Supplementary Information

Catalyst-free efficient synthesis of functionalized 1,2,4-triazole via ring opening/cyclization of arylidene thiazolone with aryl/alkyl-hydrazine

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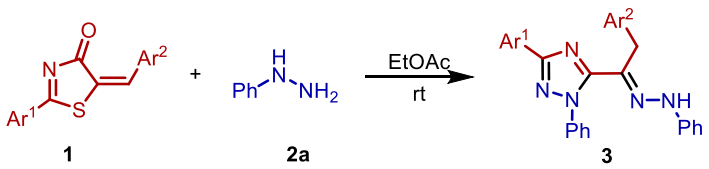
1. General Information

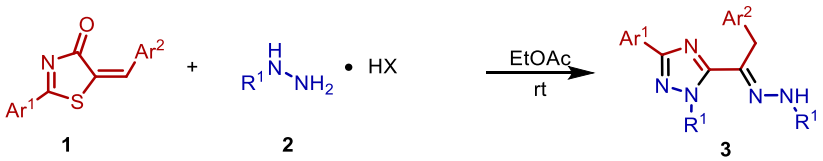
Unless otherwise noted, all reactions were carried out in a closed vial. ^{1}H NMR (400 and 500 MHz) and ^{13}C NMR (100 and 125 MHz) spectra were recorded on a Bruker High Performance Digital FT-NMR (AVANCE III HD, AscendTM WB, 500 MHz), and AVANCE NEO Ascend 400 & 500 Bruker BioSpin International AG instruments. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Oil bath on the top of the hot plate is used for heating wherever needed. TLC was performed with silica gel GF_{254} precoated on aluminium plates and spots were visualized with UV. Purification of products was performed by flash column chromatography on silica gel (100-200 mesh). High-resolution mass spectra (HRMS) were obtained by the ESI-TOF method (Agilent LC/Q-TOF 6546). For continuous flow synthesis, *Syrris Asia* pump, heater, and stainless-steel coil reactor were used. Arylidene thiazolone **1** derivatives were prepared according to the reported methods.[1] All the other reagents were purchased from commercial sources and used as received unless specified.

2. General procedure for the synthesis of 3



1 **2a** **3**

To a solution of arylidene thiazolone **1** (1 equiv., 0.2 mmol) in EtOAc (2 mL) was added hydrazine derivative **2a** (2.2 equiv., 0.44 mmol). The mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. The resulting mixture was concentrated under vacuum to give the crude product. The crude product was purified by flash column chromatography with hexane/ethyl acetate (20:1-10:1) to provide product **3.**

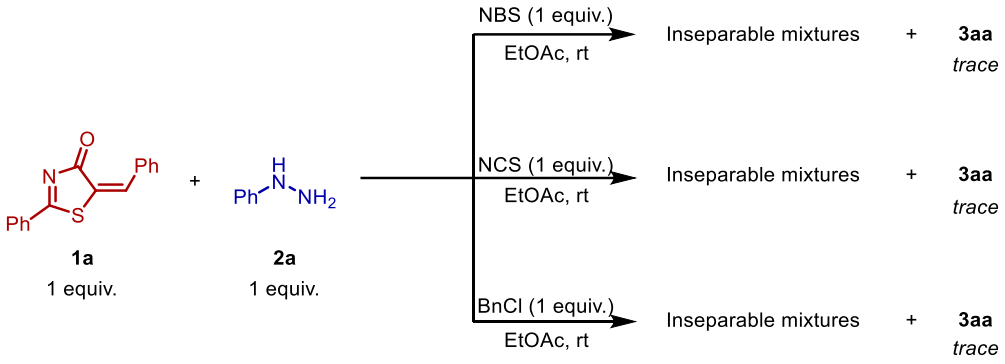


1 **2** **3**

2b, 2c, 2d; HX = HCl
2e; HX = H_2SO_4

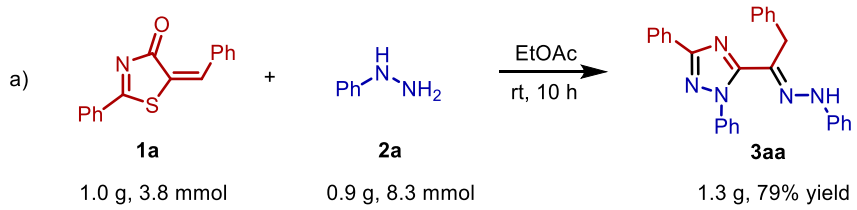
To a solution of alkyl/aryl hydrazine hydrochloride/sulphuric acid **2b/2c/2d/2e** (2.2 equiv., 0.44 mmol) in EtOAc (2 mL) was added Na_2CO_3 (2.2 equiv., 0.44 mmol) and stirred for 1 h to neutralized the solution then added arylidene thiazolone **1** (1 equiv., 0.2 mmol). The mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. The resulting mixture was concentrated under vacuum to give the crude product. The crude product was purified by flash column chromatography with hexane/ethyl acetate (20:1-10:1) to provide product **3.**

Procedure followed for three component reaction:



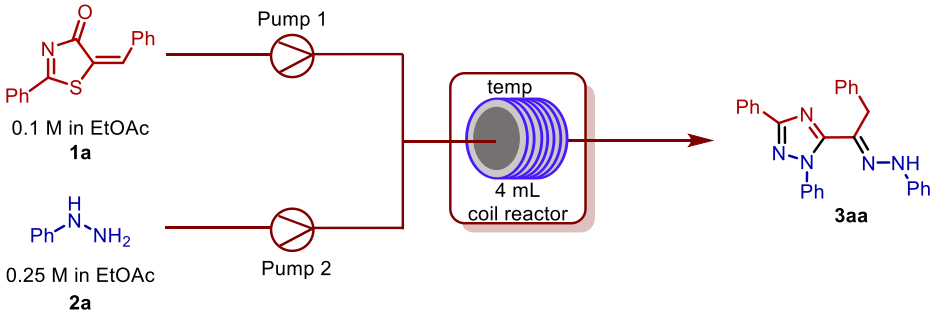
To a solution of arylidene thiazolone **1a** (1 equiv., 0.2 mmol) in EtOAc (2 mL) was added hydrazine derivative **2a** (1 equiv., 0.2 mmol) and NBS/NCS/BnCl (1 equiv., 0.2 mmol). The mixture was stirred at room temperature. The progress of the reaction was monitored by TLC, which revealed the formation of complex mixtures, making purification by column chromatography and isolation of the desired product unfeasible.

Procedure of Scale up synthesis of 3aa in batch



To a solution of arylidene thiazolone **1a** (1.0 g, 3.8 mmol) in EtOAc (25 mL) was added phenyl hydrazine derivative **2a** (0.9 g, 8.3 mmol). The mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. The resulting mixture was concentrated under vacuum to give the crude product. The crude product was purified by flash column chromatography with hexane/ethyl acetate (20:1) to provide product **3aa**.

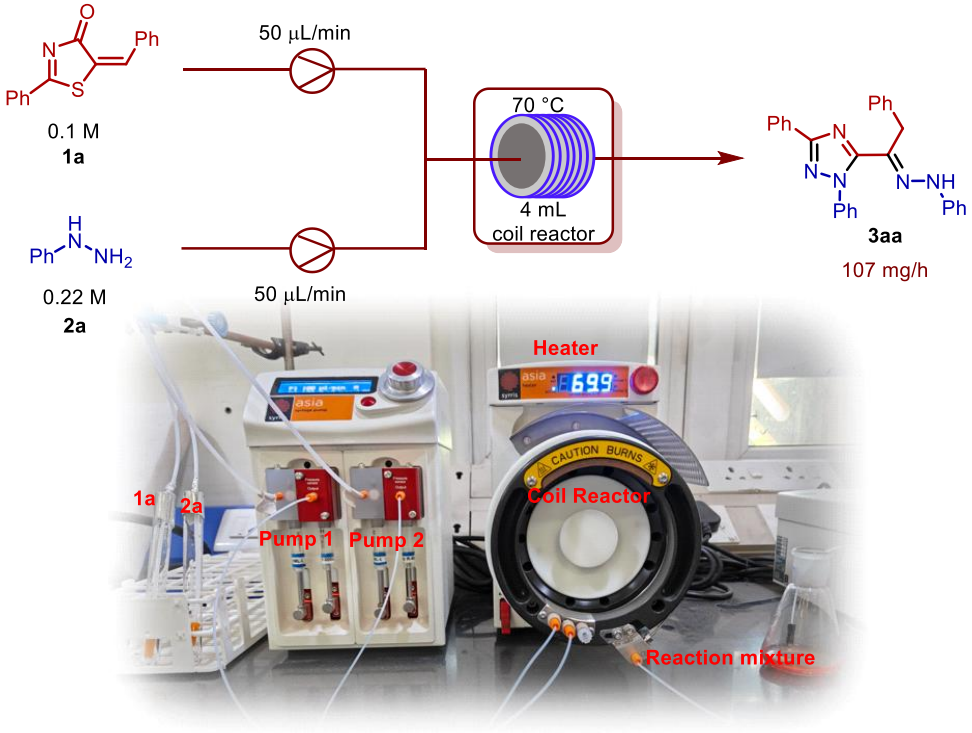
3. Optimization of reaction conditions in flow



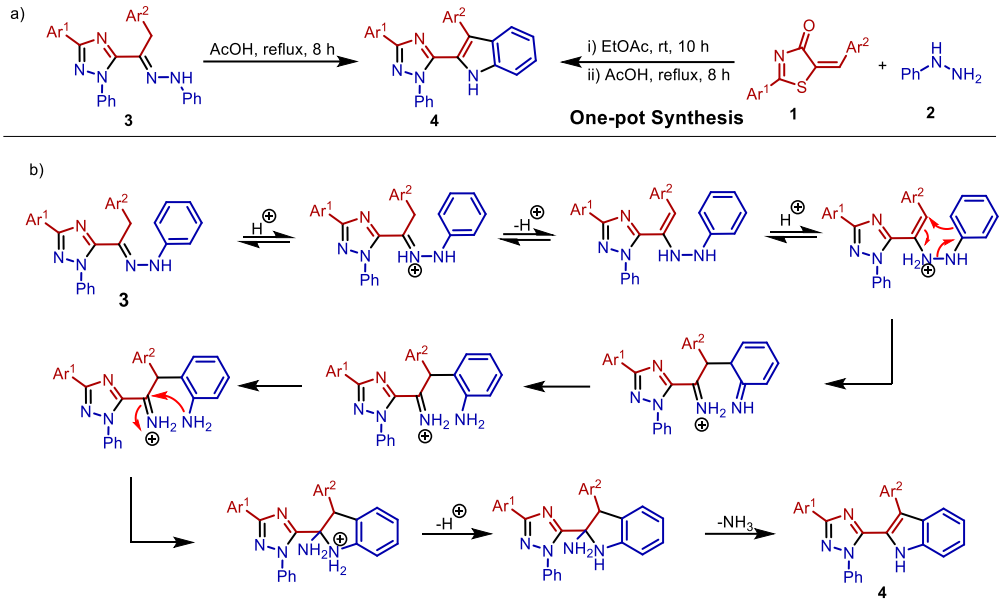
Entry	Thiazole		$PhNHNH_2$		Temp. (°C)	R_T (min)	Yield (%)	Conv. (%)
	1a [M]	Flow rate (µL/min)	2a [M]	Flow rate (µL/min)				
1	0.10	100	0.20	100	rt	20	54	63
2	0.10	100	0.25	100	rt	20	61	69
3	0.10	100	0.25	100	40	20	62	71
4	0.10	100	0.25	100	60	20	62	71
5	0.10	50	0.25	50	60	40	78	90
6	0.10	50	0.25	50	70	40	82	>99

General procedure for the gram-scale synthesis of 3aa in continuous flow

For the continuous flow experiments, the instrumental setup is schematized as below. The stainless-steel coil reactor (*Syrris Asia* coil reactor, 4 mL volume capacity) inlets were connected to syringe pumps and the reactor outlet was connected to a flask, where the product was collected. The coil reactor was assembled with a heater (*Syrris Asia* heater) which was set at the temperature of 70. After that, the pumps were associated with a solution of **1a** (1.0 equiv., 0.1 M) in EtOAc, and phenyl hydrazine **2a** (2.5 equiv., 0.25 M) in EtOAc at 50 µL/min flow rate in both the pumps (*Syrris Asia* pump). The system ran for 12.5 h. Then the complete flow system was washed with additional amount of EtOAc. All the collected reaction mixture concentrated to give the crude product followed by purification by flash column chromatography with hexane/ethyl acetate (20:1) to provide the product **3aa**.



4. a) Procedure for the synthesis of 4; b) The proposed mechanism for the synthesis of 4[2]

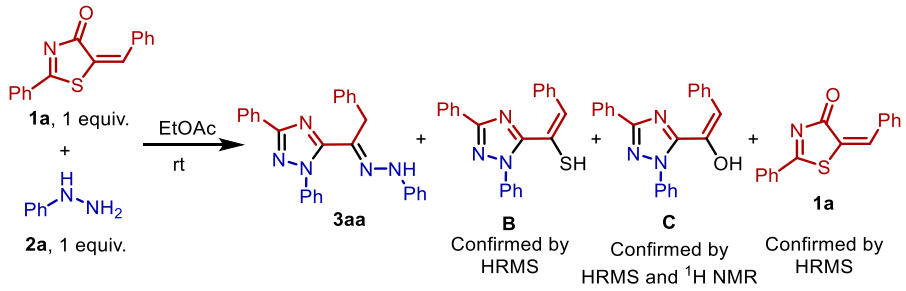


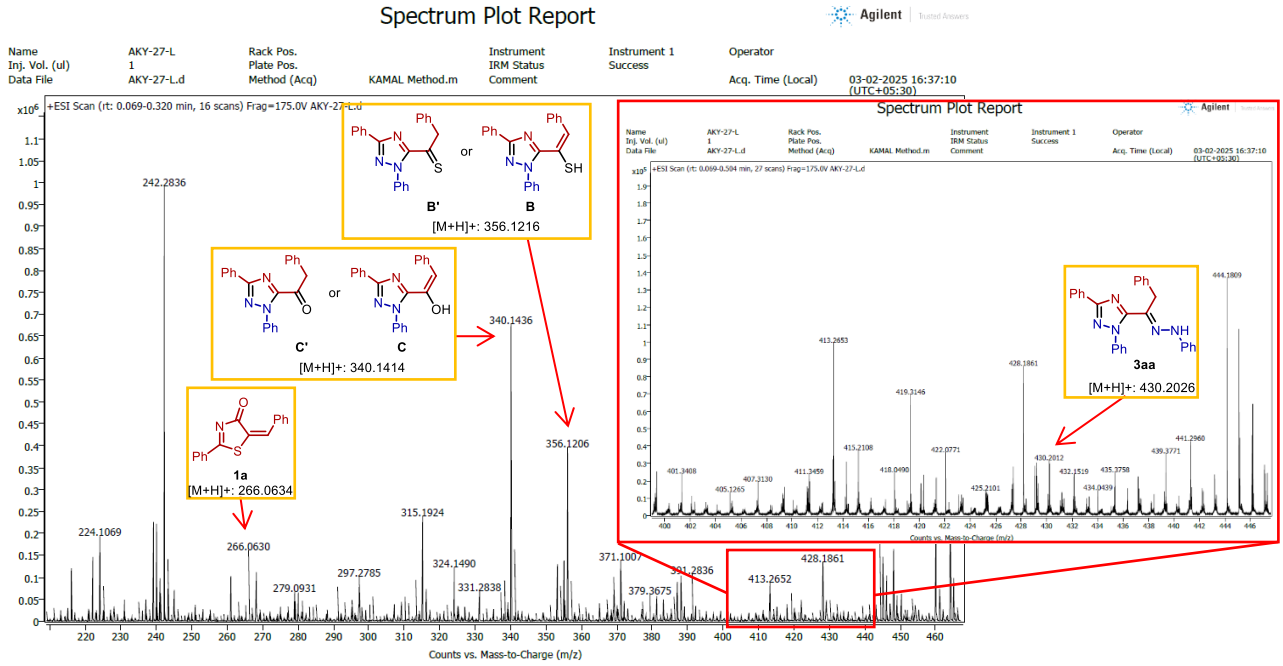
a) To a solution of 1,2,4-triazole derivative **3** (1 equiv., 0.2 mmol) in glacial acetic acid (1 mL) was added and reaction set to reflux temperature. The progress of the reaction was monitored by TLC. After completion of the reaction the mixture was quenched with saturated sodium bicarbonate solution and extracted with EtOAc (10 mL). Then the organic layer was washed with water 2 times and then dried over anhydrous sodium sulfate and concentrated to give the crude products **4.** The crude resulting mixture was purified by flash column chromatography with hexane/ethyl acetate (20:1) to give pure product **4**.

b) Under acidic conditions, phenylhydrazone undergoes tautomerization to generate an ene-hydrazine species. This intermediate then undergoes a [3,3]-sigmatropic rearrangement, leading to the formation of an iminium ion. The rearranged product subsequently undergoes intramolecular cyclization, followed by the loss of NH_3, which produces the indole ring system.[2]

One-pot synthetic procedure: To a solution of arylidene thiazolone **1** (1 equiv., 0.2 mmol) in EtOAc (2 mL) was added hydrazine derivative **2** (2.2 equiv., 0.44 mmol). The mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. When the starting materials were consumed, glacial acetic acid (1 mL) was added and the reaction was set to reflux temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was quenched with saturated sodium bicarbonate solution and extracted with EtOAc (10 mL). Then the organic layer was washed with water 2 times and then dried over anhydrous sodium sulfate and concentrated to give the crude products **4.** The crude resulting mixture was purified by flash column chromatography with hexane/ethyl acetate (20:1) to give pure product **4**.

5. Controlled experiment

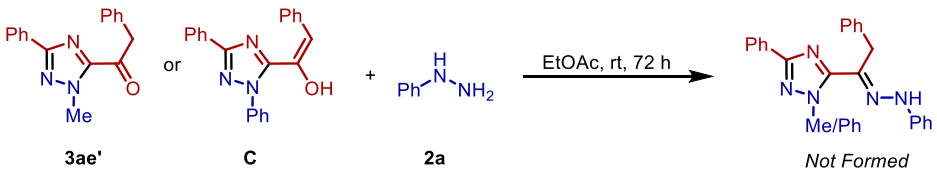




HRMS Spectra of the crude reaction mixture

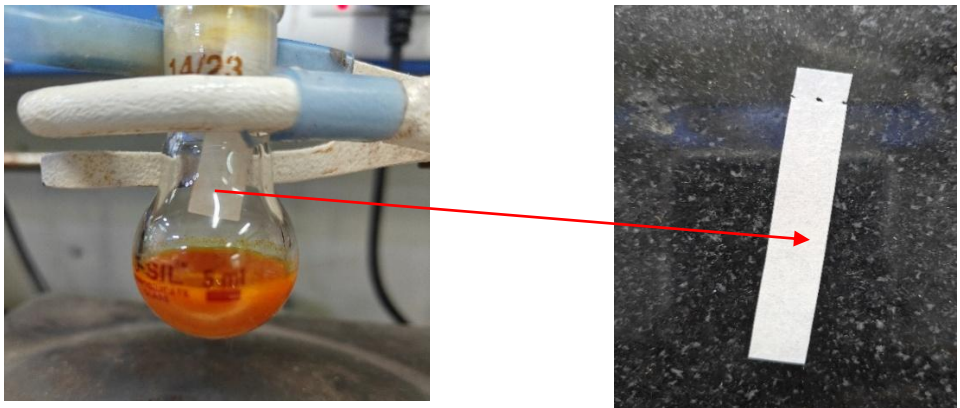
The mechanistic studies were conducted with **1a** and **2a** with equal molar ratios at room temperature. **Procedure:** To the solution of **1a** (1 equiv., 0.2 mmol) in EtOAc (2 mL), dropwise addition of **2a** (1 equiv., 0.2 mmol, dissolved in 1 mL EtOAc) over 2 h with the use of a syringe pump. The crude reaction mixture was taken after 3 h for HRMS analysis. The results show that there is the formation of intermediates **B** and **C** with **3aa** and unreacted **1a**. We have successfully isolated intermediate **C**.

Table S1: Reactions of 3ae'/C and phenyl hydrazine 2a:

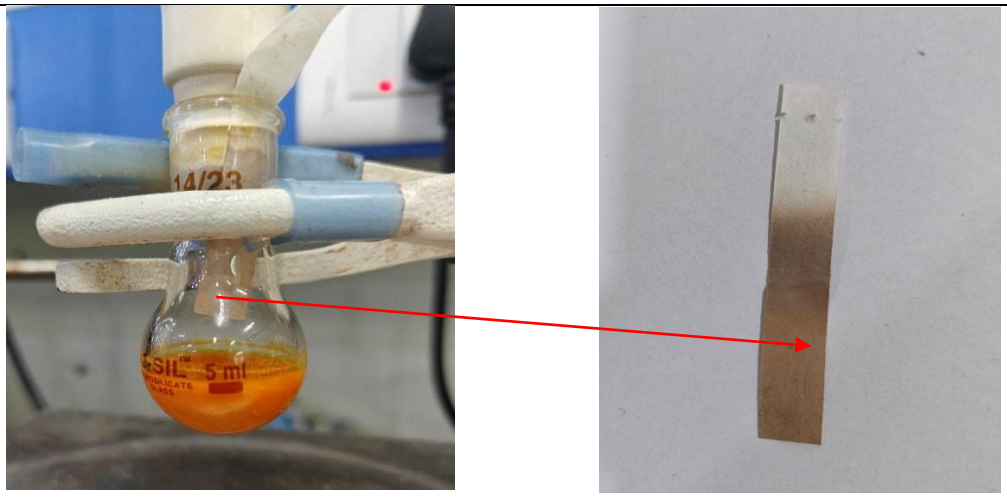


Entry	Intermediate	Time (h)	Yield (%)
1	**3ae'**	72	Not formed
2	**C**	72	Not formed

The reaction between intermediated **3ae'/C** (0.1 mmol, 1 equiv.) and phenyl hydrazine **2a** (0.1 mmol, 10.8 mg) in EtOAc (1 mL) at room temperature did not produce the final product even after continuing the stirring for 72 hours. This suggests that hydrazone **3** formed from the intermediate B/B' not from C/C'.



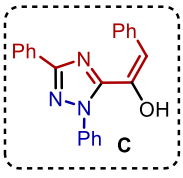
Reaction time = 0 min



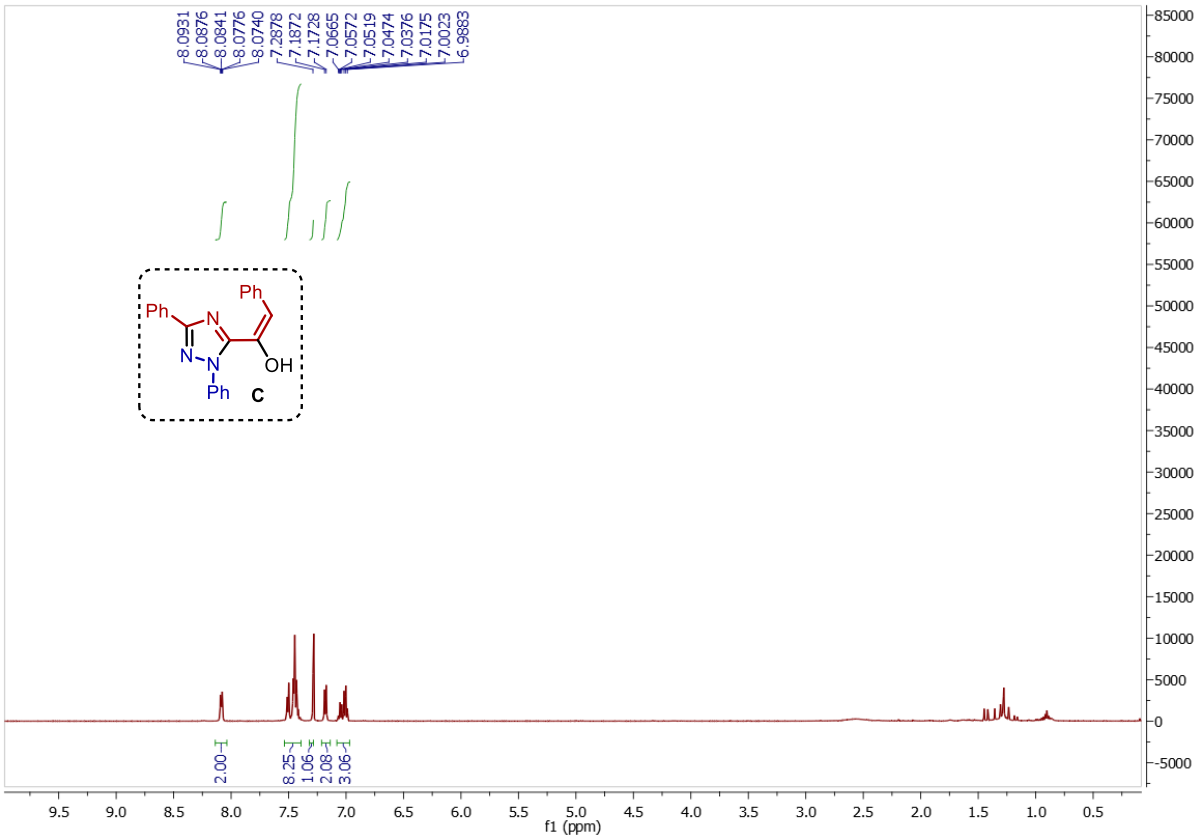
Reaction time = 5 h

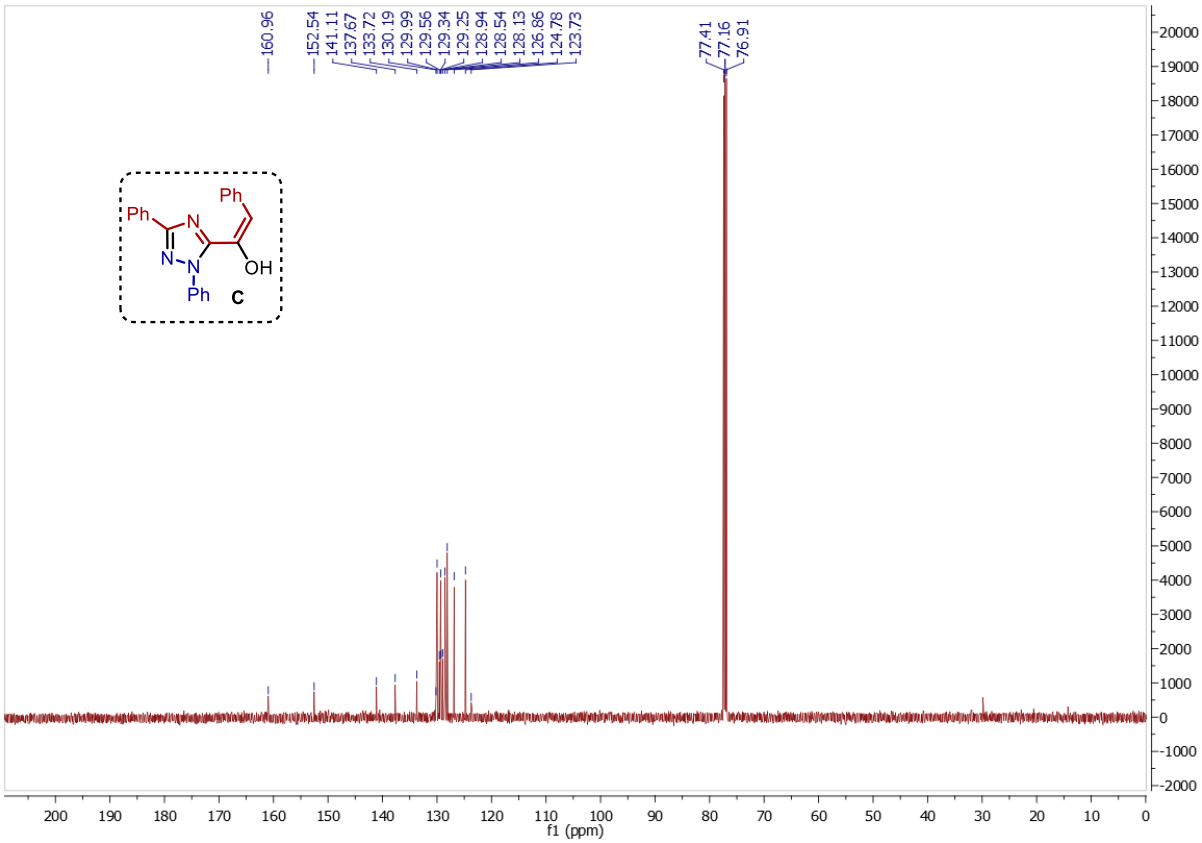
Figure S1: Experimental setup with lead-acetate paper.

To confirm the release of H_2S gas during the reaction, we conducted a lead acetate paper test by placing the paper inside the reaction vessel, as shown in Figure S1. Initially, the lead acetate paper was white. As the reaction progressed, the paper gradually darkened in colour. After 5 hours, it turned distinctly dark, indicating the presence of H_2S gas.



1-(1,3-diphenyl-1*H*-1,2,4-triazol-5-yl)-2-phenylethen-1-ol (C): Yellow solid, Yield = 17% (11.5 mg); purified using flash chromatography with hexane/ethyl acetate (10:1) as eluents and silica gel (100-200 mesh) as the stationary solid phase;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 2H), 7.54 – 7.39 (m, 8H), 7.29 (s, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.08 – 6.97 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.96, 152.54, 141.11, 137.67, 133.72, 130.19, 129.99, 129.56, 129.34, 129.25, 128.94, 128.54, 128.13, 126.86, 124.78, 123.73; HRMS (ES+) calc. for $C_{22}H_{17}N_3O$ [M+H]+ : 340.1444, found : 340.1435.

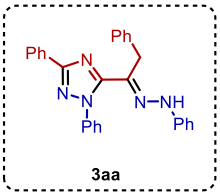




$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of intermediate **C**

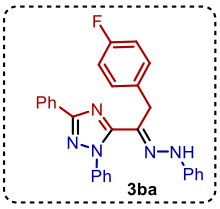
6. Characterization data of compounds 3 and 4

1,3-diphenyl-5-(2-phenyl-1-(2-phenylhydrazineylidene)ethyl)-1*H*-1,2,4-triazole (3aa)



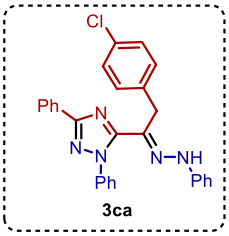
Yellow solid, Yield = 79% (67.9 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as the stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.12 (m, 2H), 7.74 (s, 1H), 7.59 – 7.49 (m, 5H), 7.49 – 7.38 (m, 5H), 7.36 (dd, *J* = 10.0, 4.7 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.01 (t, *J* = 6.5 Hz, 2H), 6.79 (t, *J* = 5.7 Hz, 1H), 6.17 (d, *J* = 6.7 Hz, 2H), 4.43 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.16, 153.29, 143.39, 140.76, 135.45, 132.60, 130.89, 129.50, 129.47, 128.99, 128.68, 128.35, 127.36, 126.69, 126.58, 121.24, 113.17, 33.29; HRMS (ES+) calc. for $C_{28}H_{23}N_5$ [M+H]+ : 430.2026, found : 430.2013.

5-(2-(4-fluorophenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3ba)



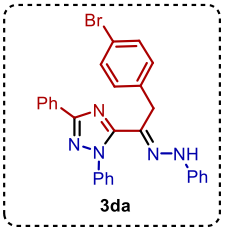
Yellow solid, Yield = 80% (71.6 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 – 8.17 (m, 2H), 7.69 (d, *J* = 19.5 Hz, 1H), 7.58 – 7.41 (m, 8H), 7.36 (dd, *J* = 8.5, 5.3 Hz, 2H), 7.03 (dd, *J* = 16.5, 8.1 Hz, 4H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.19 (d, *J* = 7.7 Hz, 2H), 4.39 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.02, 161.09, 153.07, 143.26, 140.65, 132.29, 131.045 ($J_{C\text{-}F}$ = 3.3 Hz), 130.74, 129.93, 129.87, 129.53, 129.04, 128.75, 128.71, 126.68, 126.54, 121.42, 116.31 ($J_{C\text{-}F}$ = 21.3 Hz), 113.21, 32.30; HRMS (ES+) calc. for $C_{28}H_{22}FN_5$ [M+H]+ : 448.1932, found : 448.1942.

5-(2-(4-chlorophenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3ca)



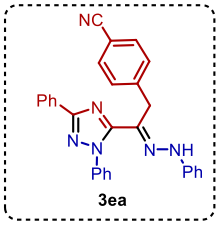
Yellow solid, Yield = 82% (76.1 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.0 Hz, 2H), 7.62 (s, 1H), 7.53 (t, *J* = 6.0 Hz, 3H), 7.52 – 7.48 (m, 2H), 7.48 – 7.40 (m, 3H), 7.32 (s, 4H), 7.03 (dd, *J* = 14.5, 6.5 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.18 (d, *J* = 8.2 Hz, 2H), 4.37 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.28, 153.09, 143.23, 140.71, 133.91, 133.20, 132.13, 130.90, 129.72, 129.57, 129.55, 129.48, 129.06, 128.75, 128.70, 126.66, 126.59, 121.46, 113.22, 32.43; HRMS (ES+) calc. for $C_{28}H_{22}ClN_5$ [M+H]+ : 464.1636, found : 464.1603.

5-(2-(4-bromophenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3da)



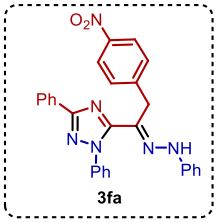
Yellow solid, Yield = 85% (86.4 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.7 Hz, 2H), 8.01 (s, 1H), 7.55 – 7.51 (m, 3H), 7.49 – 7.41 (m, 7H), 7.27 – 7.24 (m, 2H), 7.01 (t, *J* = 7.9 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.23 (d, *J* = 8.0 Hz, 2H), 4.42 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.38, 152.71, 143.19, 140.32, 134.46, 132.42, 131.06, 130.15, 130.06, 129.79, 129.55, 129.00, 128.91, 128.75, 126.79, 126.42, 121.53, 121.15, 113.34, 32.40; HRMS (ES+) calc. for $C_{28}H_{22}BrN_5$ [M+H]+ : 508.1131 & 509.1038 found : 508.1140 & 509.1047.

4-(2-(1,3-diphenyl-1*H*-1,2,4-triazol-5-yl)-2-(2-phenylhydrazineylidene)ethyl)benzonitrile (3ea)



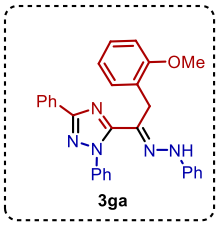
Yellow solid, Yield = 75% (68.2 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.19 (m, 2H), 7.89 (s, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.53 (m, 3H), 7.51 – 7.44 (m, 7H), 7.03 (t, *J* = 7.9 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.29 – 6.16 (m, 2H), 4.50 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.88, 152.65, 143.04, 141.25, 140.41, 132.96, 130.50, 130.41, 129.63, 129.56, 129.24, 129.03, 128.86, 128.70, 126.61, 126.45, 121.64, 118.70, 113.29, 111.10, 32.69; HRMS (ES+) calc. for $C_{29}H_{22}N_6$ [M+H]+ : 455.1979, found : 455.1985.

5-(2-(4-nitrophenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3fa)



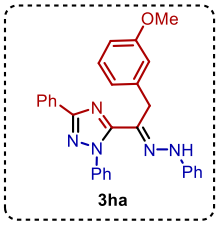
Yellow solid, Yield = 72% (68.3 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (t, *J* = 7.2 Hz, 4H), 7.89 (s, 1H), 7.58 – 7.53 (m, 5H), 7.46 (dd, *J* = 14.5, 6.8 Hz, 5H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 2H), 4.59 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.32, 152.73, 147.29, 143.23, 142.96, 140.59, 130.87, 130.74, 129.62, 129.58, 129.32, 129.14, 128.89, 128.73, 126.62, 126.59, 124.56, 121.80, 113.31, 32.57; HRMS (ES+) calc. for $C_{28}H_{22}N_6O_2$ [M+H]+ : 475.1877, found : 475.1841.

5-(2-(2-methoxyphenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3ga)



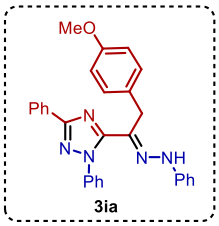
Yellow solid, Yield = 79% (72.6 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.44 – 8.19 (m, 2H), 7.74 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.57 – 7.37 (m, 8H), 7.31 – 7.11 (m, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.22 (d, *J* = 7.6 Hz, 2H), 4.37 (s, 2H), 4.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.85, 155.66, 153.57, 143.88, 140.87, 132.13, 131.50, 131.01, 129.44, 129.40, 129.03, 128.72, 128.50, 128.44, 126.71, 126.48, 124.04, 122.12, 120.65, 112.86, 110.95, 77.41, 77.16, 76.91, 55.91, 26.06; HRMS (ES+) calc. for $C_{29}H_{25}N_5O$ [M+H]+ : 460.2132, found : 460.2126.

5-(2-(3-methoxyphenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3ha)



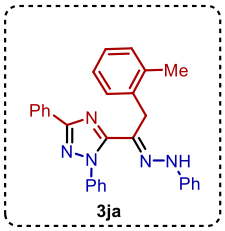
Yellow solid, Yield = 80% (73.5 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.1 Hz, 2H), 7.70 (s, 1H), 7.50 – 7.31 (m, 8H), 7.25 – 7.13 (m, 1H), 7.01 – 6.86 (m, 4H), 6.81 – 6.61 (m, 2H), 6.11 (d, *J* = 7.8 Hz, 2H), 4.33 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.49, 157.05, 153.32, 143.40, 140.76, 137.07, 132.49, 130.91, 130.46, 129.50, 129.46, 129.44, 129.00, 128.68, 126.67, 126.59, 121.24, 120.53, 114.28, 113.17, 112.62, 55.37, 33.39; HRMS (ES+) calc. for $C_{29}H_{25}N_5O$ [M+H]+ : 460.2132, found : 460.2136.

5-(2-(4-methoxyphenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3ia)



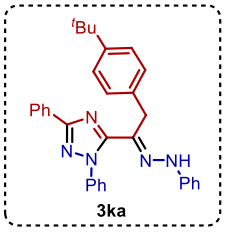
Yellow solid, Yield = 79% (72.6 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.4 Hz, 2H), 7.74 (s, 1H), 7.45 (ddd, *J* = 21.4, 20.6, 7.2 Hz, 8H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 2H), 6.88 (d, *J* = 7.4 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.17 (d, *J* = 7.7 Hz, 2H), 4.35 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.18, 158.85, 153.33, 143.45, 140.78, 133.05, 130.94, 129.49, 129.43, 129.40, 128.99, 128.68, 128.65, 127.19, 126.69, 126.58, 121.19, 114.87, 113.16, 55.44, 32.47; HRMS (ES+) calc. for $C_{29}H_{25}N_5O$ [M+H]+ : 460.2132, found : 460.2146.

1,3-diphenyl-5-(1-(2-phenylhydrazineylidene)-2-(*o*-tolyl)ethyl)-1*H*-1,2,4-triazole (3ja)



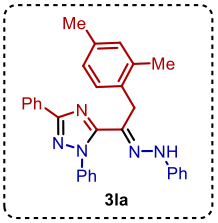
Yellow solid, Yield = 66% (58.5 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.64 (s, 1H), 7.58 – 7.48 (m, 5H), 7.46 – 7.38 (m, 3H), 7.24 (s, 1H), 7.22 – 7.17 (m, 1H), 7.17 – 7.13 (m, 2H), 7.00 (t, *J* = 7.9 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.14 (d, *J* = 7.7 Hz, 2H), 4.39 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.90, 153.19, 143.41, 140.78, 136.89, 133.02, 132.06, 132.02, 131.11, 130.71, 129.56, 129.50, 128.99, 128.77, 128.68, 127.58, 126.98, 126.71, 126.68, 121.23, 113.19, 31.56, 20.24; HRMS (ES+) calc. for $C_{29}H_{25}N_5$ [M+H]+ : 444.2183, found : 444.2191.

5-(2-(4-(*tert*-butyl)phenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3ka)



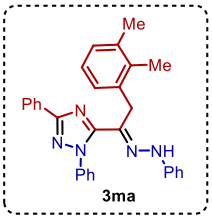
Yellow solid, Yield = 68% (66.0 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.18 (m, 2H), 7.81 (s, 1H), 7.57 – 7.48 (m, 5H), 7.48 – 7.41 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.02 (t, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.19 (d, *J* = 7.8 Hz, 2H), 4.41 (s, 2H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.91, 153.24, 150.31, 143.46, 140.71, 132.67, 132.18, 130.69, 129.52, 129.50, 128.99, 128.71, 128.69, 128.03, 126.74, 126.59, 126.38, 121.20, 113.21, 34.63, 32.74, 31.44; HRMS (ES+) calc. for $C_{32}H_{31}N_5$ [M+H]+ : 486.2652, found : 486.2623.

5-(2-(2,4-dimethylphenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3la)



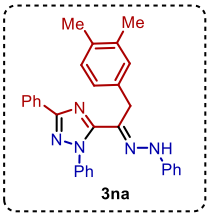
Yellow solid, Yield = 60% (55.0 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.67 (s, 1H), 7.60 – 7.49 (m, 5H), 7.47 – 7.37 (m, 3H), 7.08 – 7.03 (m, 2H), 7.01 (dd, *J* = 8.3, 7.6 Hz, 2H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.14 (d, *J* = 7.7 Hz, 2H), 4.34 (s, 2H), 2.43 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.06, 153.31, 143.50, 140.87, 137.16, 136.63, 132.50, 131.96, 130.91, 129.91, 129.57, 129.52, 129.40, 128.97, 128.71, 128.68, 128.64, 127.56, 126.68, 121.10, 113.14, 31.24, 21.07, 20.15. ; HRMS (ES+) calc. for $C_{30}H_{27}N_5$ [M+H]+ : 458.2339, found : 458.2353.

5-(2-(2,3-dimethylphenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3ma)



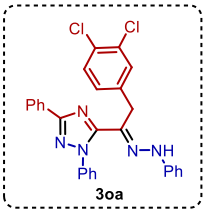
Yellow solid, Yield = 62% (56.7 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 8.17 (m, 2H), 7.73 (s, 1H), 7.59 – 7.51 (m, 5H), 7.48 – 7.38 (m, 3H), 7.14 – 7.09 (m, 1H), 7.06 (dd, *J* = 6.8, 4.3 Hz, 2H), 7.01 (t, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.13 (d, *J* = 7.8 Hz, 2H), 4.43 (s, 2H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.94, 153.27, 143.46, 140.85, 137.96, 135.54, 132.97, 132.19, 130.80, 129.52, 129.43, 129.33, 128.94, 128.69, 128.65, 126.69, 126.67, 126.38, 125.48, 121.10, 113.12, 32.53, 20.90, 15.85; HRMS (ES+) calc. for $C_{30}H_{27}N_5$ [M+H]+ : 458.2339, found : 458.2349.

5-(2-(3,4-dimethylphenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3na)



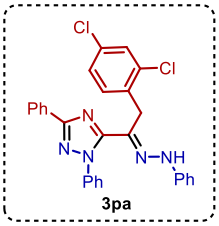
Yellow solid, Yield = 62% (56.7 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.0 Hz, 2H), 7.79 (s, 1H), 7.58 – 7.48 (m, 5H), 7.44 (dt, *J* = 22.1, 7.1 Hz, 3H), 7.15 (s, 1H), 7.10 (s, 2H), 7.01 (t, *J* = 7.8 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.17 (d, *J* = 7.8 Hz, 2H), 4.35 (s, 2H), 2.25 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.17, 153.42, 143.50, 140.81, 137.78, 135.66, 133.05, 132.72, 130.97, 130.60, 129.58, 129.46, 129.40, 128.96, 128.66, 128.62, 126.69, 126.59, 125.62, 121.09, 113.13, 33.00, 19.98, 19.51; HRMS (ES+) calc. for $C_{30}H_{27}N_5$ [M+H]+ : 458.2339, found : 458.2348.

5-(2-(3,4-dichlorophenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3oa)



Yellow solid, Yield = 81% (80.7 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.05 (s, 1H), 8.06 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 1.4 Hz, 1H), 7.58 (dd, *J* = 5.7, 2.8 Hz, 4H), 7.53 – 7.43 (m, 5H), 7.34 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 2H), 4.39 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.79, 153.02, 144.09, 140.40, 137.82, 130.94, 130.81, 130.73, 130.45, 130.23, 129.47, 129.44, 129.07, 128.85, 128.80, 128.69, 128.60, 126.28, 125.88, 120.33, 113.04, 30.99; HRMS (ES+) calc. for $C_{28}H_{21}Cl_2N_5$ [M+H]+ : 498.1247, found : 498.1204.

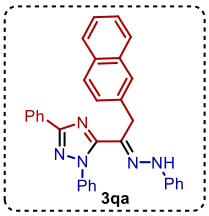
5-(2-(2,4-dichlorophenyl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3pa)



Yellow solid, Yield = 81% (80.7 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.8 Hz, 2H), 7.86 (s, 1H), 7.55 – 7.41 (m, 10H), 7.20 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.23 (d, *J* = 8.0 Hz, 2H), 4.45 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.03, 152.96, 143.03, 140.52, 133.76, 131.68, 131.33, 130.68, 130.54, 129.43, 129.37, 129.34, 128.94, 128.81, 128.64, 128.61, 128.19, 126.53, 126.42, 121.35, 113.08, 29.18; HRMS (ES+) calc. for $C_{28}H_{21}Cl_2N_5$ [M+H]+ : 498.1247, found : 498.1259.

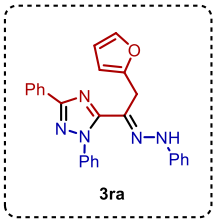
5-(2-(naphthalen-2-yl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3qa)

Yellow solid, Yield = 77% (74.0 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ



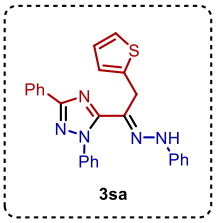
8.24 (d, *J* = 7.9 Hz, 2H), 7.91 – 7.72 (m, 5H), 7.58 – 7.40 (m, 11H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 2H), 4.59 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.25, 153.37, 143.33, 140.77, 133.83, 132.94, 132.65, 132.46, 130.94, 129.52, 129.45, 129.39, 129.01, 128.97, 128.69, 127.88, 127.67, 126.70, 126.67, 126.62, 126.57, 126.51, 126.11, 121.26, 113.19, 33.54; HRMS (ES+) calc. for $C_{32}H_{25}N_5$ [M+H]+ : 480.2183, found : 480.2191.

5-(2-(furan-2-yl)-1-(2-phenylhydrazineylidene)ethyl)-1,3-diphenyl-1*H*-1,2,4-triazole (3ra)



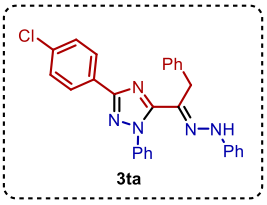
Yellow solid, Yield = 67% (56.2 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.03 (s, 1H), 8.07 (d, *J* = 7.1 Hz, 2H), 7.57 (dd, *J* = 7.9, 3.7 Hz, 4H), 7.48 (dq, *J* = 9.7, 7.0 Hz, 5H), 6.99 (t, *J* = 7.8 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.38 (dd, *J* = 2.7, 1.9 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J* = 2.9 Hz, 1H), 4.44 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.82, 152.97, 149.58, 144.15, 142.03, 140.27, 130.47, 129.41, 129.39, 128.90, 128.80, 128.56, 128.05, 126.10, 125.90, 120.13, 112.88, 110.70, 106.76, 25.73 ; HRMS (ES+) calc. for $C_{26}H_{21}N_5O$ [M+H]+ : 420.1819, found : 420.1821.

1,3-diphenyl-5-(1-(2-phenylhydrazineylidene)-2-(thiophen-2-yl)ethyl)-1*H*-1,2,4-triazole (3sa)



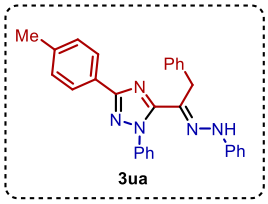
Yellow solid, Yield = 70% (61.0 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.19 (m, 2H), 7.88 (s, 1H), 7.60 – 7.49 (m, 5H), 7.47 (dd, *J* = 11.4, 4.4 Hz, 2H), 7.43 (ddd, *J* = 7.3, 3.5, 1.3 Hz, 1H), 7.22 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.04 (dd, *J* = 8.3, 7.6 Hz, 3H), 6.97 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.23 (d, *J* = 7.7 Hz, 2H), 4.59 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.19, 152.63, 143.33, 140.62, 137.23, 131.53, 130.88, 129.47, 129.45, 129.02, 128.78, 128.68, 127.41, 126.67, 126.54, 126.08, 125.05, 121.38, 113.23, 27.63; HRMS (ES+) calc. for $C_{26}H_{21}N_5S$ [M+H]+ : 436.1590, found : 436.1603.

3-(4-chlorophenyl)-1-phenyl-5-(2-phenyl-1-(2-phenylhydrazineylidene)ethyl)-1*H*-1,2,4-triazole (3ta)



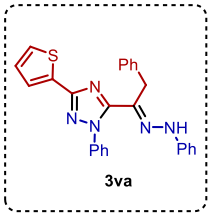
Yellow solid, Yield = 71% (66.0 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.1 Hz, 2H), 7.77 (s, 1H), 7.52 (dd, *J* = 22.5, 7.1 Hz, 5H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.36 (q, *J* = 7.9 Hz, 4H), 7.31 – 7.26 (m, 1H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.16 (d, *J* = 8.0 Hz, 2H), 4.42 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.14, 153.38, 143.28, 140.61, 135.37, 135.31, 132.23, 129.55, 129.48, 129.34, 129.00, 128.91, 128.79, 128.30, 128.00, 127.40, 126.50, 121.33, 113.17, 33.21; HRMS (ES+) calc. for $C_{28}H_{22}ClN_5$ [M+H]+ : 464.1636, found : 464.1645.

1-phenyl-5-(2-phenyl-1-(2-phenylhydrazineylidene)ethyl)-3-(*p*-tolyl)-1*H*-1,2,4-triazole (3ua)



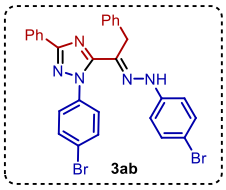
Yellow solid, Yield = 74% (65.6 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 2H), 7.78 (s, 1H), 7.57 – 7.45 (m, 5H), 7.41 – 7.32 (m, 4H), 7.27 (d, *J* = 6.1 Hz, 3H), 7.01 (t, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.17 (d, *J* = 7.8 Hz, 2H), 4.44 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.01, 153.05, 143.39, 140.69, 139.52, 135.45, 132.42, 129.49, 129.45, 129.41, 128.99, 128.68, 128.38, 127.87, 127.35, 126.66, 126.57, 121.25, 113.19, 33.31, 21.60; HRMS (ES+) calc. for $C_{29}H_{25}N_5$ [M+H]+ : 444.2183, found : 444.2191.

1-phenyl-5-(2-phenyl-1-(2-phenylhydrazineylidene)ethyl)-3-(thiophen-2-yl)-1*H*-1,2,4-triazole (3va)



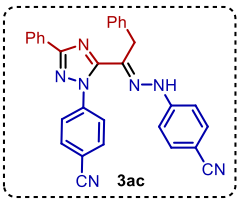
Yellow solid, Yield = 77% (67.1 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 1H), 7.77 (s, 1H), 7.52 (t, *J* = 5.7 Hz, 2H), 7.48 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.27 (d, *J* = 9.0 Hz, 1H), 7.12 (dd, *J* = 4.9, 3.7 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.15 (d, *J* = 7.8 Hz, 2H), 4.41 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.25, 153.06, 143.28, 140.46, 135.32, 133.50, 132.05, 129.54, 129.48, 129.00, 128.81, 128.35, 127.86, 127.40, 126.91, 126.83, 126.60, 121.36, 113.21, 33.26; HRMS (ES+) calc. for $C_{26}H_{21}N_5S$ [M+H]+ : 436.1590, found : 436.1597.

1-(4-bromophenyl)-5-(1-(2-(4-bromophenyl)hydrazineylidene)-2-phenylethyl)-3-phenyl-1*H*-1,2,4-triazole (3ab)



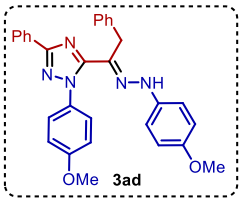
Yellow solid, Yield = 65% (76.4 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$: DMSO-d_6 (1:0.02)) δ 8.44 (s, 1H), 8.12 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.37 (dq, *J* = 14.1, 6.9 Hz, 3H), 7.28 (dt, *J* = 8.4, 5.6 Hz, 6H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.09 (d, *J* = 8.7 Hz, 2H), 4.37 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$: DMSO-d_6 (1:0.02)) δ 160.97, 152.96, 142.61, 139.46, 135.41, 132.72, 132.46, 131.69, 130.28, 129.51, 129.15, 128.56, 128.32, 128.00, 127.10, 126.51, 122.46, 114.72, 113.00, 32.77; HRMS (ES+) calc. for $C_{28}H_{21}Br_2N_5$ [M+H]+ : 586.0236 & 588.0216, found : 586.0241 & 588.0221.

4-(2-(1-(1-(4-cyanophenyl)-3-phenyl-1*H*-1,2,4-triazol-5-yl)-2-phenylethylidene)hydrazineyl)benzonitrile (3ac)



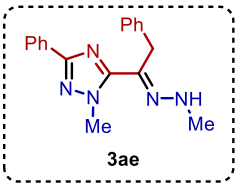
Yellow solid, Yield = 46% (44.1 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.64 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 8.07 – 8.02 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.50 (ddd, *J* = 8.3, 7.6, 2.2 Hz, 3H), 7.45 (t, *J* = 6.8 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.23 (t, *J* = 6.8 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 2H), 4.42 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.02, 153.50, 148.21, 144.20, 136.32, 135.45, 134.32, 133.53, 130.42, 130.24, 129.39, 129.20, 128.95, 127.77, 127.06, 126.45, 120.03, 118.62, 113.44, 112.07, 101.83, 32.72; HRMS (ES+) calc. for $C_{30}H_{21}N_7$ [M+H]+ : 480.1931, found : 480.1912.

1-(4-methoxyphenyl)-5-(1-(2-(4-methoxyphenyl)hydrazineylidene)-2-phenylethyl)-3-phenyl-1*H*-1,2,4-triazole (3ad)



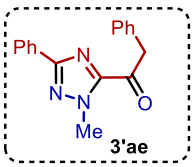
Yellow solid, Yield = 68% (66.6 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 – 8.18 (m, 2H), 7.63 (s, 1H), 7.47 – 7.39 (m, 5H), 7.35 (dt, *J* = 14.0, 6.9 Hz, 4H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 6.27 – 6.09 (m, 2H), 4.40 (s, 2H), 3.89 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.83, 159.99, 154.56, 153.42, 137.55, 135.58, 133.77, 131.83, 130.95, 129.40, 129.38, 128.65, 128.44, 128.33, 127.82, 127.26, 126.66, 114.56, 114.36, 55.81, 55.75, 33.23; HRMS (ES+) calc. for $C_{30}H_{27}N_5O_2$ [M+H]+ : 490.2238, found : 490.2259.

1-methyl-5-(1-(2-methylhydrazineylidene)-2-phenylethyl)-3-phenyl-1*H*-1,2,4-triazole (3ae)



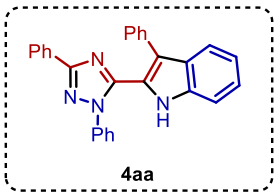
Yellow solid, Yield = 46% (28.1 mg); purified using flash chromatography with hexane/ethyl acetate (10:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.3 Hz, 2H), 7.45 – 7.35 (m, 4H), 7.32 – 7.27 (m, 4H), 4.27 (s, 2H), 4.18 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 159.35, 152.56, 135.61, 130.02, 129.02, 128.67, 128.51, 128.21, 126.86, 126.43, 126.31, 39.18, 38.23, 33.09; HRMS (ES+) calc. for $C_{18}H_{19}N_5$ [M+H]+ : 306.1713, found : 306.1765.

1-(1-methyl-3-phenyl-1*H*-1,2,4-triazol-5-yl)-2-phenylethan-1-one (3'ae)



Yellow solid, Yield = 56% (31.1 mg); purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.0 Hz, 2H), 7.46 (dq, *J* = 14.1, 7.0 Hz, 3H), 7.42 – 7.31 (m, 4H), 7.29 (t, *J* = 7.1 Hz, 1H), 4.52 (s, 2H), 4.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.05, 160.86, 149.51, 133.40, 130.47, 130.14, 129.77, 128.84, 128.80, 127.38, 126.55, 46.81, 38.87; HRMS (ES+) calc. for $C_{17}H_{15}N_3O$ [M+H]+ : 278.1288, found : 278.1307.

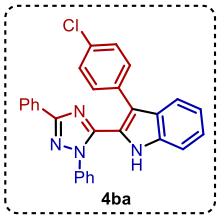
2-(1,3-diphenyl-1*H*-1,2,4-triazol-5-yl)-3-phenyl-1*H*-indole (4aa)



Yellow solid, Yield = 68% (56.1 mg) and 61% (50.3 mg) in one pot; purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.13 – 7.07 (m, 4H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.95 – 6.87 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.27, 148.73, 137.43, 136.84, 133.65, 130.41, 129.84, 129.28, 128.89, 128.77, 128.53, 128.11, 127.10, 126.72, 126.49, 124.35, 124.26, 120.84, 120.74, 120.40, 120.28, 111.90; HRMS (ES+) calc. for $C_{28}H_{20}N_4$ [M+H]+ : 413.1761, found : 413.1757.

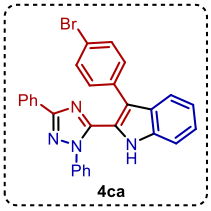
3-(4-chlorophenyl)-2-(1,3-diphenyl-1*H*-1,2,4-triazol-5-yl)-1*H*-indole (4ba)

Yellow solid, Yield = 71% (63.5 mg) and 59% (52.7 mg) in one pot; purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase;^{1}H



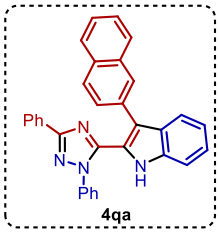
NMR (500 MHz, $CDCl_3$) δ 10.65 (s, 1H), 8.22 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.46 – 7.43 (m, 3H), 7.31 (dd, *J* = 5.7, 4.9 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.07 (dd, *J* = 15.0, 7.8 Hz, 4H), 6.86 – 6.82 (m, 4H);^{13}C NMR (125 MHz, $CDCl_3$) δ 161.78, 148.25, 137.24, 136.96, 132.57, 132.09, 130.49, 130.11, 129.71, 128.94, 128.85, 128.73, 128.48, 126.77, 126.74, 124.64, 124.29, 121.09, 120.34, 120.04, 119.19, 112.16; HRMS (ES+) calc. for $C_{28}H_{19}ClN_4$ [M+H]+ : 447.1371, found : 447.1379.

3-(4-bromophenyl)-2-(1,3-diphenyl-1*H*-1,2,4-triazol-5-yl)-1*H*-indole (4ca)



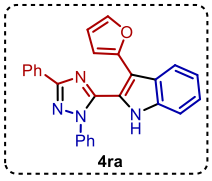
Yellow solid, Yield = 74% (72.7 mg) and 62% (61.0 mg) in one pot; purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase;^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.20 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.51 (t, *J* = 8.9 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.15 (dt, *J* = 7.4, 4.4 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.84 (d, *J* = 7.7 Hz, 2H), 6.75 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.81, 148.14, 137.17, 136.80, 132.46, 131.58, 130.75, 129.98, 129.72, 128.84, 128.77, 128.39, 126.63, 126.56, 124.56, 124.23, 121.03, 120.63, 120.36, 119.94, 119.03, 112.02; HRMS (ES+) calc. for $C_{28}H_{19}BrN_4$ [M+H]+ : 491.0866& 493.0846, found : 491.0872 & 493.0853 .

2-(1,3-diphenyl-1*H*-1,2,4-triazol-5-yl)-3-(naphthalen-2-yl)-1*H*-indole (4qa)



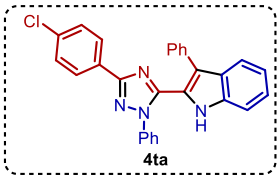
Yellow solid, Yield = 72% (66.6 mg) and 60% (55.5 mg) in one pot; purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.29 – 8.18 (m, 2H), 7.80 – 7.72 (m, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.51 – 7.41 (m, 5H), 7.35 (dd, *J* = 9.3, 5.6 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.89 (dd, *J* = 8.8, 4.5 Hz, 1H), 6.76 – 6.61 (m, 4H);^{13}C NMR (125 MHz, $CDCl_3$) δ 162.18, 148.74, 137.31, 136.90, 133.60, 132.20, 131.19, 130.27, 129.91, 128.91, 128.45, 128.13, 128.09, 127.95, 127.63, 127.57, 127.27, 126.75, 125.98, 125.76, 124.54, 124.24, 121.00, 120.95, 120.42, 120.26, 111.99; HRMS (ES+) calc. for $C_{32}H_{22}N_4$ [M+H]+ : 463.1917, found : 463.1929.

2-(1,3-diphenyl-1*H*-1,2,4-triazol-5-yl)-3-(furan-2-yl)-1*H*-indole (4ra)



Yellow solid, Yield = 76% (61.2 mg) and 62% (50.0 mg) in one pot; purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.25 – 8.12 (m, 2H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.14 (m, 7H), 6.22 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.17 (d, *J* = 3.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.73, 148.08, 147.87, 141.56, 137.43, 136.67, 129.96, 128.96, 128.87, 128.55, 126.75, 125.70, 124.65, 123.68, 121.23, 121.01, 119.98, 112.02, 111.28, 110.37, 107.22; HRMS (ES+) calc. for $C_{26}H_{18}N_4O$ [M+H]+ : 403.1553, found : 403.1565.

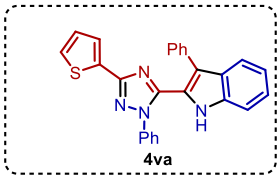
2-(3-(4-chlorophenyl)-1-phenyl-1*H*-1,2,4-triazol-5-yl)-3-phenyl-1*H*-indole (4ta)



4ta

Yellow solid, Yield = 65% (58.1 mg) and 59% (52.7 mg) in one pot; purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.17 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 9.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.11 (s, 3H), 7.02 (t, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 5.9 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.29, 148.70, 137.37, 136.75, 135.87, 133.48, 130.87, 129.48, 129.32, 129.14, 128.88, 128.58, 128.31, 128.05, 127.47, 127.17, 126.64, 124.61, 124.24, 121.04, 120.52, 111.83; HRMS (ES+) calc. for $C_{28}H_{19}ClN_4$ [M+H]+ : 447.1371, found : 447.1381.

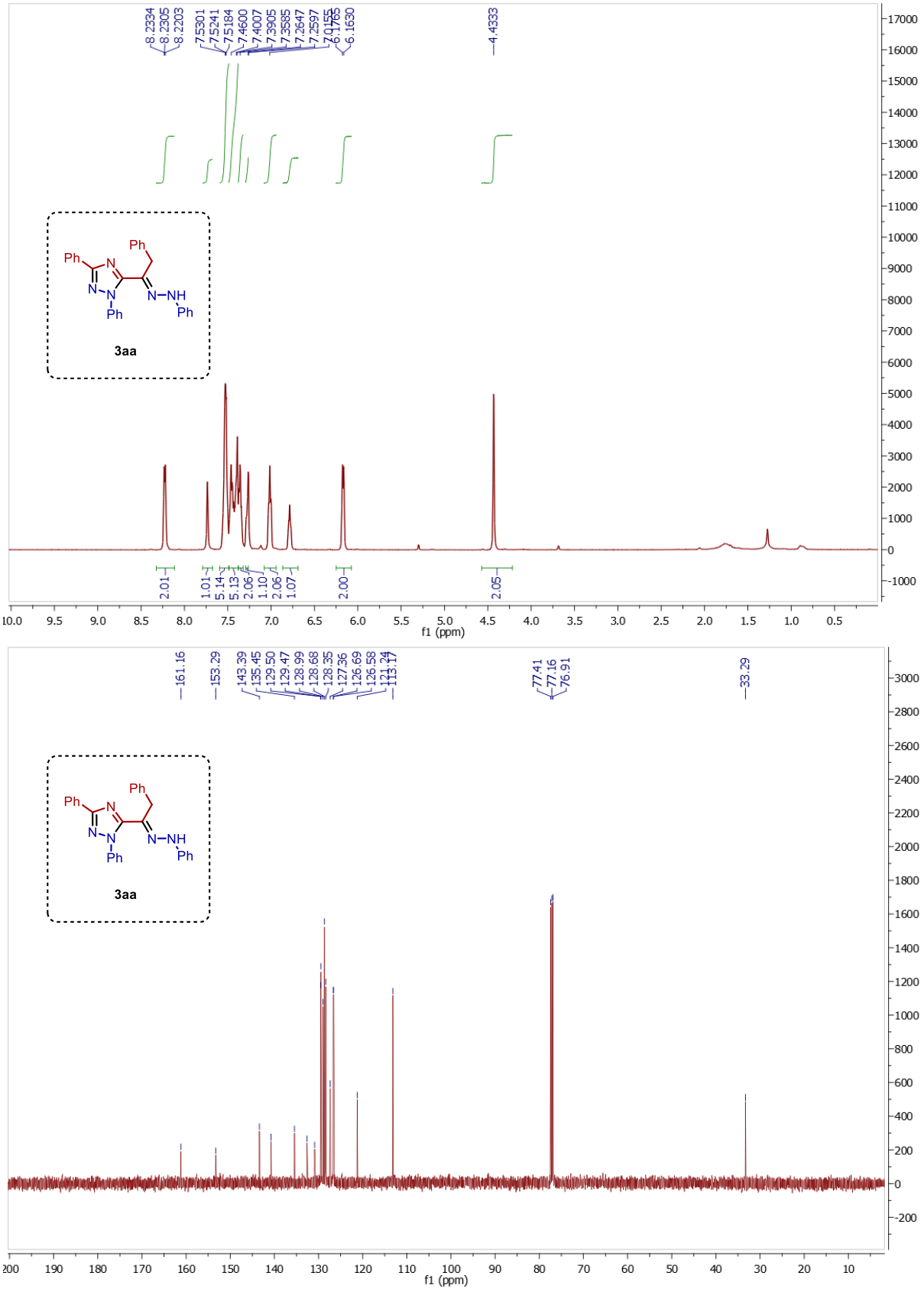
3-phenyl-2-(1-phenyl-3-(thiophen-2-yl)-1*H*-1,2,4-triazol-5-yl)-1*H*-indole (4va)



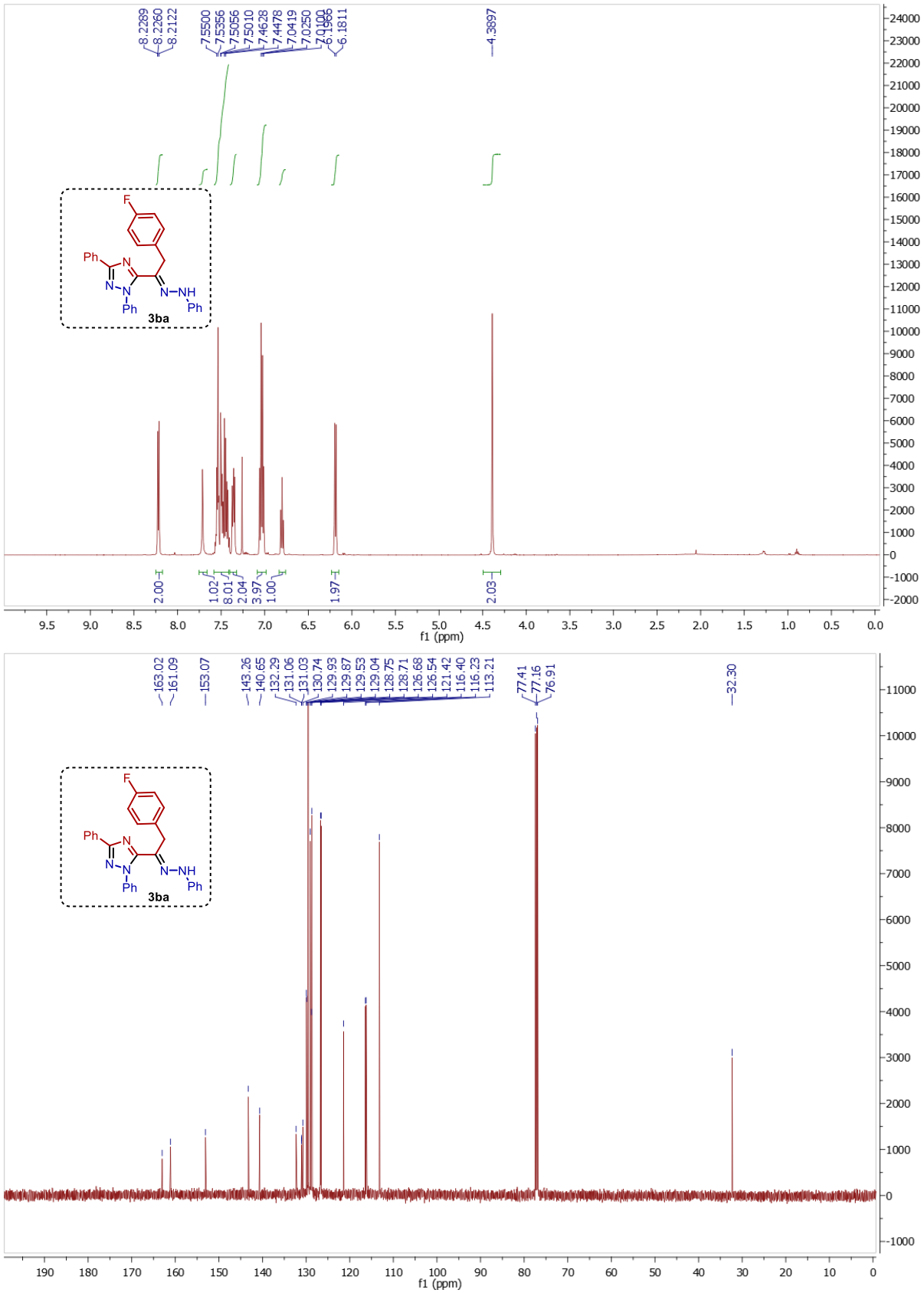
4va

Yellow solid, Yield = 70% (58.6 mg) and 61% (51.1 mg) in one pot; purified using flash chromatography with hexane/ethyl acetate (20:1) as eluents and silica gel (100-200 mesh) as stationary solid phase; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.84 (d, *J* = 3.2 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 5.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.05 (m, 6H), 7.00 (t, *J* = 7.8 Hz, 2H), 6.90 (dd, *J* = 7.2, 1.8 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.17, 148.42, 137.09, 136.74, 133.41, 132.80, 129.18, 128.69, 128.45, 128.21, 128.14, 127.95, 127.18, 127.05, 126.97, 126.45, 124.39, 124.22, 120.80, 120.46, 120.32, 111.86; HRMS (ES+) calc. for $C_{26}H_{18}N_4S$ [M+H]+ : 419.1325, found : 447.1327.

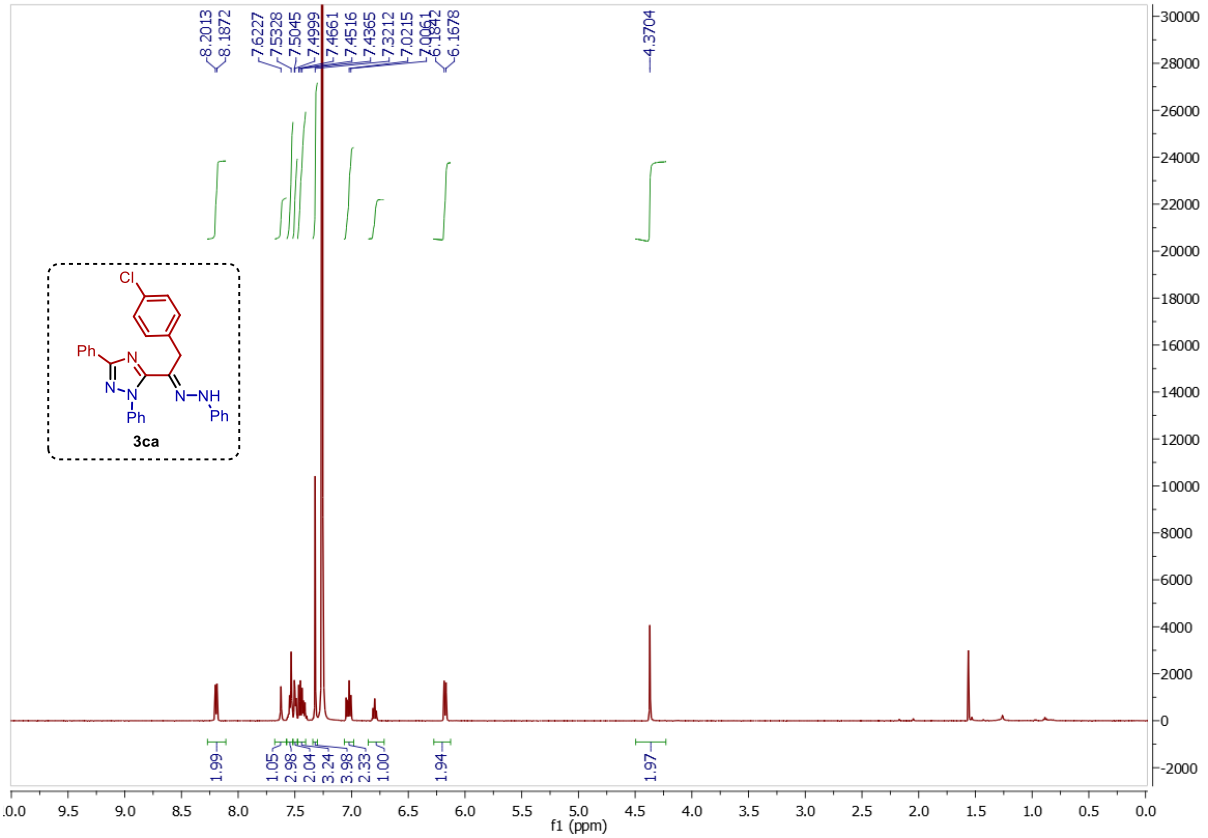
7. ^{1}H and ^{13}C NMR spectra of compounds 3 and 4

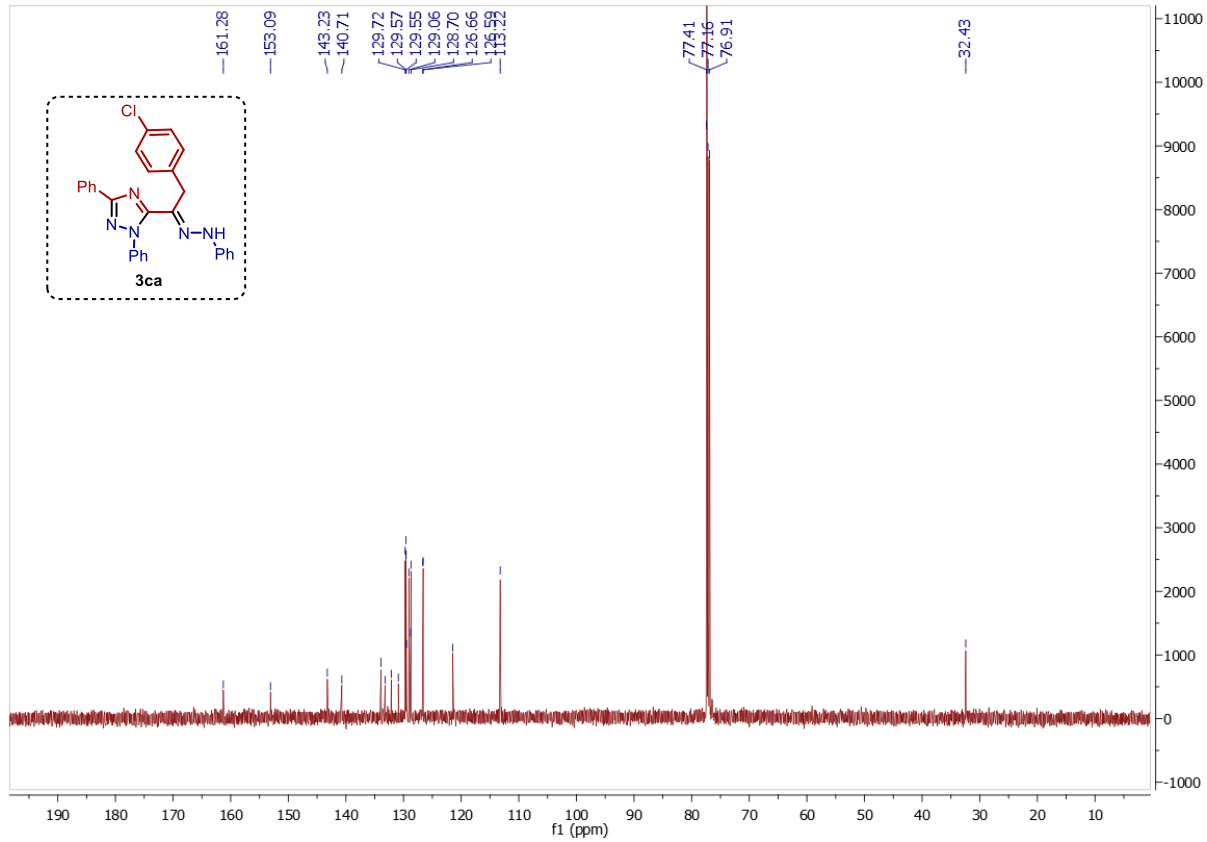


$CDCl_3$, 500 MHz ^{1}H NMR and 125 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **3aa**

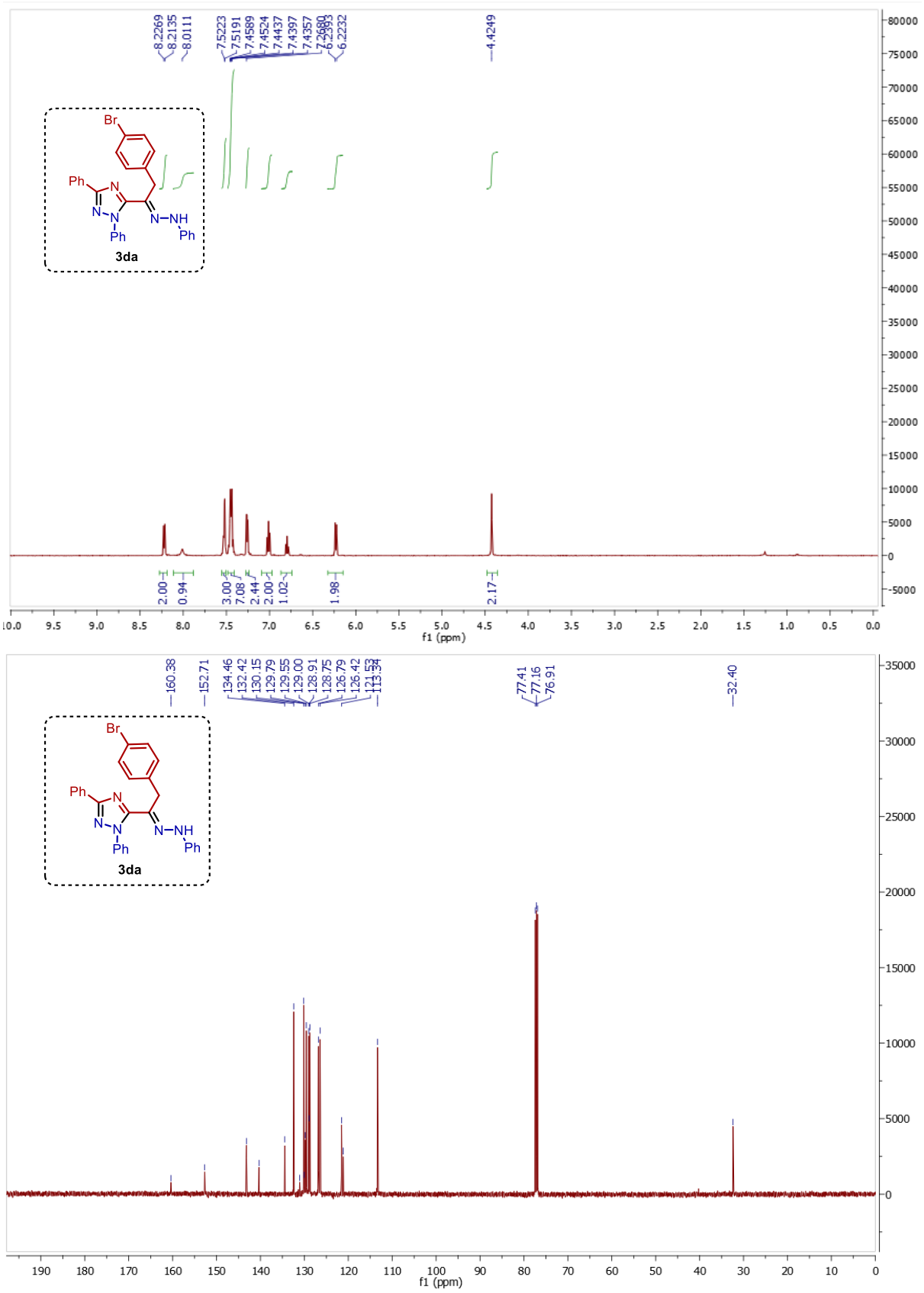


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ba**

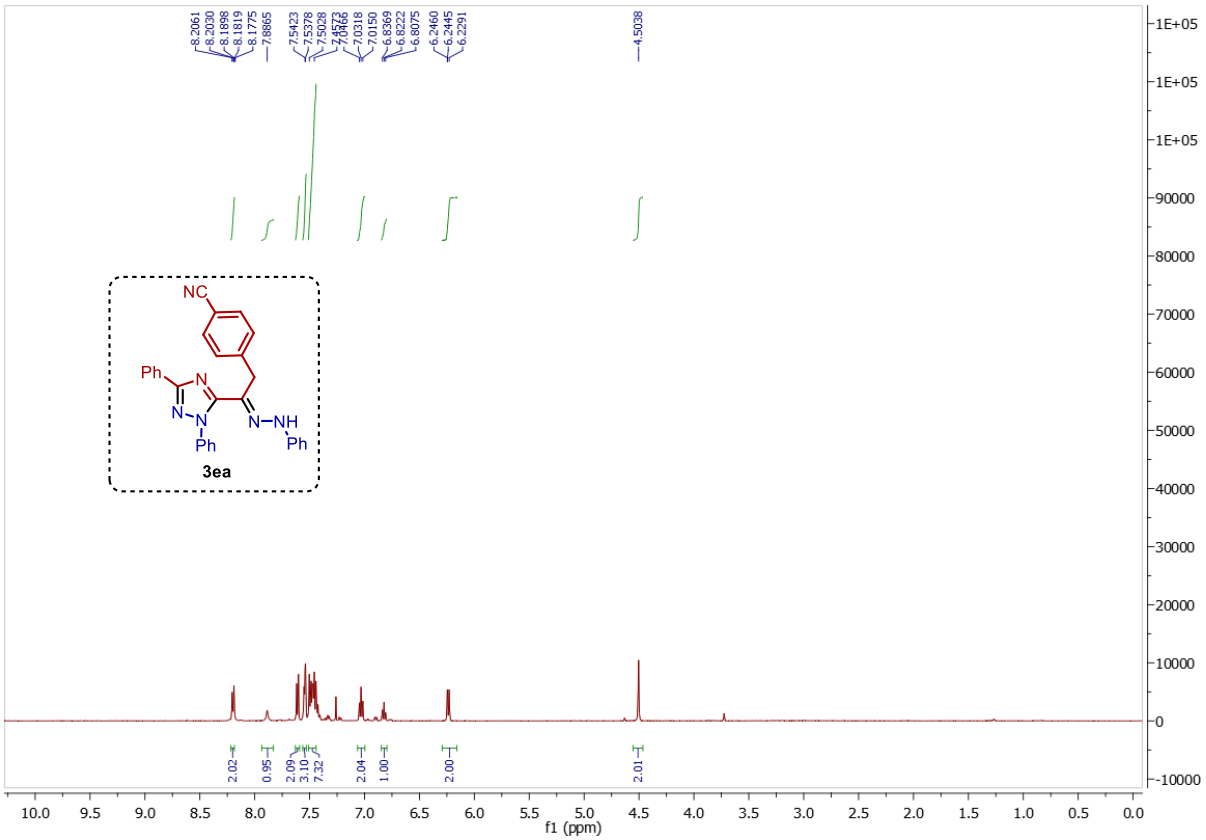


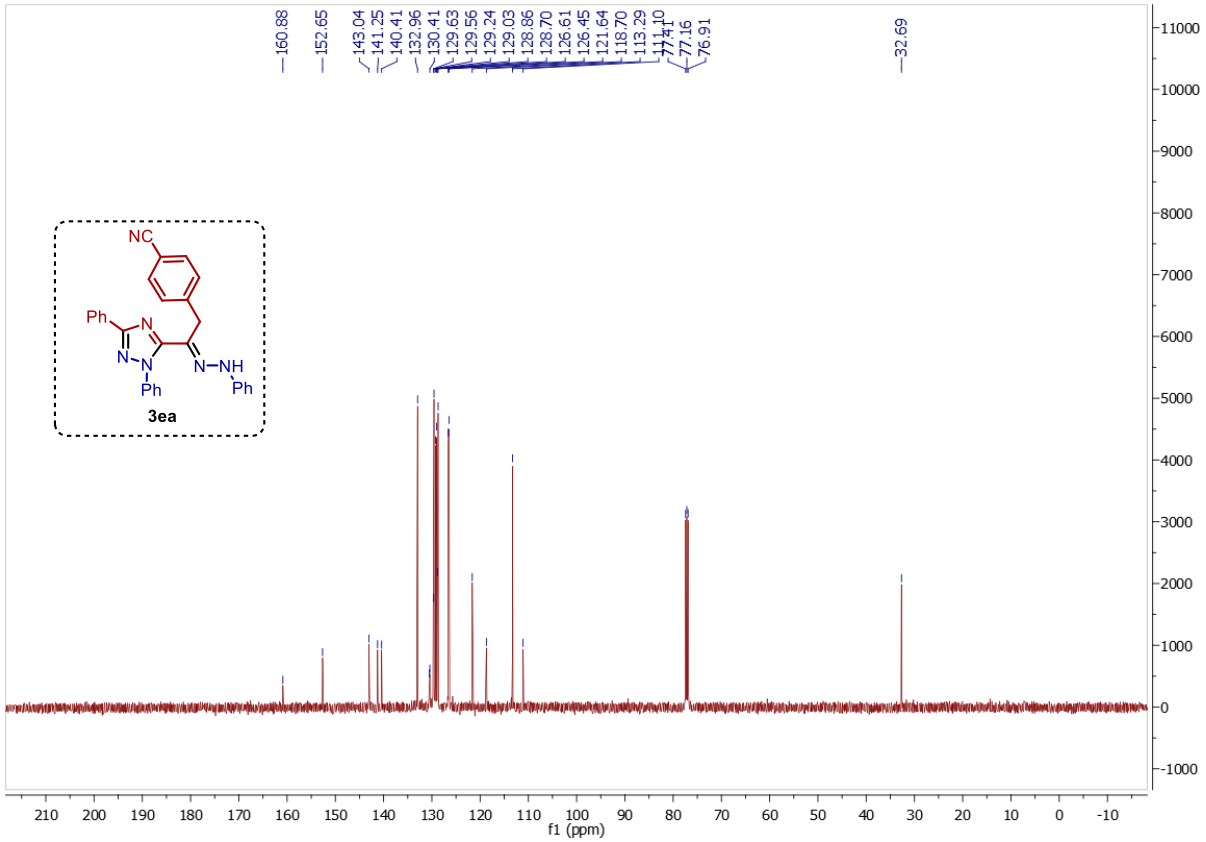


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ca**

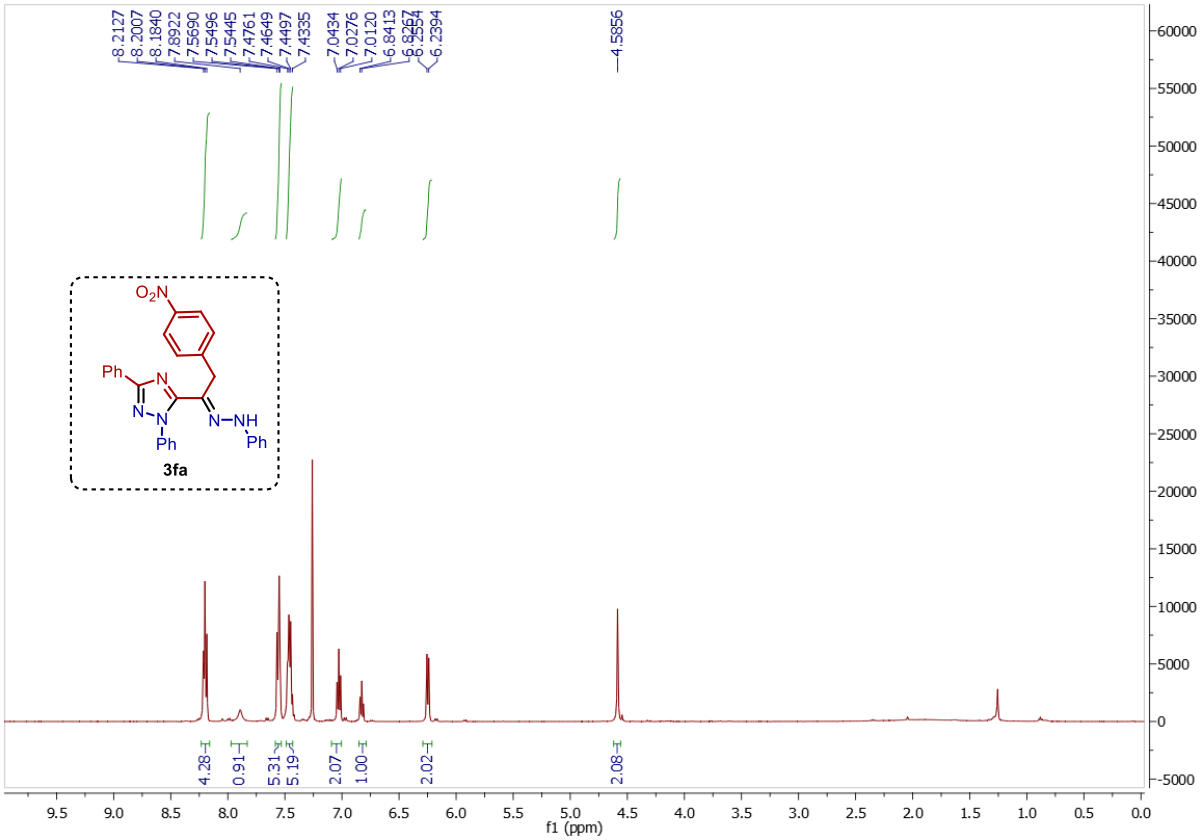


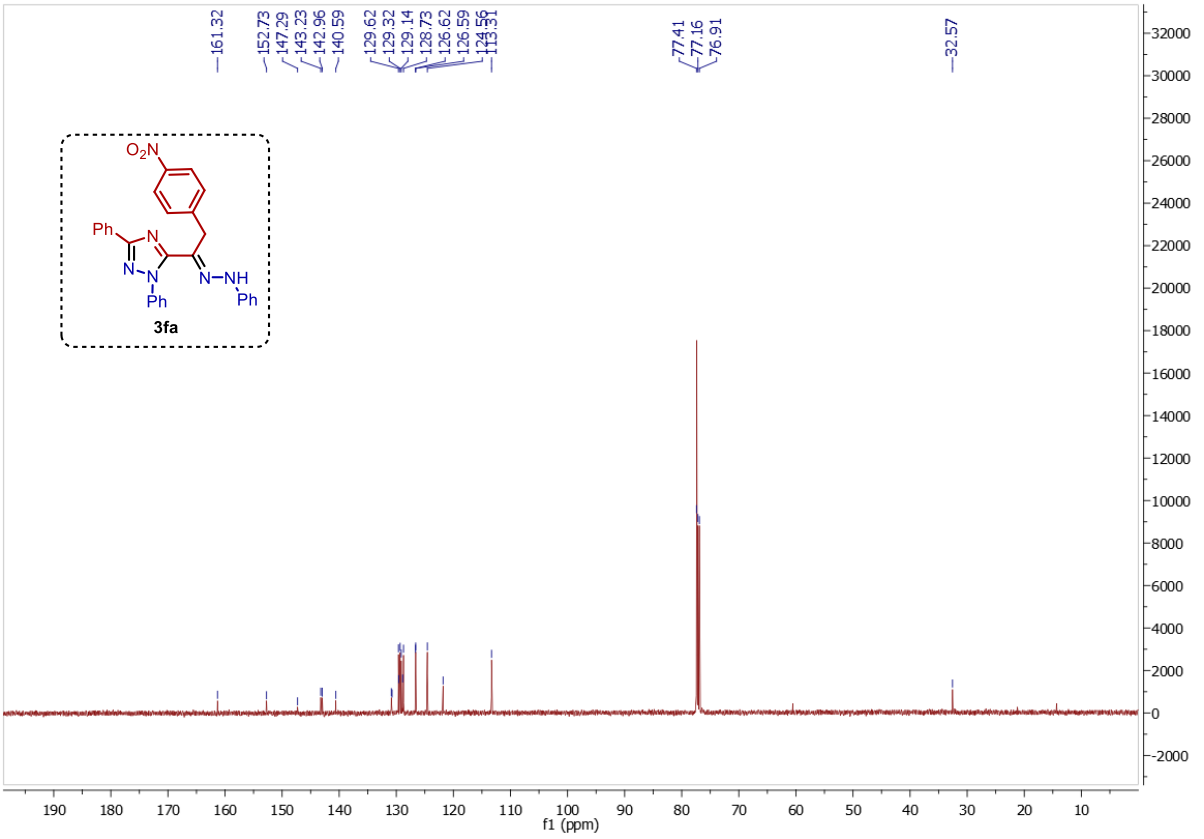
$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3da**



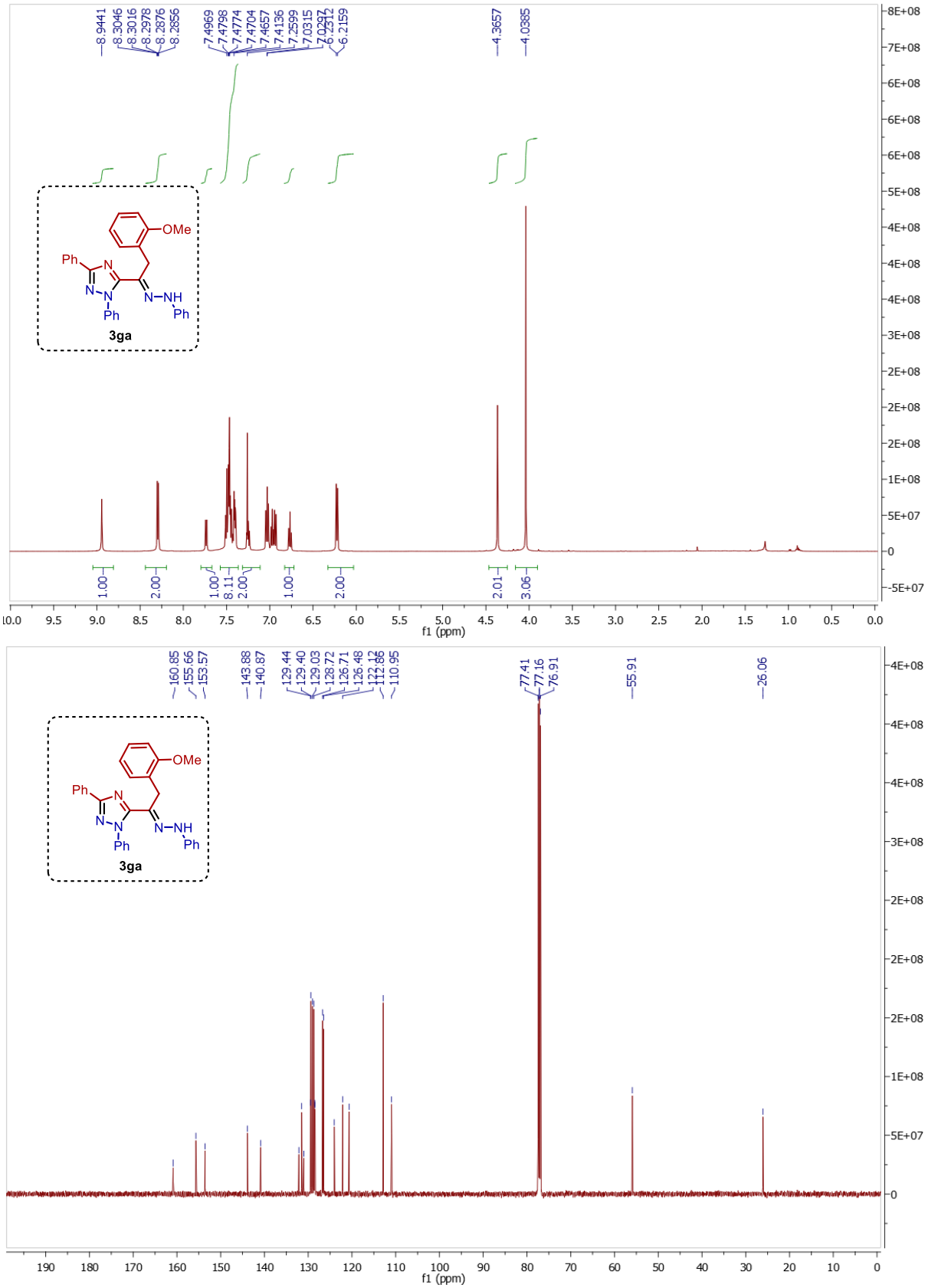


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ea**

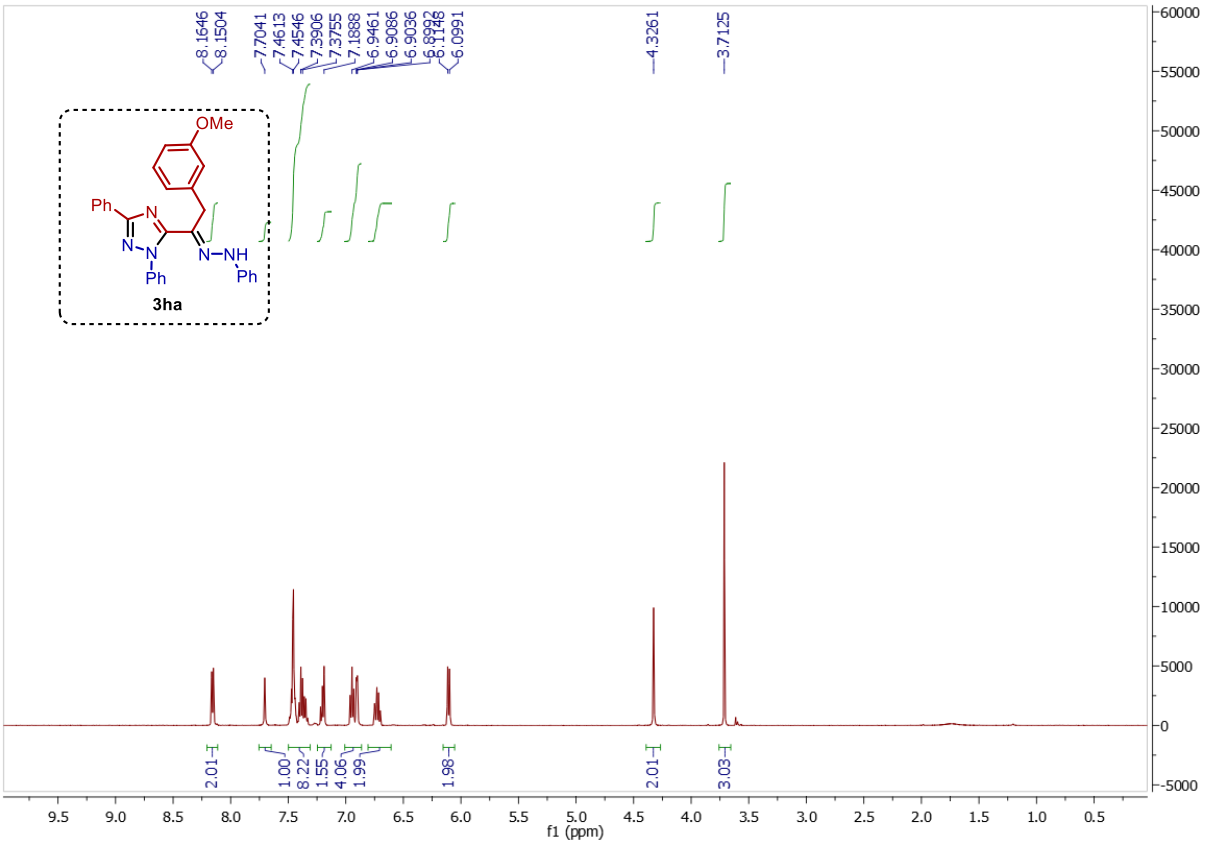


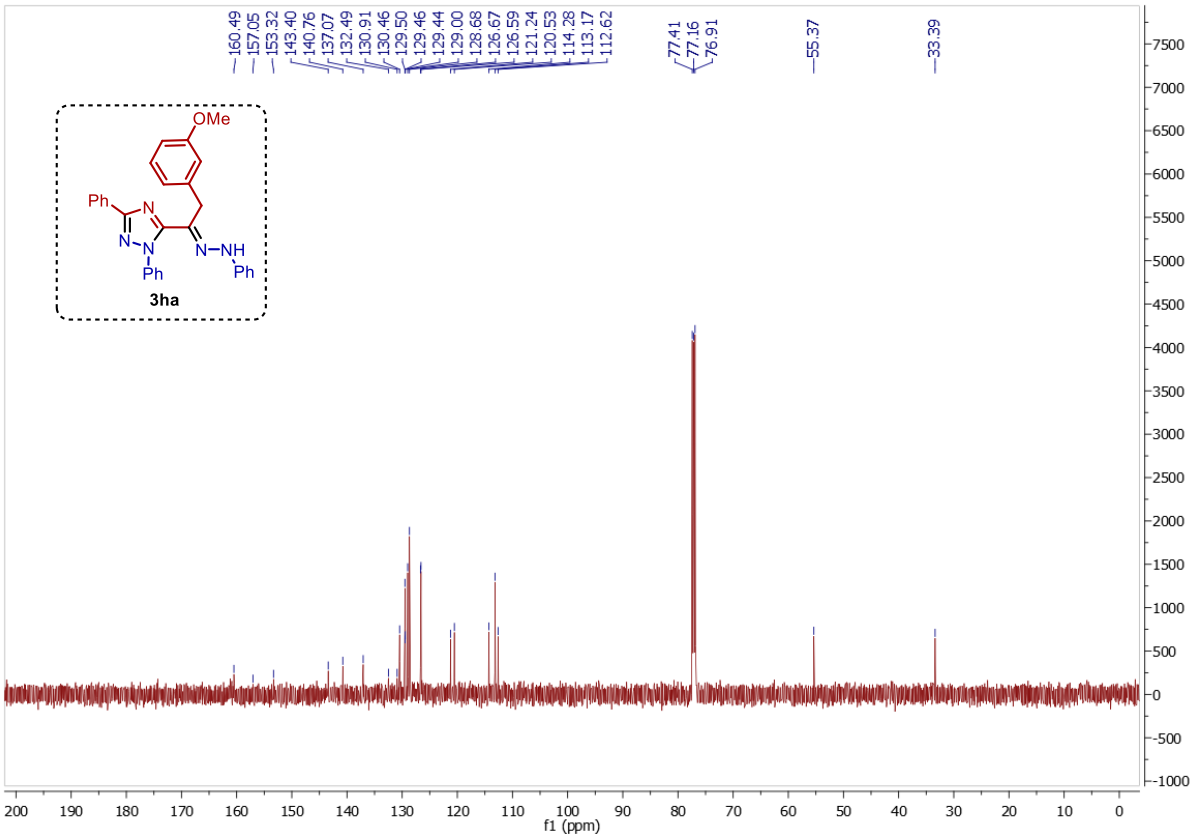


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3fa**

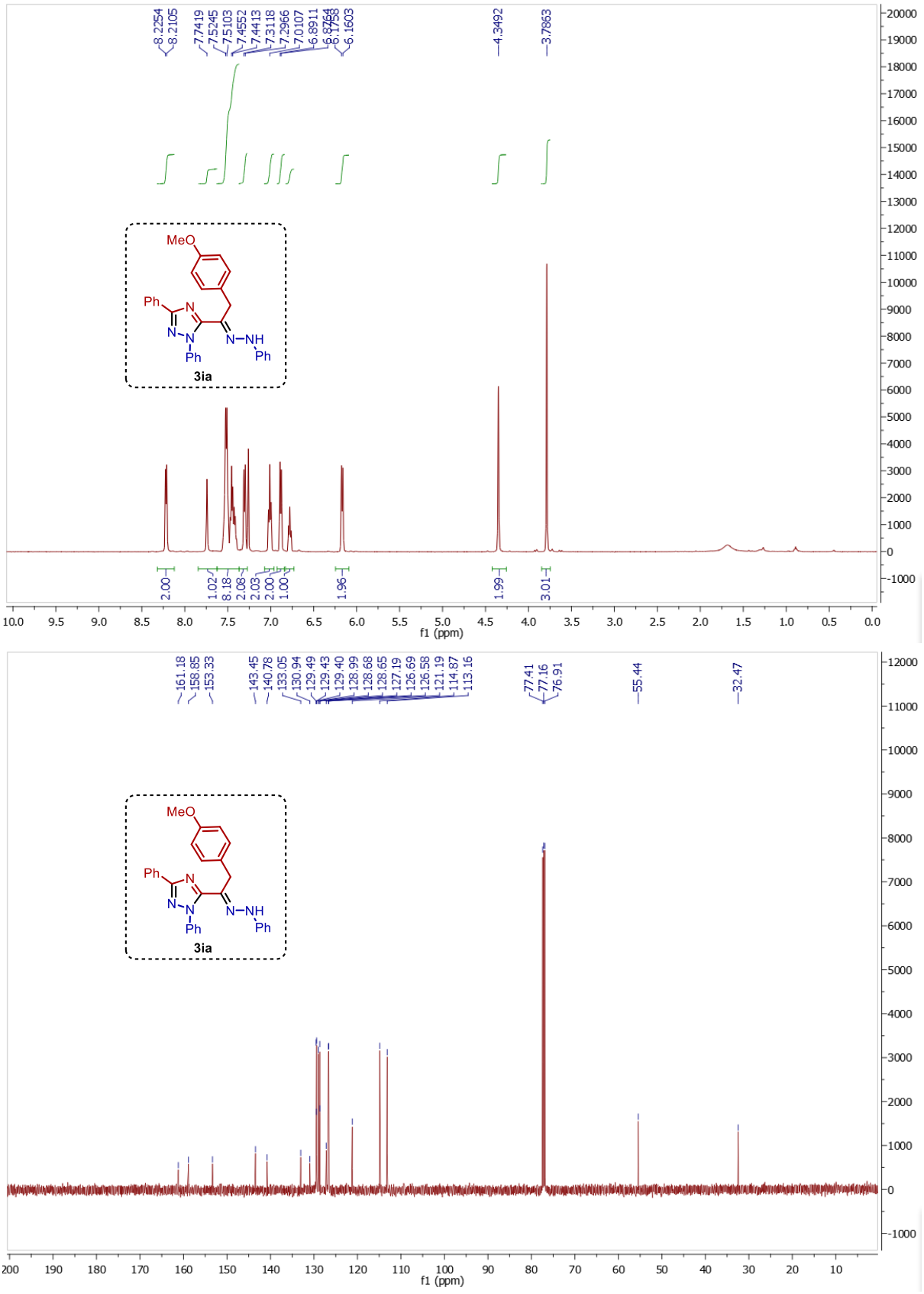


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ga**

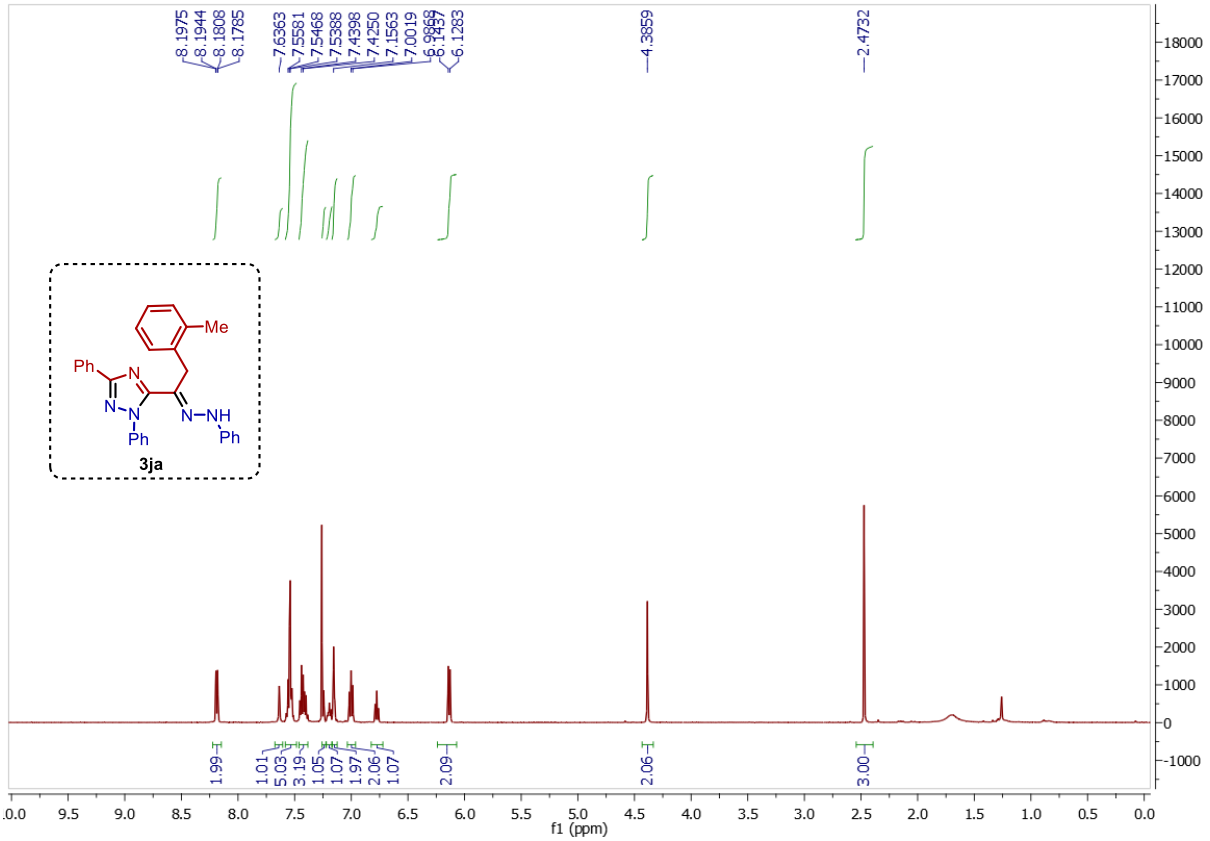


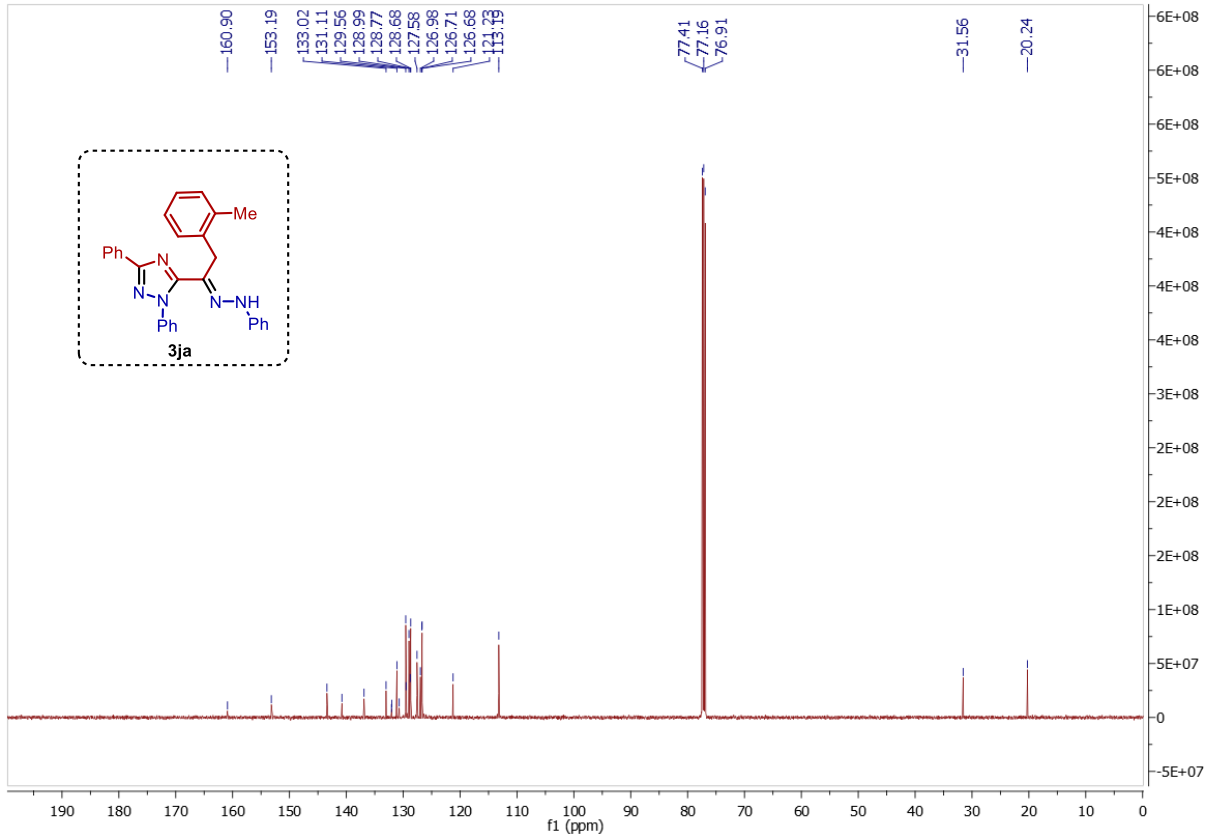


$CDCl_3$, 500 MHz ^{1}H NMR and 125 MHz $^{13}C\{^{1}H\}$ NMR Spectra of **3ha**

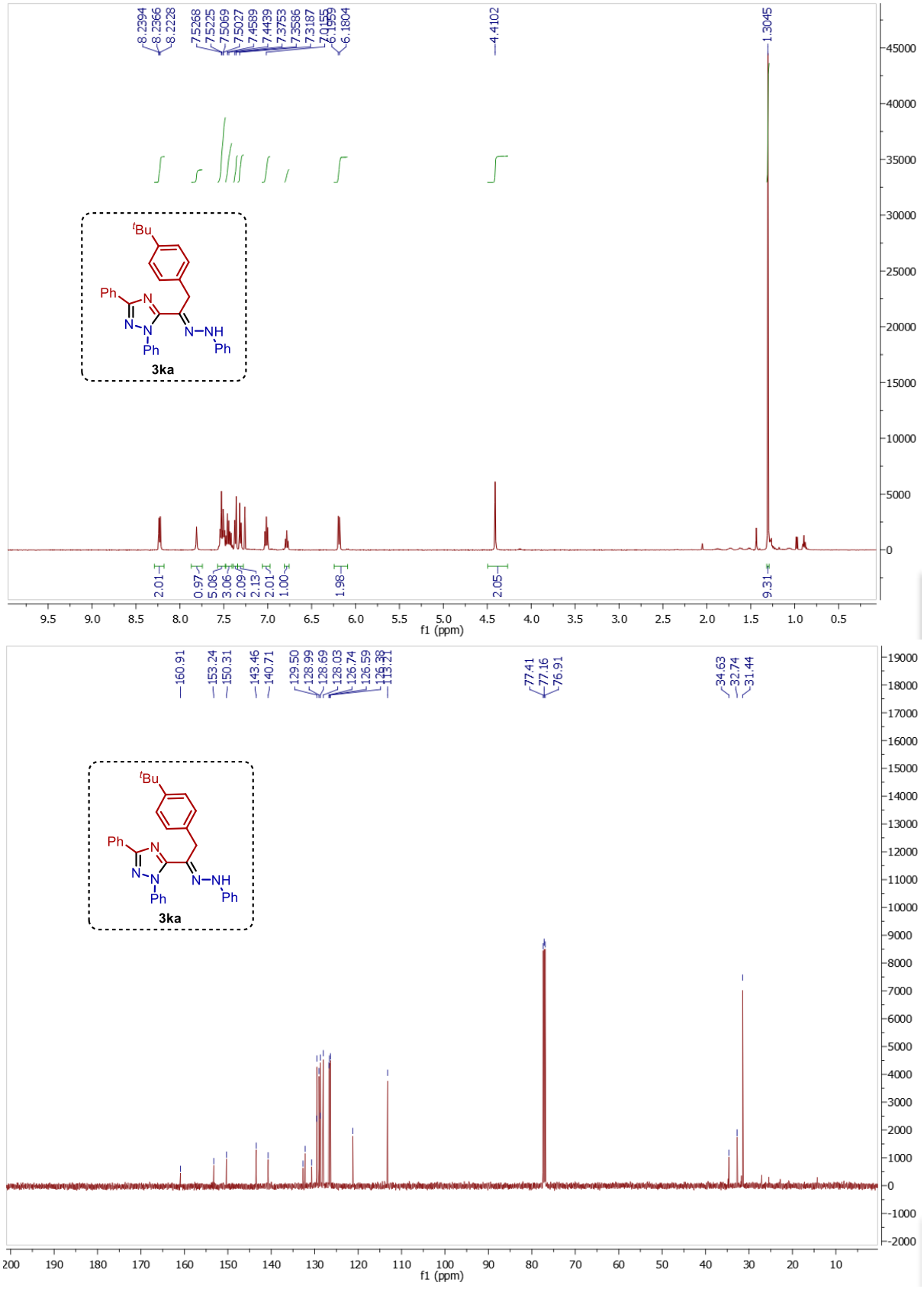


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ia**





$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ja**



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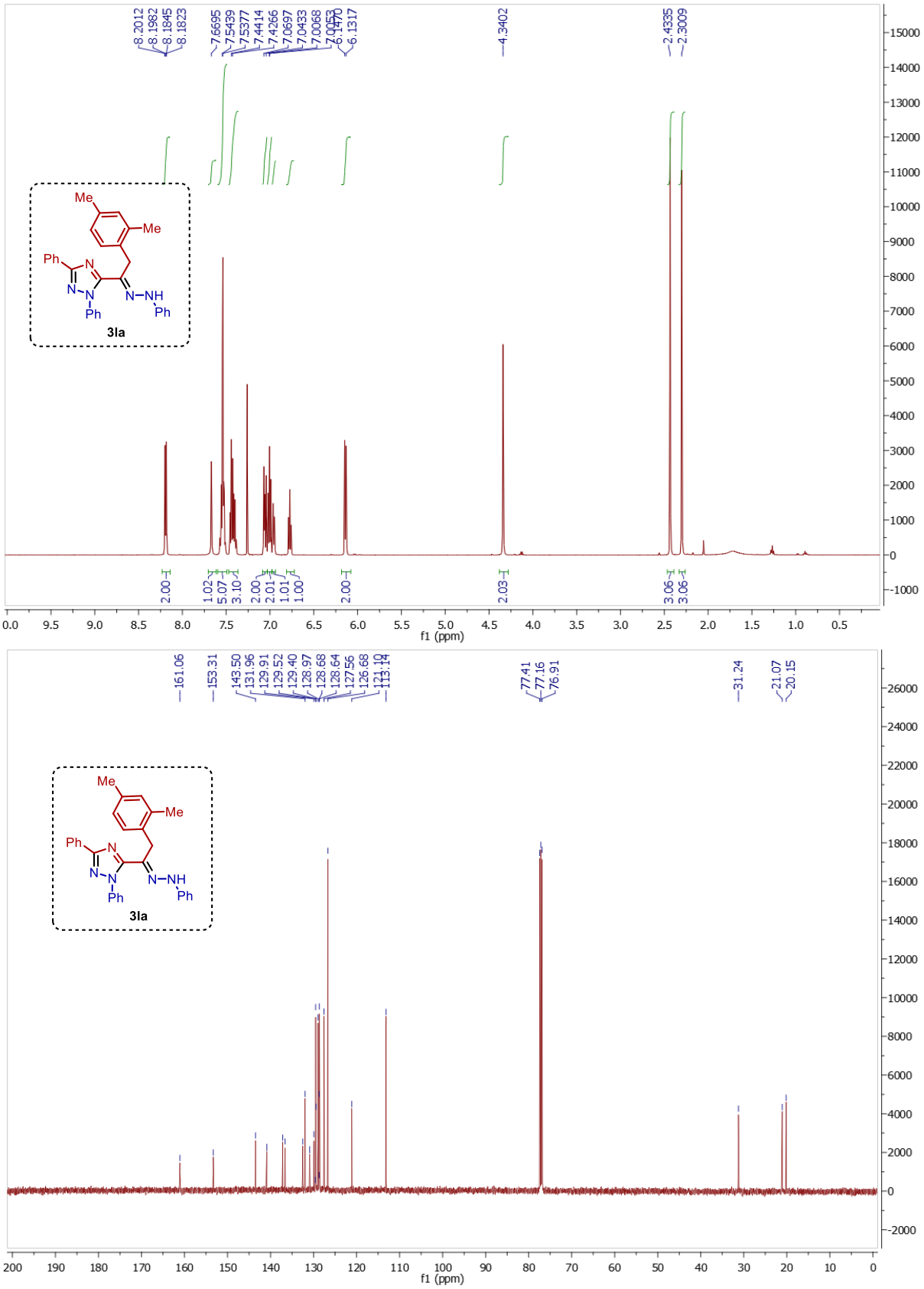
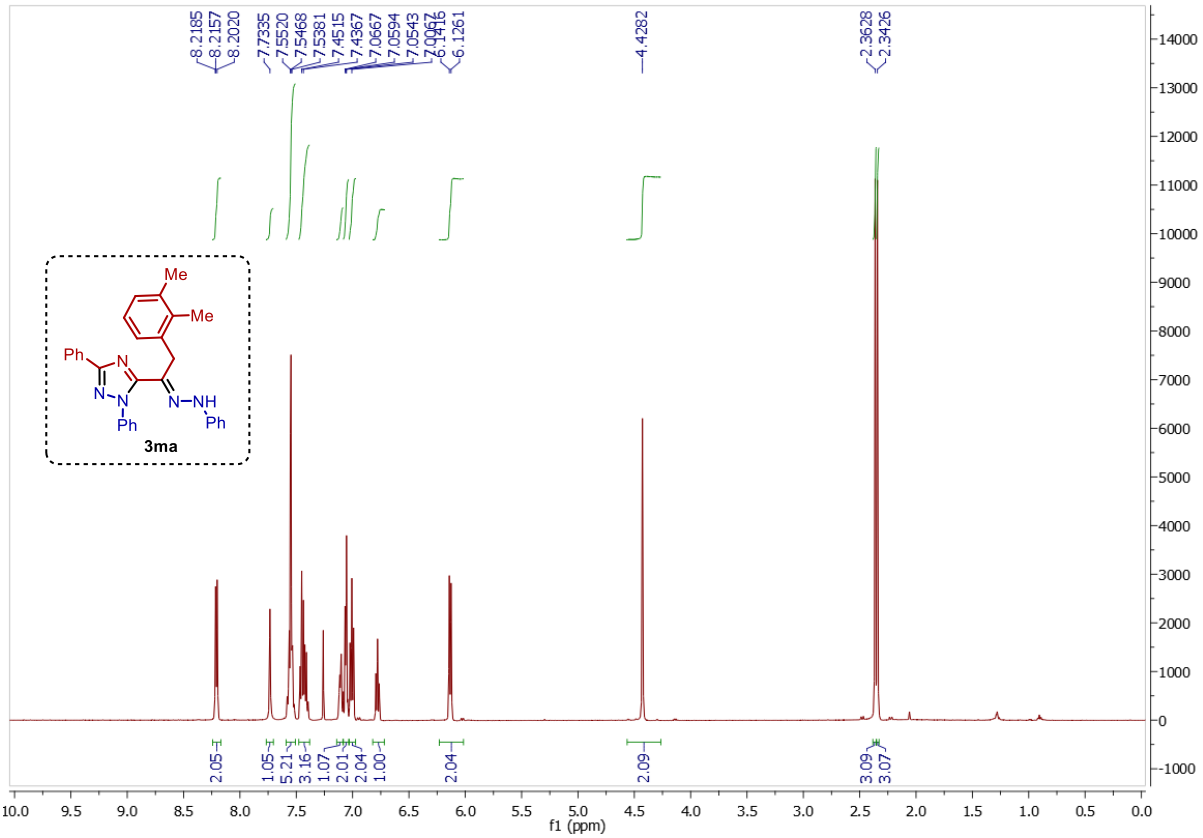
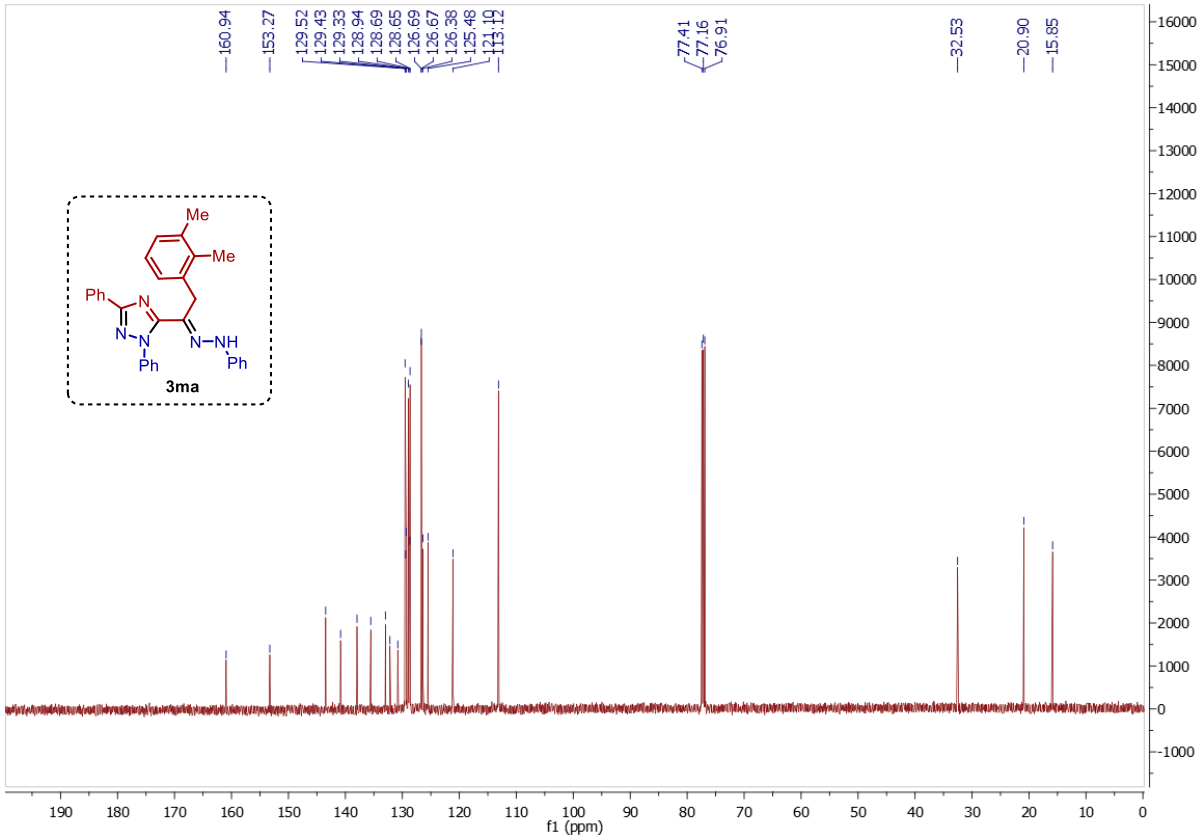
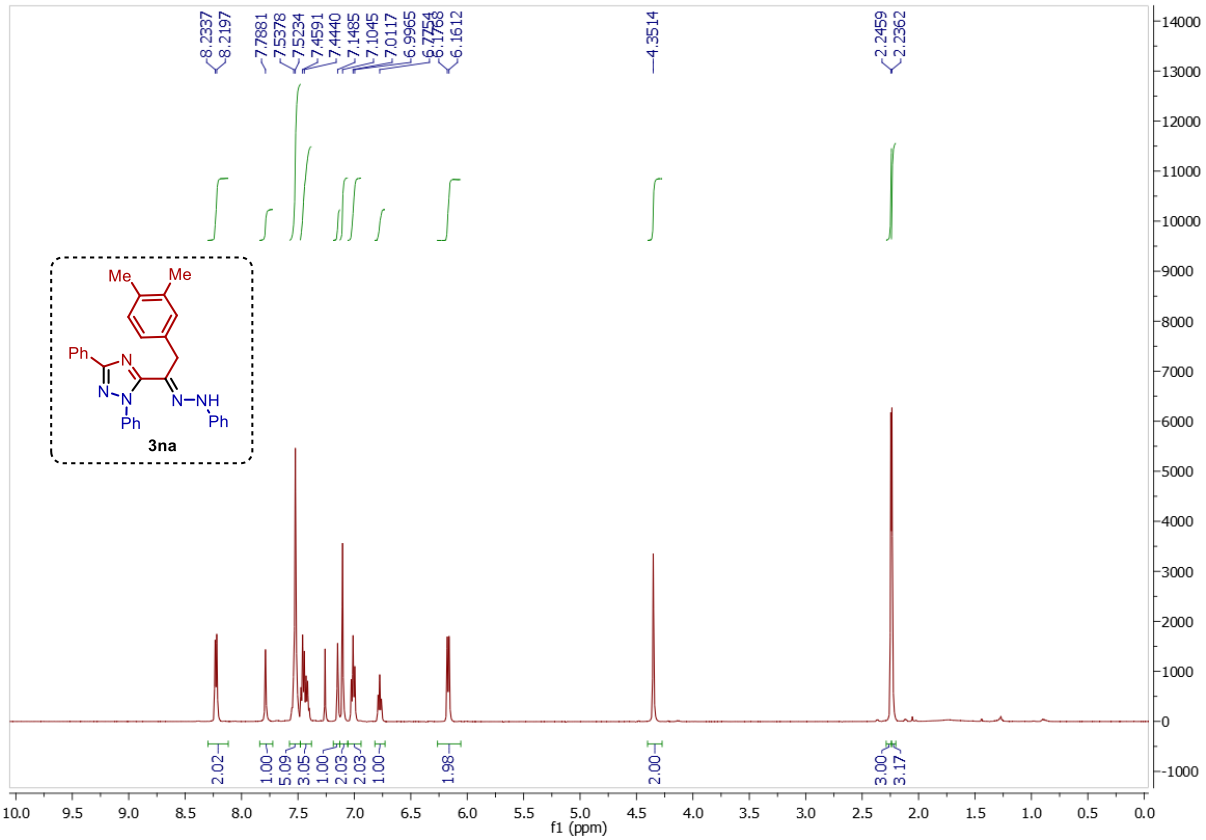


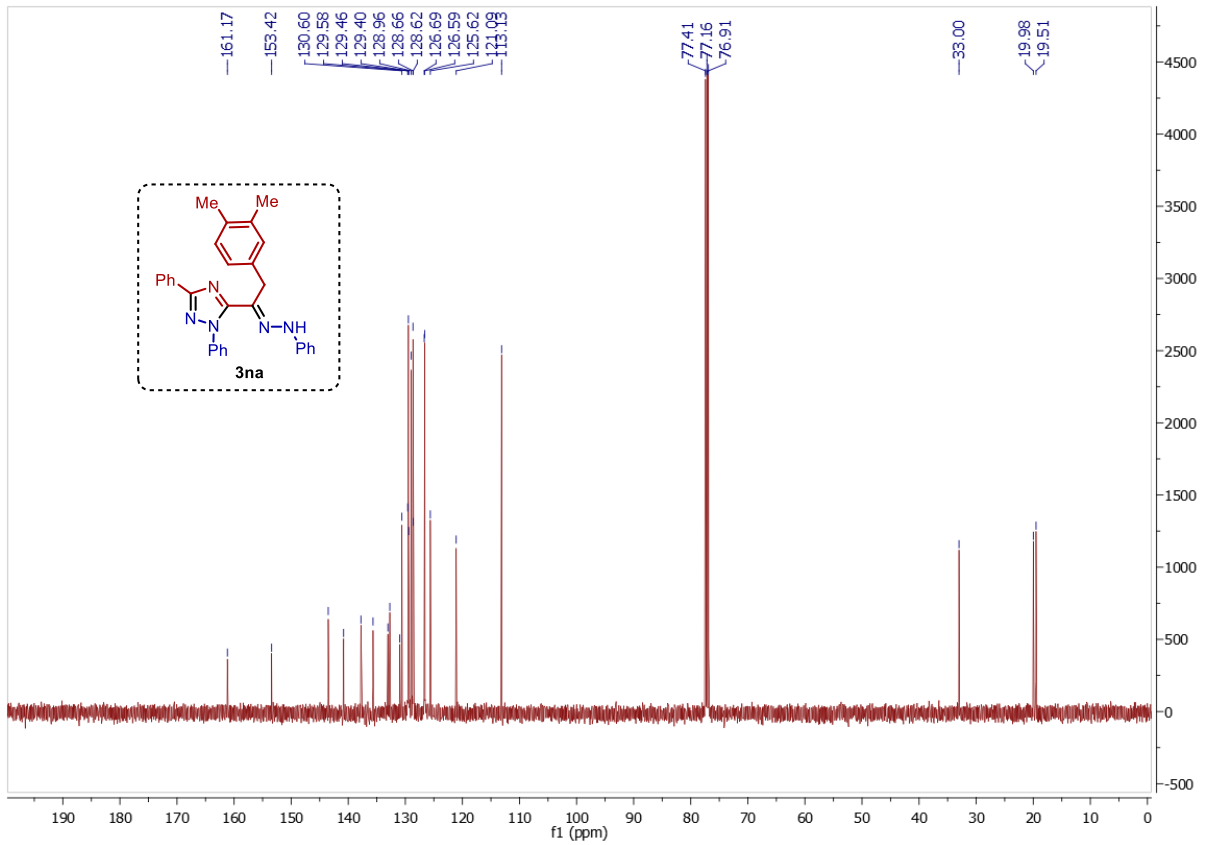
$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3la**



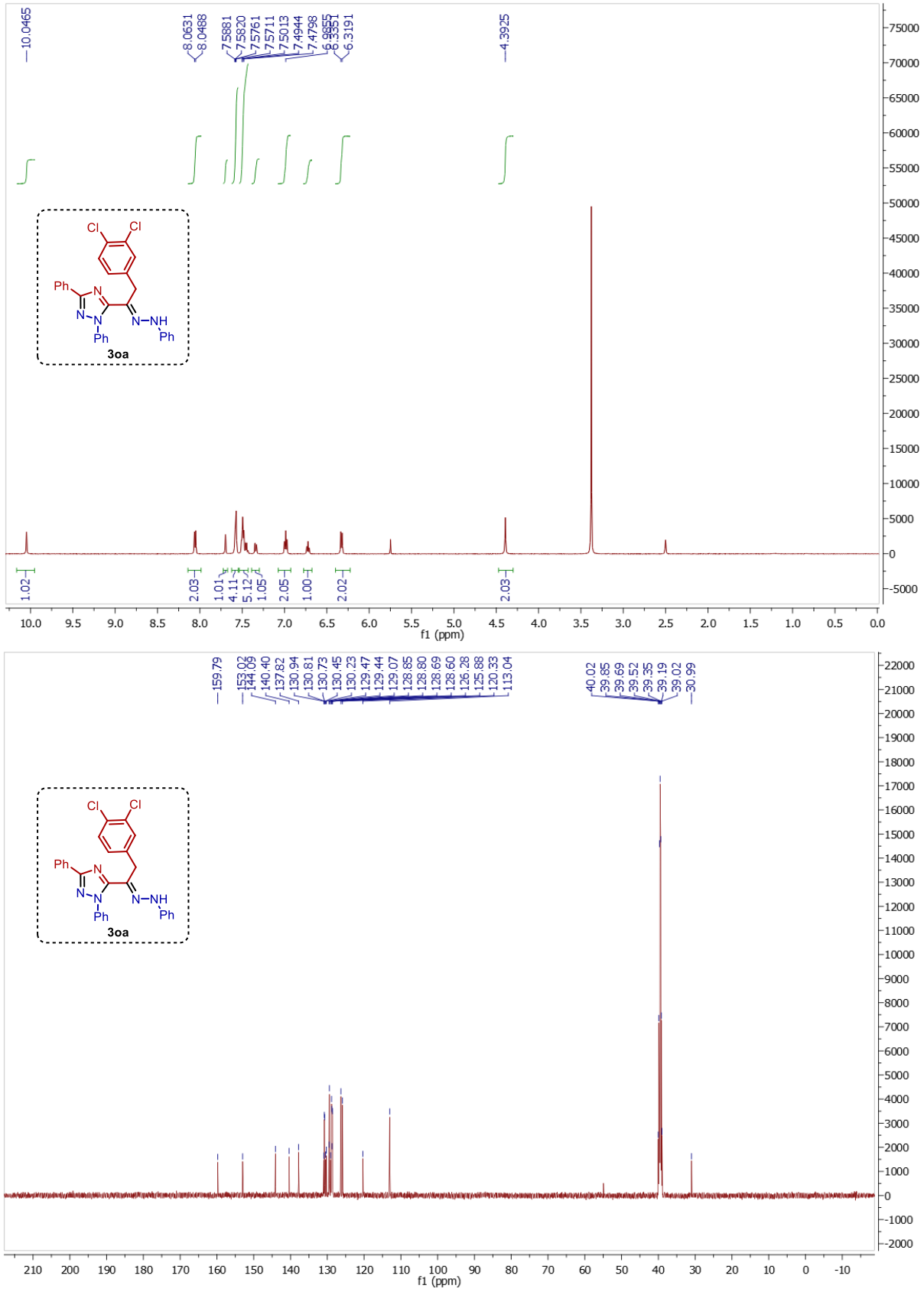


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ma**

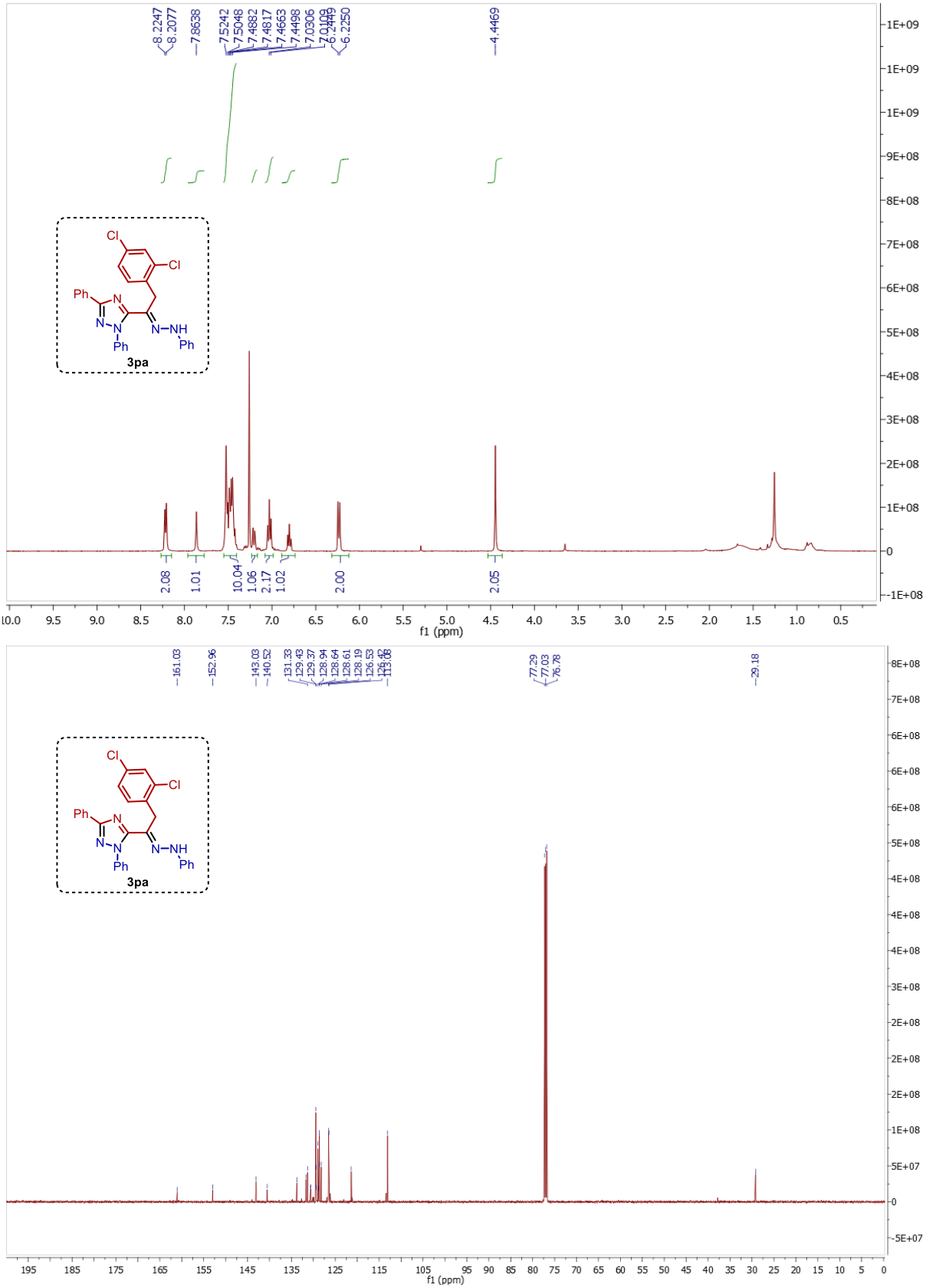




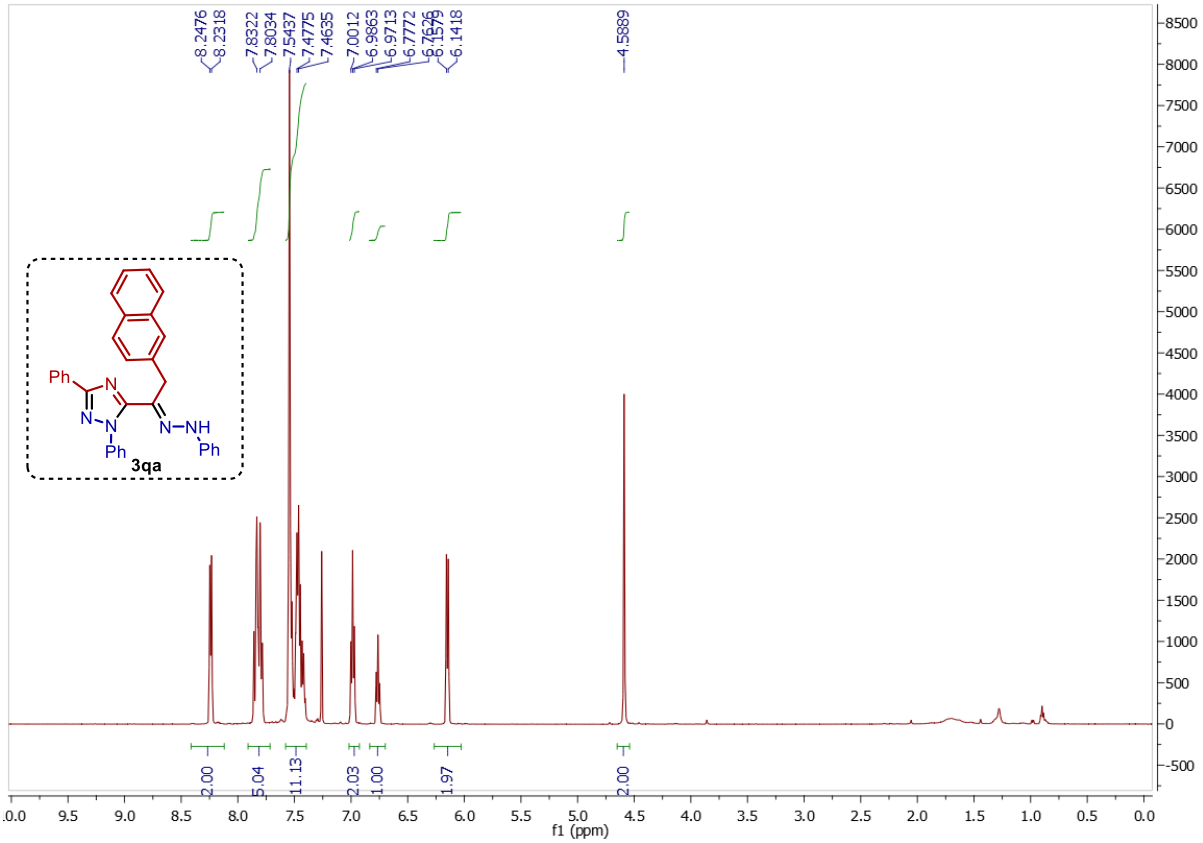
$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3na**

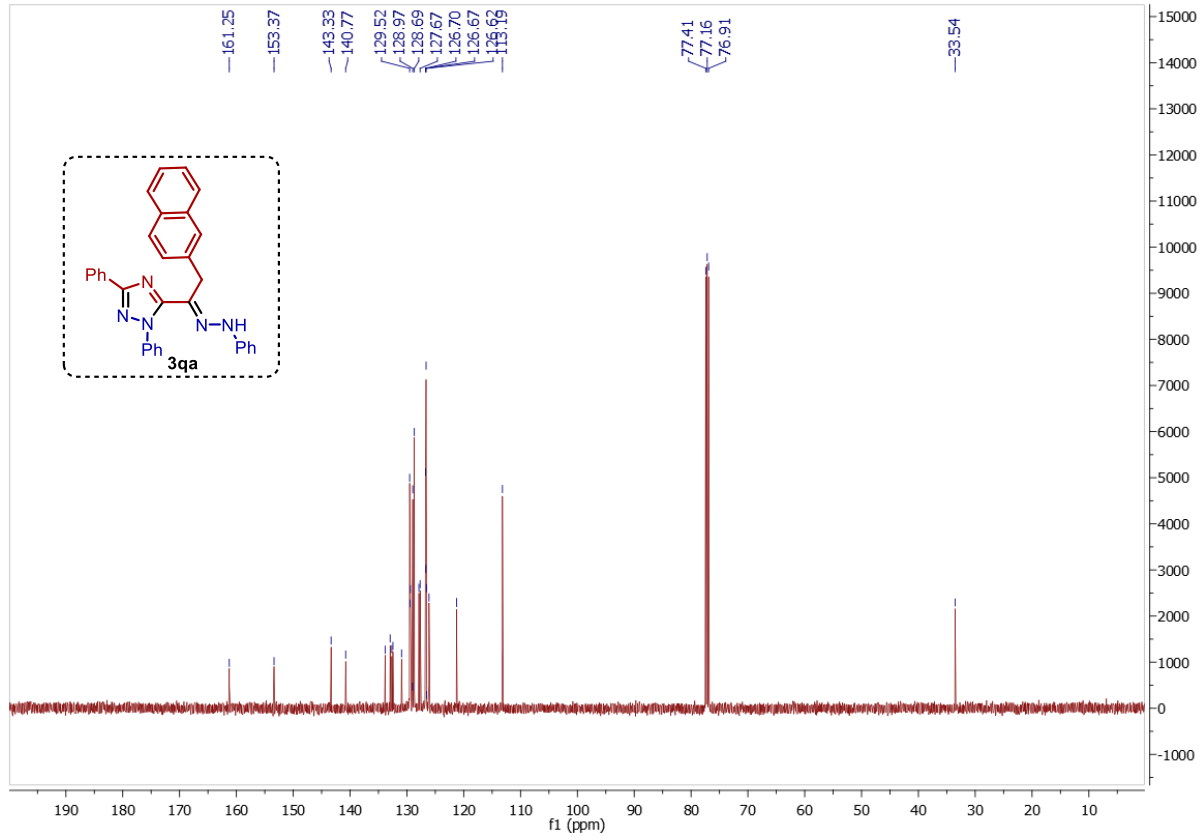


DMSO-d_6, 500 MHz ^{1}H NMR and 125 MHz ^{13}C{^{1}H} NMR Spectra of **3oa**

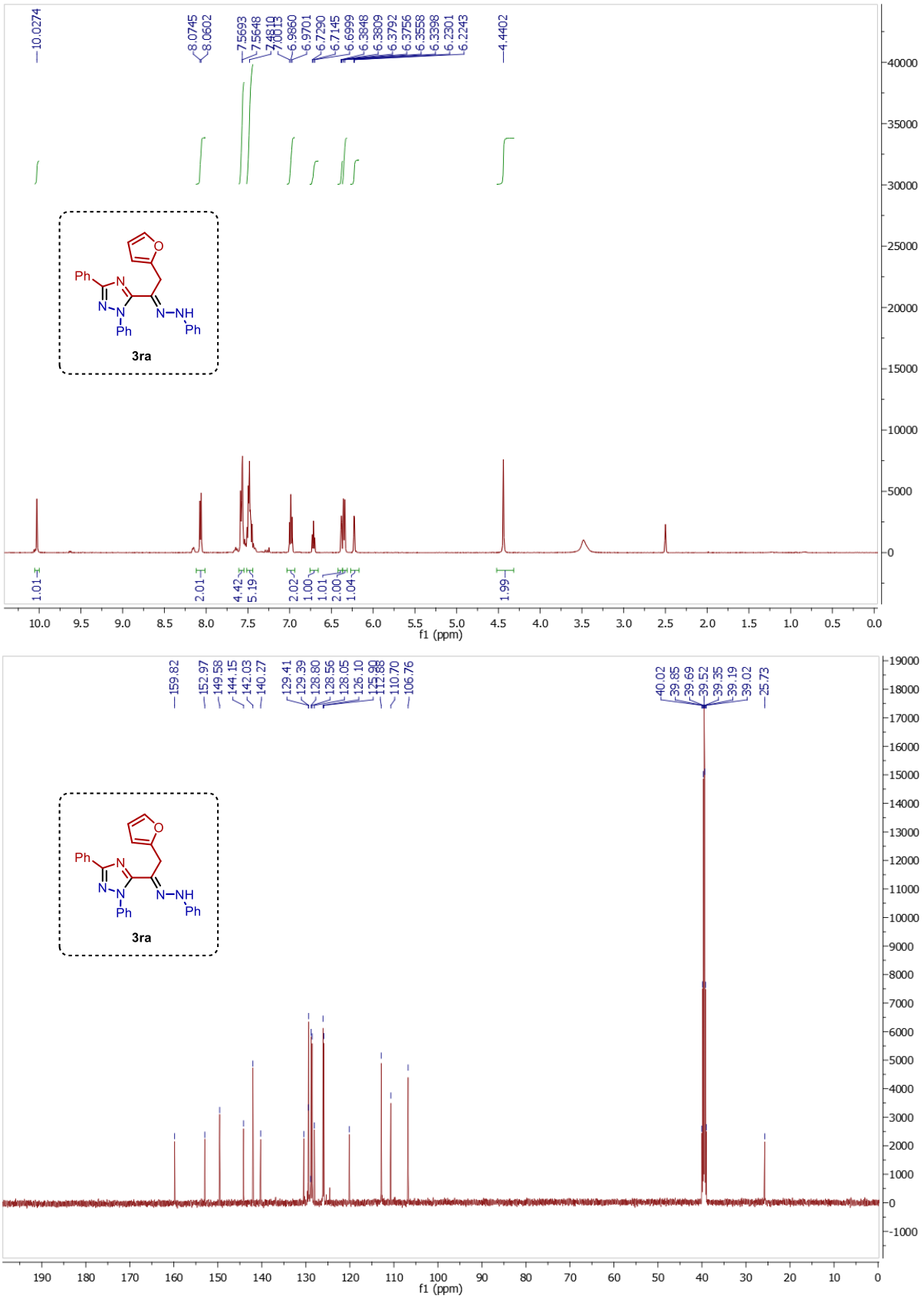


$CDCl_3$, 400 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3pa**

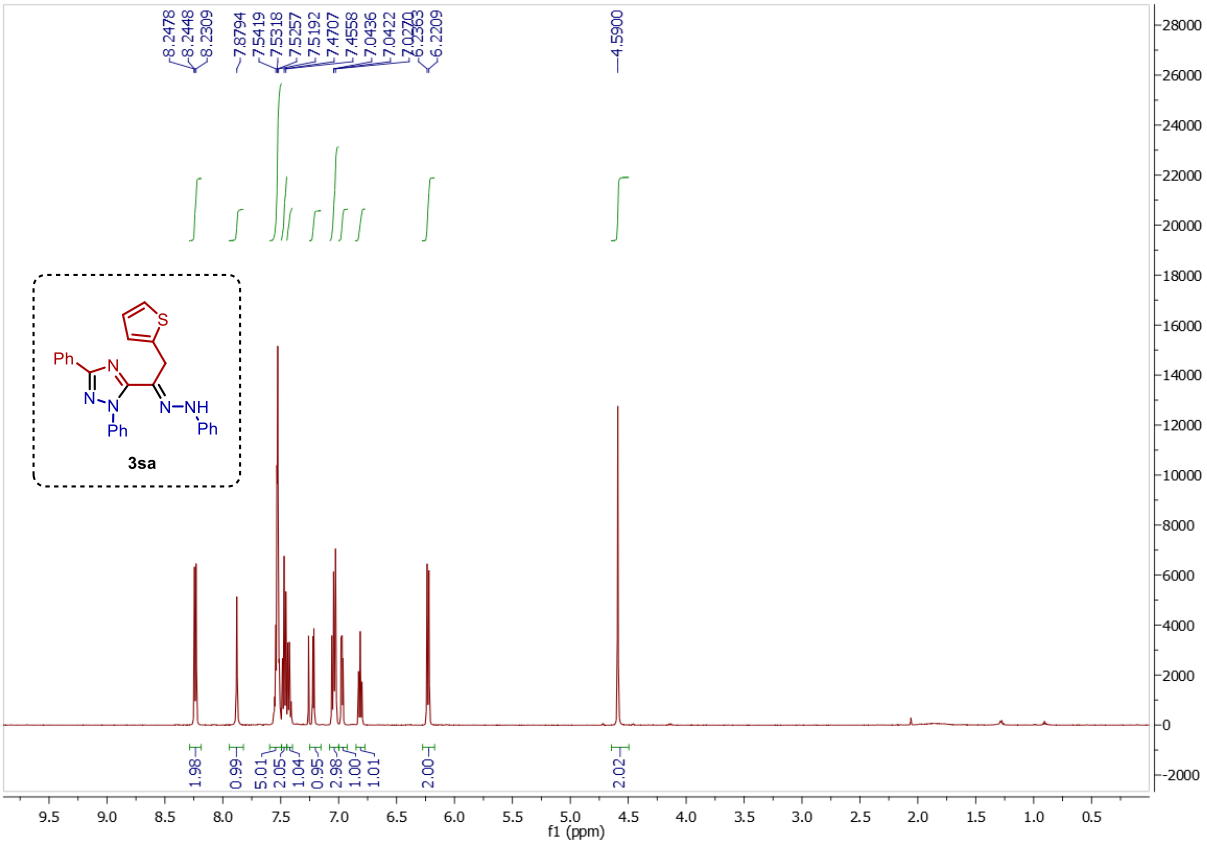


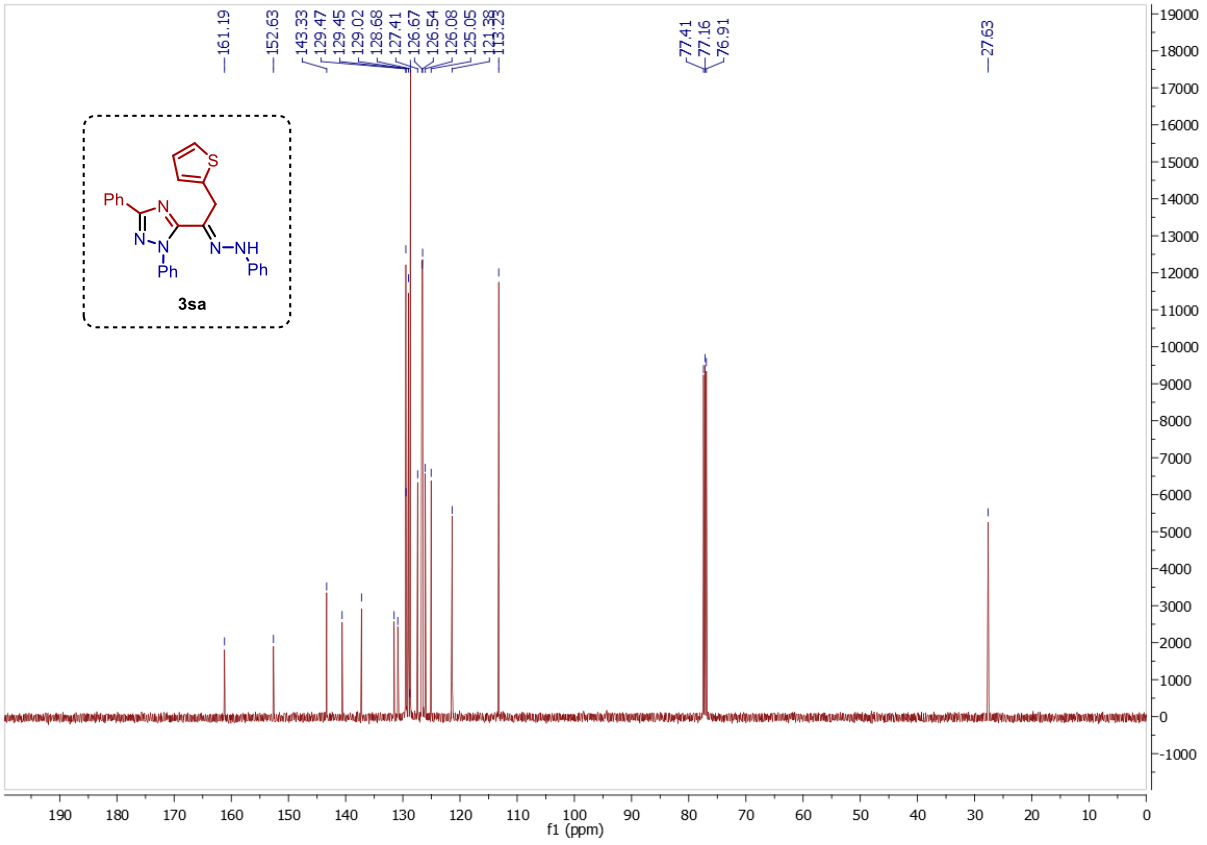


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3qa**

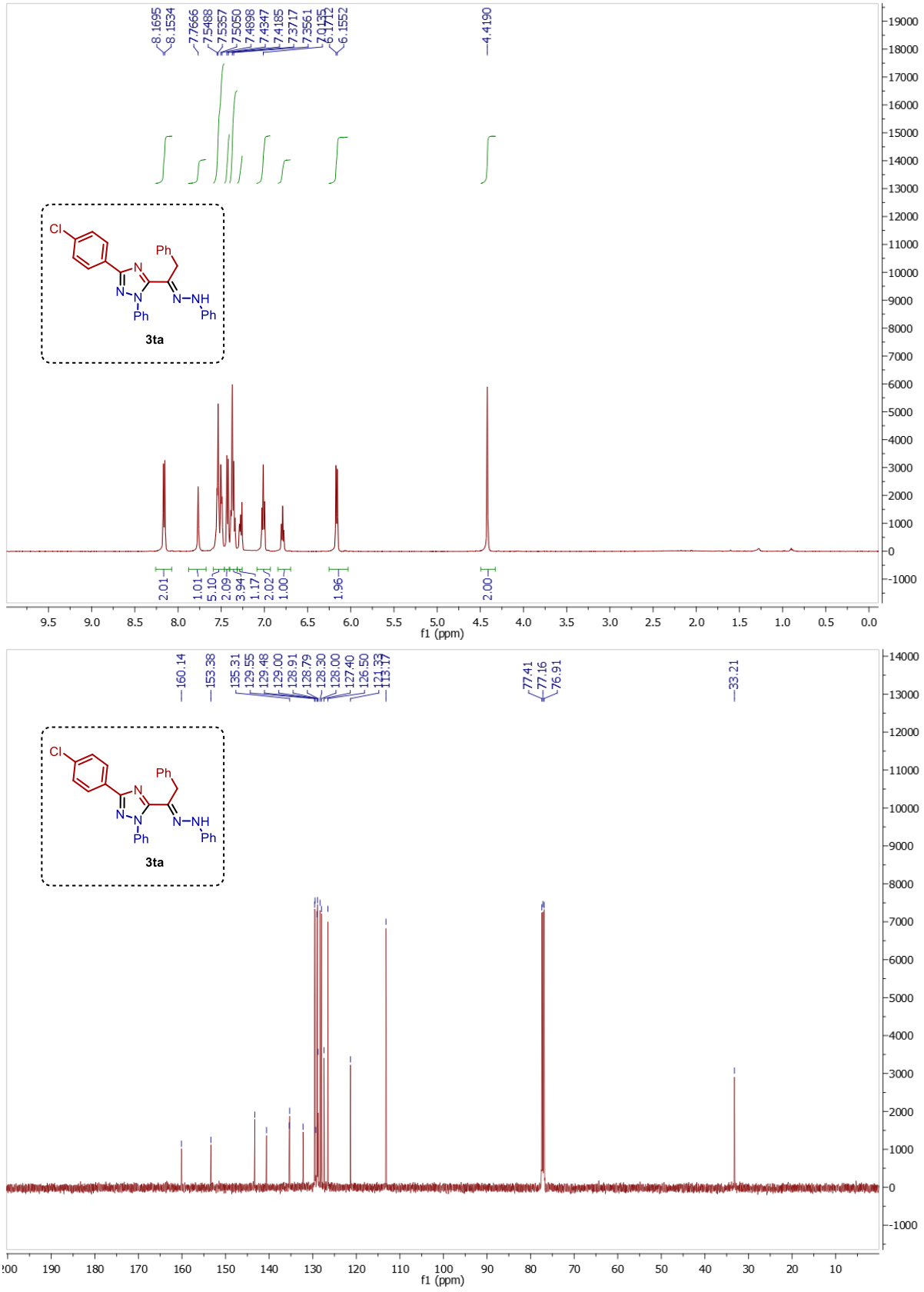


DMSO-d_6, 500 MHz ^{1}H NMR and 125 MHz ^{13}C{^{1}H} NMR Spectra of **3ra**

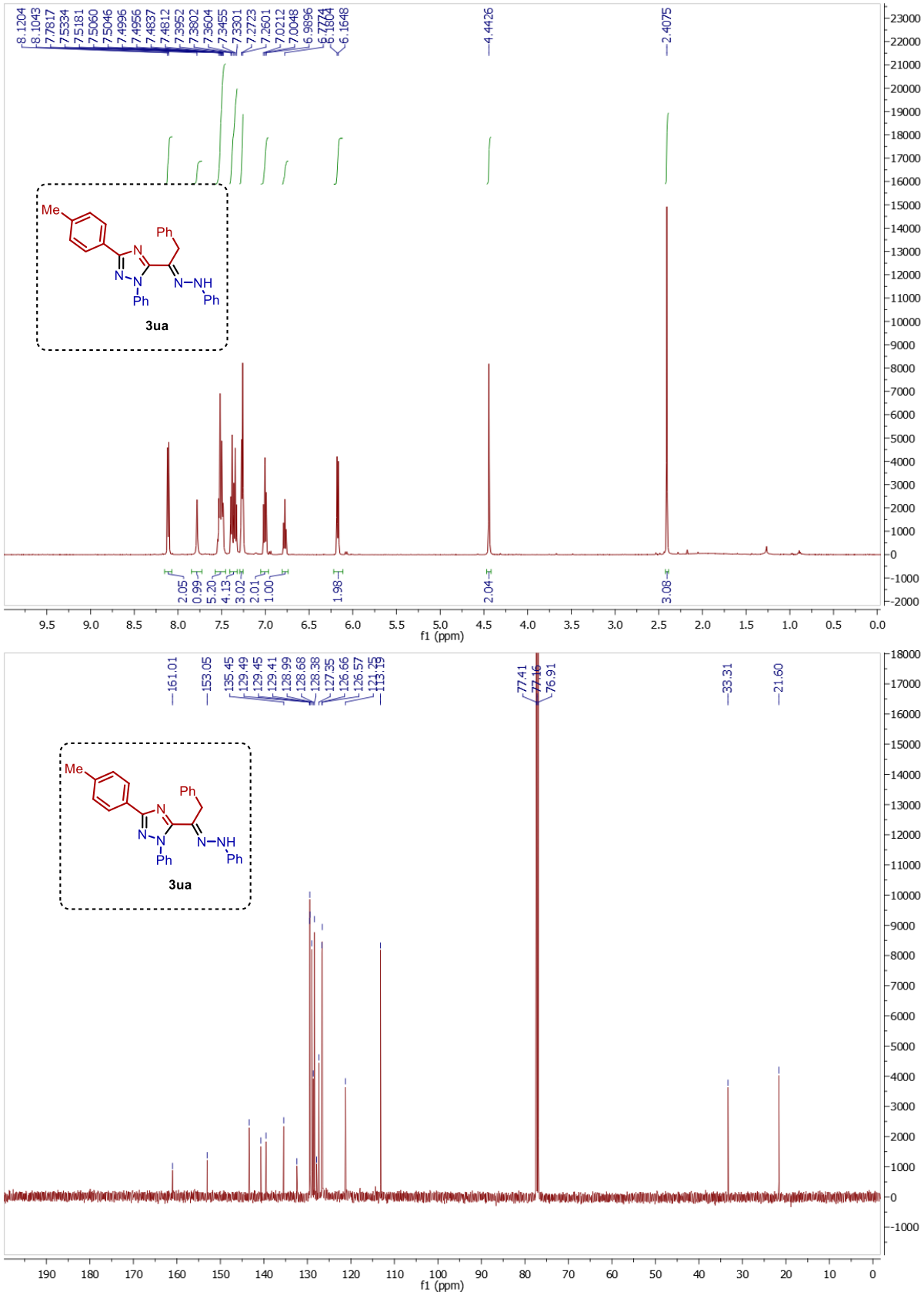




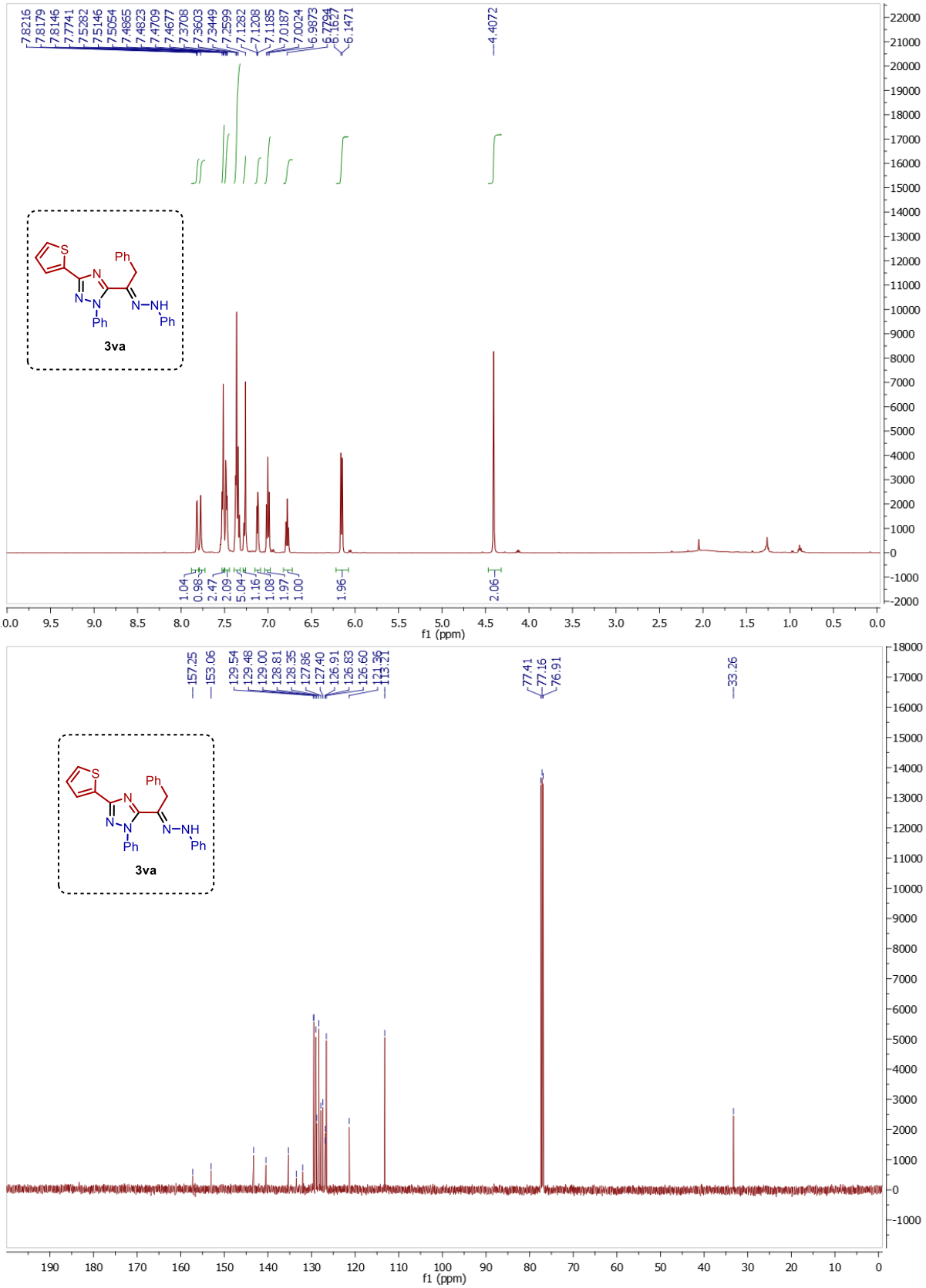
$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3sa**



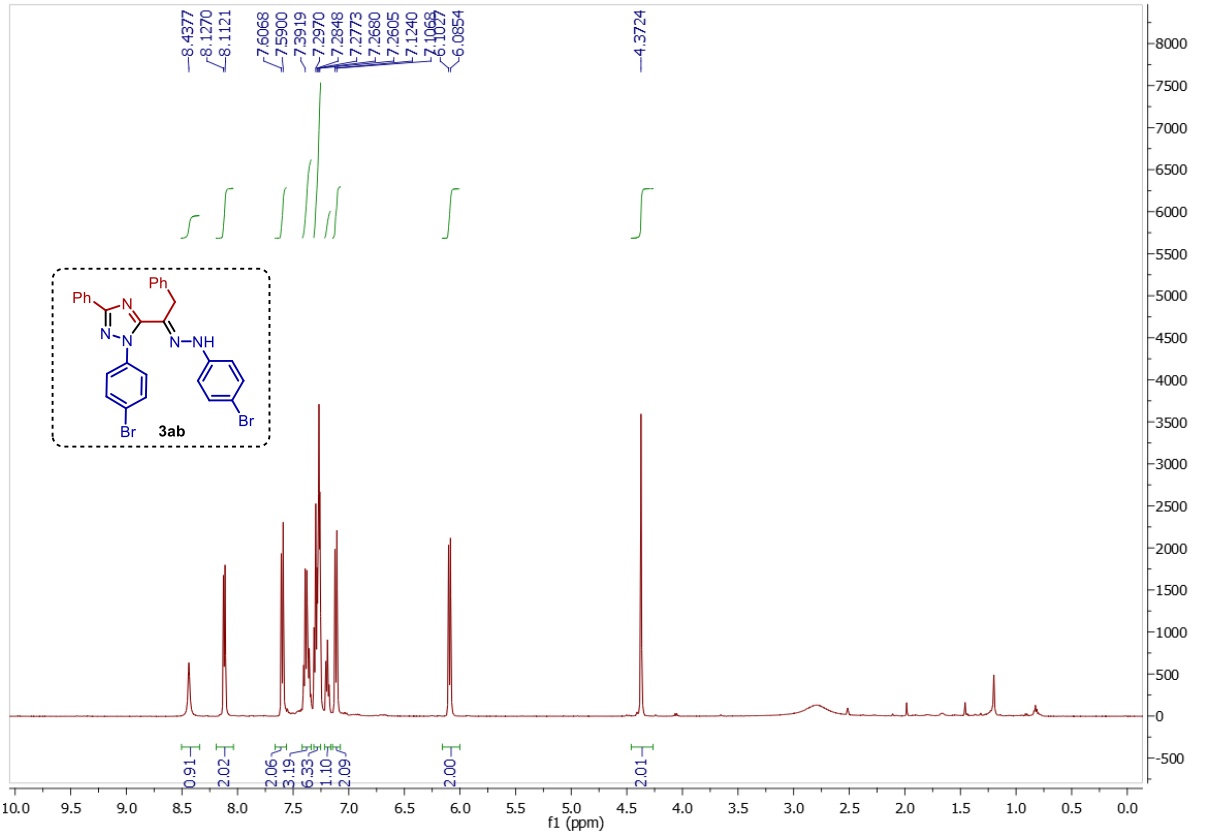
$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ta**

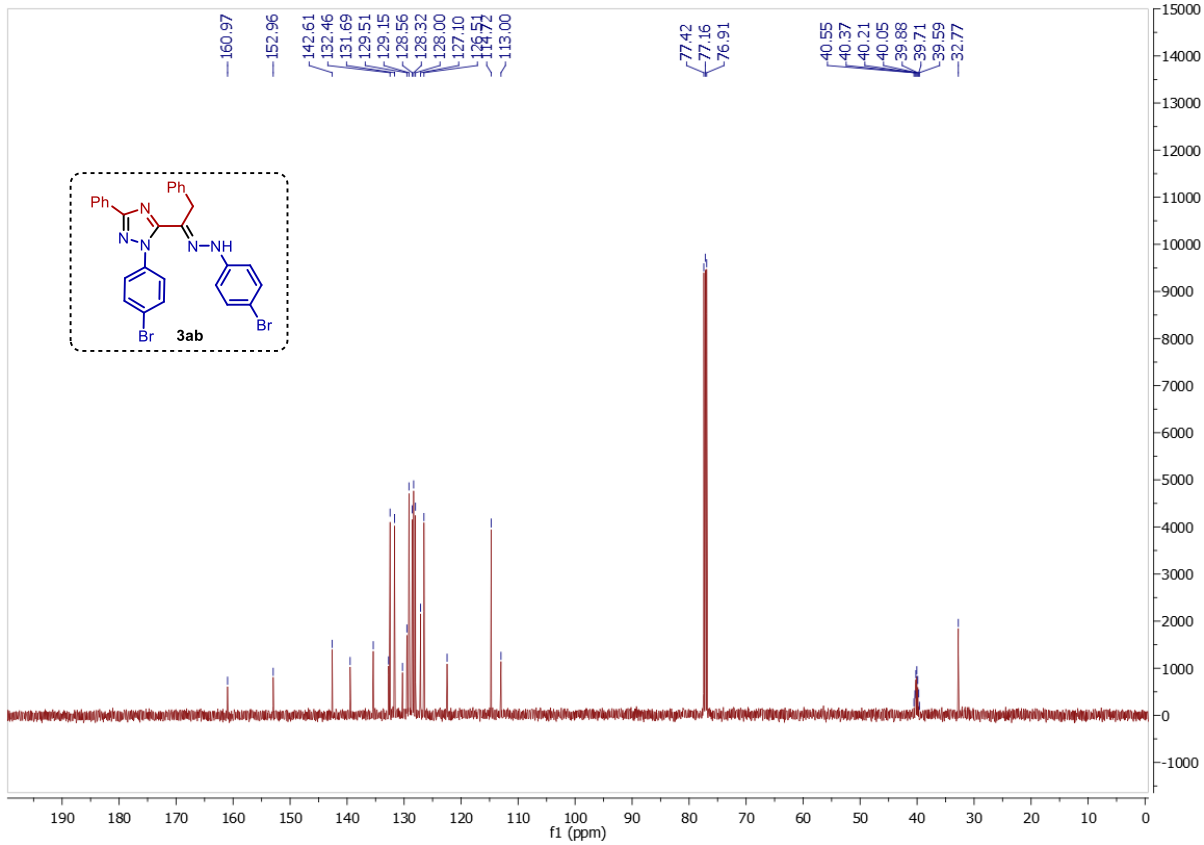


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ua**

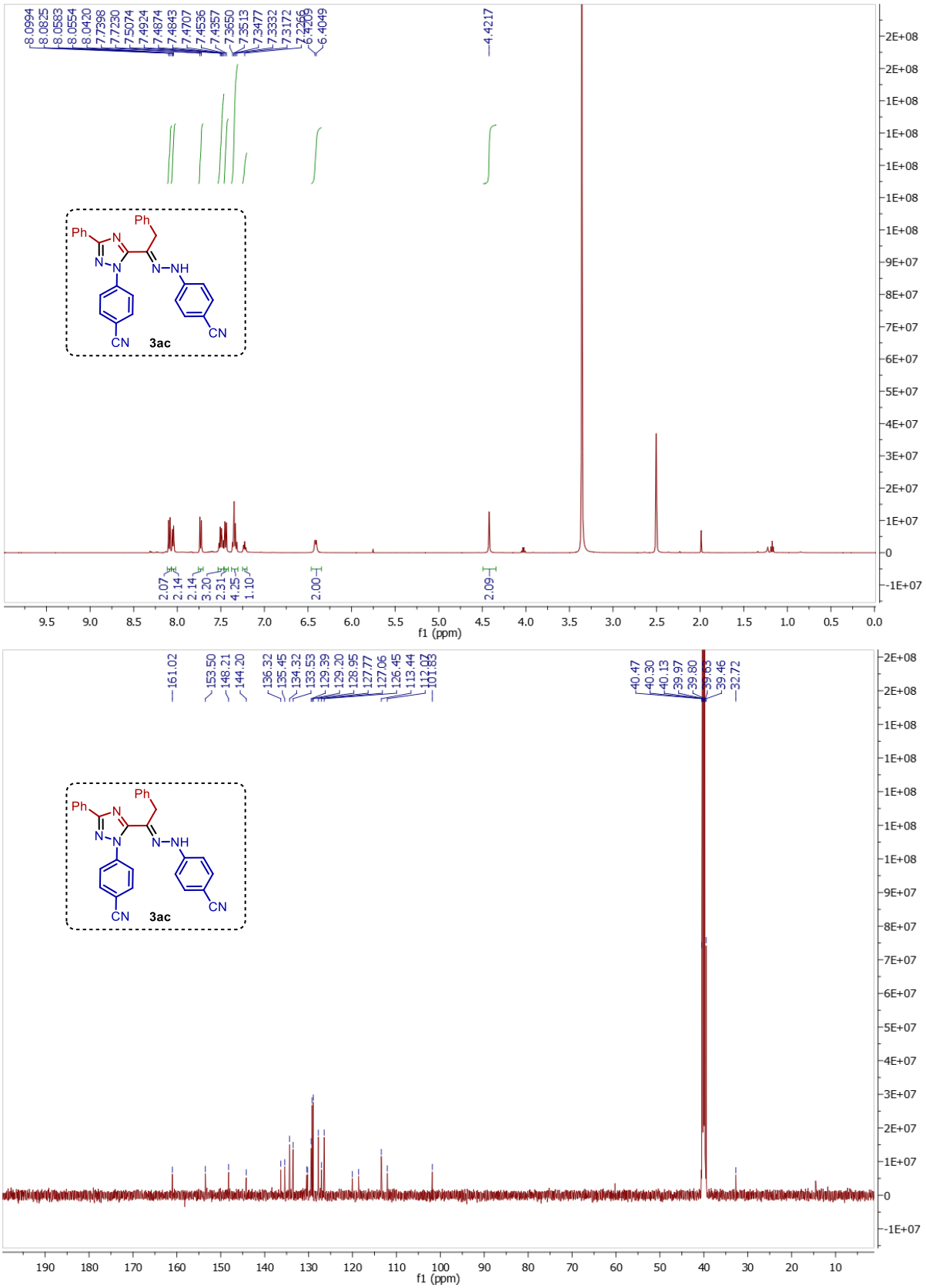


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3va**

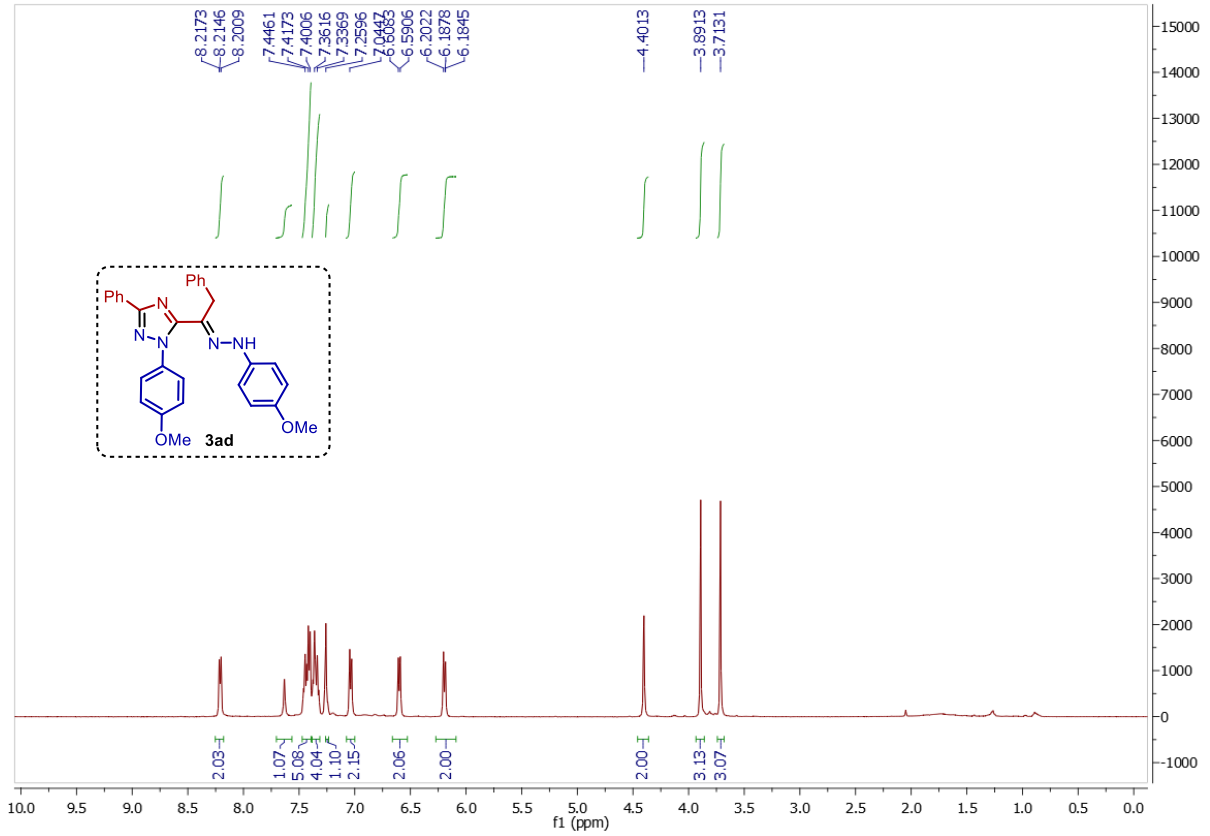


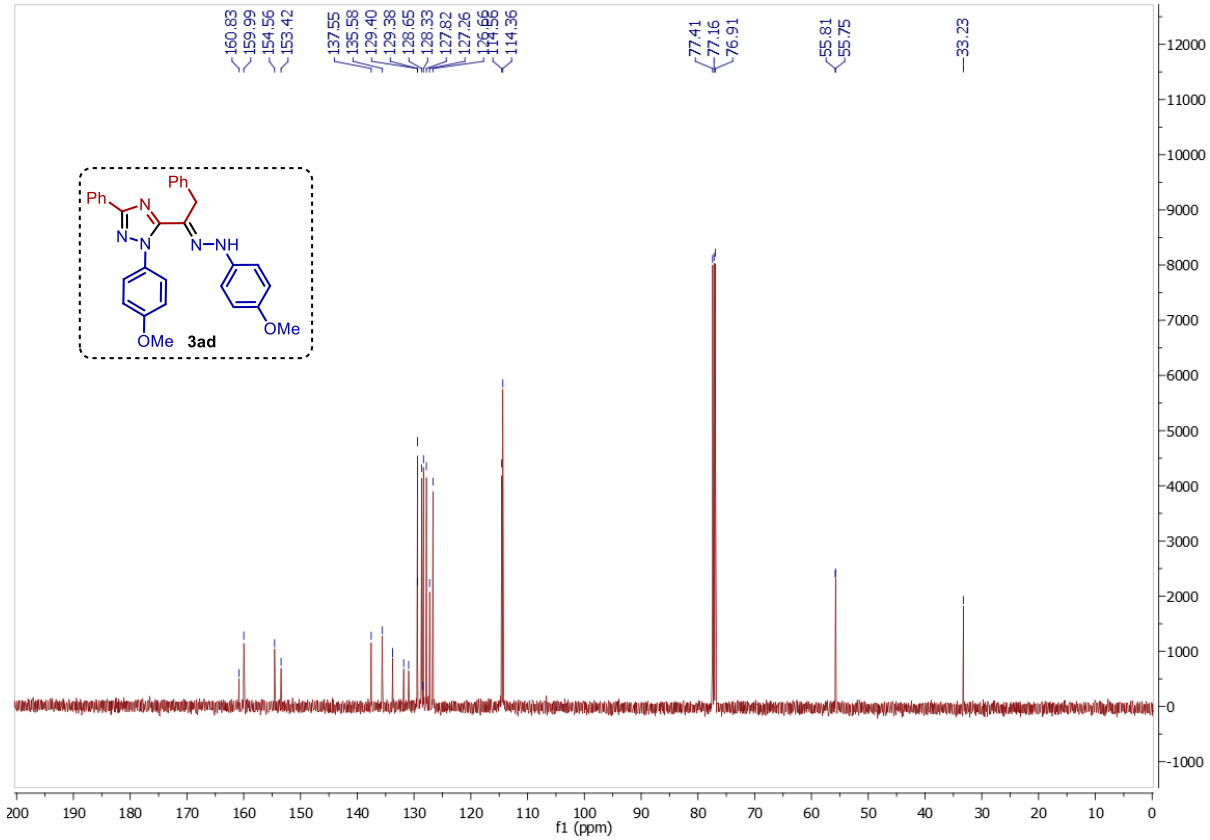


$CDCl_3$: DMSO-d_6 (1:0.02), 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ab**

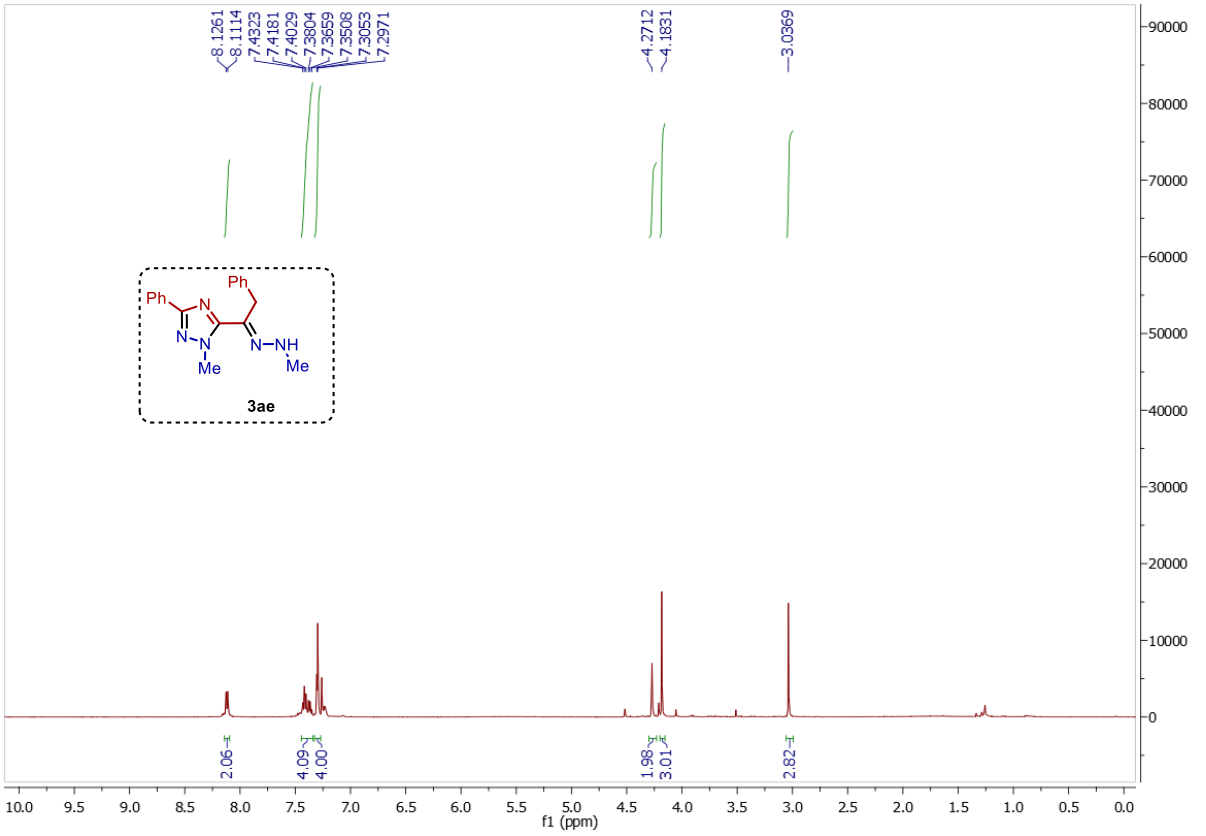


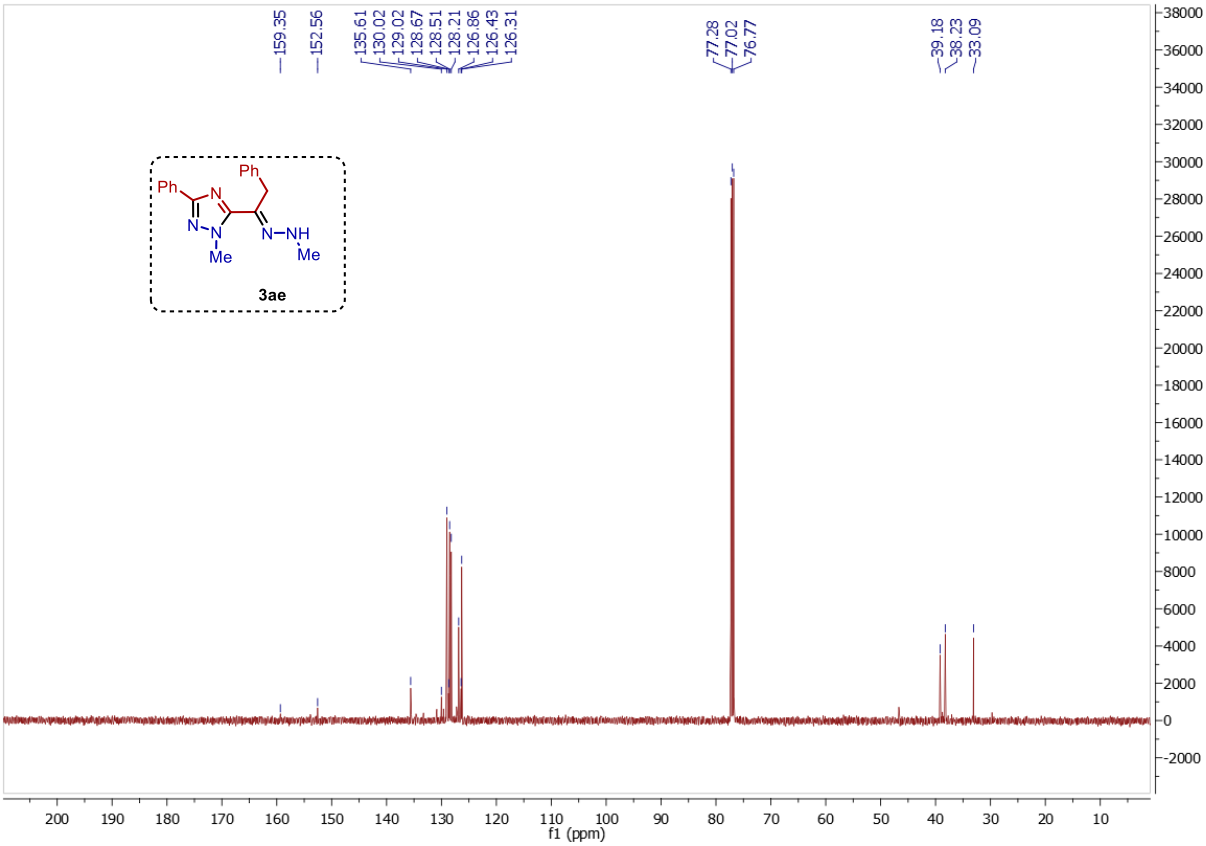
DMSO-d_6, 500 MHz ^{1}H NMR and 125 MHz ^{13}C{^{1}H} NMR Spectra of **3ac**



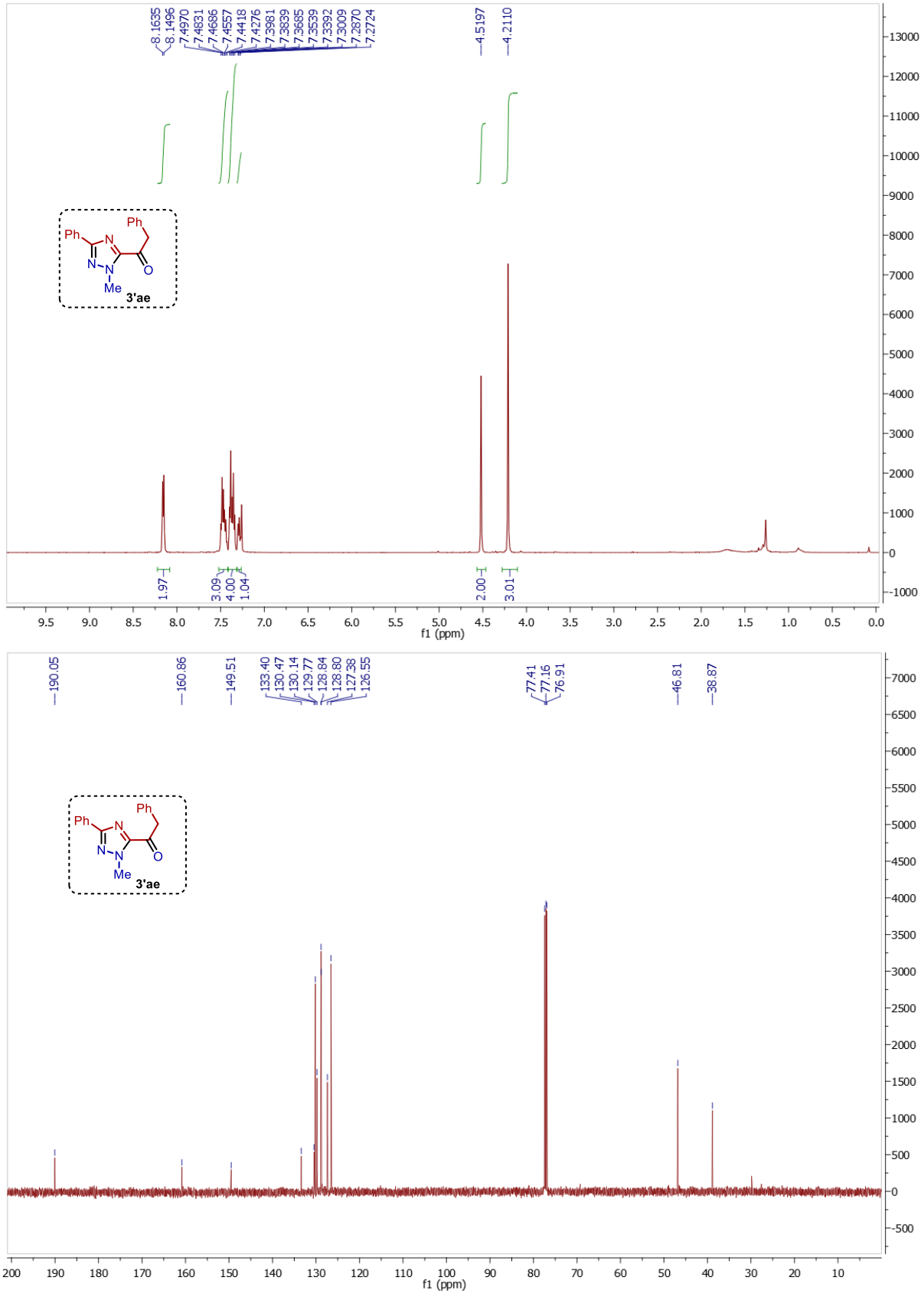


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ad**

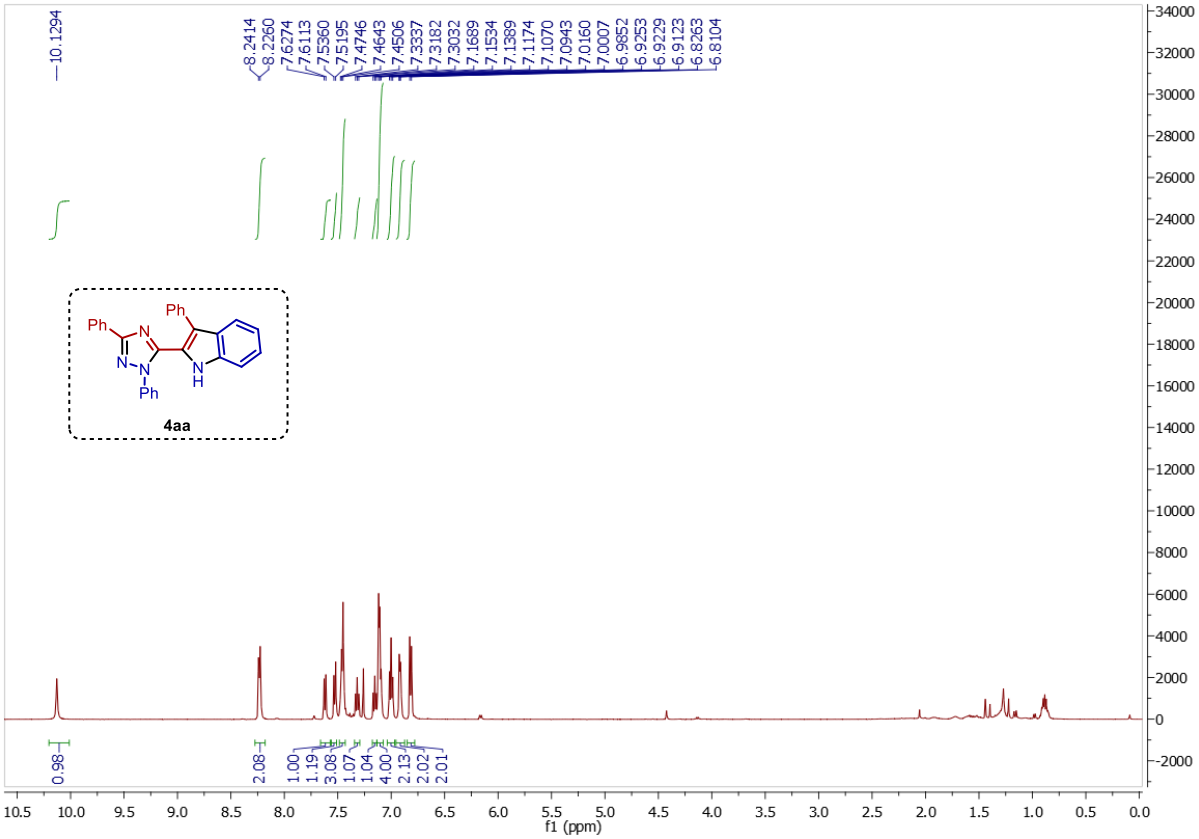


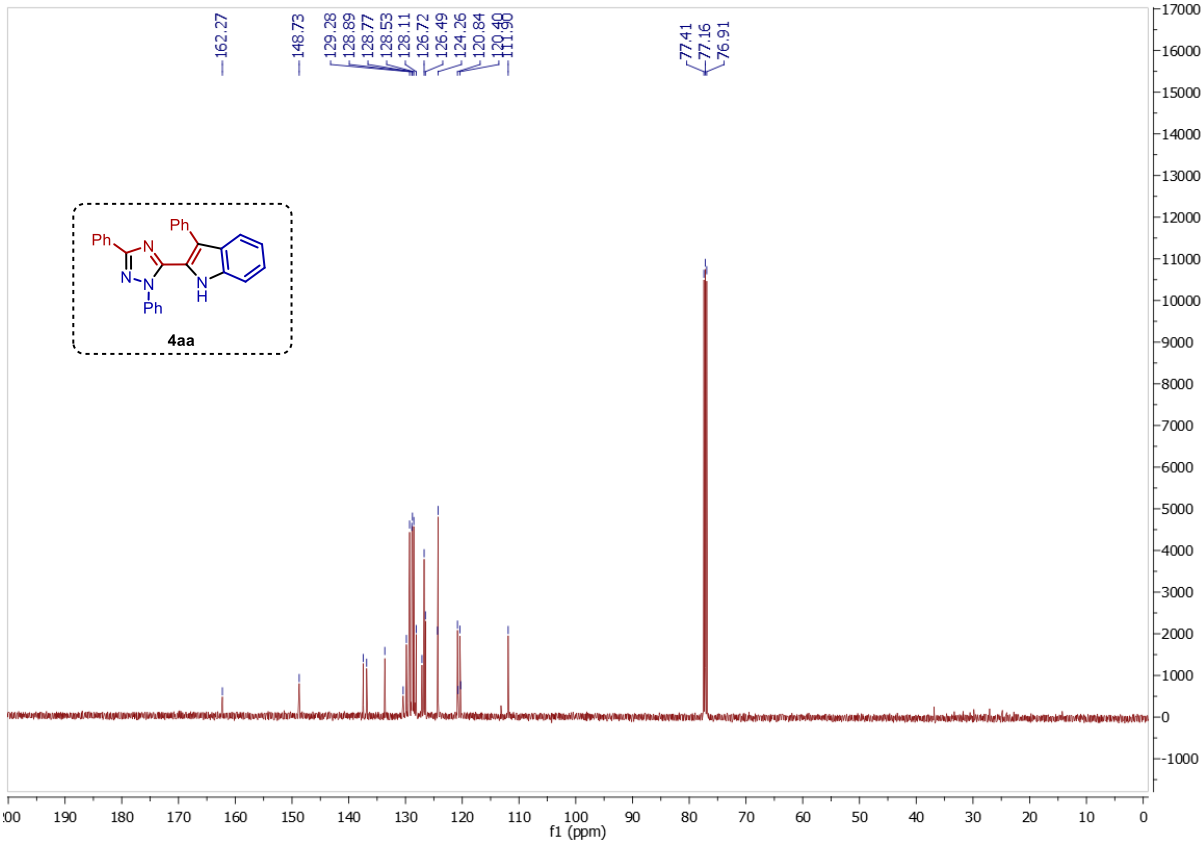


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3ae**

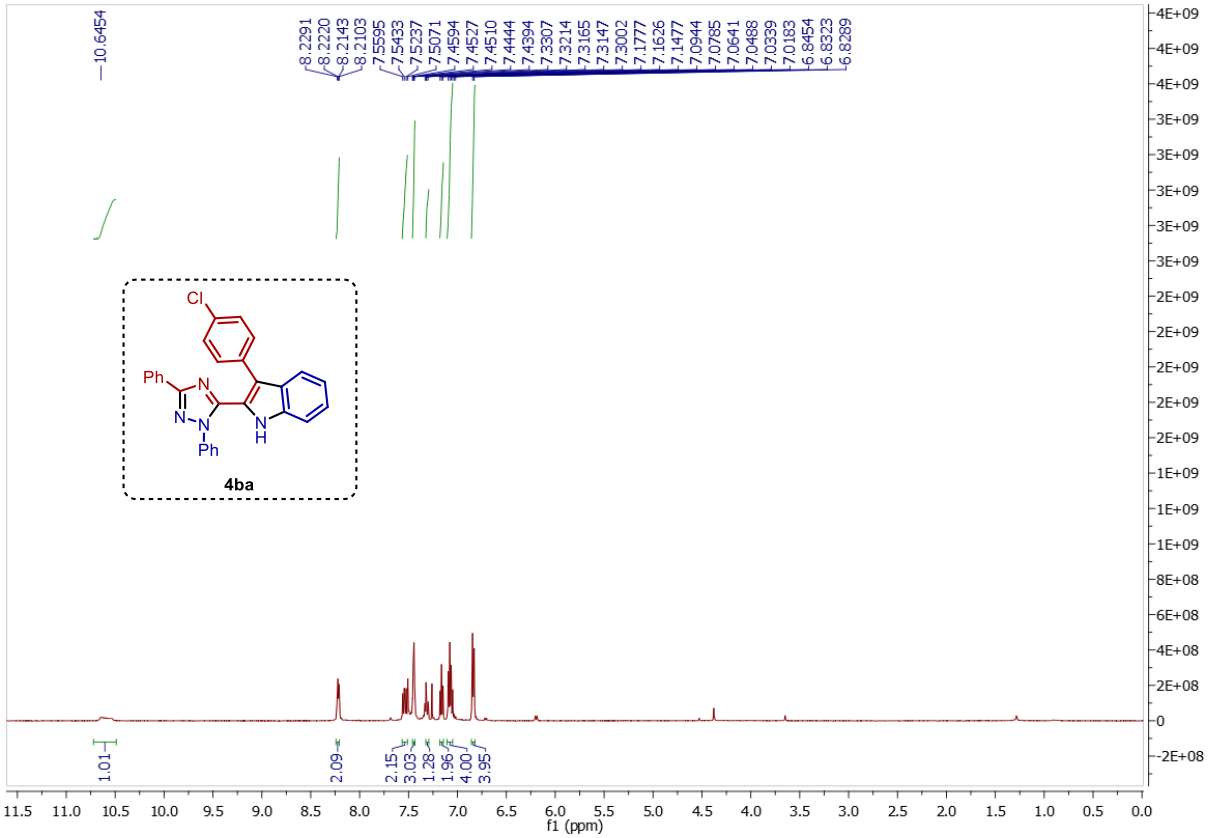


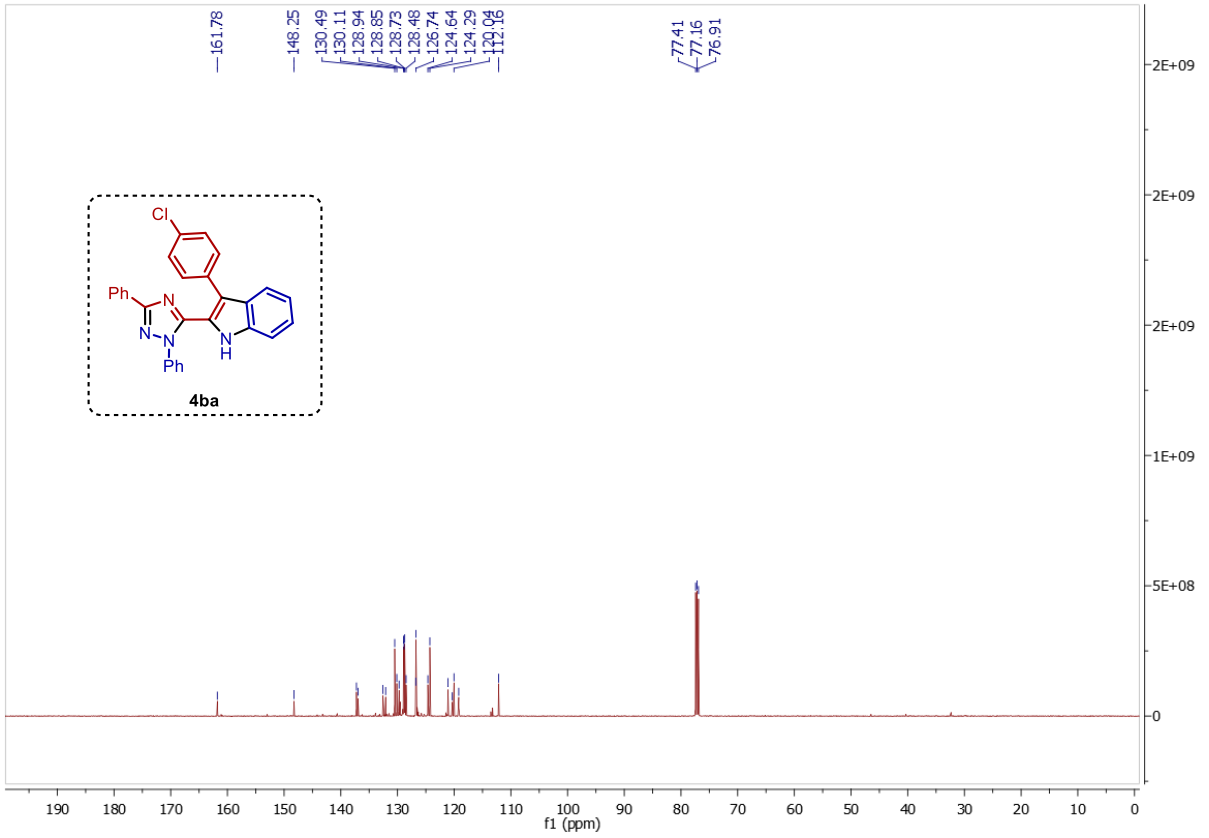
$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **3'ae**



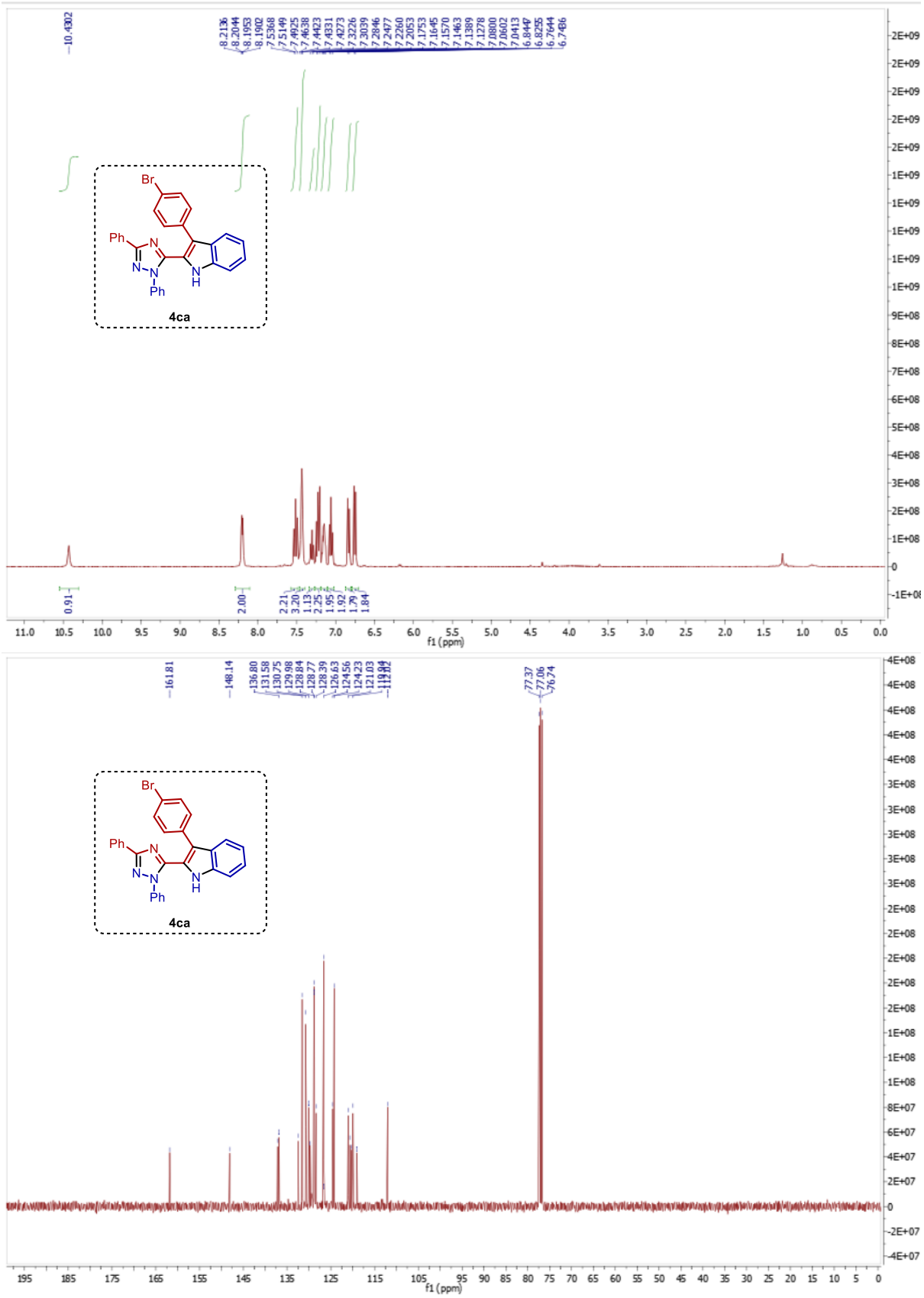


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **4aa**

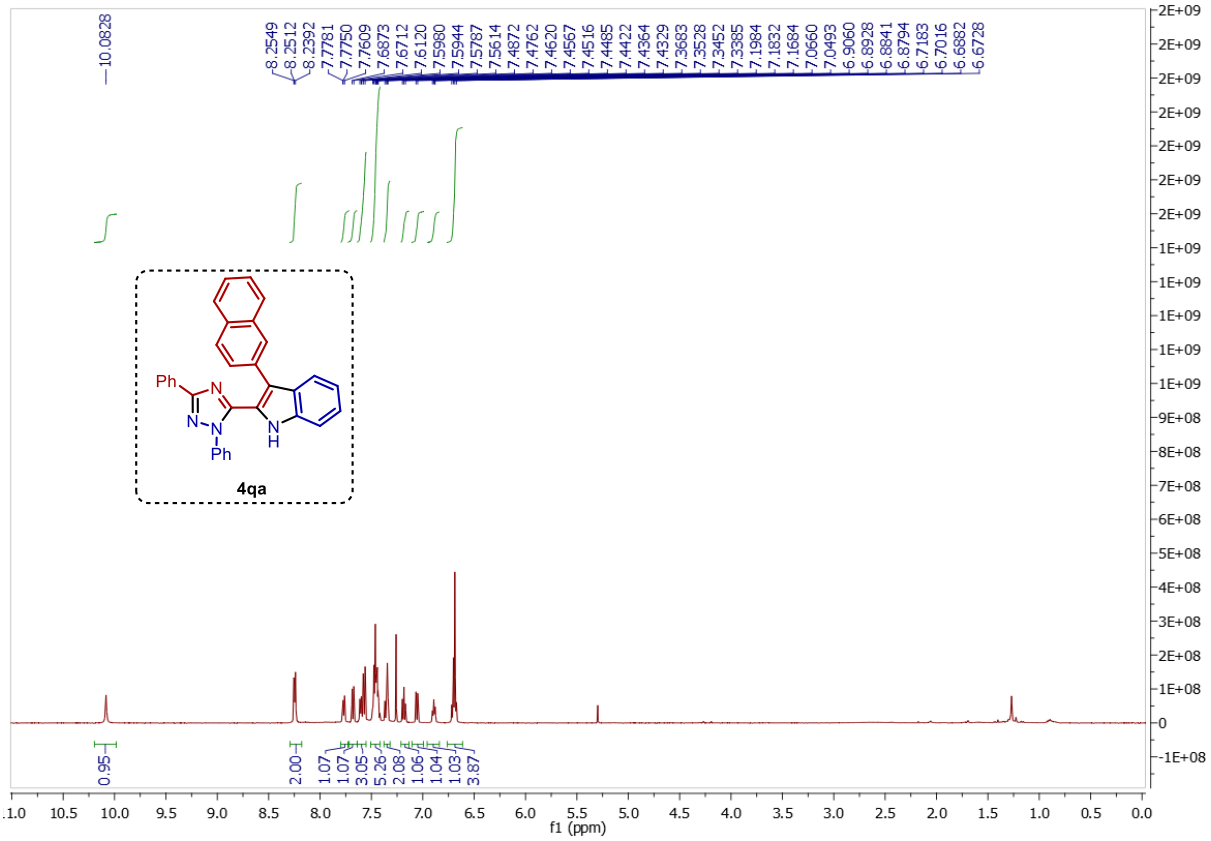


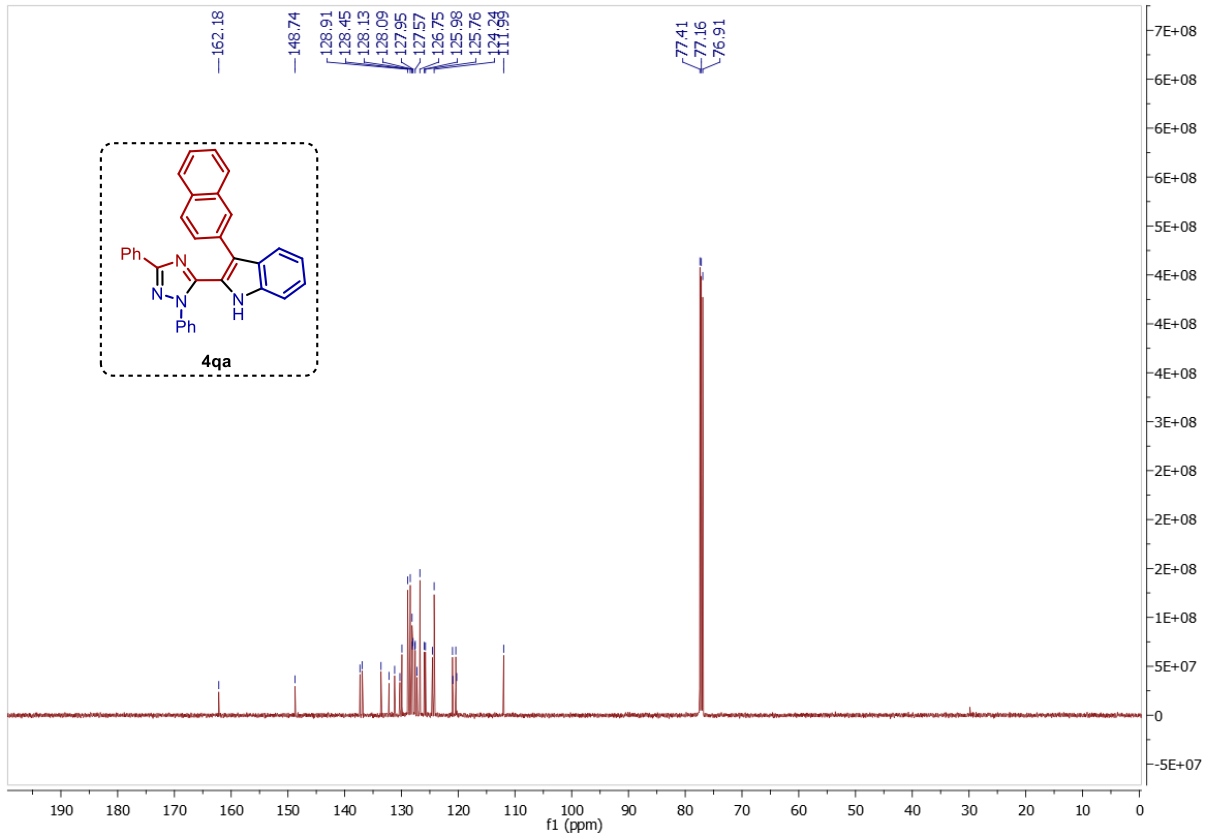


$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **4ba**

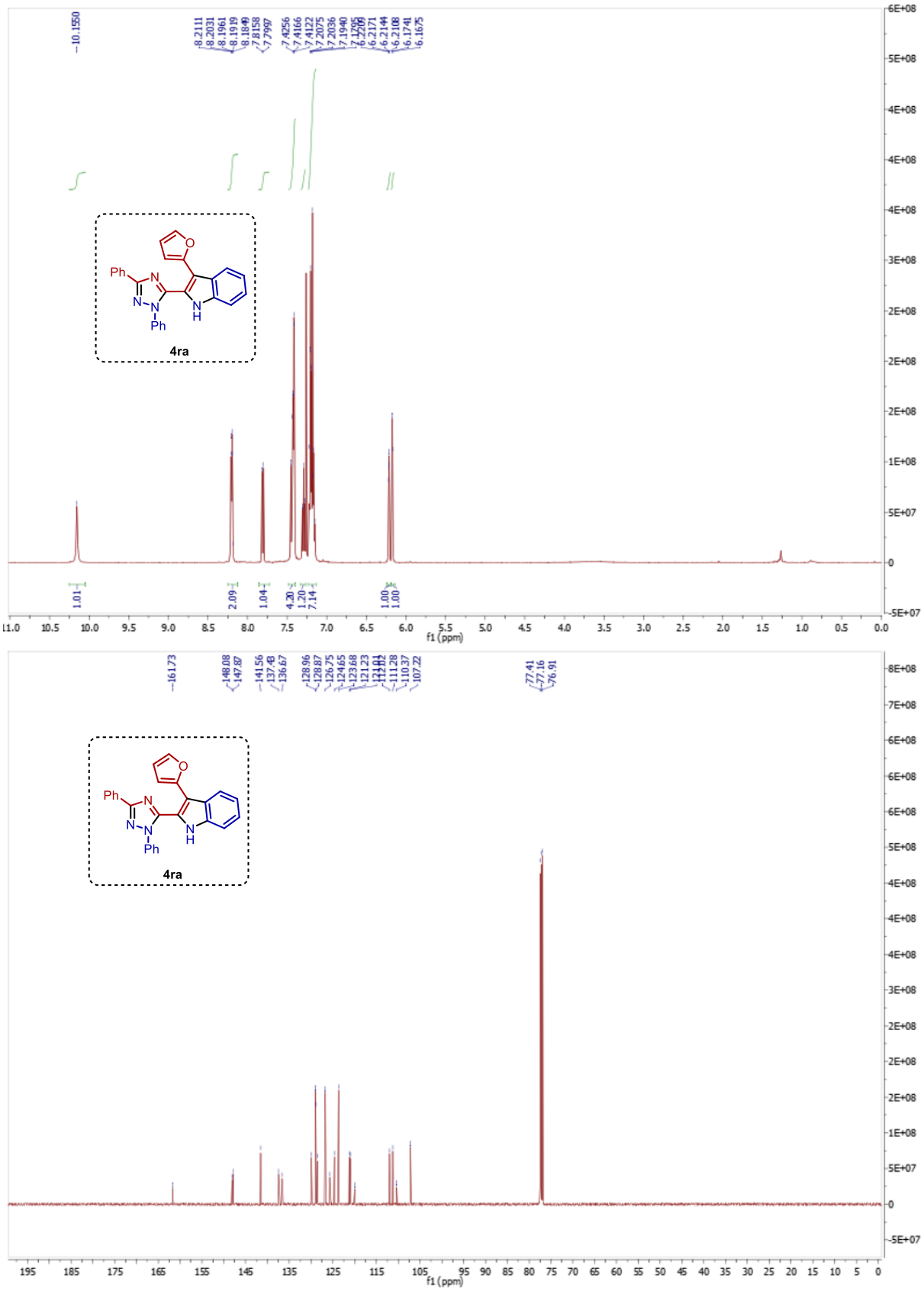


$CDCl_3$, 400 MHz ^1H NMR and 100 MHz $^{13}C\{^1H\}$ NMR Spectra of **4ca**

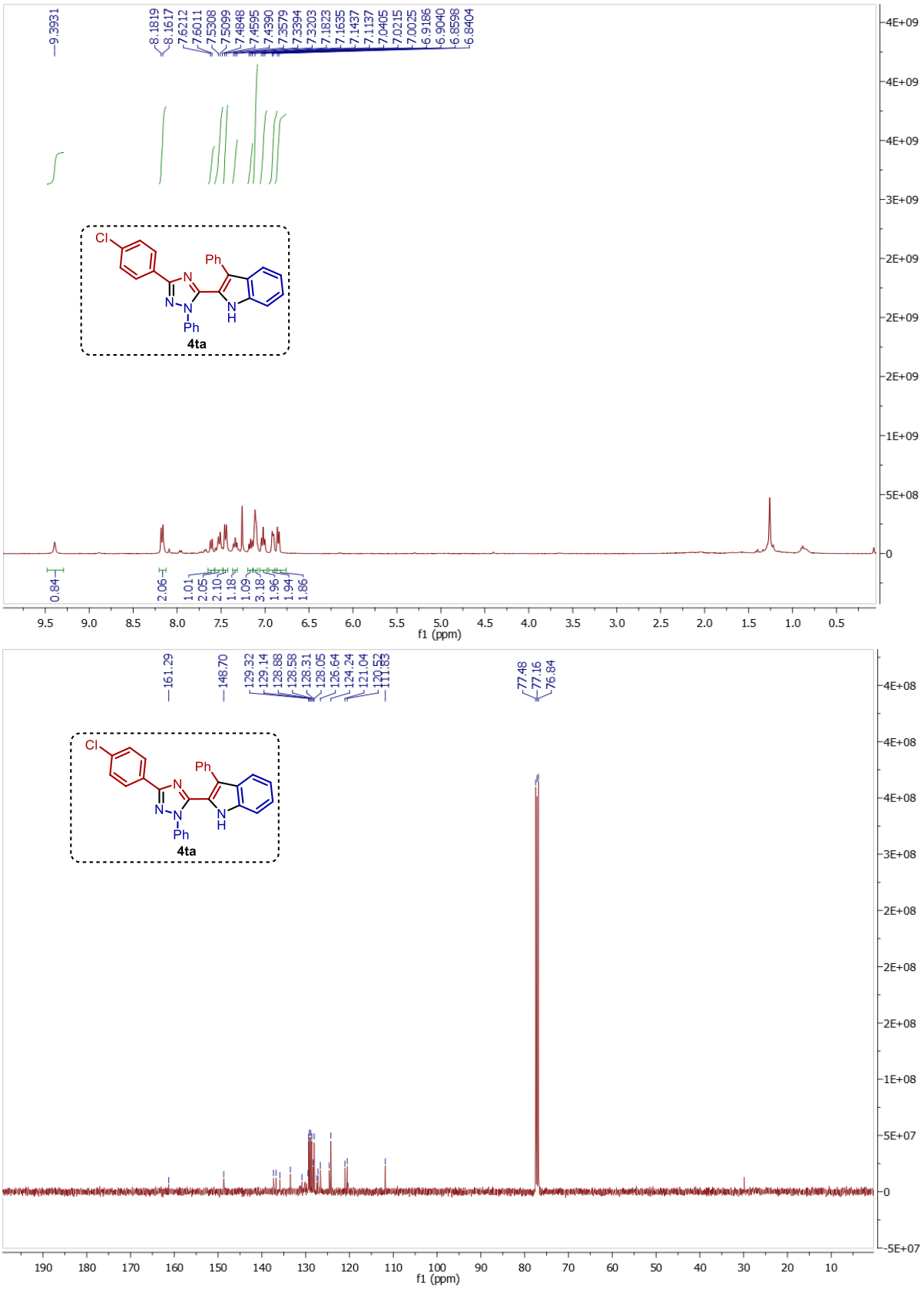




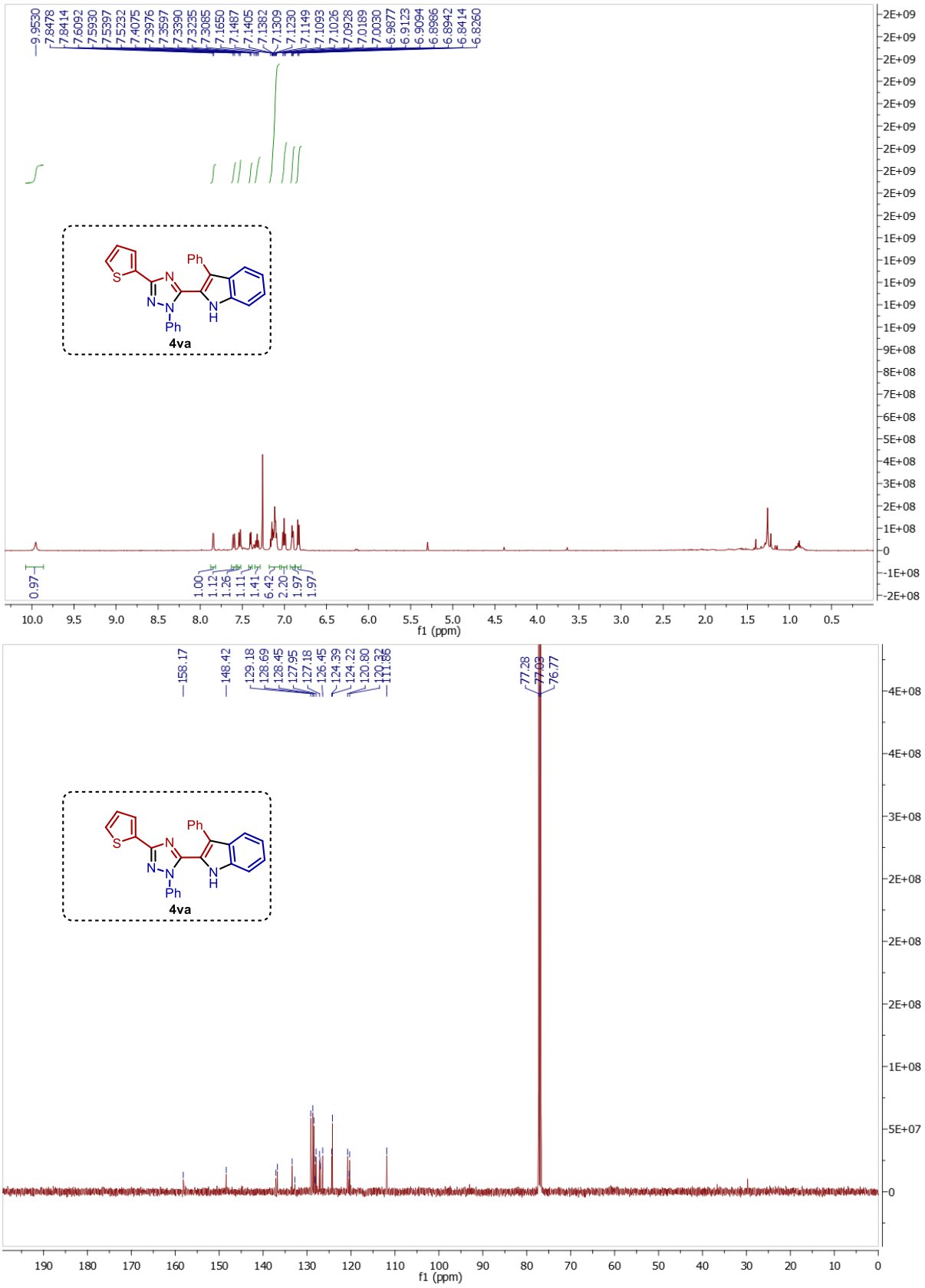
$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **4qa**



$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **4ra**



$CDCl_3$, 400 MHz ^1H NMR and 100 MHz $^{13}C\{^1H\}$ NMR Spectra of **4ta**



$CDCl_3$, 500 MHz ^1H NMR and 125 MHz $^{13}C\{^1H\}$ NMR Spectra of **4va**

8. X-ray crystal structure of 3aa

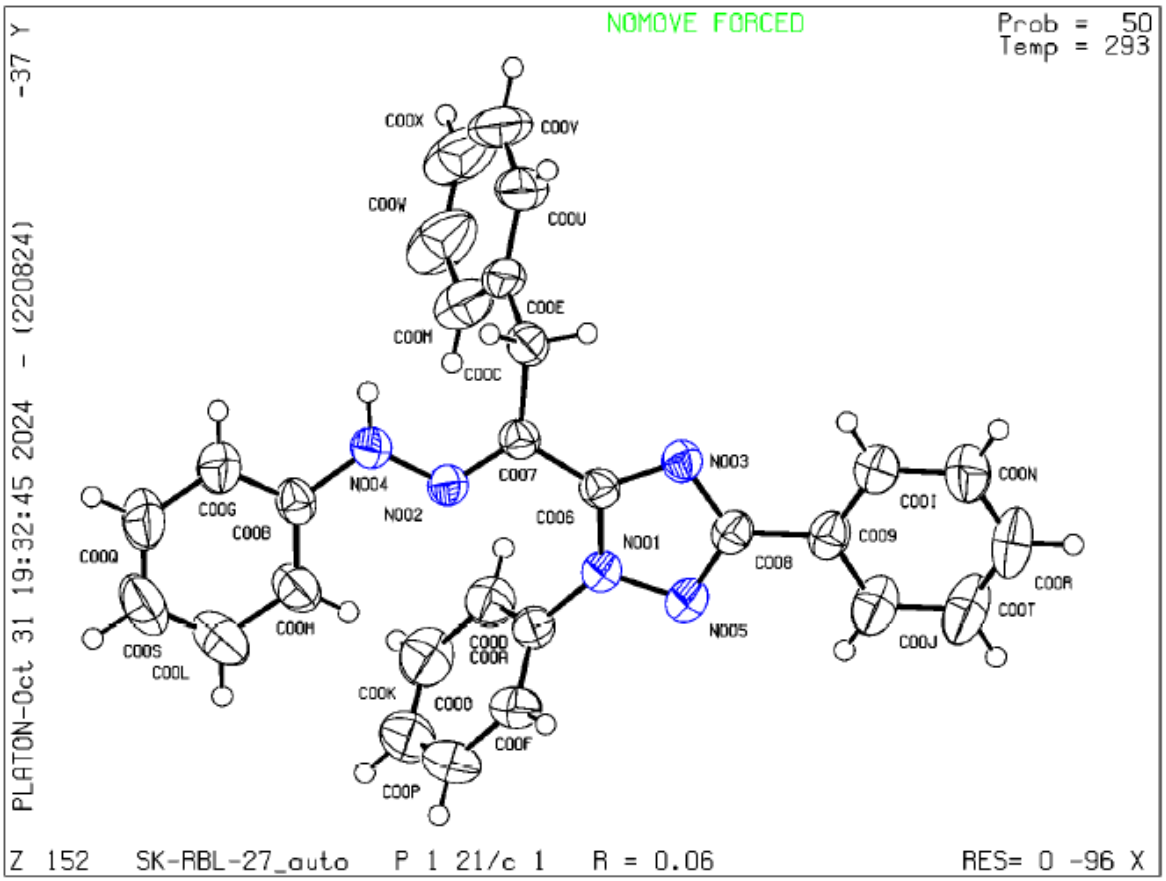


Figure S2: ORTEP Diagram of **3aa** (CCDC 2395296)

Table S2. Crystal data and structure refinement for **3aa**

Identification code	**3aa**
CCDC	2395296
Empirical formula	$C_{28}H_{23}N_5$
Formula weight	429.528
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.901(2)
b/Å	8.4370(15)
c/Å	23.343(5)
α/°	90
β/°	95.41(2)
γ/°	90
Volume/Å^3	2333.4(8)
Z	4
ρ_{calc}g/cm^3	1.223
μ/mm^{-1}	0.074
F(000)	904.3

Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.92 to 57.9
Index ranges	-14 ≤ h ≤ 15, -11 ≤ k ≤ 10, -29 ≤ l ≤ 29
Reflections collected	16067
Independent reflections	5411 [R_{int} = 0.0469, R_{sigma} = 0.0490]
Data/restraints/parameters	5411/0/299
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0617, wR_2 = 0.1629
Final R indexes [all data]	R_1 = 0.0953, wR_2 = 0.1892
Largest diff. peak/hole / e $Å^{-3}$	0.33/-0.31

9. References

1. P. V. Khairnar, Y. H. Su, Y.C. Chen, A. Edukondalu, Y.R. Chen and W. Lin, *Org. Lett*., 2020, **22**, 6868.

2. a) G. R. Humphrey and J. T. Kuethe, *Chem. Rev.*, 2006, **106**, 2875; b) C. F. H. Allen and C. V. Wilson, *J. Am. Chem. Soc*., 1943, **65**, 611.