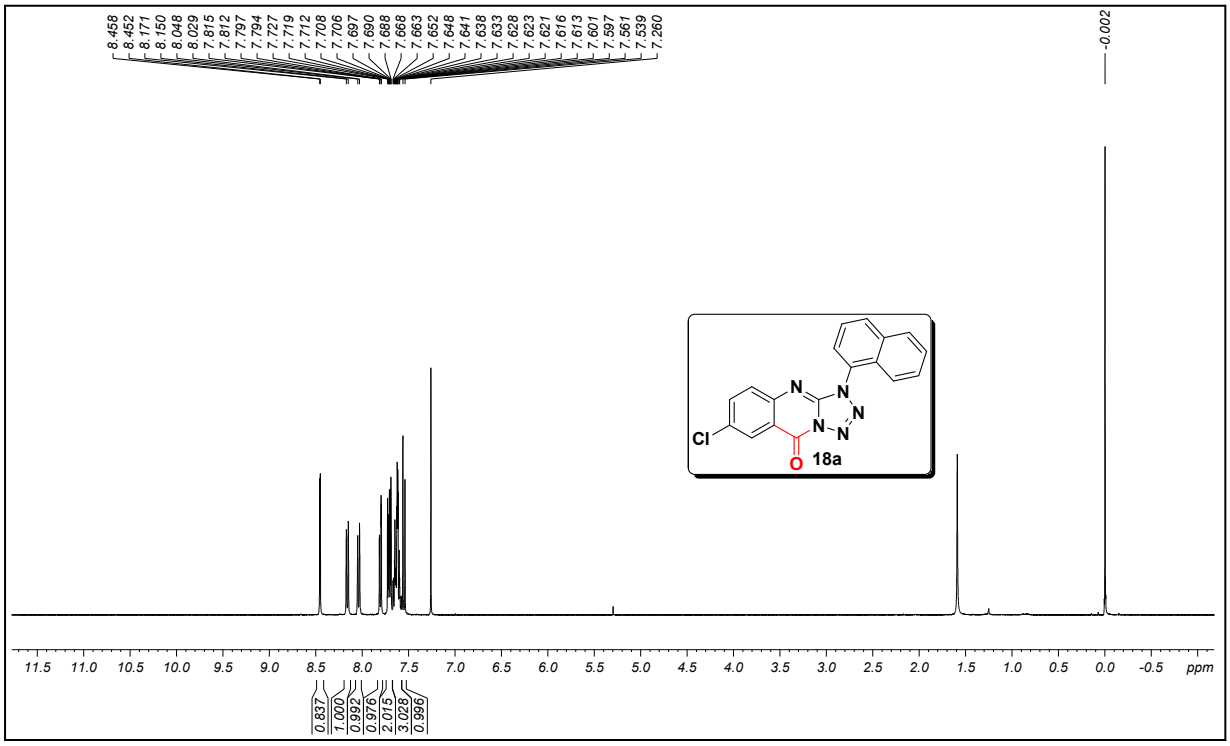


Figure S31. 400 MHz ^{1}H NMR spectrum of **18a** in $CDCl_3$

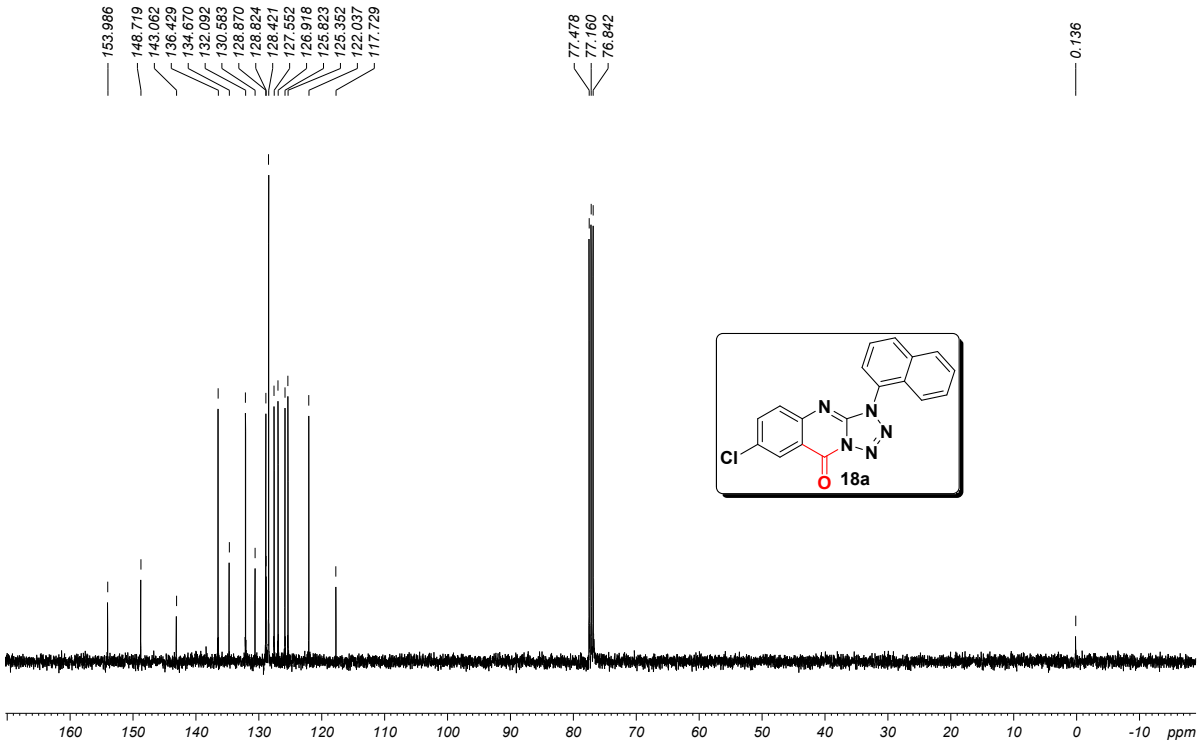


Figure S32. 100 MHz ^{13}C NMR spectrum of **18a** in $CDCl_3$

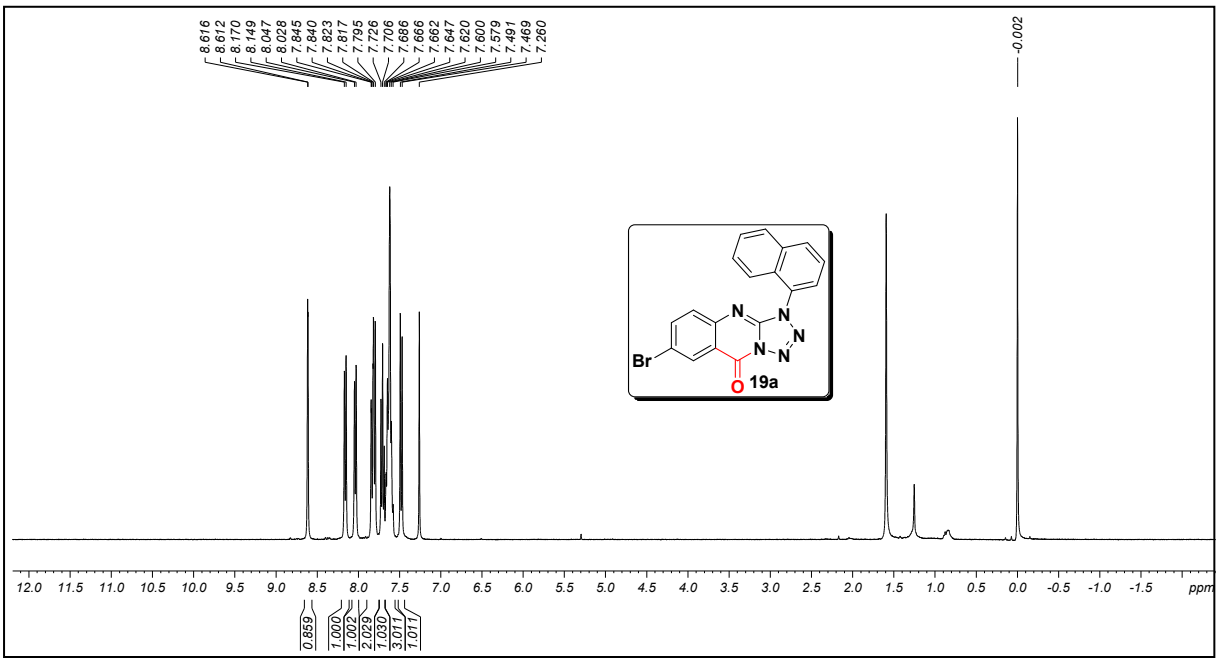


Figure S33. 400 MHz ^{1}H NMR spectrum of **19a** in $CDCl_3$

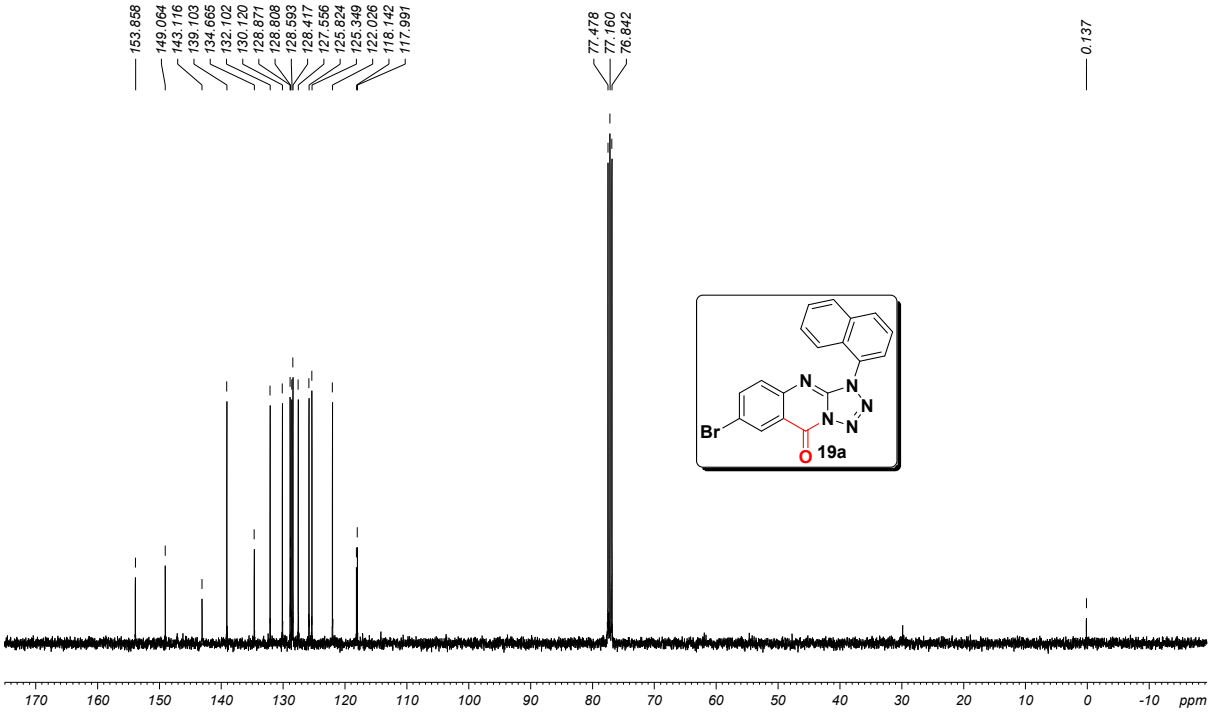


Figure S34. 100 MHz ^{13}C NMR spectrum of **19a** in $CDCl_3$

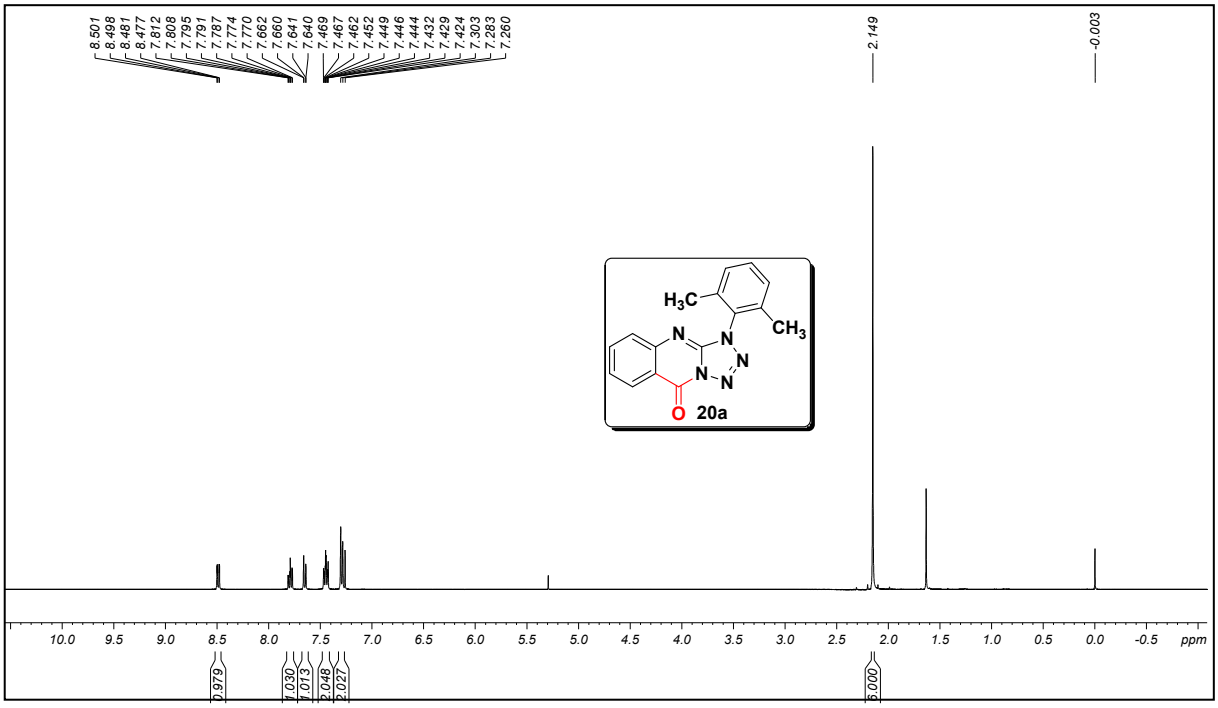


Figure S35. 400 MHz ^{1}H NMR spectrum of **20a** in $CDCl_3$

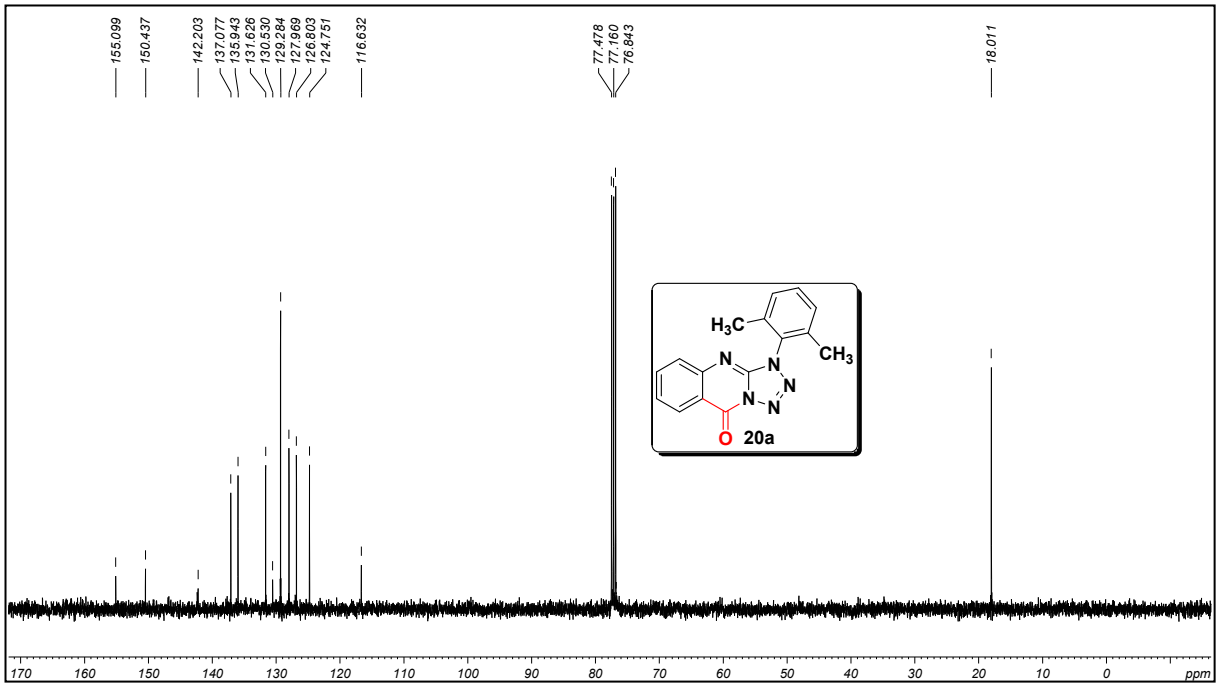


Figure S36. 100 MHz ^{13}C NMR spectrum of **20a** in $CDCl_3$

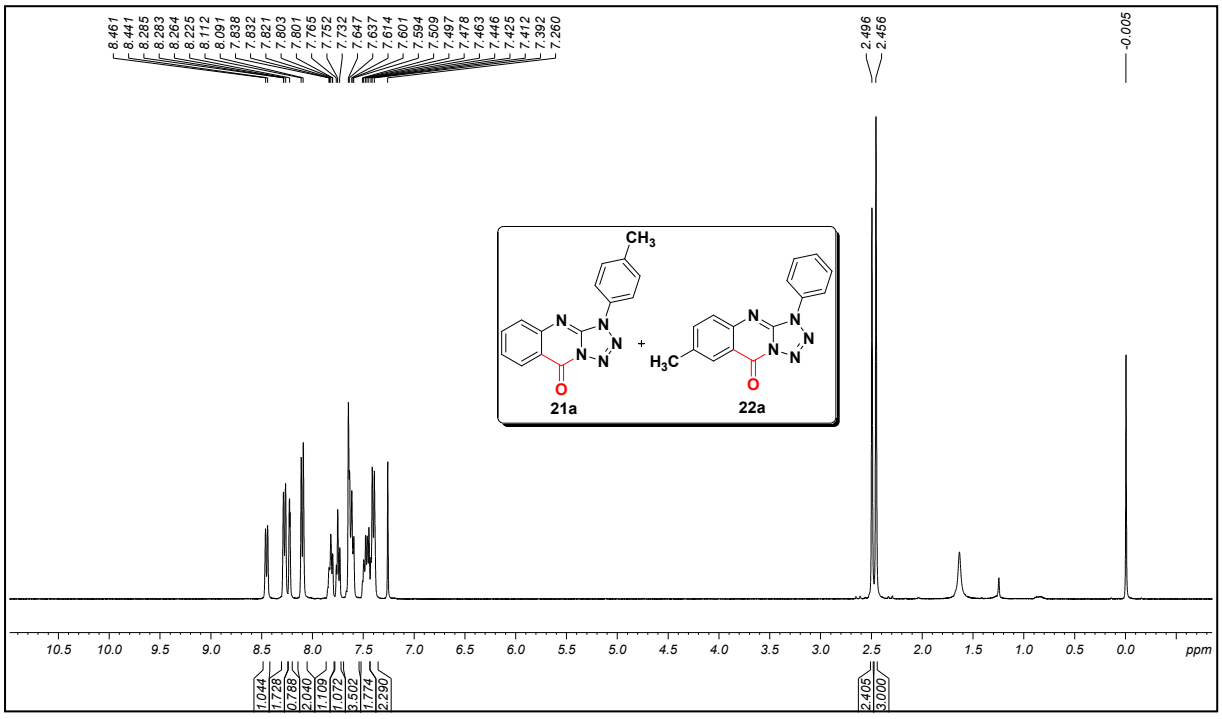


Figure S37. 400 MHz ^{1}H NMR spectrum of **21a+22a** in $CDCl_3$

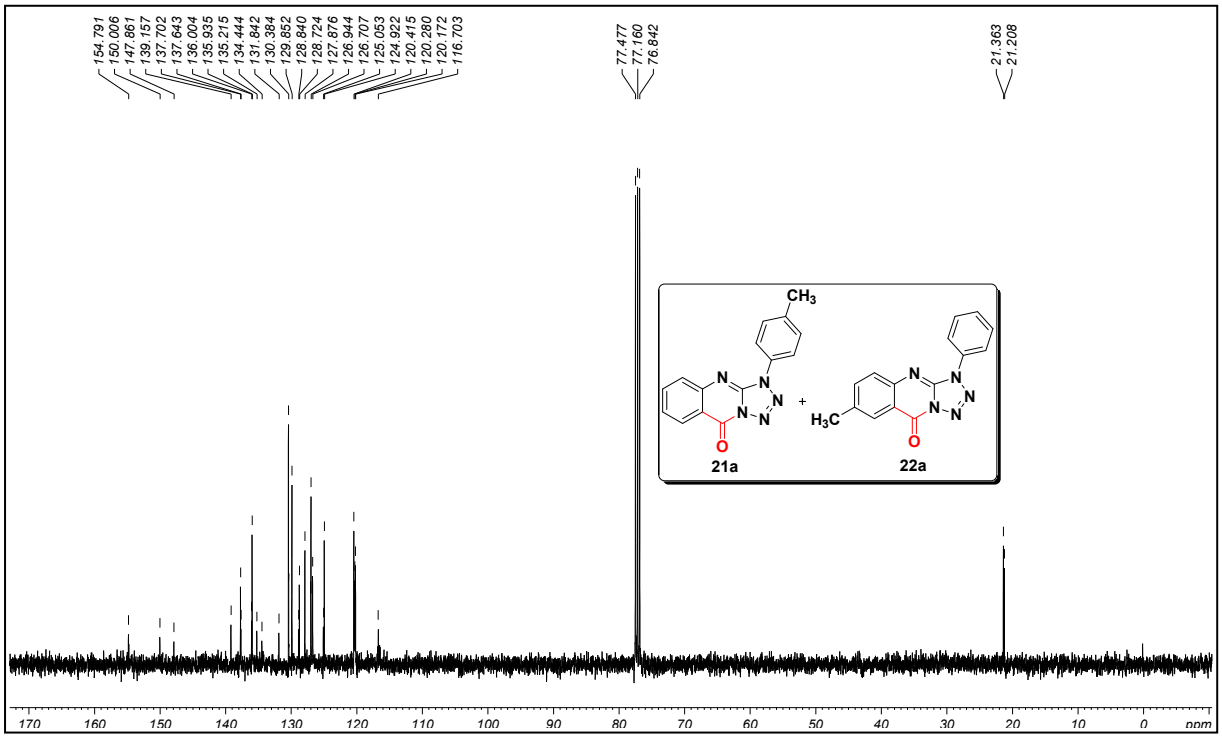


Figure S38. 100 MHz ^{13}C NMR spectrum of **21a+22a** in $CDCl_3$

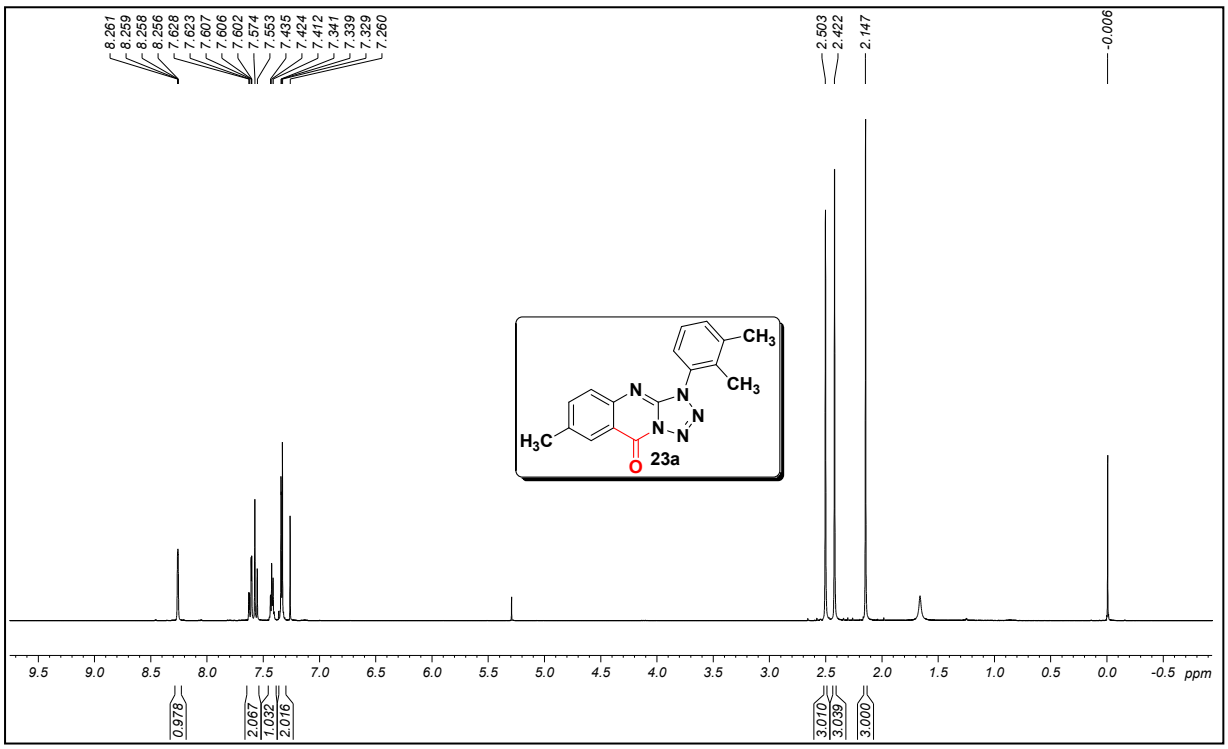


Figure S39. 400 MHz ^{1}H NMR spectrum of **23a** in $CDCl_3$

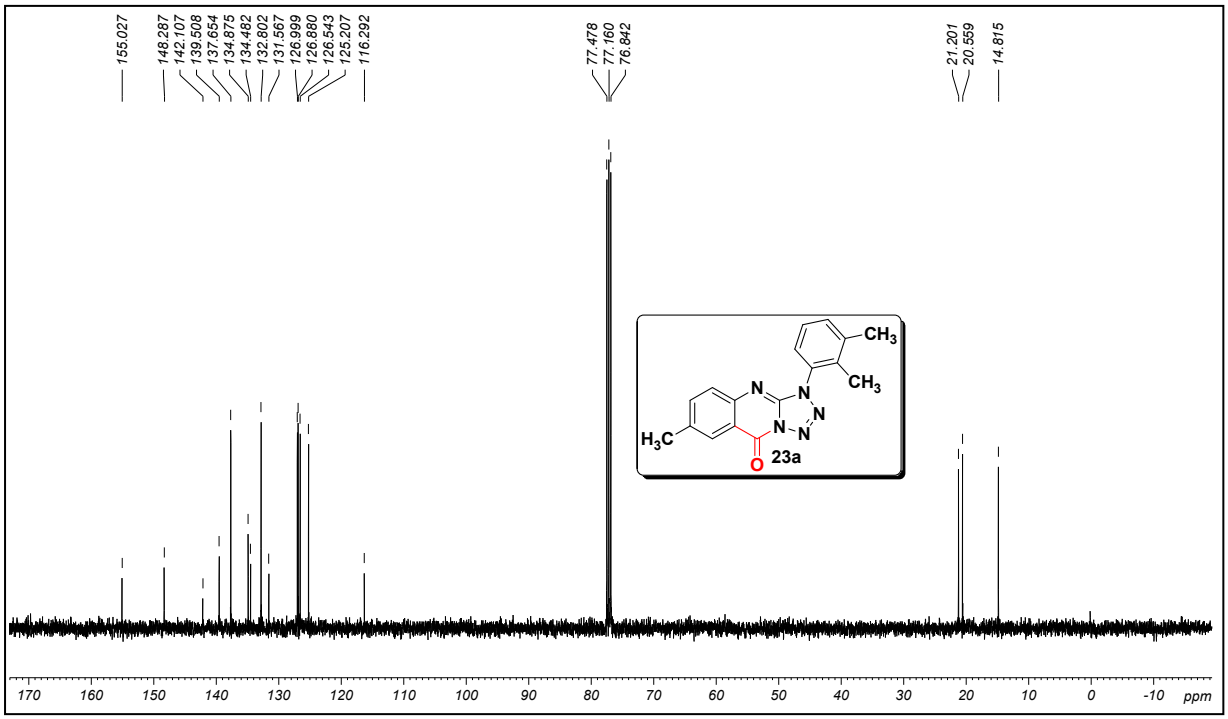


Figure S40. 100 MHz ^{13}C NMR spectrum of **23a** in $CDCl_3$

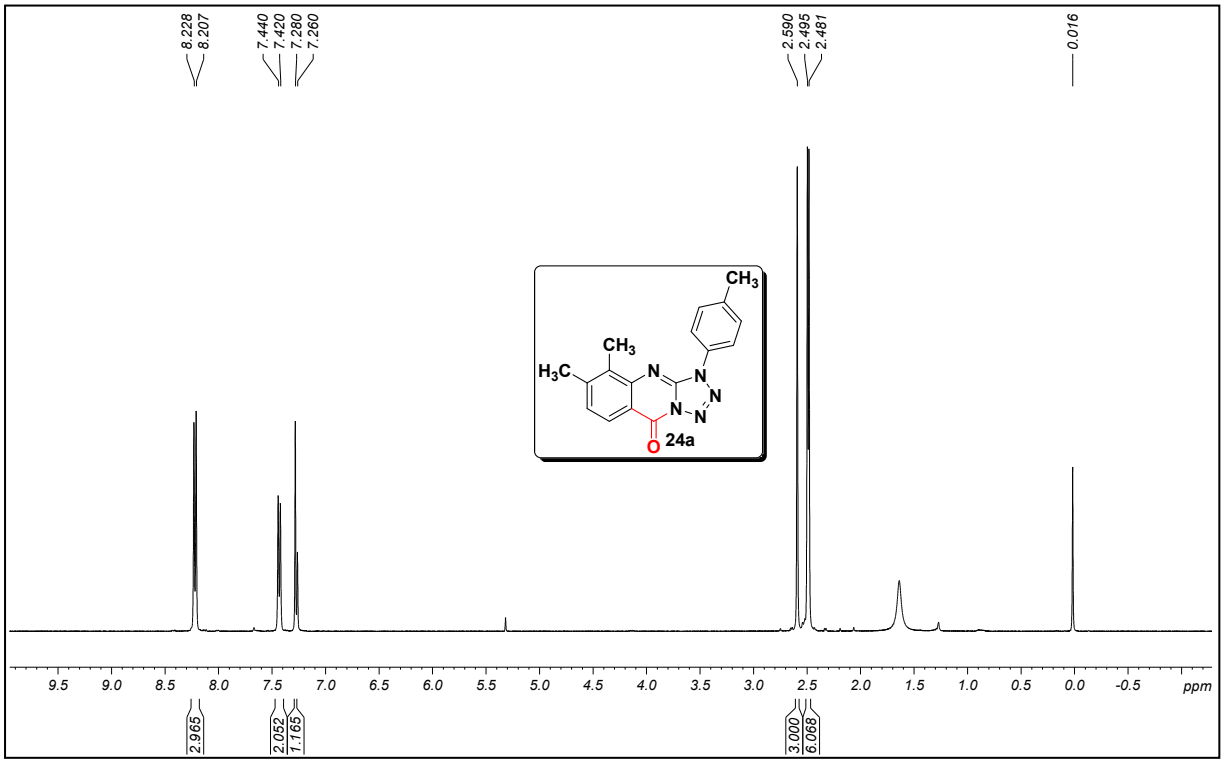


Figure S41. 400 MHz ^{1}H NMR spectrum of **24a** in $CDCl_3$

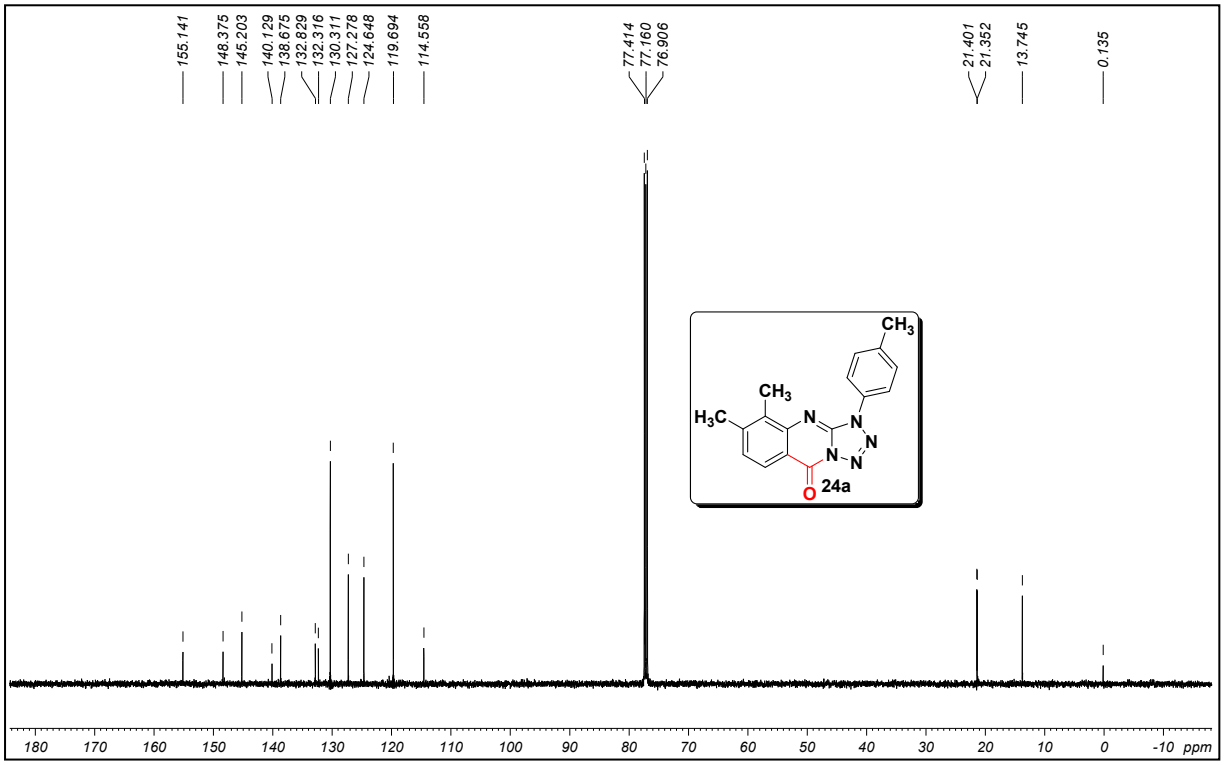


Figure S42. 125 MHz ^{13}C NMR spectrum of **24a** in $CDCl_3$

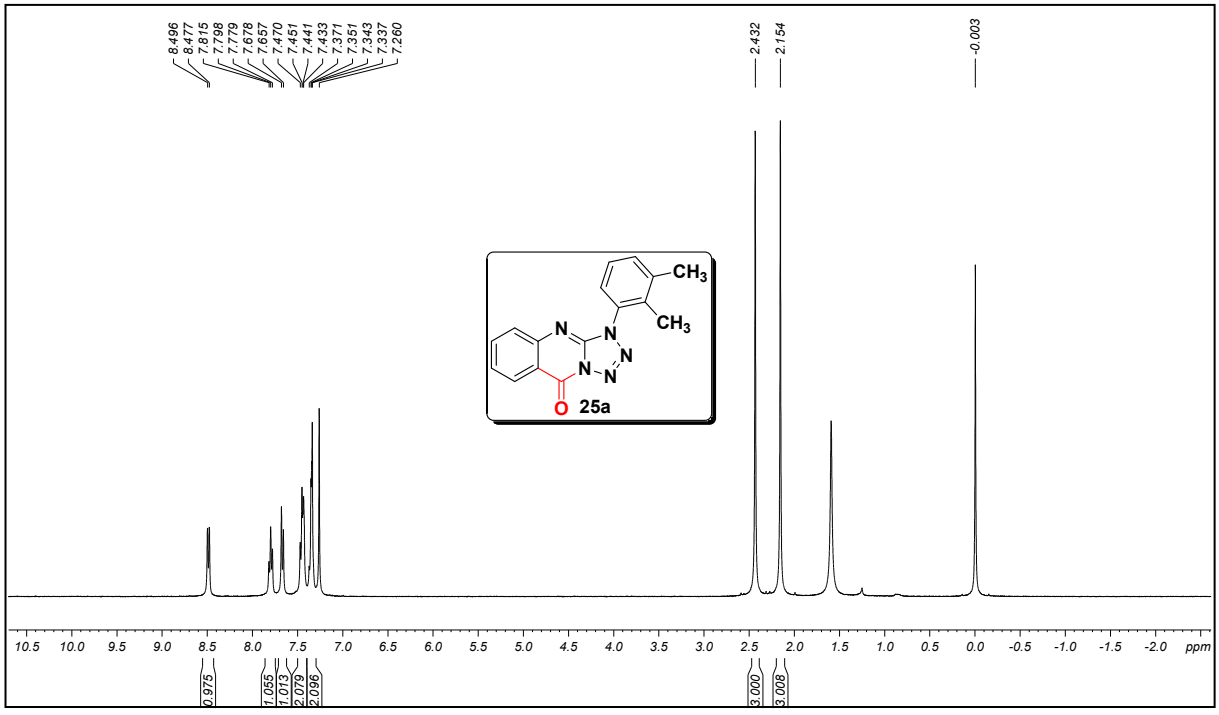


Figure S43. 400 MHz ^{1}H NMR spectrum of **25a** in $CDCl_3$

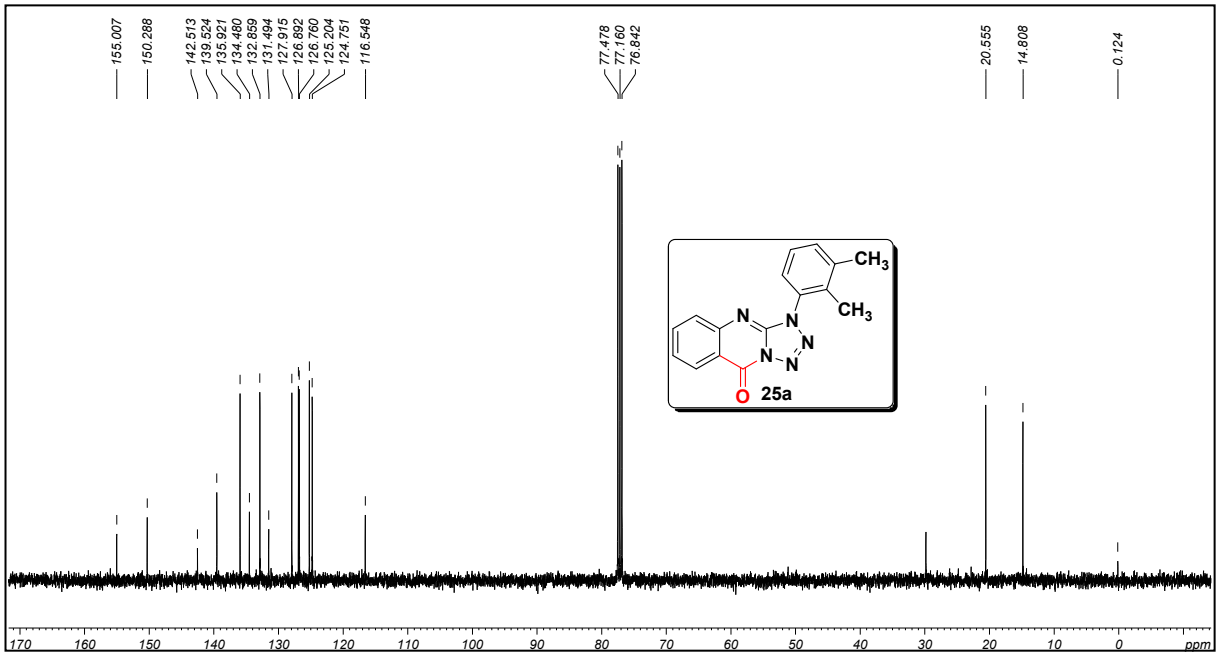


Figure S44. 100 MHz ^{13}C NMR spectrum of **25a** in $CDCl_3$

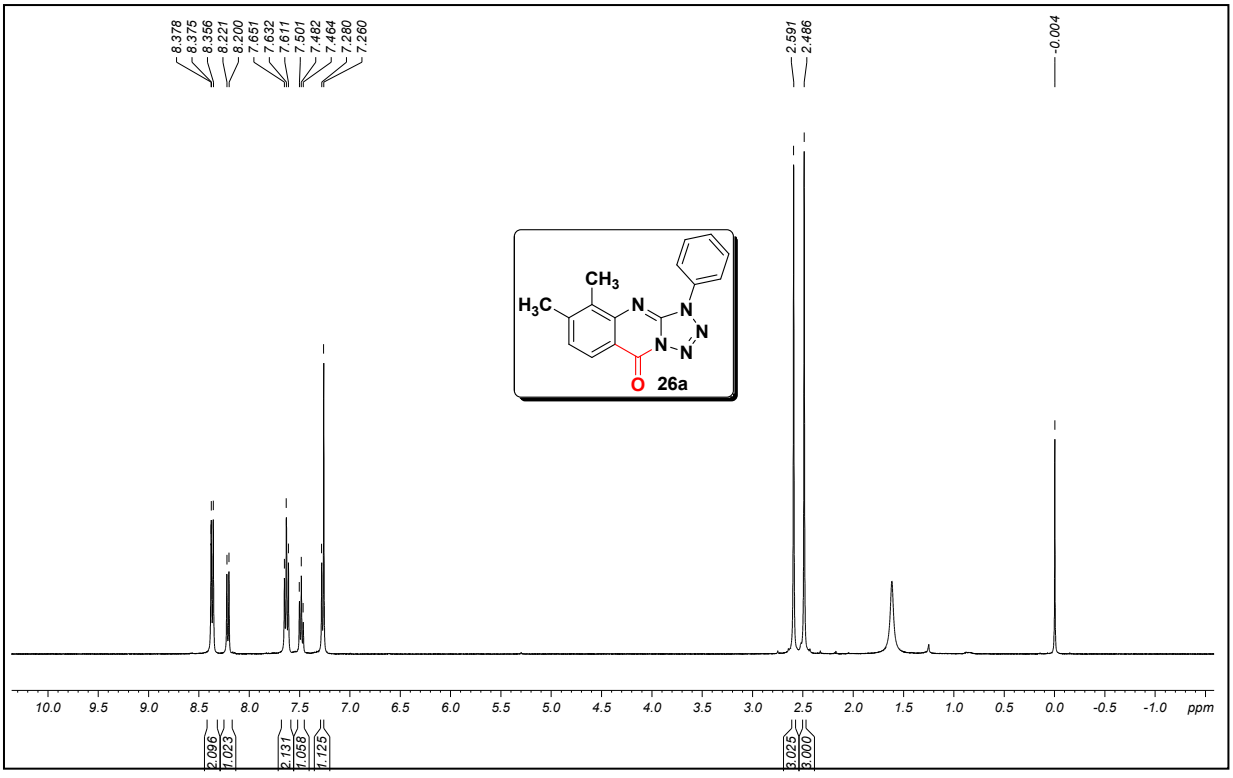


Figure S45. 400 MHz ^{1}H NMR spectrum of **26a** in $CDCl_3$

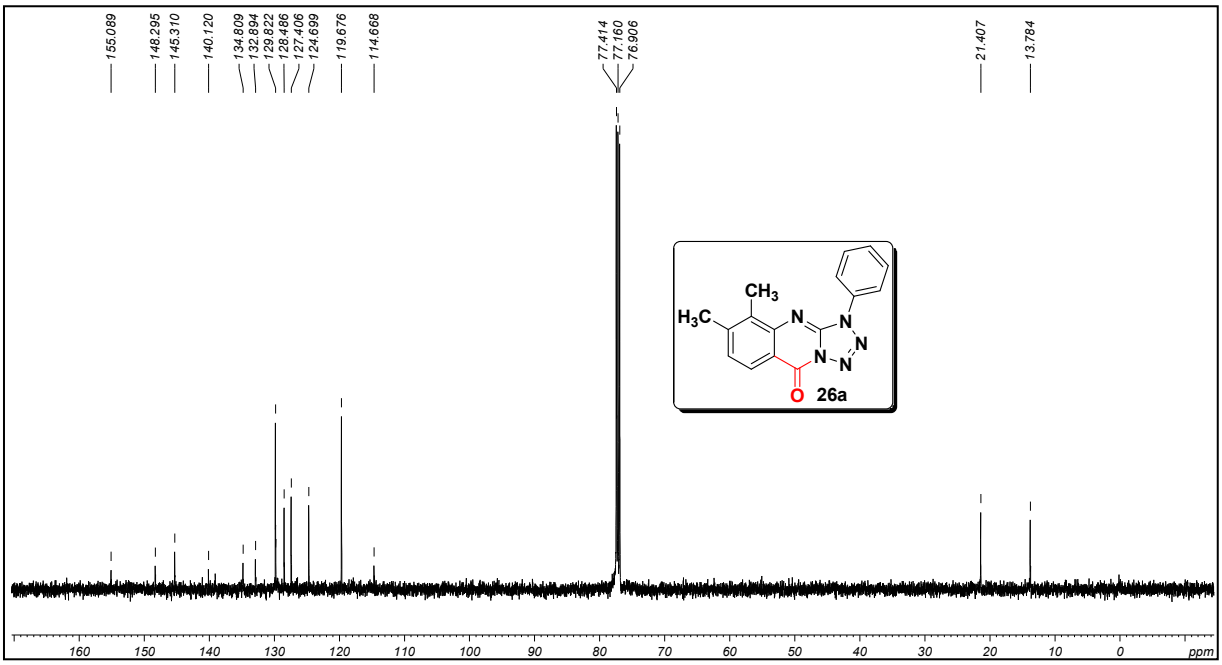


Figure S46. 125 MHz ^{13}C NMR spectrum of **26a** in $CDCl_3$

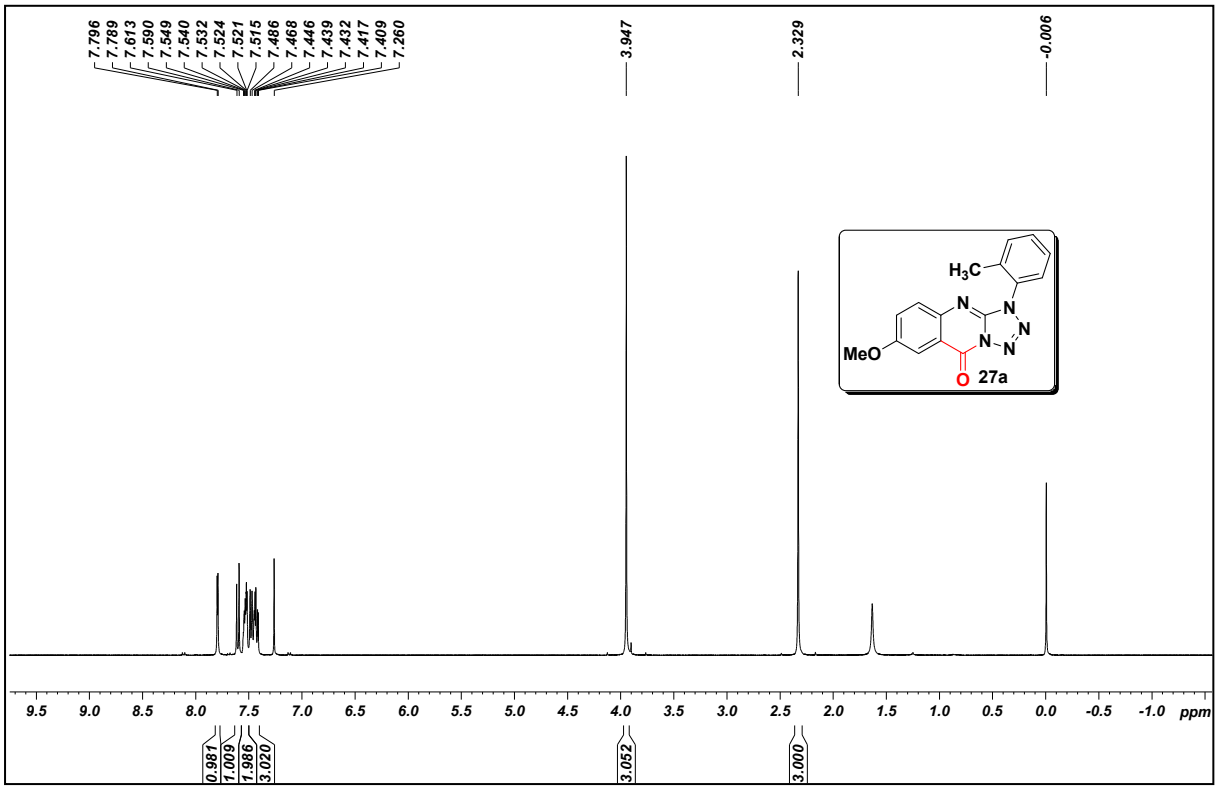


Figure S47. 400 MHz ^{1}H NMR spectrum of **27a** in $CDCl_3$

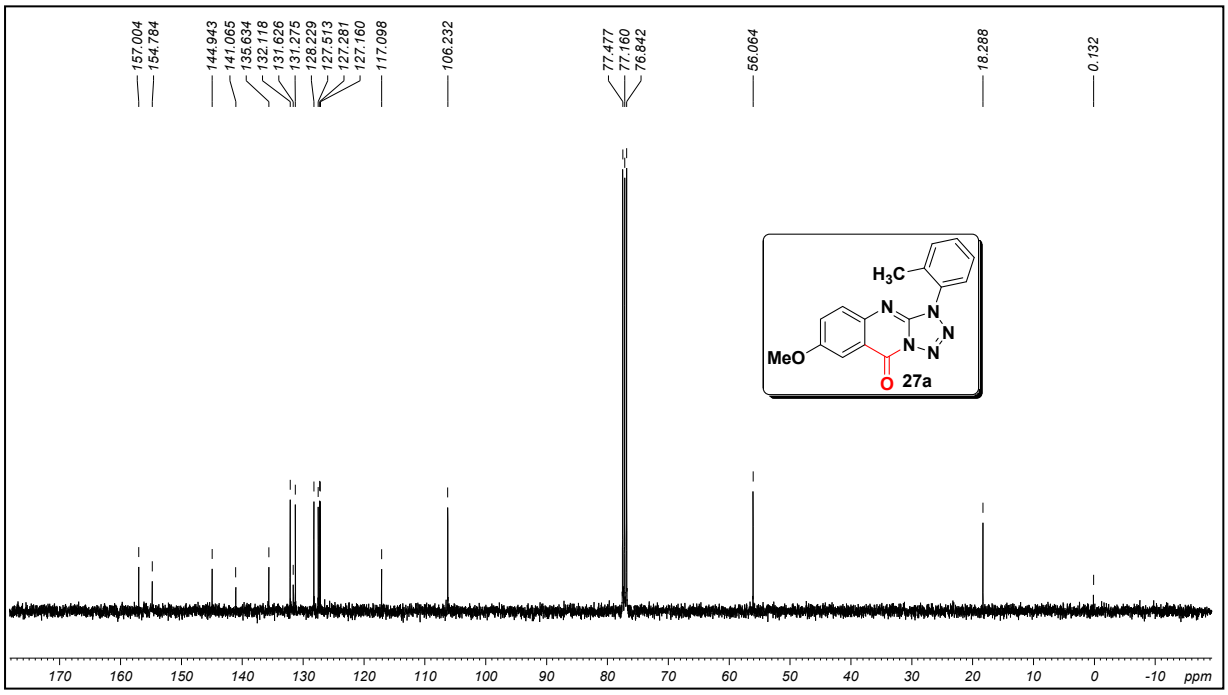


Figure S48. 100 MHz ^{13}C NMR spectrum of **27a** in $CDCl_3$

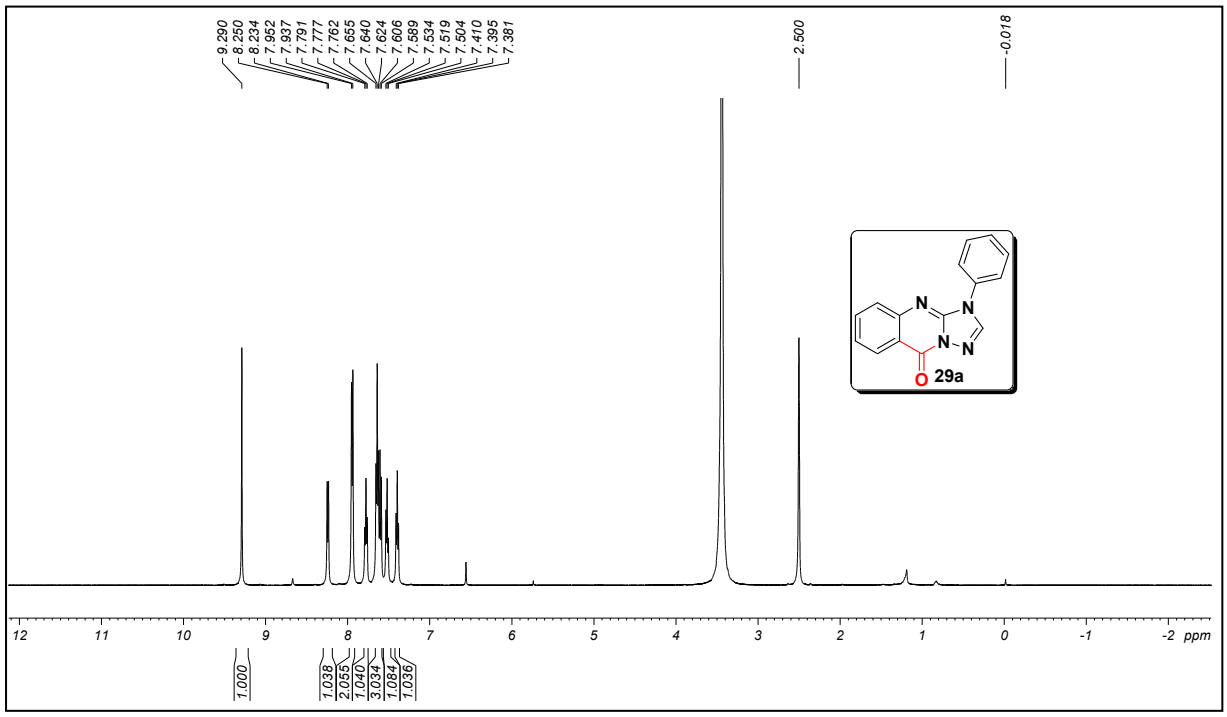


Figure S49. 500 MHz ^{1}H NMR spectrum of **29a** in DMSO-d_6

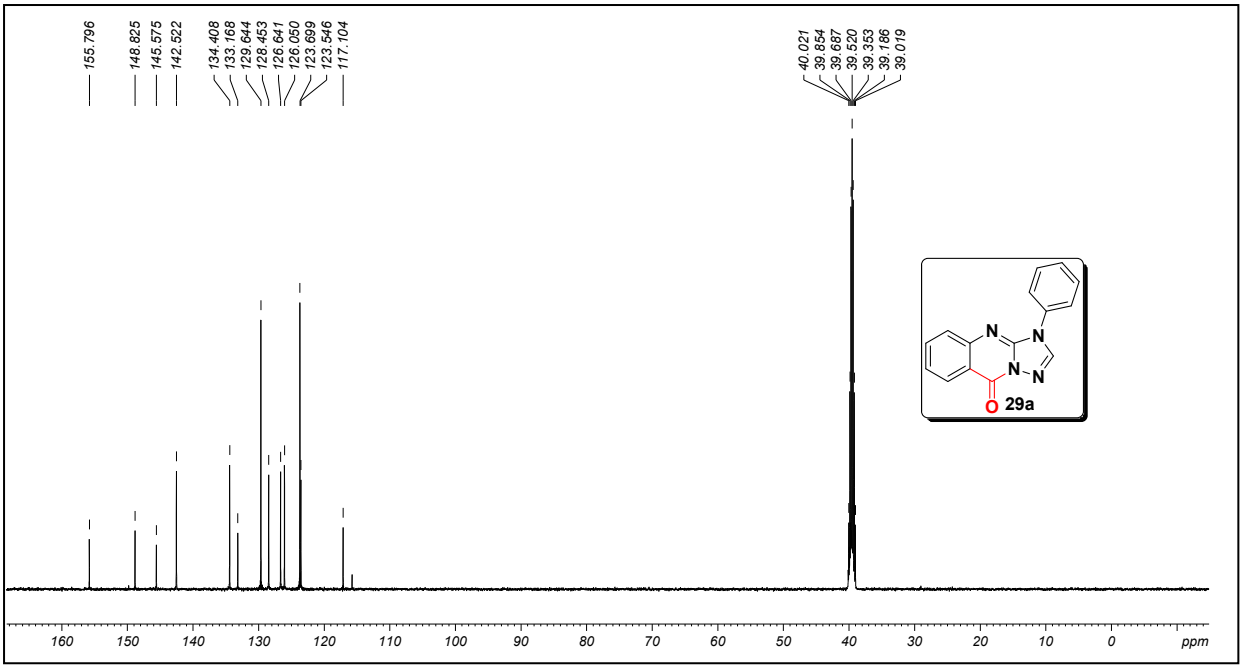


Figure S50. 125 MHz ^{13}C NMR spectrum of **29a** in DMSO-d_6

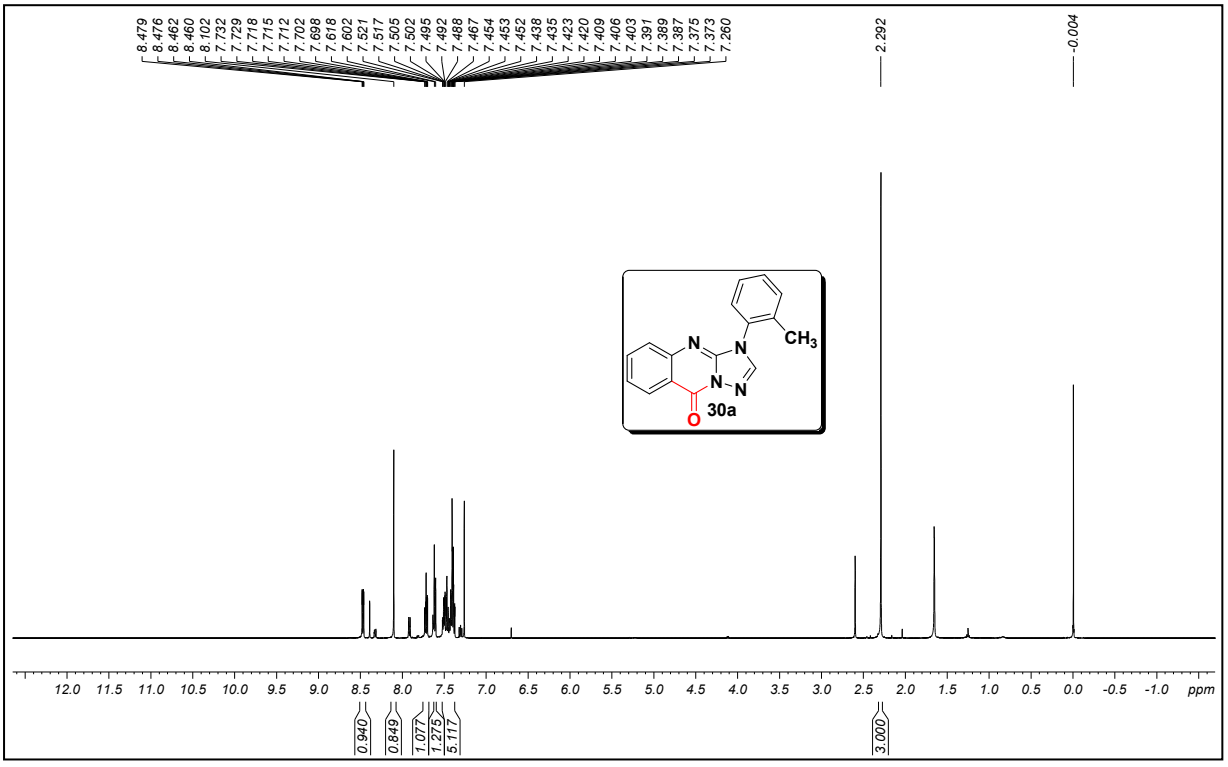


Figure S51. 500 MHz ^{1}H NMR spectrum of **30a** in DMSO-d_6

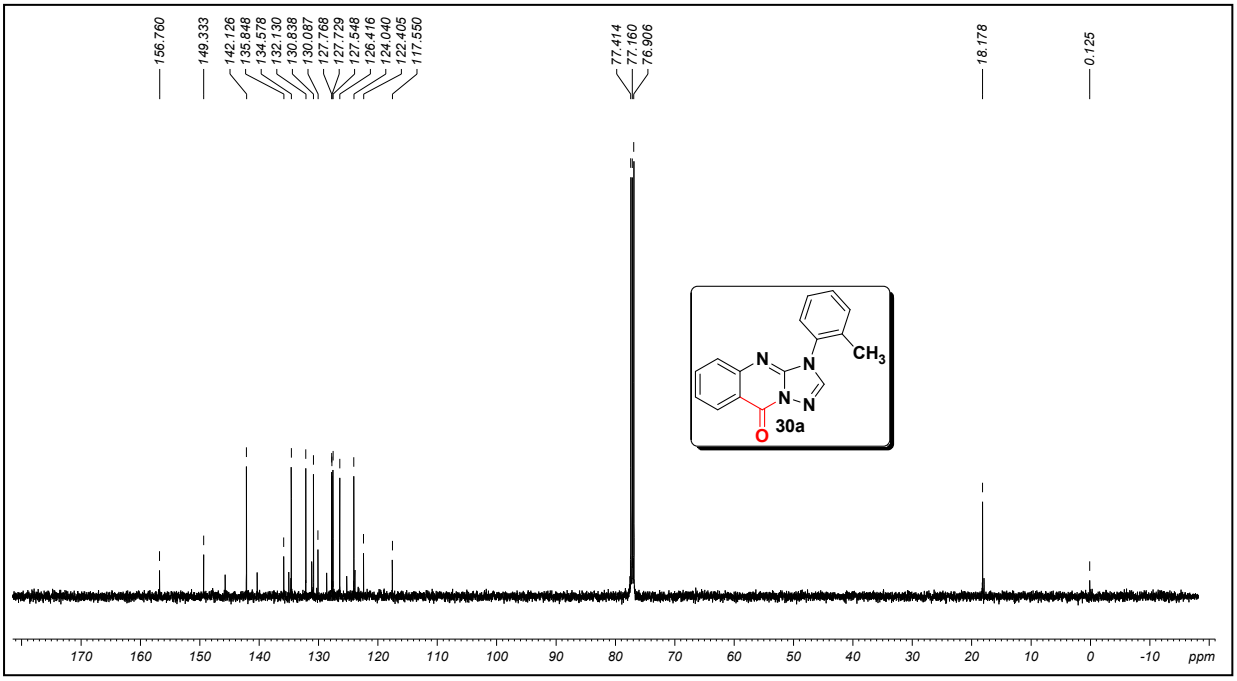


Figure S52. 125 MHz ^{13}C NMR spectrum of **30a** in DMSO-d_6

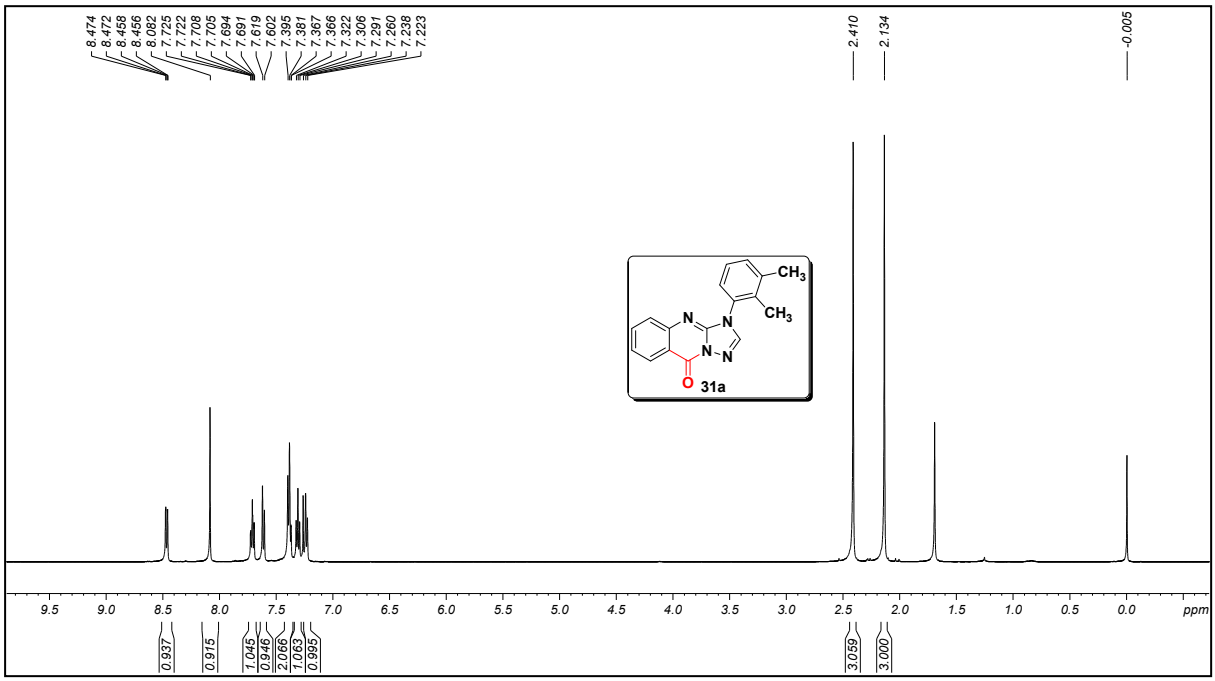


Figure S53. 500 MHz ^{1}H NMR spectrum of **31a** in $CDCl_3$

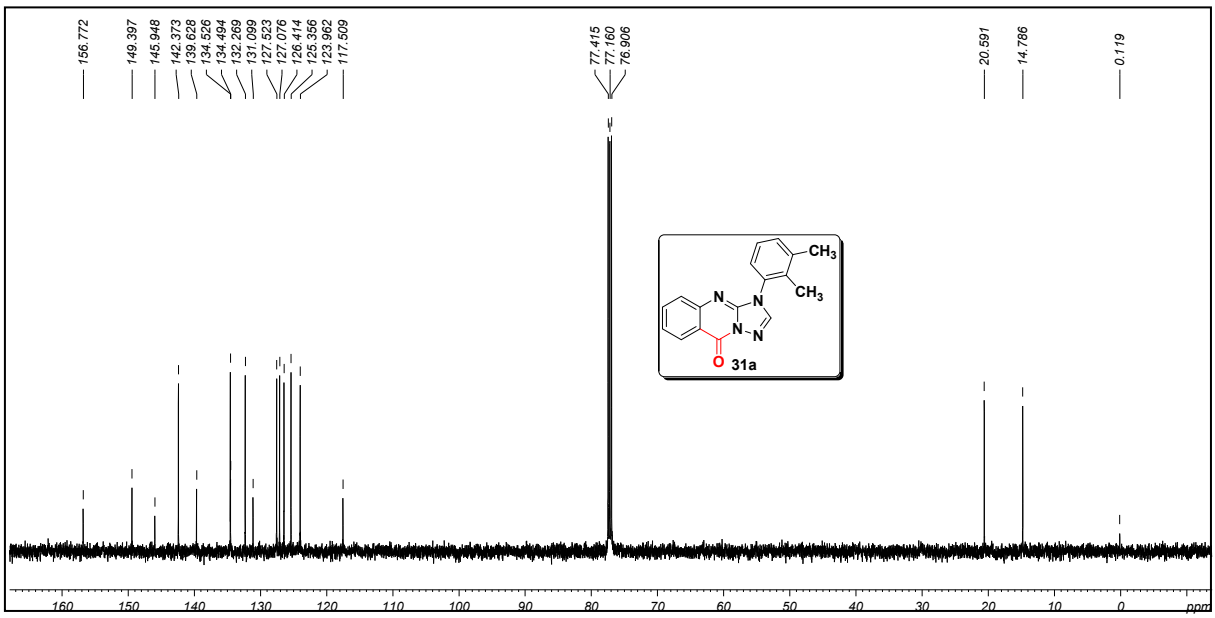


Figure S54. 125 MHz ^{13}C NMR spectrum of **31a** in $CDCl_3$

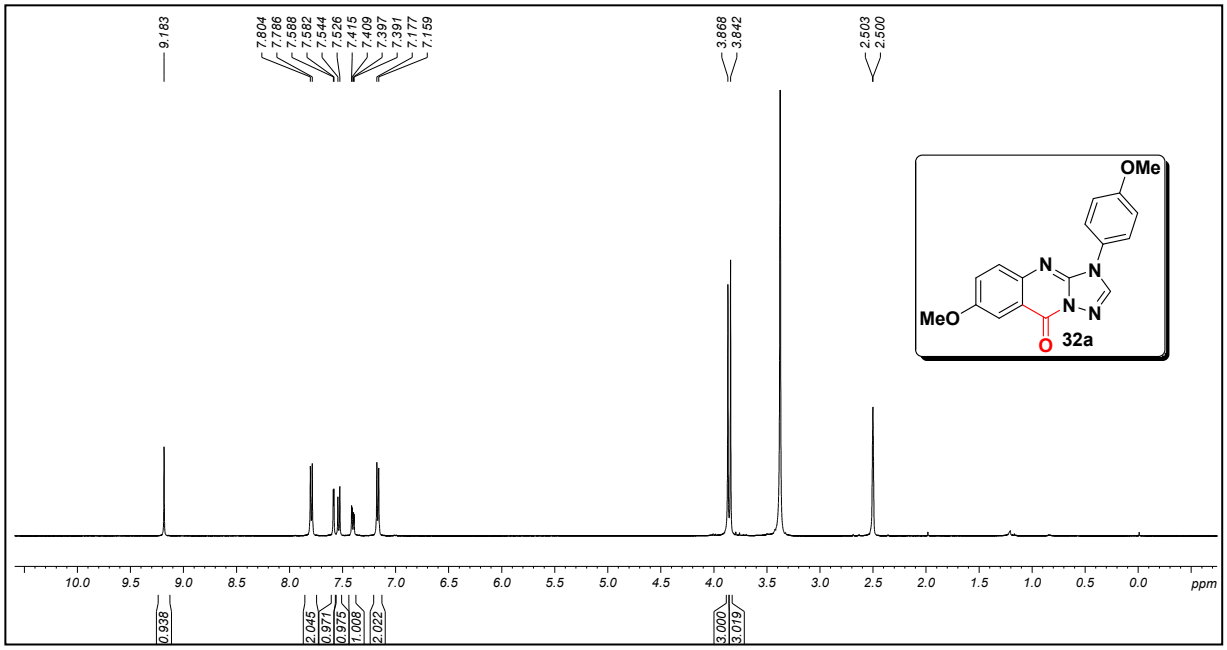


Figure S55. 500 MHz ^{1}H NMR spectrum of **32a** in DMSO-d_6

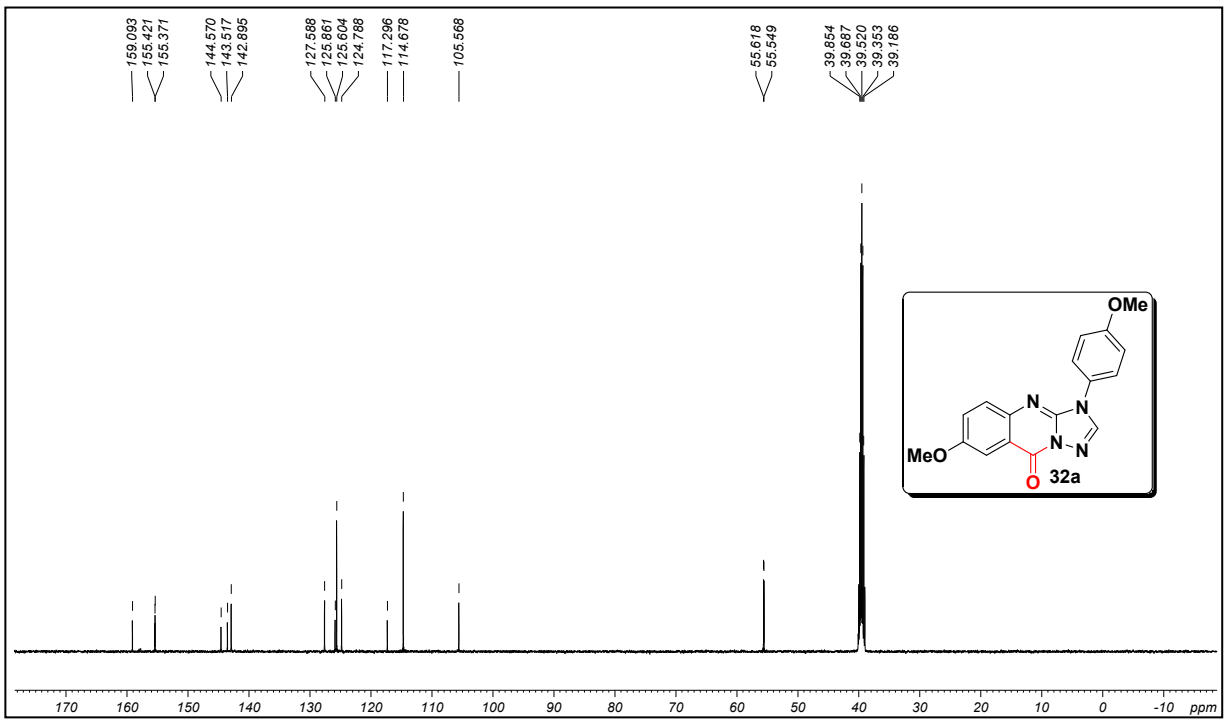


Figure S56. 125 MHz ^{13}C NMR spectrum of **32a** in DMSO-d_6

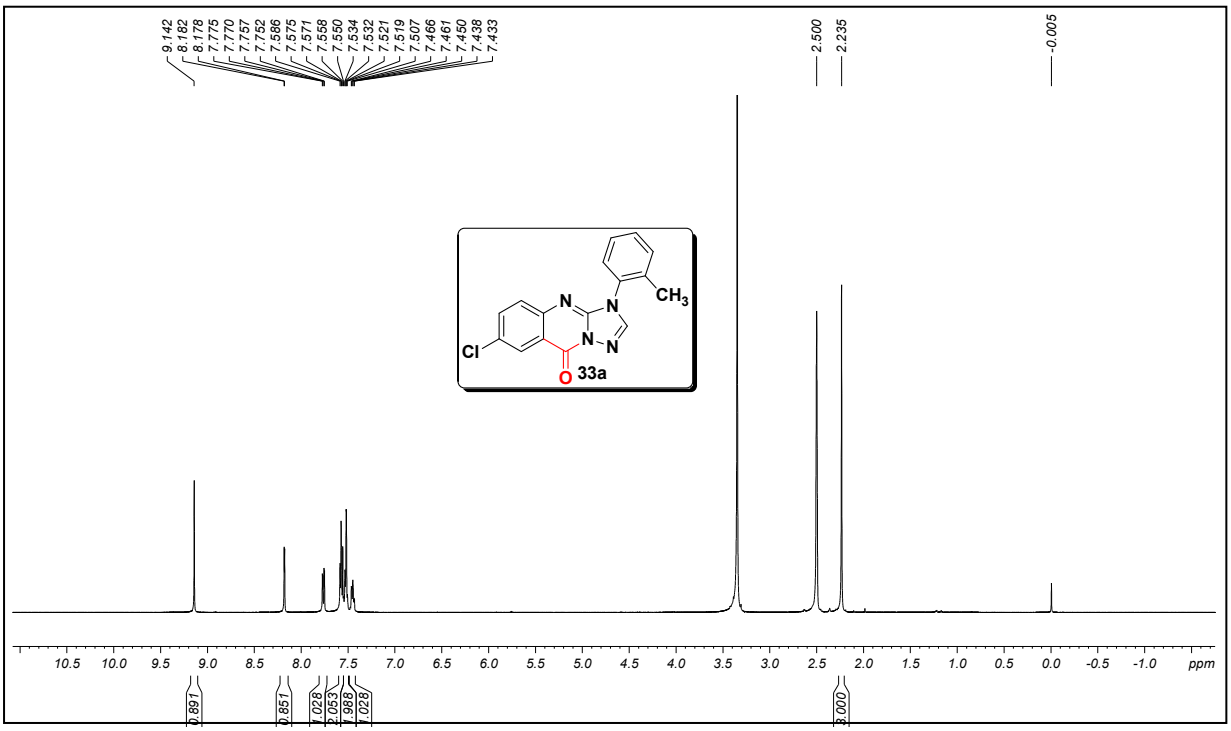


Figure S57. 500 MHz ^{1}H NMR spectrum of **33a** in DMSO-d_6

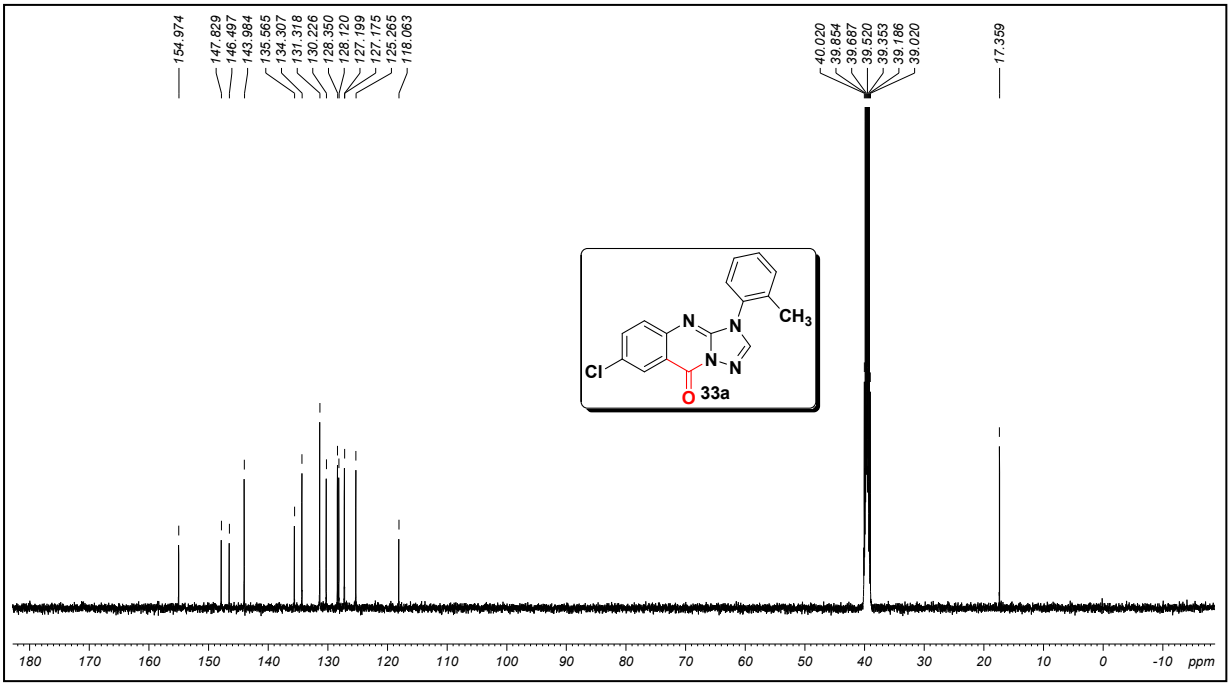


Figure S58. 125 MHz ^{1}H NMR spectrum of **33a** in DMSO-d$_6$

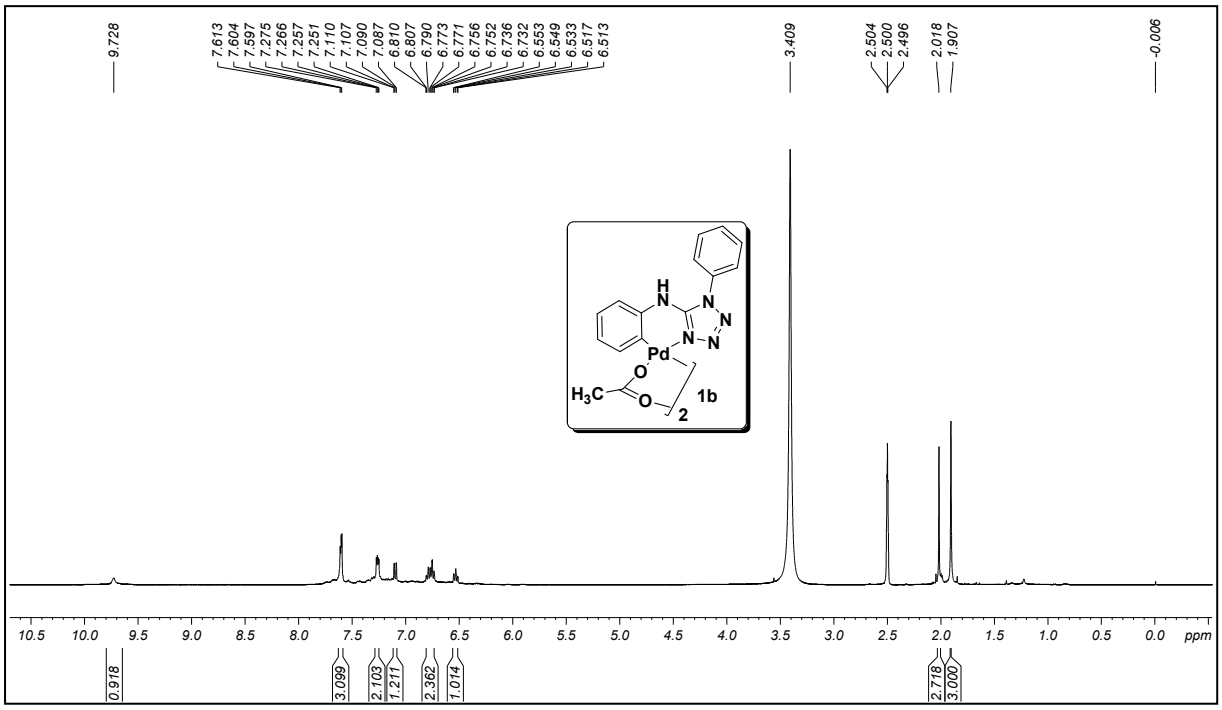


Figure S59. 400 MHz ^{1}H NMR spectrum of **1b** in DMSO-d$_6$

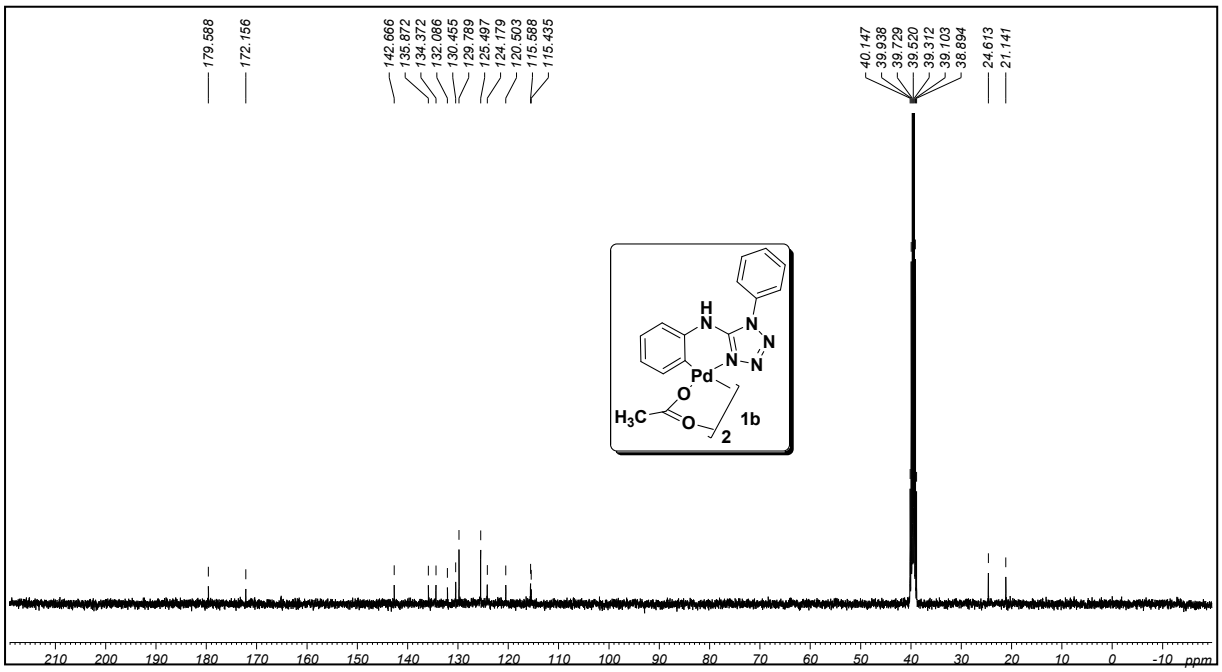


Figure S60. 100 MHz ^{13}C NMR spectrum of **1b** in DMSO-d_6

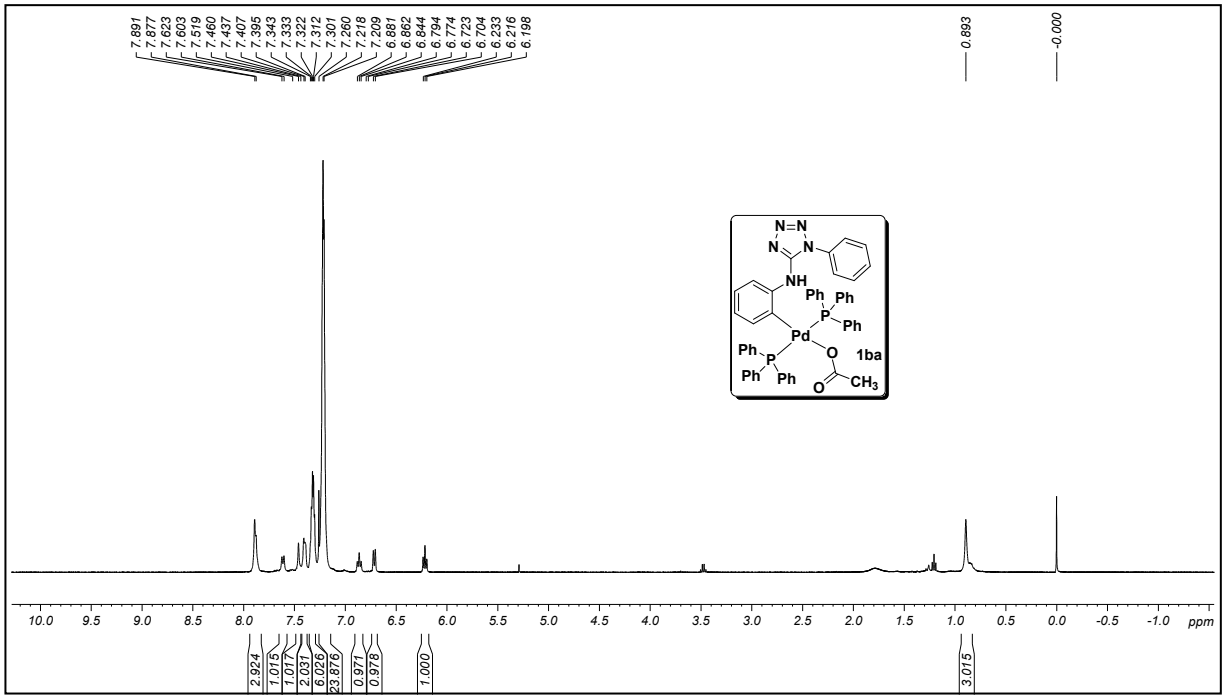


Figure S61. 400 MHz ^{1}H NMR spectrum of **1ba** in $CDCl_3$

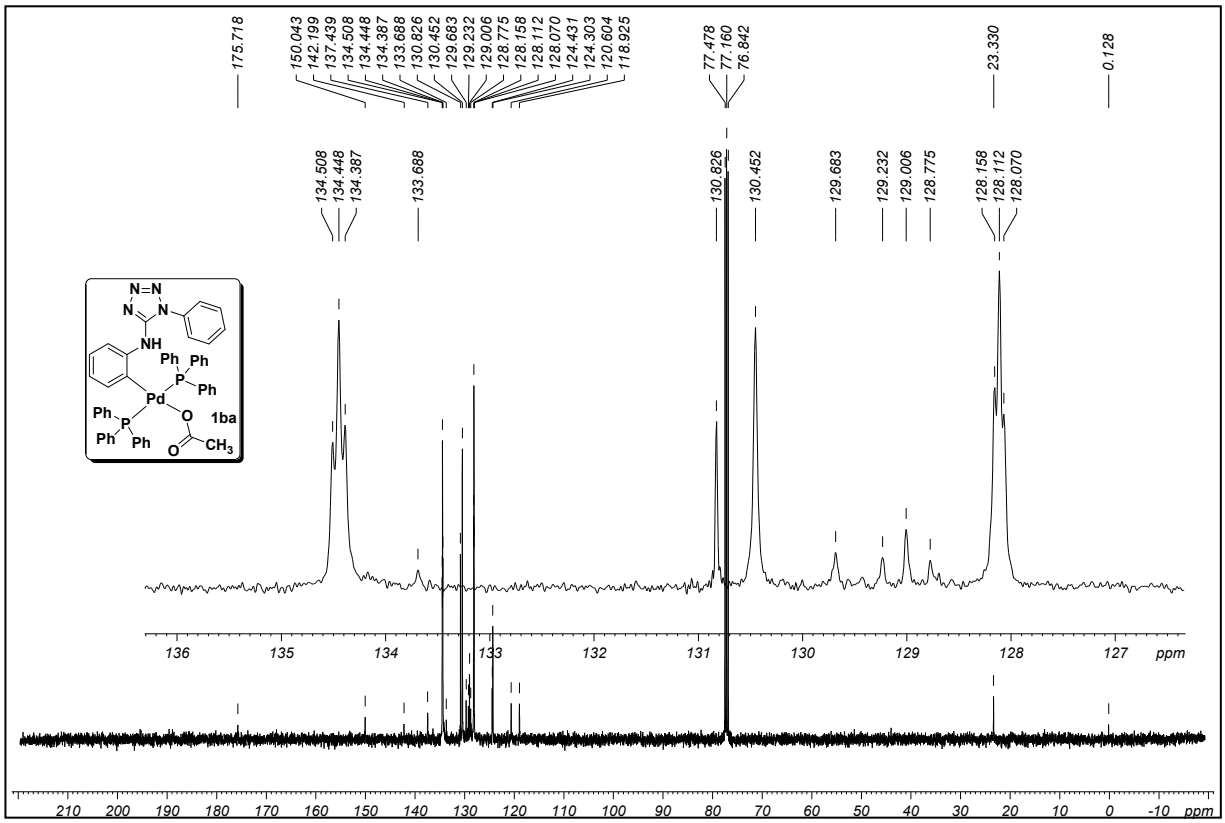


Figure S62. 100 MHz ^{13}C NMR spectrum of **1ba** in $CDCl_3$

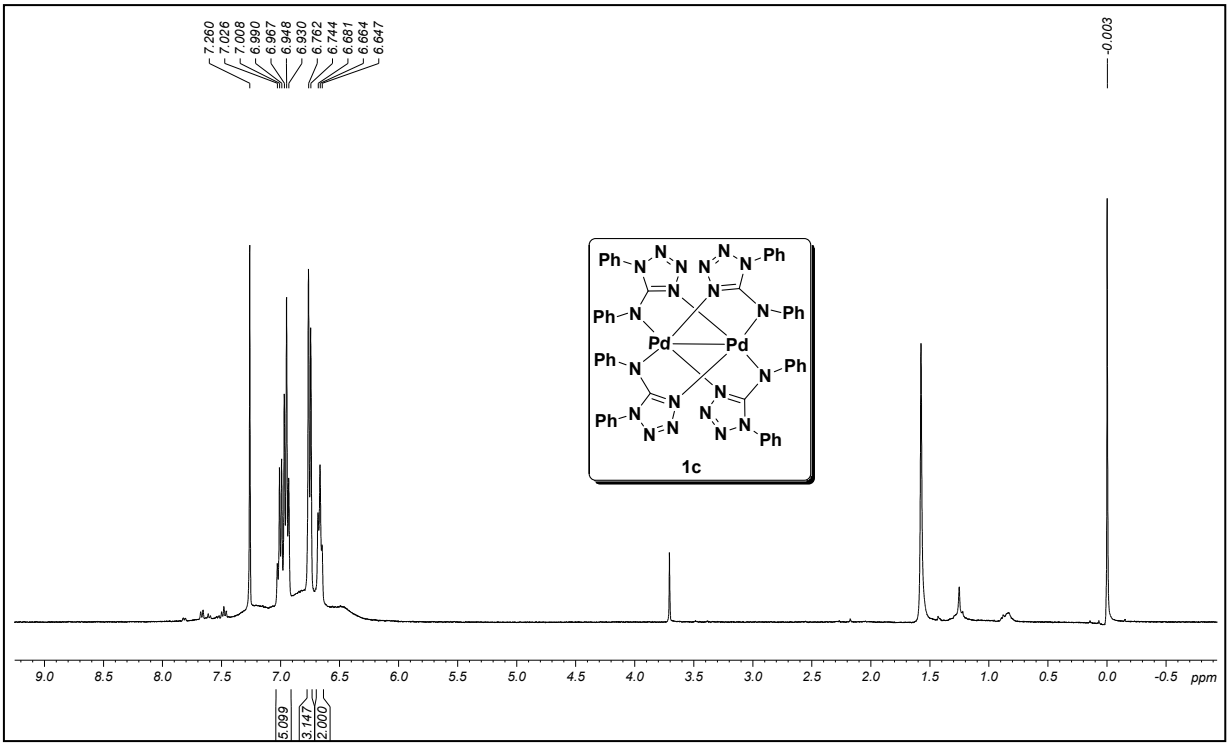


Figure S63. 400 MHz ^{1}H NMR spectrum of **1c** in $CDCl_3$

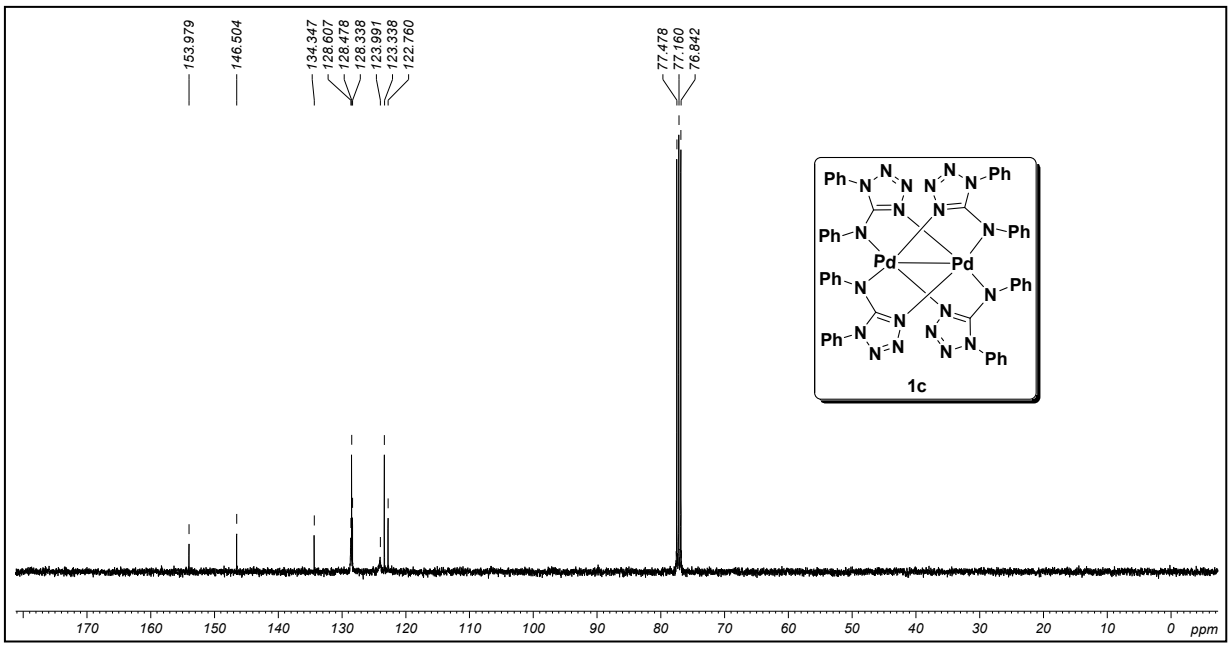


Figure S64. 100 MHz ^{13}C NMR spectrum of **1c** in $CDCl_3$

A. Intermolecular isotope experiment:

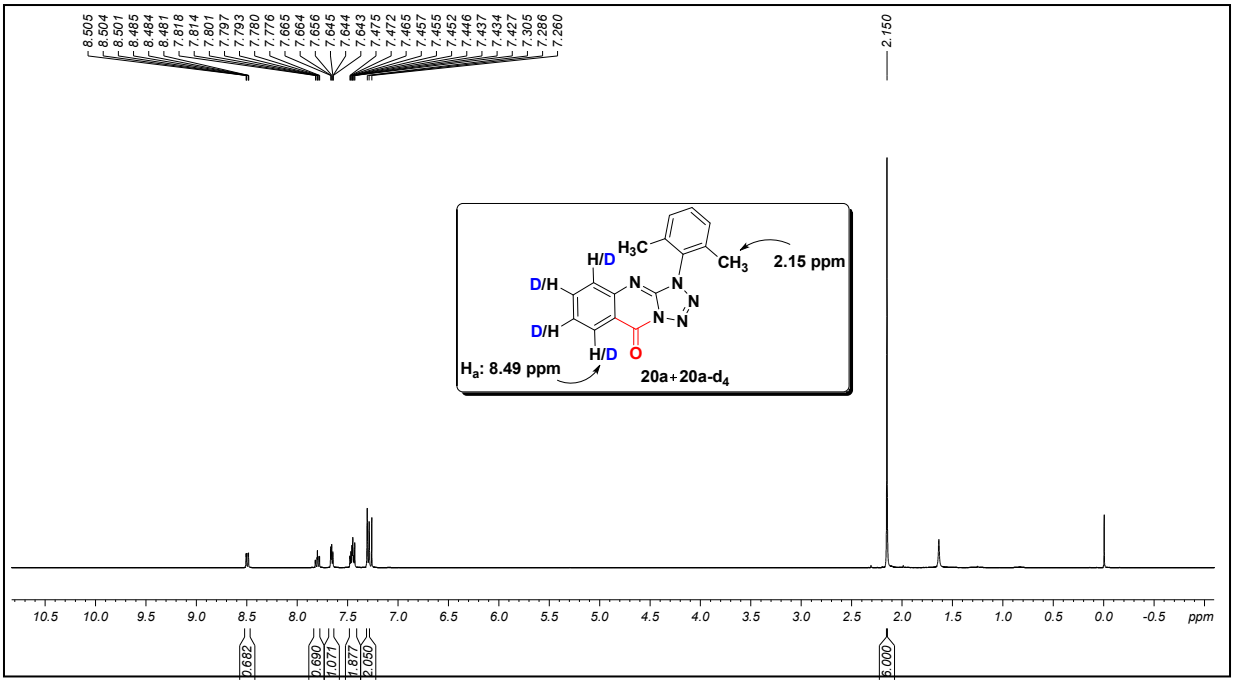


Figure S65. 400 MHz ^{1}H NMR spectrum of **20a+20a-d$_4$** in $CDCl_3$

B. Intramolecular isotope experiment:

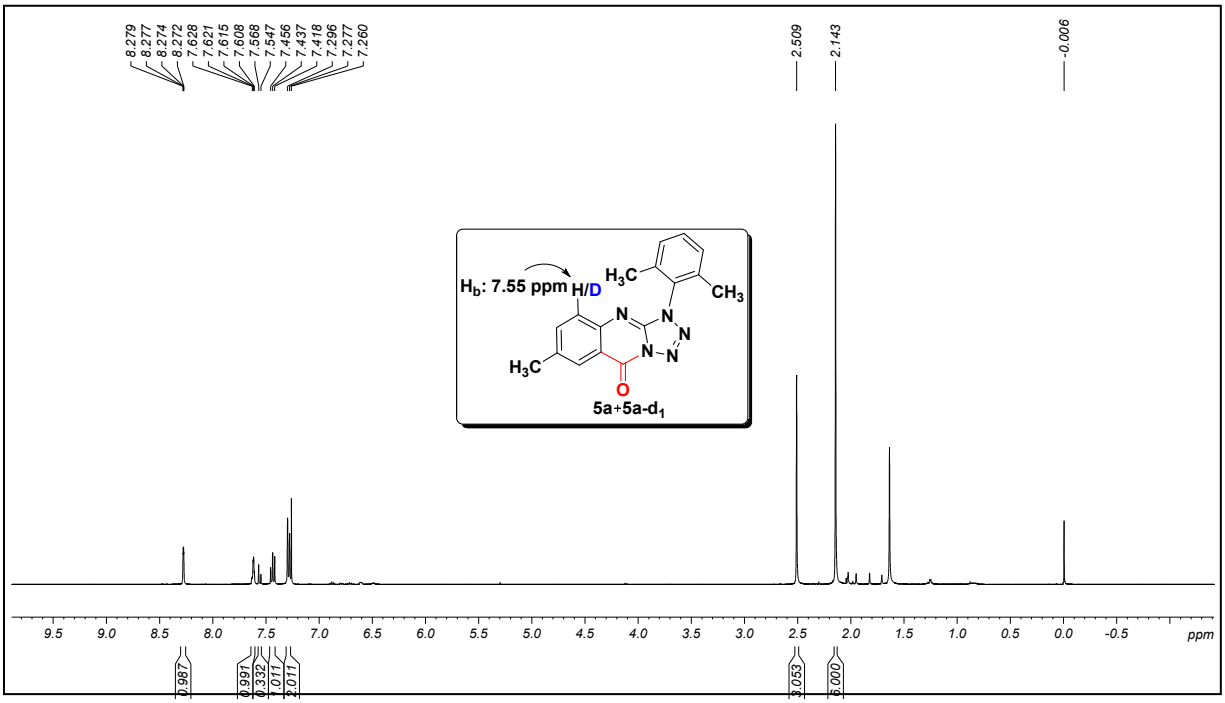


Figure S66. 400 MHz ^{1}H NMR spectrum of **5a+5a-d$_1$** in $CDCl_3$

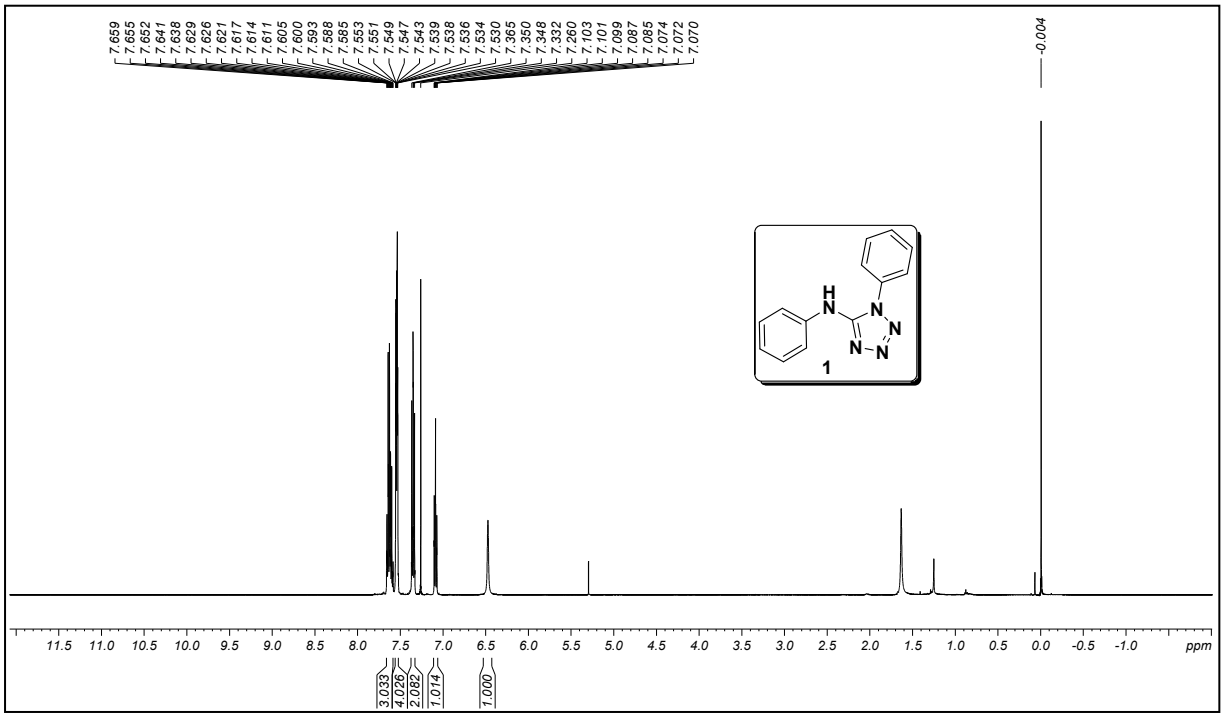


Figure S67. 500 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$

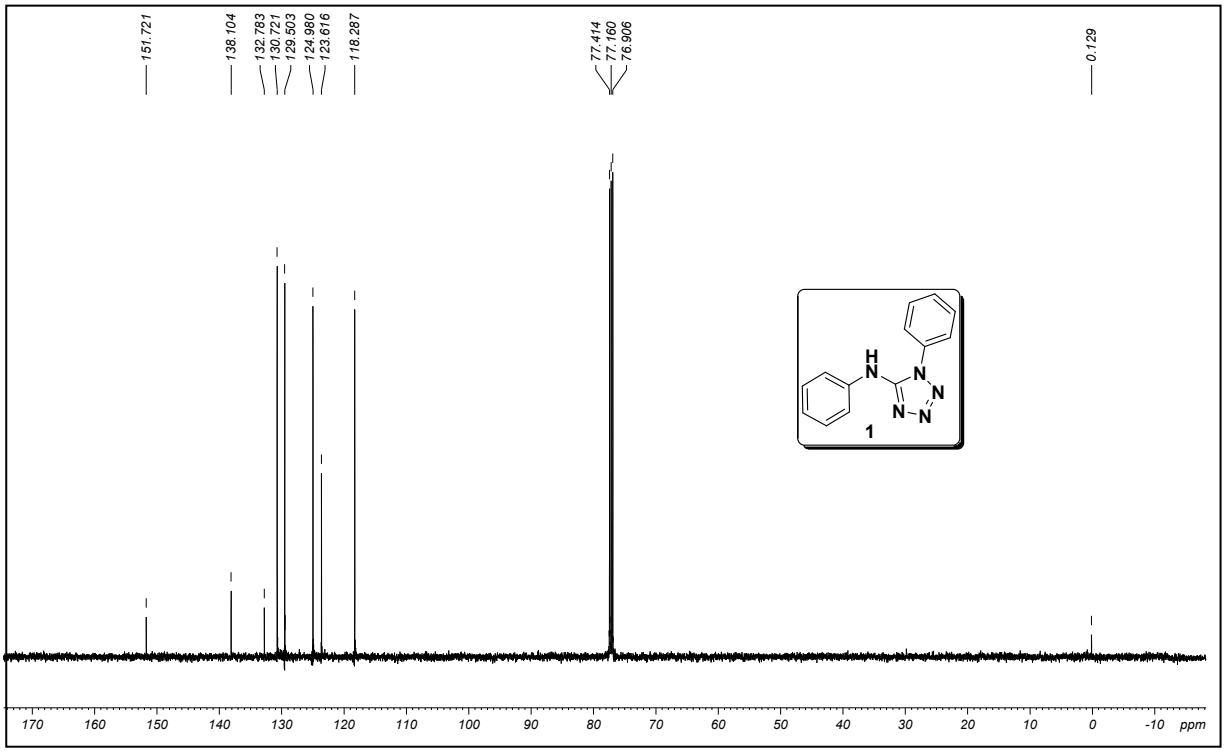


Figure S68. 125 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$

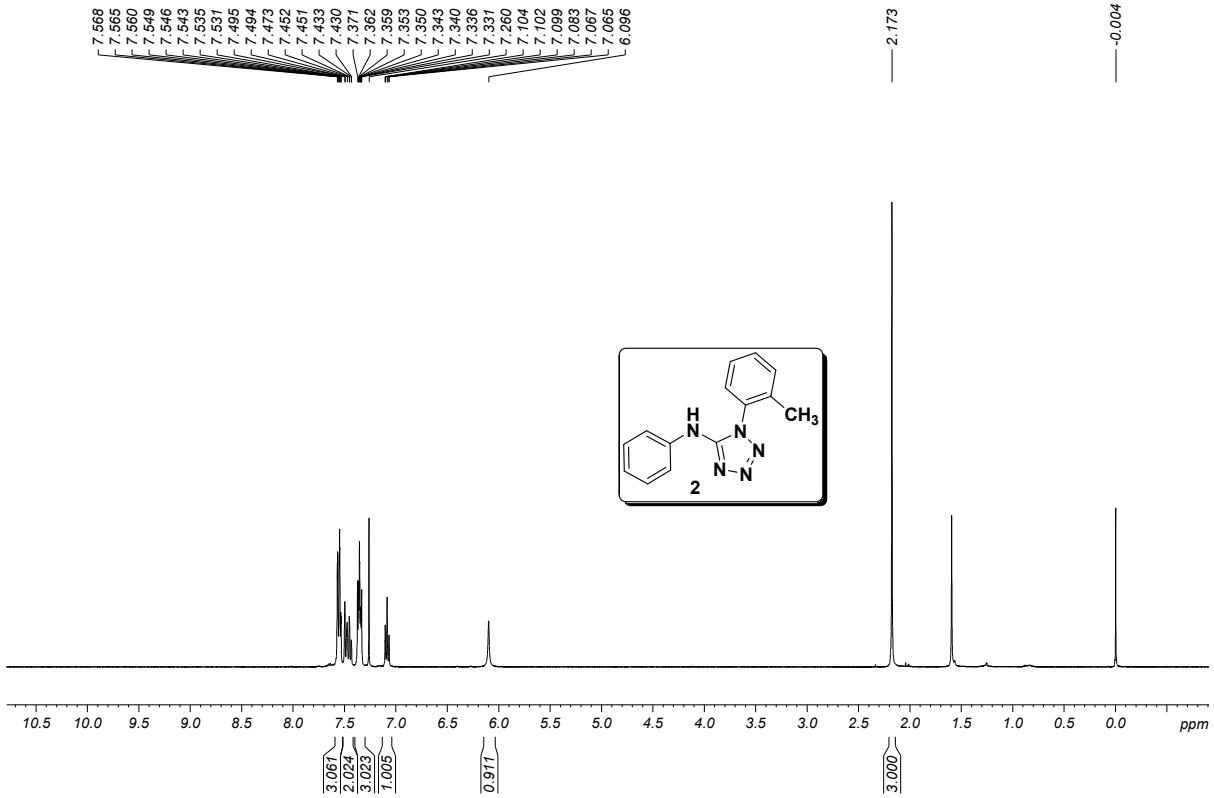


Figure S69. 400 MHz ^{1}H NMR spectrum of **2** in $CDCl_3$

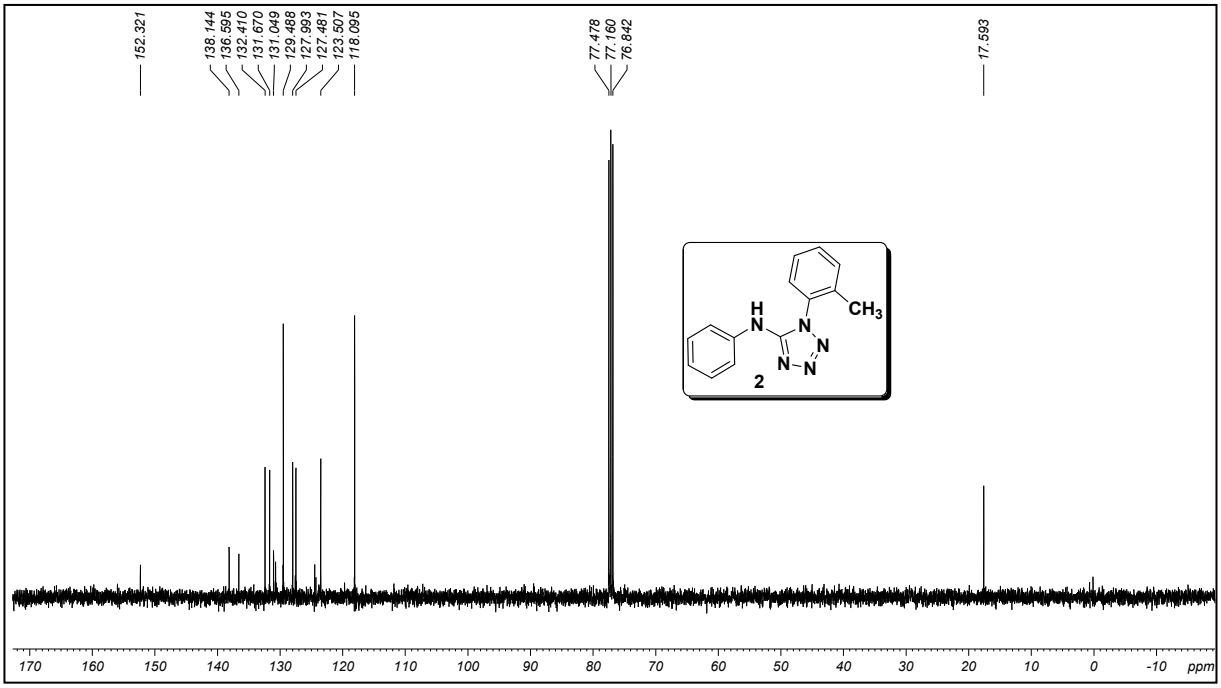


Figure S70. 100 MHz ^{13}C NMR spectrum of **2** in $CDCl_3$

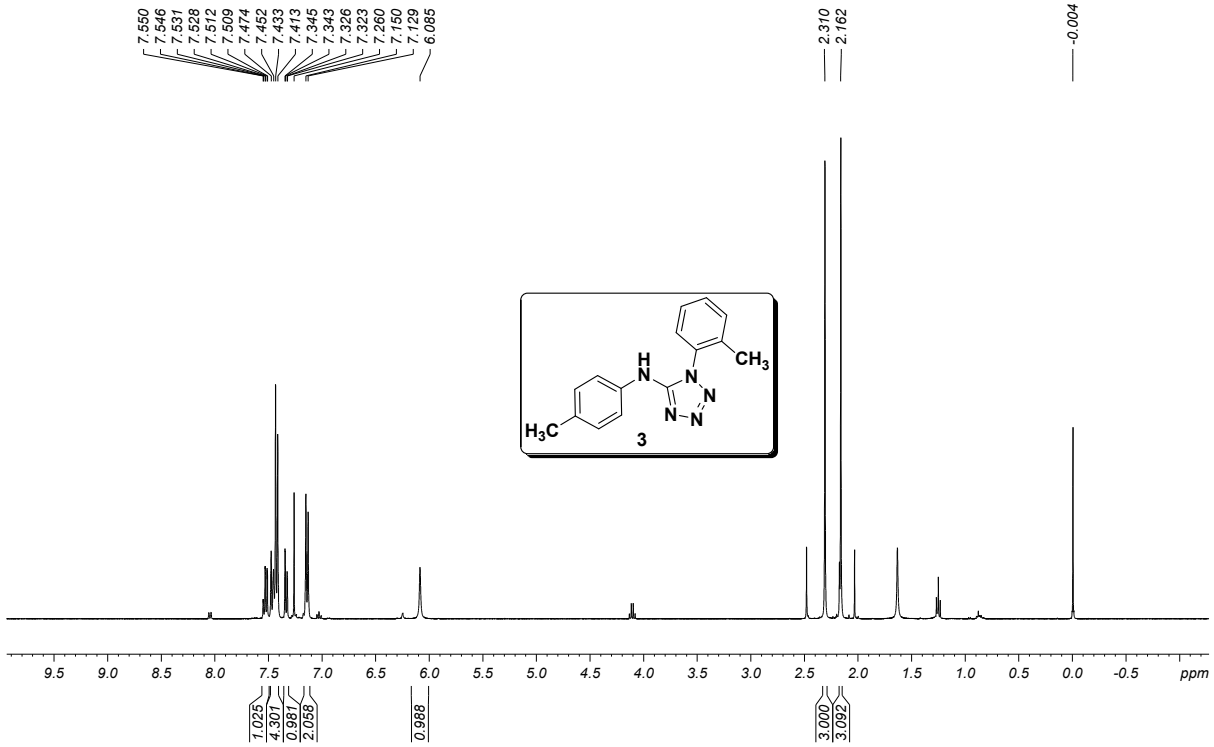


Figure S71. 400 MHz ^{1}H NMR spectrum of **3** in $CDCl_3$

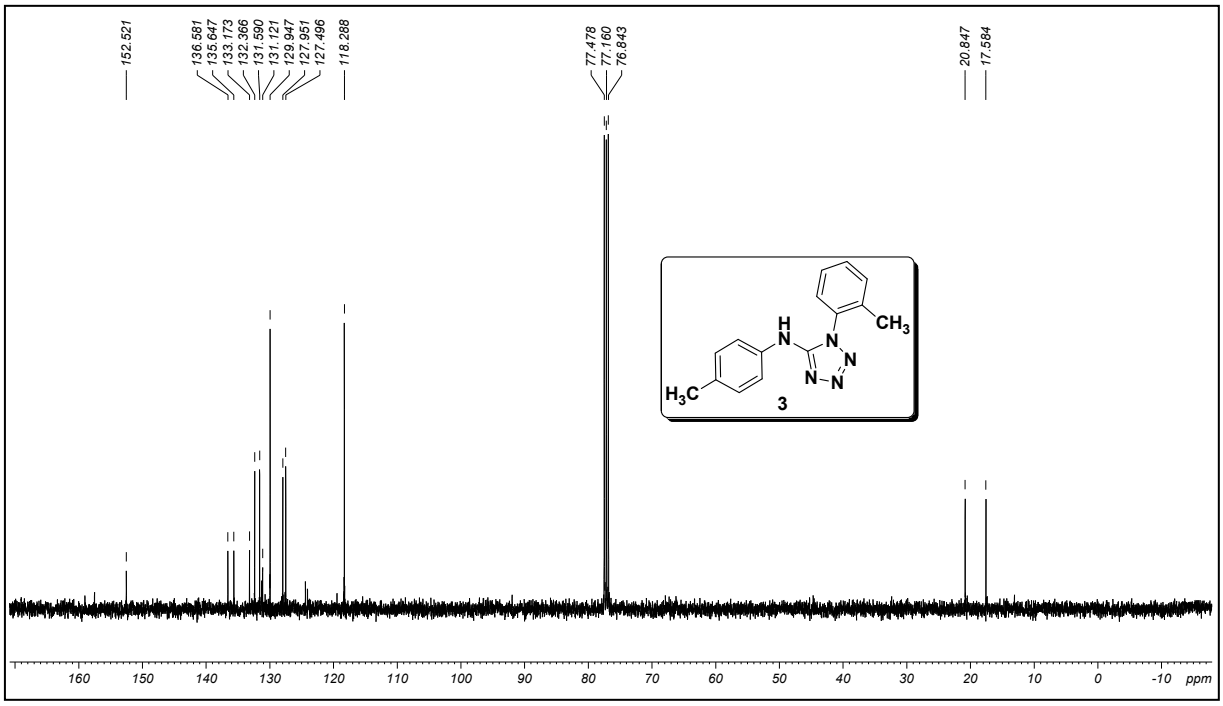


Figure S72. 100 MHz ^{13}C NMR spectrum of **3** in $CDCl_3$

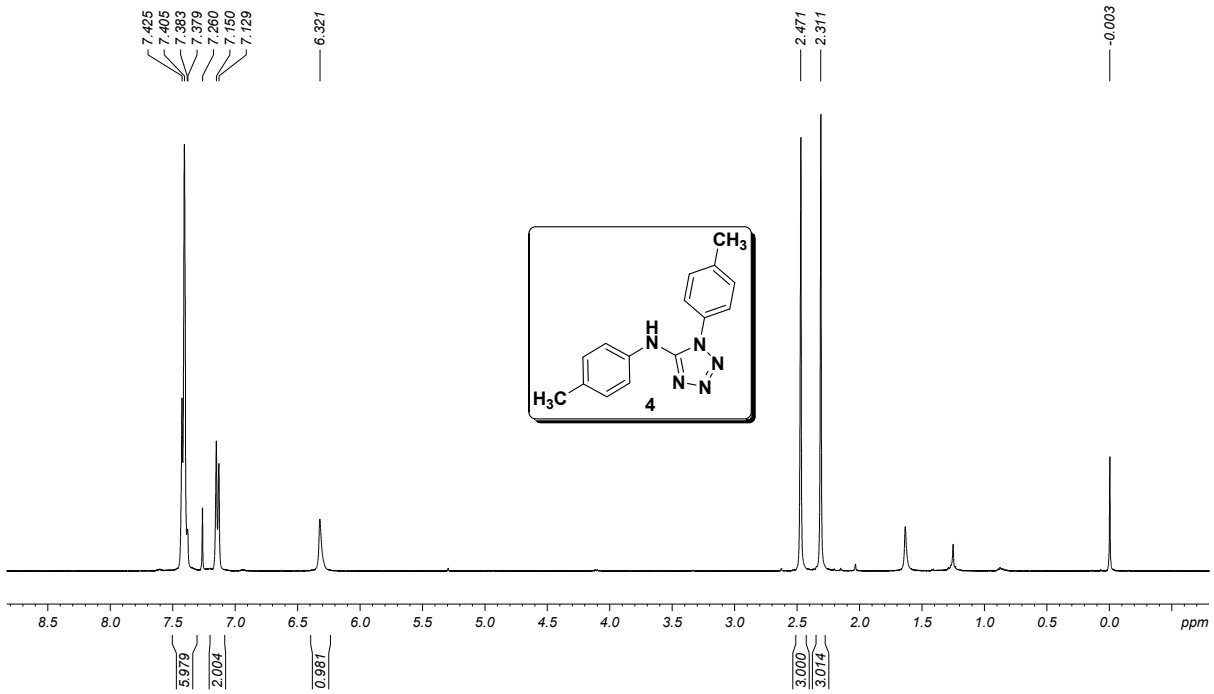


Figure S73. 400 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$

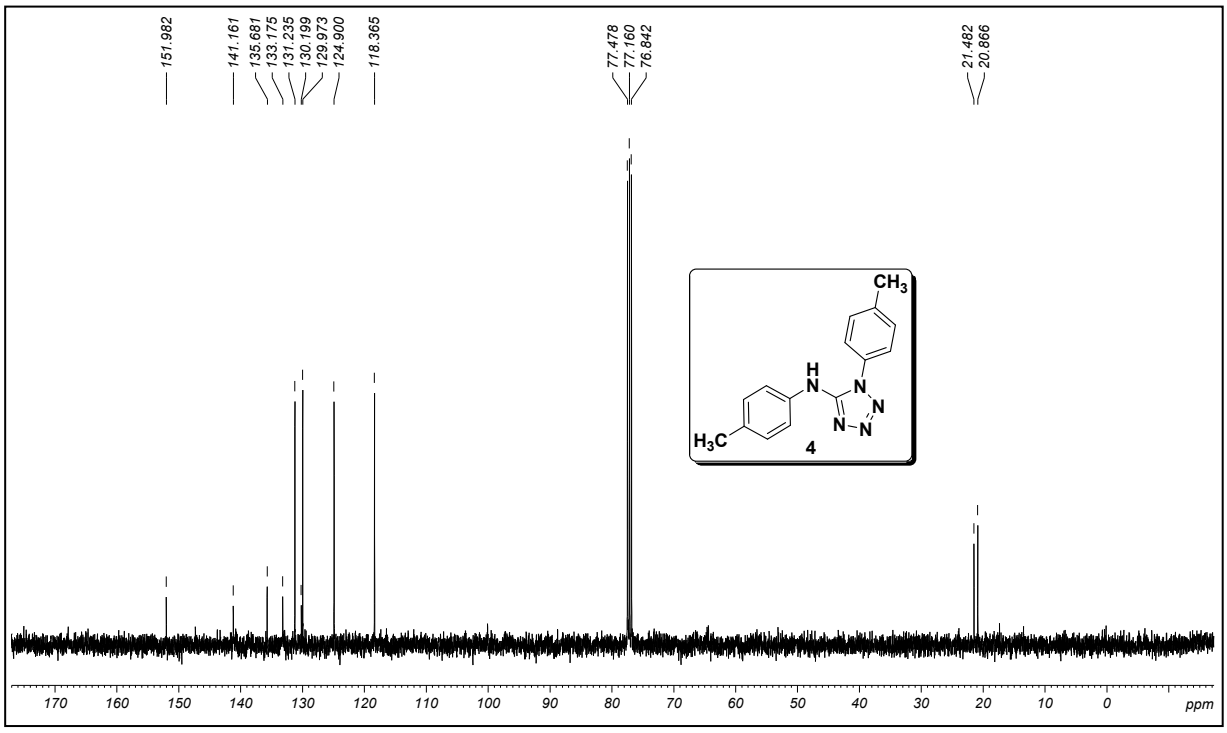


Figure S74. 100 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$

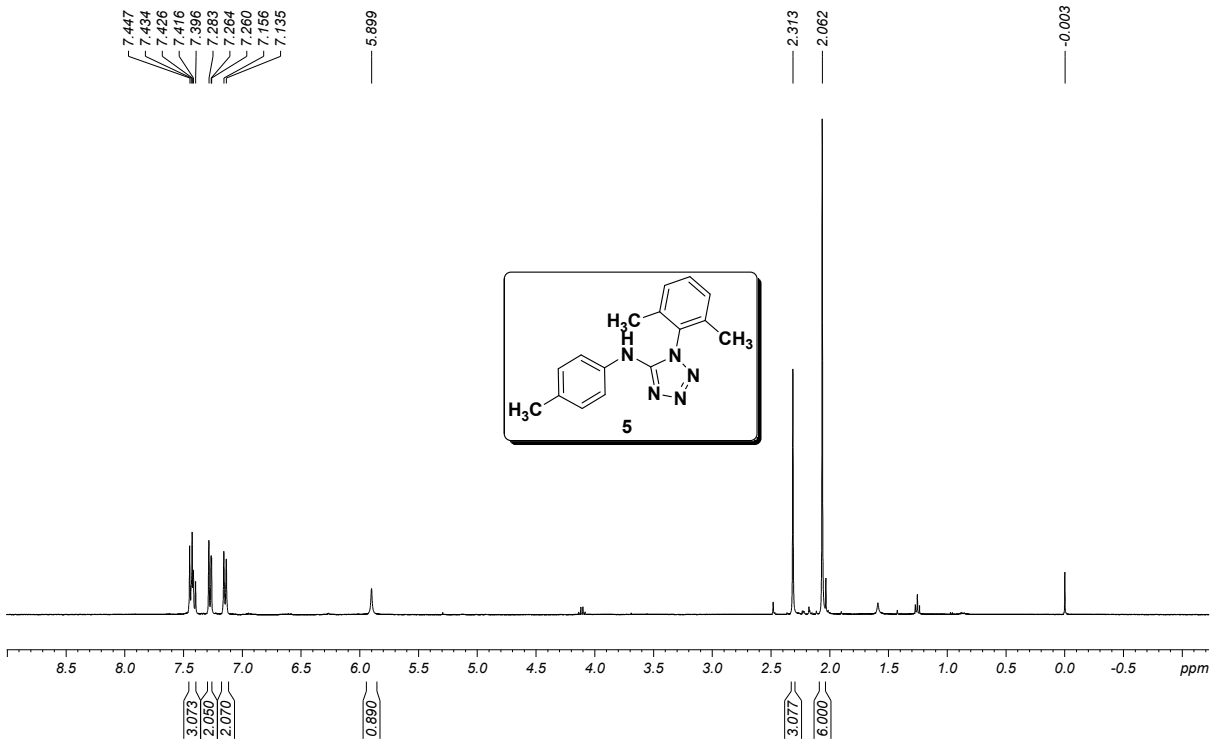


Figure S75. 400 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$

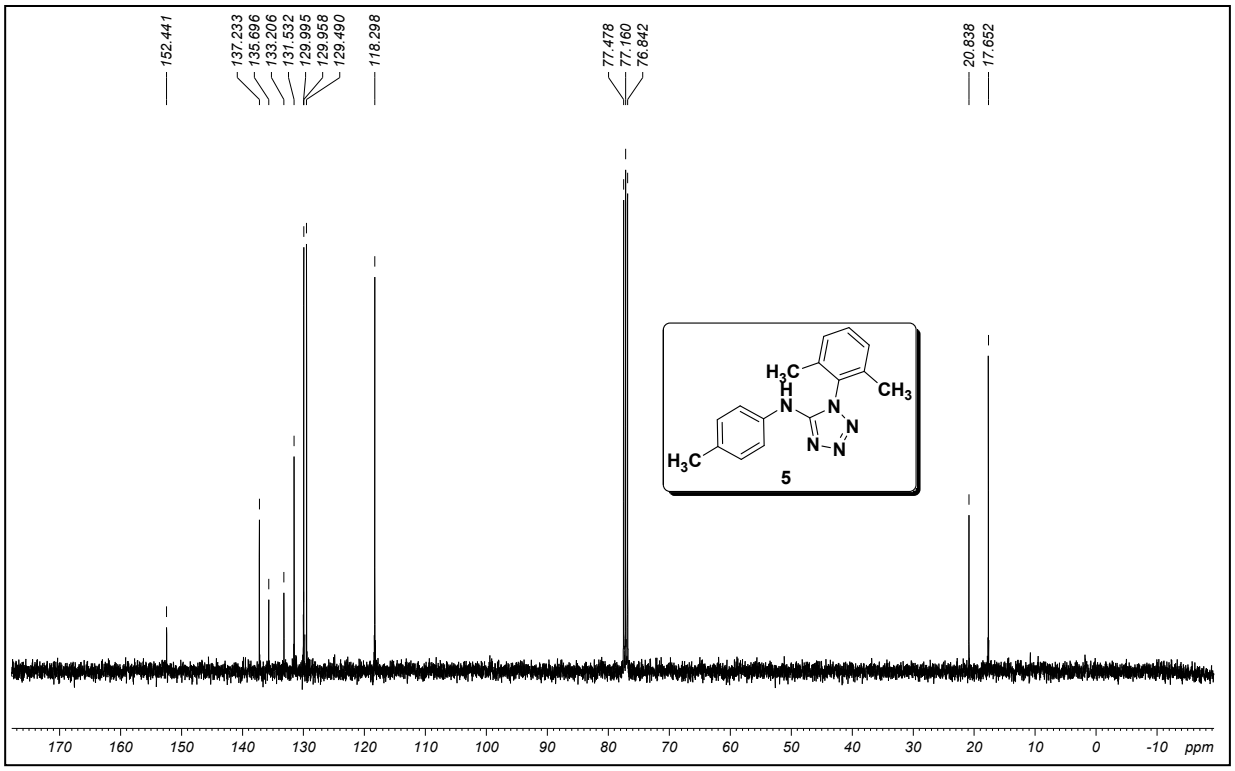


Figure S76. 100 MHz ^{13}C NMR spectrum of **5** in $CDCl_3$

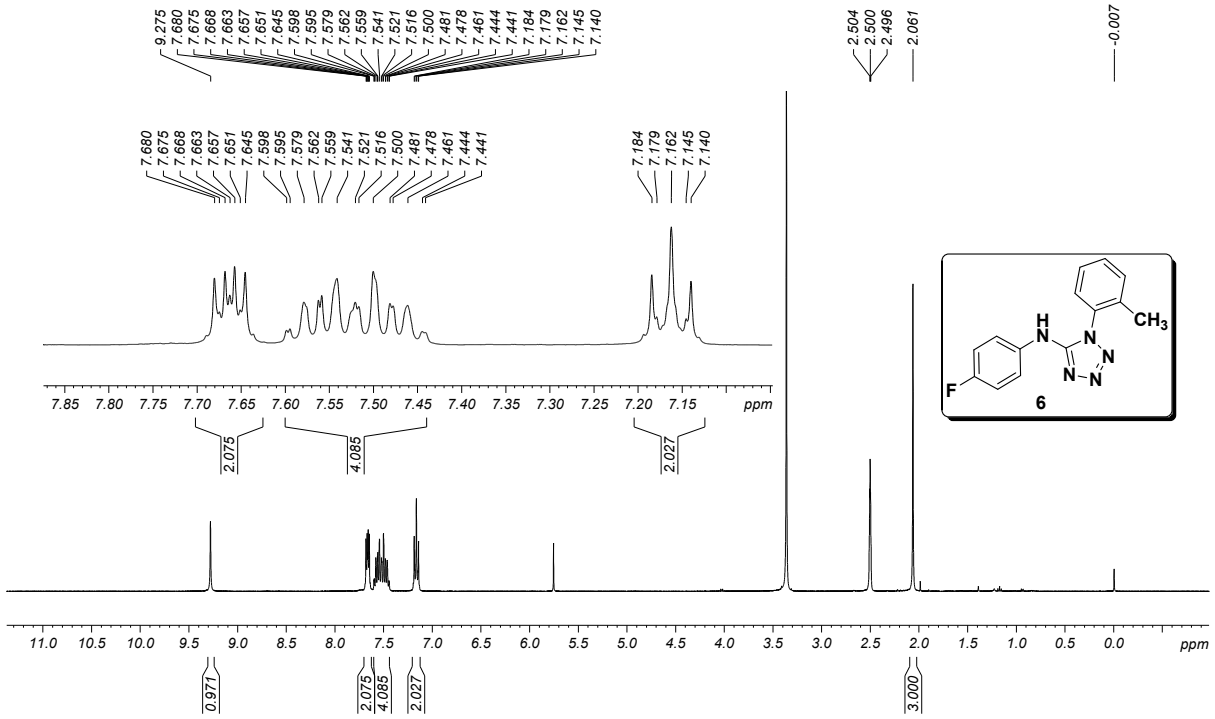


Figure S77. 400 MHz ^{1}H NMR spectrum of **6** in DMSO-d_6

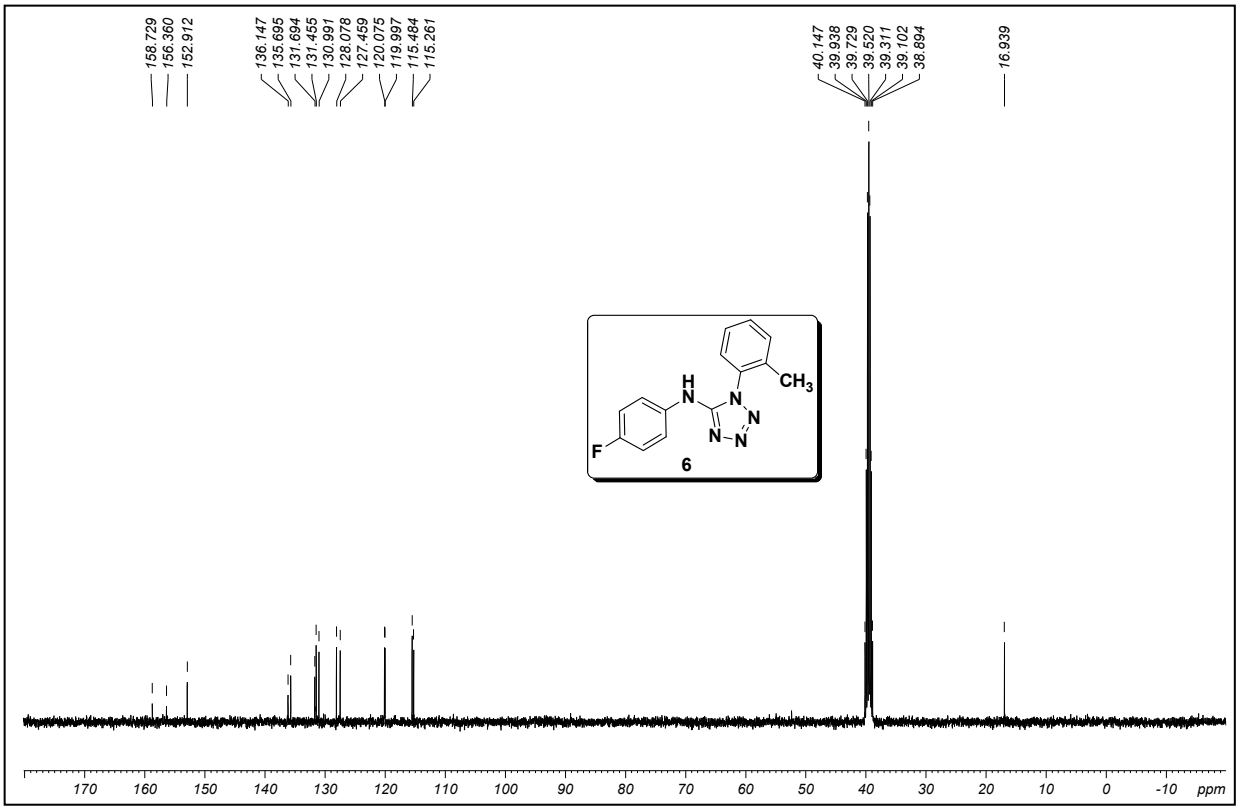


Figure S78. 100 MHz ^{13}C NMR spectrum of **6** in DMSO-d_6

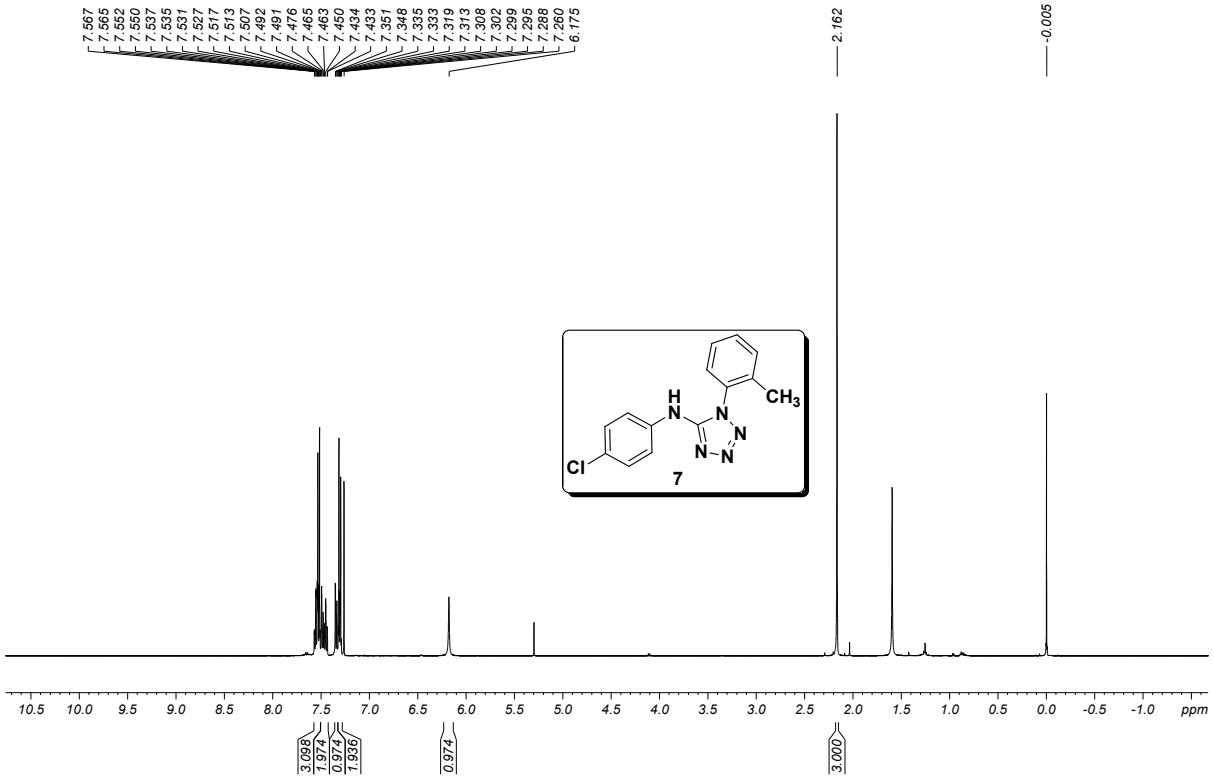


Figure S79. 500 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$

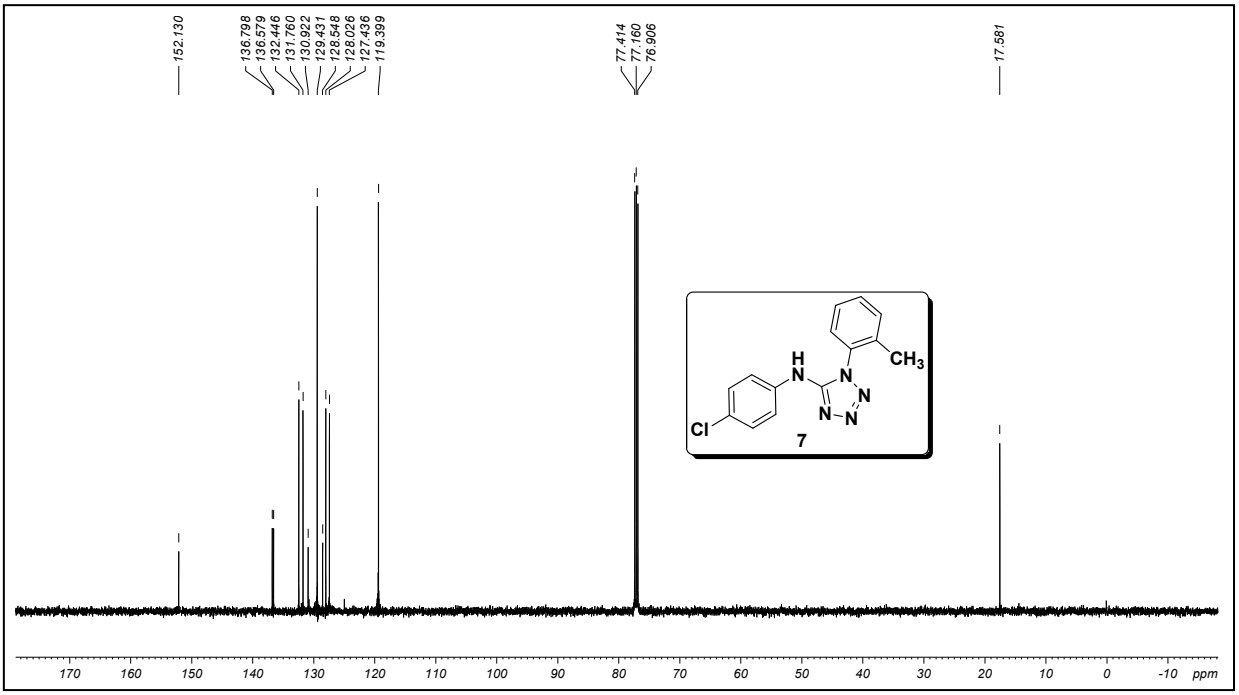


Figure S80. 125 MHz ^{13}C NMR spectrum of **7** in $CDCl_3$

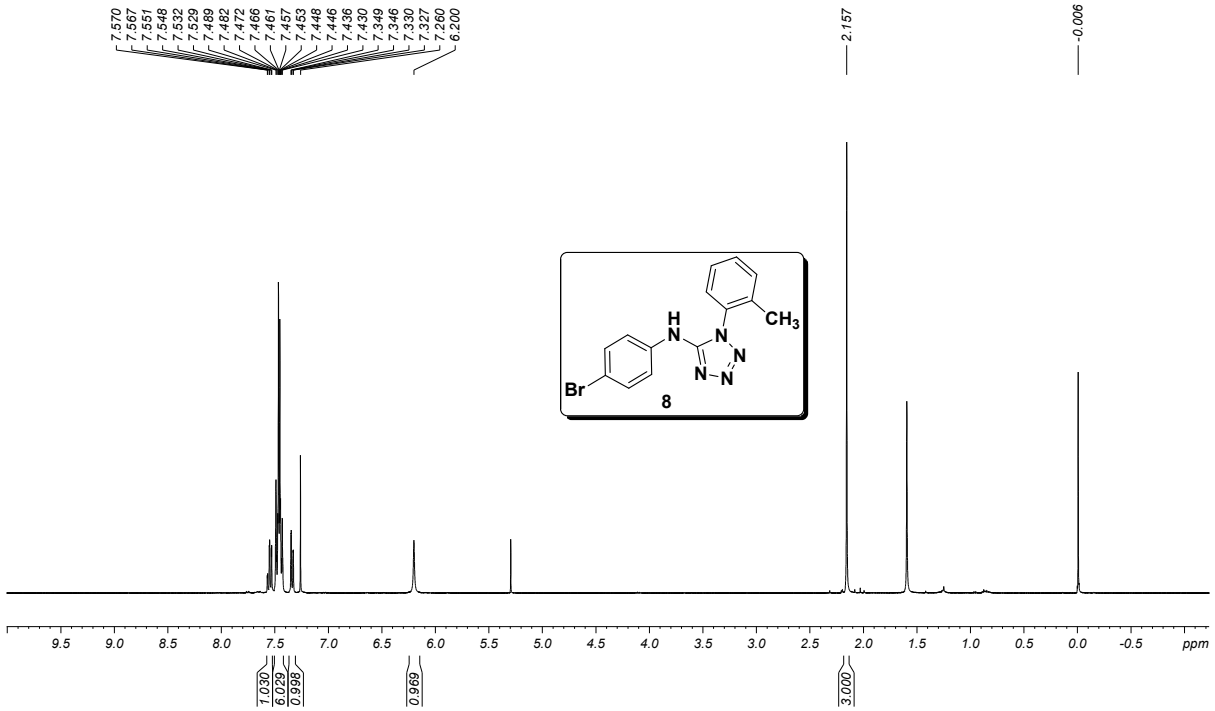


Figure S81. 400 MHz ^{1}H NMR spectrum of **8** in $CDCl_3$

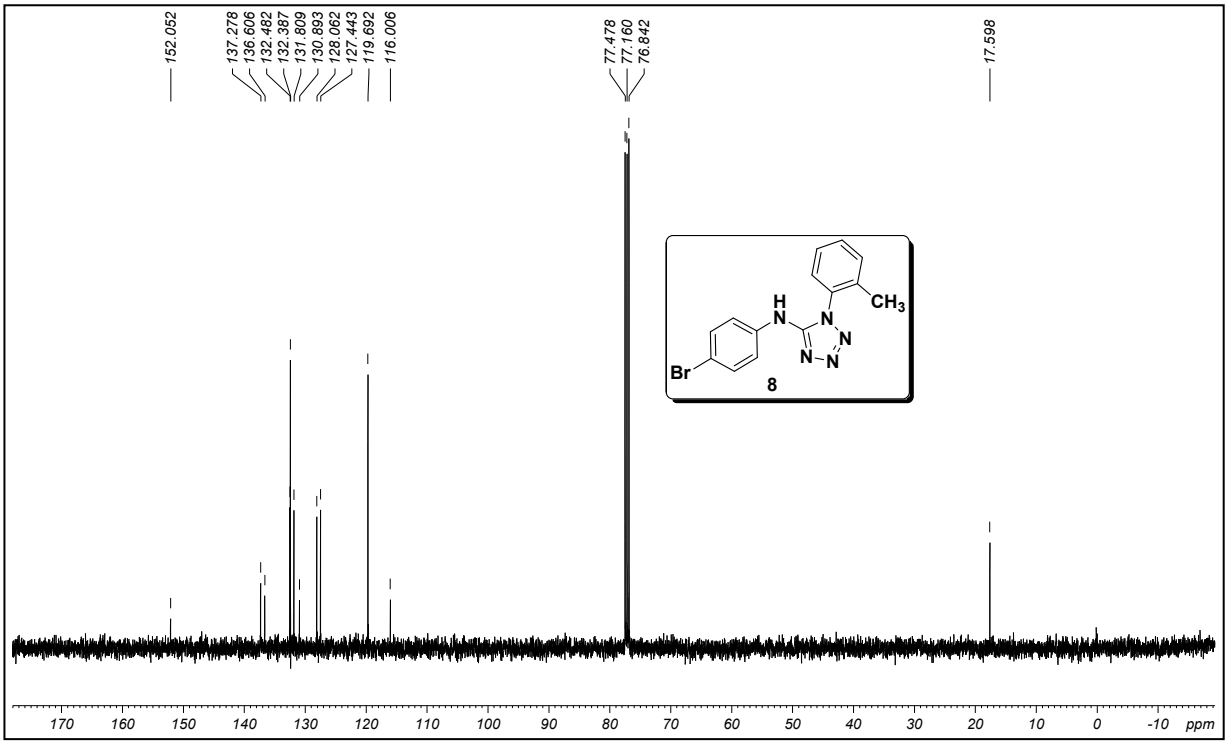


Figure S82. 100 MHz ^{13}C NMR spectrum of **8** in $CDCl_3$

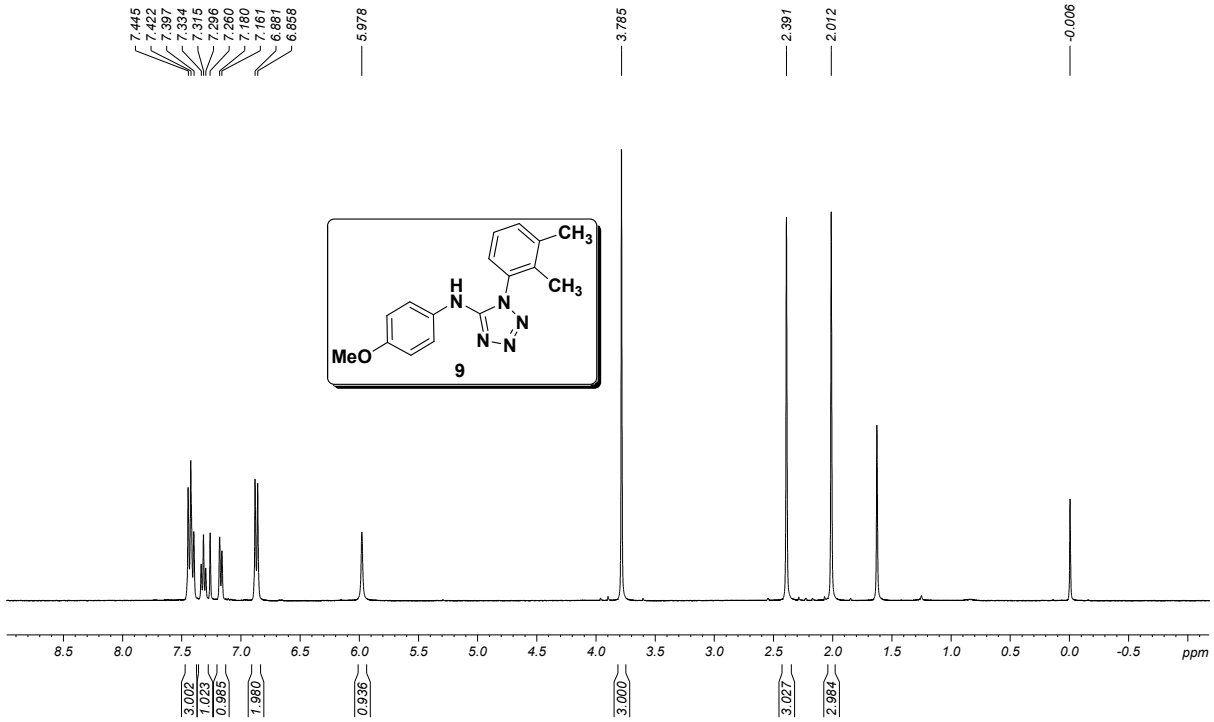


Figure S83. 400 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$

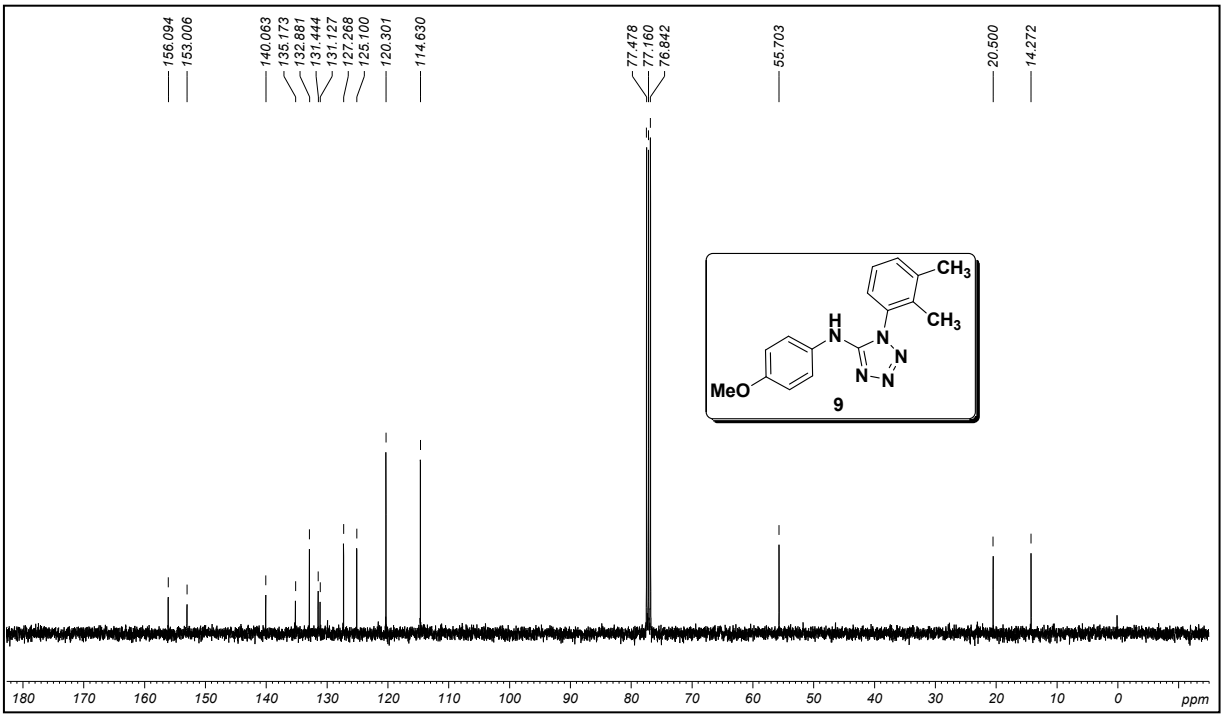


Figure S84. 100 MHz ^{13}C NMR spectrum of **9** in $CDCl_3$

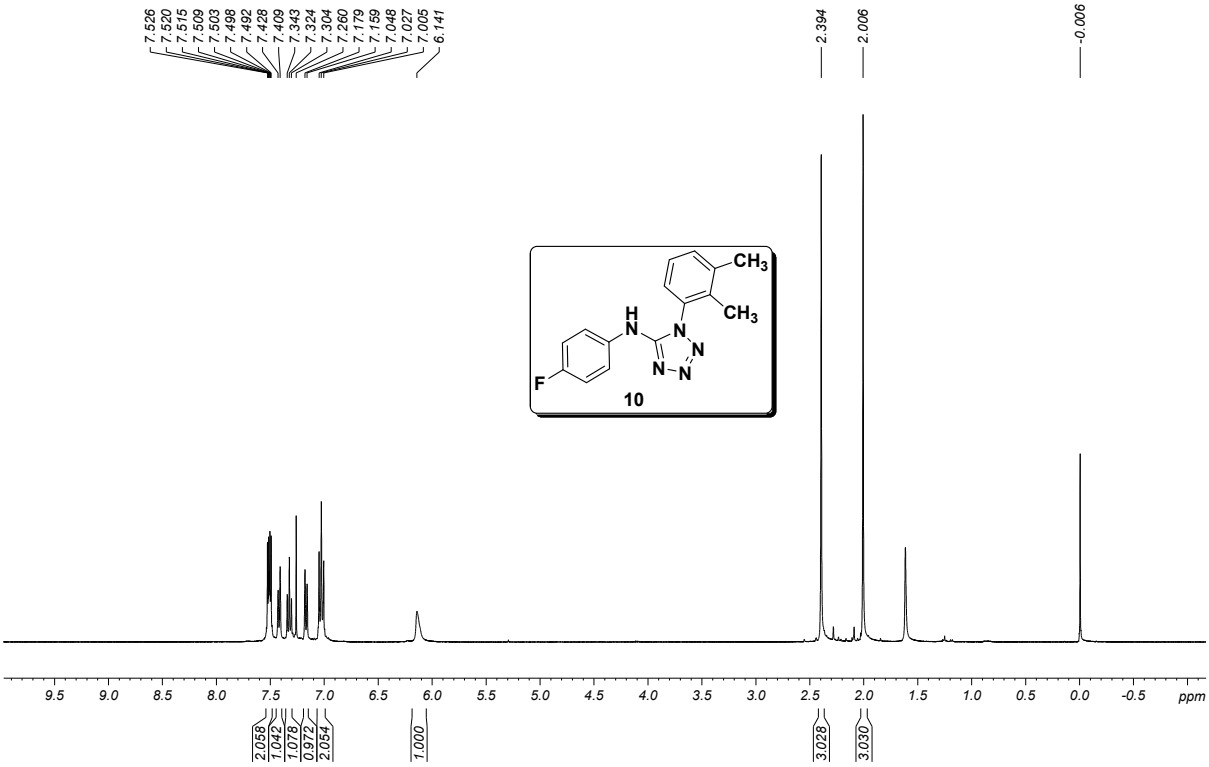


Figure S85. 400 MHz ^{1}H NMR spectrum of **10** in $CDCl_3$

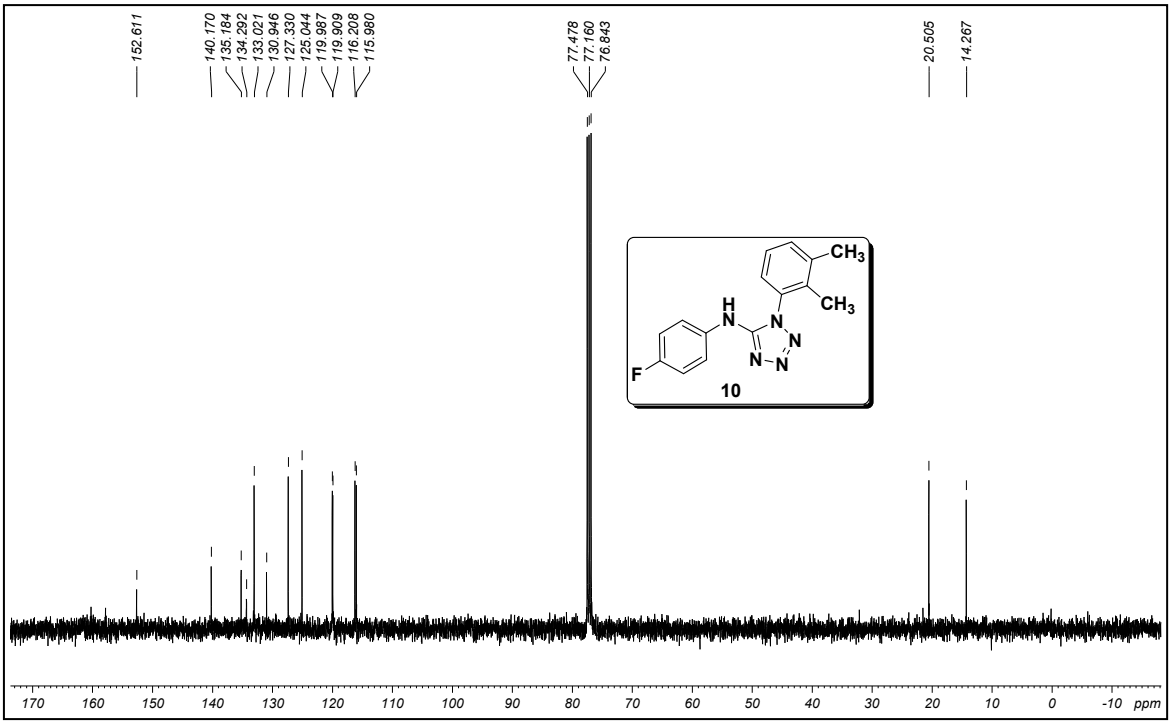


Figure S86. 100 MHz ^{13}C NMR spectrum of **10** in $CDCl_3$

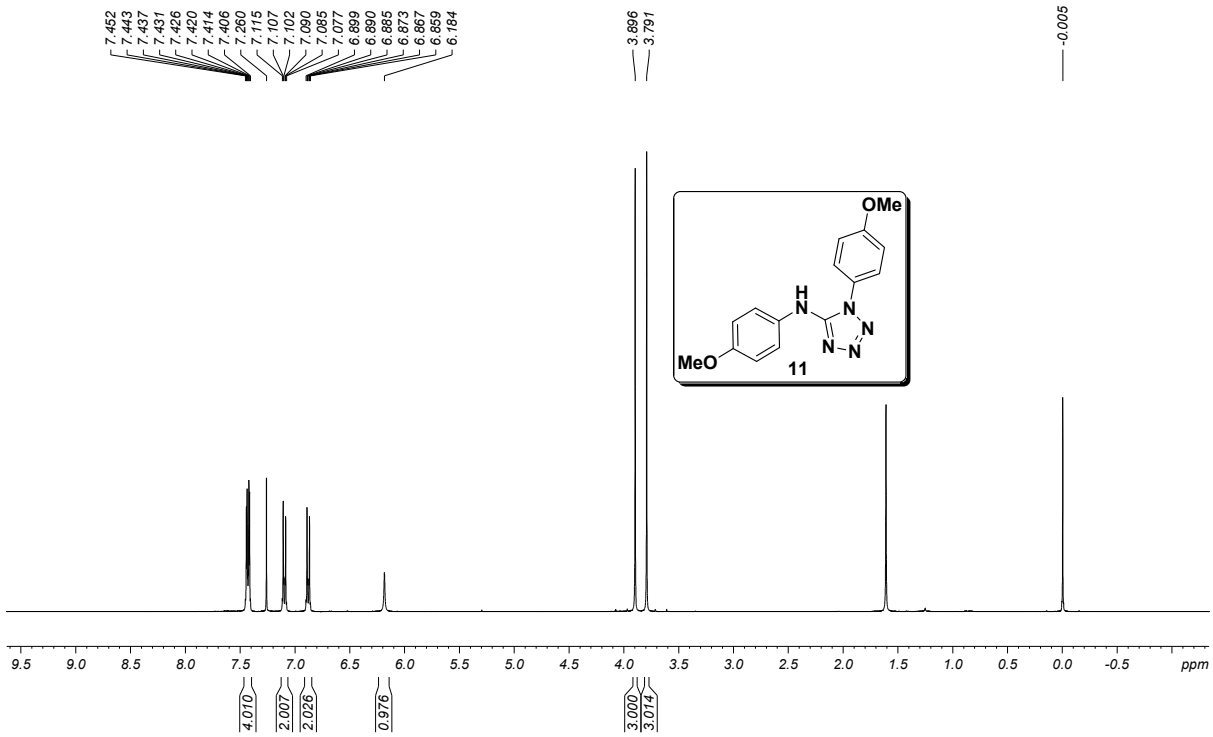


Figure S87. 400 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$

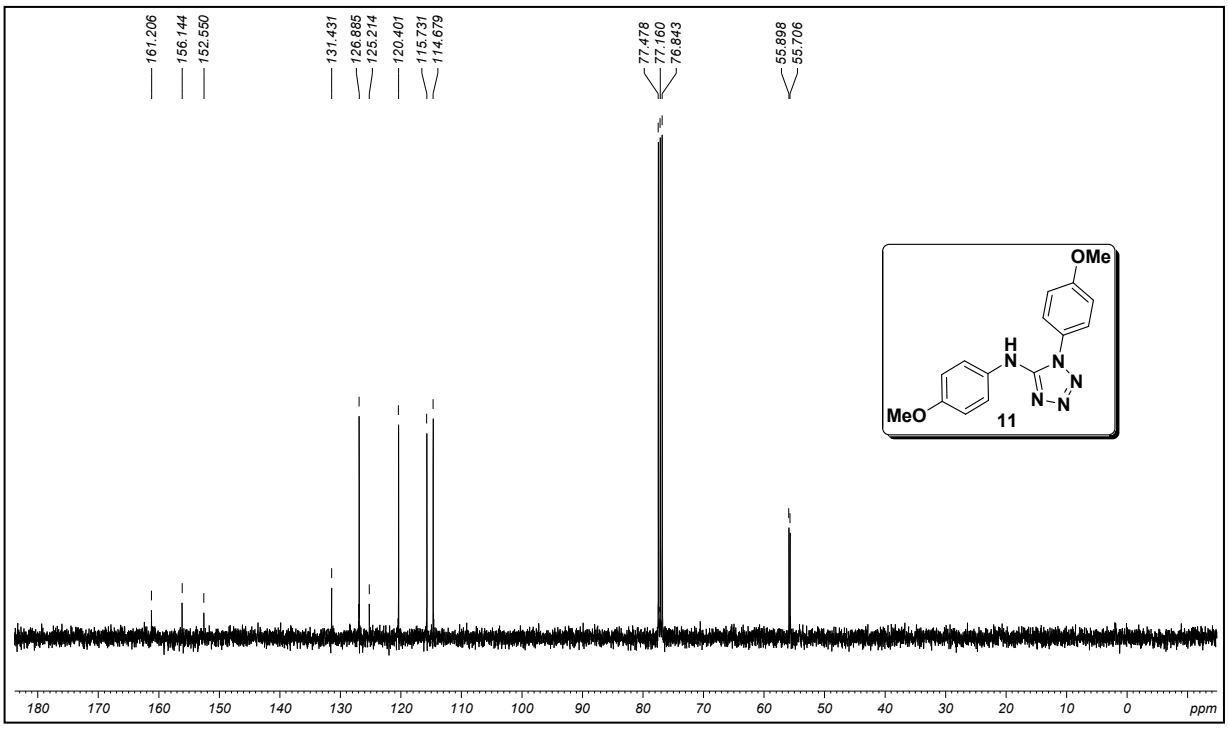


Figure S88. 100 MHz ^{13}C NMR spectrum of **11** in $CDCl_3$

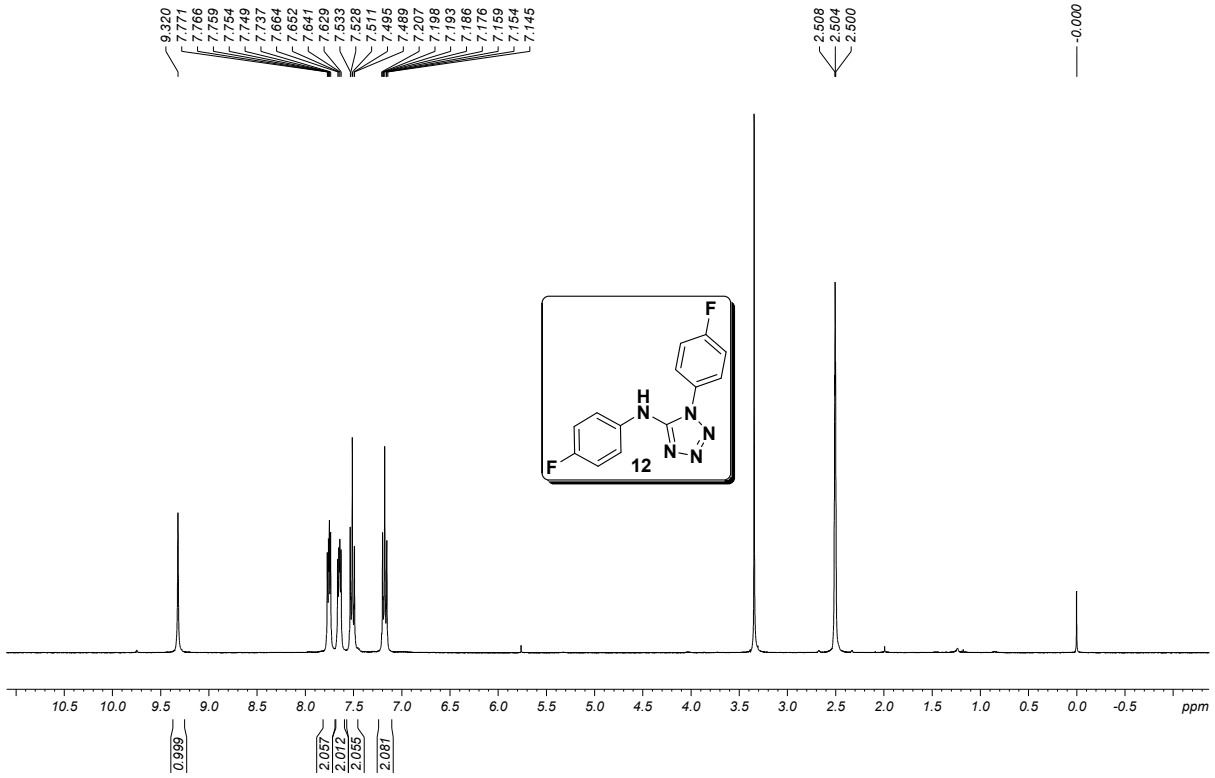


Figure S89. 400 MHz ^{1}H NMR spectrum of **12** in DMSO-d6

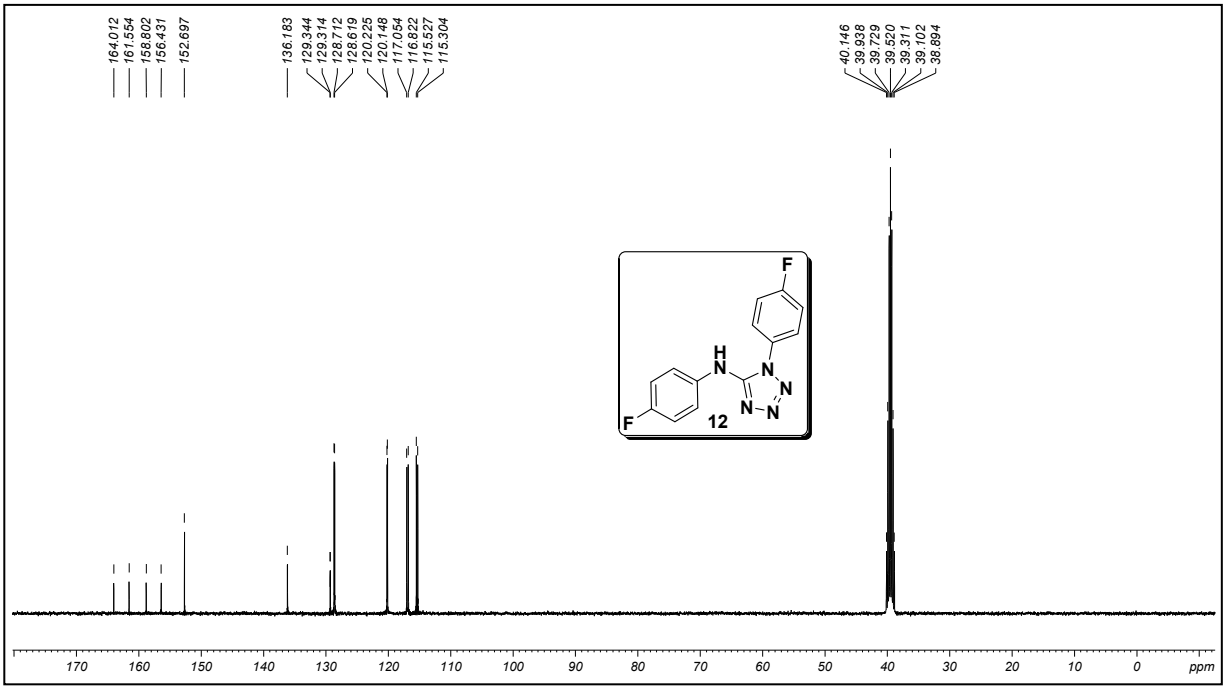


Figure S90. 100 MHz ^{13}C NMR spectrum of **12** in DMSO-d6

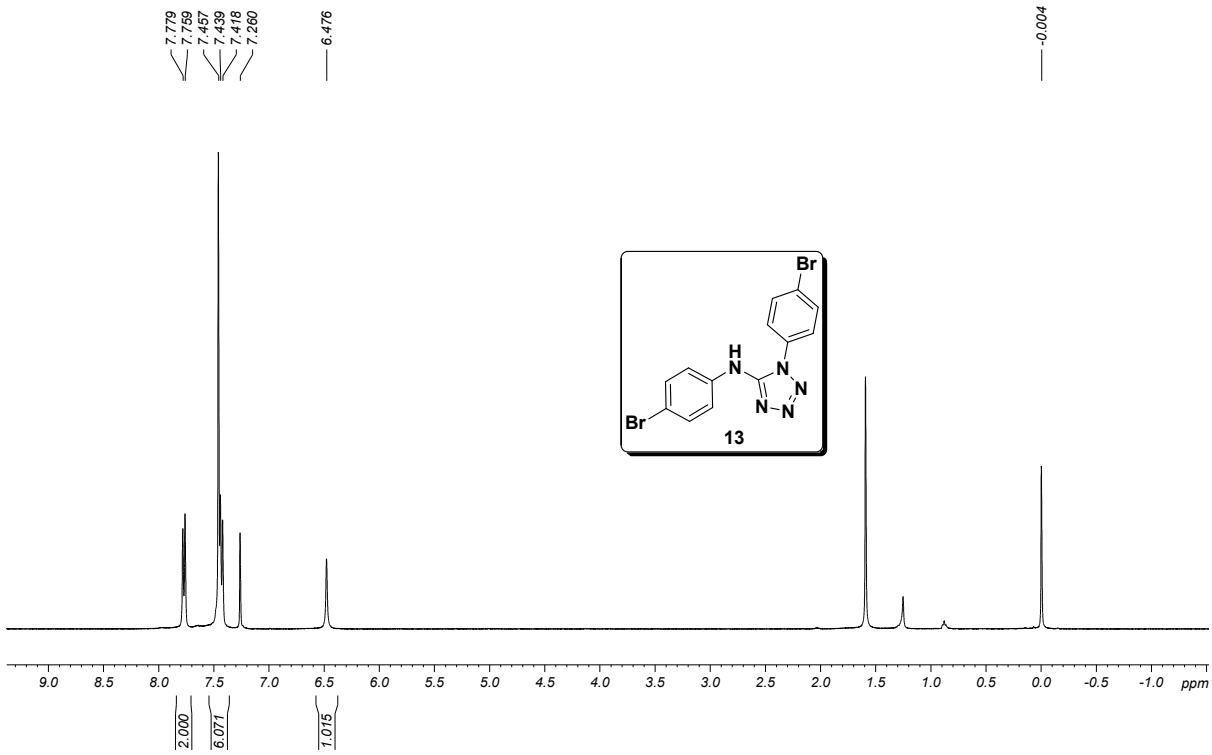


Figure S91. 400 MHz ^{1}H NMR spectrum of **13** in $CDCl_3$

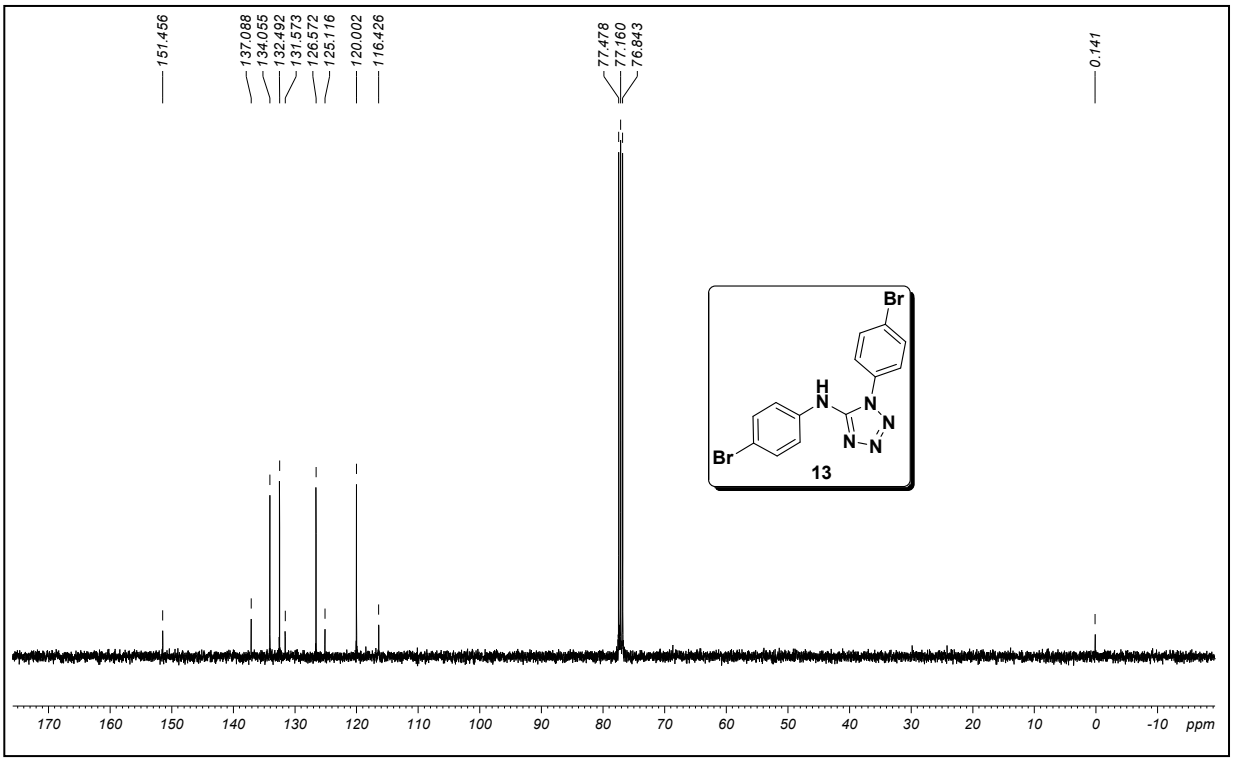


Figure S92. 100 MHz ^{13}C NMR spectrum of **13** in $CDCl_3$

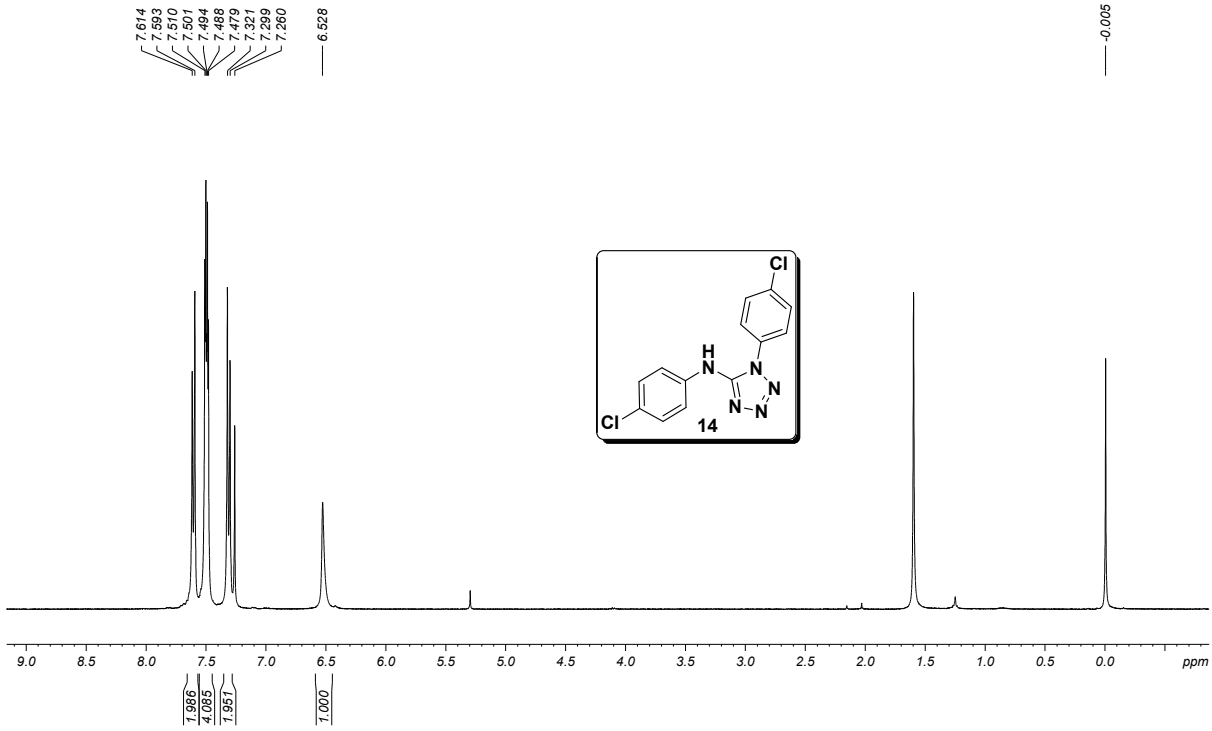


Figure S93. 400 MHz ^{1}H NMR spectrum of **14** in $CDCl_3$

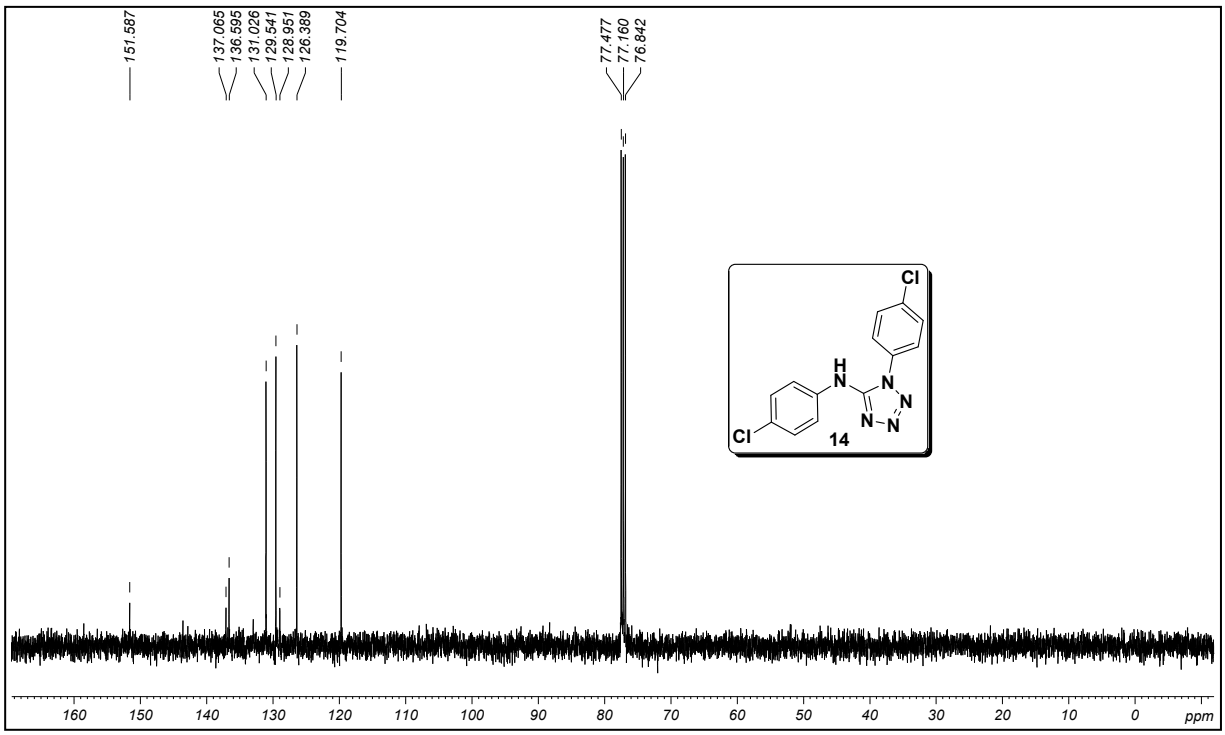


Figure S94. 100 MHz ^{13}C NMR spectrum of **14** in $CDCl_3$

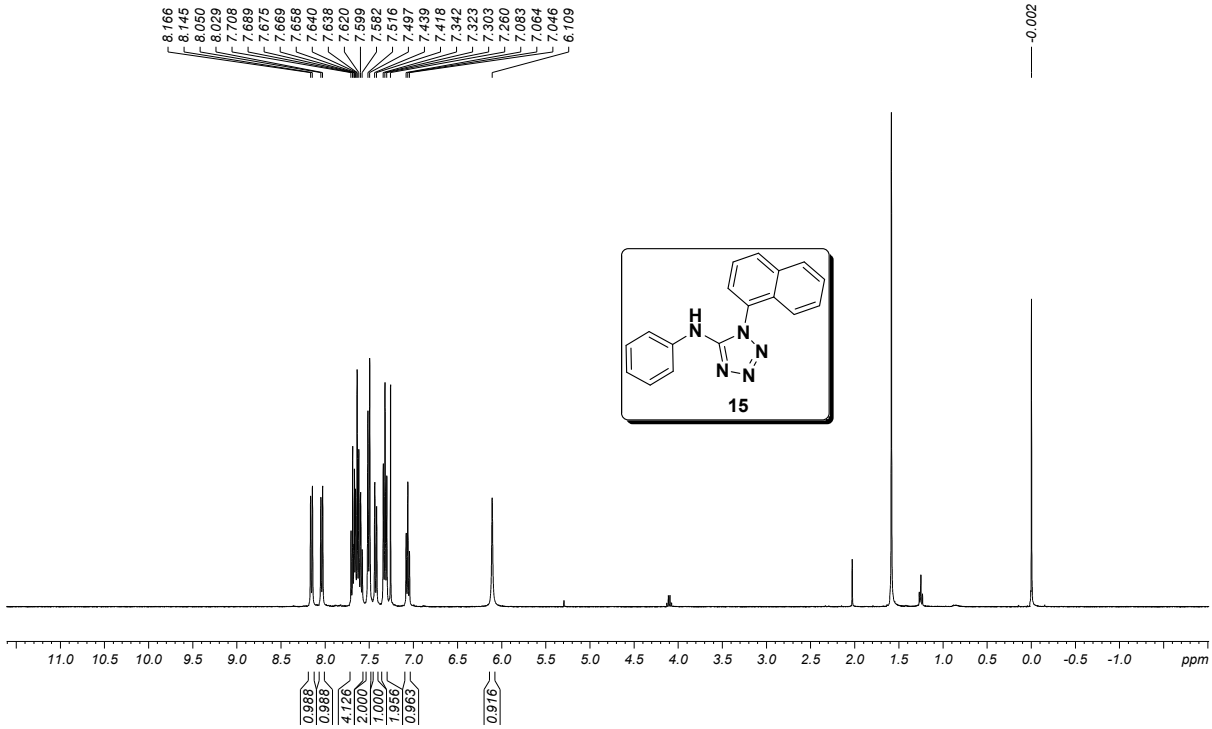


Figure S95. 400 MHz ^{1}H NMR spectrum of **15** in $CDCl_3$

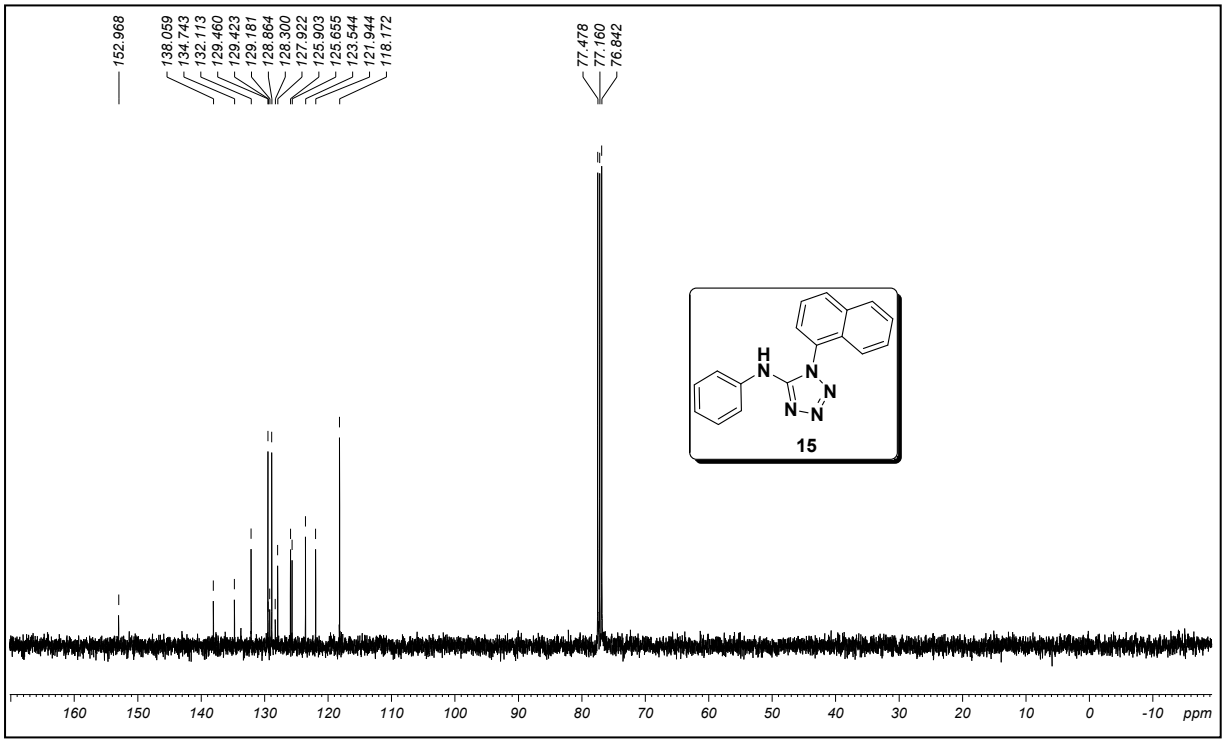


Figure S96. 100 MHz ^{13}C NMR spectrum of **15** in $CDCl_3$

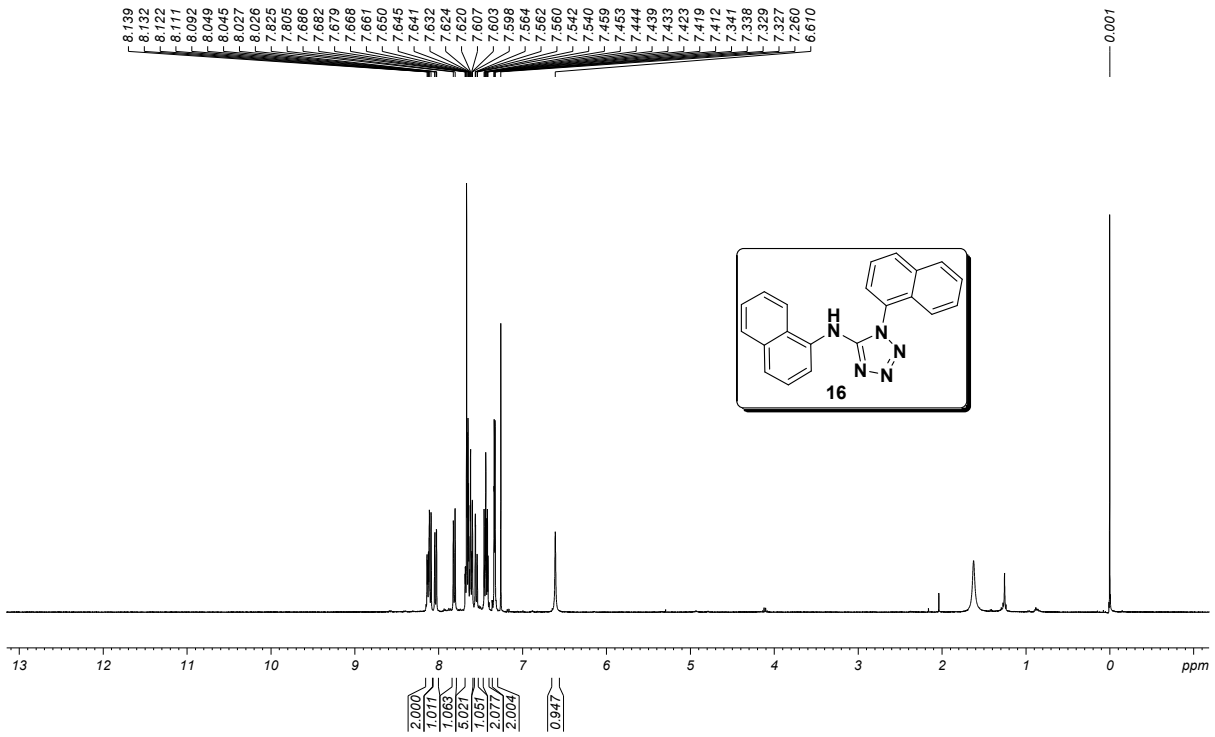


Figure S97. 400 MHz ^{1}H NMR spectrum of **16** in $CDCl_3$

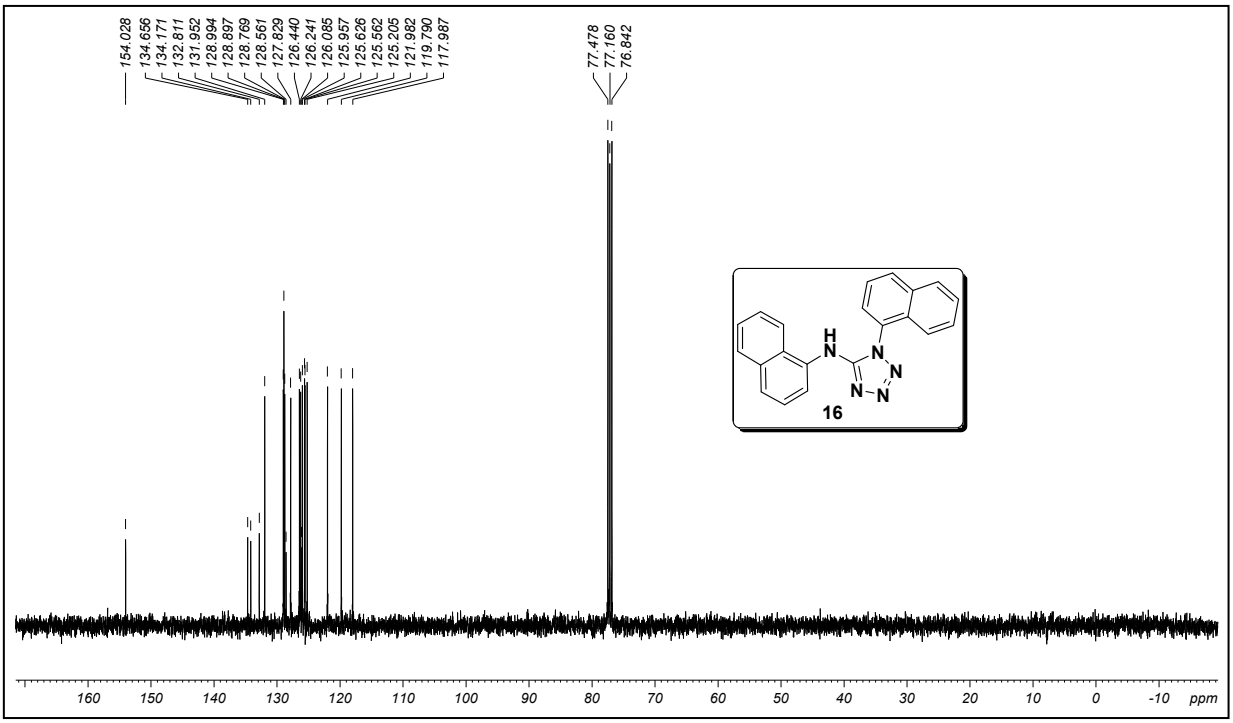


Figure S98. 100 MHz ^{13}C NMR spectrum of **16** in $CDCl_3$

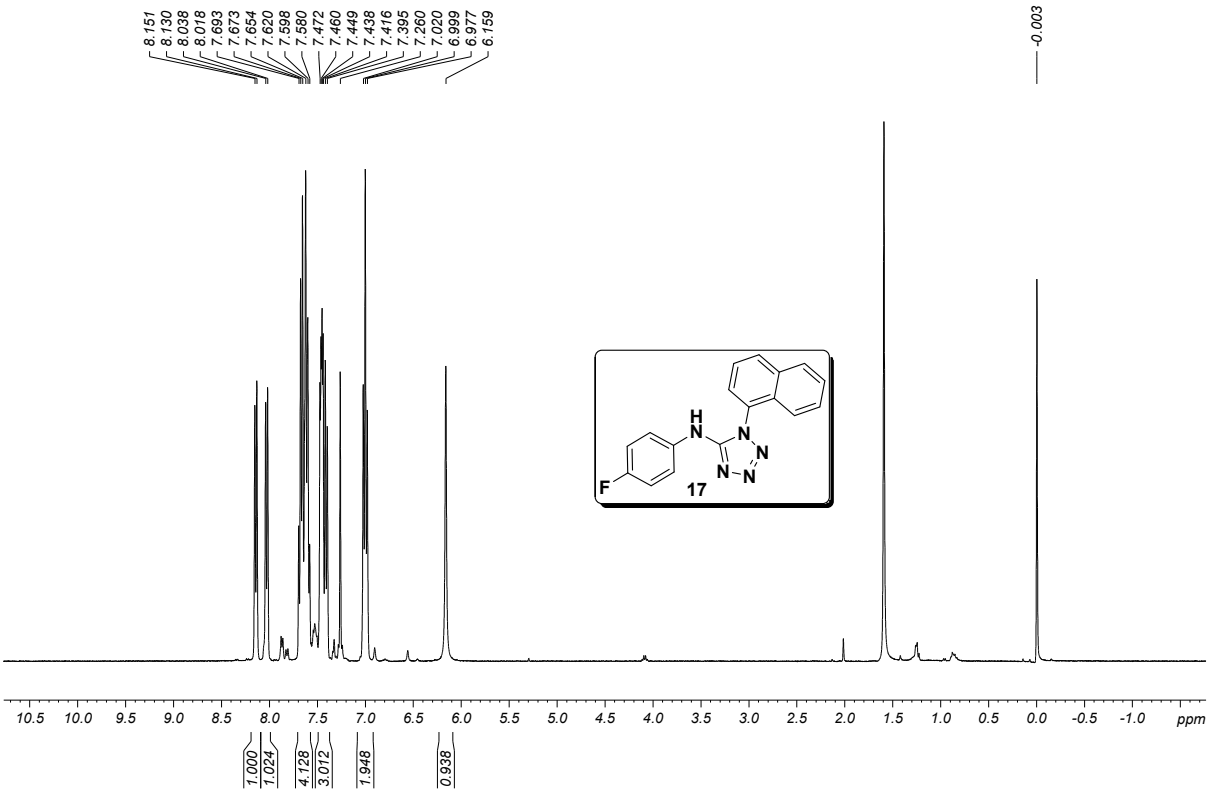


Figure S99. 400 MHz ^{1}H NMR spectrum of **17** in $CDCl_3$

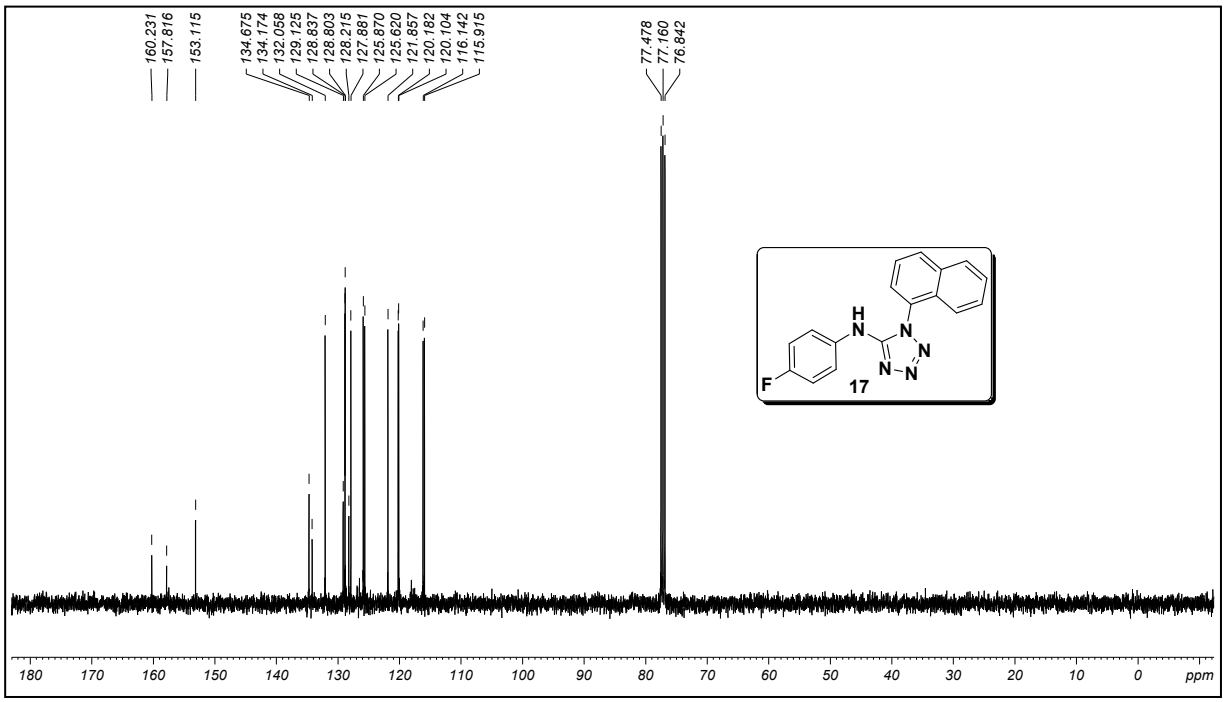


Figure S100. 100 MHz ^{13}C NMR spectrum of **17** in $CDCl_3$

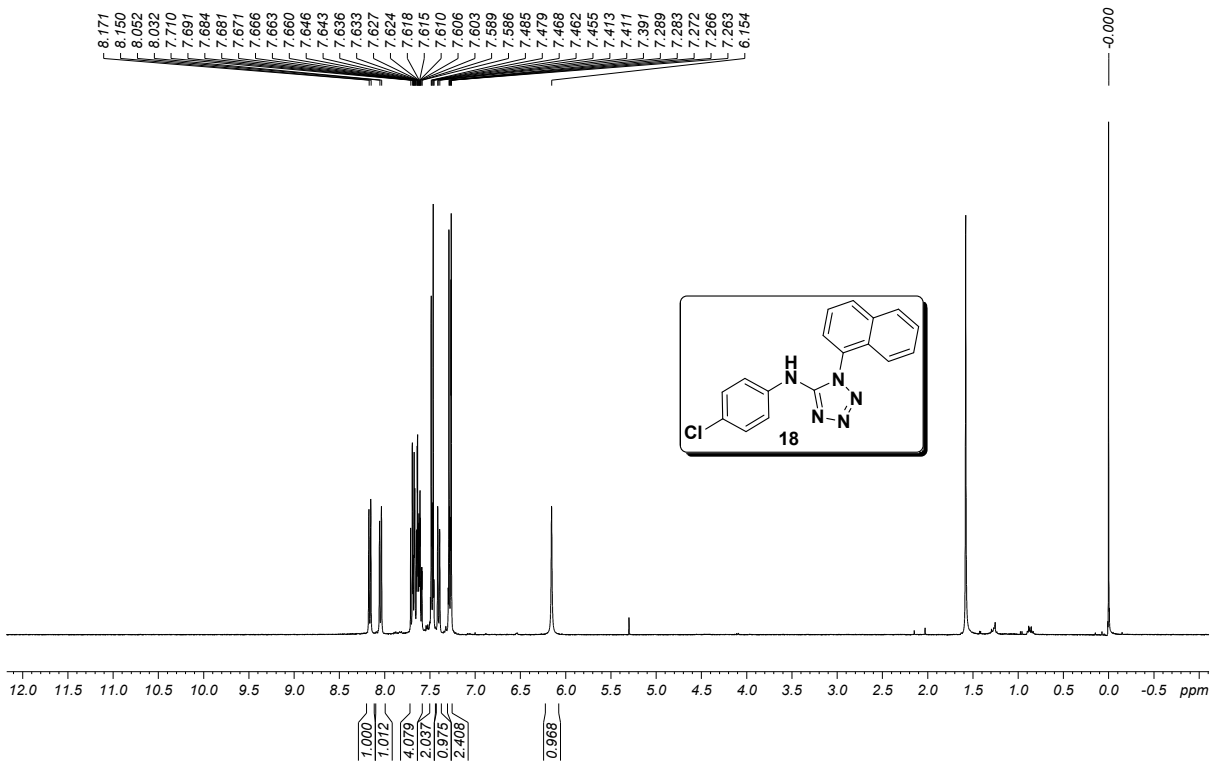


Figure S101. 400 MHz ^{1}H NMR spectrum of **18** in $CDCl_3$

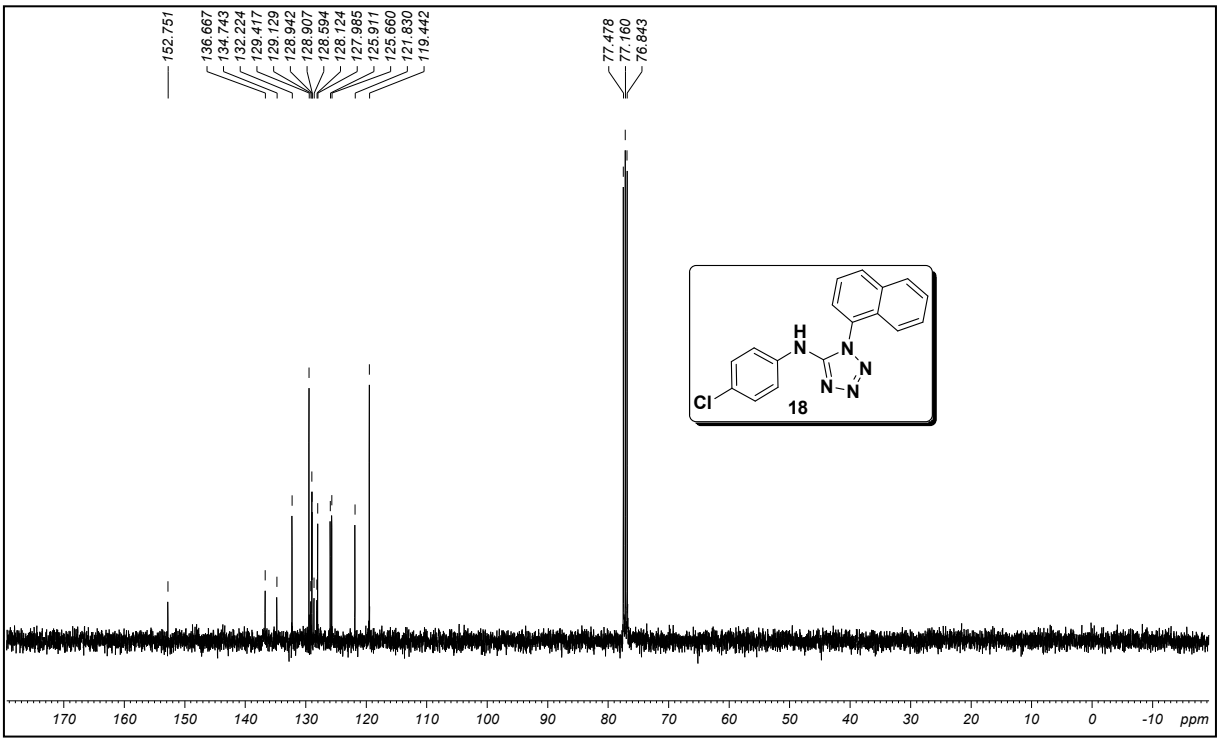


Figure S102. 100 MHz ^{13}C NMR spectrum of **18** in $CDCl_3$

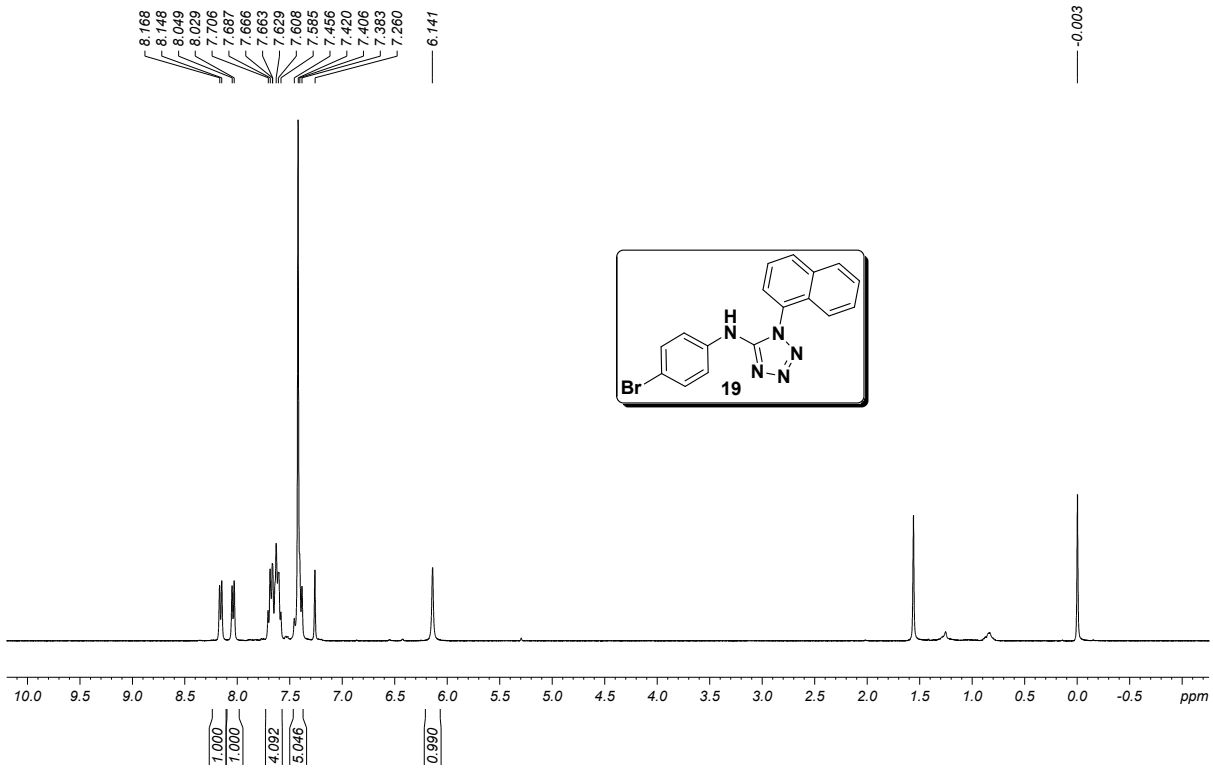


Figure S103. 400 MHz ^{1}H NMR spectrum of **19** in $CDCl_3$

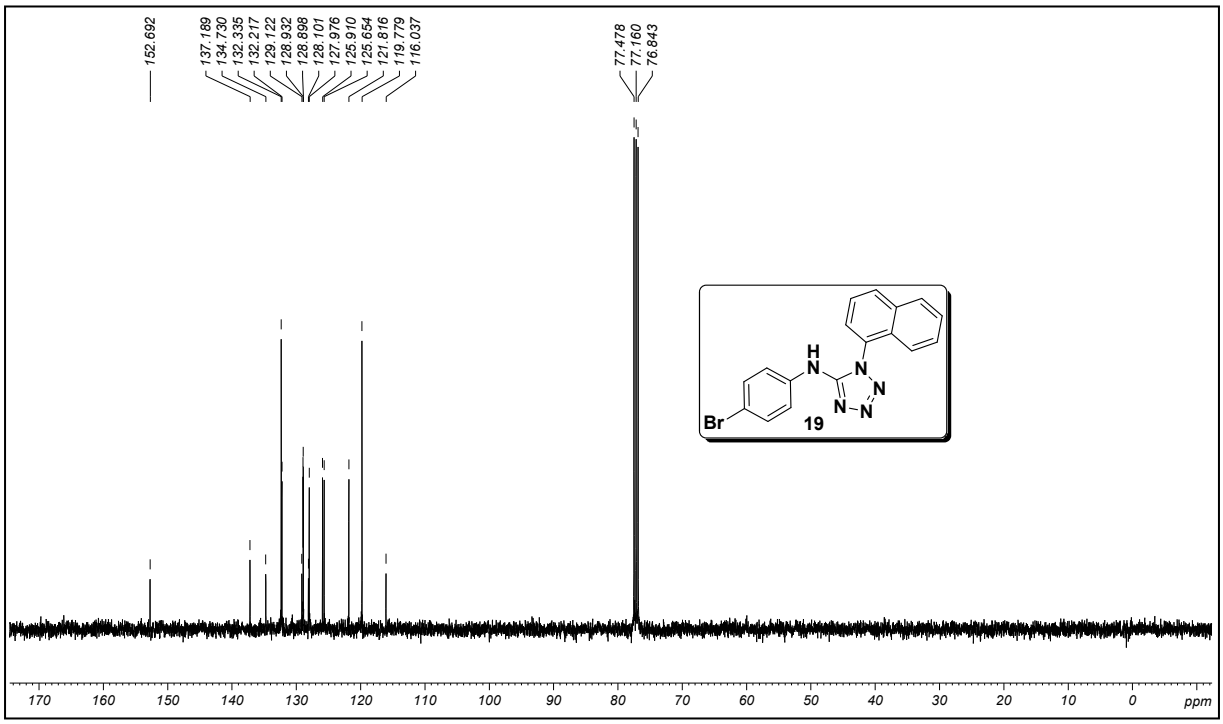


Figure S104. 100 MHz ^{13}C NMR spectrum of **19** in $CDCl_3$

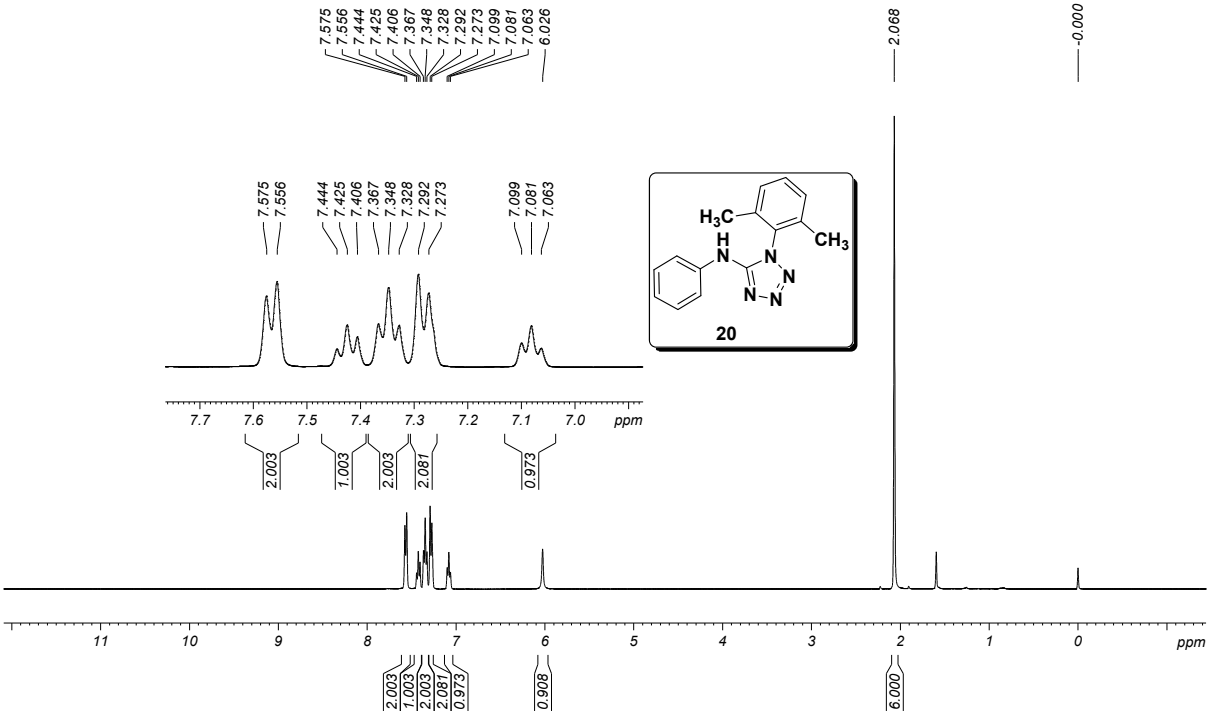


Figure S105. 400 MHz ^{1}H NMR spectrum of **20** in $CDCl_3$

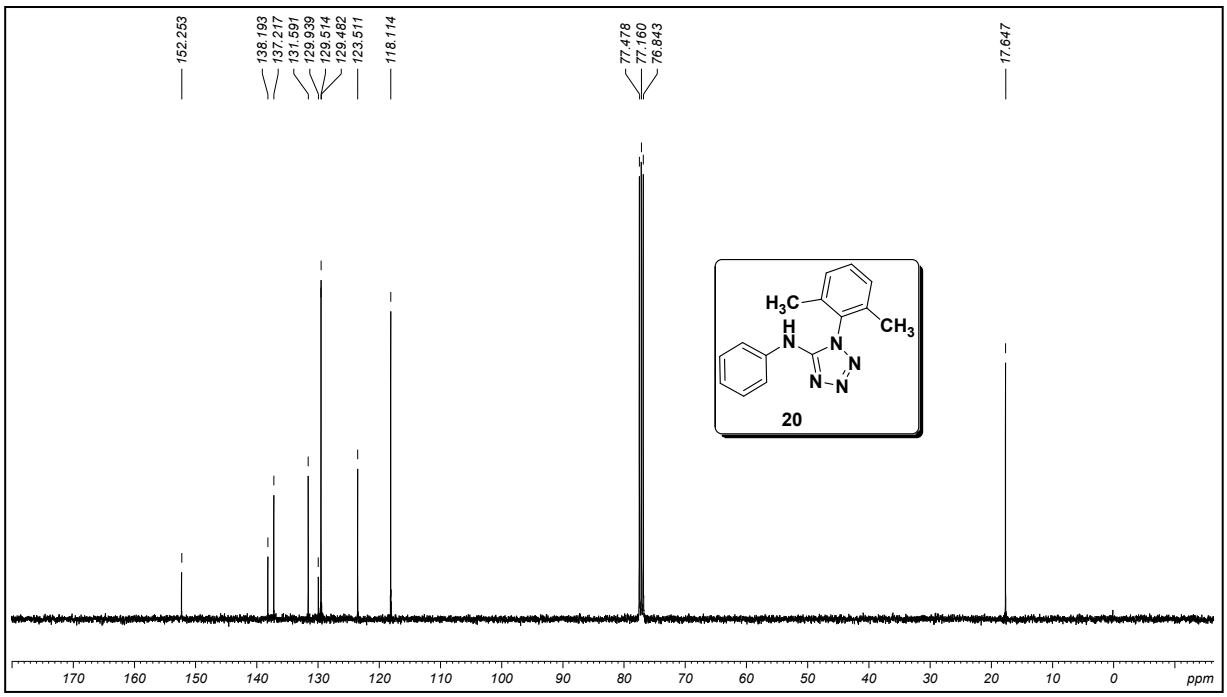


Figure S106. 100 MHz ^{13}C NMR spectrum of **20** in $CDCl_3$

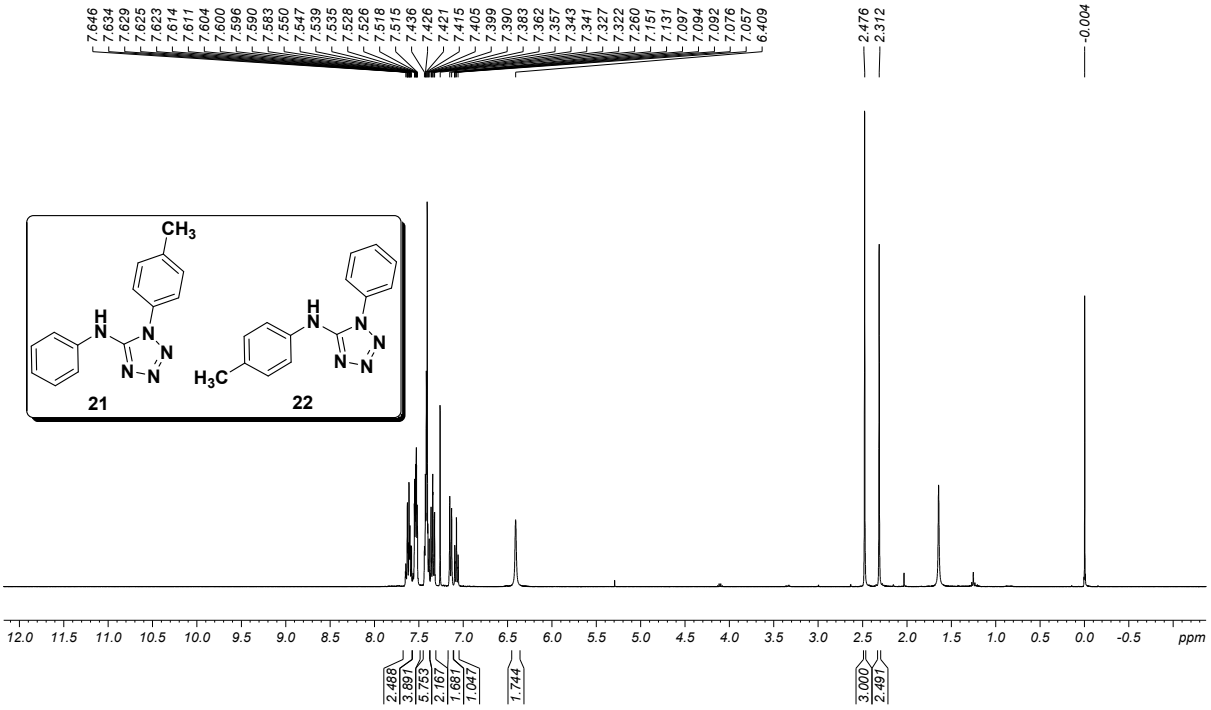


Figure S107. 400 MHz ^{1}H NMR spectrum of **21**+**22** in $CDCl_3$

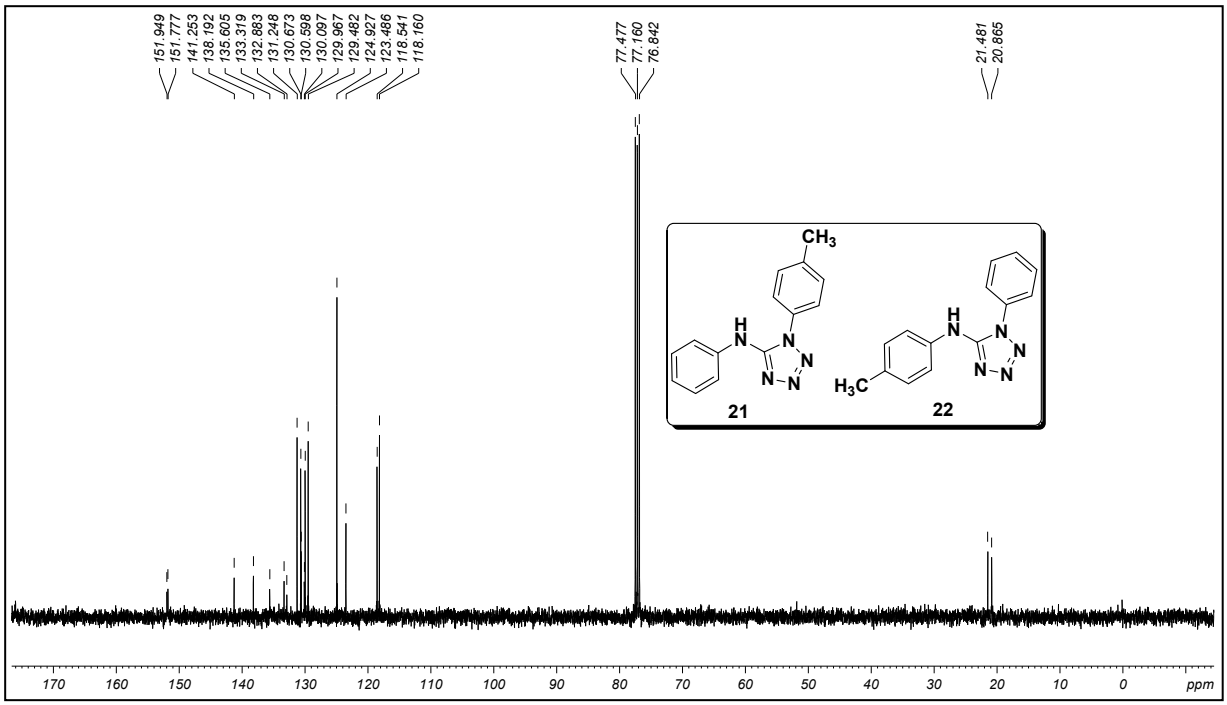


Figure S108. 100 MHz ^{13}C NMR spectrum of **21**+**22** in $CDCl_3$

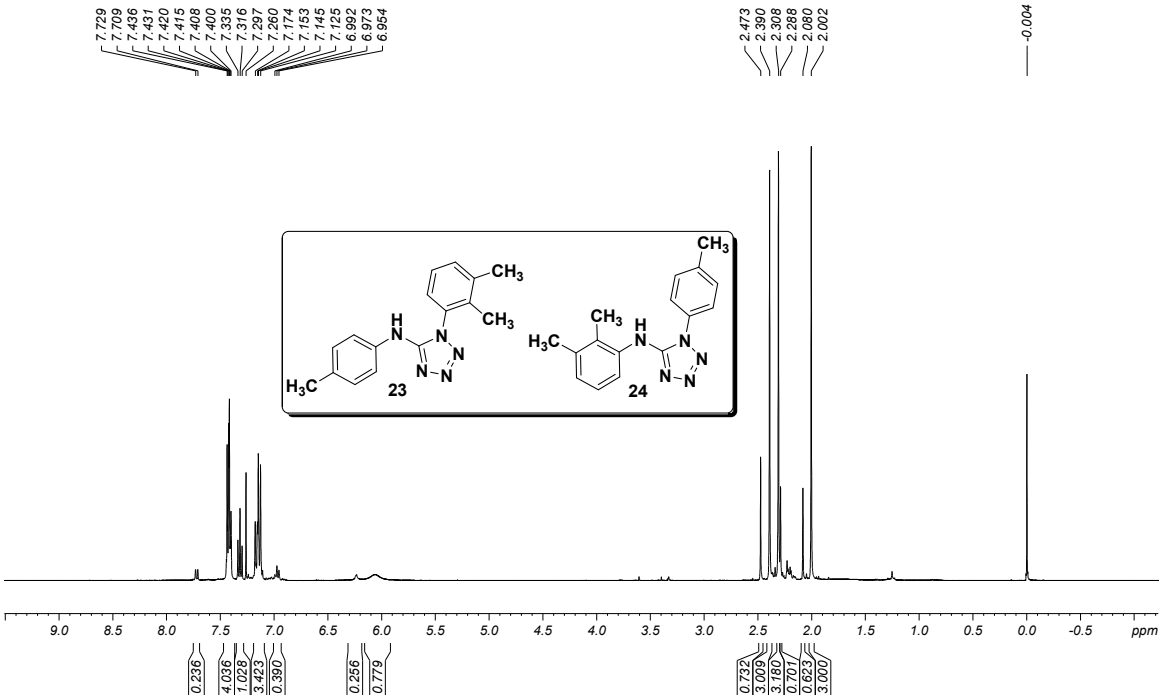


Figure S109. 400 MHz ^{1}H NMR spectrum of **23**+**24** in $CDCl_3$

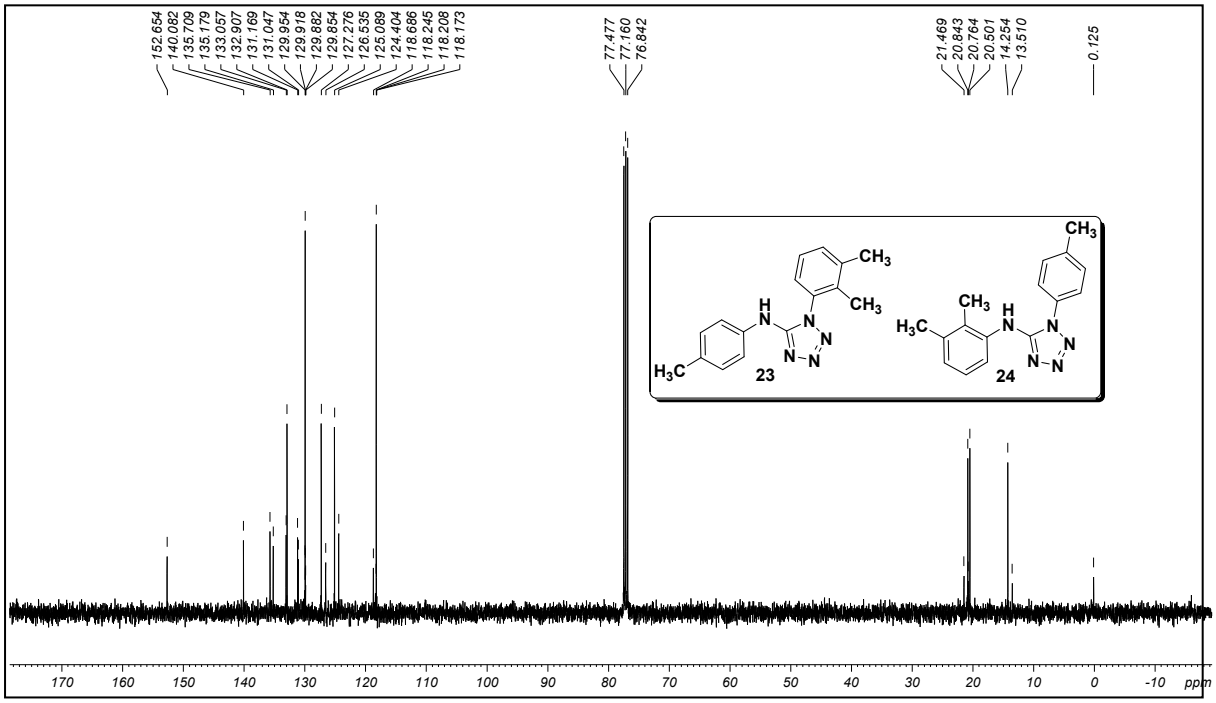


Figure S110. 100 MHz ^{13}C NMR spectrum of **23**+**24** in $CDCl_3$

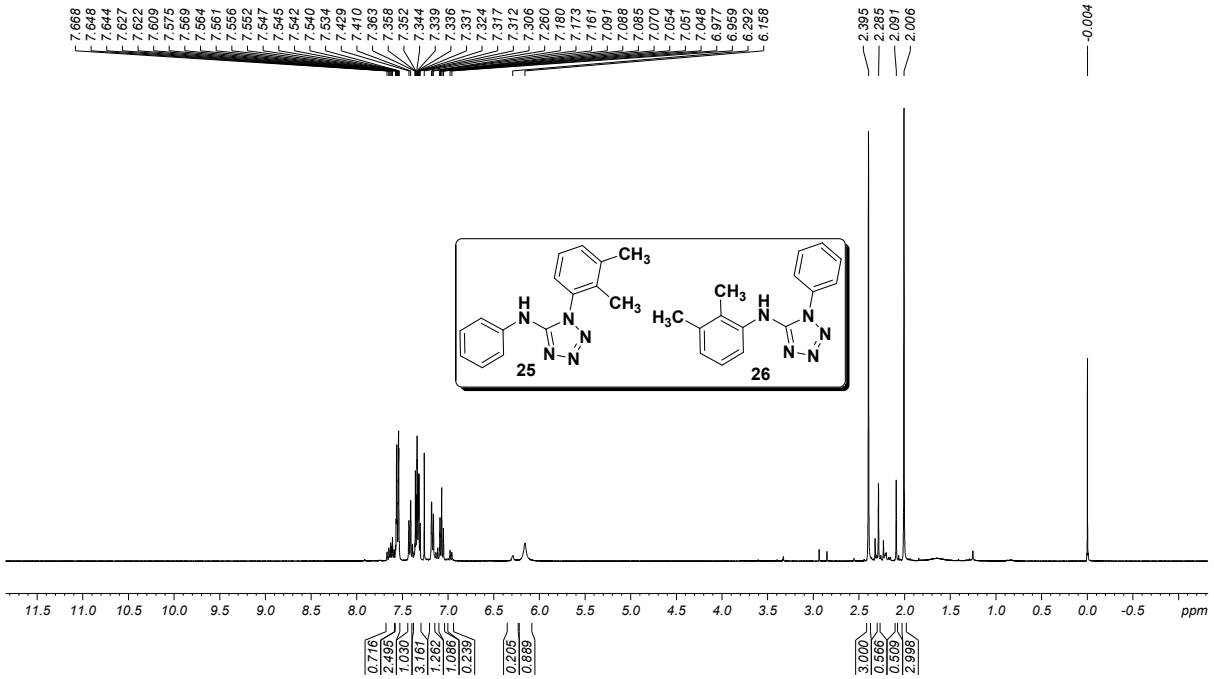


Figure S111. 400 MHz ^{1}H NMR spectrum of **25**+**26** in $CDCl_3$

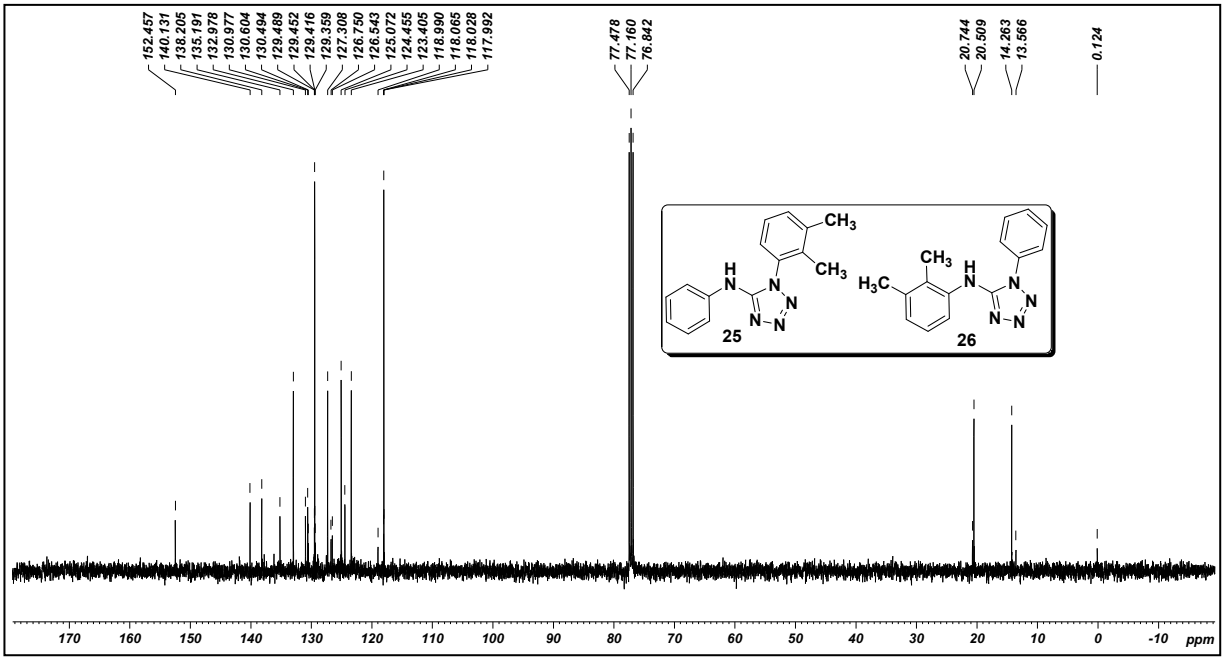


Figure S112. 100 MHz ^{13}C NMR spectrum of **25**+**26** in $CDCl_3$

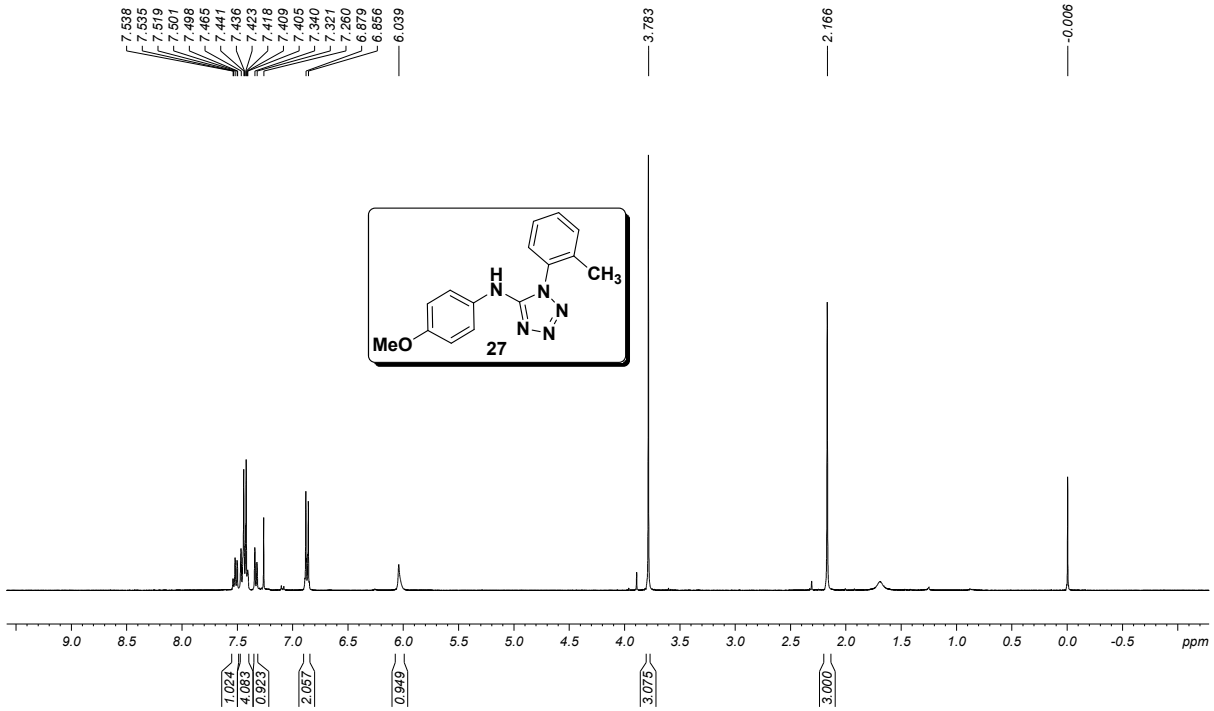


Figure S113. 400 MHz ^{1}H NMR spectrum of **27** in $CDCl_3$

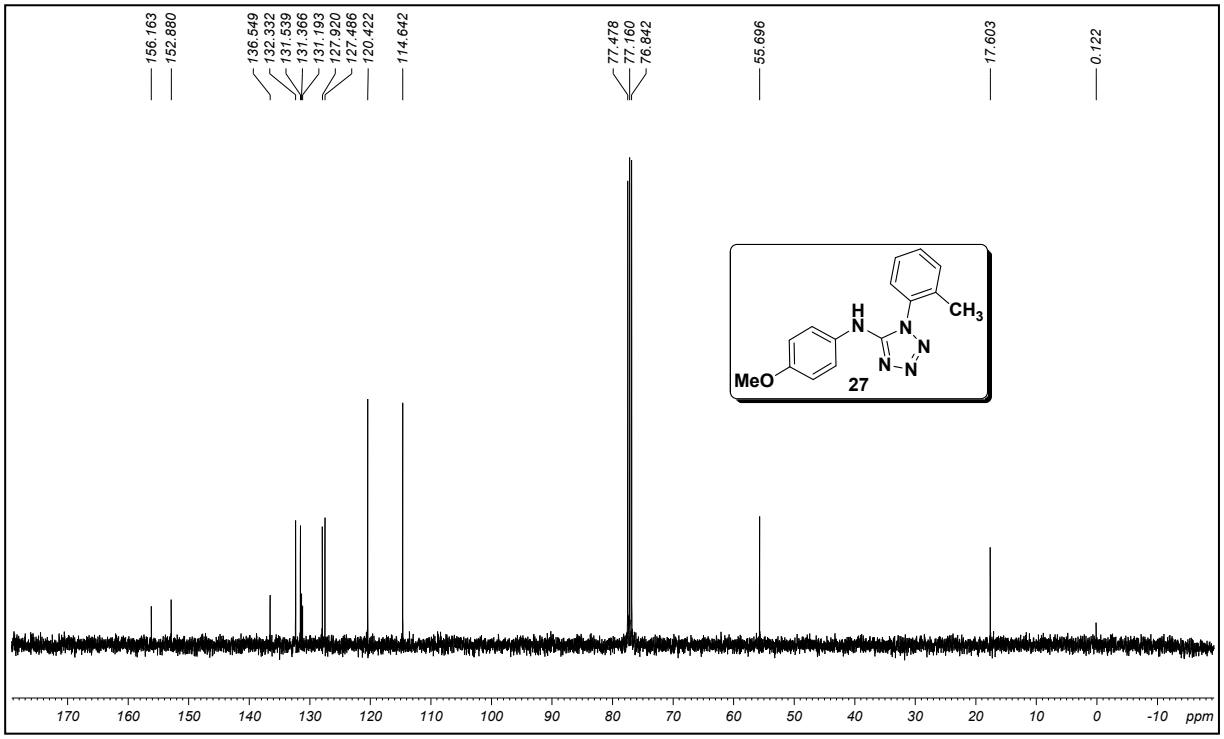


Figure S114. 100 MHz ^{13}C NMR spectrum of **25**+**26** in $CDCl_3$

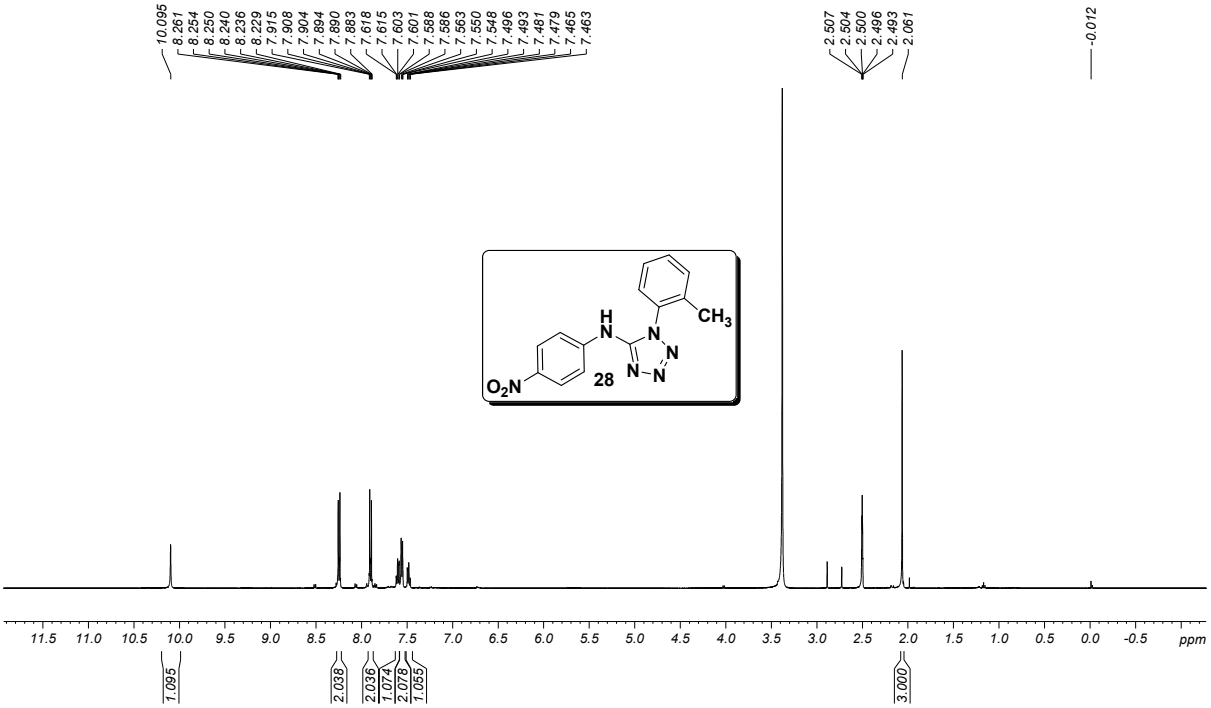


Figure S115. 400 MHz ^{1}H NMR spectrum of **28** in DMSO-d_6

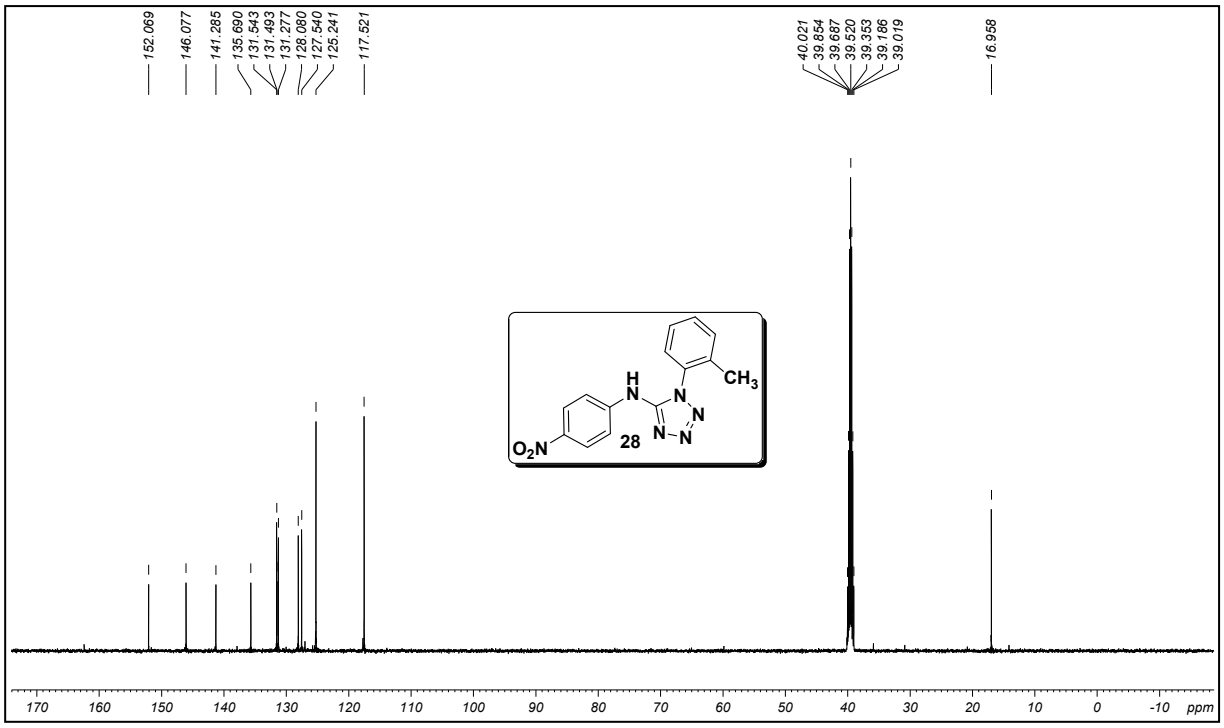


Figure S116. 100 MHz ^{13}C NMR spectrum of **28**in DMSO-d_6

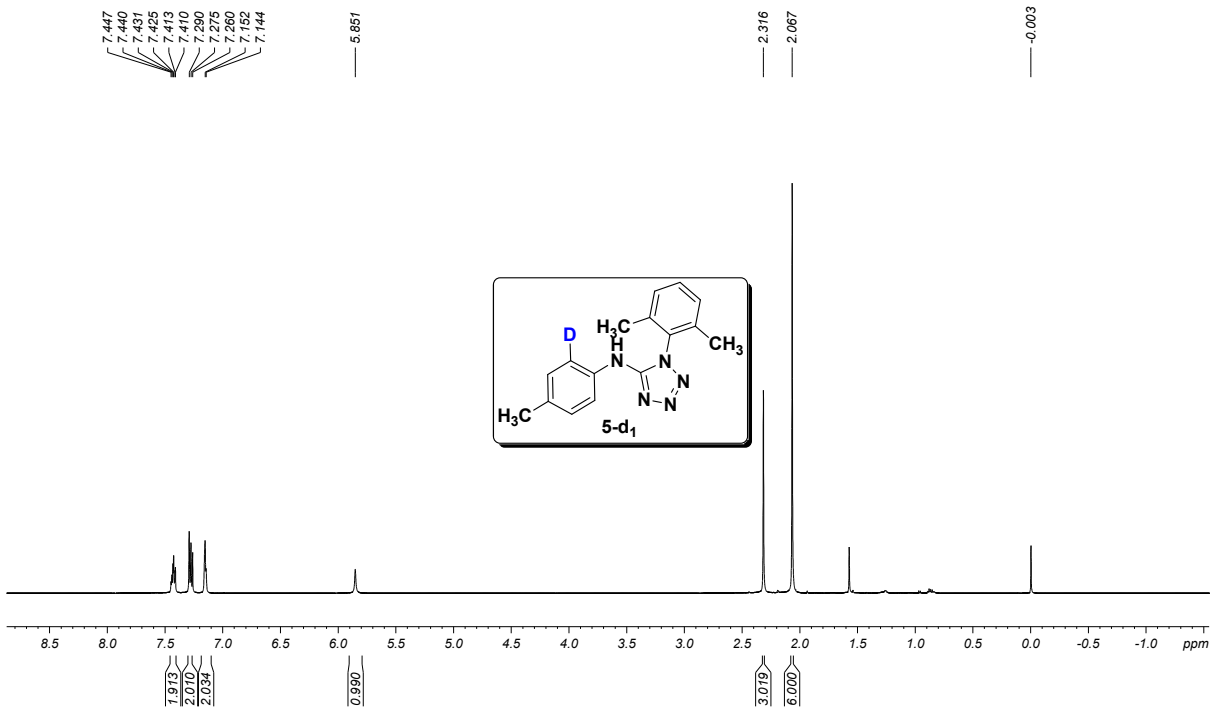


Figure S117. 500 MHz ^{1}H NMR spectrum of **5-d$_1$** in $CDCl_3$

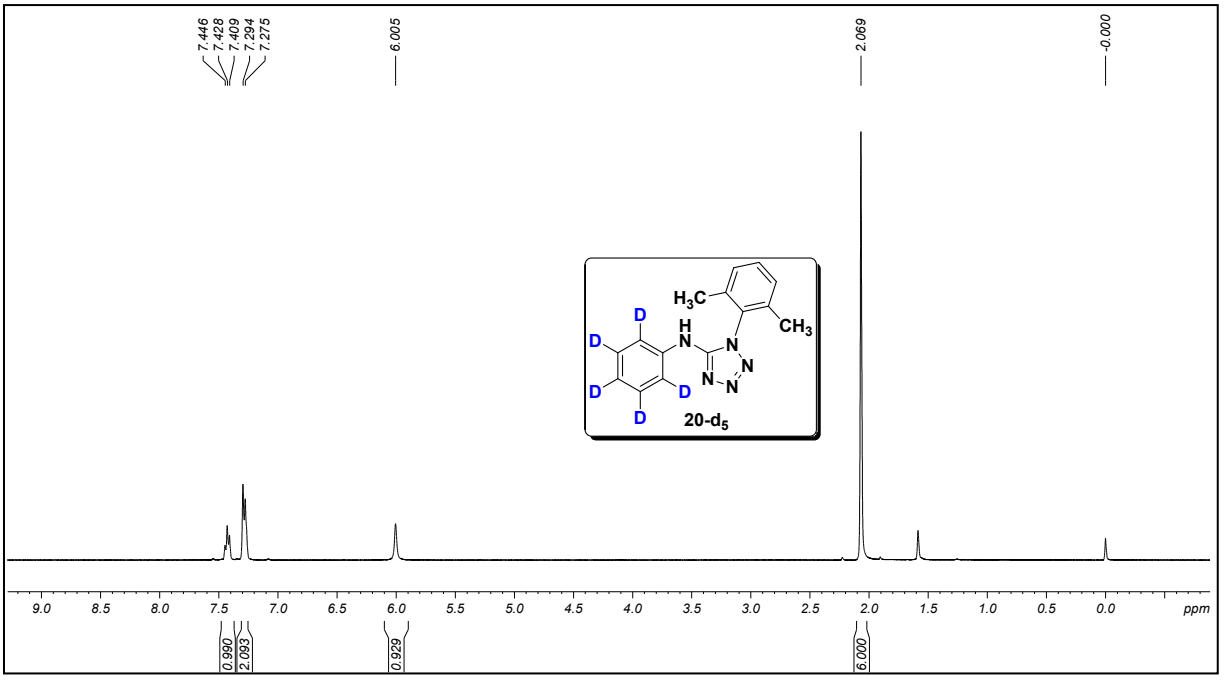


Figure S118. 400 MHz ^{1}H NMR spectrum of **20-d$_5$** in $CDCl_3$

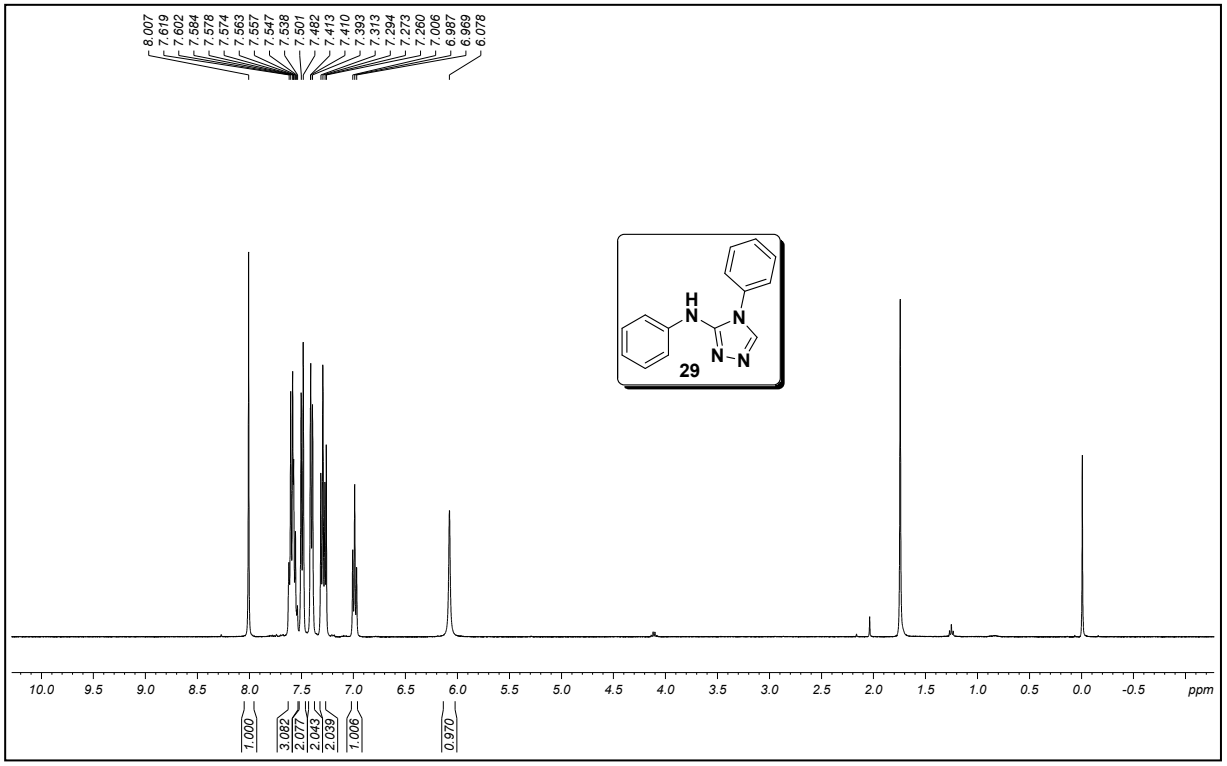


Figure S119. 400 MHz ^{1}H NMR spectrum of **29** in DMSO-d_6

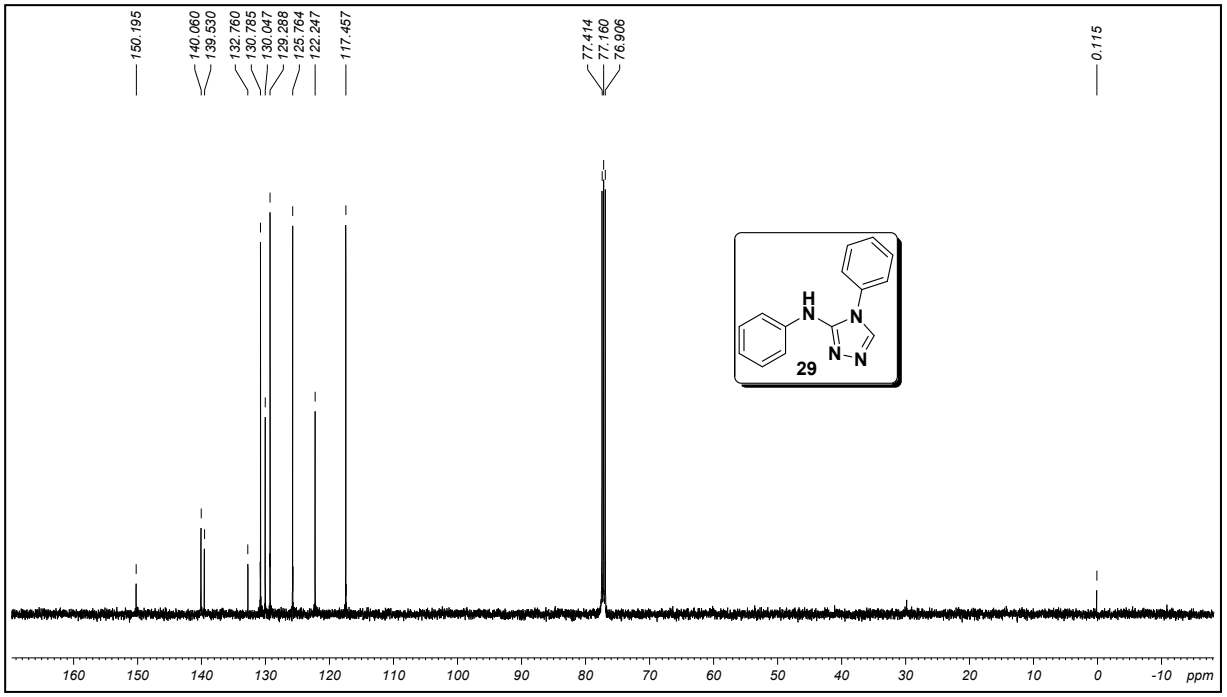


Figure S120. 100 MHz ^{13}C NMR spectrum of **29** in DMSO-d_6

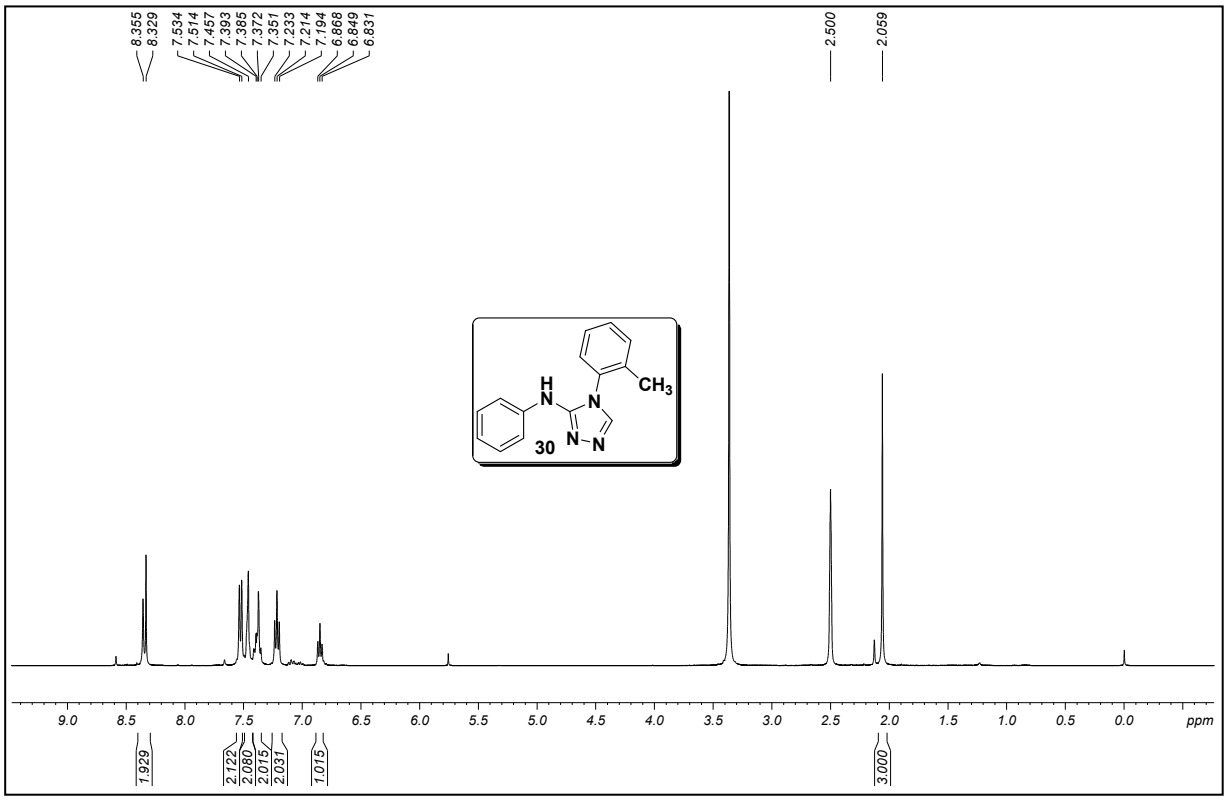


Figure S121. 400 MHz ^{1}H NMR spectrum of **30** in DMSO-d_6

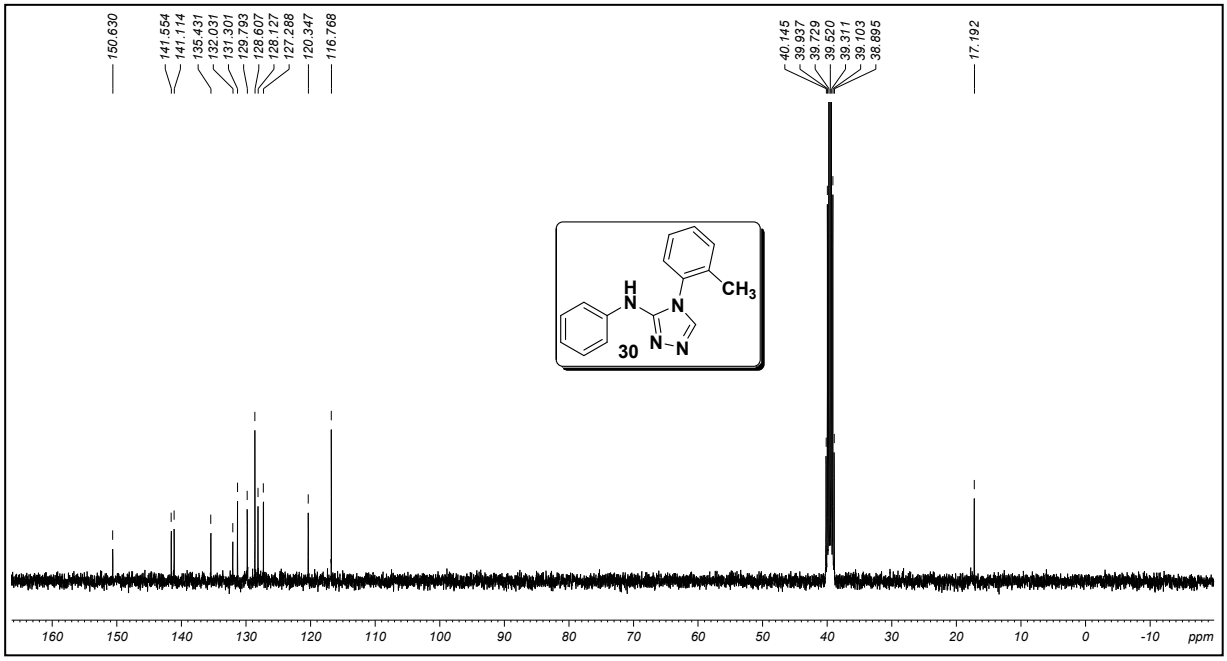


Figure S122. 100 MHz ^{13}C NMR spectrum of **30** in DMSO-d_6

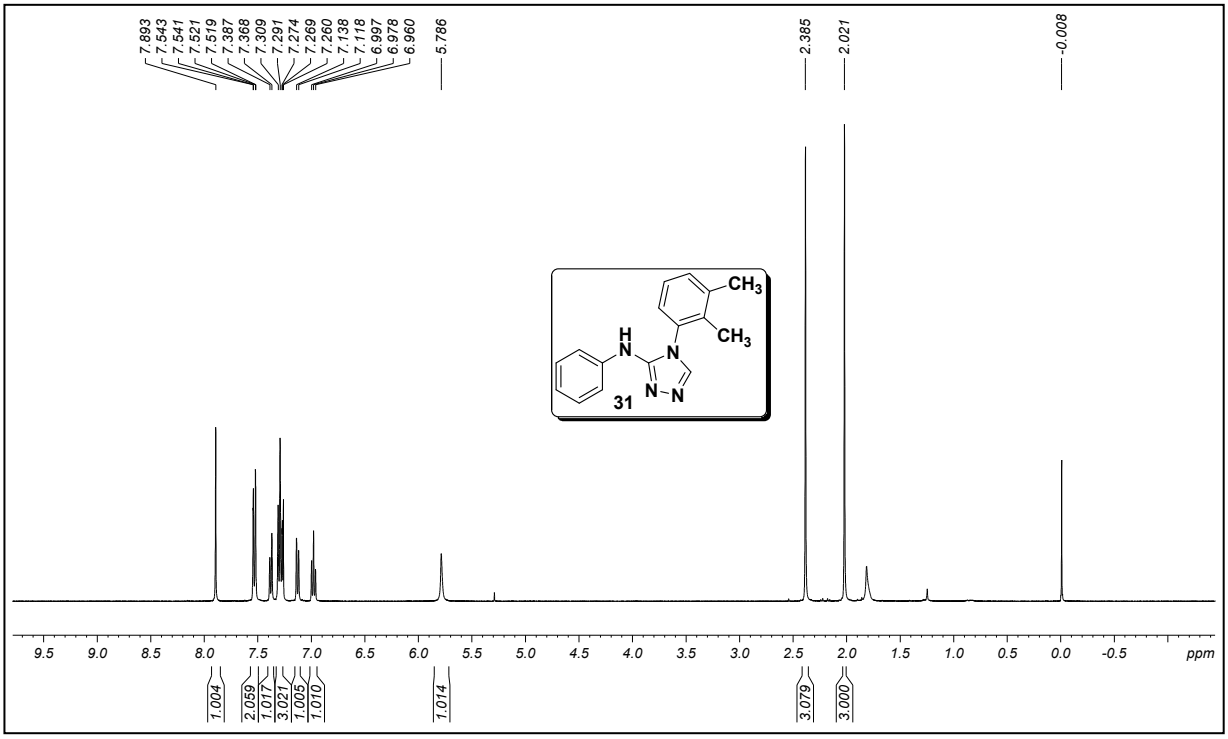


Figure S123. 400 MHz ^{1}H NMR spectrum of **31** in $CDCl_3$

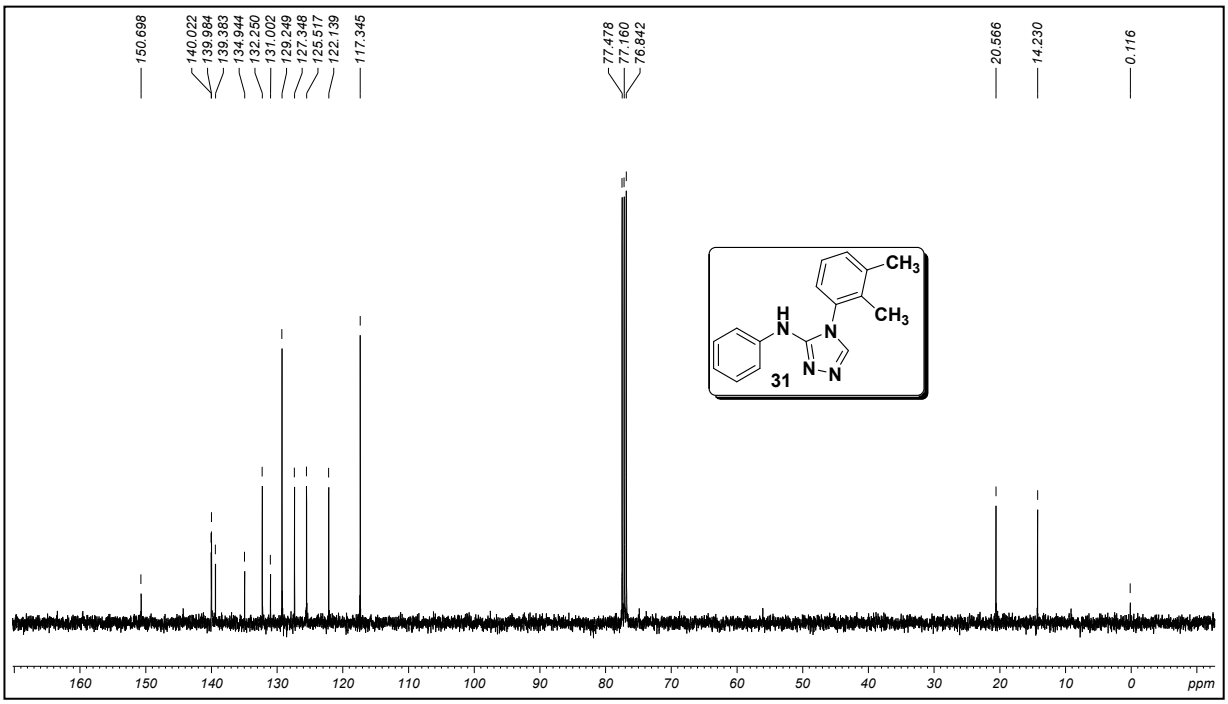


Figure S124. 100 MHz ^{13}C NMR spectrum of **31** in $CDCl_3$

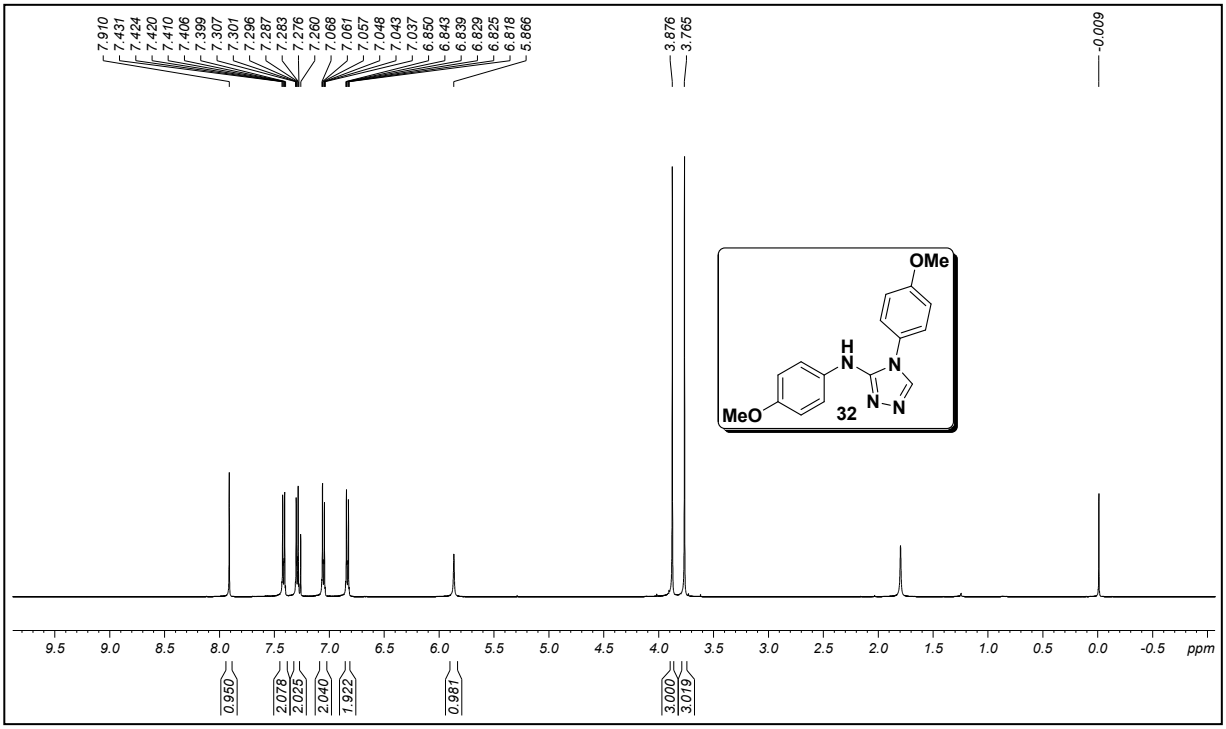


Figure S125. 500 MHz ^{1}H NMR spectrum of **32** in $CDCl_3$

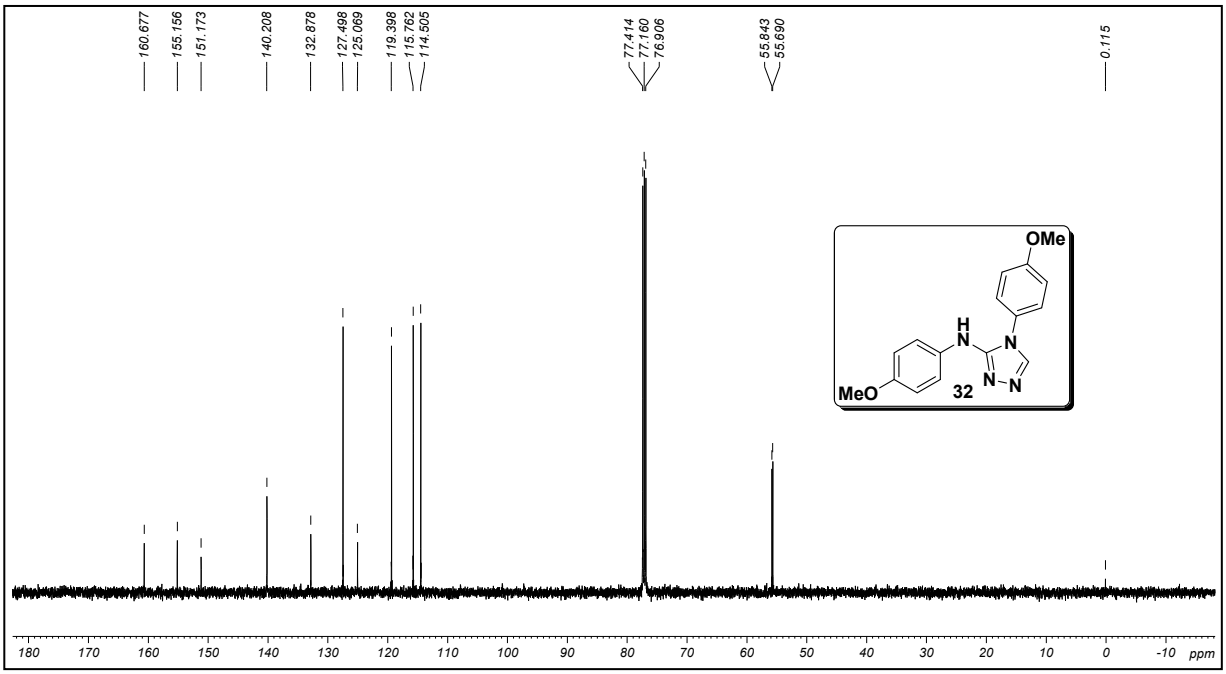


Figure S126. 125 MHz ^{13}C NMR spectrum of **32** in $CDCl_3$

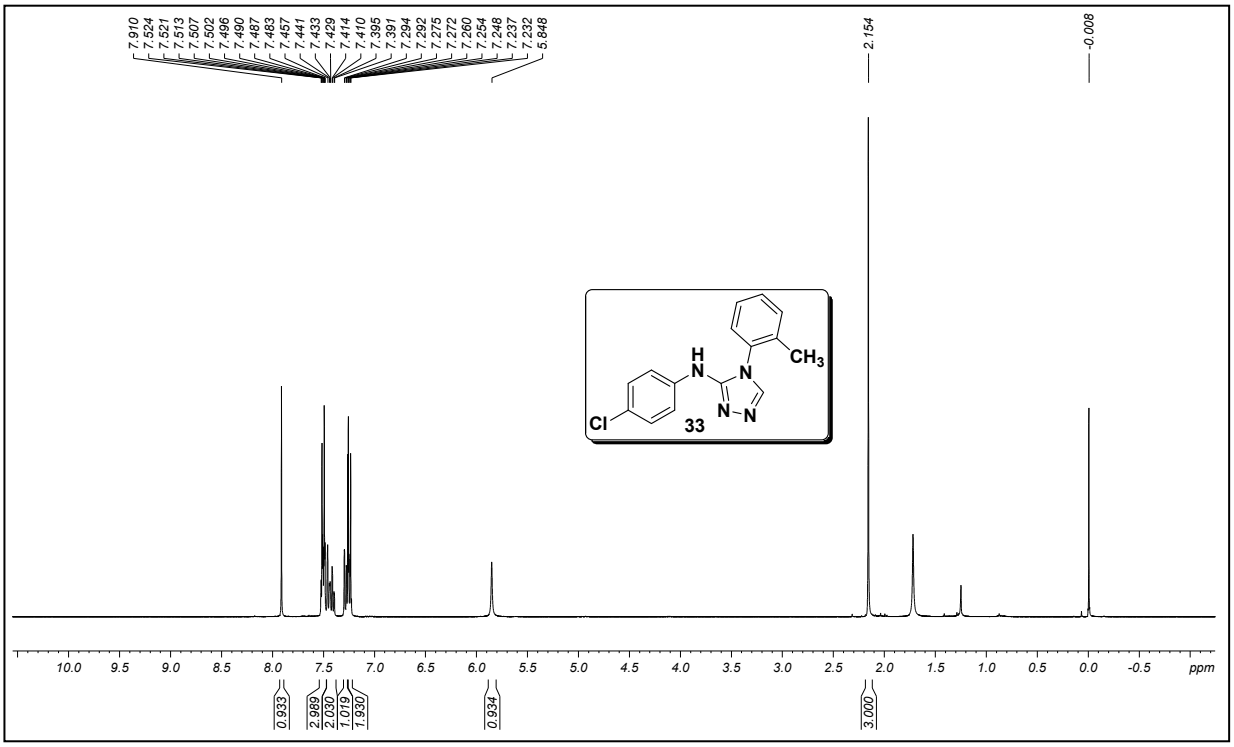


Figure S127. 400 MHz ^{1}H NMR spectrum of **33** in $CDCl_3$

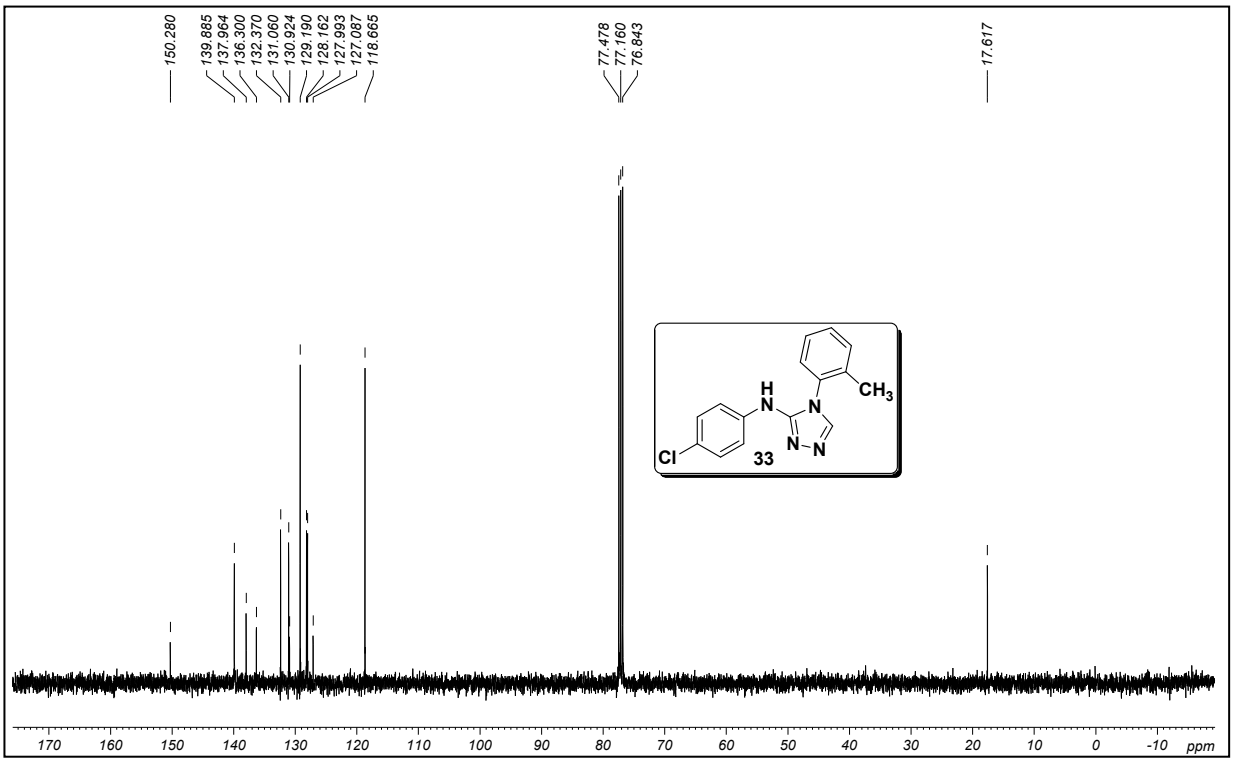
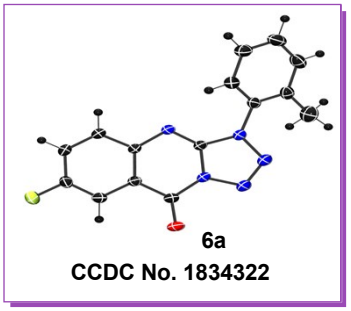


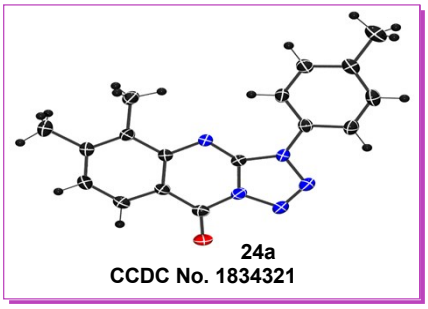
Figure S128. 100 MHz ^{13}C NMR spectrum of **33** in $CDCl_3$

Table S2. Crystal data and structure refinement for '6a'.



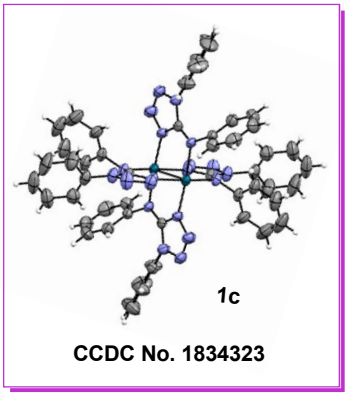
Identification code	Compound **6a**
Empirical formula	C_{15} H_{10} F N_5 O
Formula weight	295.28
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.7614(3) Å alpha = 77.8244(14) deg. b = 8.5686(4) Å beta = 77.638(2) deg. c = 11.9894(4) Å gamma = 85.281(2) deg.
Volume	662.75(5) $Å^3$
Z, Calculated density	2, 1.480 Mg/m^3
Absorption coefficient	0.109 mm^{-1}
F(000)	304
Crystal size	0.250 x 0.220 x 0.100 mm
Theta range for data collection	1.774 to 24.993 deg.
Limiting indices	-8<=h<=8, -10<=k<=9, -14<=l<=14
Reflections collected / unique	9042 / 2276 [R(int) = 0.0227]
Completeness to theta = 24.993	97.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2276 / 0 / 200
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0873
R indices (all data)	R1 = 0.0557, wR2 = 0.1018
Extinction coefficient	n/a
Largest diff. peak and hole	0.127 and -0.188 $e.Å^{-3}$

Table S3. Crystal data and structure refinement for '24a'.



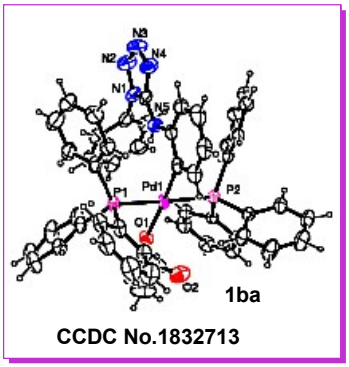
Identification code	Compound **24a**
Empirical formula	$C_{17}\ H_{15}\ N_5\ O$
Formula weight	305.34
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 8.7446(4) Å alpha = 90 deg.
	b = 11.5290(7) Å beta = 105.140(3) deg.
	c = 15.2091(8) Å gamma = 90 deg.
Volume	1480.11(14) $Å^3$
Z, Calculated density	4, 1.370 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F(000)	640
Crystal size	0.250 x 0.220 x 0.130 mm
Theta range for data collection	2.246 to 24.019 deg.
Limiting indices	-9<=h<=9, -12<=k<=13, -17<=l<=17
Reflections collected / unique	7469 / 2323 [R(int) = 0.0397]
Completeness to theta = 24.019	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2323 / 0 / 211
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1156
R indices (all data)	R1 = 0.0901, wR2 = 0.1397
Extinction coefficient	n/a
Largest diff. peak and hole	0.180 and -0.184 $e.A^{-3}$

Table S4. Crystal data and structure refinement for '1C'.



Identification code	Compound **1C**
Empirical formula	$C_{26}\ H_{20}\ N_{10}\ Pd$
Formula weight	578.92
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 14.0025(17) Å alpha = 90 deg.
	b = 13.5967(18) Å beta = 116.114(5) deg.
	c = 15.1462(14) Å gamma = 90 deg.
Volume	2589.3(5) $Å^3$
Z, Calculated density	4, 1.485 Mg/m^3
Absorption coefficient	0.752 mm^{-1}
F(000)	1168
Crystal size	0.180 x 0.120 x 0.100 mm
Theta range for data collection	1.652 to 24.997 deg.
Limiting indices	-16<=h<=16, -15<=k<=16, -18<=l<=12
Reflections collected / unique	16326 / 4545 [R(int) = 0.0884]
Completeness to theta = 24.997	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4545 / 0 / 334
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.0889
R indices (all data)	R1 = 0.1008, wR2 = 0.1127
Extinction coefficient	n/a
Largest diff. peak and hole	0.451 and -0.584 $e.Å^{-3}$

Table S5. Crystal data and structure refinement for 1ba.



Identification code	Compound **1ba**	
Empirical formula	$C_{53}\ H_{45}\ Cl_6\ N_5\ O_2\ P_2\ Pd$	
Formula weight	1164.98	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.2631(4) Å	a= 71.606(2)°.
	b = 13.7670(4) Å	b= 87.408(3)°.
	c = 19.0767(6) Å	g = 63.9440(10)°.
Volume	2728.97(15) $Å^3$	
Z	2	
Density (calculated)	1.418 Mg/m^3	
Absorption coefficient	0.736 mm^{-1}	
F(000)	1184	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.068 to 25.000°.	
Index ranges	-14<=h<=14, -16<=k<=16, -22<=l<=22	
Reflections collected	49975	
Independent reflections	9643 [R(int) = 0.0704]	
Completeness to theta = 25.000°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9643 / 680 / 763	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1275	
R indices (all data)	R1 = 0.1193, wR2 = 0.1648	
Extinction coefficient	0.0019(4)	
Largest diff. peak and hole	0.535 and -0.504 $e.Å^{-3}$	