Supporting Information

Pyridine promoted umpolung strategy for the *α*-amination of styrenes via pyridinium salt intermediates

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1. General information

Chemicals. Unless otherwise stated, commercial grade chemicals and extra dry solvents (THF, Et_2O, MeCN, DMF and 1,4-dioxane) were used without further purification. Commercially available chemicals were obtained from Energy Chemical, TCI and Aladin. Volume reduction and drying steps were performed *in vacuo*. (*α*-Phenylvinyl)pyridinium trifluoromethanesulfonate (**5a'**) was synthesized according to the literature procedure.[1]

General Physical Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on JNM-ECZ400S, Bruker Avance III (400 MHz) or Bruker AVANCE NEO 500. Chemical shifts were measured relative to the residual solvent resonance for ^{1}H and ^{13}C NMR ($CDCl_3$ = 7.26 ppm for ^{1}H and 77.2 ppm for ^{13}C, DMSO-d_6 = 2.50 ppm for ^{1}H and 39.2 ppm for ^{13}C). Coupling constants *J* are reported in hertz (Hz). The following abbreviations were used to designate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet, p, pentet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dt, double of triplet; ddt, doublet of doublet of triplet; m, multiplet; br, broad. HR-MS (ESI) spectra were obtained using a Shimadzu LCMS-IT-TOF time off light mass spectrometer.

2. Experimental procedure

2.1 Optimization of the formation of acetophenone azine.

Table S1. Optimization of the formation of acetophenone azine (**6a**).[a]

entries	additive	base	solvent	T / °C	t / h	atamosphere	amount of N_2H_4	yield
1	**pyridine**	**K_2CO_3**	**THF**	**70**	**12**	**air**	**2 eq.**	**82%**
2	**4-MeO-pyridine**	K_2CO_3	THF	70	12	air	2 eq.	10%
3	**4-CN-pyridine**	K_2CO_3	THF	70	12	air	2 eq.	0%
4	pyridine	**KOH**	THF	70	12	air	2 eq.	trace
5	pyridine	**Et_3N**	THF	70	12	air	2 eq.	0%
6	pyridine	**Na_2CO_3**	THF	70	12	air	2 eq.	75%
7	pyridine	**Cs_2CO_3**	THF	70	12	air	2 eq.	83%
8	pyridine	K_2CO_3	**DMF**	70	12	air	2 eq.	25%
9	pyridine	K_2CO_3	**MeCN**	70	12	air	2 eq.	66%

entries	additive	base	solvent	T / °C	t / h	atamosphere	amount of N_2H_4	yield
10	pyridine	K_2CO_3	**1,4-dioxane**	70	12	air	2 eq.	80%
11	pyridine	K_2CO_3	**H_2O**	70	12	air	2 eq.	0%
12	pyridine	K_2CO_3	THF	**60**	12	air	2 eq.	75%
13	pyridine	K_2CO_3	THF	**80**	12	air	2 eq.	82%
14	pyridine	K_2CO_3	THF	70	**8**	air	2 eq.	77%
15	pyridine	K_2CO_3	THF	70	**16**	air	2 eq.	82%
16	pyridine	K_2CO_3	THF	70	12	**N_2**	2 eq.	83%
17	pyridine	K_2CO_3	THF	70	12	air	**1.5 eq.**	55%
18	pyridine	K_2CO_3	THF	70	12	air	**3 eq.**	78%

[a]Reaction conditions: **1a** (0.40 mmol), **2a**, additive (0.40 mmol), I_2 (0.80 mmol), base (1.60 mmol), solvent (2 mL); [b]Isolated yields.

2.2 Experimental procedure for the synthesis of 6.

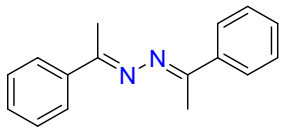
General procedure for the synthesis of 6a – 6u: A mixture of styrene derivatives **1** (0.40 mmol), pyridine (0.40 mmol, 31.6 mg) and iodine (0.80 mmol, 203.2 mg) was stirred at room temperature for 10 minutes. K_2CO_3 (1.60 mmol, 221.1 mg), 85 wt% Hydrazine hydrate (0.80 mmol, 47.1 mg) and THF (2.0 mL) was added sequentially to the mixture, and the resulted solution was stirred at 70 °C (heated by oil bath) for 12 h in air. After cooling to room temperature, 0.5 mL HAcO was added to the reaction mixture and stirred for 10 min. After stirring, the mixture was diluted with EtOAc (10 mL) and washed with brine (2×10 mL). The organic layer was collected and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/ethyl acetate (10:1-5:1 v/v) to afford the product **6a – 6u**.

Experimental procedure for the scale-up synthesis of 6a: A mixture of styrene **1a** (10 mmol, 1.04 g), pyridine (10 mmol, 0.79 g) and iodine (20 mmol, 5.08 g) was stirred at room temperature for 30 minutes. K_2CO_3 (40 mmol, 5.53 g), 85 wt% Hydrazine hydrate (20 mmol, 1.18 g) and THF (30 mL) was slowly and carefully added to the mixture (Warning: Nitrogen was generated and significant heat was released during the process). The resulted solution was refluxed at 70 °C (heated by oil bath) for 12 h in air. After cooling to room temperature, 10 mL HAcO was added to the reaction mixture and stirred for 20 min. After stirring, the mixture was diluted with EtOAc (30 mL) and washed with brine (3×30 mL). The organic layer was collected and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/ethyl acetate (10:1 v/v) to afford the product **6a** in 68% yield (0.80 g).

General procedure for the synthesis of 6v: A mixture of styrene **1a** (0.40 mmol, 41.7 mg), pyridine (0.40 mmol, 31.6 mg) and iodine (0.80 mmol, 203.2 mg) was stirred at room temperature for 10 minutes. Hydroxylamine sulfate (0.80 mmol, 131.3 mg) and THF (2.0 mL) was added sequentially to the mixture, and the resulted solution was stirred with K_2CO_3 (2.40 mmol, 331.7 mg) at 70 °C (heated by oil bath) for 12 h in air. After cooling to room temperature, 0.5 mL HAcO was added to the reaction mixture and stirred for 10 min. After stirring, the mixture was diluted with EtOAc (10 mL) and washed with brine (2×10 mL). The organic layer was collected and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/ethyl acetate (7:1 v/v) to afford the product **6v** (39.2 mg, 72%).

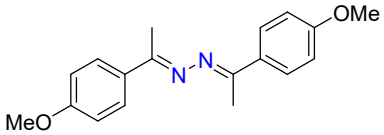
General procedure for the synthesis of 6w: A mixture of styrene **1a** (0.40 mmol, 41.7 mg), pyridine (0.40 mmol, 31.6 mg) and iodine (0.80 mmol, 203.2 mg) was stirred at room temperature for 10 minutes. Phenyl hydrazine (0.80 mmol, 86.5 mg) and THF (2.0 mL) was added sequentially to the mixture, and the resulted solution was stirred with K_2CO_3 (1.60 mmol, 221.1 mg) at 70 °C (heated by oil bath) for 12 h in air. After cooling to room temperature, 1 mL HAcO was added to the reaction mixture and stirred for 10 min. After stirring, the mixture was diluted with EtOAc (10 mL) and washed with brine (2×10 mL). The organic layer was collected and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/ethyl acetate (7:1 v/v) to afford the product **6w** (38.6 mg, 46%).

1,2-bis(1-phenylethylidene)hydrazine (6a)



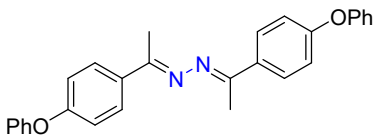
Yield, 82% (38.5 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 4H), 7.48 – 7.38 (m, 6H), 2.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 138.5, 129.6, 128.4, 126.6, 15.1. This compound is known.[2]

1,2-bis(1-(4-methoxyphenyl)ethylidene)hydrazine (6b)



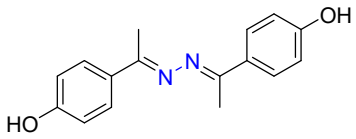
Yield, 80% (47.6 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.9 Hz, 4H), 6.94 (d, J = 8.9 Hz, 4H), 3.86 (s, 6H), 2.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 157.8, 131.4, 128.1, 113.6, 55.4, 14.8. This compound is known.[3]

1,2-bis(1-(4-phenoxyphenyl)ethylidene)hydrazine (6c)



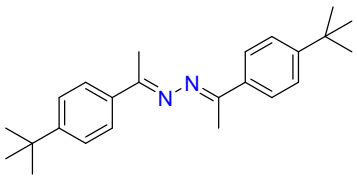
Yield, 76% (64.0 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 4H), 7.40 – 7.34 (m, 4H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 4H), 7.03 (d, *J* = 8.8 Hz, 4H), 2.33 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 157.7, 156.6, 133.4, 129.9, 128.3, 123.8, 119.4, 118.2, 15.0. HR-MS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{25}N_2O_2$, 421.1916; found, 421.1906.

1,2-bis(1-(4-phenoxyphenyl)ethylidene)hydrazine (6d')



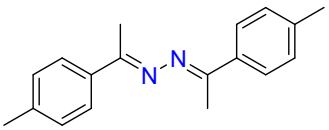
Yield, 70% (39.2 mg); white solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.80 (s, 2H), 7.76 (d, *J* = 8.8 Hz, 4H), 6.82 (d, *J* = 8.8 Hz, 4H), 2.25 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.4, 158.1, 129.6, 128.4, 115.5, 14.8. HR-MS (ESI) *m/z* $[M-H]^-$ calcd for $C_{16}H_{15}N_2O_2$, 267.1134; found, 267.1142.

1,2-bis(1-(4-(tert-butyl)phenyl)ethylidene)hydrazine (6e)



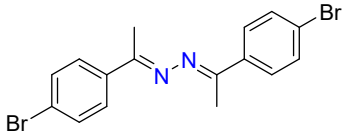
Yield, 82% (56.9 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 4H), 7.44 (d, *J* = 8.5 Hz, 4H), 2.29 (s, 6H), 1.35 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 152.8, 135.8, 126.4, 125.3, 34.8, 31.3, 15.0. This compound is known.[4]

1,2-bis(1-(p-tolyl)ethylidene)hydrazine (6f)



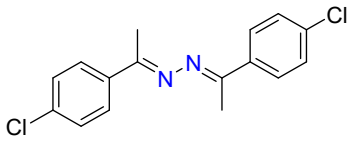
Yield, 82% (43.5 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 4H), 7.23 (d, *J* = 8.0 Hz, 4H), 2.40 (s, 6H), 2.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 139.7, 135.8, 129.0, 126.6, 21.4, 15.0. This compound is known.[2]

1,2-bis(1-(4-bromophenyl)ethylidene)hydrazine (6g)



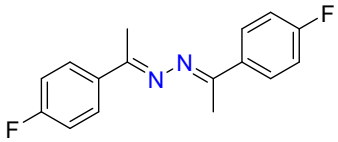
Yield, 78% (61.8 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 4H), 7.55 (d, *J* = 8.6 Hz, 4H), 2.29 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 137.1, 131.5, 128.2, 124.2, 14.9. This compound is known.[2]

1,2-bis(1-(4-chlorophenyl)ethylidene)hydrazine (6h)



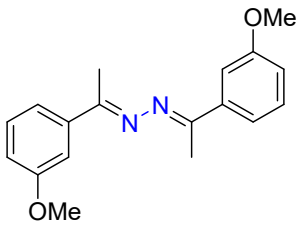
Yield, 79% (47.8 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 4H), 7.39 (d, *J* = 8.6 Hz, 4H), 2.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 136.7, 135.8, 128.6, 127.9, 14.9. This compound is known.[2]

1,2-bis(1-(4-fluorophenyl)ethylidene)hydrazine (6i)



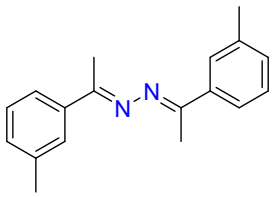
Yield, 80% (43.7 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.9, 5.5 Hz, 4H), 7.02 (t, *J* = 8.7 Hz, 4H), 2.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8 (d, *J* = 249.7 Hz), 134.6 (d, *J* = 3.2 Hz), 128.6 (d, *J* = 8.4 Hz), 115.3 (d, *J* = 21.6 Hz), 15.0. This compound is known.[2]

1,2-bis(1-(3-methoxyphenyl)ethylidene)hydrazine (6j)



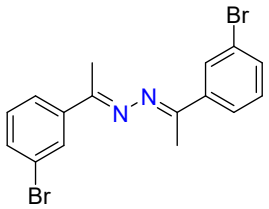
Yield, 77% (45.8 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 6.97 (ddd, *J* = 8.2, 2.6, 0.7 Hz, 2H), 3.87 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 157.2, 139.8, 129.3, 119.3, 115.6, 111.7, 55.4, 15.2. This compound is known.[5]

1,2-bis(1-(m-tolyl)ethylidene)hydrazine (6k)



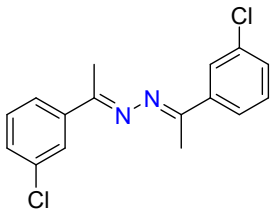
Yield, 83% (43.6 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 2.41 (s, 6H), 2.29 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 138.5, 138.0, 130.4, 128.3, 127.2, 123.8, 21.6, 15.2. HR-MS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{21}N_2$, 265.1705; found, 265.1698.

1,2-bis(1-(3-bromophenyl)ethylidene)hydrazine (6l)



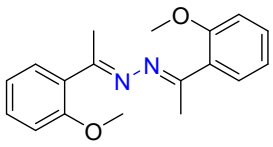
Yield, 78% (61.1 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (t, *J* = 1.7 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.47 (dd, *J* = 7.9, 0.8 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 2H), 2.22 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 140.2, 132.7, 129.9, 129.7, 125.2, 122.7, 29.7, 15.1. HR-MS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}Br_2N_2$, 392.9602; found, 392.9595.

1,2-bis(1-(3-chlorophenyl)ethylidene)hydrazine (6m)



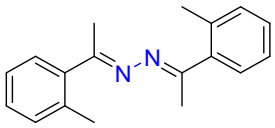
Yield, 76% (46.2 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (t, *J* = 1.8 Hz, 2H), 7.77 (dt, *J* = 7.5, 1.4 Hz, 2H), 7.41 – 7.34 (m, 4H), 2.31 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 140.3, 135.0, 130.0, 129.8, 126.9, 124.8, 15.1. This compound is known.[6]

1,2-bis(1-(2-methoxyphenyl)ethylidene)hydrazine (6n)



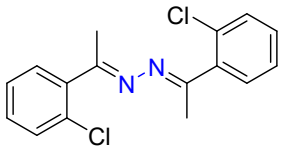
Yield, 30% (17.9 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.38 - 7.33 (m, 2H), 7.00 (t, *J* = 7.5, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 3.86 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 157.6, 130.1, 129.7, 129.6, 120.7, 111.2, 55.5, 18.8. This compound is known.[7]

1,2-bis(1-(o-tolyl)ethylidene)hydrazine (6o)



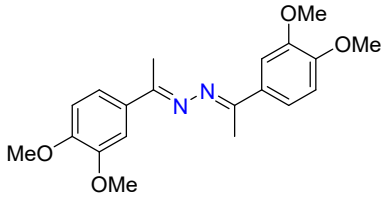
Yield, 42% (21.9 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 2H), 7.27 – 7.22 (m, 6H), 2.47 (s, 6H), 2.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 140.3, 135.6, 130.9, 128.7, 128.1, 126.0, 20.6, 19.3. This compound is known.[8]

1,2-bis(1-(2-chlorophenyl)ethylidene)hydrazine (6p)



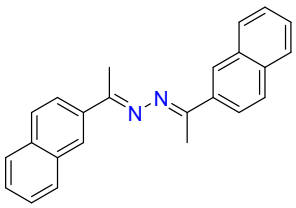
Yield, 10% (6.4 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.45 – 7.39 (m, 2H), 7.33 – 7.29 (m, 4H), 2.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 139.4, 132.2, 130.8, 130.1, 129.1, 127.0, 19.4. This compound is known.[6]

1,2-bis(1-(3,4-dimethoxyphenyl)ethylidene)hydrazine (6q)



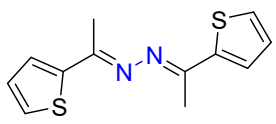
Yield, 77% (55.0 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 2.0 Hz, 2H), 7.37 (dd, J = 8.4, 2.0 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 3.96 (s, 6H), 3.94 (s, 6H), 2.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 150.6, 148.8, 131.4, 119.9, 110.3, 109.0, 56.0, 14.8. HR-MS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_4$, 357.1815; found, 357.1807.

1,2-bis(1-(naphthalen-2-yl)ethylidene)hydrazine (6r)



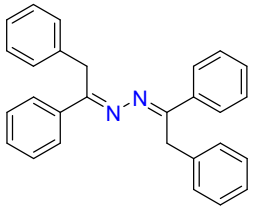
Yield, 82% (54.8 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 – 8.22 (m, 4H), 7.89 (ddd, J = 9.4, 7.7, 5.1 Hz, 6H), 7.54 – 7.48 (m, 4H), 2.48 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 135.9, 134.1, 133.1, 128.7, 128.0, 127.7, 126.9, 126.7, 126.4, 124.1, 15.0. This compound is known.[7]

1,2-bis(1-(thiophen-2-yl)ethylidene)hydrazine (6s)



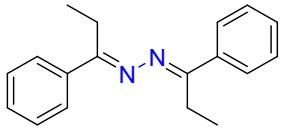
Yield, 77% (38.4 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 3.5 Hz, 2H), 7.39 (d, J = 5.0 Hz, 2H), 7.10 – 7.06 (m, 2H), 2.46 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 144.7, 128.8, 127.7, 127.4, 15.2. This compound is known.[2]

1,2-bis(1,2-diphenylethylidene)hydrazine (6t)



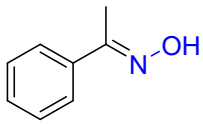
Yield, 60% (46.5 mg); light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 4H), 7.38 – 7.32 (m, 6H), 7.20 – 7.09 (m, 10H), 4.35 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 137.5, 129.9, 128.7, 128.6, 128.4, 127.5, 126.1, 34.8. This compound is known.[9]

1,2-bis(1-phenylpropylidene)hydrazine (6u)



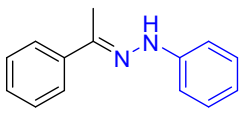
Yield, 62% (32.9 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.8, 1.8 Hz, 4H), 7.49 – 7.39 (m, 6H), 2.89 (q, *J* = 7.6 Hz, 4H), 1.13 (t, *J* = 7.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 137.4, 129.5, 128.4, 126.9, 22.0, 11.4. This compound is known.[7]

1-phenylethan-1-one oxime (6v)



Yield, 72% (39.2 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.62 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.44 – 7.34 (m, 3H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 136.5, 129.3, 128.5, 126.1, 12.4. This compound is known.[10]

1-phenyl-2-(1-phenylethylidene)hydrazine (6w)

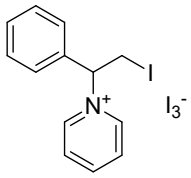


Yield, 46% (38.6 mg); white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.18 (dd, *J* = 15.6, 8.1 Hz, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 141.2, 139.2, 129.3, 128.4, 128.0, 125.6, 120.2, 113.3, 11.9. This compound is known.[3]

2.3 Experimental procedure for the reactions shown in the Fig. 3.

(a) A mixture of styrene (0.40 mmol, 41.7 mg), pyridine (0.40 mmol, 31.6 mg) and iodine (0.80 mmol, 203.2 mg) was stirred for 10 min to give some black oil and washed with Et_2O (3 × 5 mL). The black oil was collected and dried under reduced pressure to afford product **3a** in yield 96% (262.2 mg).

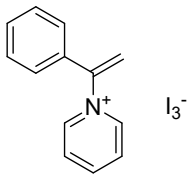
1-(2-iodo-1-phenylethyl)pyridinium triiodide (3a)



^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (d, *J* = 5.7 Hz, 2H), 8.68 (t, *J* = 7.8 Hz, 1H), 8.33 – 8.22 (m, 2H), 7.65 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.55 – 7.40 (m, 3H), 6.40 (t, *J* = 8.0 Hz, 1H), 4.45 – 4.35 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.5, 143.8, 135.7, 130.7, 130.0, 129.5, 128.1, 75.1, 5.4. This compound is known.[11]

(b) A solution of **3a** (0.40 mmol, 276.4 mg) in THF (5 mL) was added with K_2CO_3 (0.60 mmol, 82.9 mg) and stirred at room temperature for 1 h. The reaction mixture was filtered and concentrated under reduced pressure. The residue was purified on a silica gel column eluted with absolute ethyl acetate to afford the product **4a** in 95% yield (NMR yield, 99%).

(α-phenylvinyl)pyridinium triiodide (4a)



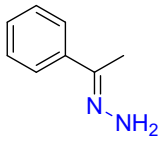
^{1}H NMR (500 MHz, DMSO-d_6) δ 9.22 (d, *J* = 5.5 Hz, 2H), 8.89 (t, *J* = 7.9 Hz, 1H), 8.35 (dd, *J* = 7.7, 6.8 Hz, 2H), 7.58 – 7.47 (m, 3H), 7.39 (d, *J* = 6.8 Hz, 2H), 6.48 (d, *J* = 2.7 Hz, 1H), 6.12 (d, *J* = 2.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.6, 148.0, 145.4, 133.2, 131.0, 129.7, 129.0, 126.8, 117.4. HR-MS (ESI) *m/z* $[M\text{-}I_3]^+$ calcd for $C_{13}H_{12}N$, 182.0970; found, 182.0979.

(c) A mixture of **4a** (0.40 mmol, 225.2 mg), 85 wt% Hydrazine hydrate (0.80 mmol, 47.1 mg) and K_2CO_3 (1.60 mmol, 221.1 mg) was treated with THF (2 mL). The mixture was stirred at 70 ^{o}C (heated by oil bath) for 12 h in air. After cooling to room temperature, the mixture was diluted with EtOAc (10 mL) and washed with brine (2×10 mL). The organic layer was collected and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/ethyl acetate (10:1) to afford the product **6a** in 85% yield (40.0 mg). The yield of pyridine (90%) is determined by NMR.

(d) A mixture of **4a** (0.80 mmol, 450.4 mg), 85 wt% Hydrazine hydrate (1.60 mmol, 94.2 mg) and K_2CO_3 (3.20 mmol, 442.2 mg) was treated with THF (4 mL). The mixture was stirred at 70 ^{o}C (heated by oil bath) for 6 h in air. After cooling to room temperature, the mixture was diluted with EtOAc (20 mL) and washed with brine (2×20 mL). The organic layer was collected and

concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/ethyl acetate (10:1 - 7:1) to afford the products **5a** (7.6 mg, 7%) and **6a** (37.8 mg, 40%).

(1-phenylethylidene)hydrazine (5a)



Yield, 7% (7.6 mg); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.1 Hz, 1H), 7.32 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.3 Hz, 1H), 5.36 (s, 2H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 139.4, 128.3, 128.1, 125.5, 11.7. This compound is known.[12]

(e) A mixture of **4a'** (0.40 mmol, 132.5 mg), **5a** (0.40 mmol, 53.7 mg) and K_2CO_3 (1.60 mmol, 221.1 mg) was treated with THF (2 mL). The mixture was stirred at 70 °C (heated by oil bath) for 12 h in air. After cooling to room temperature, the mixture was diluted with EtOAc (10 mL) and washed with brine (2×10 mL). The organic layer was collected and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/ethyl acetate (10:1 - 7:1) to afford the products **6a** in 90% yield (84.7 mg).

3. Computational details

Gaussian09 software package specifically the Becke-3-Lee-Yang-Parr (B3LYP) approach was utilized for conducting the DFT simulations.[13] During geometry optimization and frequency calculations, the 6-311G basis set was applied to all atoms.[14] All possible geometries for each species were taken into consideration when determining the optimized configurations. The outcomes suggest that the configurations presented in this article as optimized are the most stable among the considered alternatives.

4. References

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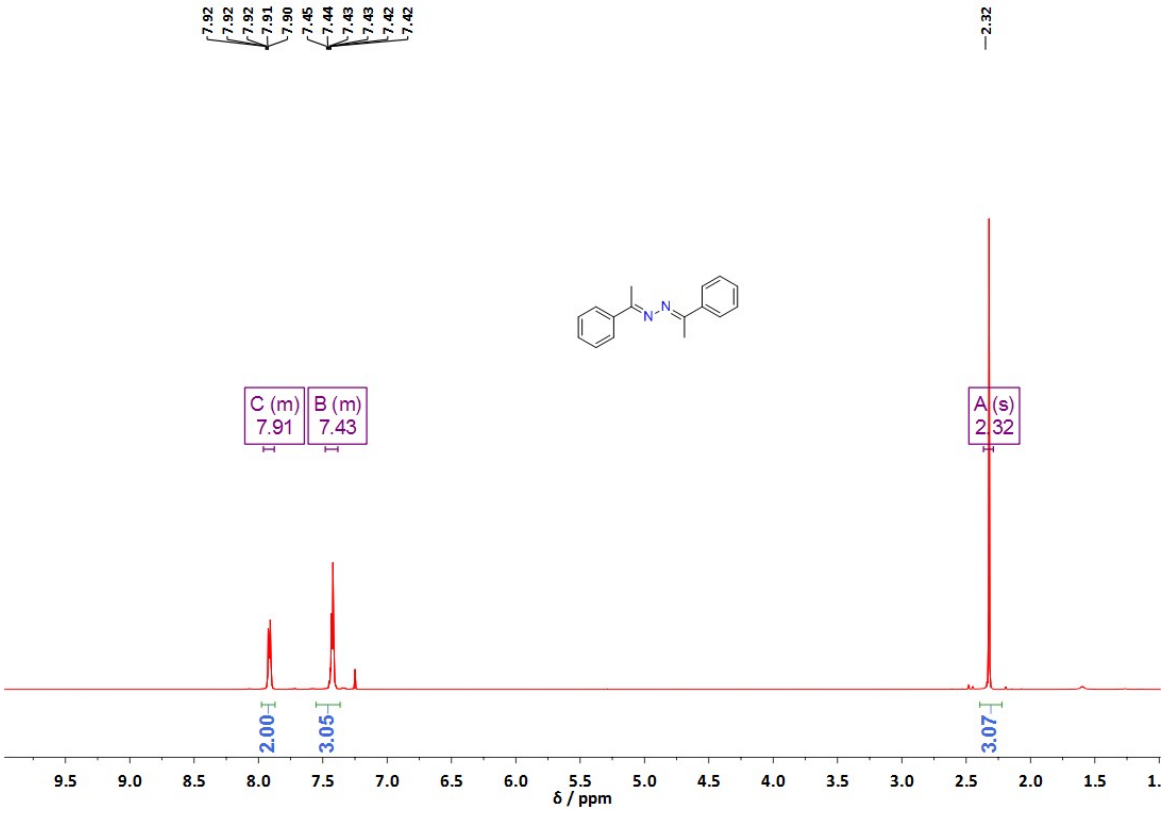
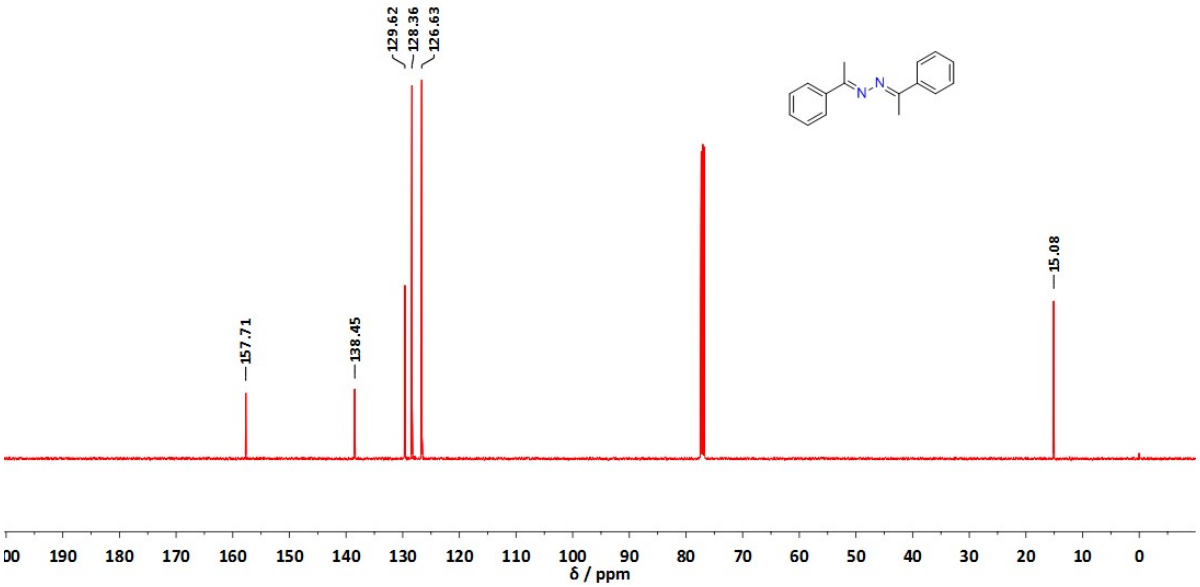
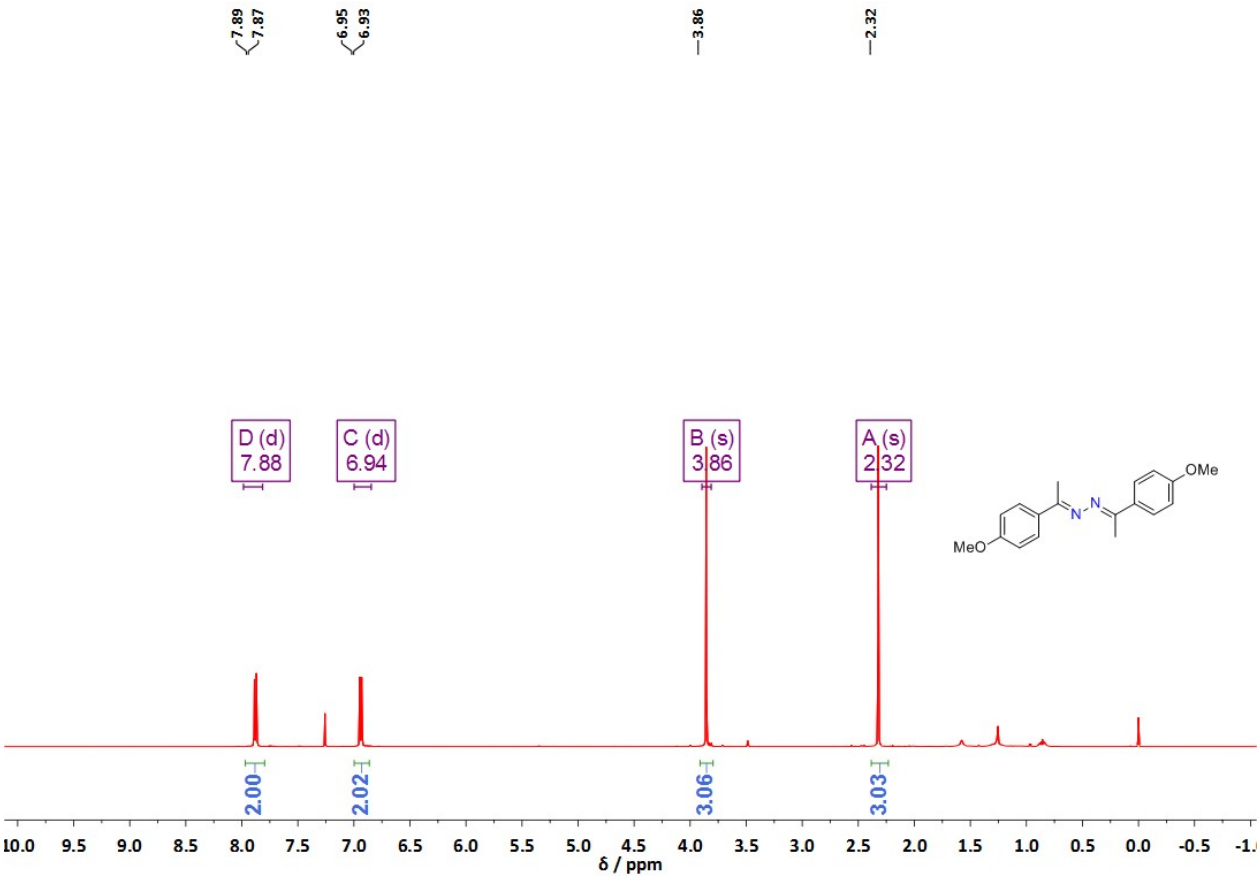
5. ^{1}H NMR and ^{13}C NMR spectra of compounds

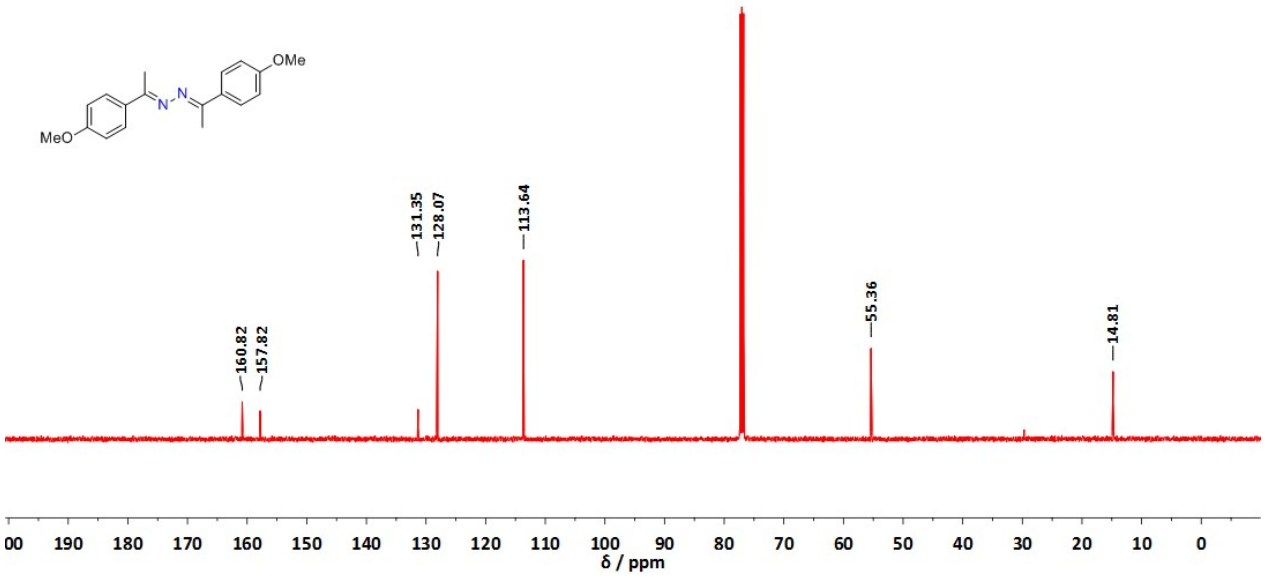
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6a



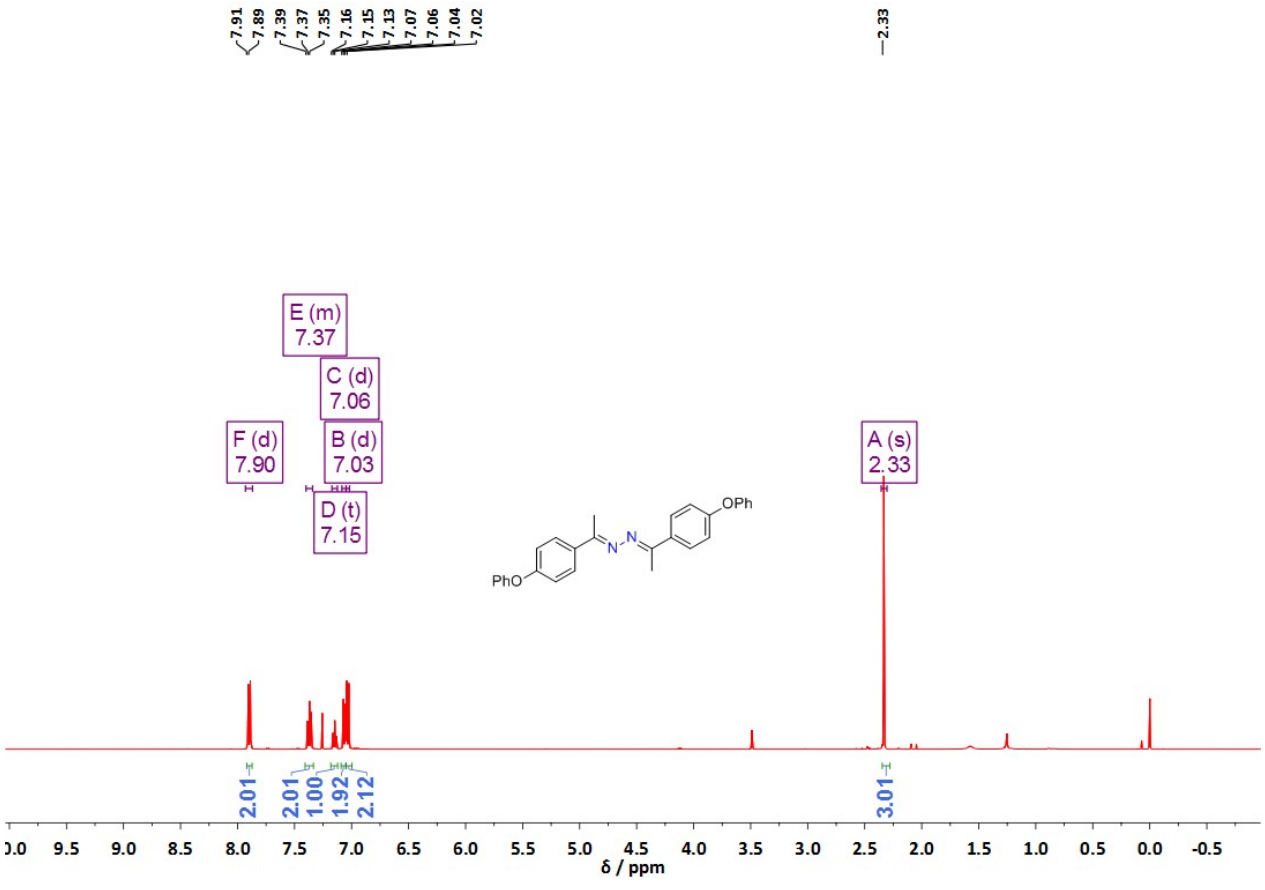


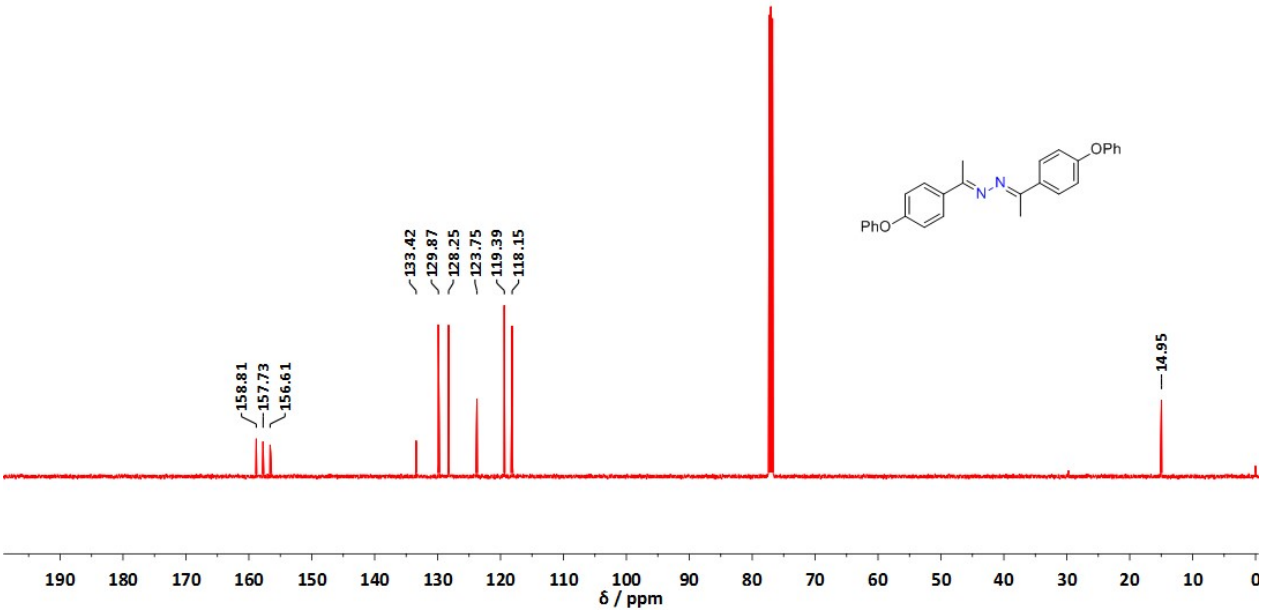
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6b



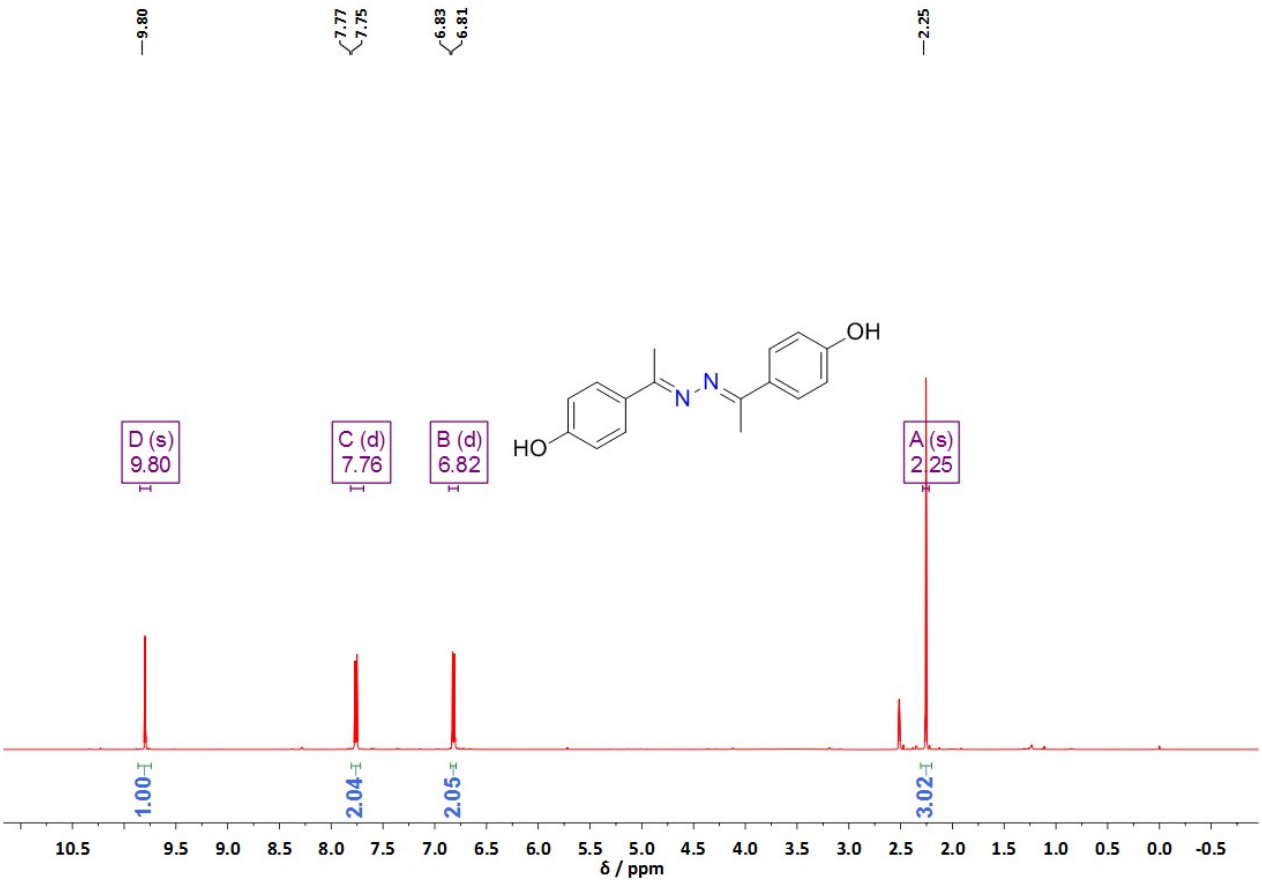


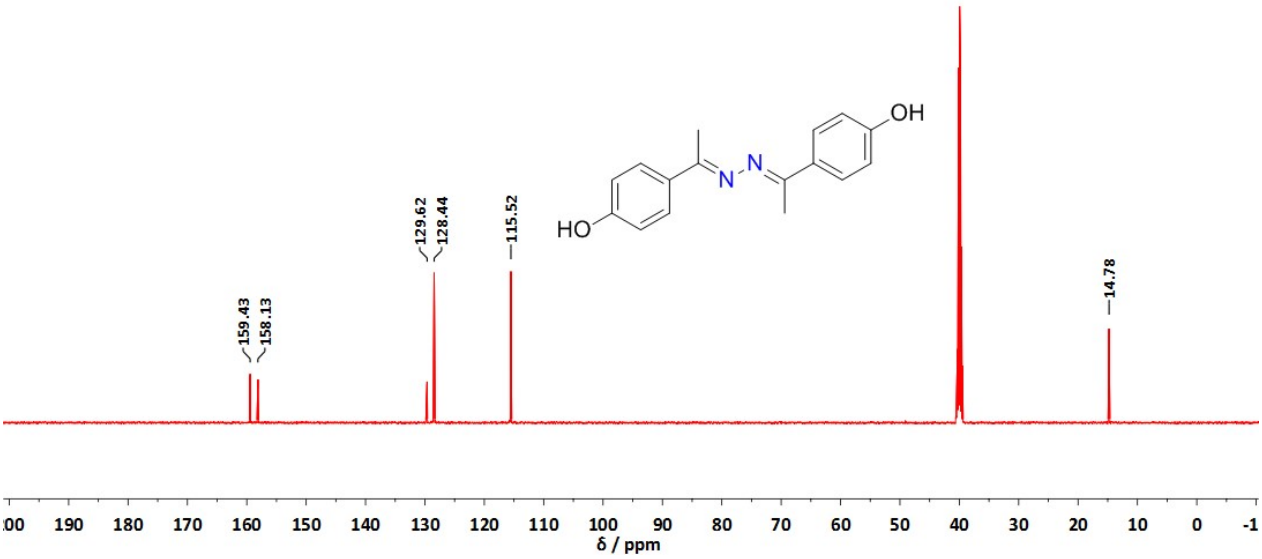
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6c



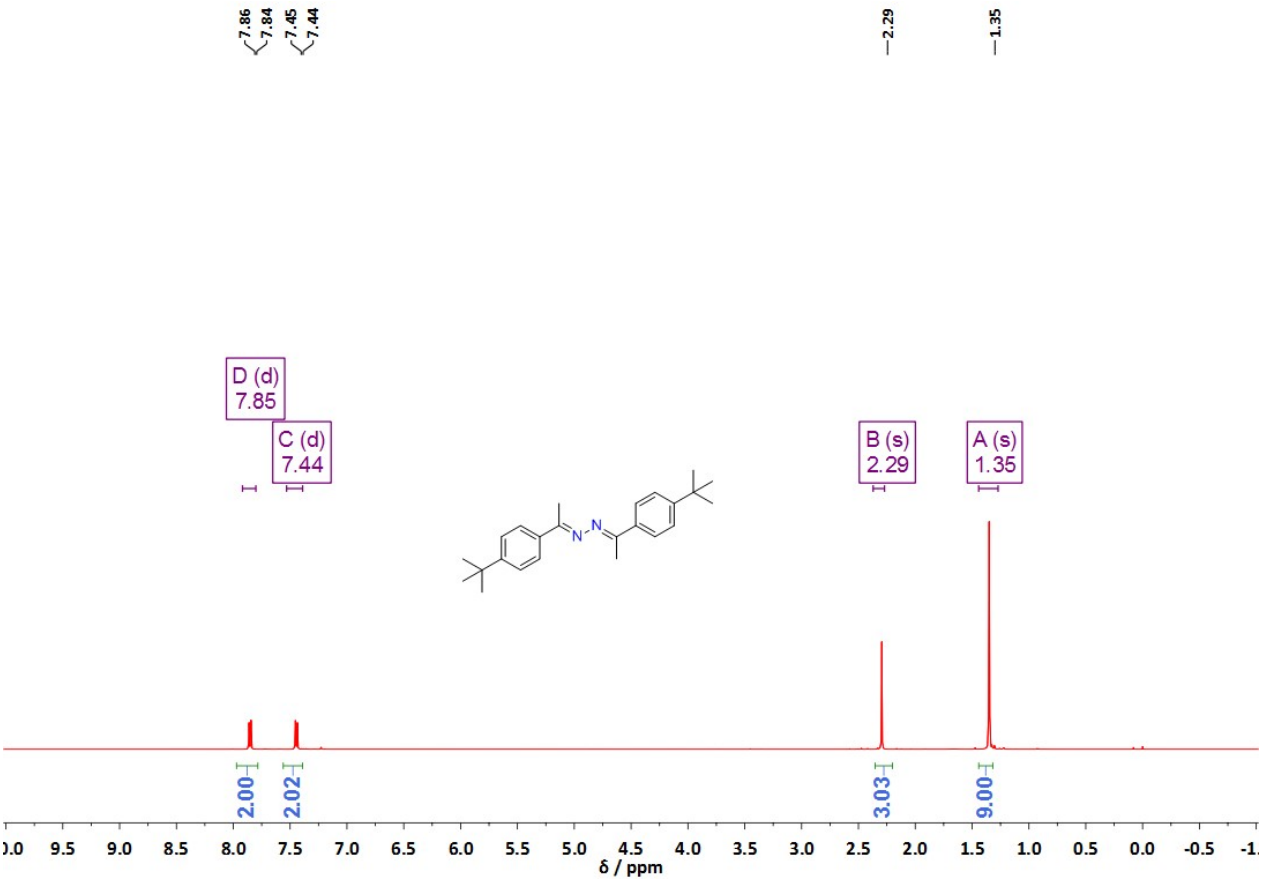


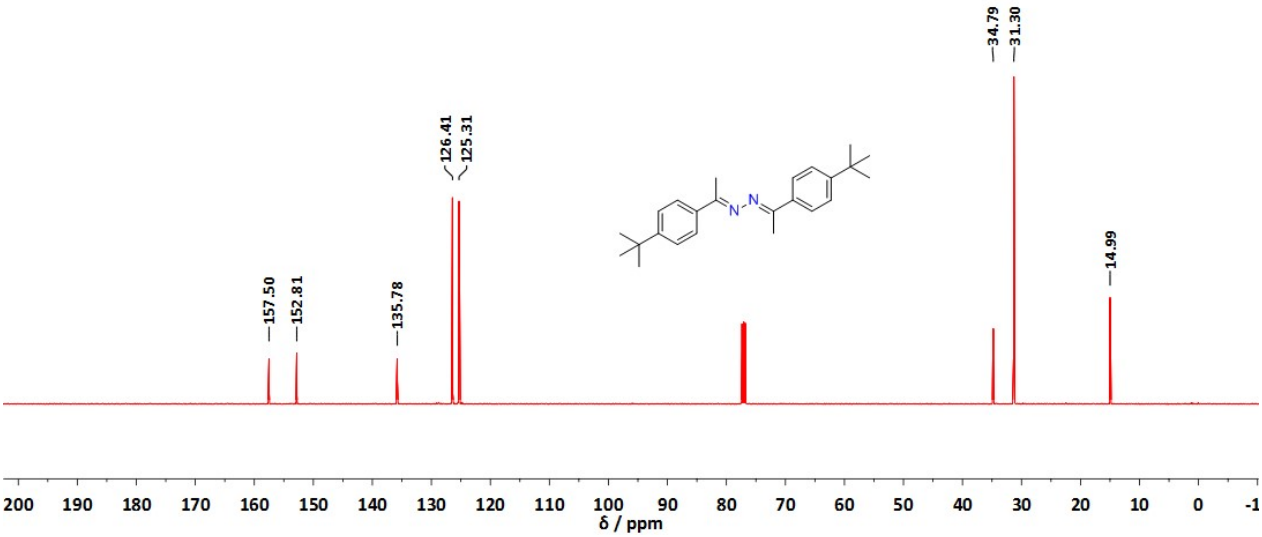
^{1}H NMR spectrum (500 MHz, DMSO-d_6) and ^{13}C NMR spectrum (126 MHz, DMSO-d_6) of 6d'



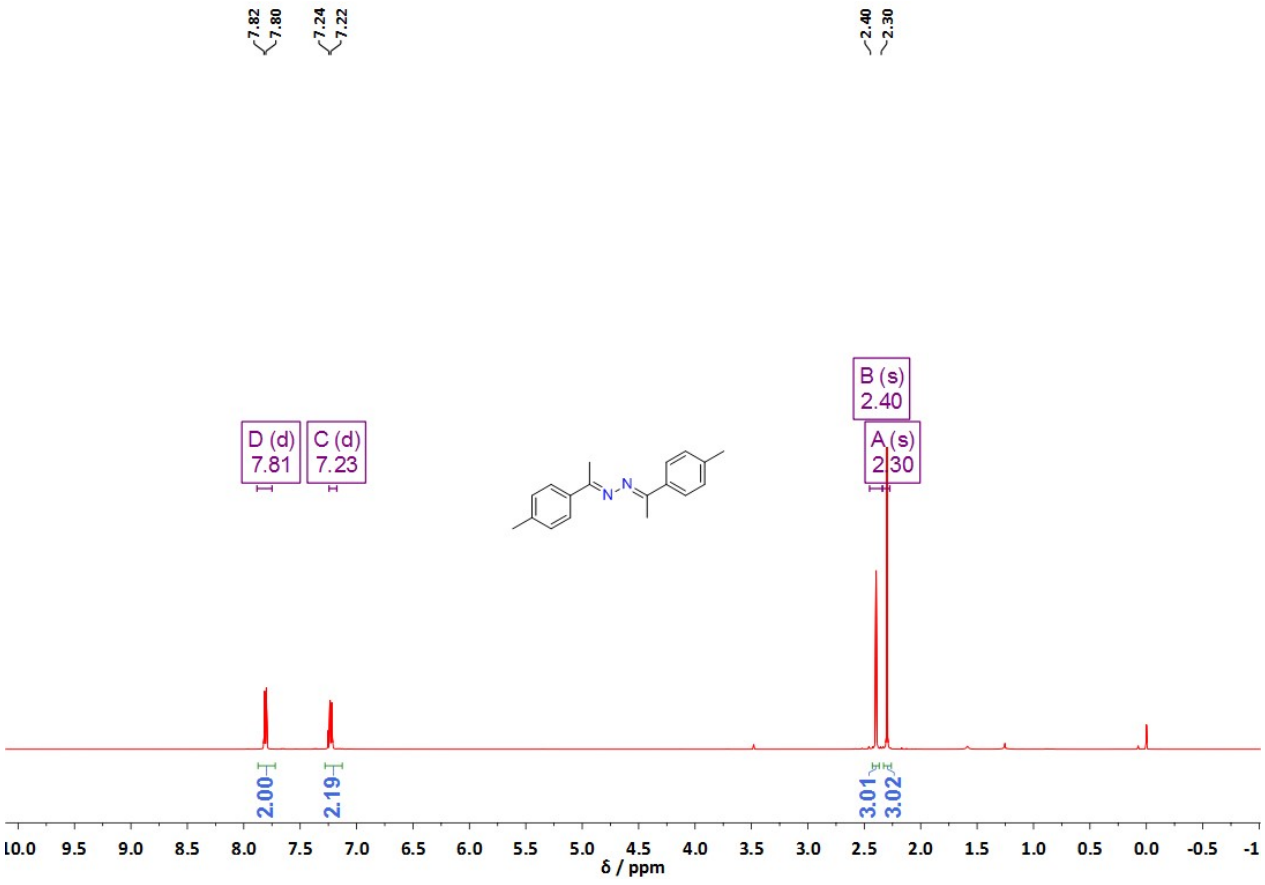


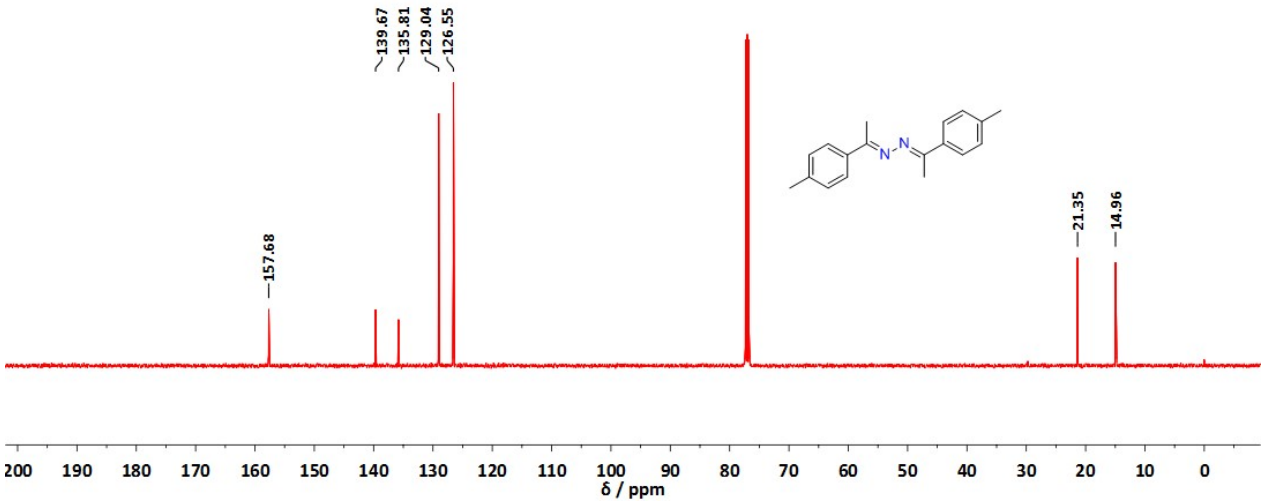
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6e



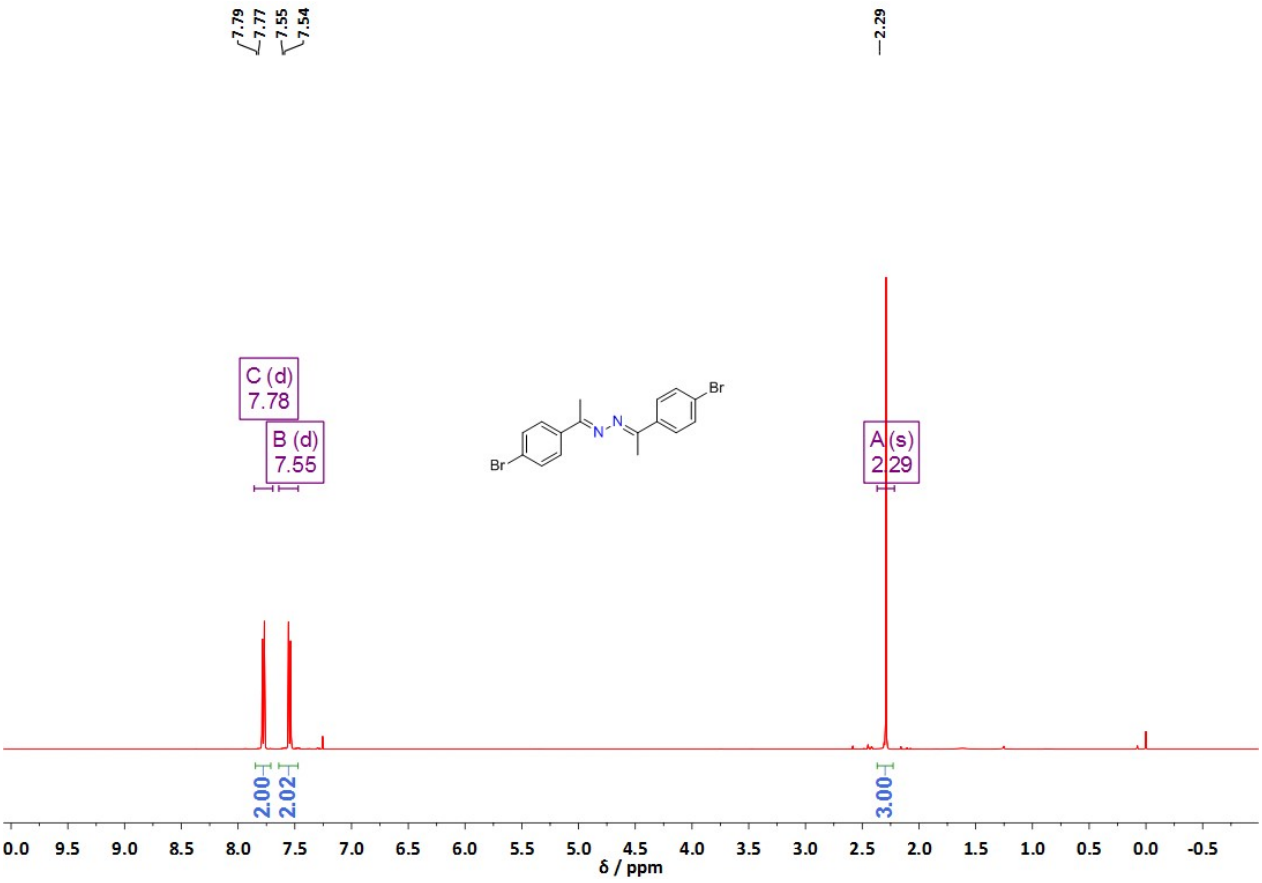


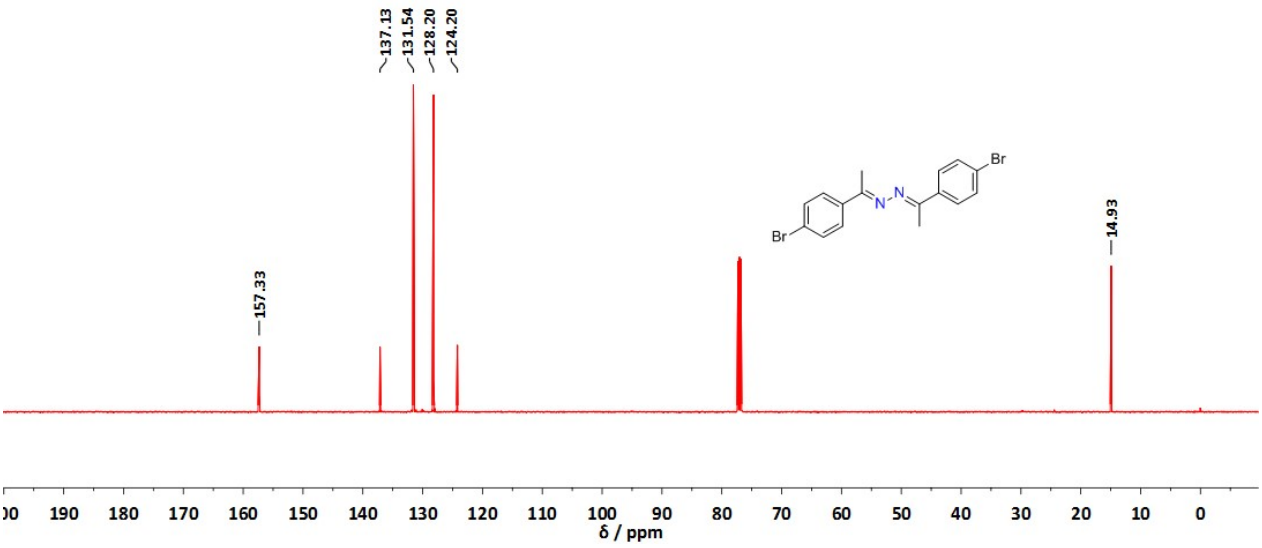
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6f



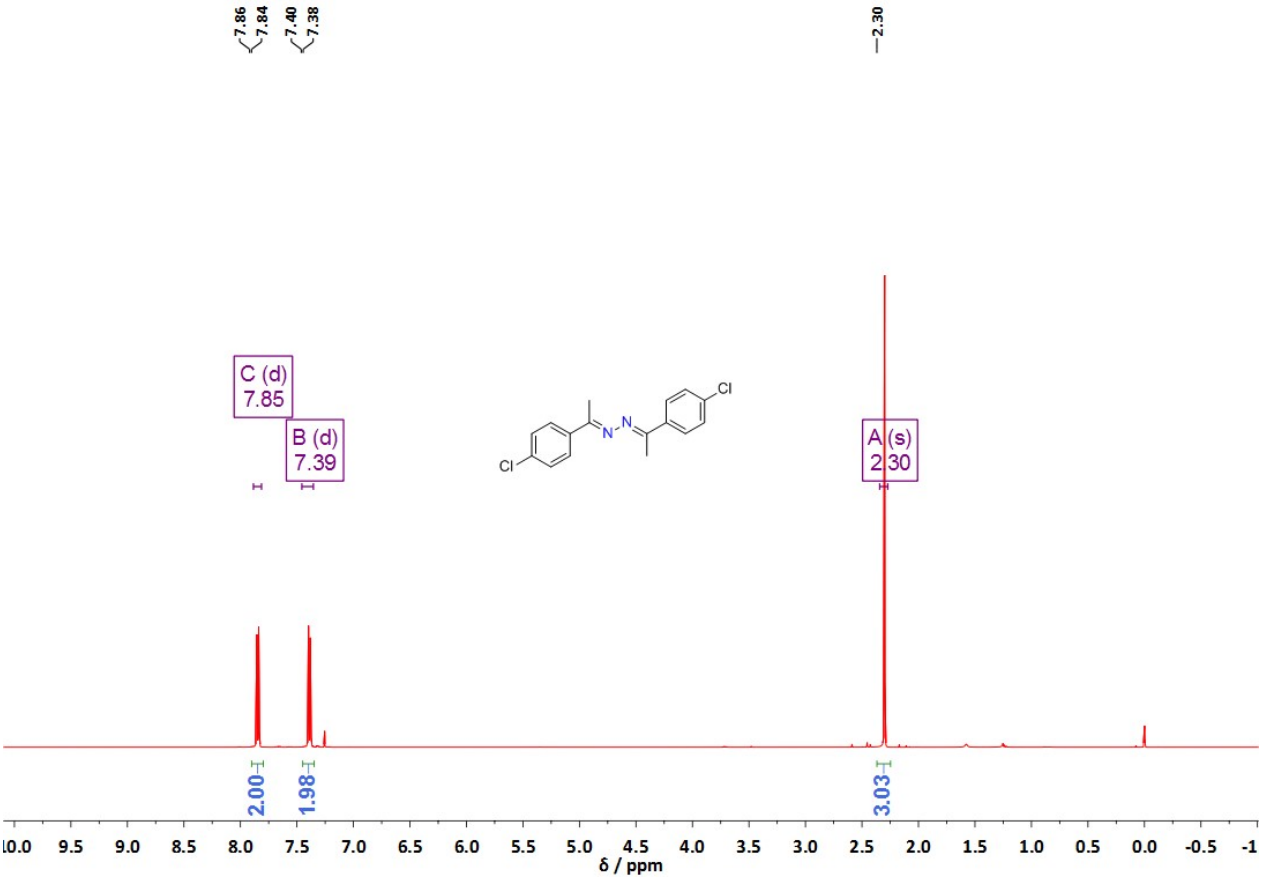


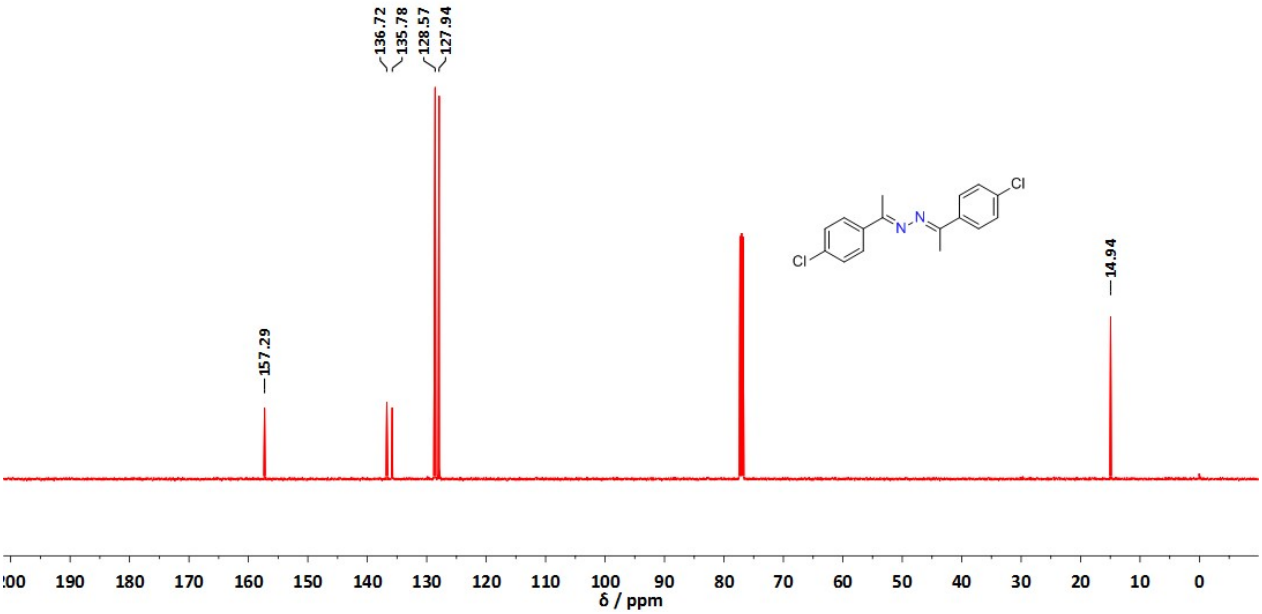
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6g



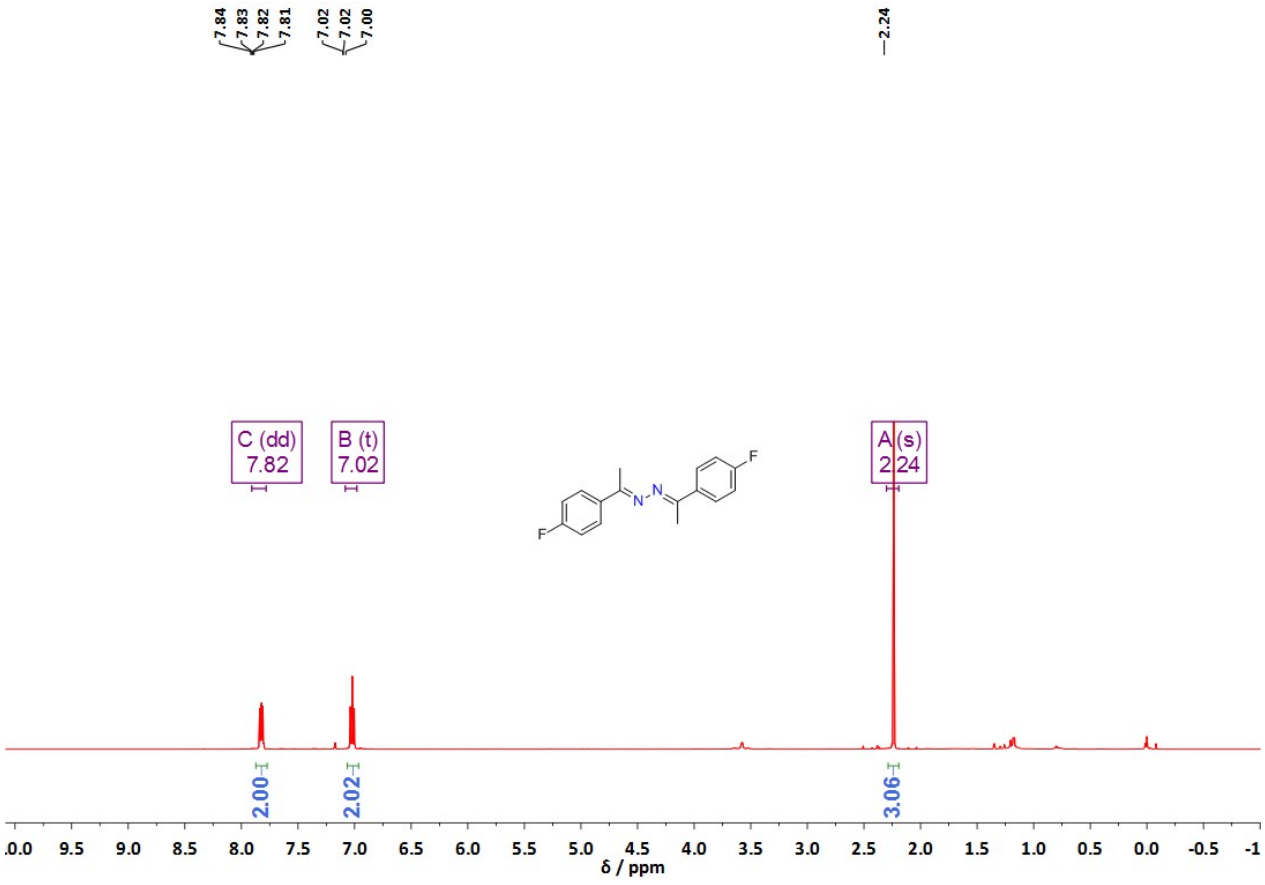


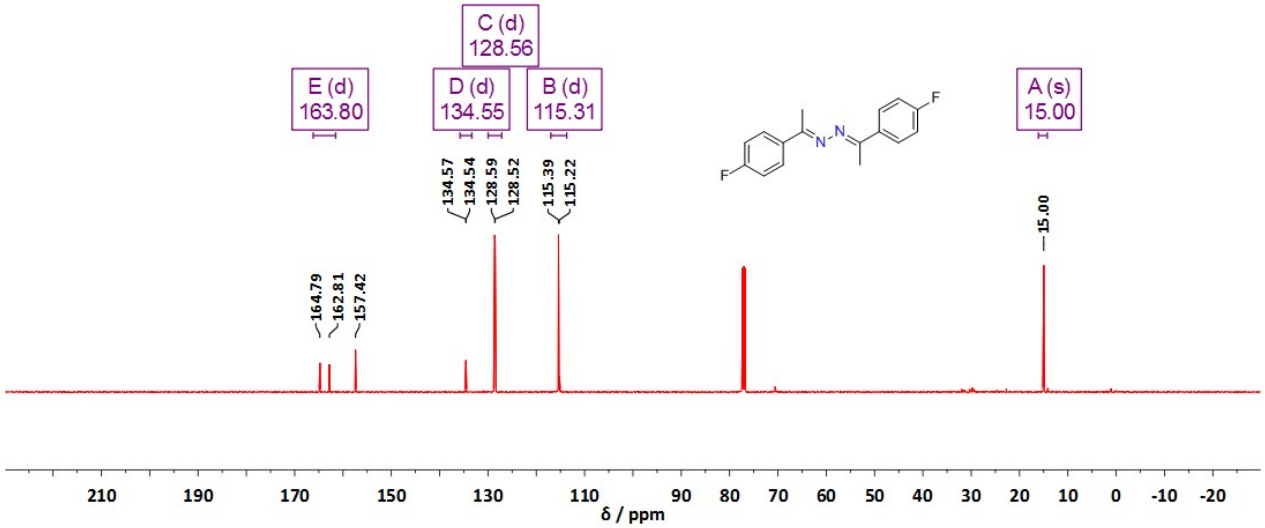
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6h



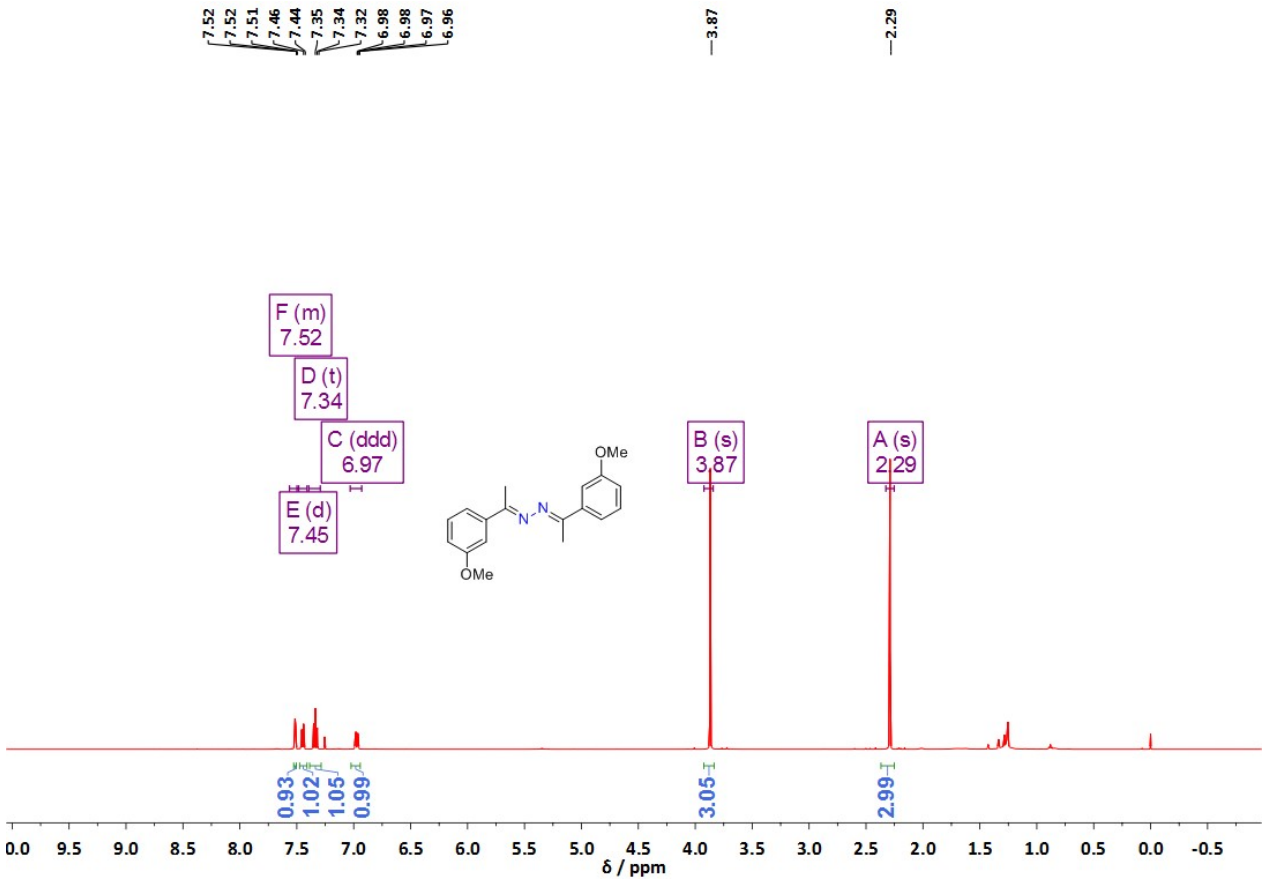


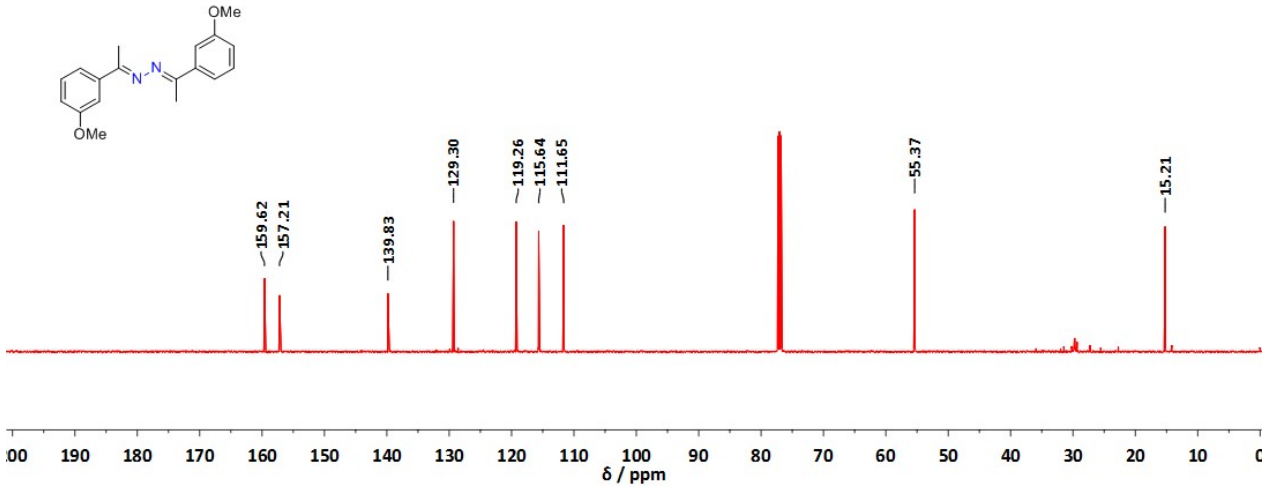
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6i



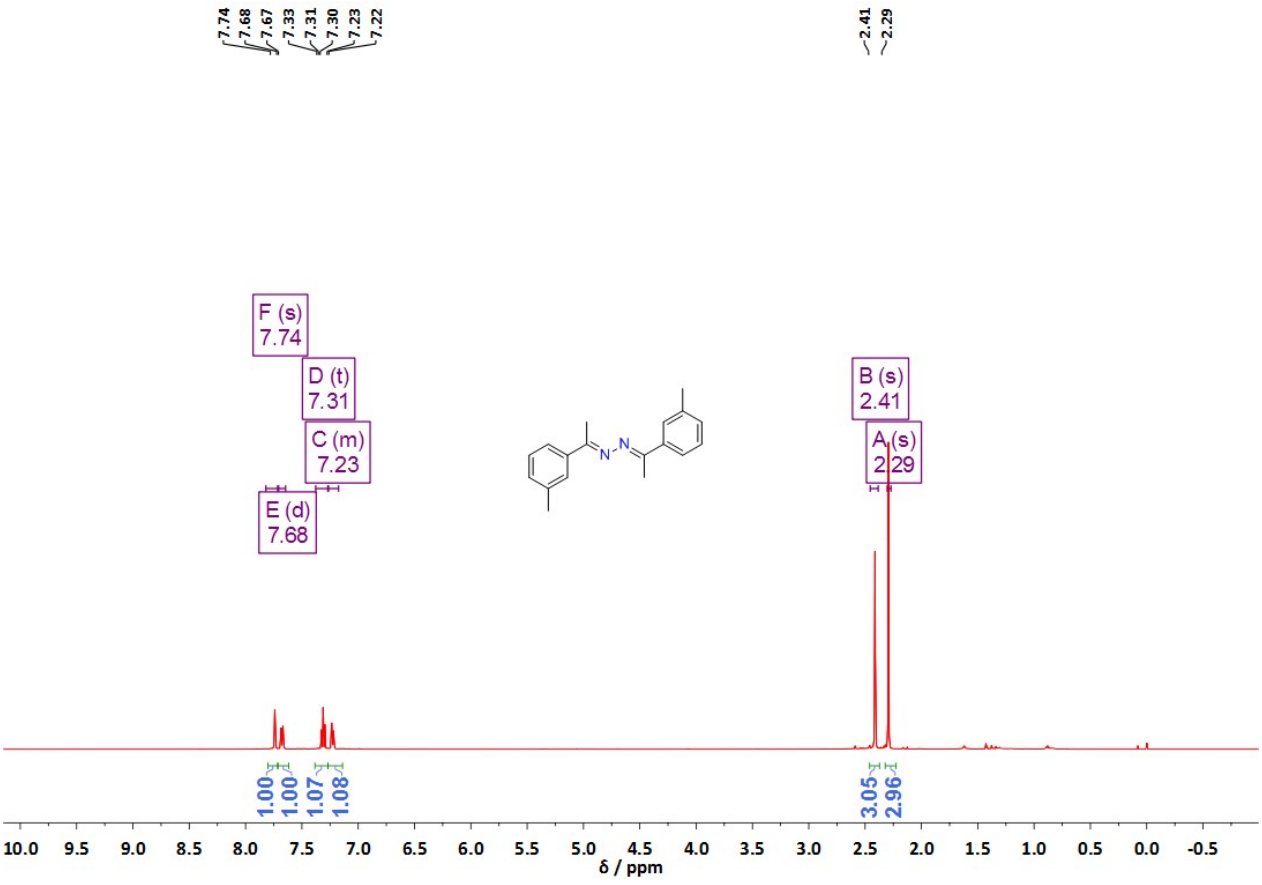


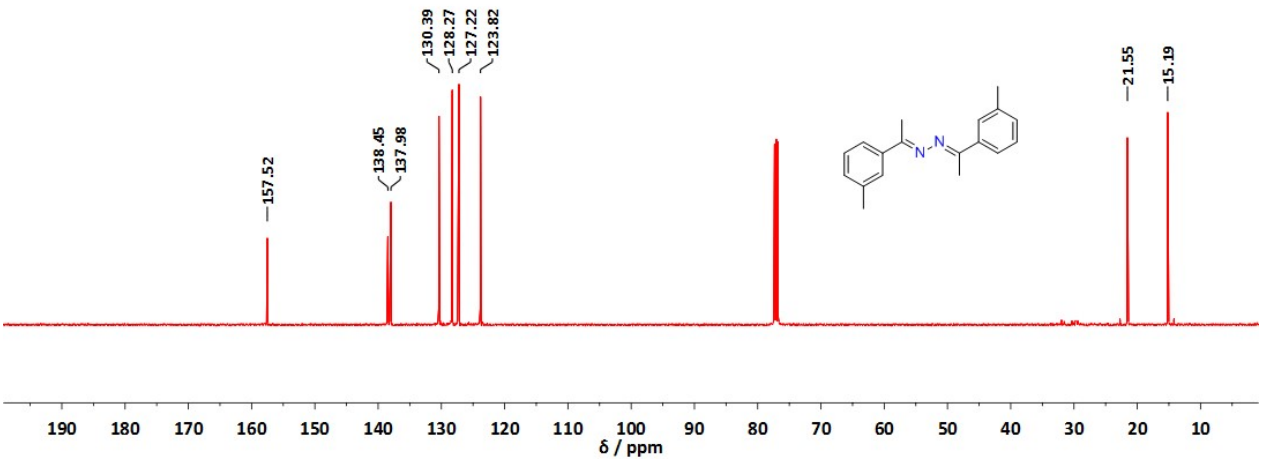
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6j



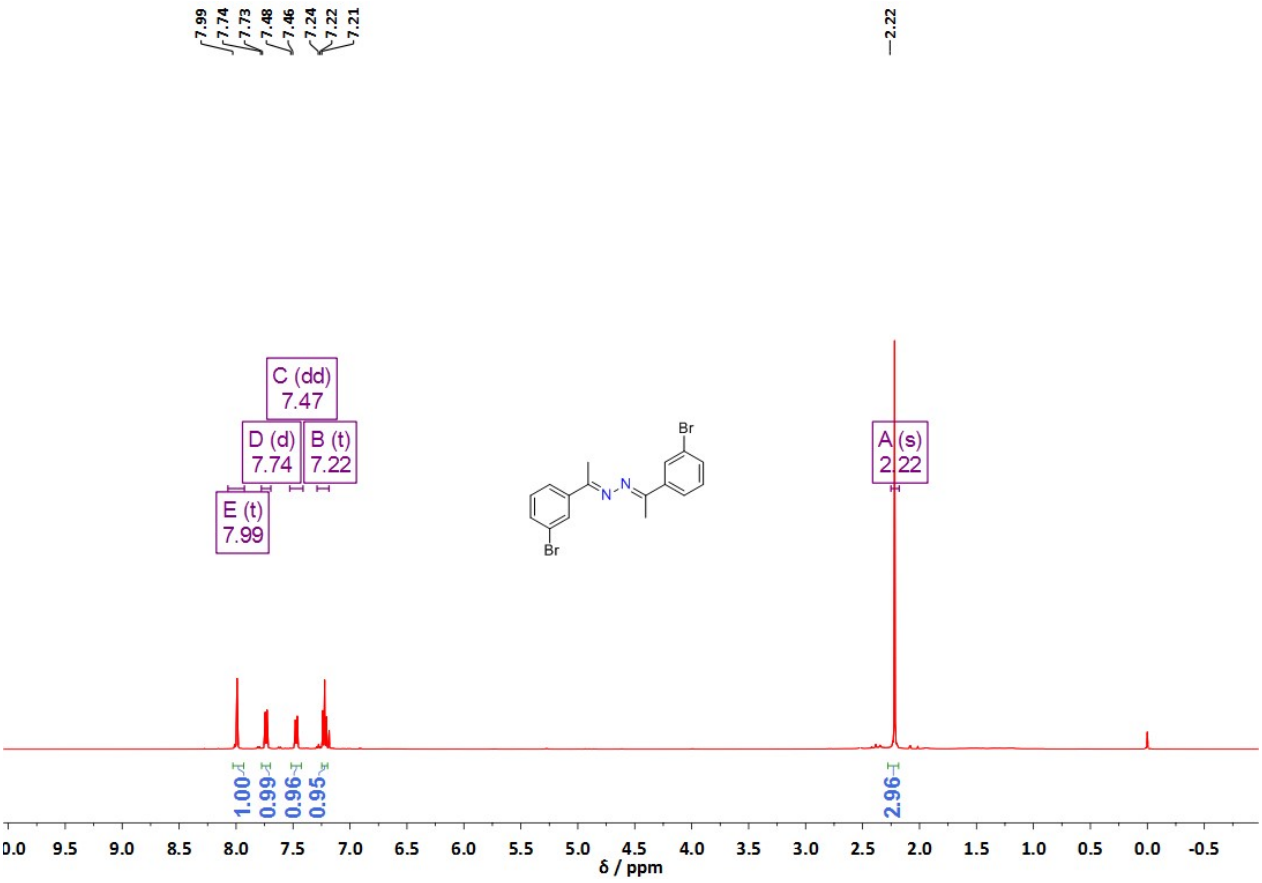


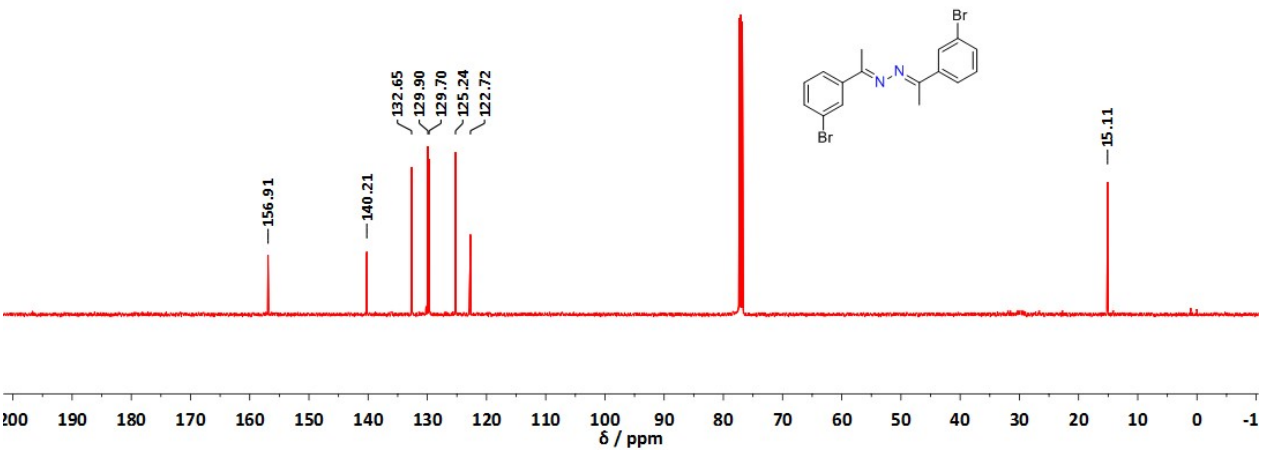
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6k



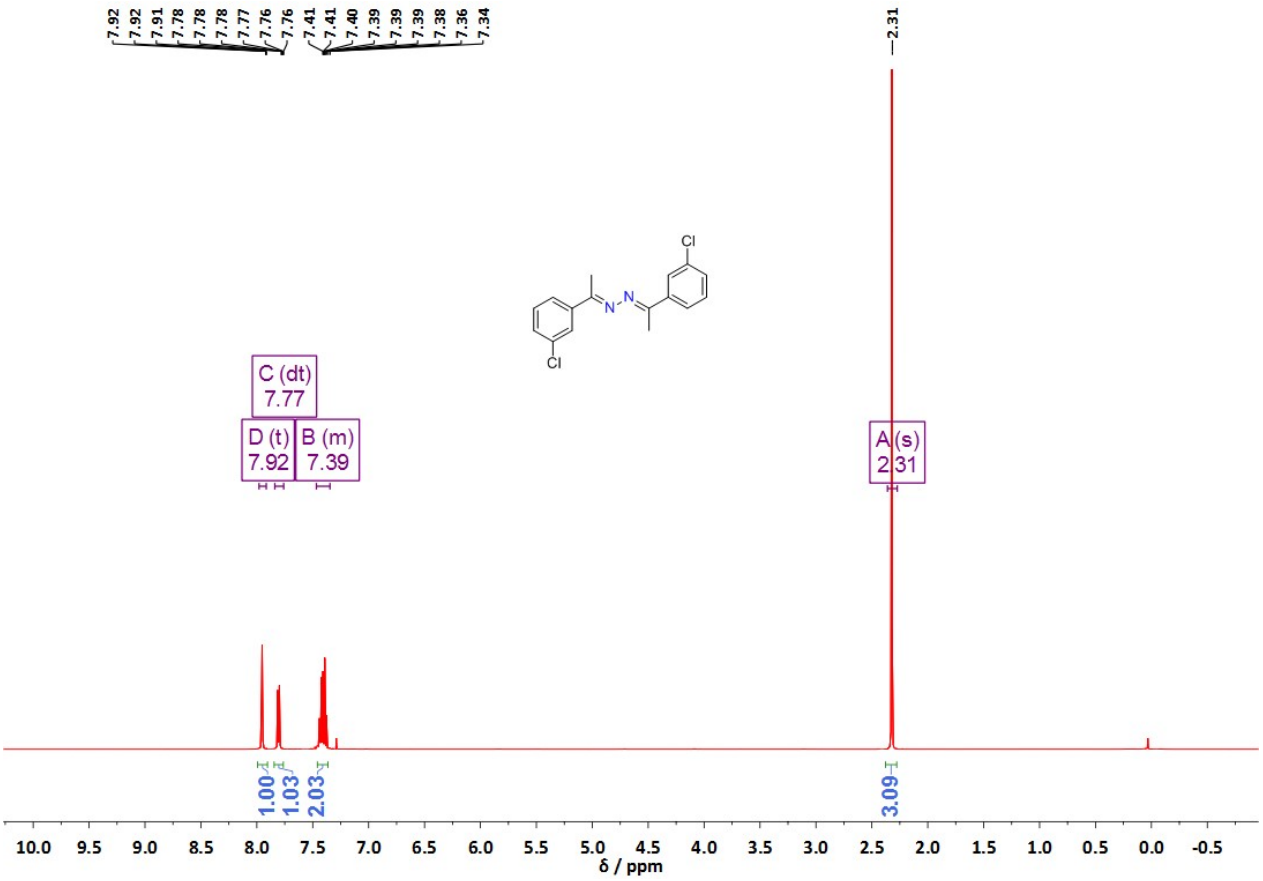


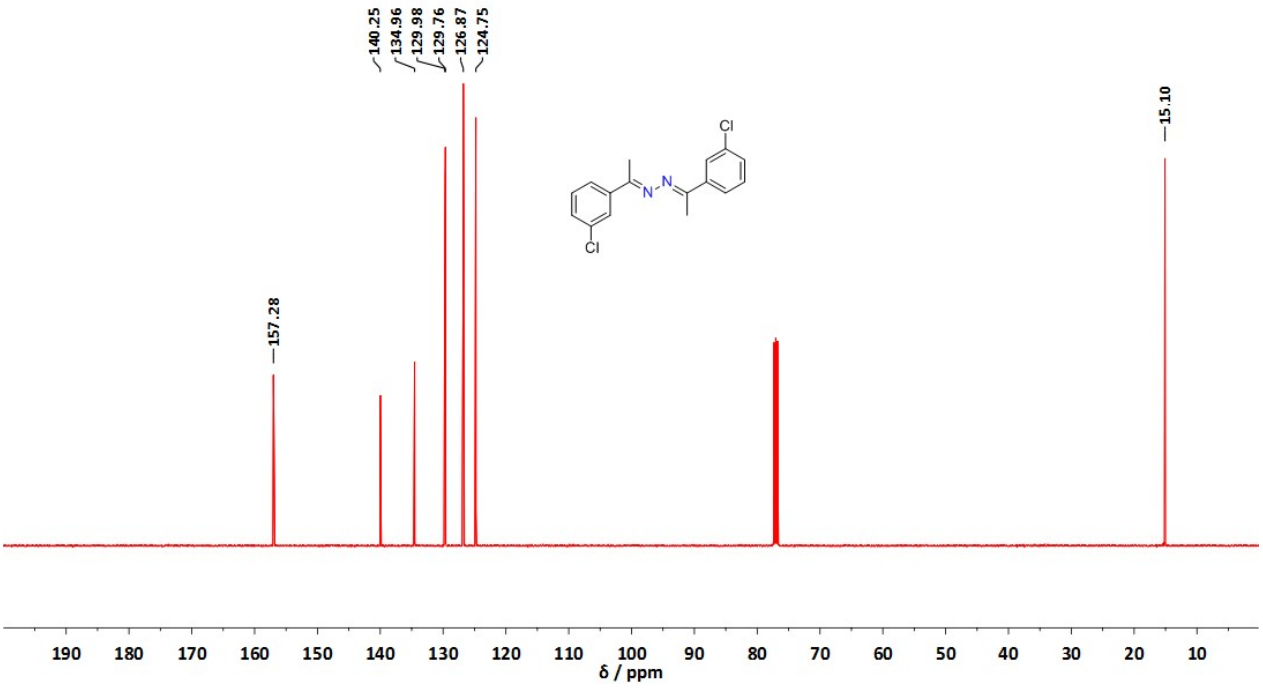
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6l



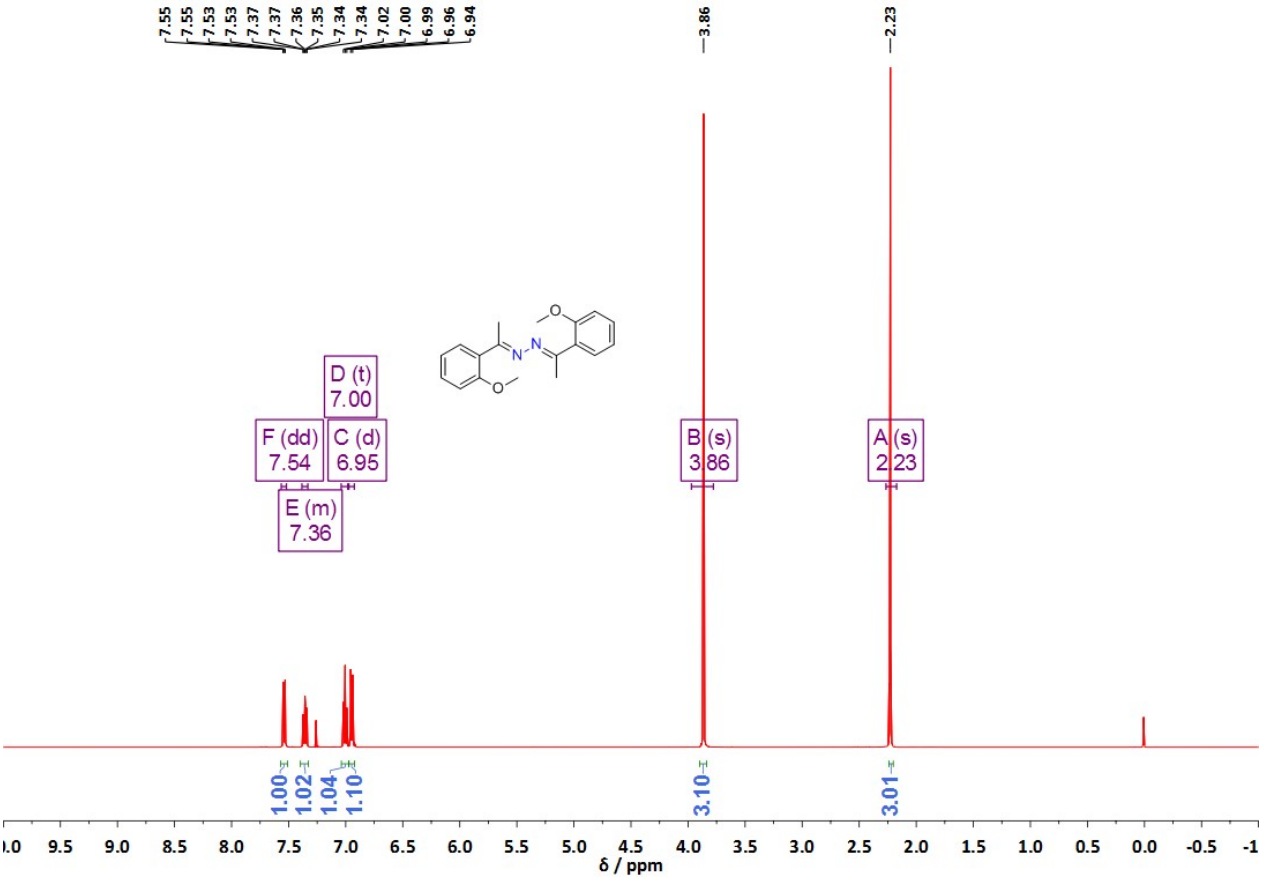


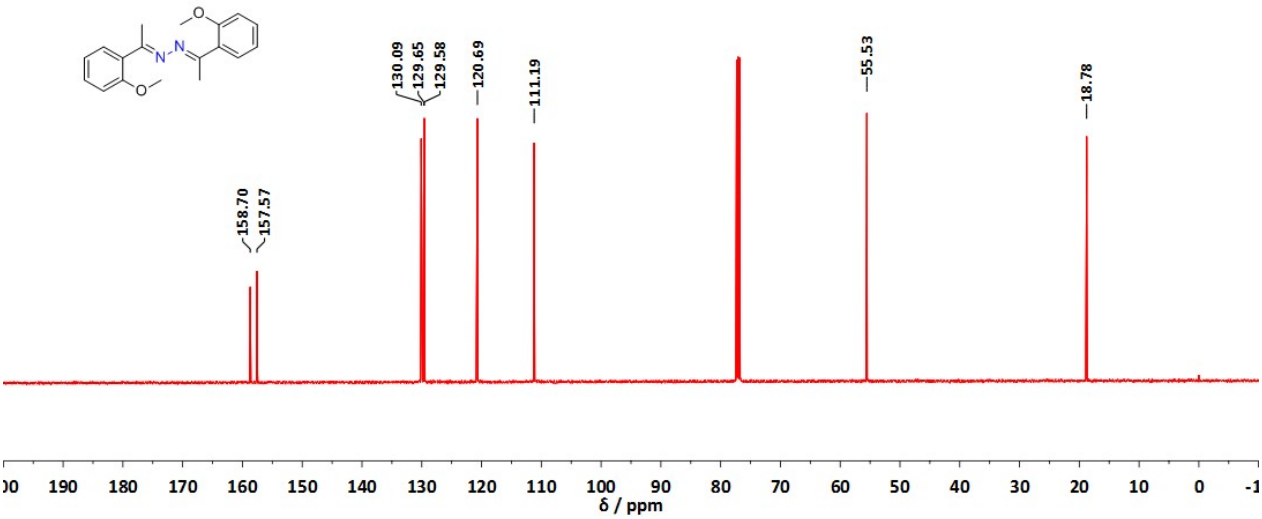
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6m



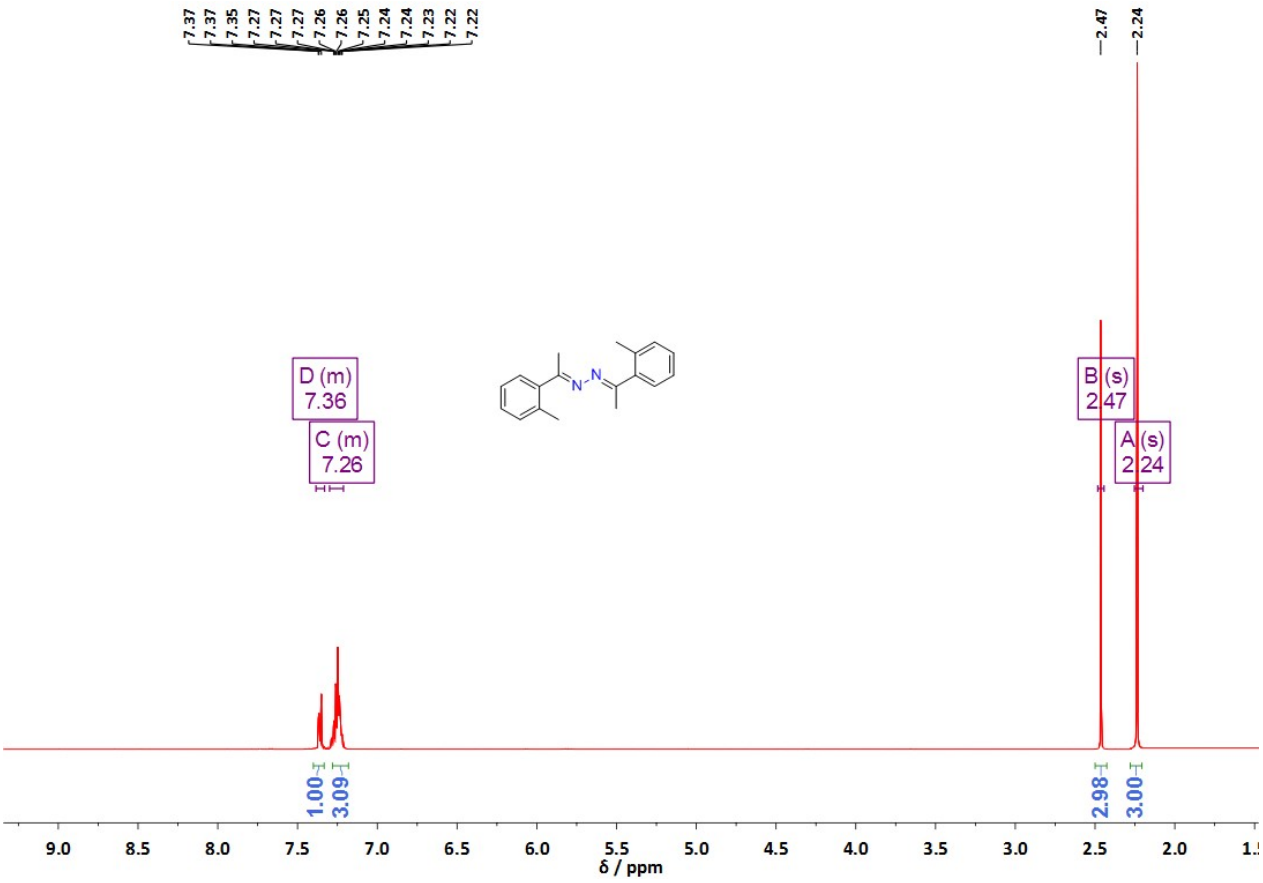


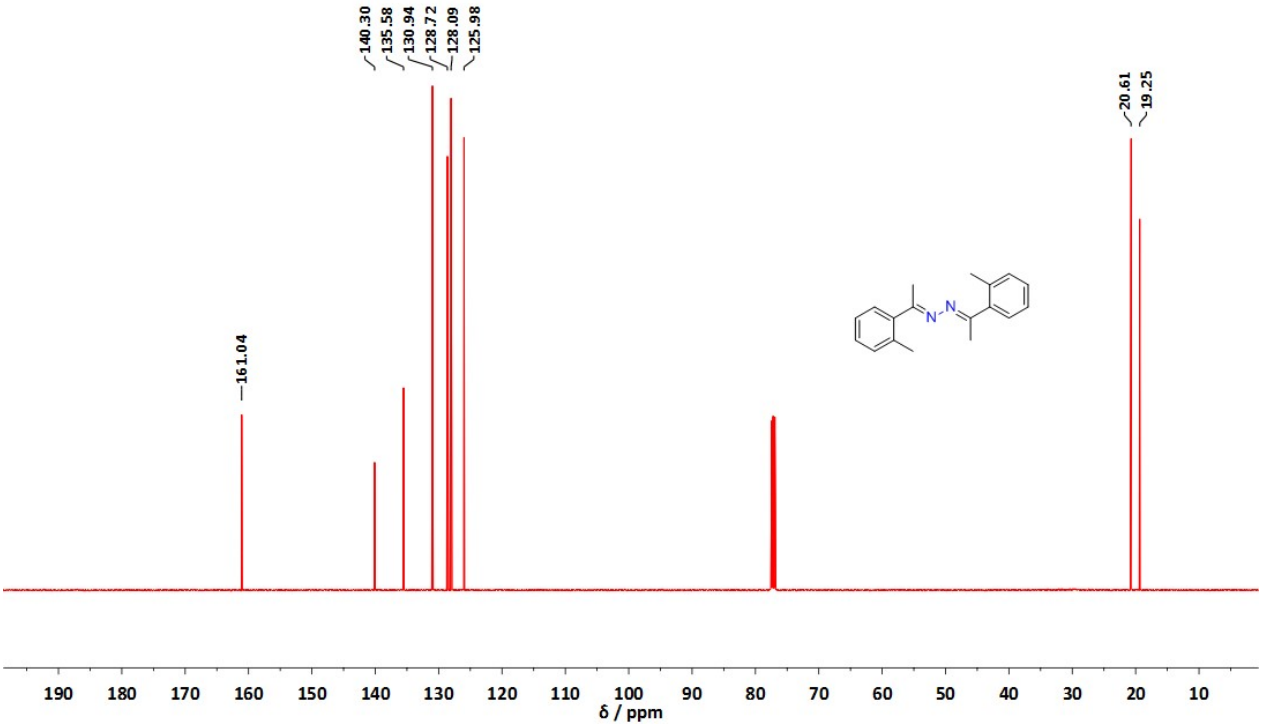
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6n



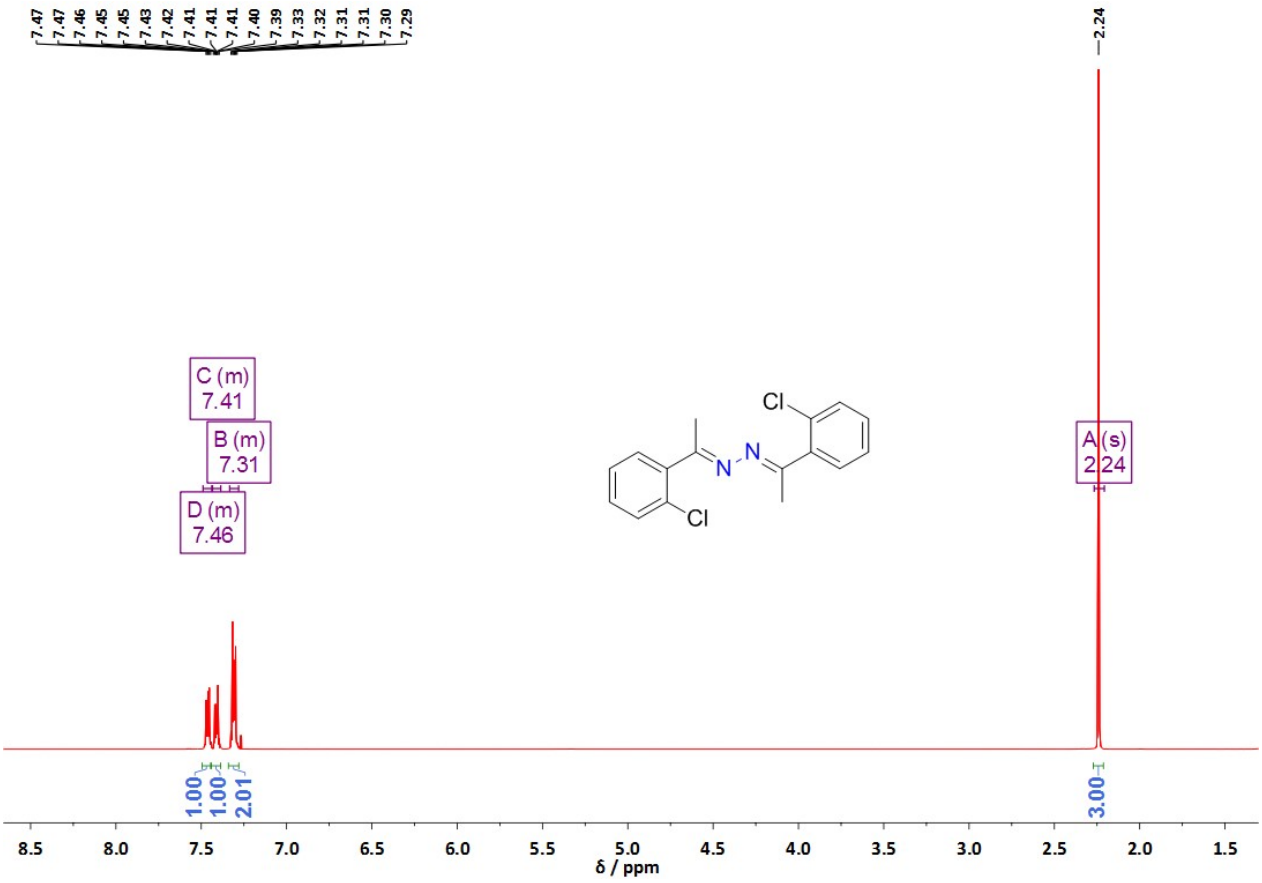


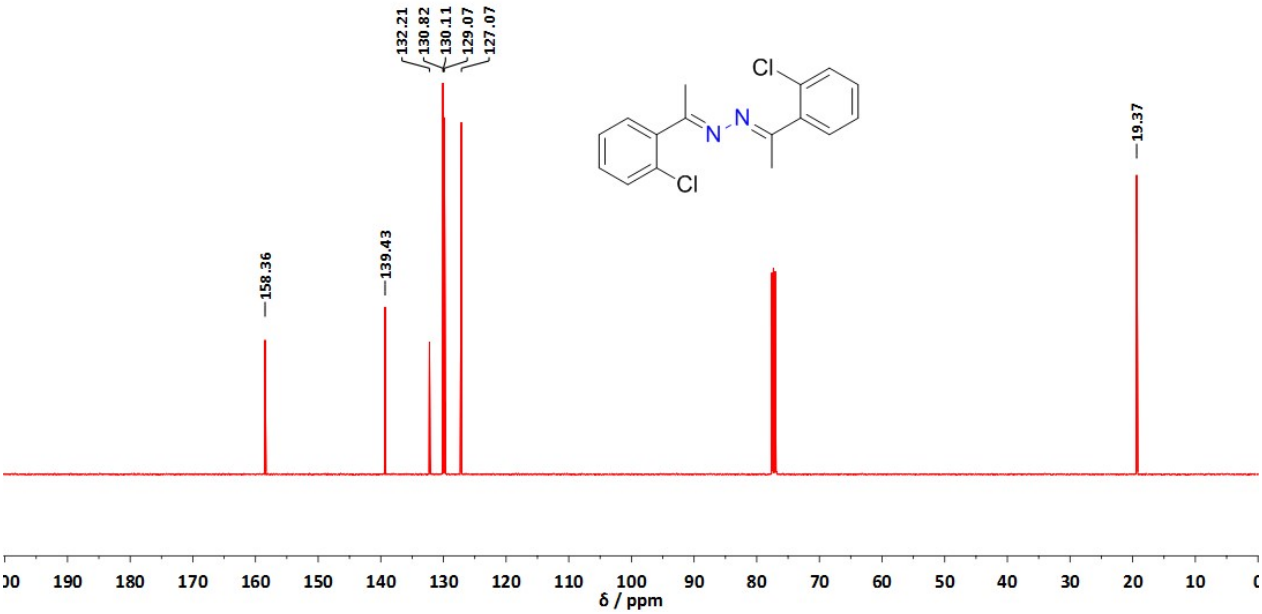
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6o



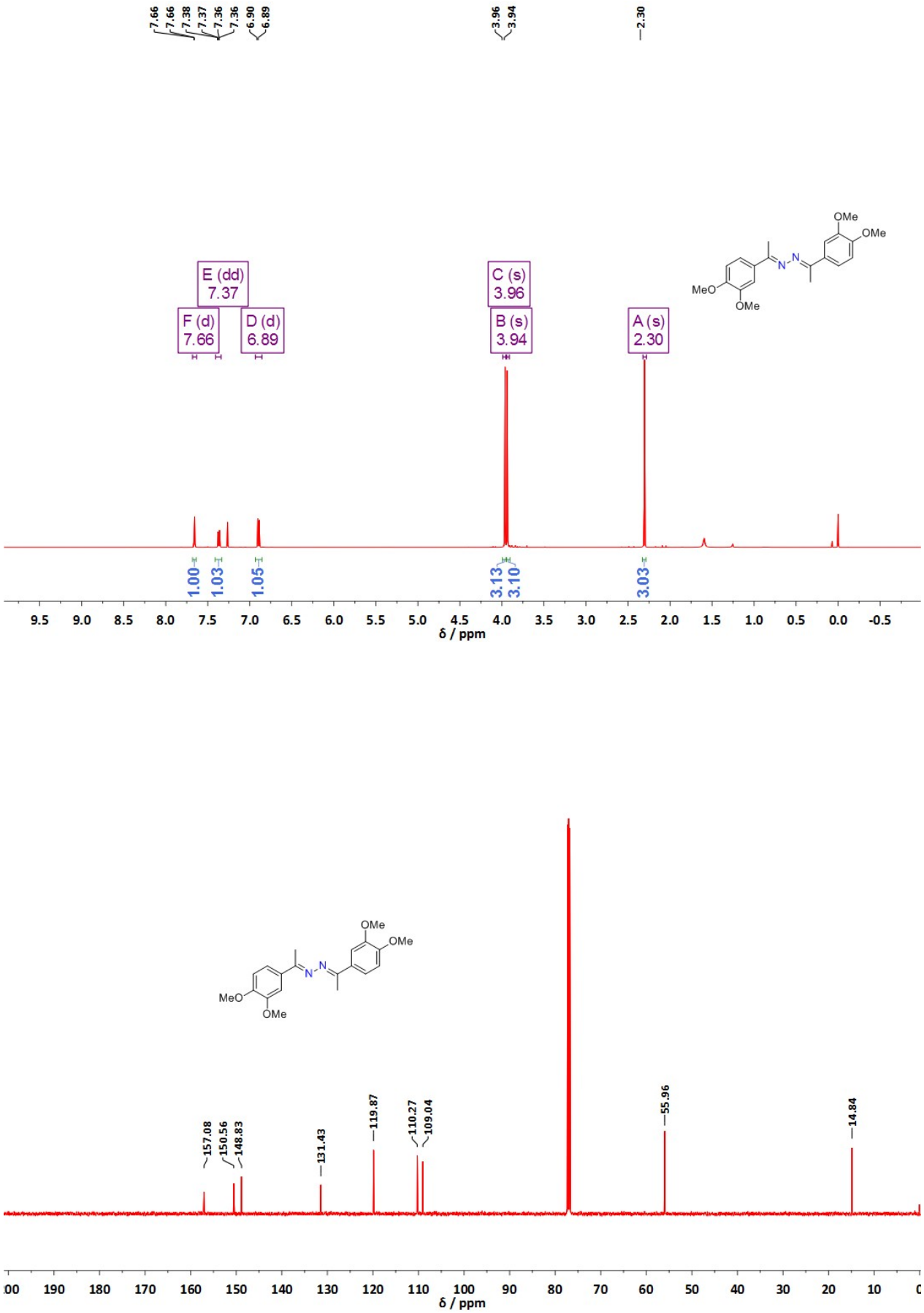


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6p

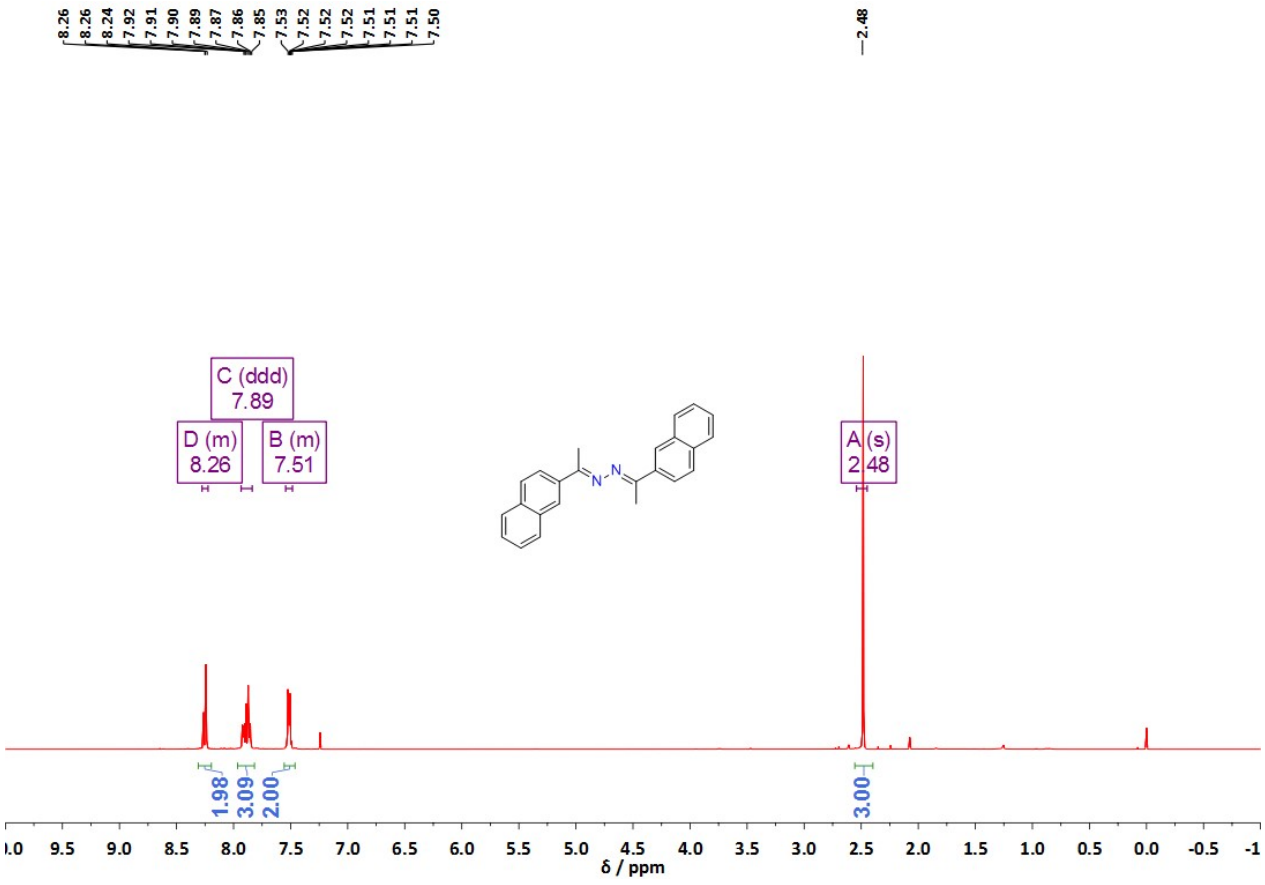


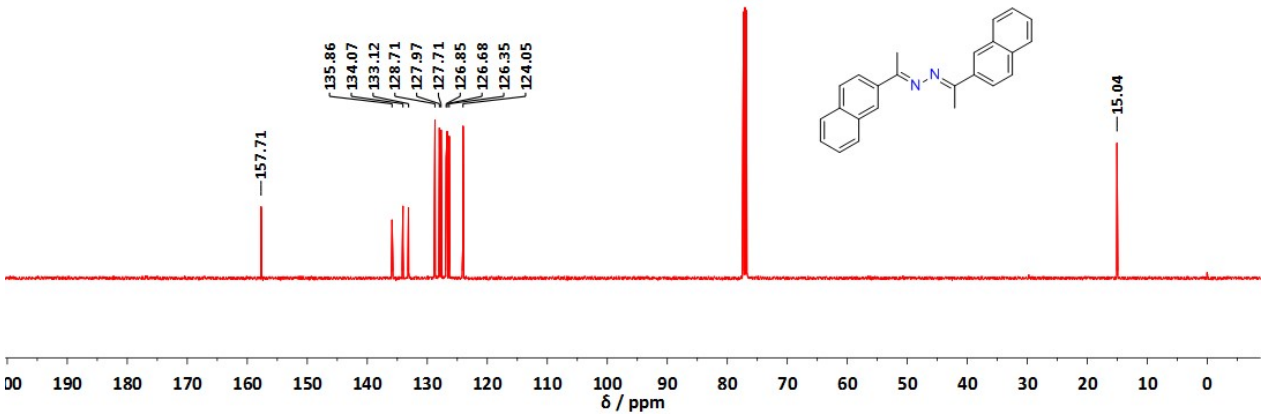


^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6q

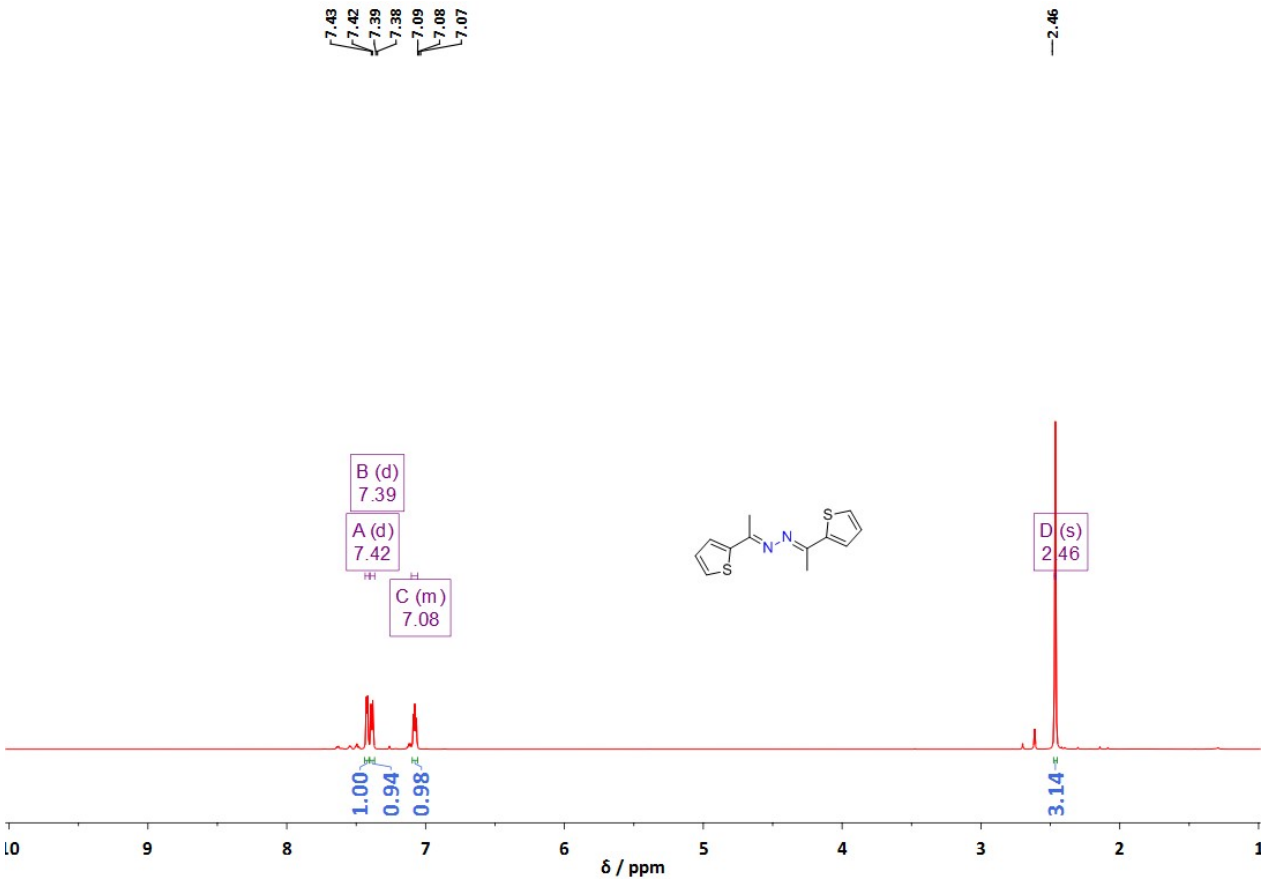


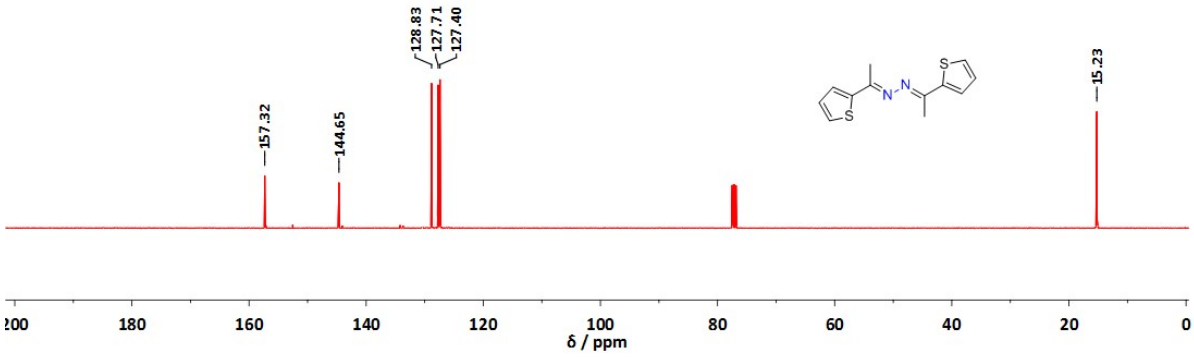
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6r



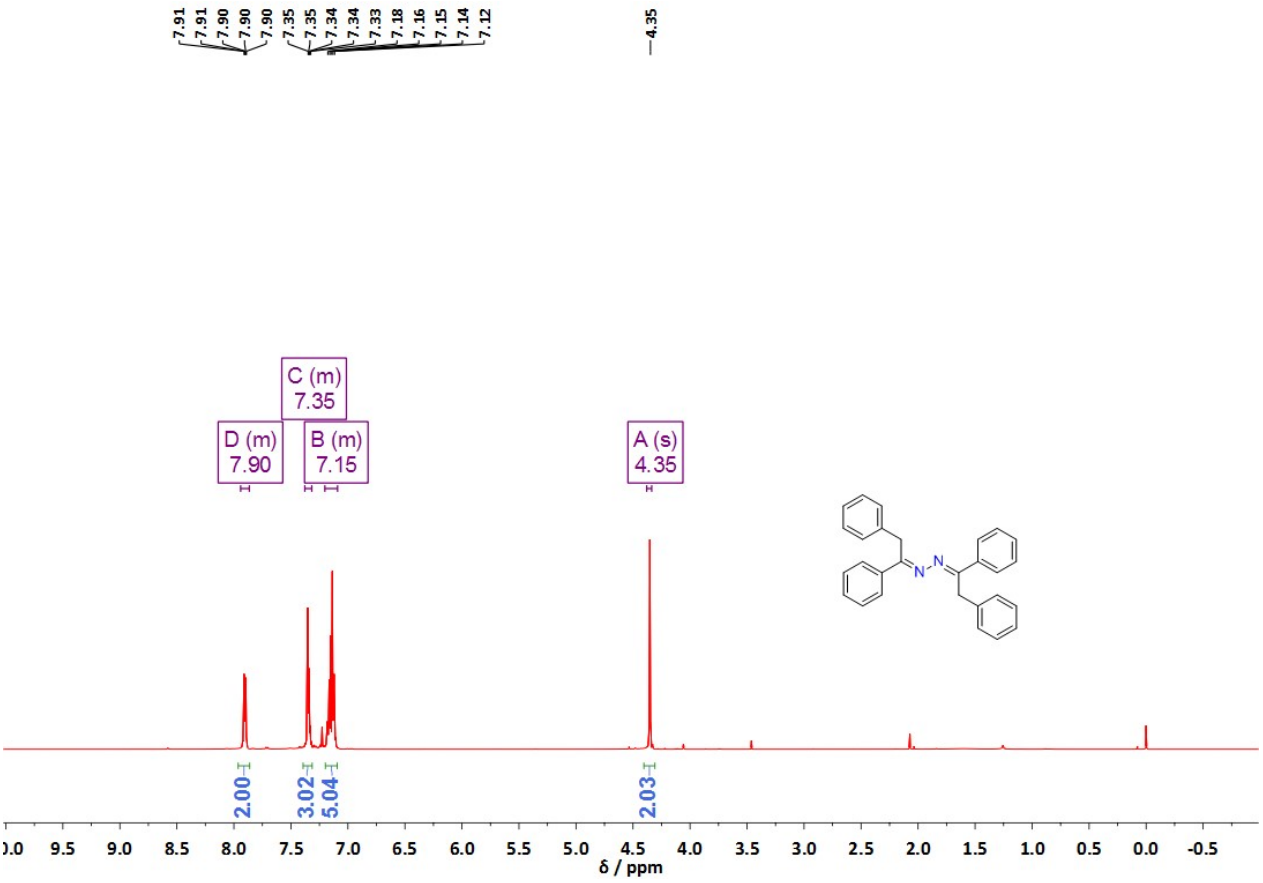


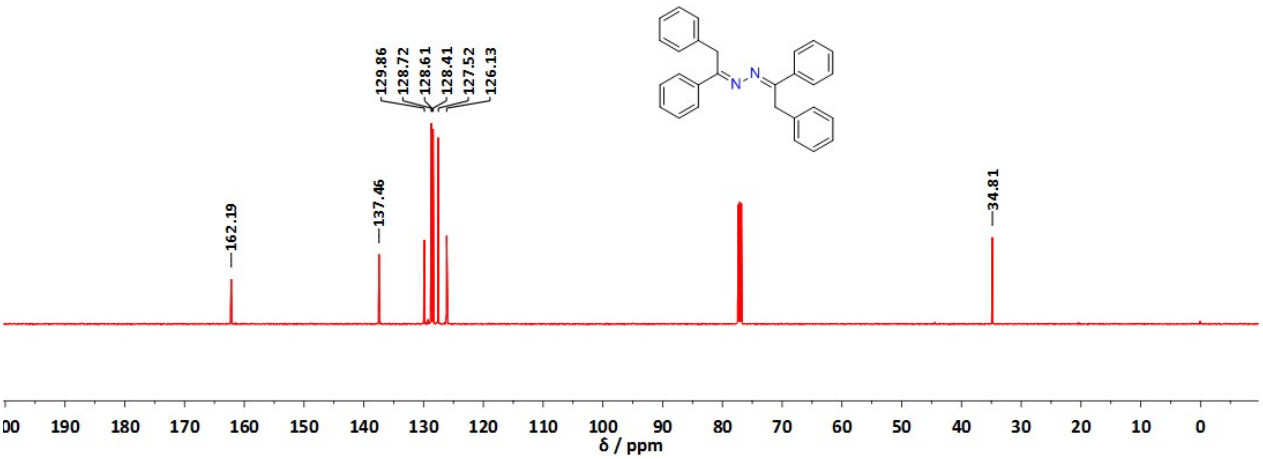
^{1}H NMR spectrum (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 6s



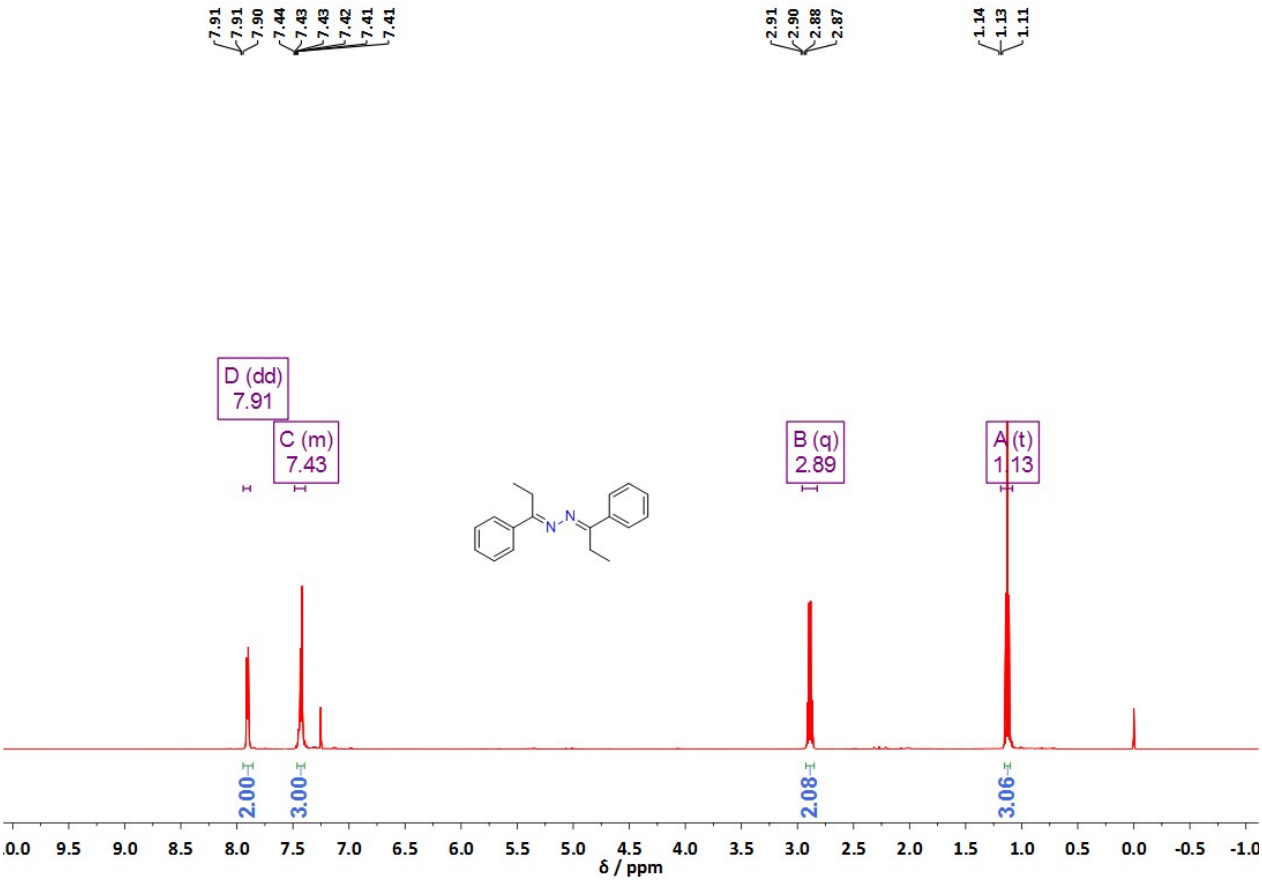


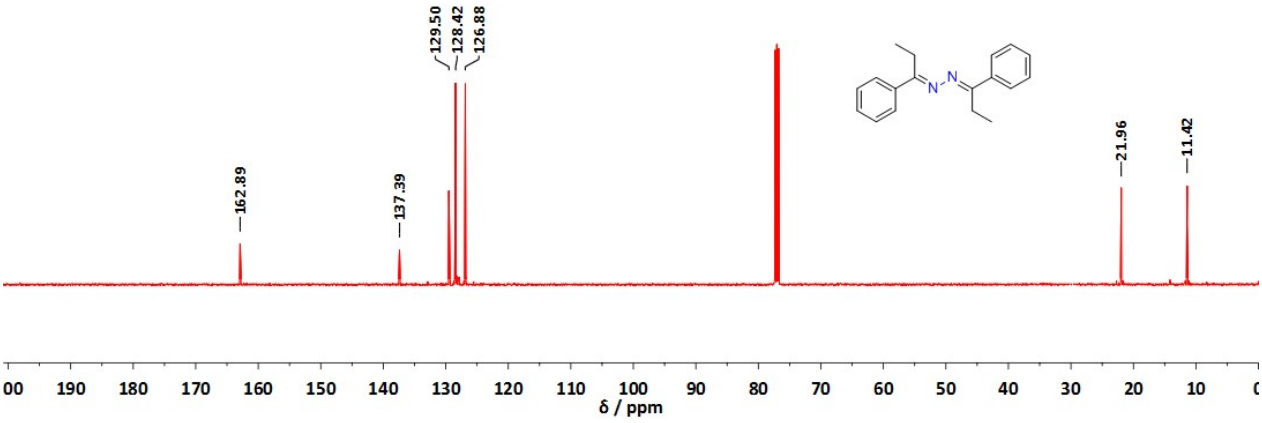
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6t



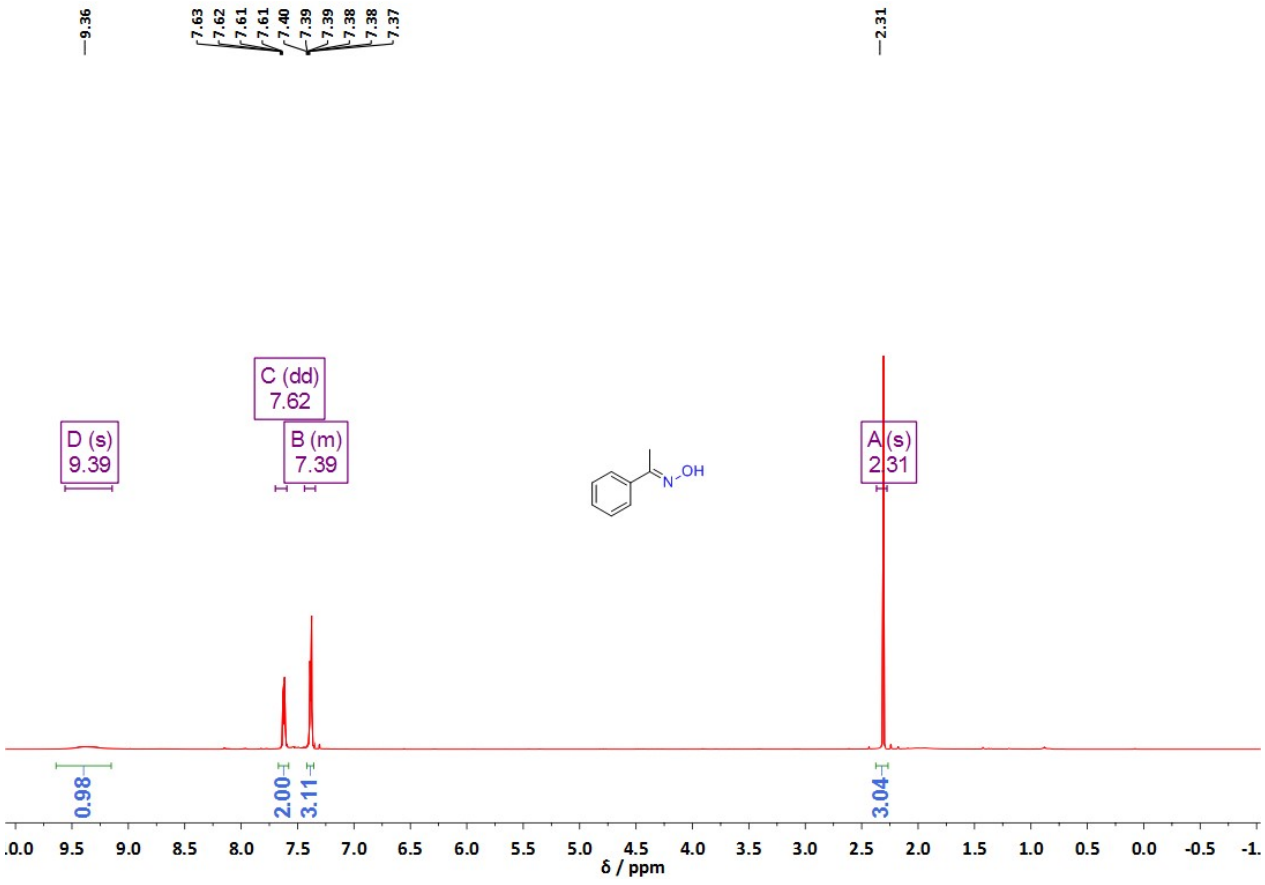


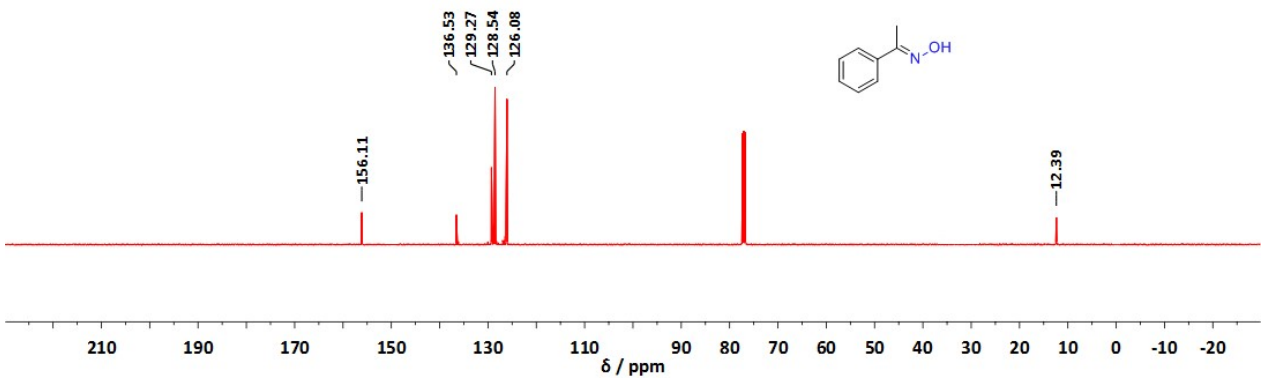
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6u



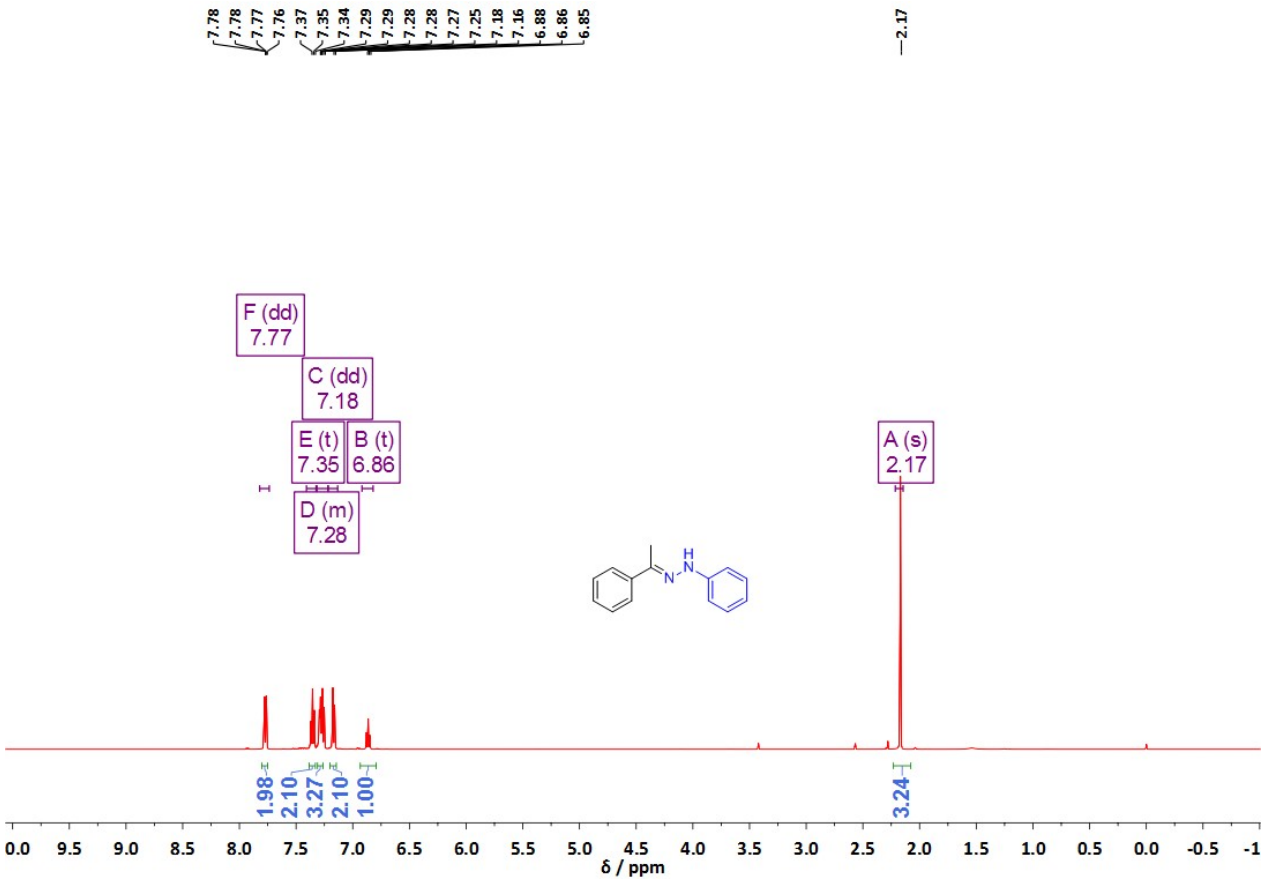


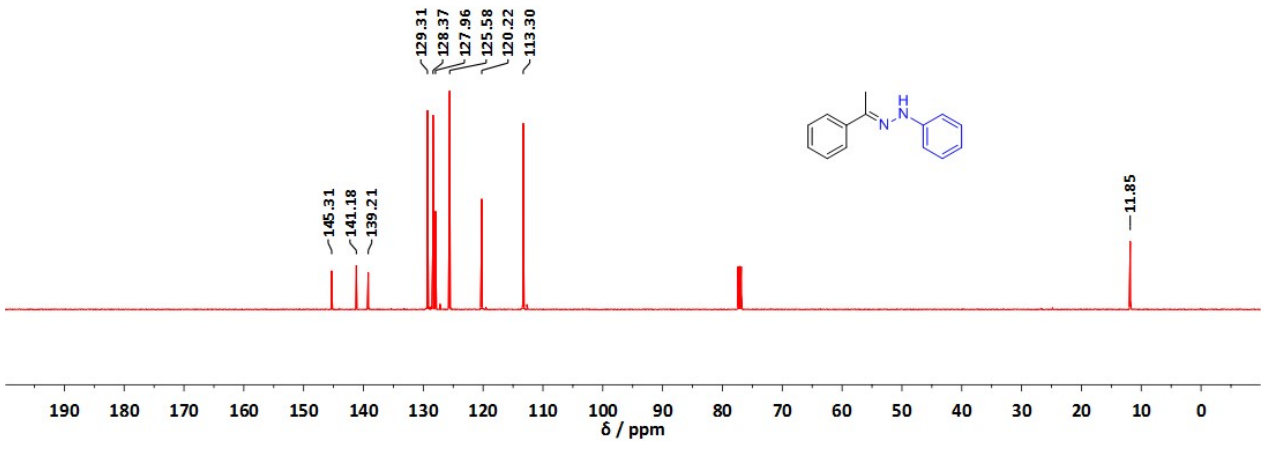
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6v





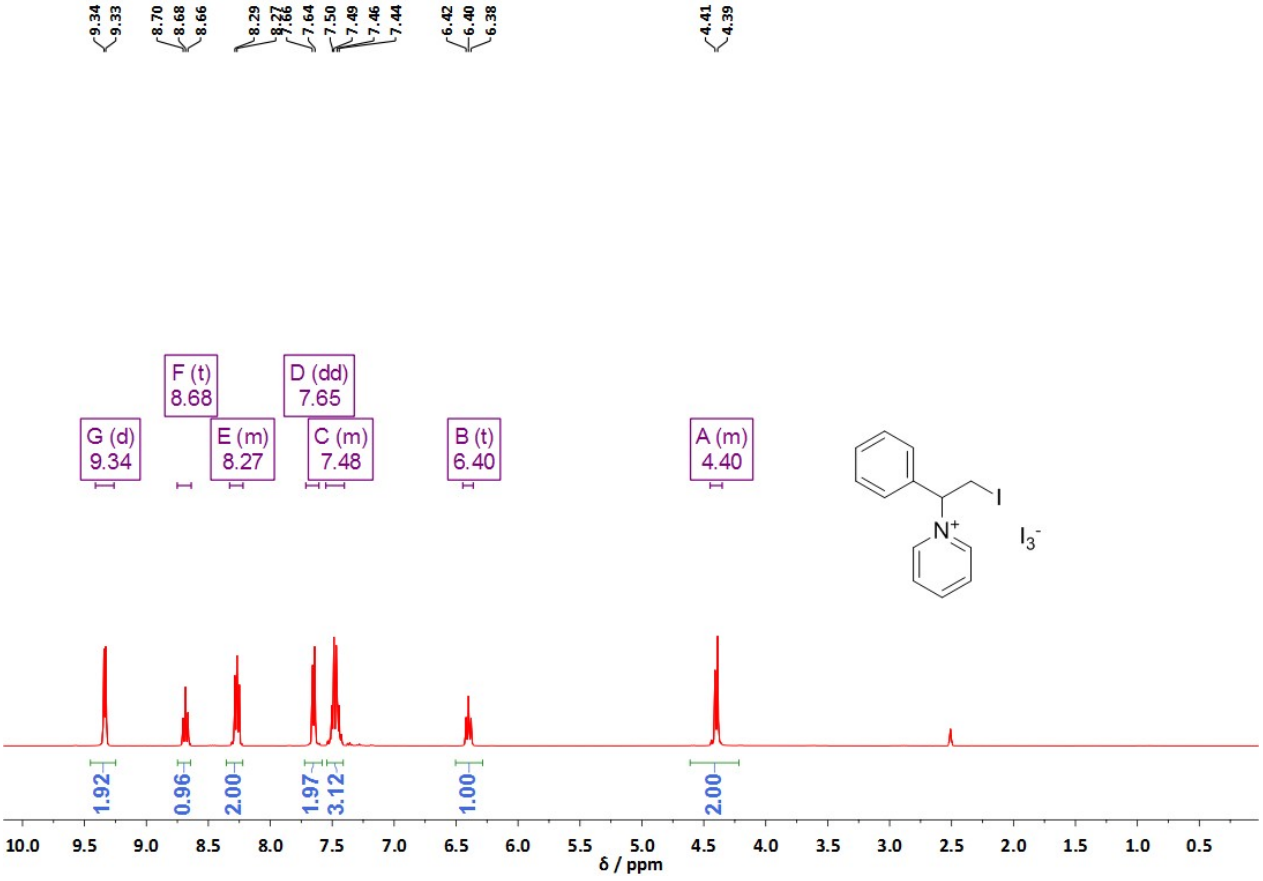
^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 6w

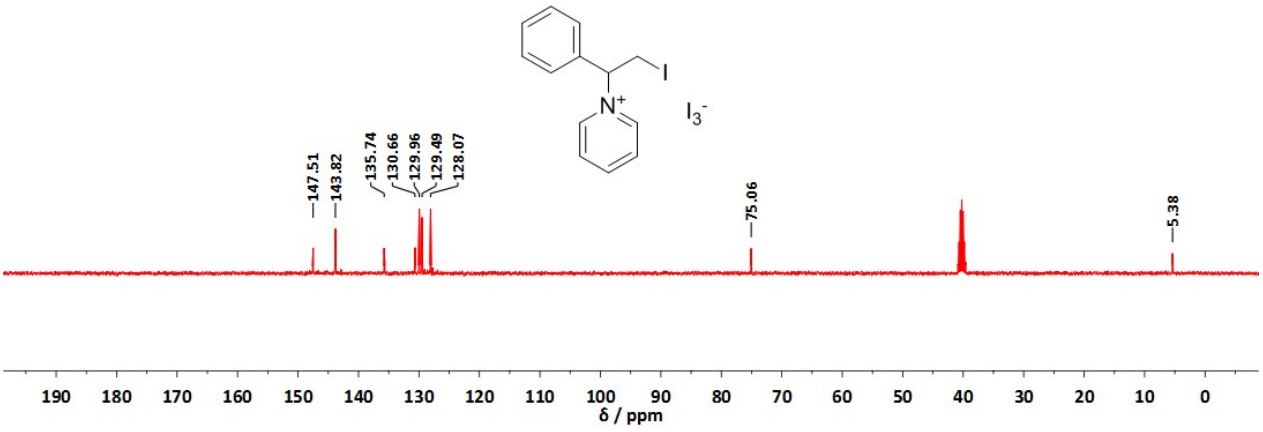




^{1}H NMR spectrum (400 MHz, DMSO-d_6) and ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of

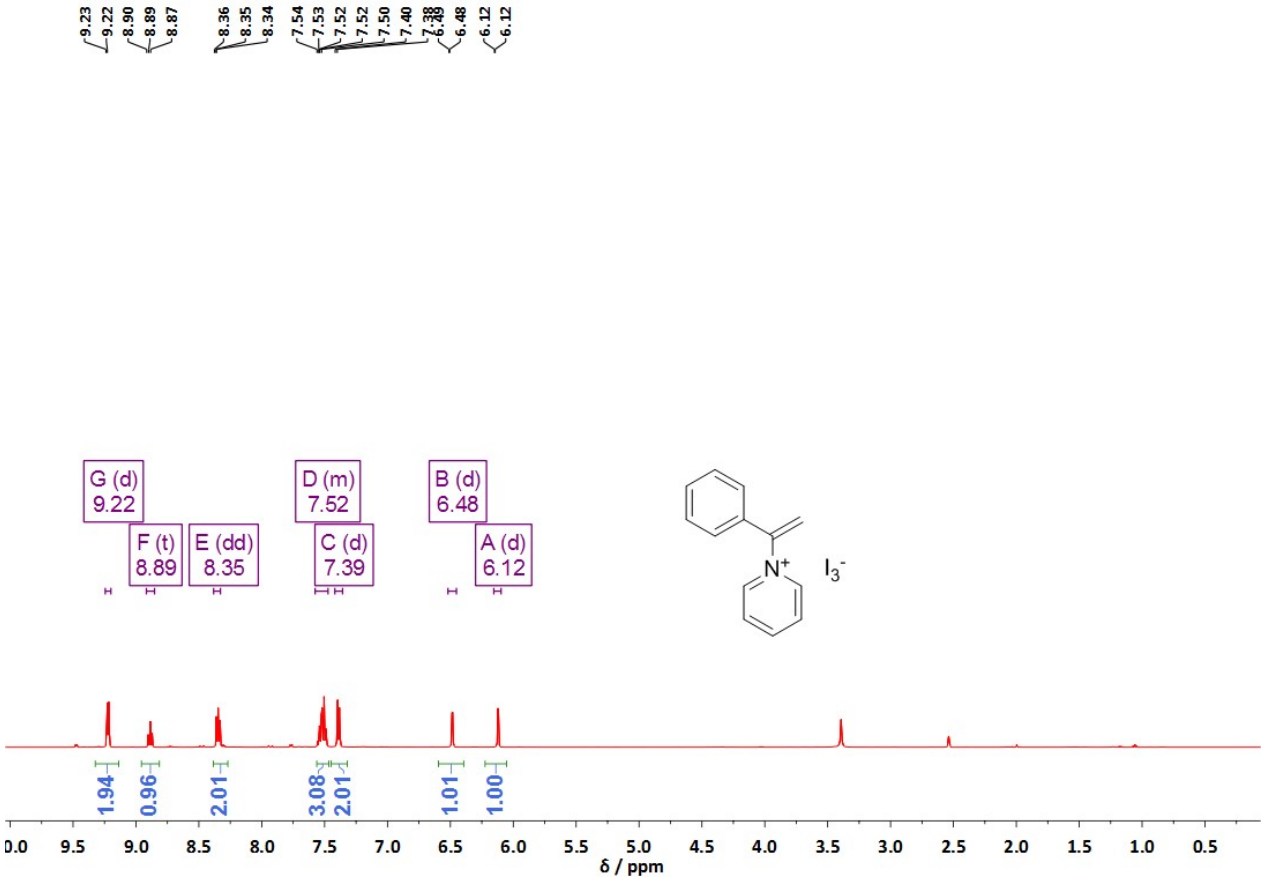
3a

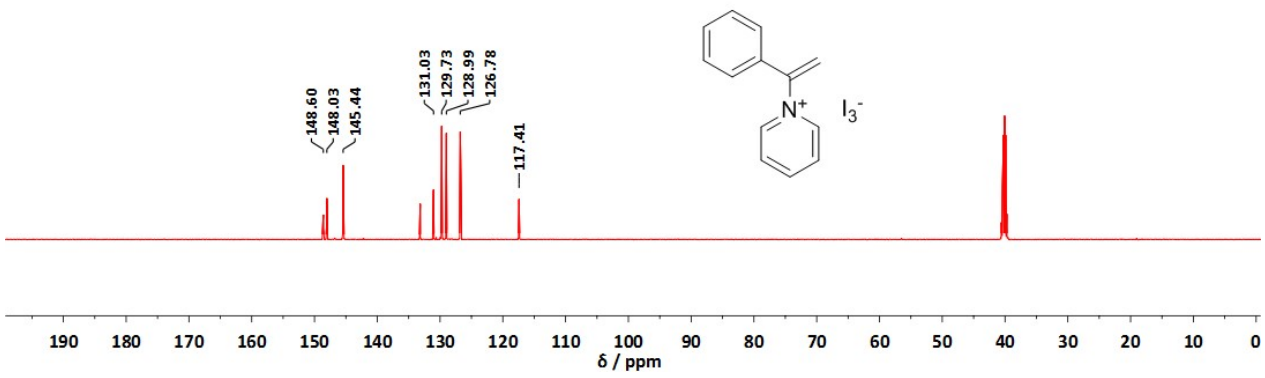




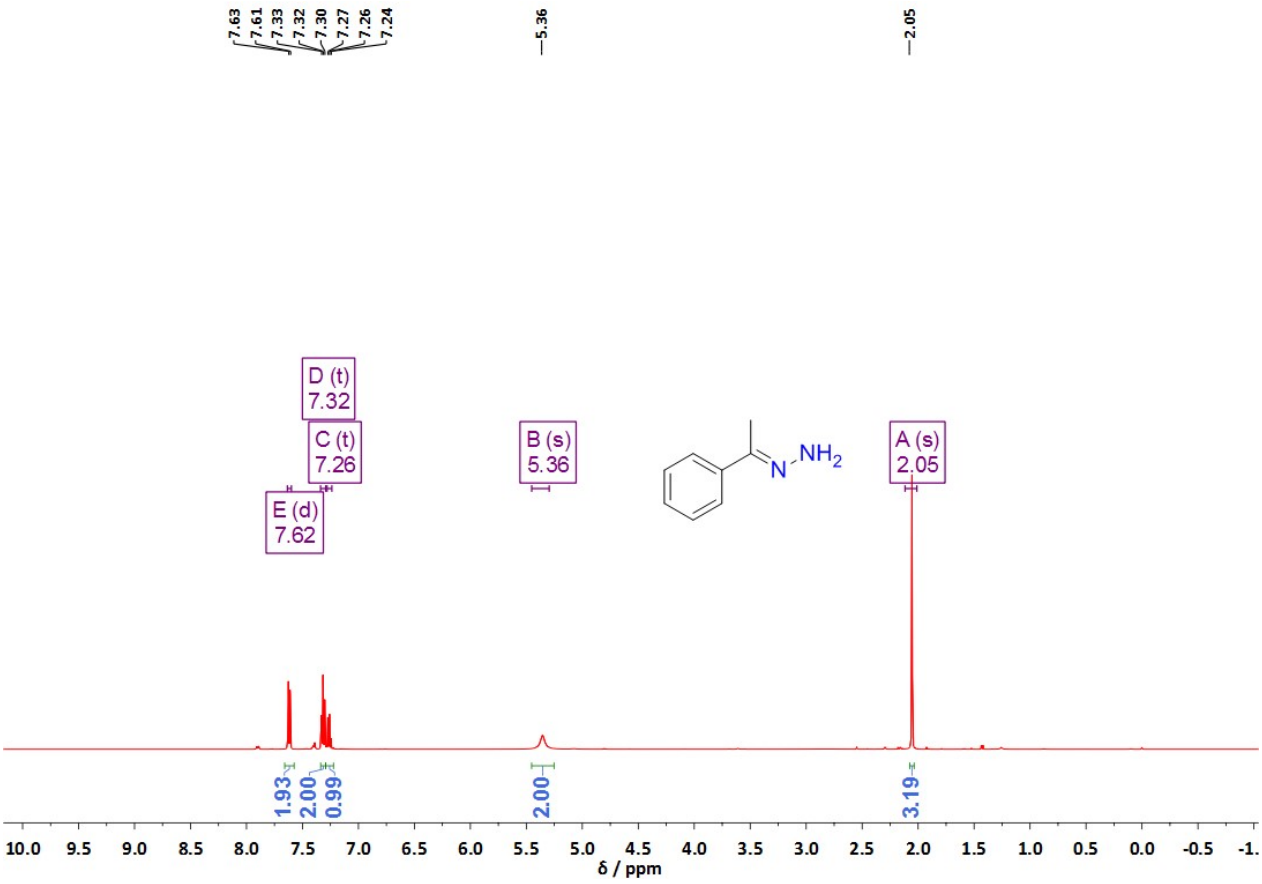
^{1}H NMR spectrum (500 MHz, DMSO-d_6) and ^{13}C NMR spectrum (126 MHz, DMSO-d_6) of

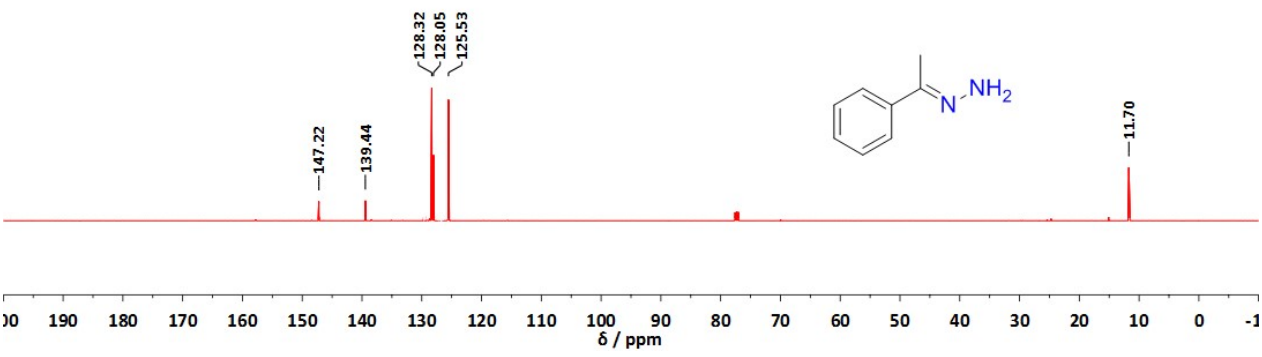
4a





^{1}H NMR spectrum (500 MHz, $CDCl_3$) and ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of 5a


7.63
7.61
7.33
7.32
7.30
7.27
7.26
7.24
5.36
2.05
D (t)
7.32
C (t)
7.26
E (d)
7.62
B (s)
5.36
A (s)
2.05
NH2
1.93
2.00
0.99
2.00
3.19
δ / ppm


128.32
128.05
125.53
147.22
139.44
NH2
11.70
δ / ppm