Supporting Information

1,1-Diaminoazines as Organocatalysts in phospha-Michael addition reaction

Aabid A. Wani,[a] Sumit S. Chourasiya,[a] Deepika Kathuria[b] and Prasad V. Bharatam*[a]

Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research (NIPER), SAS Nagar – 160062, Punjab, India.

Email: pvbharatam@niper.ac.in

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1. General Information

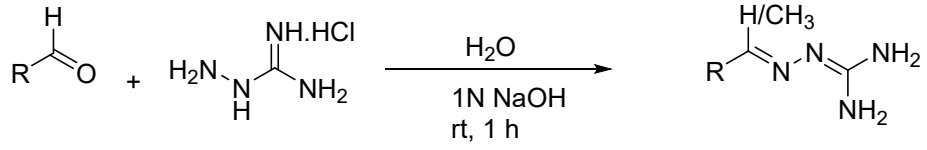
The reagents and chemicals required for the study were procured and all the reagents were used as such without further purification unless otherwise mentioned. The progress of the reaction was monitored by Thin Layer Chromatography (TLC) performed on silica gel aluminium plates and visualization was done by UV light. ^{1}H NMR and ^{13}C NMR spectra were recorded at 500 MHz

and 100 MHz respectively, with TMS as an internal standard. ^{31}P NMR was recorded at 202.4 MHz with TMS as an internal standard. The ^{1}H NMR and ^{13}C NMR spectra were recorded using $CDCl_3$ at 7.25 ppm and 77.31 ppm and for a few compounds DMSO-*d6* at 2.50 ppm and 39.51 ppm respectively. Chemical shift (δ) are reported in parts per million (ppm). Coupling constants (*J*) were reported in hertz (Hz). The abbreviations used to characterize the signals are as follows: s = singlet, m = multiplet, d = doublet, br. s. = broad singlet, dd = doublet of doublet, t = triplet. High resolution mass spectra were recorded using ESI-TOF method.

2. Synthetic Procedures

2.1 Synthesis of organocatalyst (C):

To the substituted carboxaldehyde and aminoguanidine hydrochloride solution in H_2O was added 1N NaOH (2 mL) and the reaction mixture was stirred for 1-2 h, until precipitate is formed. The resultant precipitate was filtered and dried to afford the desired organocatalysts in 88 to 95 % yields.[1]



5 mmol 5 mmol (**C**)

R= Ph, 2,4,6-OMePh, 1-Naphthalene Biphenyl

The products were obtained as a solid precipitates which were filtered, washed with water and dried under vacuum.

2.2 Synthesis of 3:

To the neat and dried round bottom flask with 25 mL capacity, β-nitrostyrene (**1**) (50 mg, 0.33 mmol), biphenylphosphine oxide (**2**) (66 mg, 0.33 mmol) and 1,1-diaminoazine (**C1**) (5 mg, 10 mol%) were charged followed by addition of 1mL MeCN. The reaction mass was stirred at rt for 3 hours. The progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mass was extracted with ethyl acetate (3×5 mL). The organic layers were combined and subjected to drying by rota evaporator to get crude **3** which was purified using column chromatography (hexane-EtOAc). This representative procedure was employed for the synthesis of **6** and **7** using water for former and toluene for the later as solvent.

2.3 Procedure of the three-component addition:

Benzaldehyde (50 mg, 0.45 mmol) and malononitrile (30 mg, 0.45 mmol) were added to round bottom flask with 25 mL capacity followed by addition of 1mL of toluene. This is followed by **C1** (11 mg, 10 mol%). After sometime (1-2 min), diphenylphosphine oxide (90 mg, 0.45 mmol) was added into the stirring reaction mixture. The reaction was completed in 15 min. The product **7** was obtained as a white solid (152 mg, 92%) after column chromatography.

3. Medicinal application of organophosphorus compounds

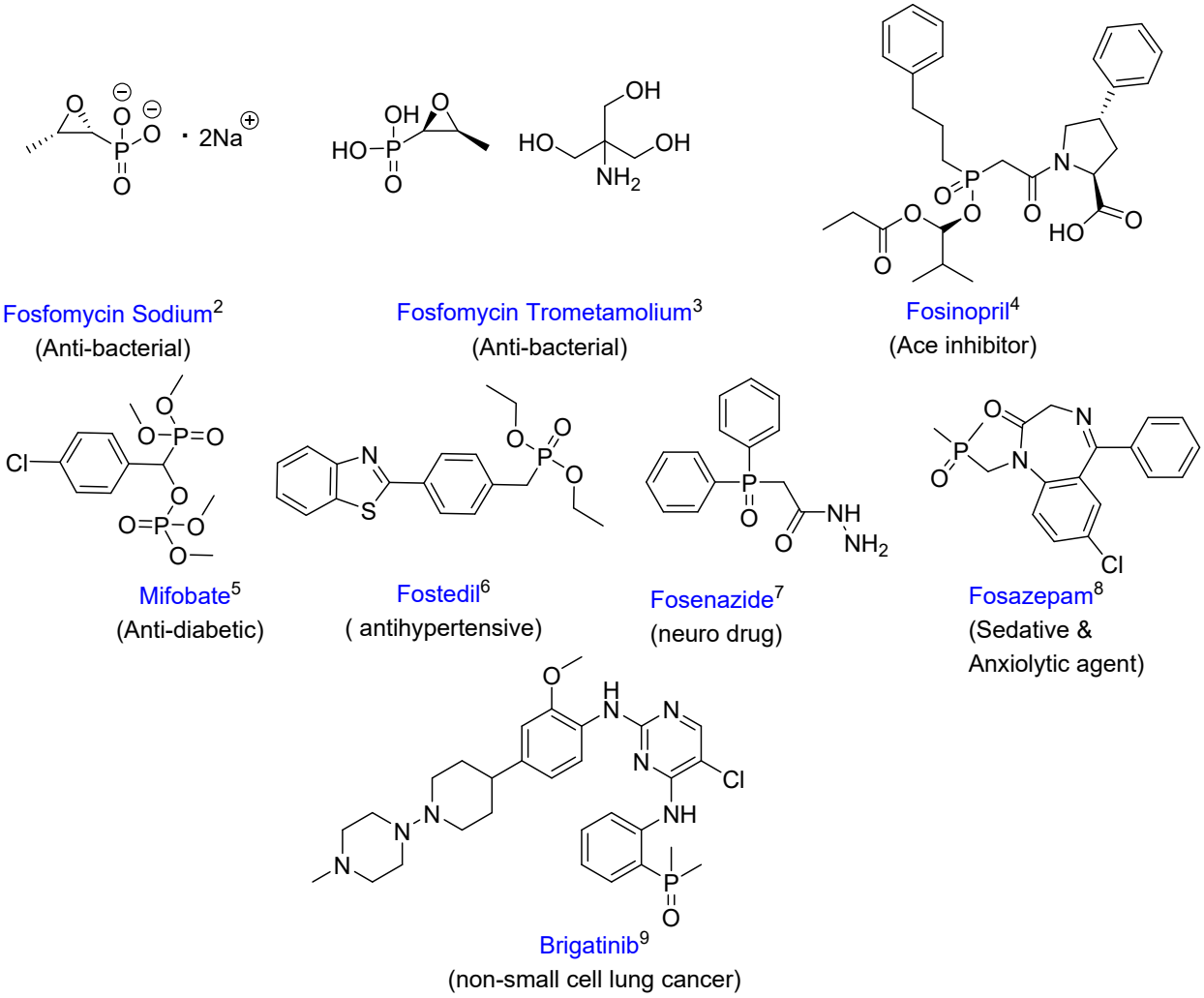


Figure S1: A selected list of organophosphorus compounds which found applications as drugs/leads in medicinal chemistry.

4. Mass and ^{1}H NMR evidences in support of proposed mechanism:

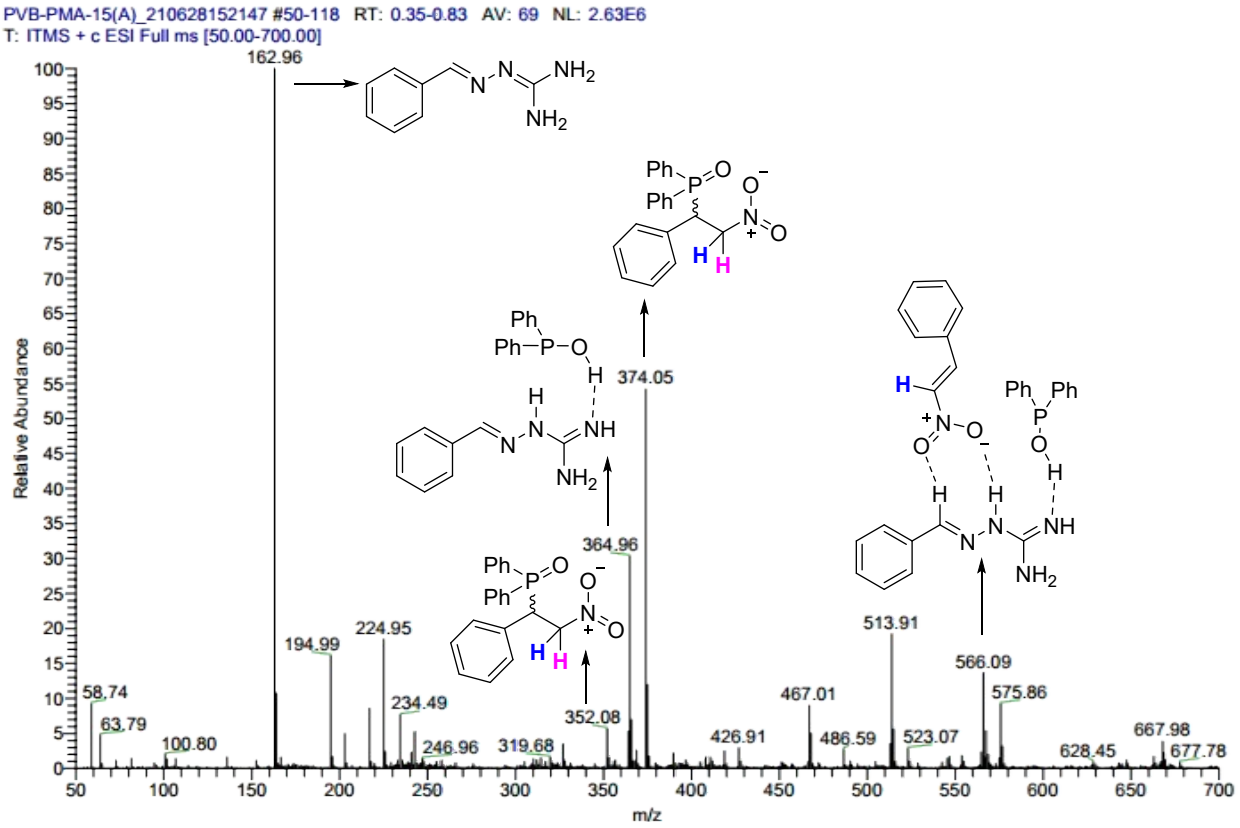


Figure S2: Mass spectrum of reaction mixture after 10 min. of stirring.

The mass spectral evidence for the proposed mechanism is further supported by evidences from ^{1}H NMR. A few characteristic peaks can be clearly seen from the ^{1}H NMR of the reaction mixture which say that 1,1-diaminoazine behaves as a bifunctional organocatalyst (Figure S-3A). A broad singlet appears at 13.14 ppm. A Very similar peak can be seen in the ^{1}H NMR spectrum of protonated azine (**C6**) (Figure S-3B) which is having a chemical shift value of 12.11 ppm. However, there is no such peak in or around this region for 1,1-diaminoazine (**C1**) (Figure S-3C). This observation clearly shows that during reaction **C1** undergoes protonation at N2. Hence, the peak at 13.11 can be attributed to –NH (N2 position) for **C1**. Furthermore, this peak (13.11 ppm) is somewhat more deshielded than the –NH peak of the **C6**. This deshielding provides the clue for –NH being hydrogen bonded, holding the reactants together. For **C1** and **C6**, the iminic CH

appears at 7.95 ppm and 8.15 ppm respectively. In case of reaction mixture, one extra peak can be seen at 8.54 ppm (Figure S-3A). It may be a –CH peak which is hydrogen bonded and may belong to **Int-1**. In case of **C1**, the two $–NH_2$ peaks appear at 5.89 ppm and 5.50 ppm. There are two peaks visible in the ^1H NMR of the reaction mixture at 6.83 ppm and 6.55 ppm which can be two $–NH_2$ groups. These peaks also appear in split forms (more like doublets). This splitting can be due to the hydrogen bonding of **C1** in protonated form with starting materials. Over all, the appearance of –NH (13.11 ppm), -CH (8.54 ppm), and two $–NH_2$ groups (6.83 ppm and 6.55 ppm) provide sufficient evidences for the formation of **Int-1** in the reaction which make **C1** a bifunctional organocatalyst.

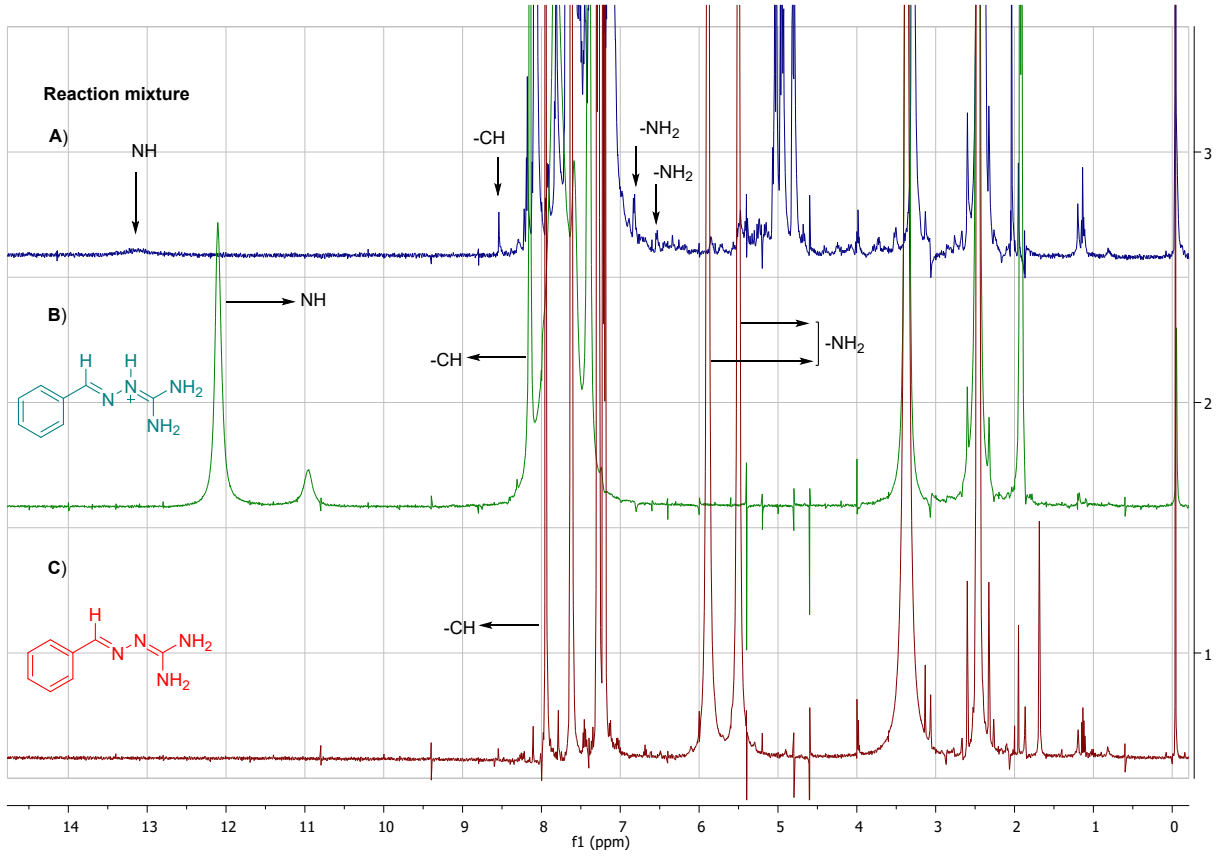


Figure S3: Overlapped 1H NMR Spectrum A) Reaction mixture, B) Protonated azine (**C6**), C) 1,1-diaminoazine (**C1**).

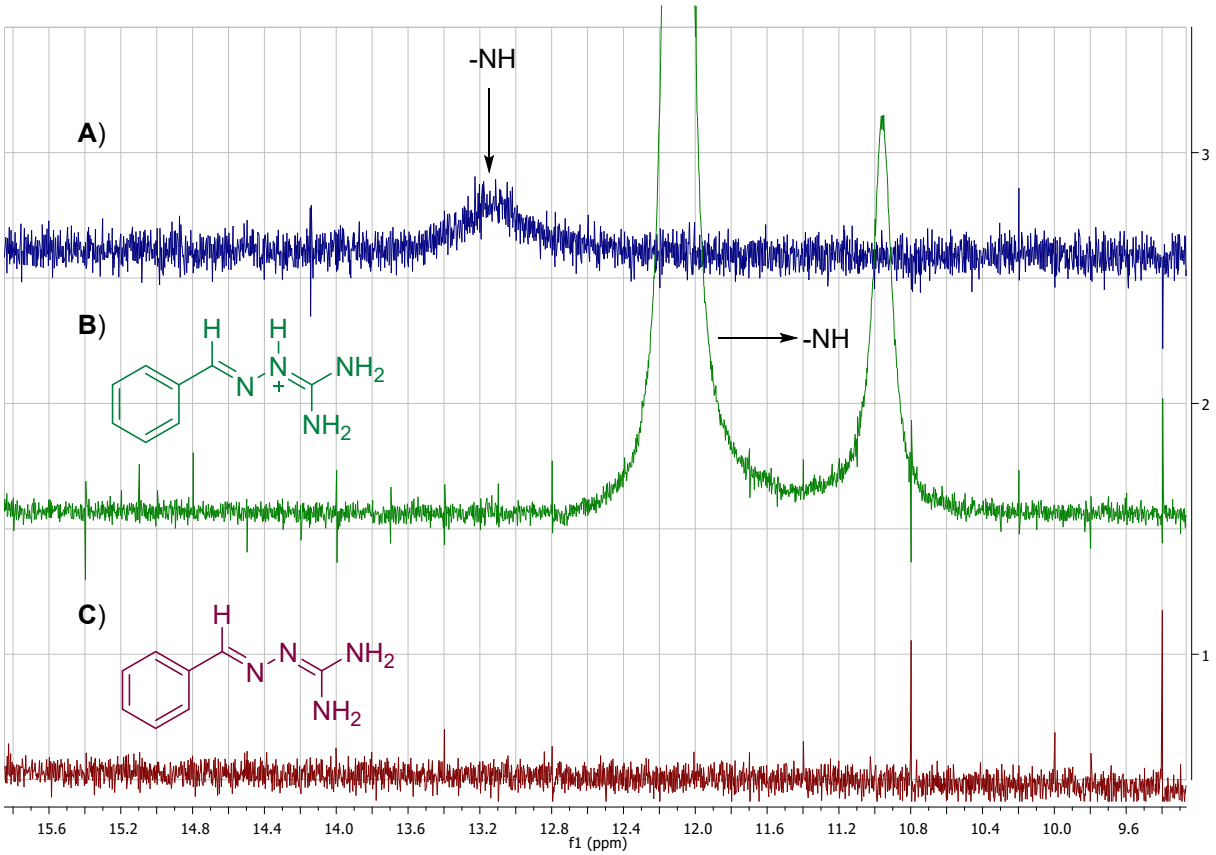


Figure S4: Expanded ^{1}H NMR spectrum (For clear visibility of –NH peak).

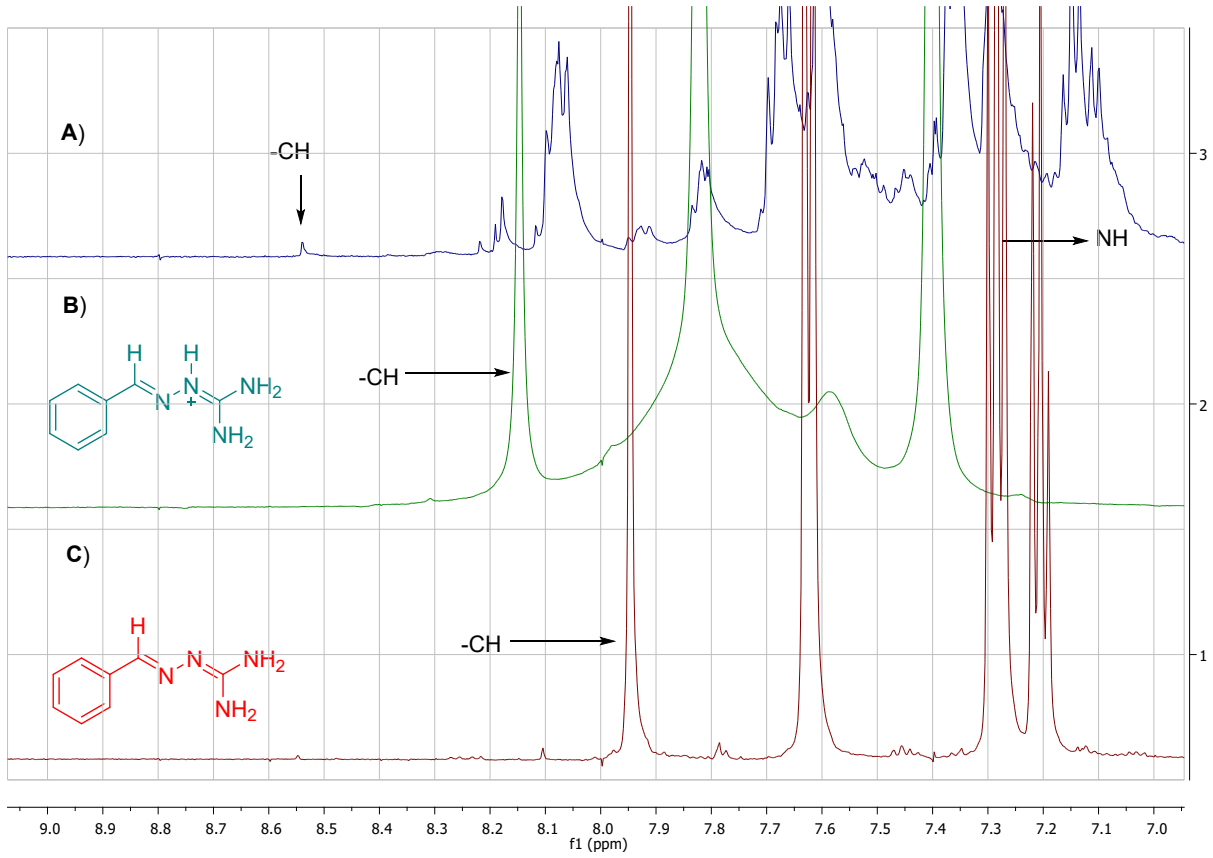


Figure S5: Expanded ^{1}H NMR spectrum of C1 and its protonated form (For clear visibility of –CH peak).

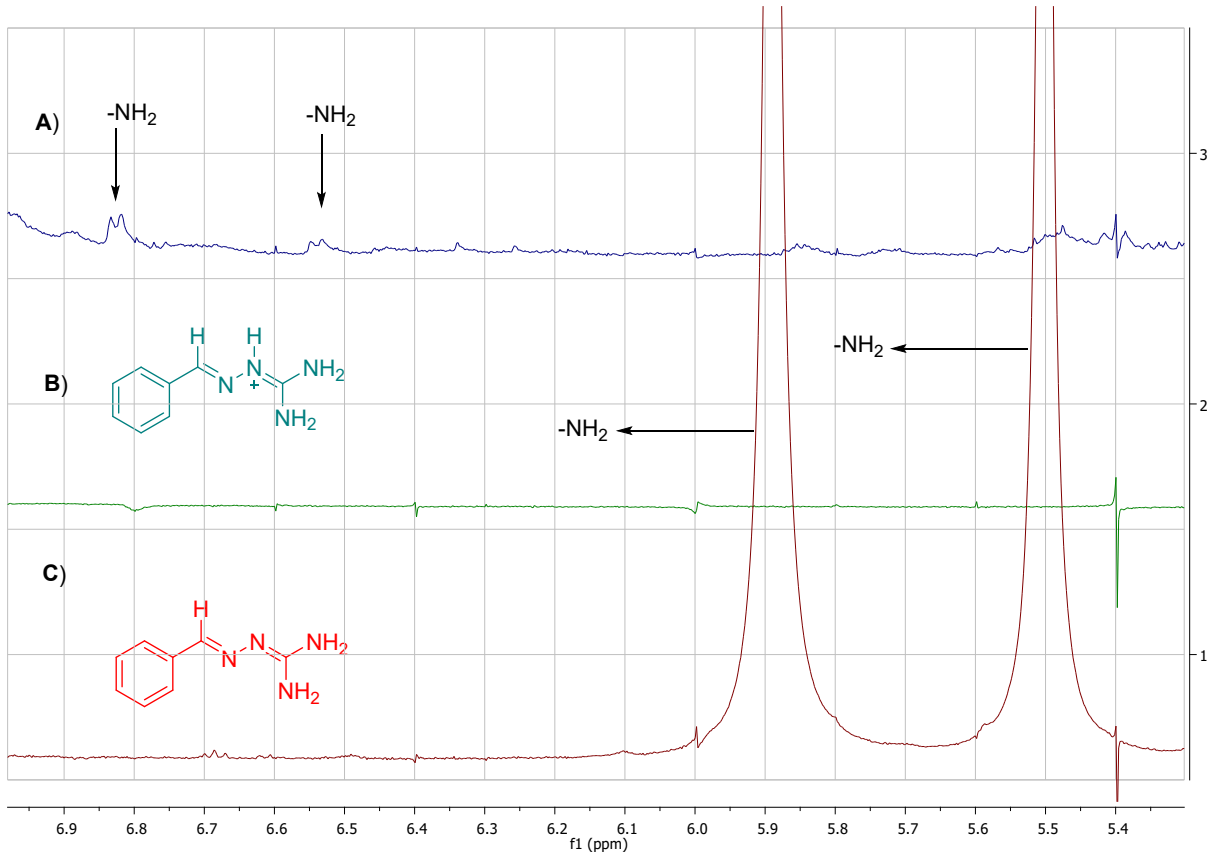
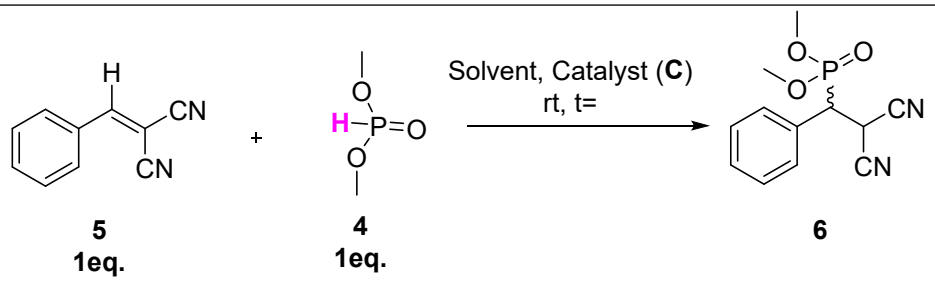


Figure S6: Expanded ^{1}H NMR spectrum of C1 and its protonated form (For clear visibility of –NH_2 peaks).

Table S1: 1,1-diaminoazine catalysed reaction between dimethyl phosphite and benzylidene malononitrile.



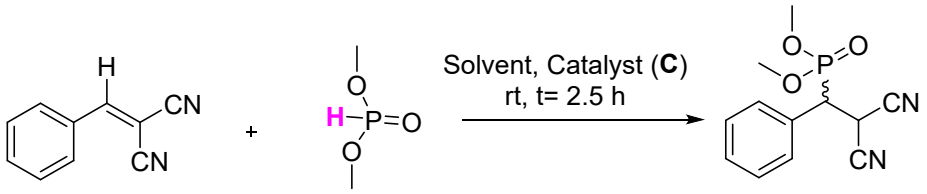
5 1eq. **4** 1eq. **6**

S.No	Solvent	Catalyst (10 mol %)	Time (h)	% yield
1.	**MeCN**	**C1**	**1.5**	**63**
2.	EtOH	C1	1.5	52
3.	MeOH	C1	1.5	64
4.	**1,4-Dioxane**	**C1**	**1.5**	**96**
5.	NMP	C1	1.5	41
6.	THF	C1	1.5	87
7.	**Toluene**	**C1**	**1.5**	**99**
8.	**Water**	**C1**	**1.5**	**No Reaction**
9.	**Toluene**	C2	1.5	43
10.	**Toluene**	C3	1.5	84
11.	**Toluene**	C4	1.5	87
12.	**Toluene**	C5	1.5	88
13.	**Toluene**	**C6**	**1.5**	**No Reaction**
14.	**Toluene**	C7	1.5	23
15.	**Toluene**	No catalyst	1.5	No Reaction

Reaction conditions: **5** (0.32 mmol, 50 mg), **4** (0.32 mmol, 35 mg), **C** (10 mol%, 5 mg) rt, 1,4-Dioxane (1 mL).
*** Isolated Yield**

Scale up Reaction:

The reaction between benzylidene malononitrile and dimethyl phosphite (Scheme 1) was tried at gram scale level (10 mmol) to prove the scalability of the optimized reaction condition. The reaction complies in 2.5 h wherein both the starting materials i.e. benzylidene malononitrile and dimethyl phosphite were consumed completely (TLC). The product was isolated with yield of 97% suggest that the optimized reaction condition is scalable and thus can found its potential application in industry. The isolation and purification of the product was done by column chromatography, by using 50% Ethylacetate/Hexane as an eluent. The gram scale application of the developed method is now provided in the revised version of the manuscript.



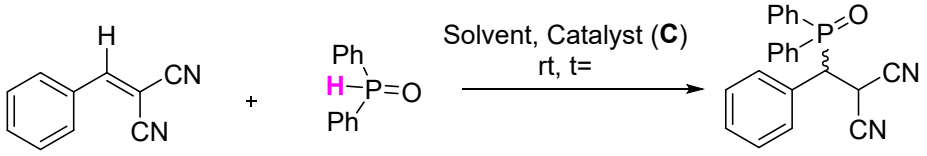
A **B** **6**

10 mmol **10 mmol** **Yield= 97%**

1.54 g **1.10 g** **2.58 g**

Scheme 1: Gram scale synthesis of P-C adduct.

Table S2: 1,1-diaminoazine catalysed reaction between biphenylphosphine oxide and benzylidene malononitrile.

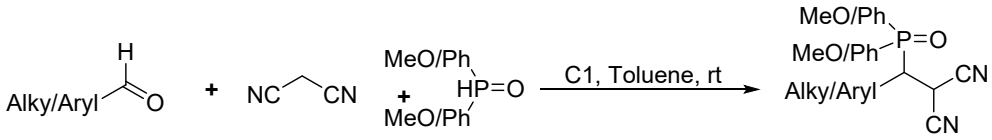


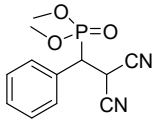
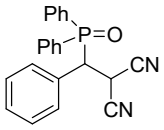
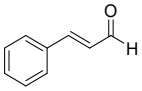
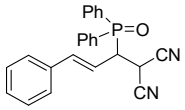
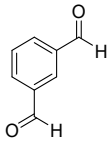
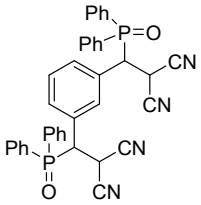
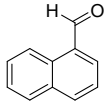
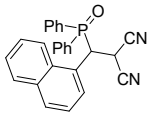
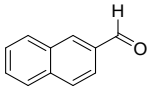
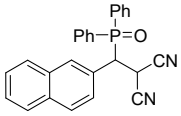
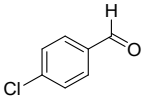
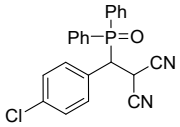
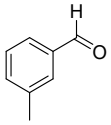
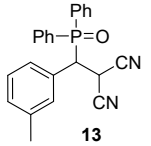
5 **1** **7**

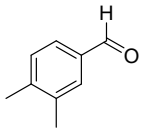
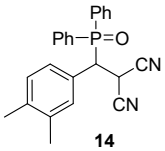
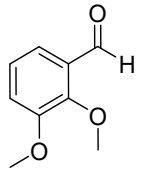
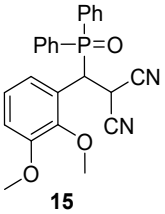
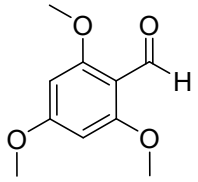
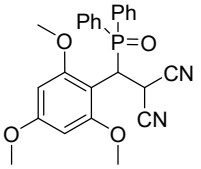
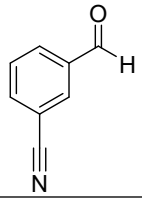
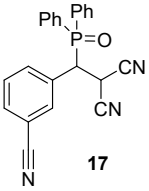
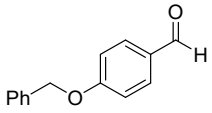
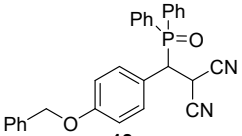
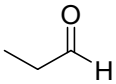
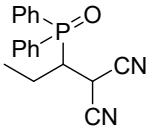
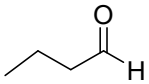
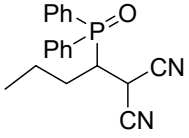
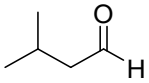
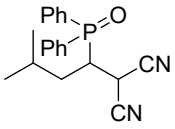
1eq. **1eq.**

S.no	Solvent	Catalyst (10 mol %)	Time (h)	% yield
1.	**MeCN**	**C1**	**1**	**88**
2.	EtOH	C1	1	71
3.	MeOH	C1	1.5	76
4.	**1,4-Dioxane**	**C1**	**0.5**	**98**
5.	NMP	C1	1	74
6.	THF	C1	1	87
7.	Toluene	C1	1.5	77
8.	**Water**	**C1**	**0.4**	**95**
9.	Water	C2	0.4	49
10.	Water	C3	0.4	52
11.	Water	C4	0.4	70
12.	Water	C5	0.4	66
13.	Water	C6	0.4	63
14.	Water	C7	0.4	39
15.	Water	No catalyst	0.4	Traces
Reaction conditions: **5** (1 mmol, 154 mg), **1** (1 mmol, 202 mg), **C** (10 mol%, 16 mg) rt, Water (1.5 mL).				
*** Isolated Yield**				

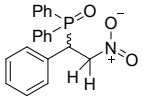
Table S3: Applications of **C1** in catalysing multicomponent reactions.



S. No.	Aldehyde	Product	Time (h)	Yield (%)
1	Benzaldehyde	 **6**	2 h	85
2	Benzaldehyde	 **7**	15 min	92
3		 **8**	2 h	91
4		 **9**	1h	66
5		 **10**	2 h	91
6		 **11**	2 h	85
7		 **12**	2 h	88
8		 **13**	2 h	91

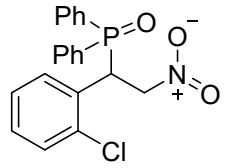
9		 **14**	2 h	89
10		 **15**	2 h	91
11		 **16**	2h	84
12		 **17**	2h	90
13		 **18**	2h	92
14		 **19**	2h	75
15		 **20**	2h	71
16		 **21**	2h	88
Reaction conditions: **Aldehyde** (0.37 mmol), **malononitrile** (0.37 mmol), **C** (15 mol%) rt, Toluene (1.5 mL).				

5. Characterization Data of the Corresponding Products:



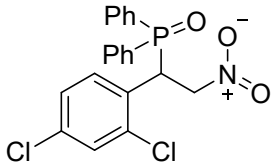
(2-nitro-1-phenylethyl)diphenylphosphine oxide (**3a**)

[10]Yield: 108 mg, 95%, white solid, m.p= 202-204 °C, [α] $^{25}_{589} = -4\ (c\ 0.1, CHCl3)$; 1H NMR (500MHz, DMSO-d6) δ 8.10 – 8.06 (t, J = 10 Hz, 2 H), 7.70 - 7.66 (dd, J = 7.68 Hz, 2 H), 7.61 - 7.60 (m, 3 H), 7.37 - 7.34 (m, 3 H), 7.30 – 7.29 (m, 2 H), 7.16 – 7.08 (m, 3 H), 5.07 – 5.01 (m, 1 H), 4.98 – 4.94 (m, 1 H), 4.83 – 4.78 (m, 1 H); 13C NMR 133.3, 132.9, 132.2, 131.4, 131.3, 131.2, 131.1, 129.9, 129.9, 129.6, 129.5, 128.8, 128.7, 128.2, 121.2, 76.6, 76.5, 44.4, 43.8; 31P NMR (202.4 MHz, DMSO) δ 29.39: IR (FTIR) NO_2 (1550 cm-1), P=O (1185 cm-1). HRMS (ESI) m/z 352.1112 (M+H+), calc. for C20H19NO3P+ 352.1097.



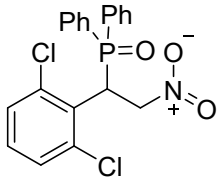
(1-(2-chlorophenyl)-2-nitroethyl)diphenylphosphine oxide **(3b)**

Yield: 90 mg, 86%, white solid, m.p= 188-190 °C; 1H NMR (500MHz, CDCl3) δ 8.07 – 8.03 (m, 2 H), 7.85 – 7.84 (d, J = 7.84 Hz, 1 H), 7.68 – 7.62 (m, 3 H)7.44 – 7.35 (m, 3 H), 7.31 – 7.27 (m, 1 H), 7.24 – 7.20 (m, 2 H), 7.14 – 7.13 (d, J = 5 Hz, 2 H), 5.24 – 5.20 (m, 1 H), 5.14 – 5.08 (m, 1 H) 4.77 – 4.73 (m, 1 H); 13C NMR 135.0, 134.9, 133.0, 131.3, 131.0, 130.2, 130.0, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 128.2, 128.1, 127.5, 75.4, 75.4, 41.2, 40.7; 31P NMR (202.4MHz, CDCl3) δ 31.30; IR (FTIR) NO_2 (1540 cm-1), P=O (1193 cm-1). HRMS (ESI) m/z 386.0717 (M+H+), calc. for $C_{20}H_{18}ClNO_3P^+$ 386.0707



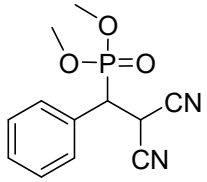
(1-(2,4-dichlorophenyl)-2-nitroethyl)diphenylphosphine oxide **(3c)**

Yield: 78 mg, 81%, white solid, m.p= 185-187 °C; [1]H NMR (500MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 2 H), 7.82 – 7.80 (dd, *J* = 7.81 Hz, 1 H), 7.69 – 7.62 (m, 3 H), 7.47 – 7.40 (m, 3 H), 7.29 – 7.25 (m, 3 H), 7.18 (br.s., 1 H), 5.17 – 5.12 (m, 1 H), 5.08 – 5.02 (m, 1 H) 4.75 – 4.70 (m, 1 H); [13]C NMR 135.6, 134.8, 133.2, 132.6, 131.2, 130.9, 130.8, 130.4, 129.9, 129.7, 129.6, 129.5, 129.1, 128.5, 127.9, 75.3, 40.8, 40.3; [31]P NMR (202.4MHz, $CDCl_3$) δ 31.40; IR (FTIR) NO_2 (1437 cm-1), P=O (1182 cm^{-1}). HRMS (ESI) m/z 420.0325 ($M+H^+$), calc. for $C_{20}H_{17}Cl_2NO_3P^+$ 420.0318



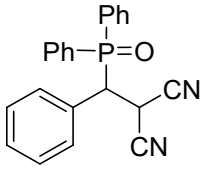
(1-(2,6-dichlorophenyl)-2-nitroethyl)diphenylphosphine oxide **(3d)**

Yield: 82 mg, 85%, white solid, m.p= 186-188 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 8.10 – 8.07 (t, J = 10.0 Hz, 2 H), 7.61 – 7.53 (m, 5 H), 7.34 – 7.31 (t, J = 10.0 Hz, 1 H), 7.20 (br.s., 2 H), 7.15 – 7.14 (d, J = 5.0 Hz, 2 H), 7.01 – 6.98 (t, J = 10.0 Hz, 1 H), 5.67 – 5.63 (m, 2 H), 5.13 – 5.08 (m, 1 H); ^{13}C NMR 137.1, 137.0, 135.7, 135.7, 132.8, 132.2, 131.7, 131.4, 131.3, 130.9, 130.2, 130.2, 129.7, 129.3, 129.2, 128.5, 128.0, 127.9, 72.7, 43.0, 42.5; ^{31}P NMR (202.4MHz, $CDCl_3$) δ 30.32; IR (FTIR) NO_2 (1445 cm-1), P=O (1188 cm^{-1}). HRMS (ESI) m/z 420.0318 ($M+H^+$), calc. for $C_{20}H_{17}Cl_2NO_3P^+$ 420.0332



dimethyl (2,2-dicyano-1-phenylethyl)phosphonate (**6**)

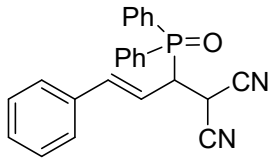
^{11}Yield: 254 mg, 96%, white solid, m.p= 126-128 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 5 H), 4.51 – 4.48 (t, J = 4.50 Hz, 1 H), 3.82-3.80 (d, J = 10 Hz, 3 H), 3.65 – 3.59 (dd, J = 3.62 Hz, 1 H), 3.54 – 3.52 (d, J = 10 Hz, 3 H); ^{13}C NMR 129.9, 129.9, 129.8, 129.6, 111.2, 111.2, 111.1, 111.0, 54.8, 54.7, 53.6, 53.5, 45.2, 44.0, 25.5; ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 22.38:IR (FTIR) CN (2340 cm^{-1}), P=O (1180 cm^{-1}). HRMS (ESI) m/z 287.0565 ($M+Na^+$), calc. for $C_{12}H_{13}N_2O_3PNa^+$ 287.0561.



2-((diphenylphosphoryl)(phenyl)methyl)malononitrile (**7**)

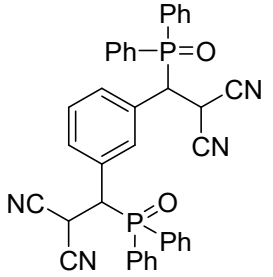
^{11}Yield: 220 mg, 95%, white solid, m.p= 195-197 °C; ^{1}H NMR (500MHz, DMSO-*d6*) δ 8.12 – 8.08 (dd, J = 8.10 Hz, 2 H), 7.62 – 7.60 (m, 5 H), 7.55 –7.53 (d, J = 7.54 Hz, 2 H), 7.35 – 7.32 (t, J = 7.33 Hz, 1 H), 7.29 – 7.28 (m, 2 H), 7.24 – 7.17 (m, 3 H), 5.42 – 5.39 (t, J = 5.41 Hz, 1 H), 5.08 – 5.06 (t, J = 5.07 Hz, 1 H) ; ^{13}C NMR ($CDCl_3$) 133.2, 132.4, 131.4, 131.3, 131.2, 130.8, 130.8, 130.3, 129.8, 129.7, 129.4, 129.3, 128.8, 128.6, 128.5, 128.4, 111.4, 111.3, 111.2, 47.4, 46.9, 24.8; ^{31}P NMR

(204.2MHz, DMSO) δ28.82: IR (FTIR) CN (2340.42 cm^{-1}), P=O (1179cm^{-1}). HRMS (ESI) m/z 357.1163 ($M+H^+$), calc. for $C_{22}H_{18}N_2OP^+$ 357.1151.



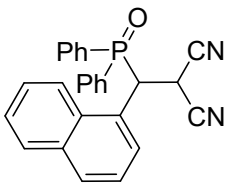
(*E*)-2-(1-(diphenylphosphoryl)-3-phenylallyl)malononitrile (**8**)

[11]Yield: 130 mg, 91%, white solid, m.p= 136-138 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ7.90 – 7.80 (m, 4 H), 7.64 – 7.60 (dd, *J* = 7.62 Hz, 2 H), 7.56 –7.51 (m, 4 H), 7.35 – 7.31 (m, 3 H), 7.28 – 7.27 (m, 2 H), 6.08 – 6.64 (dd, *J* = 6.66 Hz, 1 H), 6.08 – 6.02 (m, 1 H), 4.81 – 4.79 (dd, *J* = 4.80 Hz, 1 H), 3.77 – 3.72 (m, 1 H) ; ^{13}C NMR 139.7, 139.6, 136.0, 133.3, 132.4, 132.3, 131.2, 131.1, 129.3, 129.2, 129.2, 129.0, 128.9, 128.9, 126.9, 117.3, 117.2, 112.0, 111.9, 110.4, 46.6, 46.1, 23.9; ^{31}P NMR (202.4MHz, $CDCl_3$) δ28.41: IR (FTIR) CN (2340 cm^{-1}), P=O (1180 cm^{-1}). HRMS (ESI) m/z 383.1314 ($M+H^+$), calc. for $C_{24}H_{20}N_2OP^+$ 383.1308.



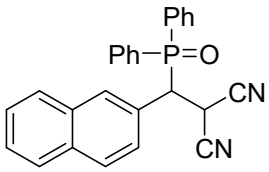
2,2'-(1,3-phenylenebis((diphenylphosphoryl)methylene))dimalononitrile (**9**)

Yield: 319, 66%, light brown solid, m.p= 159-161 °C; $[\alpha]_{589}^{25} = 3\ (c\ 0.1, MeOH)$; ^{1}H NMR (500MHz, $CDCl_3$) δ7.98 – 7.92 (t, *J* = 7.95 Hz, 5 H), 7.78 (br. s., 1 H), 7.66 –7.64 (d, *J* = 7.65 Hz, 3 H), 7.63 – 7.59 (m, 6 H), 7.51 – 7.48 (m, 5 H), 7.38 – 7.35 (m, 4 H), 4.71 – 4.68 (t, *J* = 4.70 Hz, 1 H), 4.55 – 4.52 (t, *J* = 4.53 Hz, 1 H), 4.02 – 4.00 (t, *J* = 4.01 Hz, 1 H); ^{13}C NMR (500MHz, $CDCl_3$ + DMSO-*d6*) 133.1, 133.0, 132.9, 132.9, 132.9, 132.5, 132.5, 132.3, 132.2, 132.14, 132.0, 131.9, 131.7, 131.7, 131.7, 131.6, 131.5, 131.4, 131.4, 131.3, 131.1, 130.9, 130.8, 130.7, 130.1, 129.7, 129.2, 129.2, 128.8, 128.6, 128.5, 111.6, 111.6, 111.4, 111.4, 27.7, 27.2, 25.1, 24.77. ^{31}P NMR (202.4MHz, $CDCl_3$ + DMSO-*d6*) δ34.32: IR (FTIR) CN (2351 cm^{-1}), P=O (1179 cm^{-1}). HRMS (ESI) m/z 635.1755 ($M+H^+$), calc. for $C_{38}H_{29}N_4O_2P_2^+$ 635.1760.



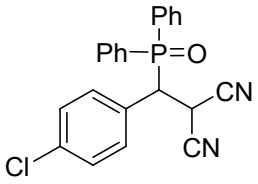
2-((diphenylphosphoryl)(naphthalen-1-yl)methyl)malononitrile (**10**)

Yield: 118 mg, 91%, white solid, m.p= 210-214 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 8.56 – 8.55 (d, J = 8.56 Hz, 1 H), 8.28 – 8.24 (dd, 2 H), 8.18 – 8.17 (d, J = 8.17 Hz, 1 H), 7.80 – 7.77 (t, J = 7.79 Hz, 2 H), 7.68 – 7.63 (m, 3 H), 7.52 – 7.47 (dd, J = 7.50 Hz, 2 H), 7.44 – 7.41 (m, 1 H), 7.39 – 7.35 (dd, J = 7.37 Hz, 2 H), 5.71 – 5.68 (t, J = 5.69 Hz, 1 H), 5.60 – 5.57 (t, J = 5.59 Hz, 1 H) ; ^{13}C NMR 133.7, 133.2, 132.2, 132.1, 131.9, 131.5, 131.1, 130.7, 130.5, 130.4, 129.7, 129.5, 129.4, 129.0, 129.0, 128.4, 128.4, 126.9, 126.3, 125.5, 124.1, 113.7, 113.6, 113.2, 113.1, 37.4, 36.9, 26.0; ^{31}P NMR (202.4MHz, DMSO-*d6*) δ 29.55. IR (FTIR) CN (1953 cm^{-1}), P=O (1181 cm^{-1}). HRMS (ESI) m/z 407.1320 ($M+H^+$), calc. for $C_{26}H_{20}N_2OP^+$ 407.1308.



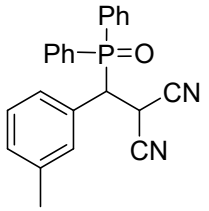
2-((diphenylphosphoryl)(naphthalen-2-yl)methyl)malononitrile (**11**)

Yield: 110 mg, 85%, white solid, m.p= 190-192 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 8.00 – 7.96 (dd, J = 7.98 Hz, 1 H), 7.86 (br. s., 1 H), 7.78 – 7.74 (m, 3 H), 7.67 – 7.64 (t, J = 7.66 Hz, 1 H), 7.61 – 7.59 (t, J = 7.66 Hz, 2 H), 7.52 – 7.47 (m, 4 H), 7.44 – 7.42 (d, J = 7.43 Hz, 1 H), 7.33 – 7.30 (t, J = 7.31 Hz, 1 H), 7.22 – 7.18 (m, 2 H), 4.84 – 4.81 (t, J = 4.82 Hz, 1 H), 4.21 – 4.18 (t, J = 4.82 Hz, 2 H); ^{13}C NMR 133.2, 133.2, 133.0, 132.5, 131.3, 131.2, 130.4, 129.7, 129.6, 129.3, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7, 127.0, 126.8, 126.4, 126.4, 111.3, 111.3, 111.2, 47.5, 46.8, 24.9; ^{31}P NMR (202.4MHz, CDCl3) δ 29.33: IR (FTIR) CN (2340 cm^{-1}), P=O (1173 cm^{-1}). HRMS (ESI) m/z 407.1320 ($M+H^+$), calc. for $C_{26}H_{20}N_2OP^+$ 407.1308.



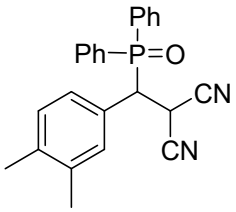
2-((4-chlorophenyl)(diphenylphosphoryl)methyl)malononitrile (**12**)

Yield: 122 mg, 88%, white solid, m.p= 179-181 °C; ^{1}H NMR (500MHz, DMSO-*d6*) δ 8.08 – 8.07 (m, 2 H), 7.63 – 7.60 (m, 7 H), 7.35 – 7.32 (m, 5 H), 5.43 (br. s., 1 H), 5.15 – 5.14 (m, 1 H) ; ^{13}C NMR 133.9, 133.2, 132.5, 132.3, 132.3, 131.9, 131.6, 131.6, 130.8, 130.8, 129.6, 129.5, 129.1, 129.0, 128.9, 113.3, 113.2, 113.0, 112.9, 42.3, 41.8, 25.4 ; ^{31}P NMR (202.4MHz, DMSO) δ28.80: IR (FTIR) CN (2053 cm^{-1}), P=O (1174 cm^{-1}). HRMS (ESI) m/z 391.0768 (M+H^{+}), calc. for $C_{22}H_{17}ClN_2OP^{+}$ 391.0762.



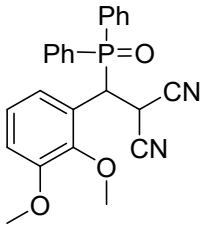
2-((diphenylphosphoryl)(*m*-tolyl)methyl)malononitrile (**13**)

Yield: 135 mg, 91%, white solid, m.p= 178-180 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 8.10 – 8.07 (m, 2 H), 7.60 – 7.57 (m, 5 H), 7.33 – 7.28 (m, 5 H), 7.12 – 7.09 (m, 5 H), 5.40 – 5.38 (t, *J* = 5.39 Hz, 1 H), 5.01 – 4.99 (d, *J* = 5.00 Hz, 1 H) ; ^{13}C NMR 133.2, 133.2, 133.0, 132.5, 131.3, 131.2, 130.4, 129.7, 129.6, 129.5, 129.4, 129.3, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.0, 126.8, 126.4, 126.4, 111.3, 111.3, 111.2, 47.5, 46.8, 24.9; ^{31}P NMR (202.4MHz, $CDCl_3$) δ29.43: IR (FTIR) CN (2348 cm^{-1}), P=O (1179 cm^{-1}). HRMS (ESI) m/z 371.1319 (M+H^{+}), calc. for $C_{23}H_{20}N_2OP^{+}$ 371.1308.



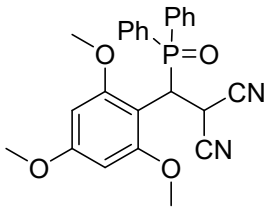
2-((3,4-dimethylphenyl)(diphenylphosphoryl)methyl)malononitrile (**14**)

Yield: 126 mg, 89%, white solid, m.p= 185-187 °C; ^{1}H NMR (500MHz, DMSO-*d6*) δ 8.08 – 8.05 (m, 2 H), 7.64 – 7.57 (m, 5 H), 7.35 – 7.27 (m, 5 H), 6.99 – 6.98 (d, *J* = 6.99 Hz, 1 H), 5.32 – 5.29 (t, *J* = 5.30 Hz, 1 H), 4.98 – 4.95(t, *J* = 4.96 Hz, 1 H), 2.07 (s, 6 H) ; ^{13}C NMR 137.0, 136.7, 133.0, 132.3, 132.2, 131.6, 131.5, 131.4, 131.4, 131.3, 130.9, 130.8, 130.1, 129.5, 129.4, 129.2, 128.9, 128.8, 128.6, 113.5, 113.2, 42.5, 42.0, 20.0, 19.53; ^{31}P NMR (202.4MHz, DMSO-*d6*) δ 28.86: IR (FTIR) CN (1960 cm^{-1}), P=O (1179 cm^{-1}). HRMS (ESI) m/z 385.1476 (M+H^{+}), calc. for $C_{24}H_{22}N_2OP^{+}$ 385.1464.



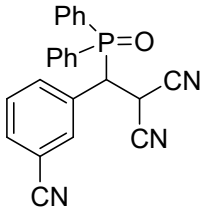
2-((2,3-dimethoxyphenyl)(diphenylphosphoryl)methyl)malononitrile (**15**)

Yield: 105 mg, 91%, white solid, m.p= 195-197 °C; ^{1}H NMR (500MHz, DMSO-*d6*) δ 8.06 – 8.02 (m, 2 H), 7.63 – 7.59 (m, 3 H), 7.47 – 7.43 (m, 3 H)7.28 – 7.27 (m, 3 H), 6.99 – 6.98 (t, J = 6.98 Hz, 1 H), 6.91 – 6.89 (d, J = 6.90 Hz, 1 H), 5.42 – 5.39 (t, J = 5.40 Hz, 1 H), 5.05 – 5.03 (t, J = 5.04 Hz, 1 H), 3.68 – 3.67 (m, 6 H) ; ^{13}C NMR 156.3, 152.3, 133.1, 132.4, 131.8, 131.7, 130.9, 130.8, 129.5, 129.5, 128.7, 128.6, 124.2, 114.1, 114.0, 61.3, 56.2, 25.3, 21.86; ^{31}P NMR (202.4MHz, DMSO-*d6*) δ 29.42; IR (FTIR) CN (2342 cm^{-1}), P=O (1182 cm^{-1}). HRMS (ESI) m/z 417.1377 (M+H^{+}), calc. for $C_{24}H_{22}N_2O_3P^{+}$ 417.



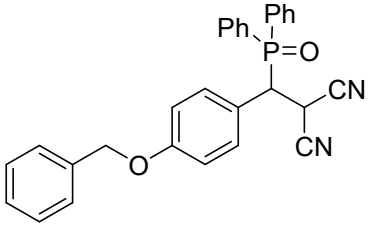
2-((diphenylphosphoryl)(2,4,6-trimethoxyphenyl)methyl)malononitrile **(16)**

Yield: 92 mg, 84%, white solid, m.p= 178-180 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.91 – 7.87 (t, J = 10 Hz 2 H), 7.59 (br.s., 3 H), 7.34 – 7.21 (m, 5 H), 6.11 (br.s., 1 H), 5.86 (br.s., 1 H), 5.56 – 5.52 (t, J = 10 Hz, 1 H), 4.92 – 4.88 (t, J = 10 Hz, 1 H), 3.79 (s, 3 H), 3.64(s, 3 H), 3.42 (s, 3 H) ; ^{13}C NMR 162.1, 159.4, 158.3, 132.6, 132.0, 130.9, 130.7, 129.5, 129.4, 128.0, 127.9, 114.3, 114.0, 113.9, 101.3, 91.2, 56.7, 55.8, 55.7, 40.1, 40.0, 39.8, 39.6, 23.3; ^{31}P NMR (202.4MHz, $CDCl_3$) δ 29.40; IR (FTIR) CN (2332 cm^{-1}), P=O (1175 cm^{-1}). HRMS (ESI) m/z 447.1482 (M+H^{+}), calc. for $C_{25}H_{24}N_2O_4P^{+}$ 447.1468



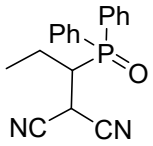
2-((3-cyanophenyl)(diphenylphosphoryl)methyl)malononitrile **(17)**

Yield: 120 mg, 90%, white solid, m.p= 192-194 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 8.01 – 7.97 (dd, J = 8 Hz, 2 H), 7.79-7.77 (d, J = 10 Hz, 1 H), 7.70 – 7.68 (t, J = 8 Hz, 2 H), 7.64-7.62 (m, 3 H), 7.59-7.57 (d, J = 10 Hz, 1 H), 7.52 – 7.48 (m, 2 H), 7.45 – 7.42 (t, J = 10 Hz, 2 H), 7.34-7.30 (m, 2 H), 4.67-4.66 (t, J = 5 Hz, 1 H), 4.08-4.05 (t, J = 5 Hz, 1 H) ; ^{13}C NMR 133.9, 133.8, 133.7, 133.4, 133.3, 133.0, 132.9, 132.8, 132.7, 131.3, 130.2, 129.7, 129.6, 129.3, 129.1, 128.9, 128.8, 128.3, 117.7, 113.5, 110.8, 110.7, 46.7, 46.2, 24.5; ^{31}P NMR (202.4MHz, $CDCl_3$) δ 28.97; IR (FTIR) CN (2333 cm^{-1}), P=O (1175 cm^{-1}). HRMS (ESI) m/z 382.1115 ($M+H^+$), calc. for $C_{23}H_{17}N_3OP^+$ 382.1104



2-((4-(benzyloxy)phenyl)(diphenylphosphoryl)methyl)malononitrile **(18)**

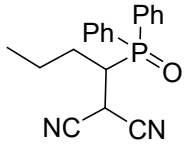
Yield: 112 mg, 92%, white solid, m.p= 184-186 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.96 – 7.92 (dd, J = 10 Hz, 2 H), 7.65-7.63 (t, J = 5 Hz, 1 H), 7.60 – 7.57 (m, 2 H), 7.51-7.47 (dd, J = 10 Hz , 2 H), 7.40-7.37 (m, 5 H), 7.31 – 7.28 (m, 5 H), 6.88 – 6.86 (d, J = 10 Hz, 2 H), 4.99 (s, 2 H), 4.66-4.63 (t, J = 8 Hz, 1 H), 3.99-3.96 (t, J = 8 Hz, 1 H) ; ^{13}C NMR 159.5, 131.4, 131.3, 131.1, 129.4, 129.3, 128.7, 128.5, 128.4, 128.2, 127.6, 115.6, 111.5, 111.4, 111.3, 70.1, 46.7, 46.2, 25.1; ^{31}P NMR (202.4MHz, $CDCl_3$) δ 29.19; IR (FTIR) CN (2341 cm^{-1}), P=O (1180 cm^{-1}). HRMS (ESI) m/z 463.1579 ($M+H^+$), calc. for $C_{29}H_{24}N_2O_2P^+$ 463.1570



2-(1-(diphenylphosphoryl)propyl)malononitrile **(19)**

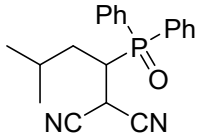
Yield: 83 mg, 75%, white solid, m.p= 155-157 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 4 H), 7.65 – 7.60 (q, J = 7.6 Hz, 2 H), 7.58 – 7.52 (m, 4 H), 4.57 – 4.54 (dd, J = 5 Hz, 1 H), 2.91

– 2.86 (m, 1 H), 2.00 – 1.81 (m, 2 H), 1.16 – 1.13 (t, J = 7.6 Hz, 3 H); ^{13}C NMR 133.3, 133.2, 133.1, 131.8, 131.7, 131.1, 131.0, 129.5, 129.4, 129.1, 129.0, 128.6, 127.8, 113.0, 1112.9, 110.3, 41.9, 41.4, 21.6, 21.1, 12.8, 12.7; ^{31}P NMR (202.4MHz, $CDCl_3$) δ 31.30; IR (FTIR) CN (2335 cm^{-1}), P=O (1183 cm^{-1}). HRMS (ESI) m/z 309.1165 ($M+H^+$), calc. for $C_{18}H_{18}N_2OP^+$ 309.1151



2-(1-(diphenylphosphoryl)butyl)malononitrile **(20)**

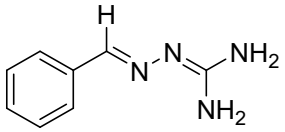
Yield: 82 mg, 71%, white solid, m.p= 150-152 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 4 H), 7.65 – 7.61 (dd, J = 7.6 Hz, 2 H), 7.58 – 7.53 (m, 4 H), 4.56 – 4.53 (dd, J = 5 Hz, 1 H), 2.99 – 2.94 (m, 1 H), 1.87 – 1.80 (m, 2 H), 1.69 – 1.62 (m, 1 H), 1.46 – 1.38 (m, 1 H), 0.90 – 0.87 (t, J = 10 Hz, 3 H); ^{13}C NMR 133.3, 133.2, 133.1, 131.8, 131.7, 129.5, 129.4, 129.3, 129.0, 128.5, 127.7, 113.0, 112.9, 110.3, 40.2, 39.6, 29.5, 21.9, 21.2, 21.1, 13.8; ^{31}P NMR (202.4MHz, $CDCl_3$) δ 32.40; IR (FTIR) CN (2338 cm^{-1}), P=O (1178 cm^{-1}). HRMS (ESI) m/z 323.1322 ($M+H^+$), calc. for $C_{19}H_{20}N_2OP^+$ 323.1308



2-(1-(diphenylphosphoryl)-3-methylbutyl)malononitrile **(21)**

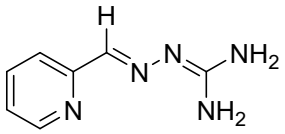
Yield: 102 mg, 88%, white solid, m.p= 146-148 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.83 – 7.77 (dd, J = 7.8 Hz 4 H), 7.65 – 7.62 (dd, J = 7.63 Hz, 2 H), 7.58 – 7.53 (m, 4 H), 4.58 – 4.55 (dd, J = 10 Hz, 1 H), 3.06 – 3.02 (m, 1 H), 1.87 – 1.80 (m, 2 H), 1.86 – 1.78 (m, 2 H), 1.61 – 1.54 (m, 1 H), 0.93 – 0.90 (t, J = 10 Hz, 6 H); ^{13}C NMR 133.3, 133.2, 132.0, 131.9, 131.1, 129.9, 129.6, 129.5, 129.1, 129.0, 128.1, 127.4, 113.0, 112.9, 110.2, 38.2, 37.6, 36.2, 25.9, 25.8, 23.2, 22.0, 21.1; ^{31}P NMR (202.4MHz, $CDCl_3$) δ 32.93; IR (FTIR) CN (2342 cm^{-1}), P=O (1181 cm^{-1}). HRMS (ESI) m/z 337.1473 ($M+H^+$), calc. for $C_{20}H_{22}N_2OP^+$ 337.1464

6 Characterization Data of the catalysts:



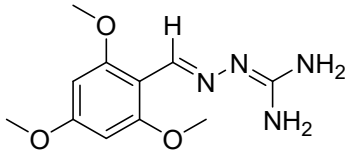
C1

Yield: 580 mg, 95%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 7.95 (s, 1H), 7.63-7.62 (d, *J* = 7.62 Hz, 2H), 7.30-7.27 (t, *J* = 7.28 Hz, 2H), 7.22-7.19 (t, *J* = 7.21 Hz, 1H), 5.89 (br.s, 1H), 5.80 (br. s., 1H) - ; ^{13}C NMR 161.1, 143.6, 137.4, 128.8, 128.2, 126.7; IR (FTIR) -NH (3428 cm^{-1}), C=N (1637 cm^{-1}). HRMS (ESI) m/z 163.0978 ($M+H^+$), calc. for $C_8H_{11}N_4^+$ 163.1024.



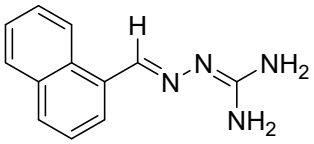
C2

Yield: 510 mg, 84%, white solid; ^{1}H NMR (500 MHz, DMSO- *d6*) δ 8.43 – 8.42 (d, *J* = 8.42 Hz, 1H), 8.04 – 8.03 (d, *J* = 8.03 Hz, 1H), 7.93 (br. s., 1H), 7.68 - 7.65 (t, *J* = 7.66 Hz, 1H), 7.18 – 7.16 (dd, *J* = 7.17 Hz, 1H), 6.15 (br.s, 1H), 5.87 (br. s., 1H); ^{13}C NMR 161.7, 156.2, 149.3, 143.8, 136.4, 122.7, 119.8; IR (FTIR) -NH (3456 cm^{-1}), C=N (1567 cm^{-1}). HRMS (ESI) m/z 164.0953 ($M+H^+$), calc. for $C_7H_{10}N_5^+$ 164.0931.



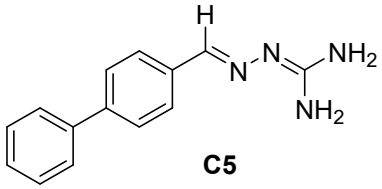
C3

Yield: 464 mg, 90%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 8.09 (br. s., 1H), 6.19 (br. s., 2H), 5.54 (br. s., 2H), 5.23 (br. s., 2H), 3.75 (br. s., 3H), 3.75 (br. s., 6H); 13C NMR 160.8, 159.8, 159.7, 139.5, 107.2, 91.7, 56.3, 55.7; IR (FTIR) CN (2342 cm-1), P=O (1182 cm-1). HRMS (ESI) m/z 253.1280 ($M+H^+$), calc. for $C_{11}H_{17}N_4O_3^+$ 253.1295.



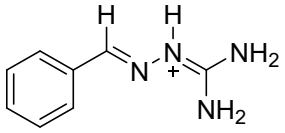
C4

Yield: 502 mg, 92%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 8.68 (br. s., 1H), 8.63 – 8.62 (d, *J* = 8.62 Hz, 1H), 7.98 – 7.96 (d, *J* = 7.97 Hz, 1H), 7.90 – 7.88 (d, *J* = 7.87 Hz, 1H), 7.81 – 7.79 (d, *J* = 7.80 Hz, 1H), 7.54 – 7.44 (m, 4H), 5.94 (br. s., 2H), 5.60 (br. s., 2H),; 13C NMR 161.2, 142.5, 134.0, 132.7, 130.7, 129.0, 128.3, 126.9, 126.2, 126.0, 125.4, 124.5; IR (FTIR) -NH (3451 cm-1), C=N (1637 cm-1). HRMS (ESI) m/z 213.1187 ($M+H^+$), calc. for $C_{12}H_{13}N_4^+$ 213.1135.



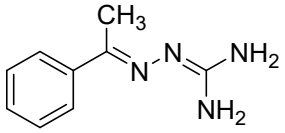
C5

Yield: 495 mg, 94%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 7.99 (br. s., 1H), 7.73 – 7.71 (d, *J* = 7.72 Hz, 2H), 7.66 – 7.64 (d, *J* = 7.65 Hz, 2H), 7.61 – 7.59 (d, *J* = 7.60 Hz, 2H), 7.44 – 7.41 (t, *J* = 7.42 Hz, 2H), 7.33 – 7.30 (t, *J* = 7.32 Hz, 1H), 6.04 (br. s., 2H), 5.67 (br. s., 2H); 13C NMR 161.1, 143.1, 140.3, 139.7, 136.6, 129.4, 127.9, 127.3, 127.1, 126.9; IR (FTIR) -NH (3450 cm-1), C=N (1586 cm-1). HRMS (ESI) m/z 239.1345 ($M+H^+$), calc. for $C_{14}H_{15}N_4^+$ 239.1291.



C6

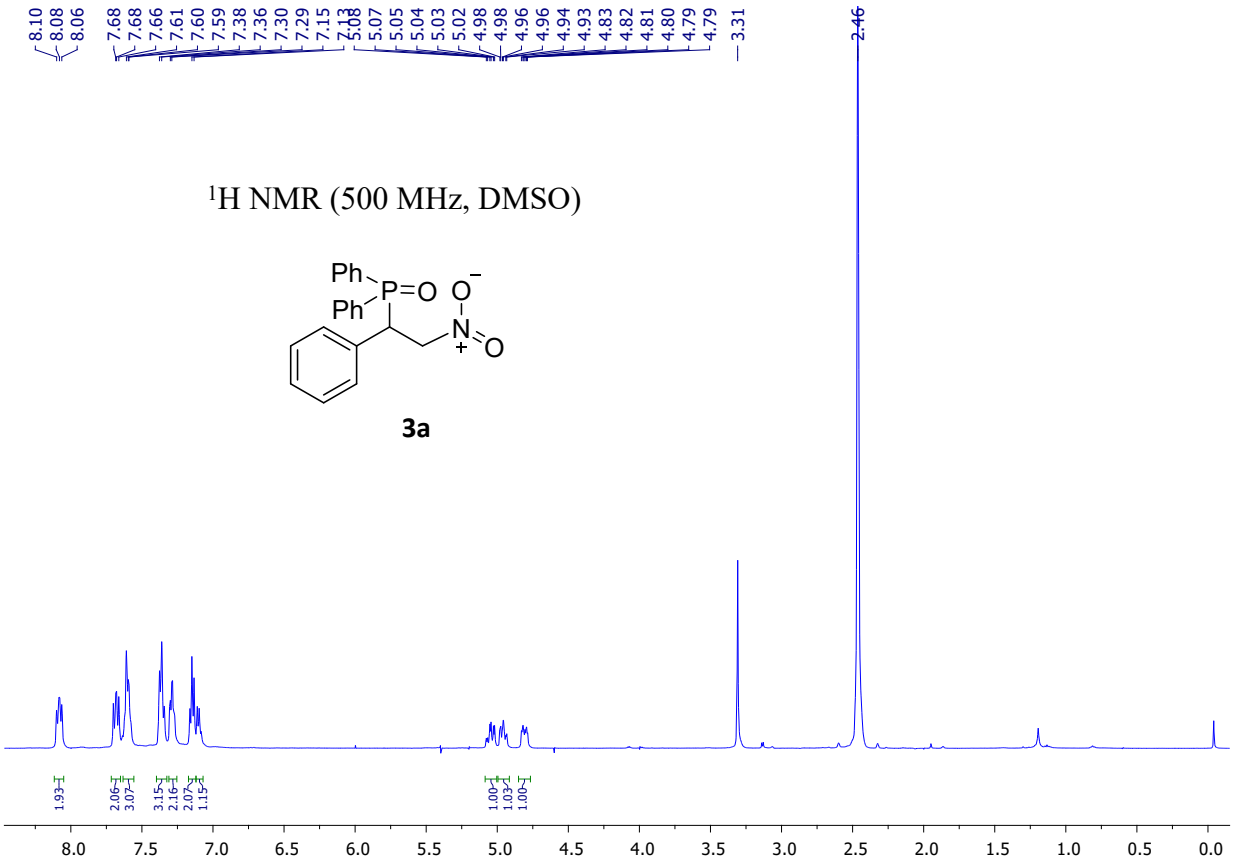
Yield: 563 mg, 92%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 12.10(br. s., 1H), 8.15 (br. s., 1H), 7.82 (br. s., 4H), 7.59 (br. s., 1H), 7.40 (br. s., 3H); 13C NMR 156.0, 147.2, 133.9, 130.9, 129.2, 128.1; IR (FTIR) -NH (3099 cm-1), C=N (1657 cm-1). HRMS (ESI) m/z 163.1003 ($M+H^+$), calc. for $C_8H_{11}N_4^+$ 163.0978.



C7

Yield: 525 mg, 88%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 7.75 – 7.74 (d, *J* = 7.74 Hz, 2H), 7.29 – 7.26 (t, *J* = 7.20 Hz, 2H), 7.21 – 7.19 (t, *J* = 7.20 Hz, 1H), 5.84 (br. s., 1H), 5.45 (br. s., 1H), 3.34 (br. s., 1H), 3.32 (br. s., 1H), 2.18 (br. s., 3H); 13C NMR 160.2, 140.7, 128.4, 127.6, 125.8, 13.8; IR (FTIR) -NH (3458 cm-1), C=N (1621 cm-1). HRMS (ESI) m/z 177.1135 ($M+H^+$), calc. for $C_9H_{13}N_4^+$ 177.1182.

7 ^{1}H , ^{13}C and ^{31}P NMR spectra of Products:



^{1}H NMR (500 MHz, DMSO)

3a

8.10
8.08
8.06
7.70
7.68
7.68
7.66
7.62
7.61
7.60
7.59
7.58
7.38
7.36
7.34
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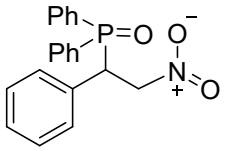
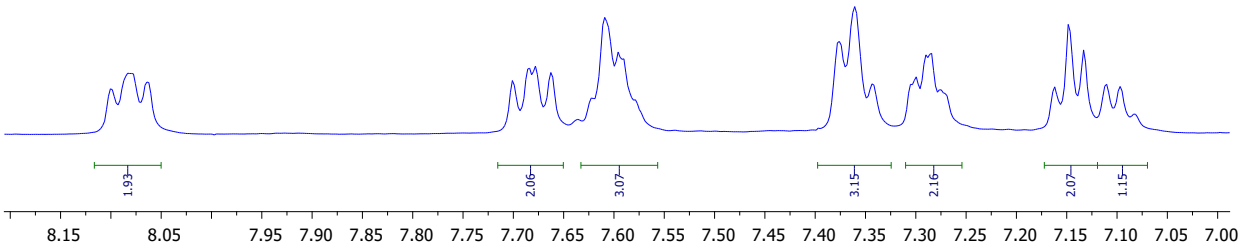
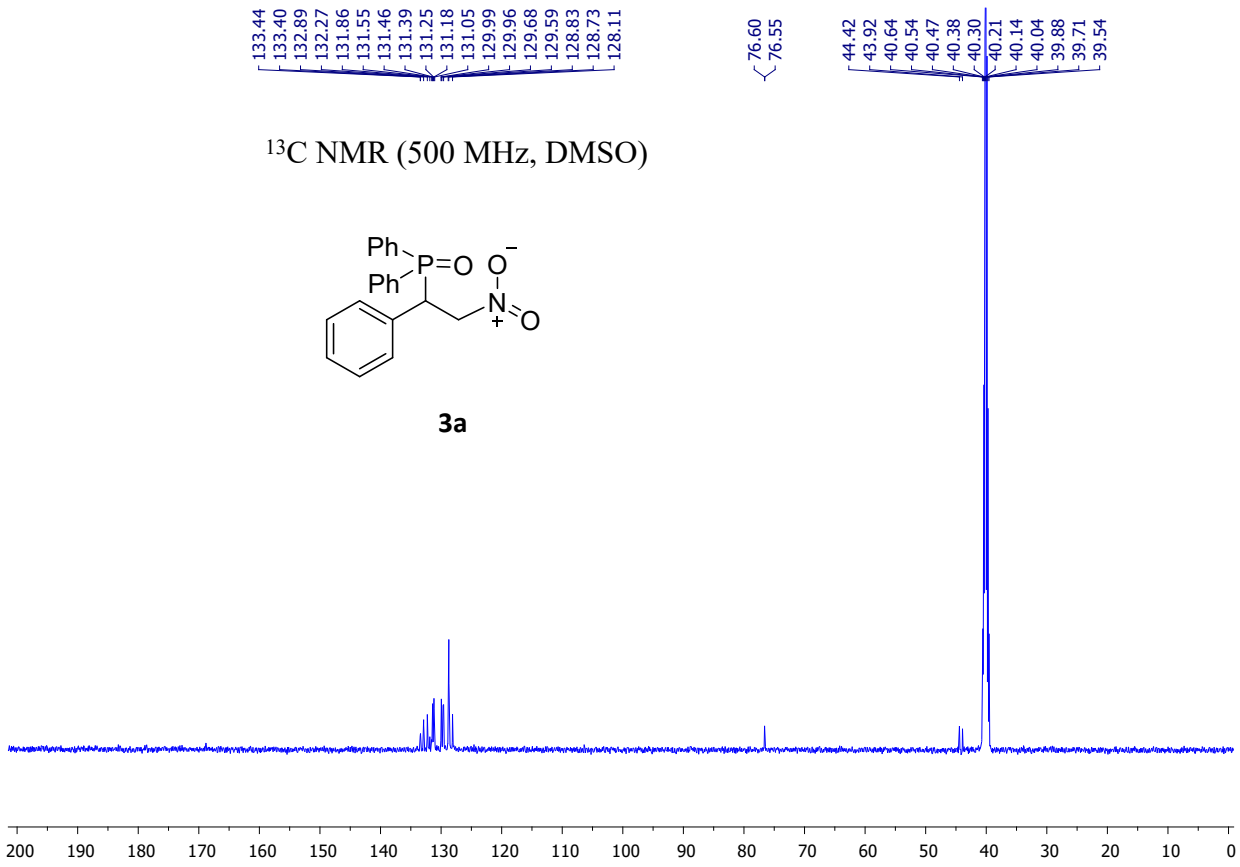
7.28
7.16
7.15
7.13
7.11
7.10
7.08

^{1}H NMR (500 MHz, DMSO)



3a



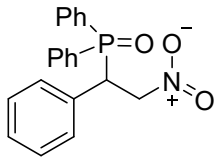


^{13}C NMR (500 MHz, DMSO)

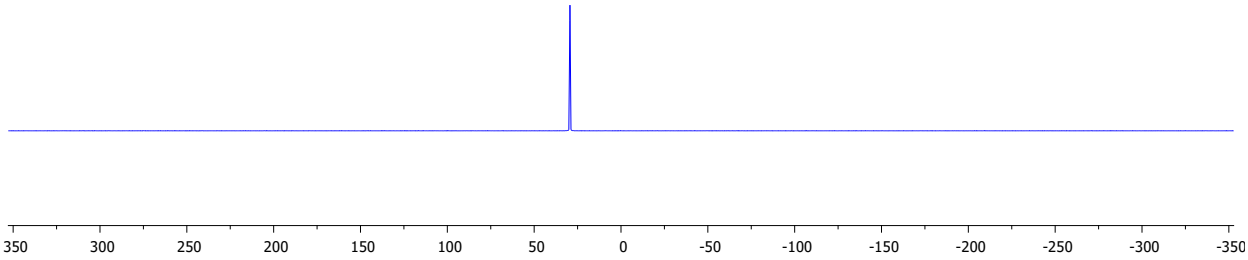
3a

29.39

^{31}P NMR (202.4 MHz, DMSO

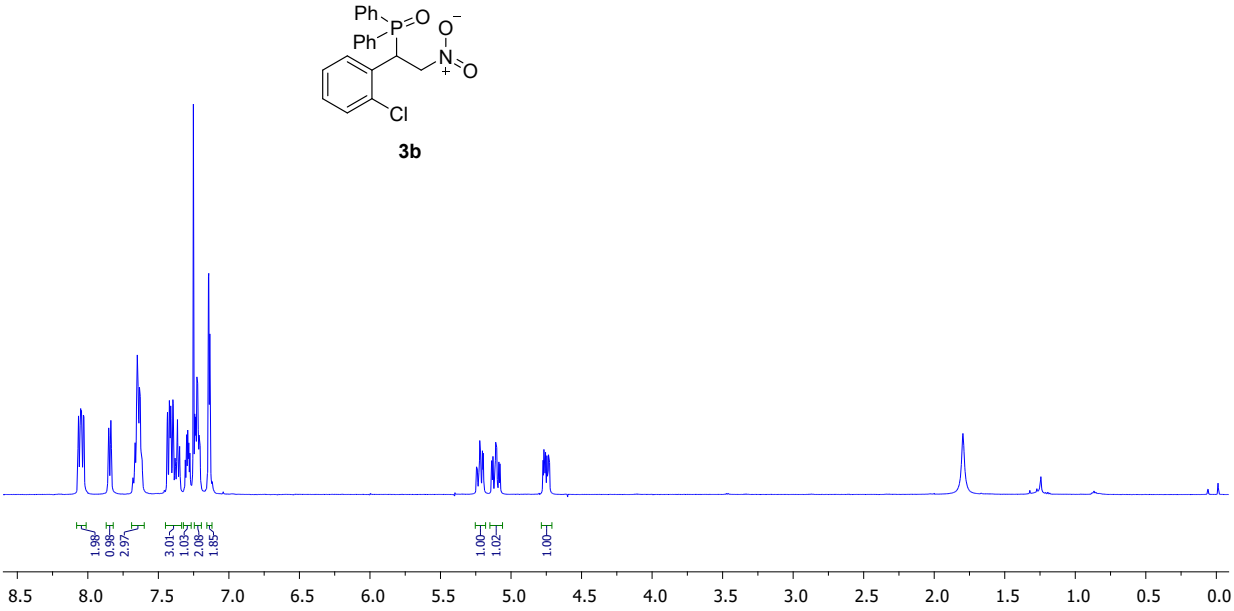


3a



8.05 8.05 8.03 8.03 7.65 7.63 7.63 7.44 7.42 7.41 7.40 7.25 7.23 7.22 7.14 7.14 5.22 5.22 5.20 5.20 5.13 5.11 5.11 5.10 4.77 4.76 4.76 4.75 4.74 4.73 4.73 1.80

^{1}H NMR (500 MHz, $CDCl_3$)



3b

8.07
8.05
8.05
8.03
8.03
7.85
7.84
7.68
7.67
7.65
7.63
7.63
7.62
7.44
7.42
7.41
7.40
7.38
7.37
7.35
7.30
7.29
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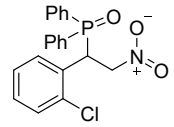
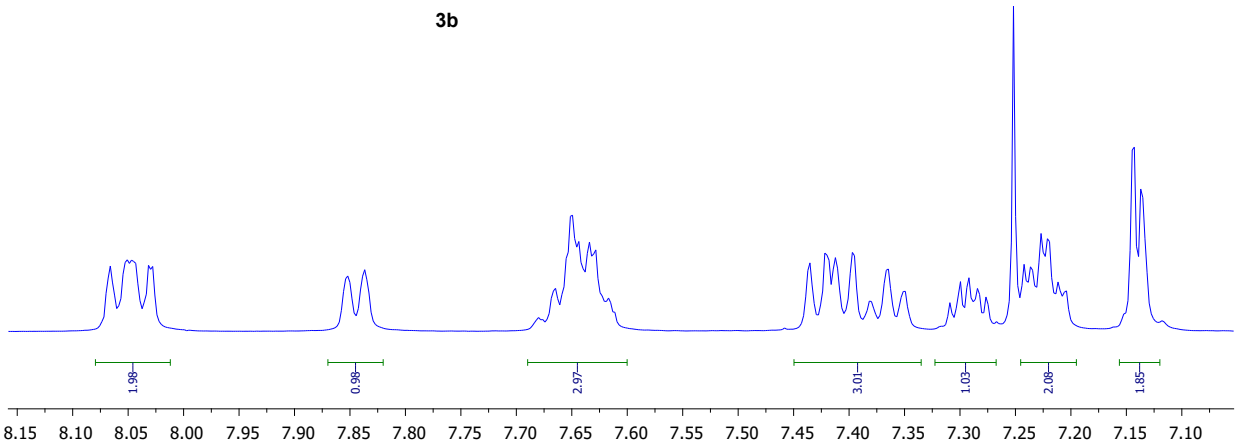
7.24
7.24
7.23
7.22
7.21
7.14

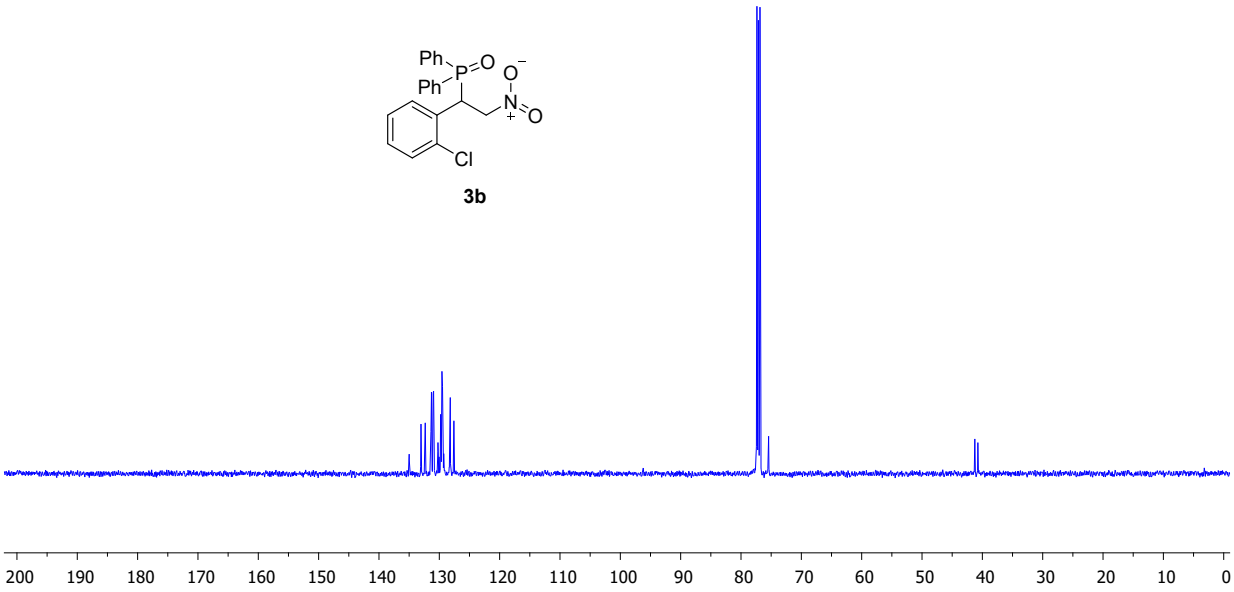
^{1}H NMR (500 MHz, $CDCl_3$)



3b

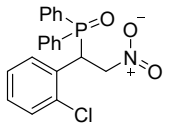


^{13}C NMR (500 MHz, $CDCl_3$)

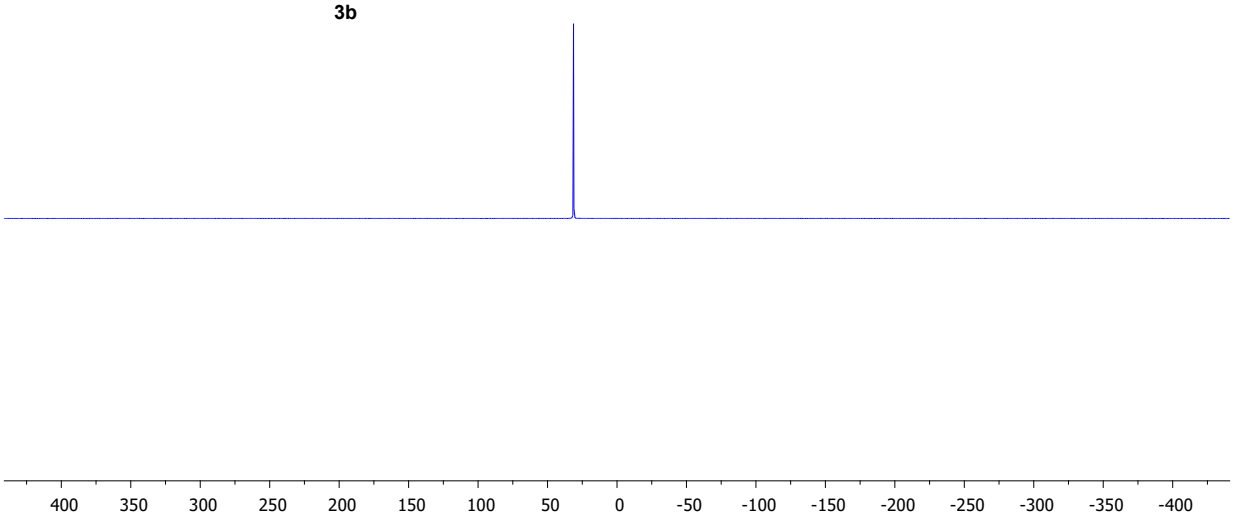


31.30

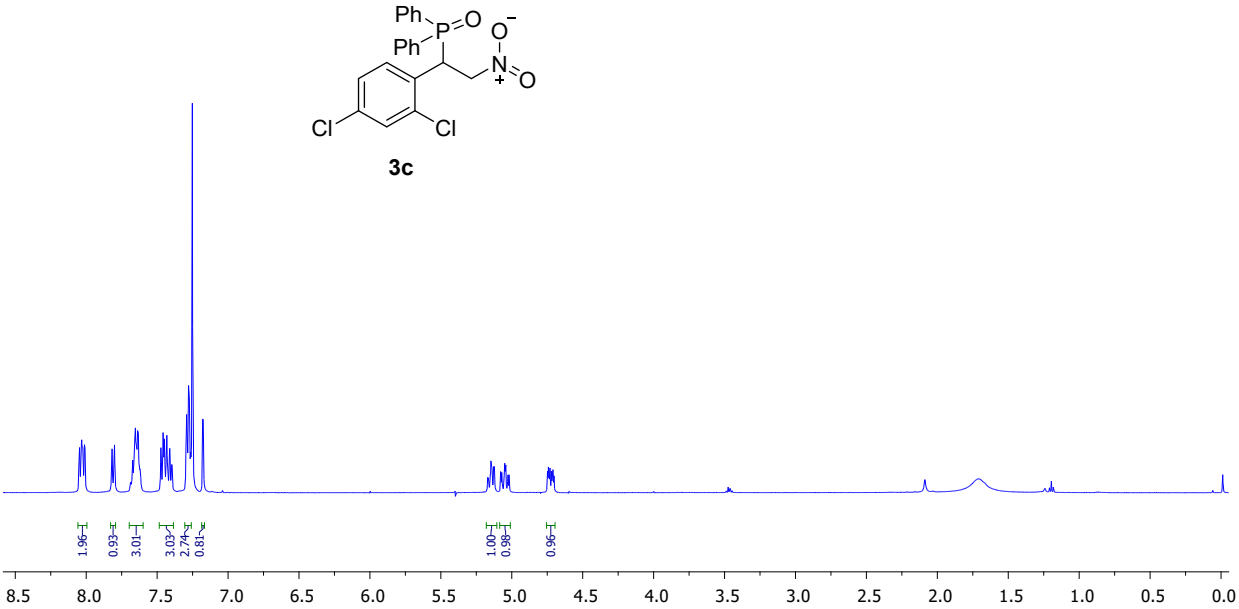
^{31}P NMR (202.4 MHz, $CDCl_3$)



3b



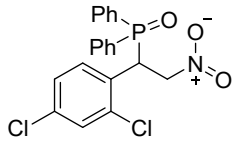
^{1}H NMR (500 MHz, $CDCl_3$)



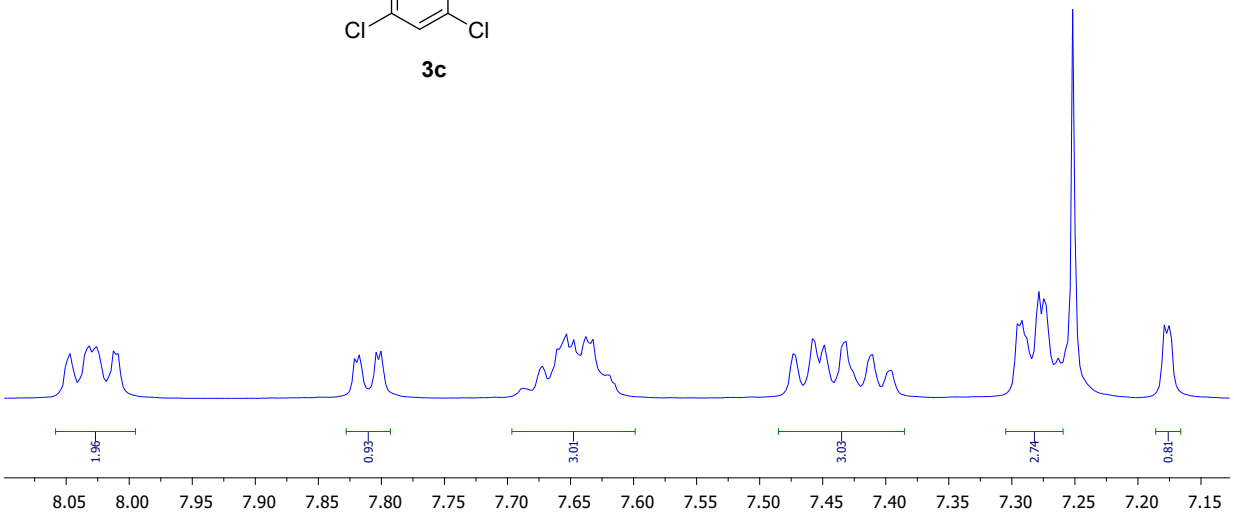
3c

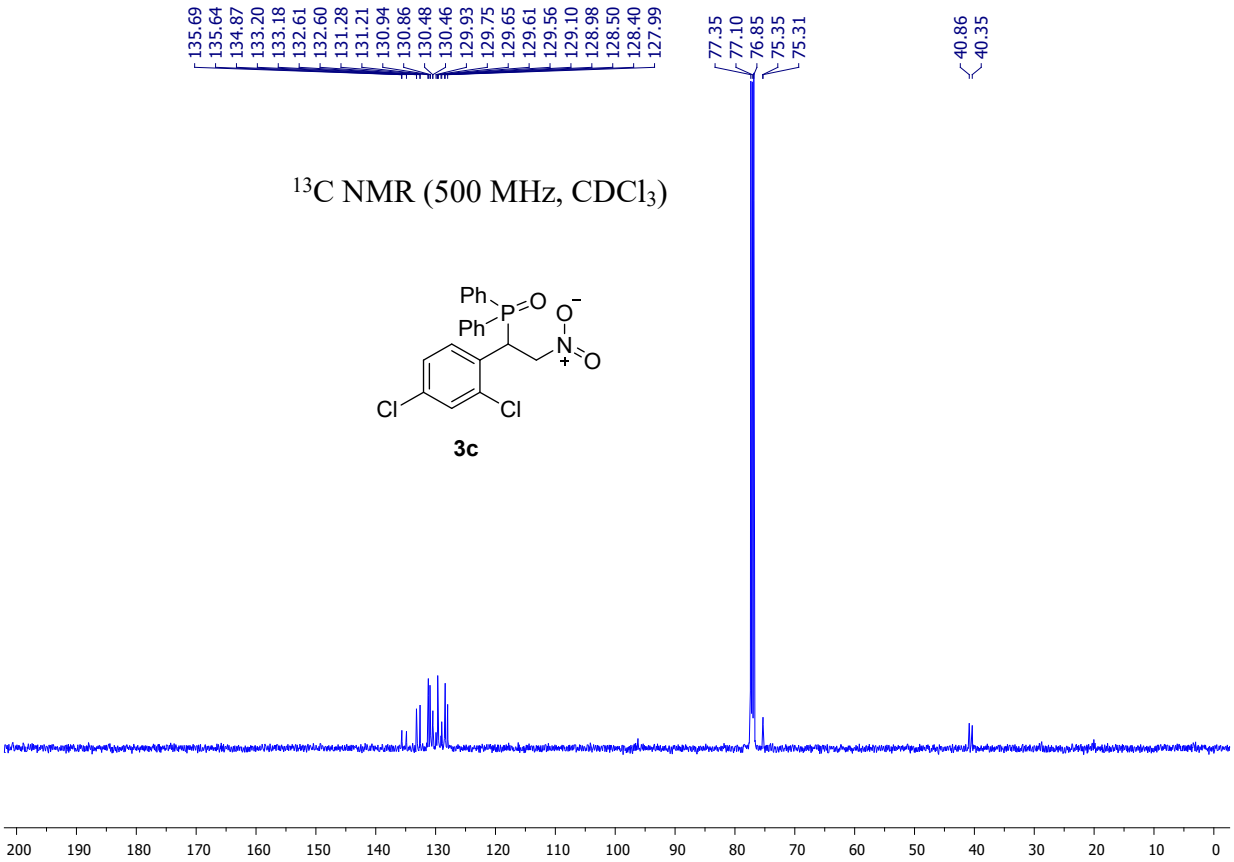
8.05 8.03 8.03 8.01 8.01 7.82 7.82 7.80 7.80 7.69 7.67 7.66 7.65 7.65 7.64 7.63 7.62 7.47 7.46 7.45 7.43 7.41 7.40 7.29 7.29 7.28 7.27 7.25 7.18 7.18

^{1}H NMR (500 MHz, $CDCl_3$)



3c

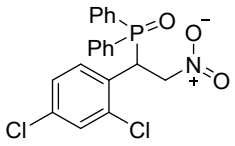




^{13}C NMR (500 MHz, $CDCl_3$)

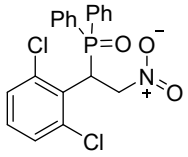
3c

^{31}P NMR (500 MHz, $CDCl_3$)

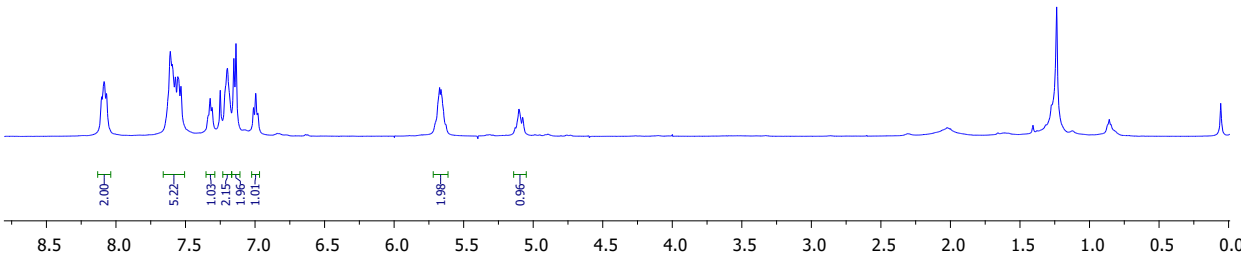


3c

^{1}H NMR (500 MHz, $CDCl_3$)

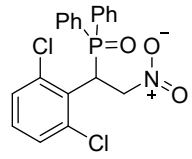


3d

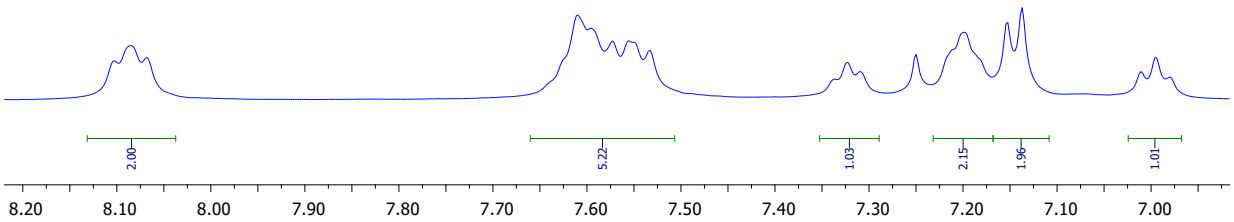


8.10
8.09
8.07
7.61
7.60
7.57
7.56
7.55
7.53
7.34
7.32
7.31
7.25
7.20
7.15
7.14
7.01
7.00
6.98

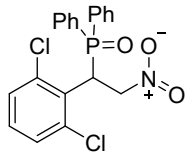
^{1}H NMR (500 MHz, $CDCl_3$)



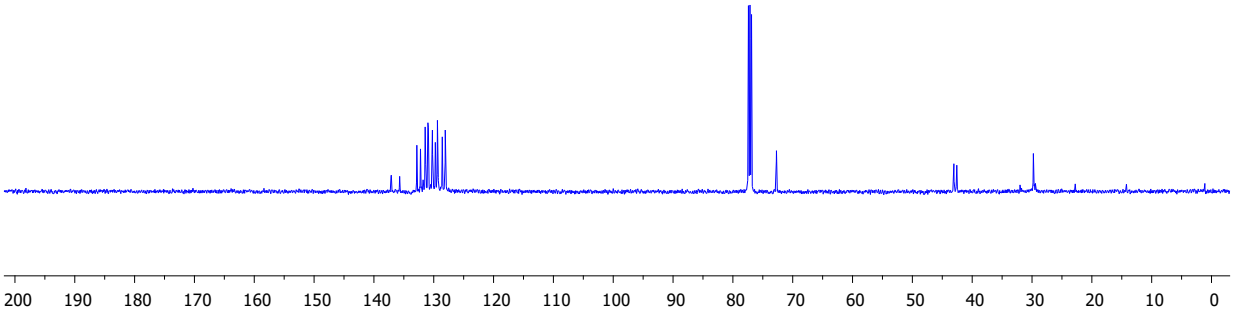
3d



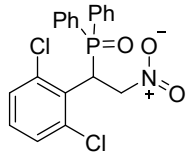
^{13}C NMR (500 MHz, $CDCl_3$)



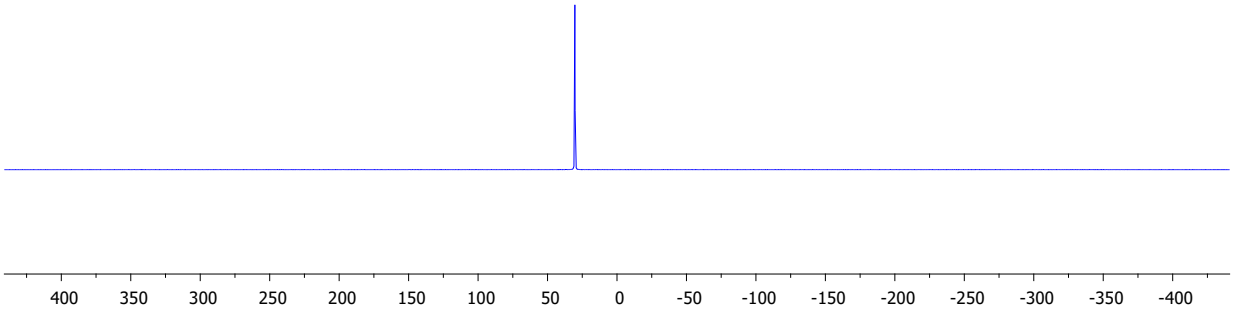
3d



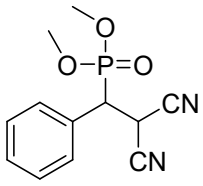
30.32


Ph
Ph
Cl
P=O
O
N
O
Cl

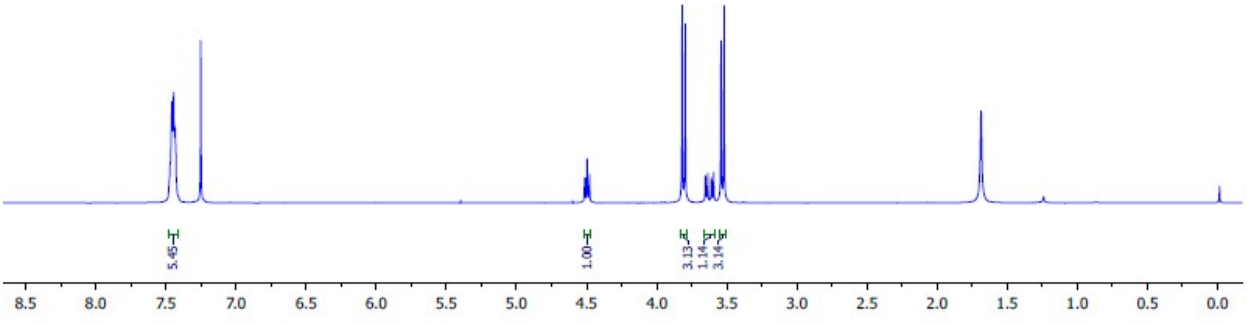
3d


400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400

^{1}H NMR (500 MHz, $CDCl_3$)

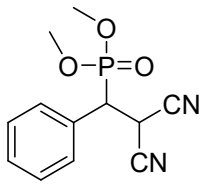


6



4.51
4.50
4.48
3.82
3.80
3.65
3.64
3.61
3.59
3.54
3.52

^{1}H NMR (500 MHz, $CDCl_3$)



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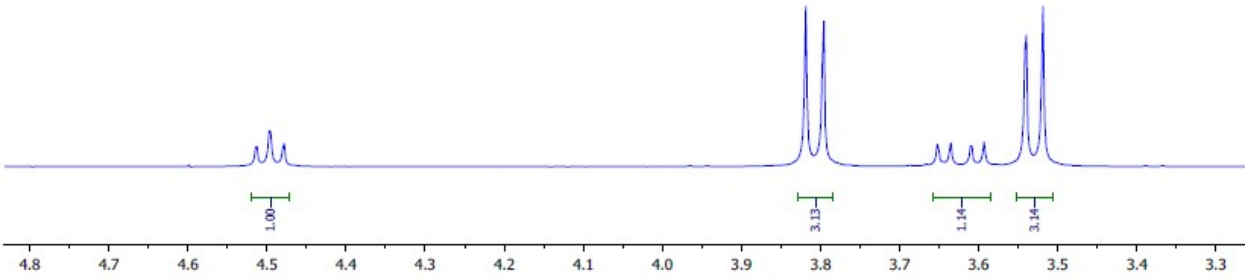
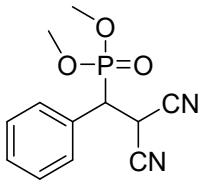


^{13}C NMR (500 MHz, $CDCl_3$)



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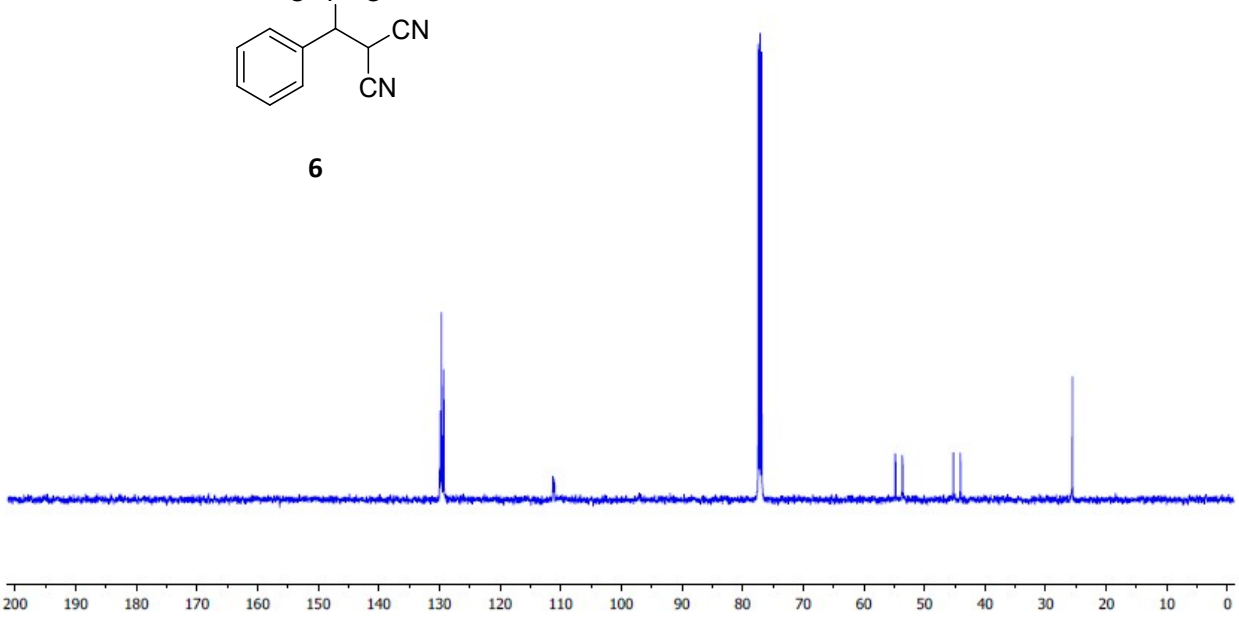
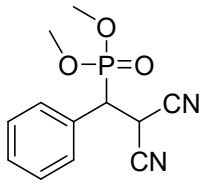


— 22.38

^{31}P NMR (202.4 MHz, $CDCl_3$)



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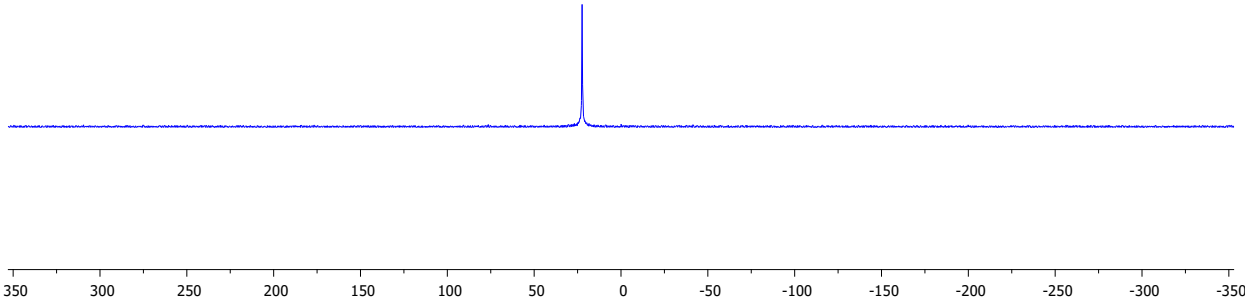
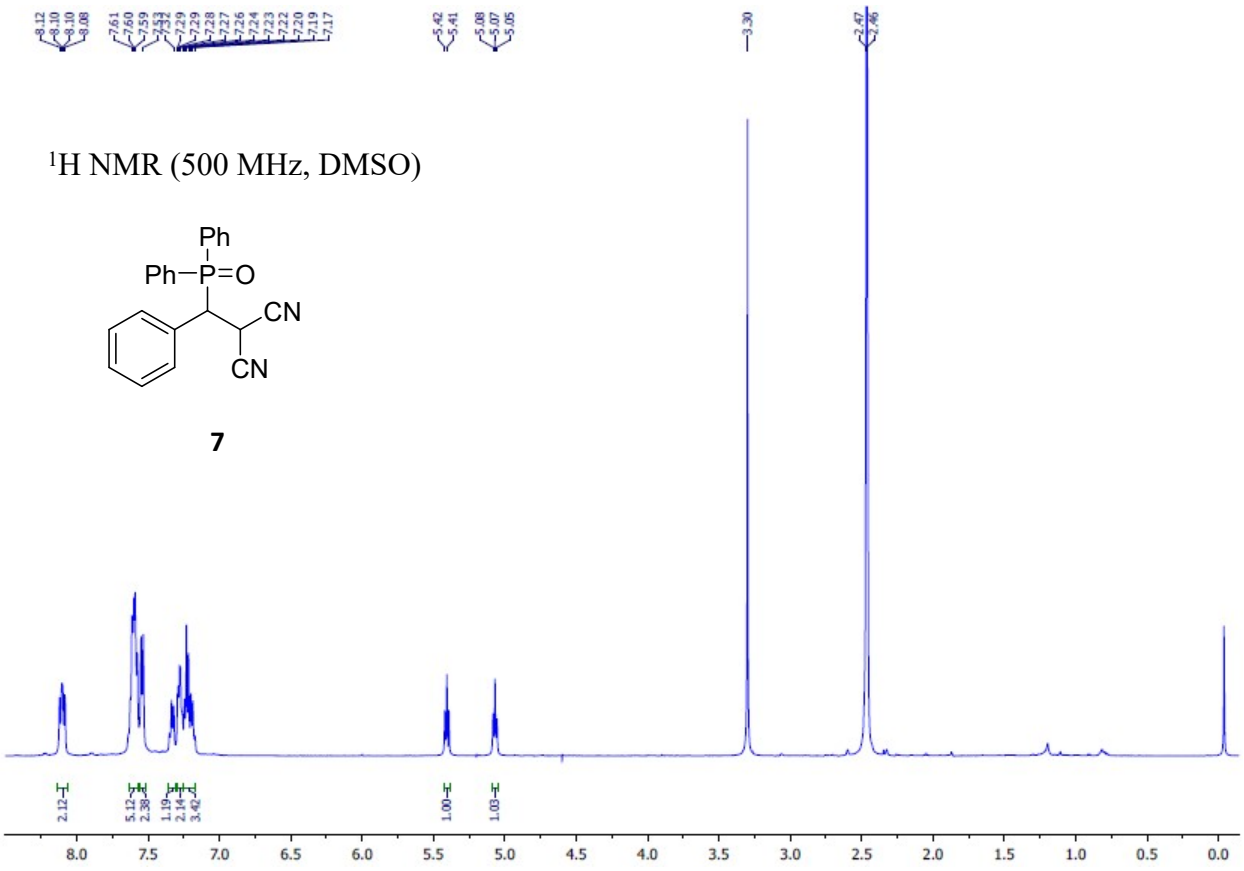


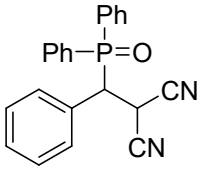


^{1}H NMR (500 MHz, DMSO)

7

5.42 5.41 5.08 5.07 5.05

^{1}H NMR (500 MHz, DMSO)



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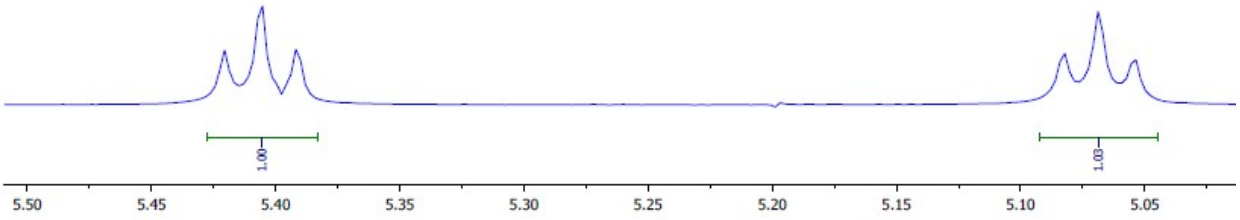
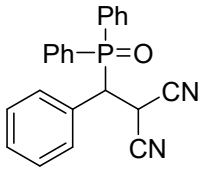


^{13}C NMR (500 MHz, $CDCl_3$)



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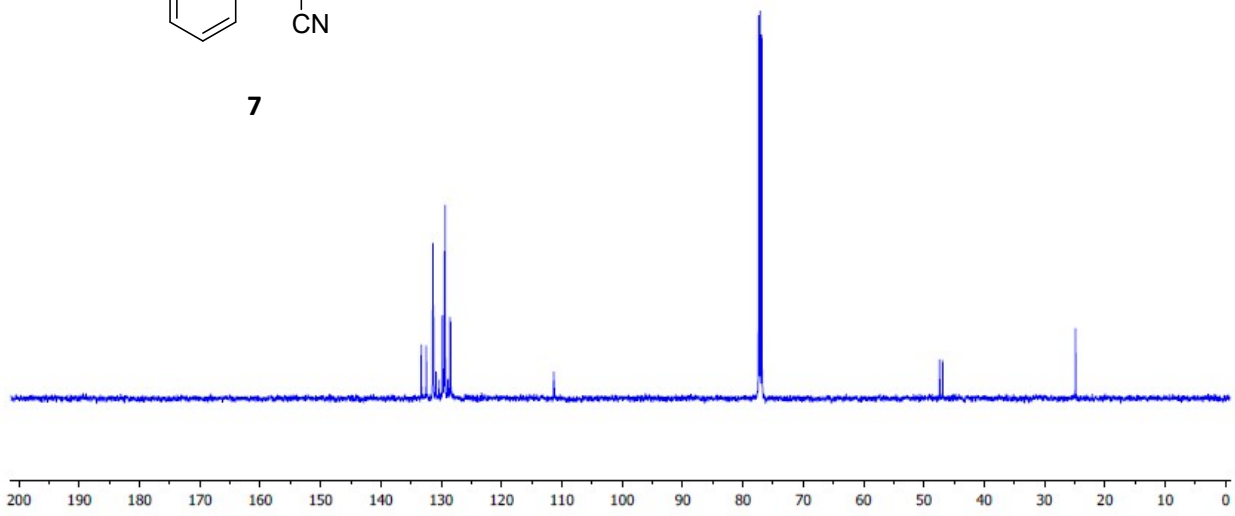
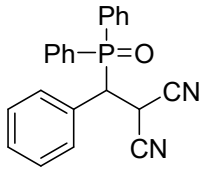


28.82

^{31}P NMR (202.4 MHz, DMSO)



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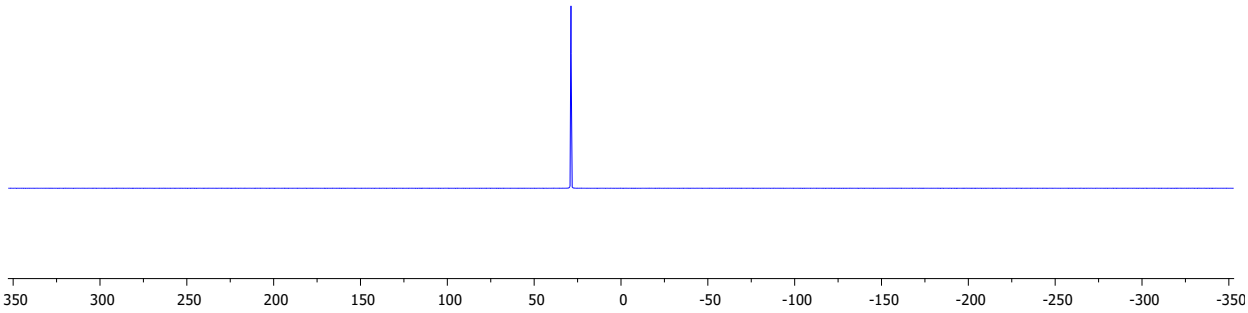
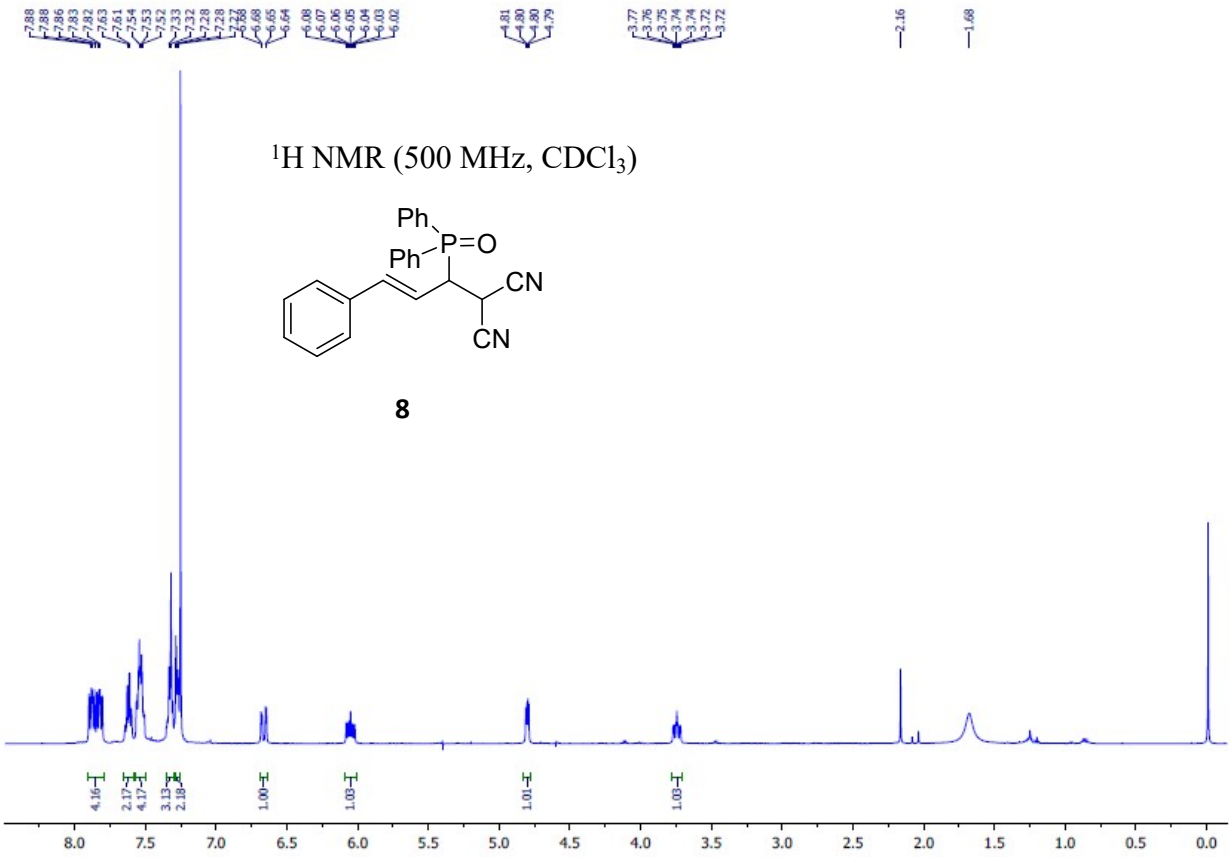
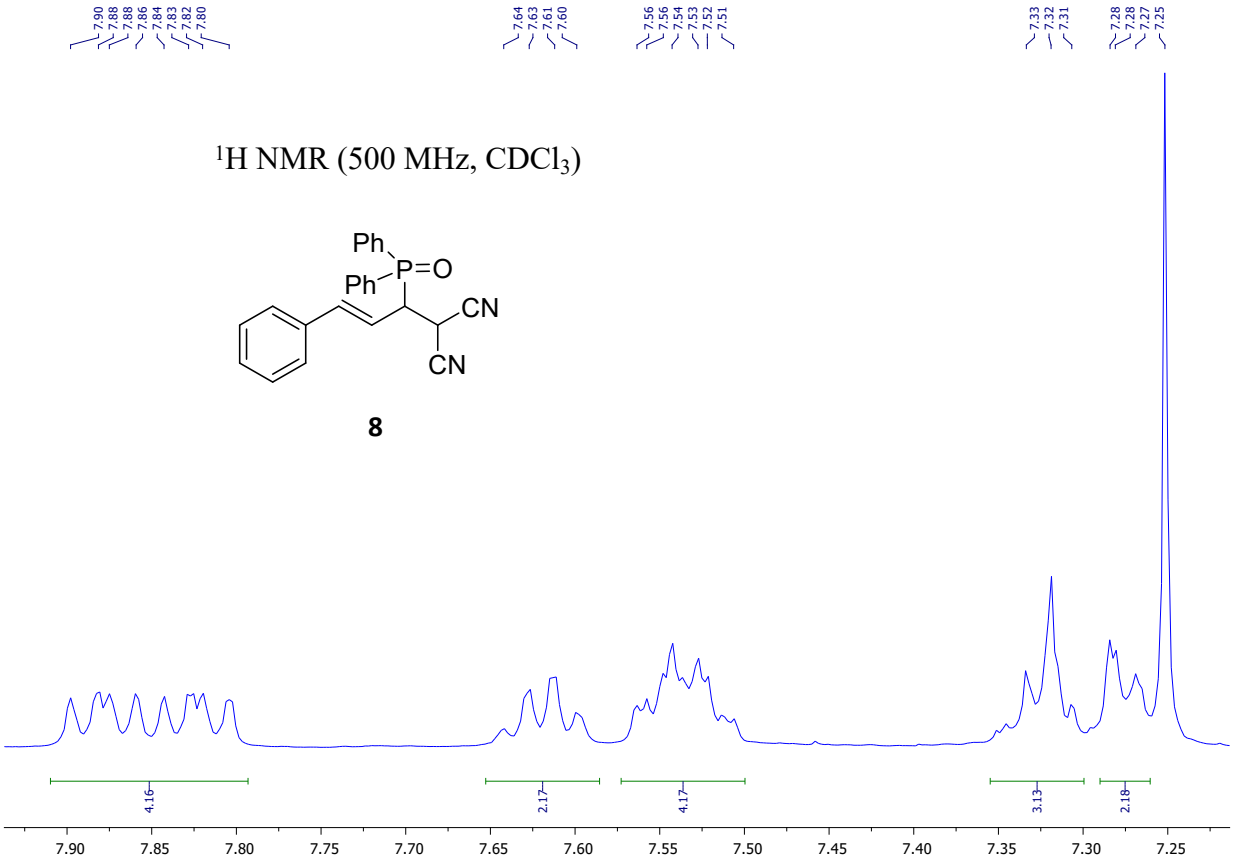




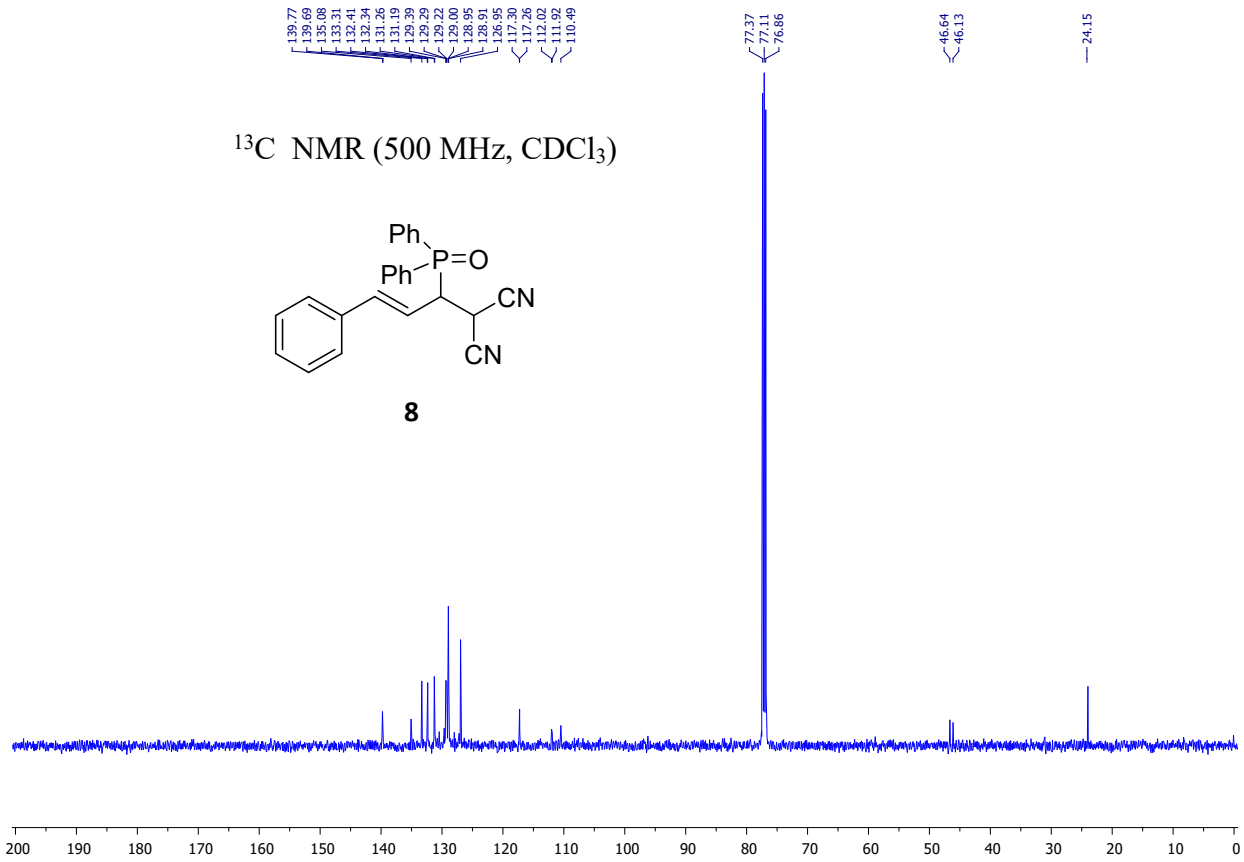
^{1}H NMR (500 MHz, $CDCl_3$)

8



^{1}H NMR (500 MHz, $CDCl_3$)

8

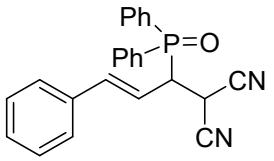


^{13}C NMR (500 MHz, $CDCl_3$)

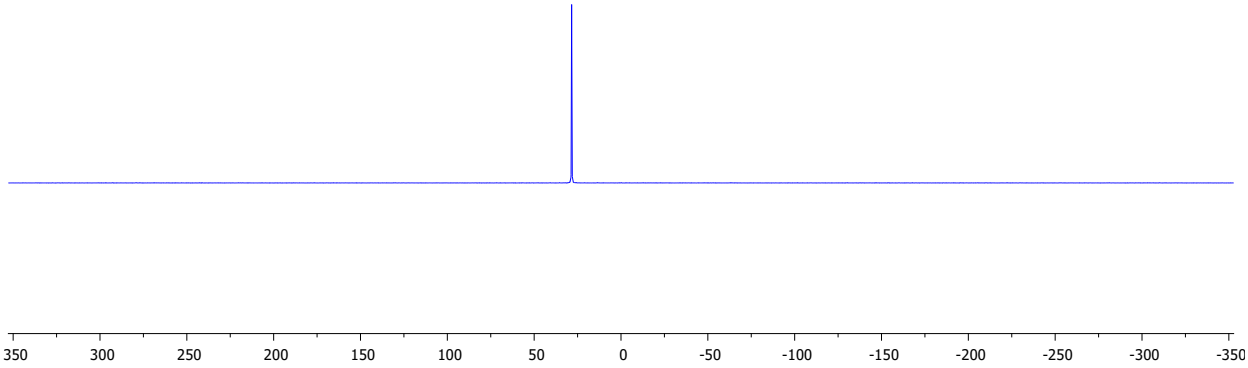
8

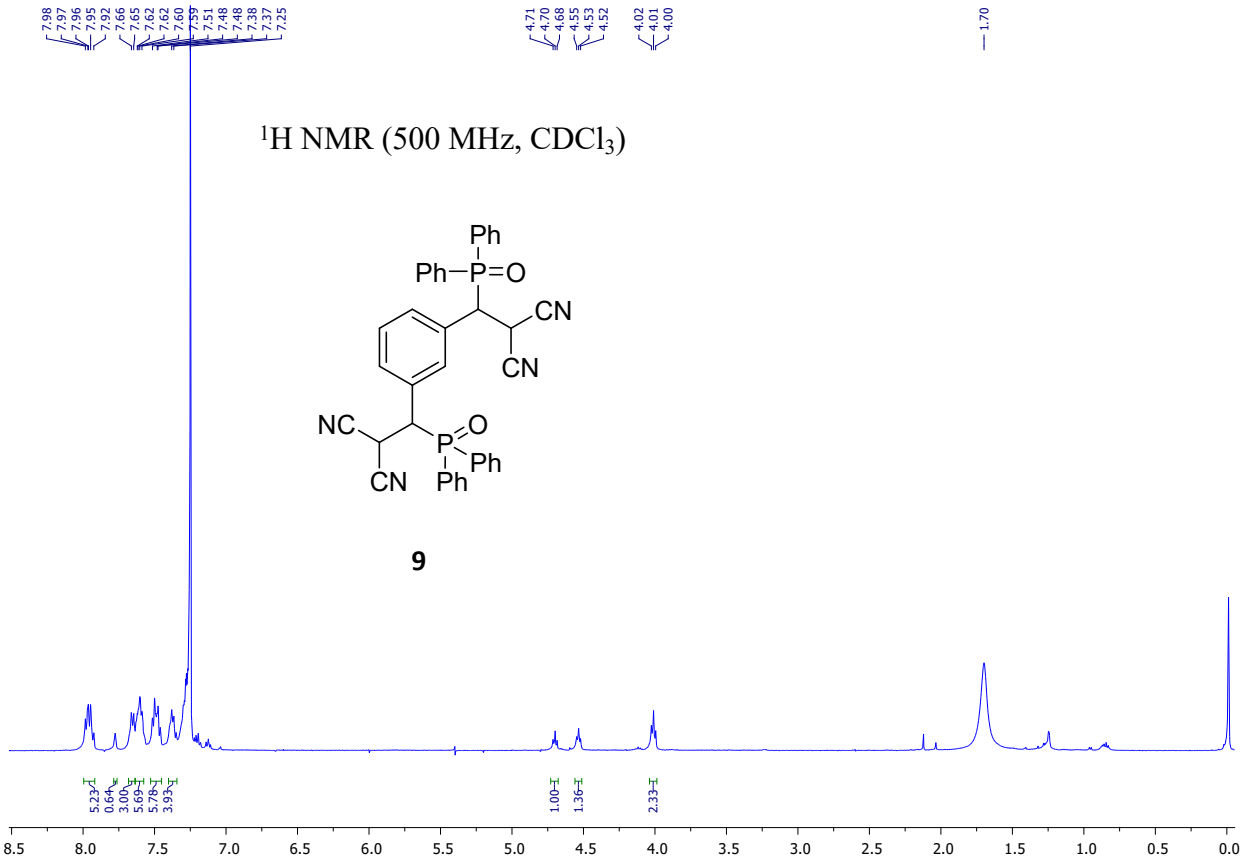
28.41

^{13}C NMR (202.4 MHz, $CDCl_3$)



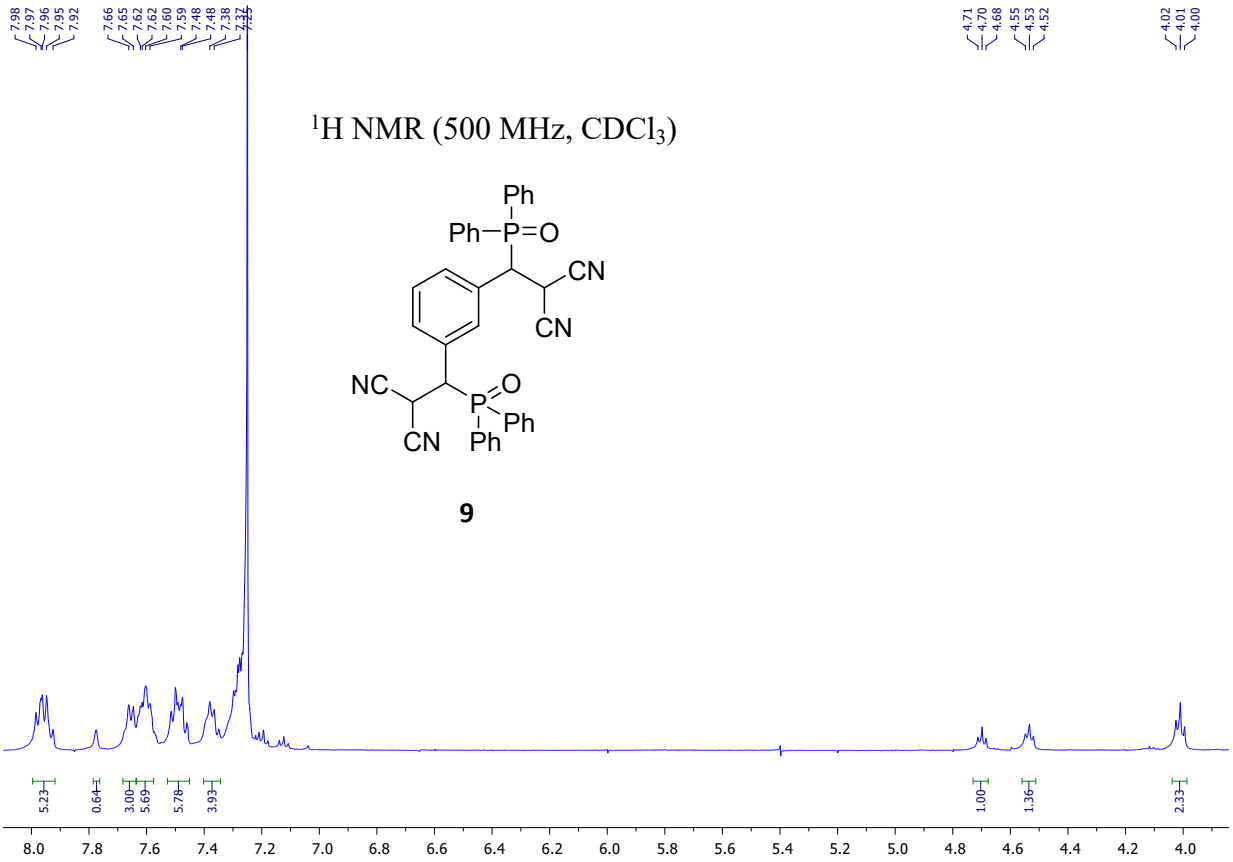
8





^{1}H NMR (500 MHz, $CDCl_3$)

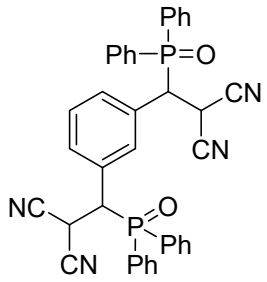
9



^{1}H NMR (500 MHz, $CDCl_3$)

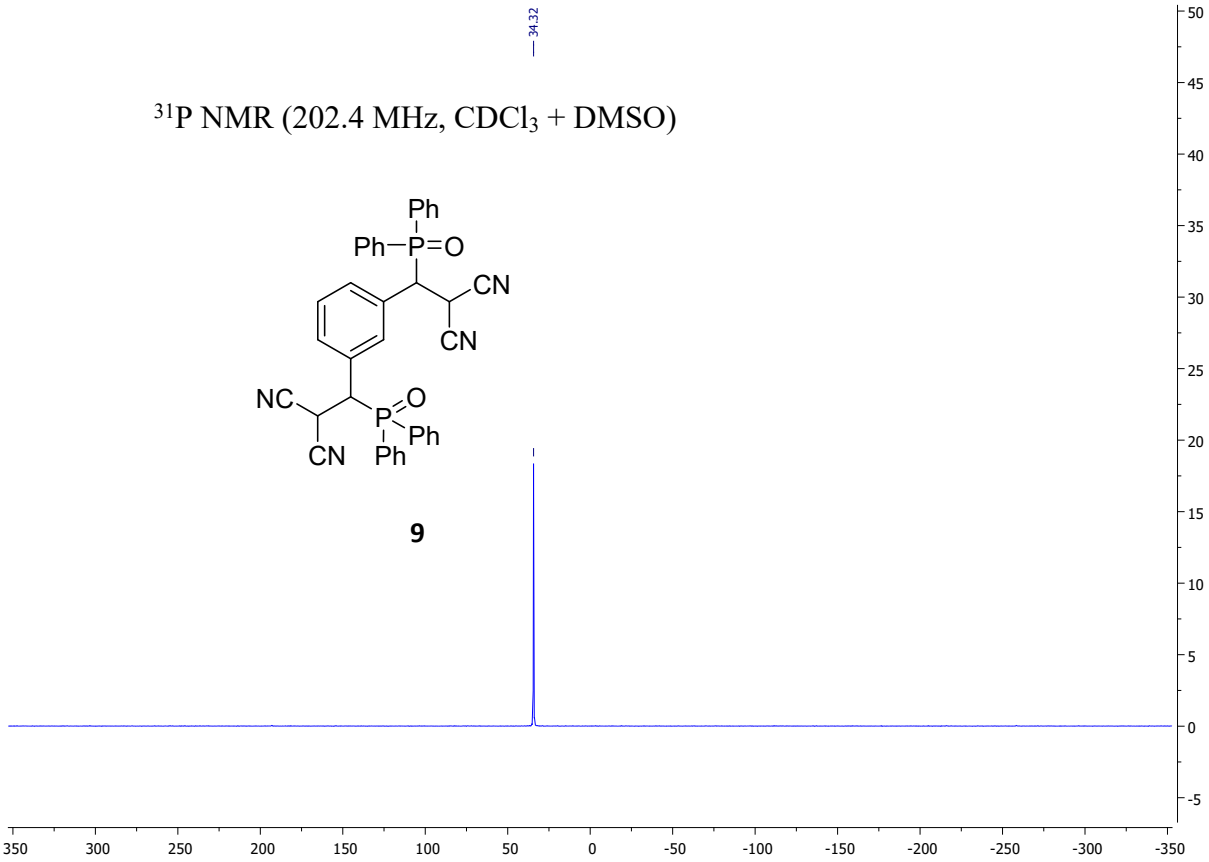
9

^{13}C NMR (500 MHz, $CDCl_3$ + DMSO)

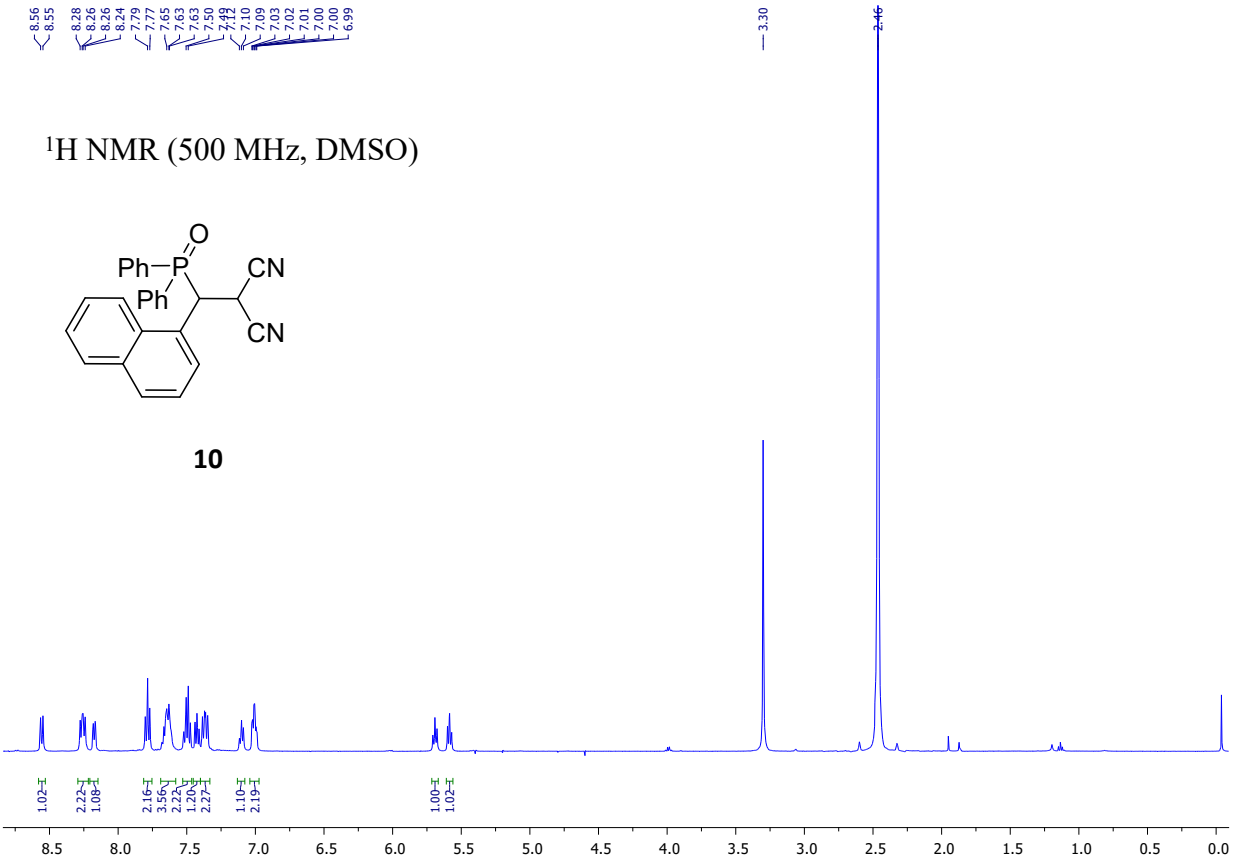


9

^{31}P NMR (202.4 MHz, $CDCl_3$ + DMSO)



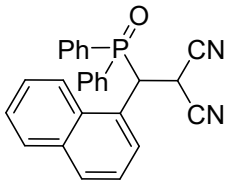
9



^{1}H NMR (500 MHz, DMSO)

10

^{1}H NMR (500 MHz, DMSO)



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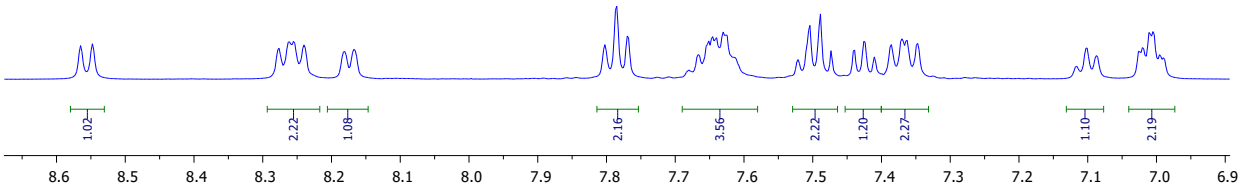
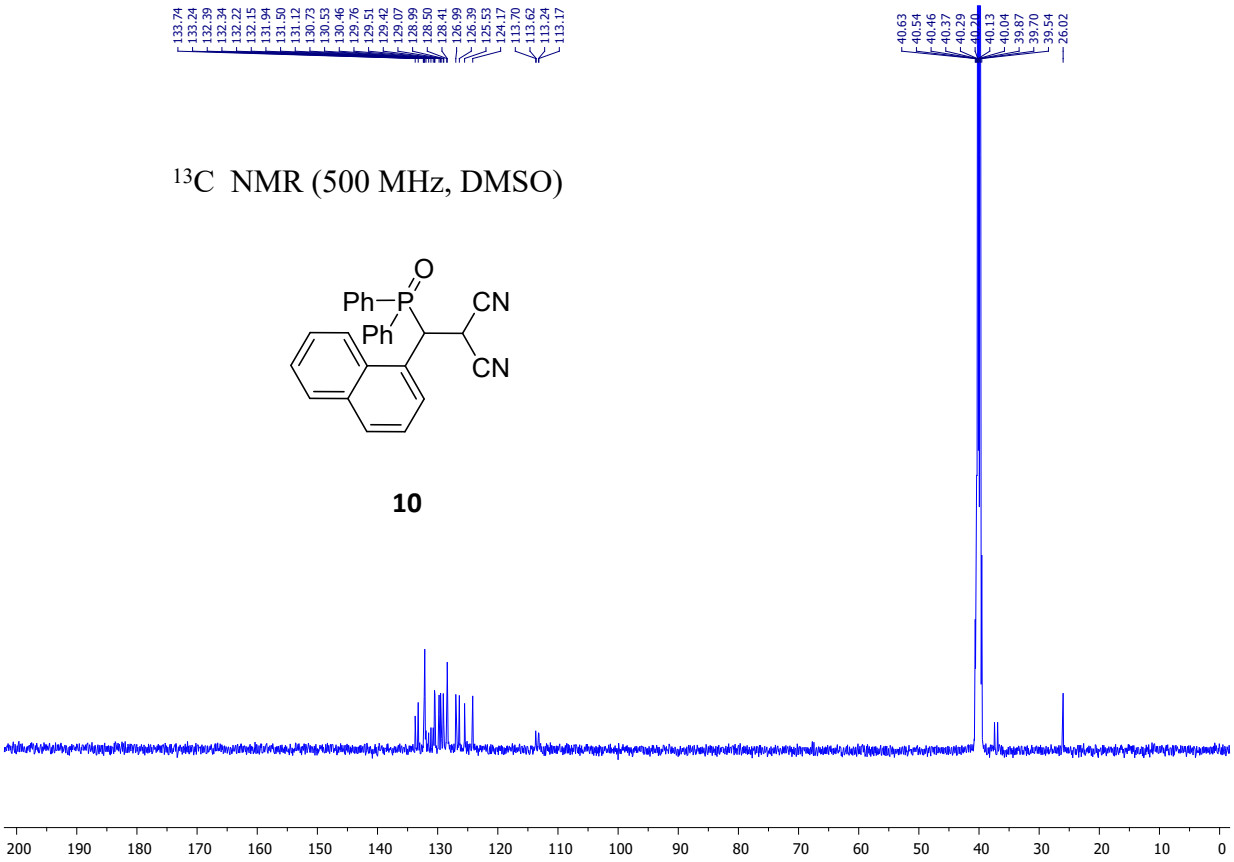


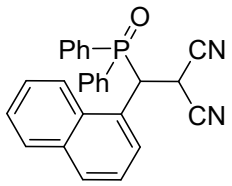


^{13}C NMR (500 MHz, DMSO)

10

29.55

^{31}P NMR (202.4 MHz, DMSO)



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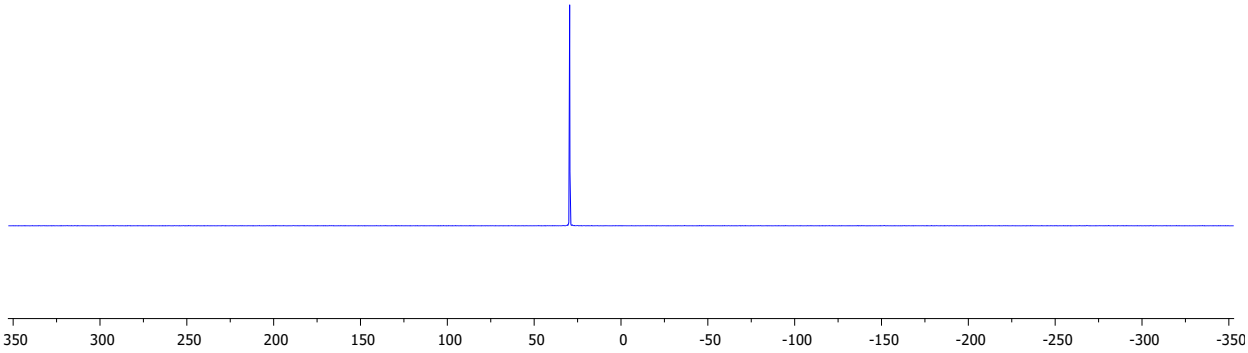
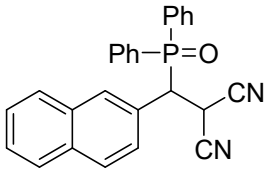
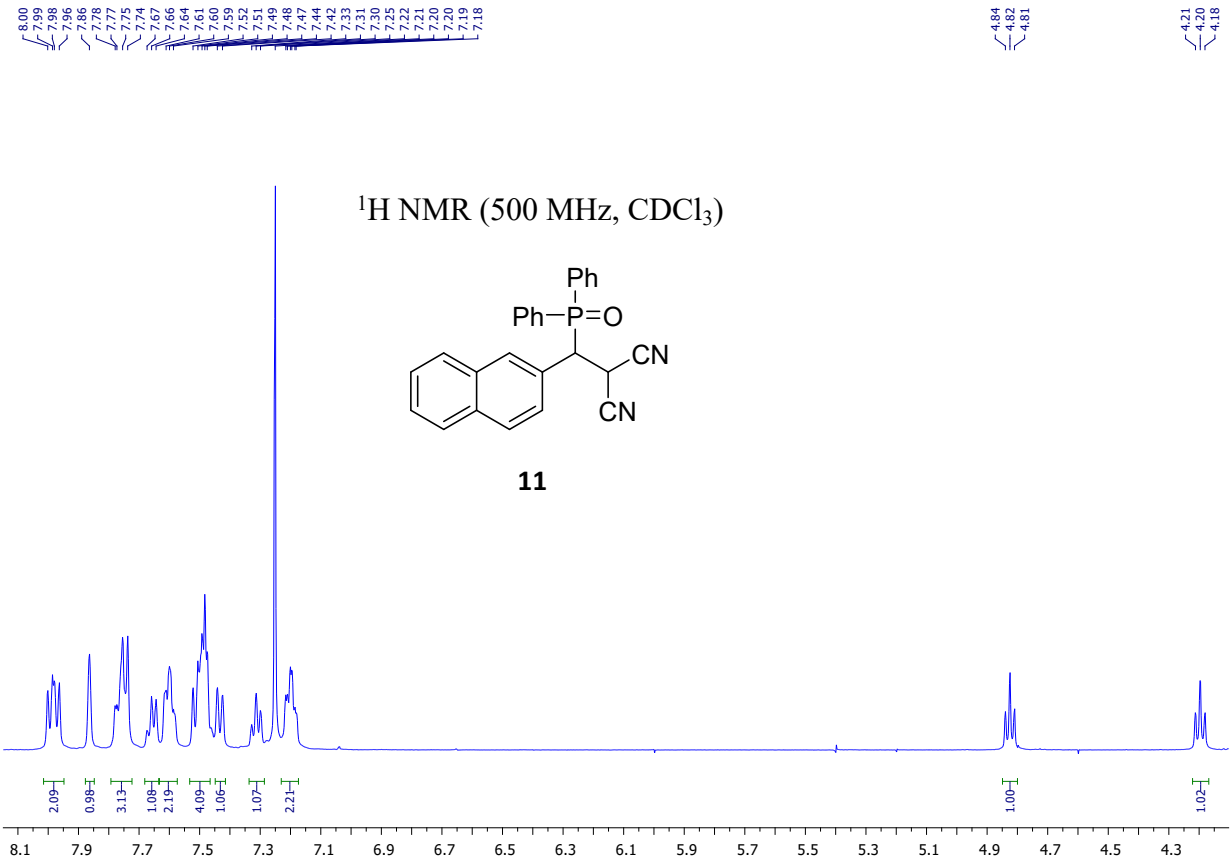


^{1}H NMR (500 MHz, $CDCl_3$)



11


8.00
7.99
7.98
7.96
7.86
7.78
7.77
7.75
7.74
7.67
7.66
7.64
7.61
7.60
7.59
7.52
7.51
7.49
7.48
7.47
7.44
7.42
7.33
7.31
7.30
7.25
7.22
7.21
7.20
7.19
7.18
4.84
4.82
4.81
4.21
4.20
4.18
^{1}H NMR (500 MHz, $CDCl_3$)
Ph
Ph—P=O
CN
CN
11
2.09
0.98
3.13
1.08
2.19
4.09
1.06
1.07
2.21
1.00
1.02
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
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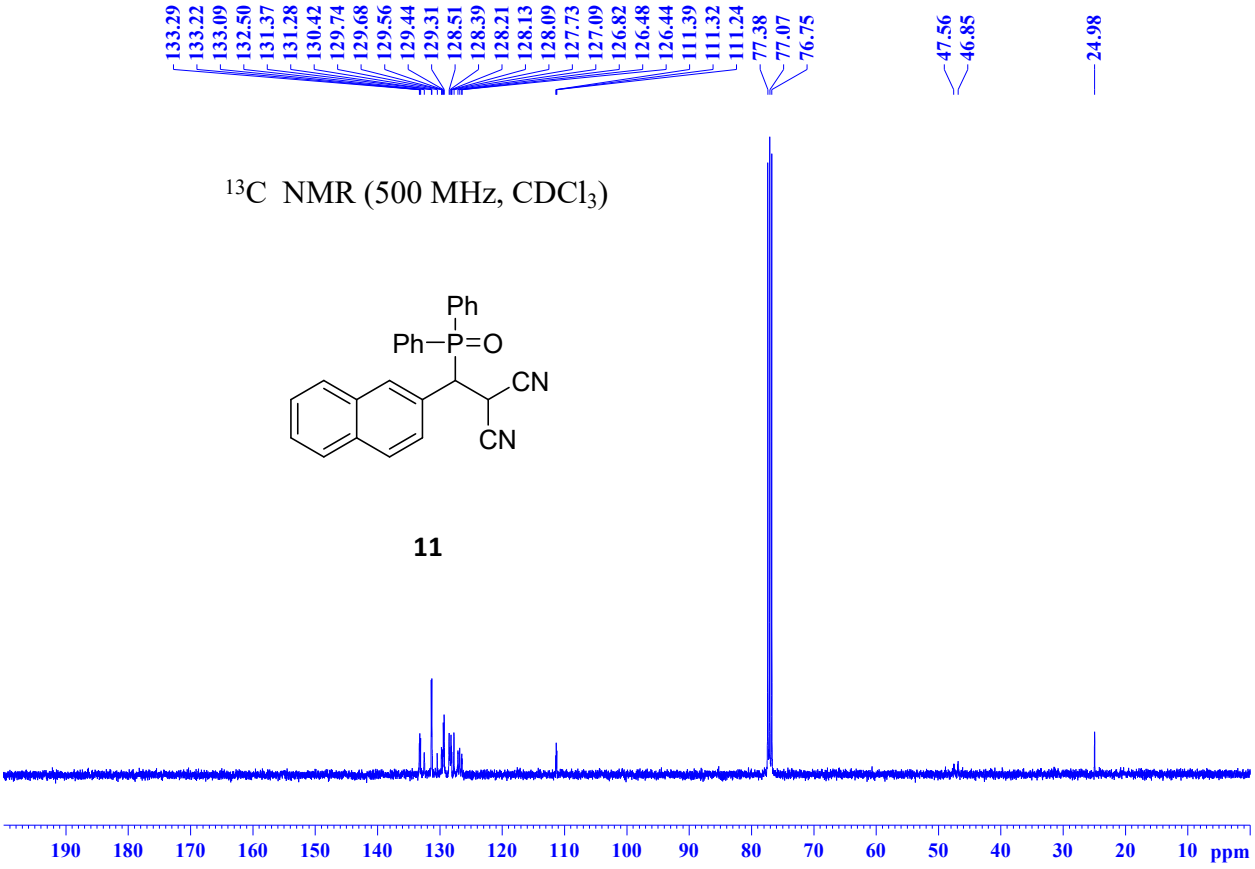
5.3
5.1
4.9
4.7
4.5
4.3

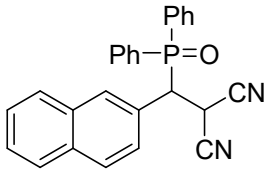


^{13}C NMR (500 MHz, $CDCl_3$)

11

29.33

^{31}P NMR (202.4 MHz, $CDCl_3$)



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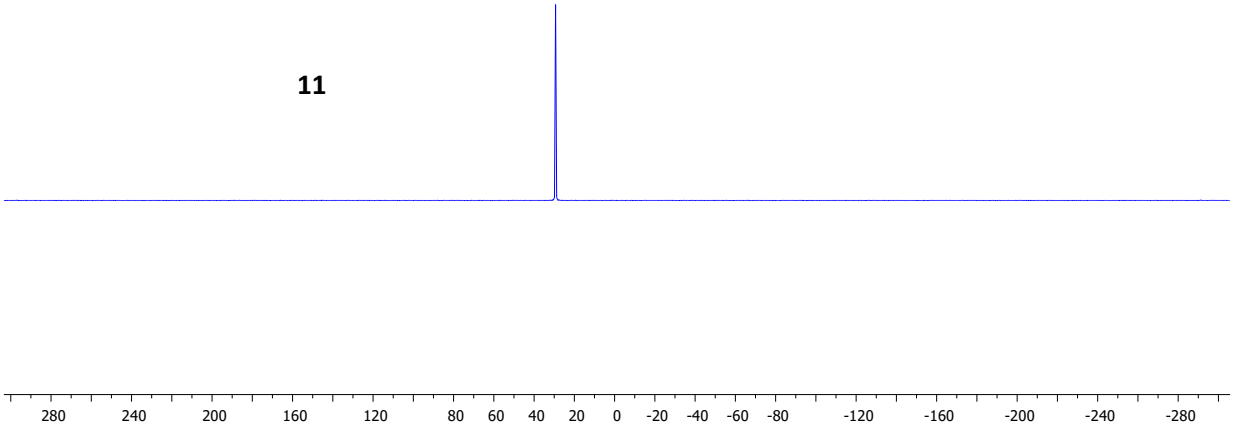
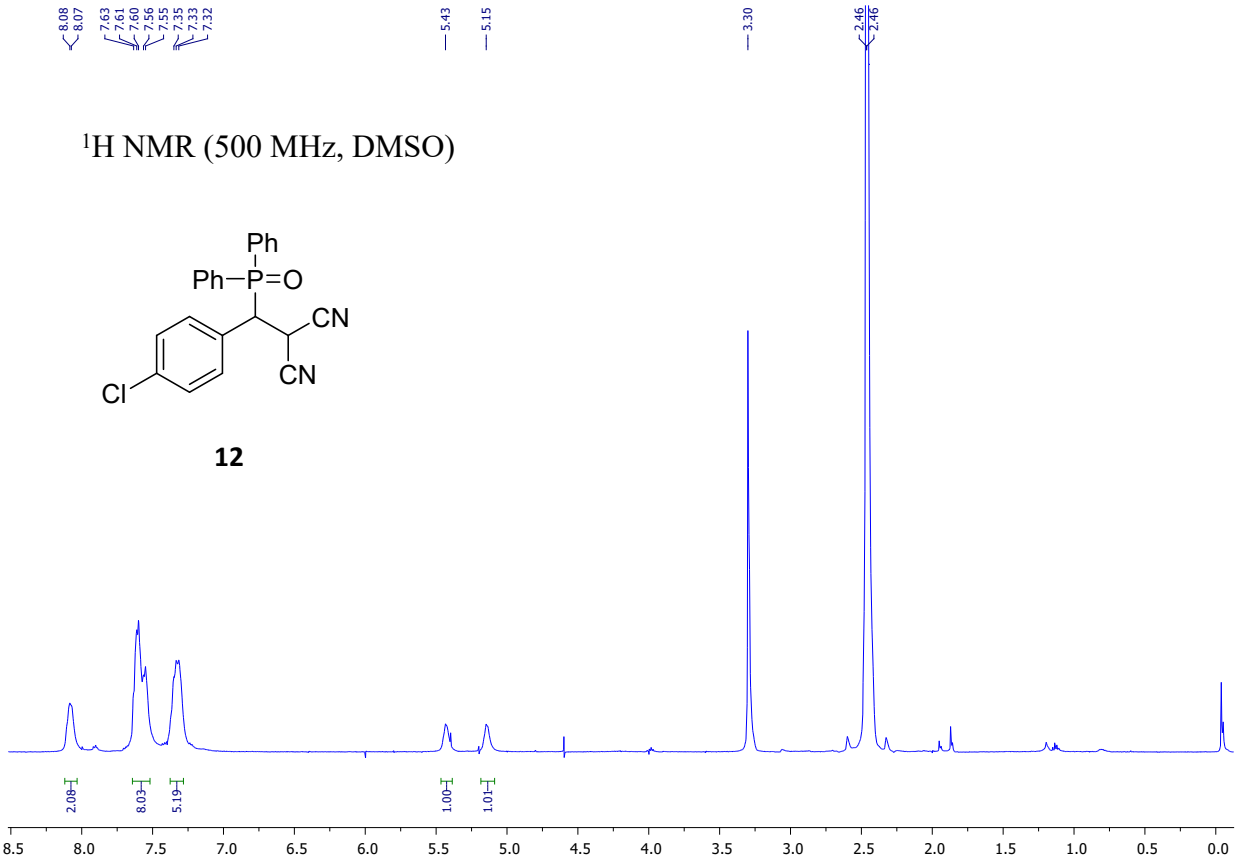


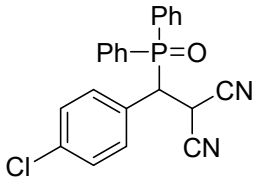


^{1}H NMR (500 MHz, DMSO)

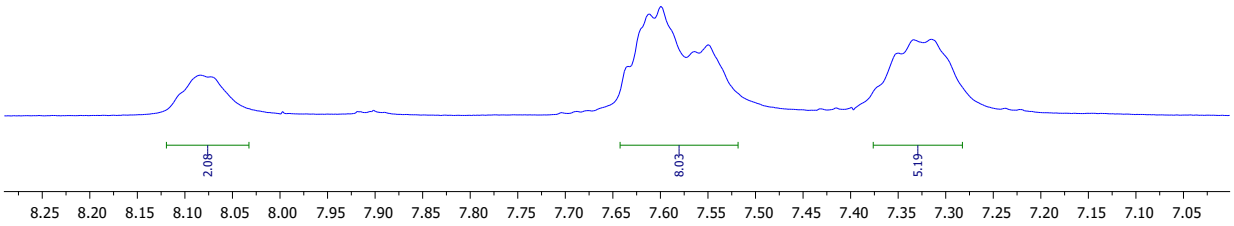
12

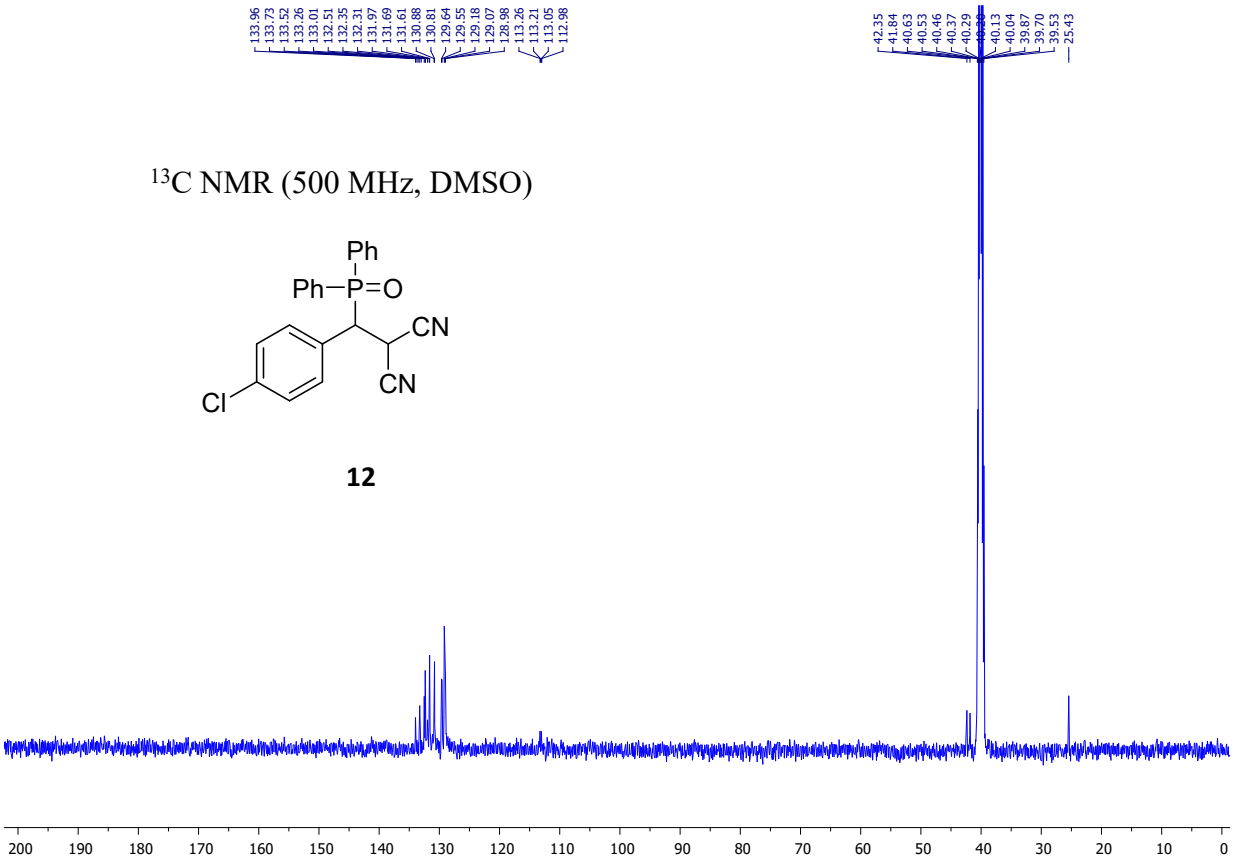
8.08
8.07
7.63
7.61
7.60
7.56
7.55
7.35
7.33
7.32

^{1}H NMR (500 MHz, DMSO)



12

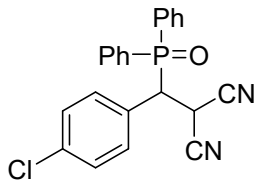




^{13}C NMR (500 MHz, DMSO)

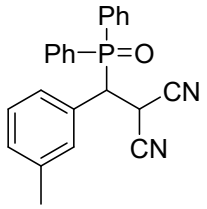
12

^{31}P NMR (202.4 MHz, DMSO)

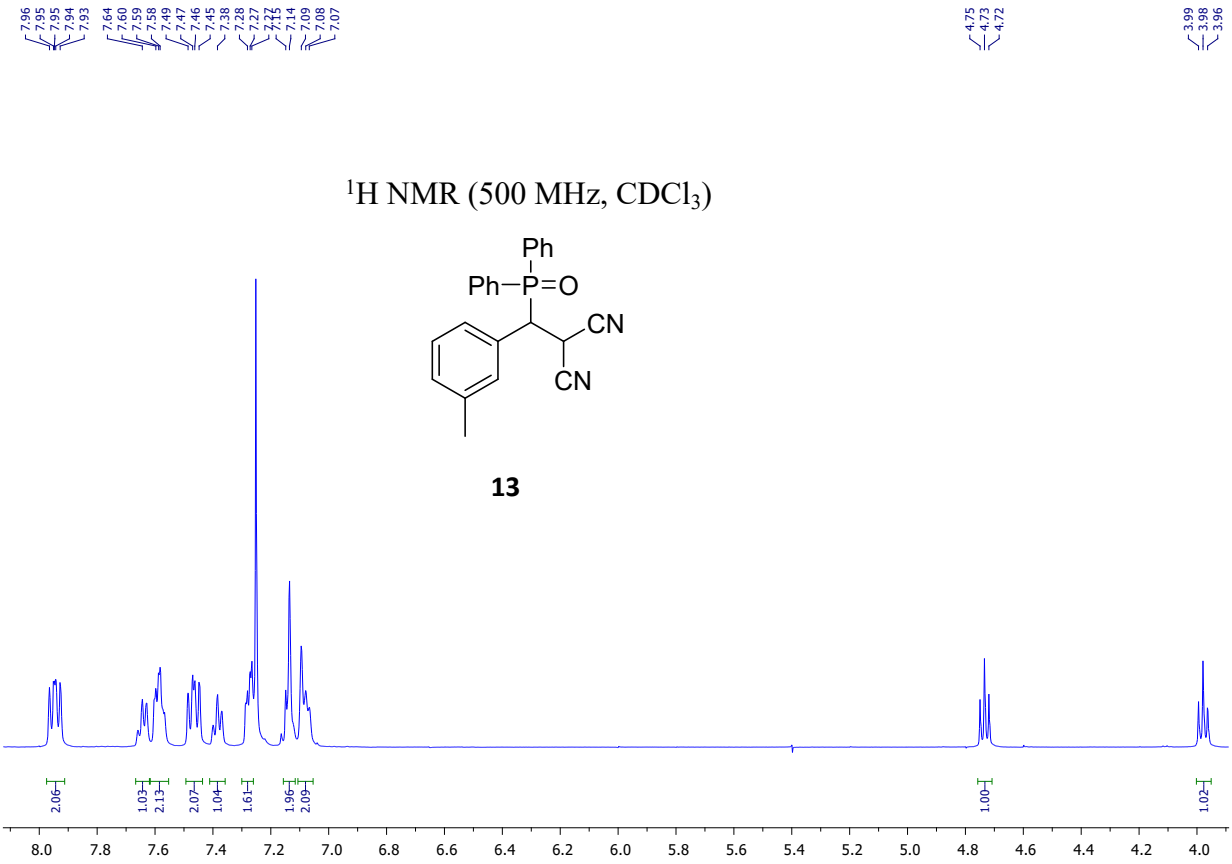


12

^{1}H NMR (500 MHz, $CDCl_3$)

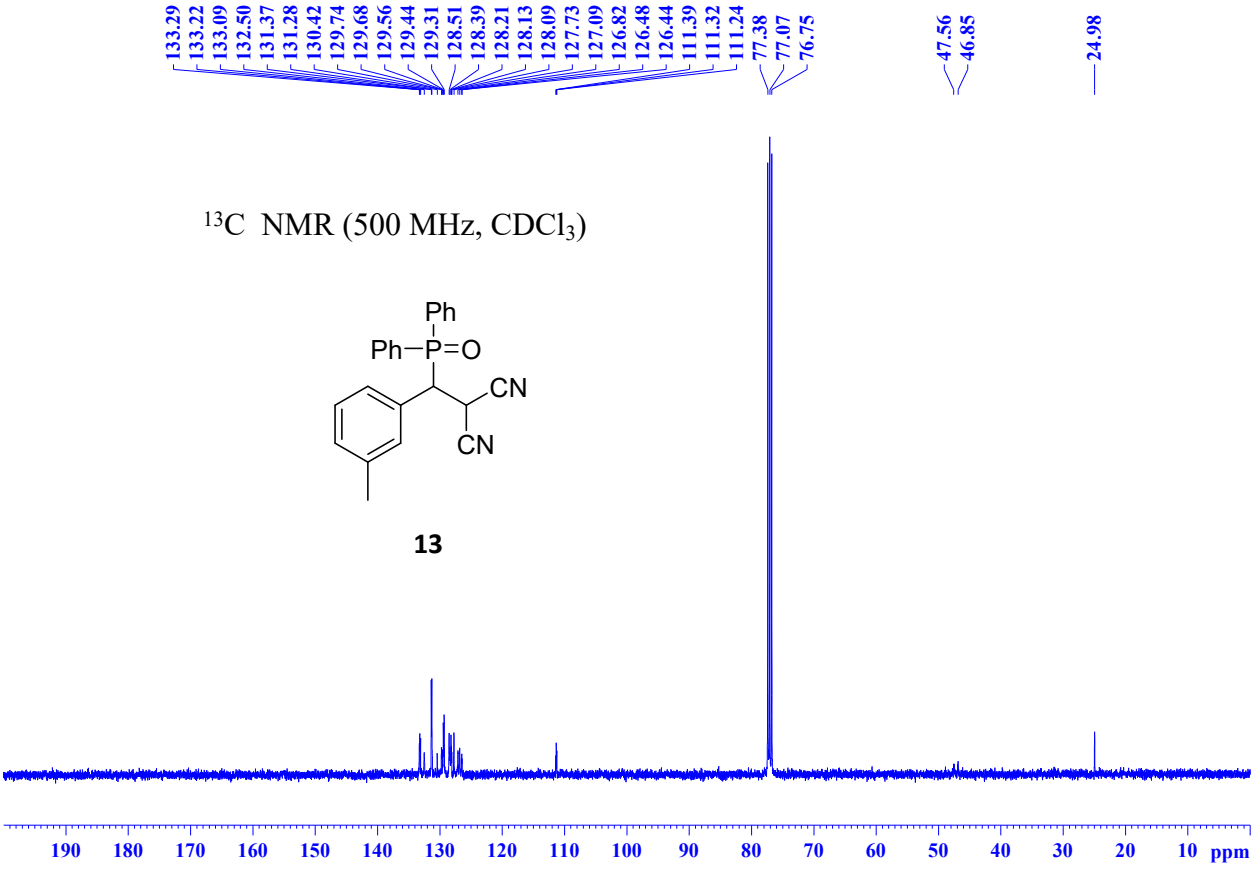


13



^{1}H NMR (500 MHz, $CDCl_3$)

13

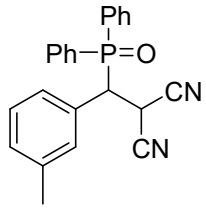


^{13}C NMR (500 MHz, $CDCl_3$)

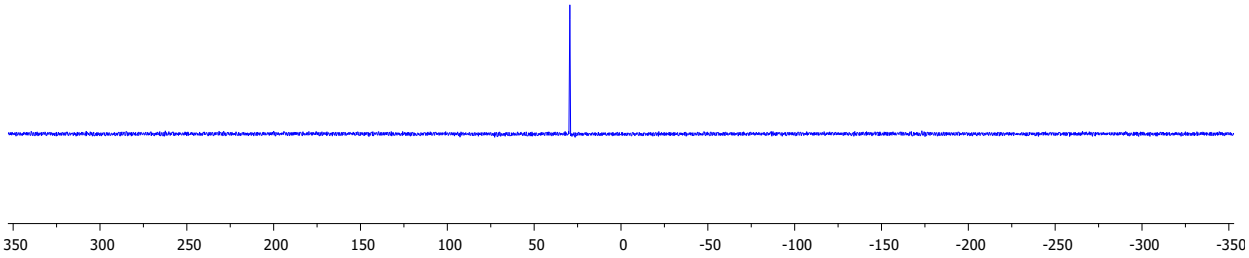
13

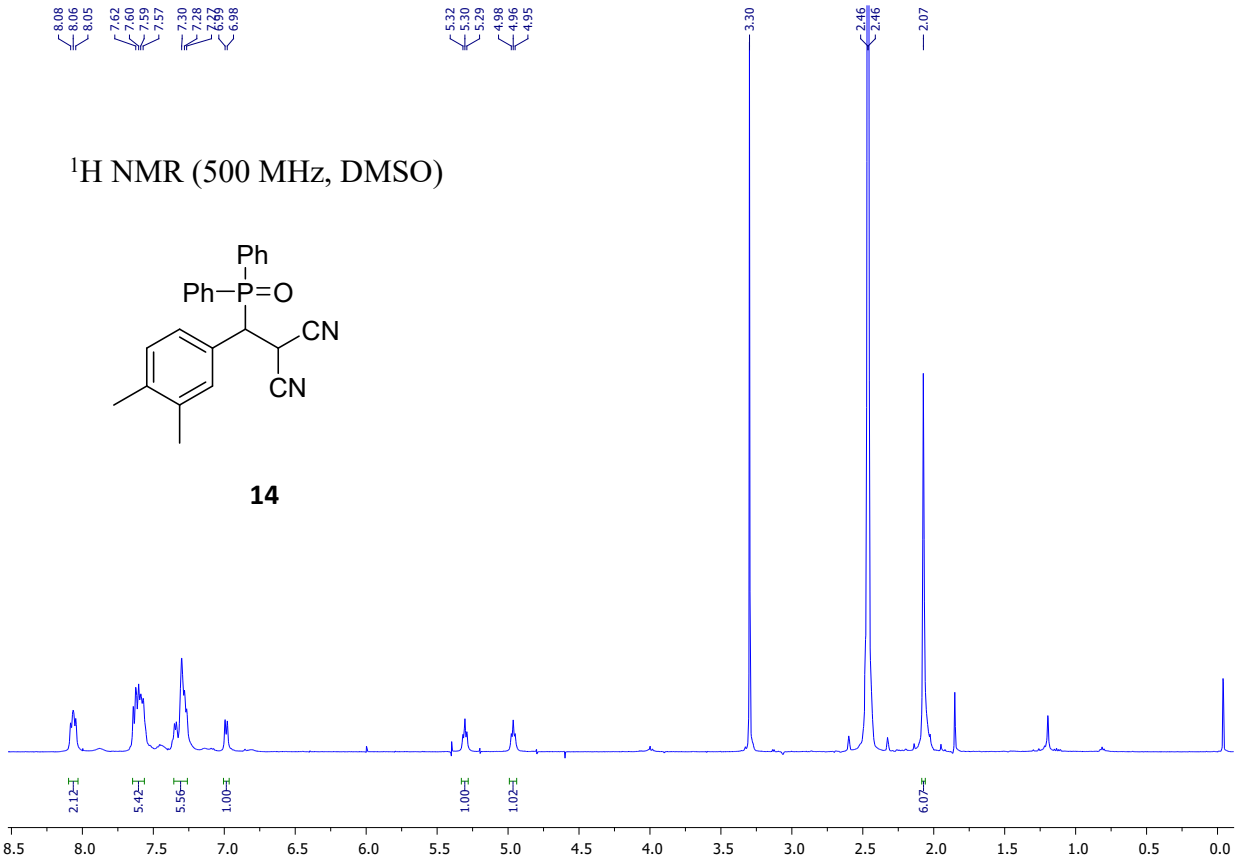
29.43

^{31}P NMR (202.4 MHz, DMSO)



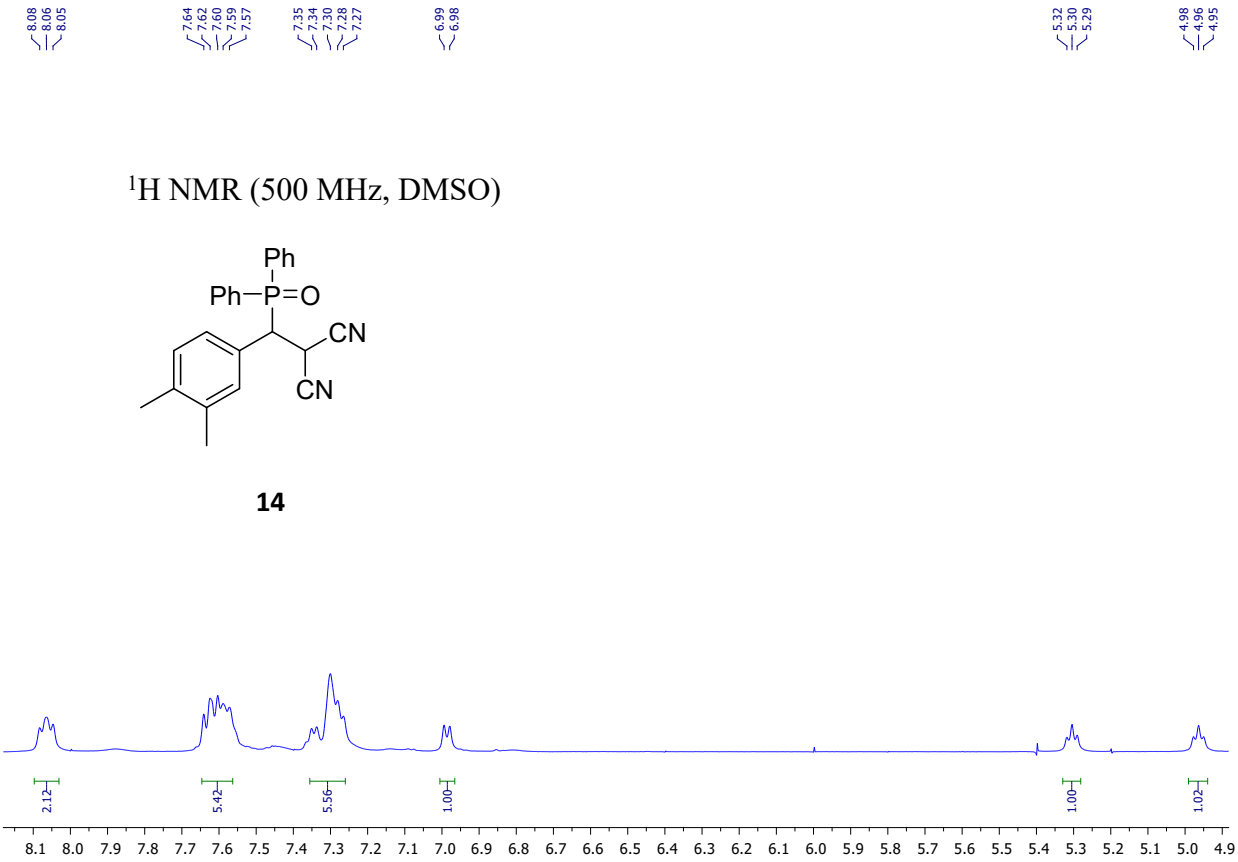
13





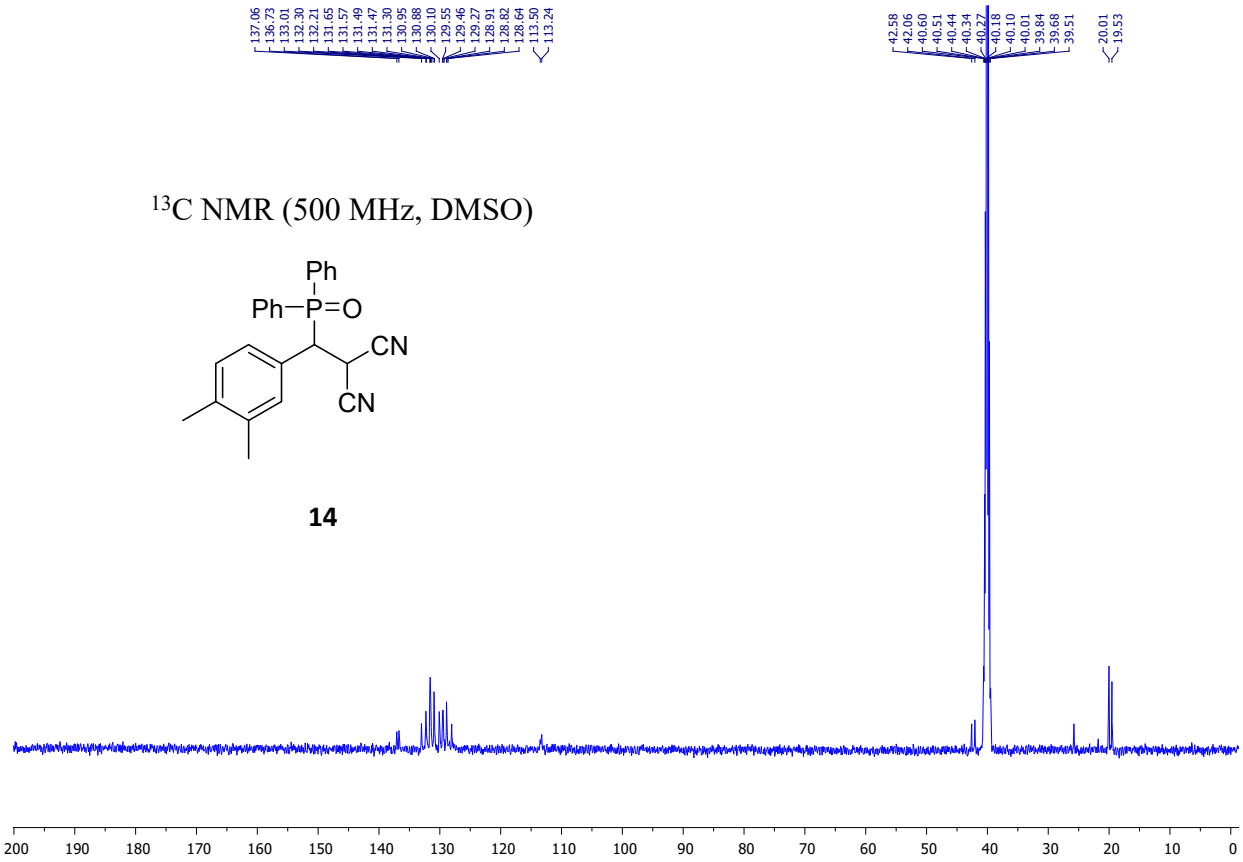
^{1}H NMR (500 MHz, DMSO)

14



^{1}H NMR (500 MHz, DMSO)

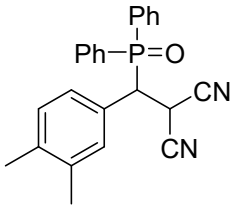
14



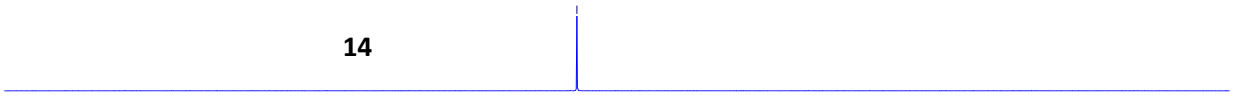
^{13}C NMR (500 MHz, DMSO)

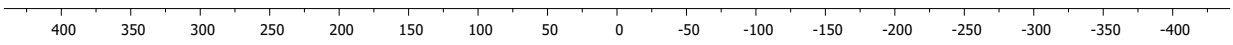
14

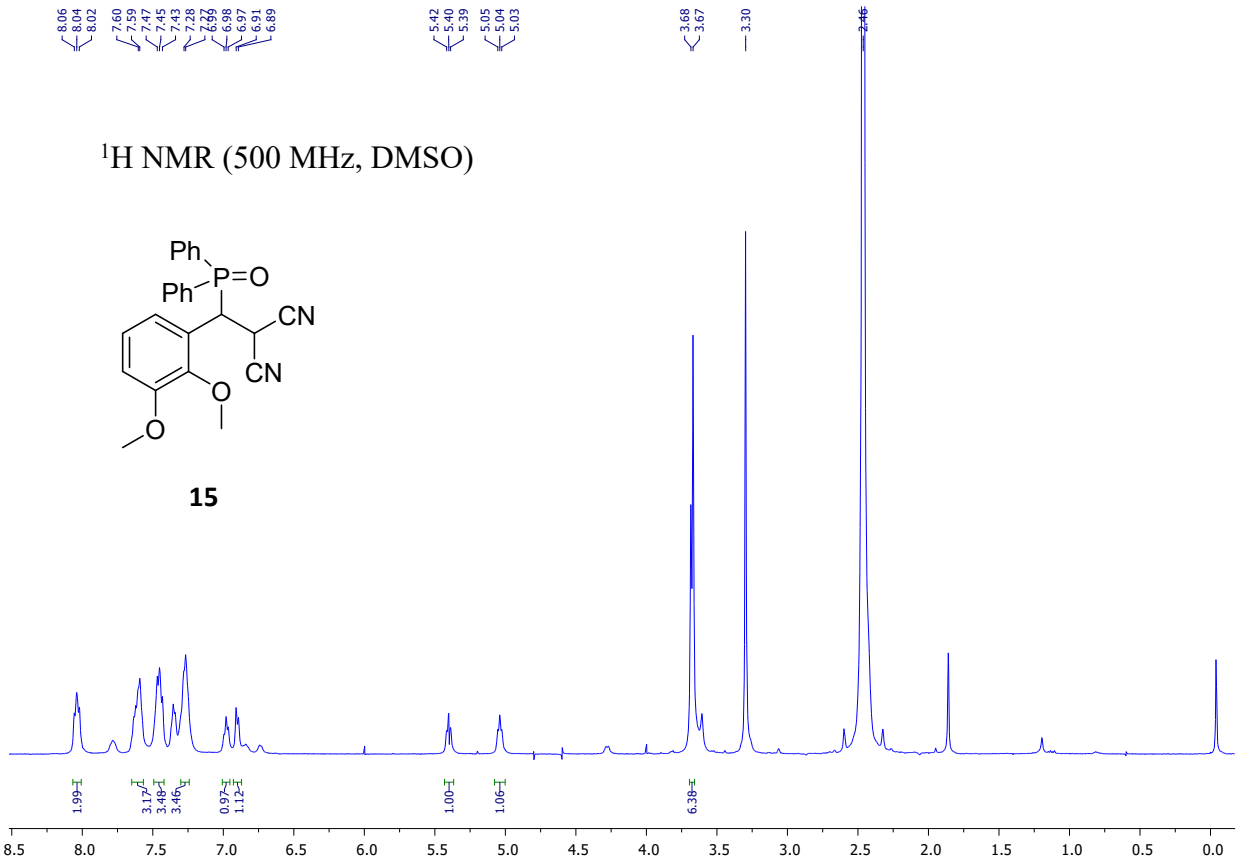
^{31}P NMR (202.4 MHz, DMSO)



14

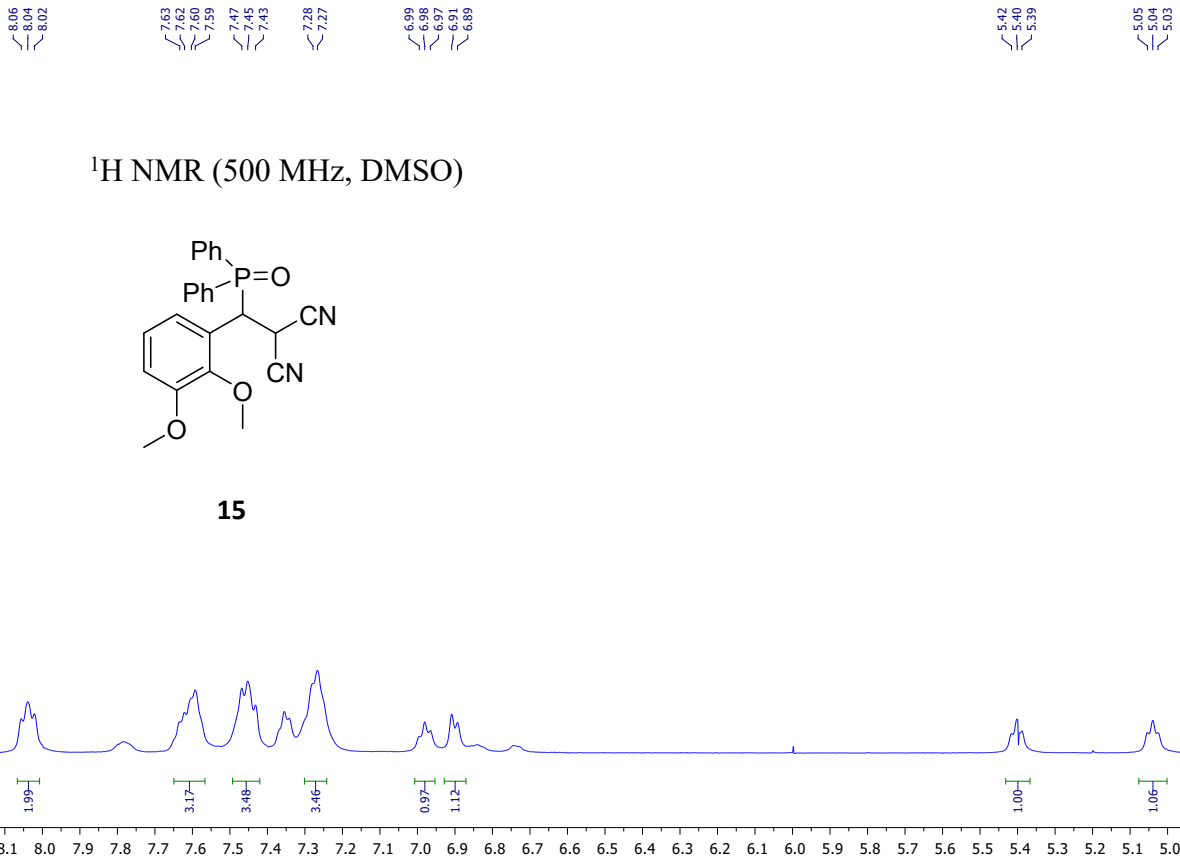






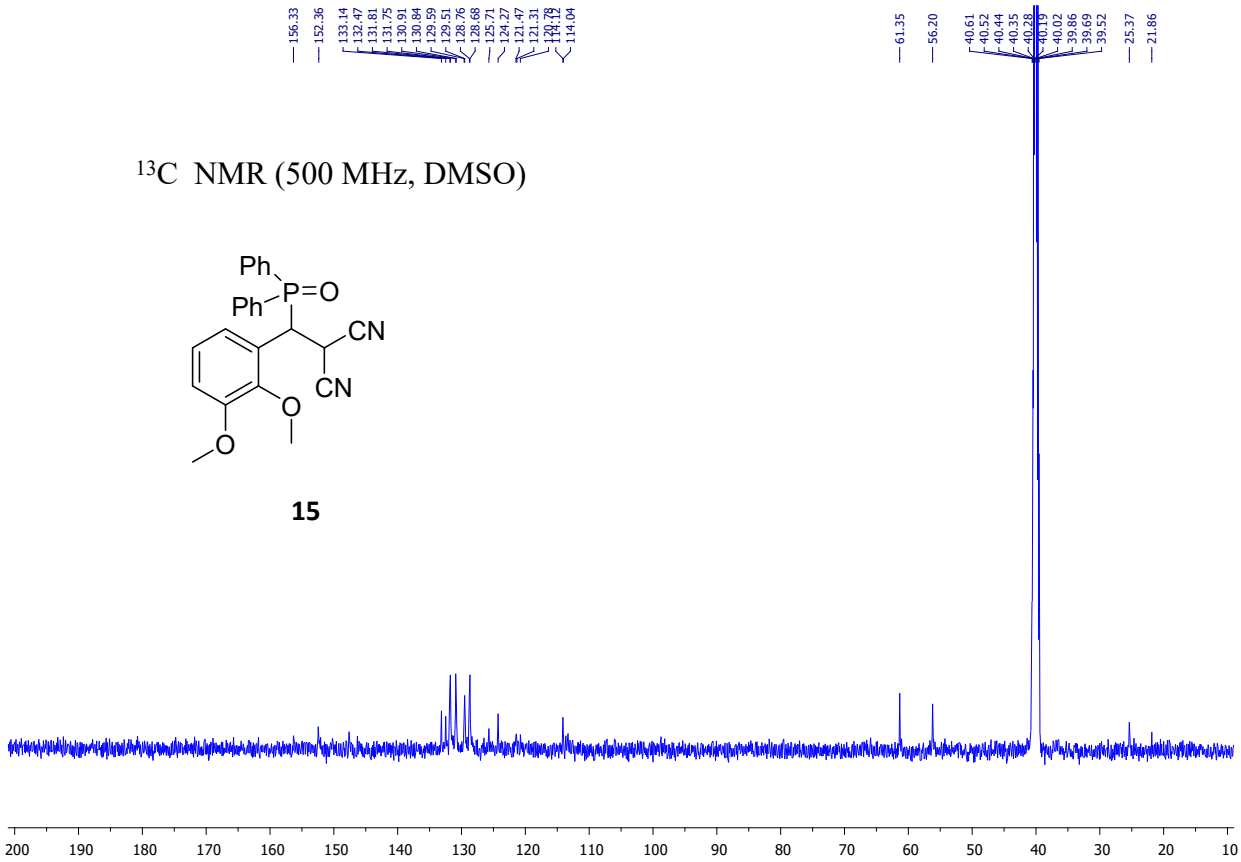
^{1}H NMR (500 MHz, DMSO)

15



^{1}H NMR (500 MHz, DMSO)

15

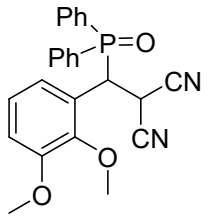


^{13}C NMR (500 MHz, DMSO)

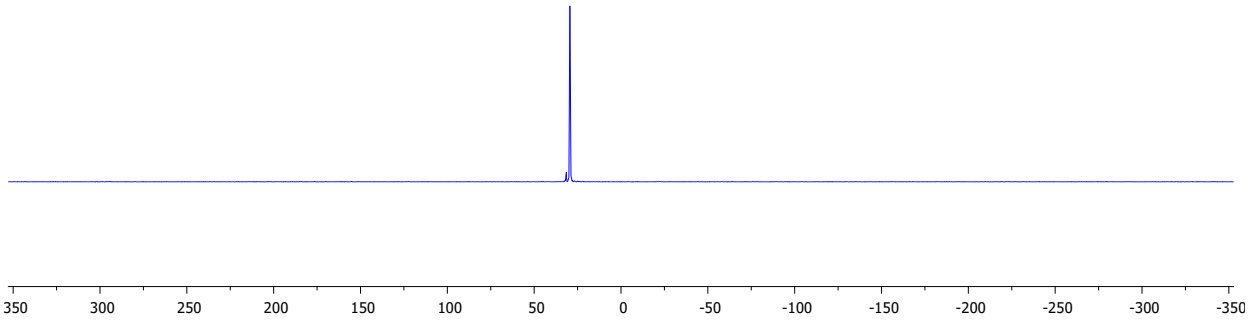
15

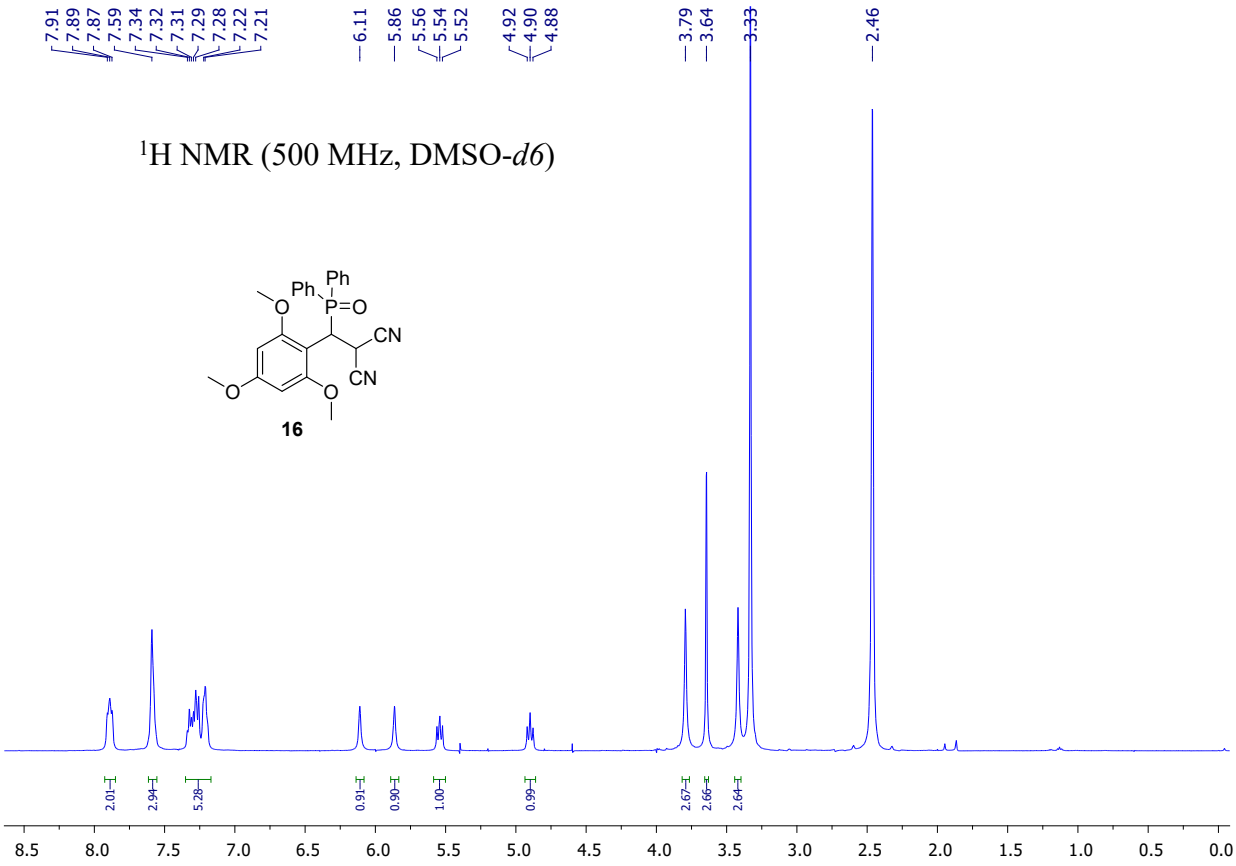
29.42

^{31}P NMR (202.4 MHz, DMSO)



15



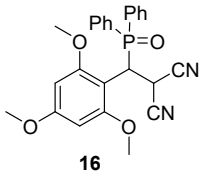


^{1}H NMR (500 MHz, DMSO-*d6*)

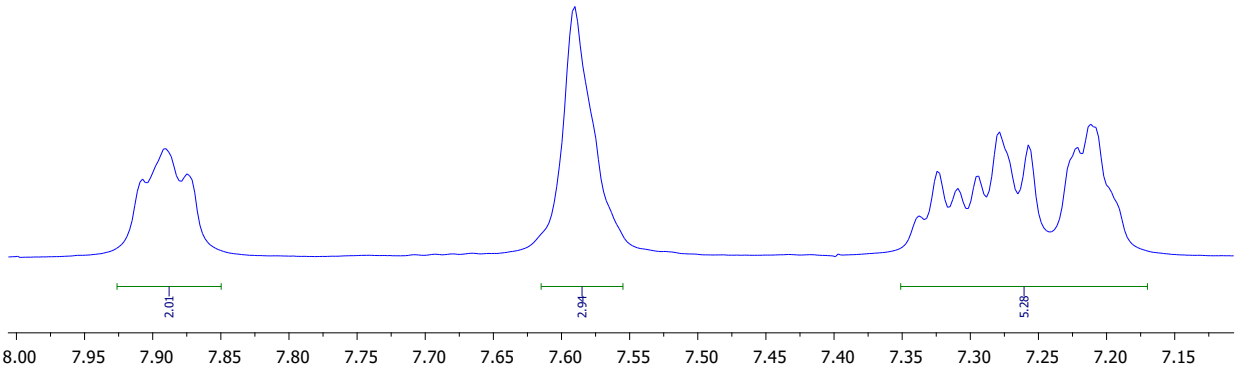
16

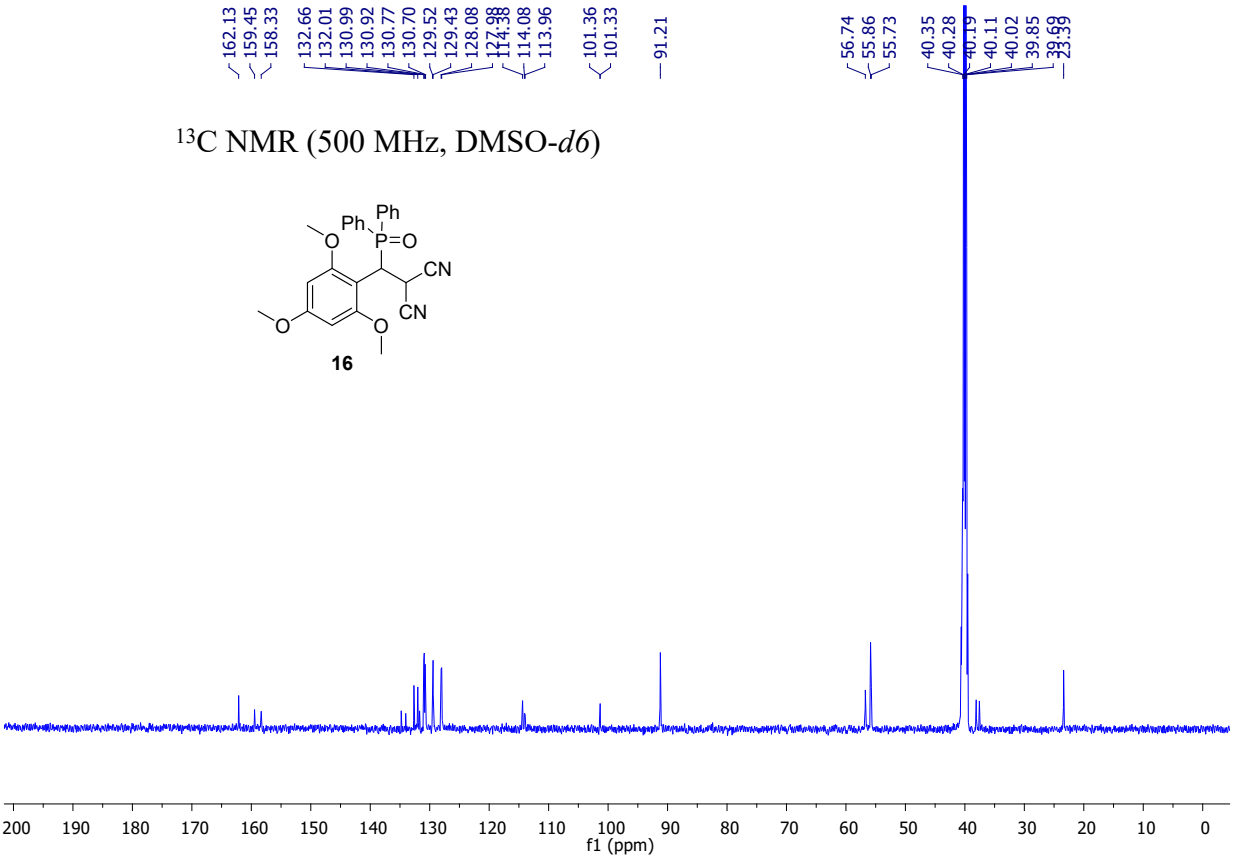
7.91
7.89
7.87
7.59
7.34
7.32
7.31
7.29
7.28
7.22
7.21

^{1}H NMR (500 MHz, DMSO-*d6*)



16



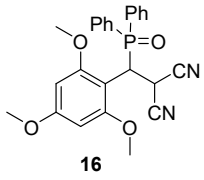


^{13}C NMR (500 MHz, DMSO-*d6*)

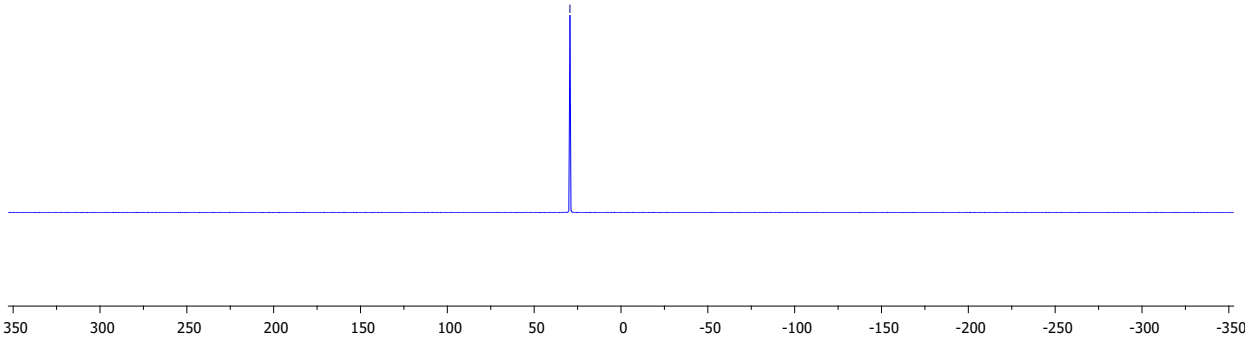
16

29.40

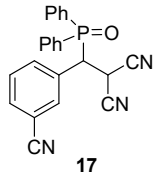
^{31}P NMR (500 MHz, DMSO-*d6*)



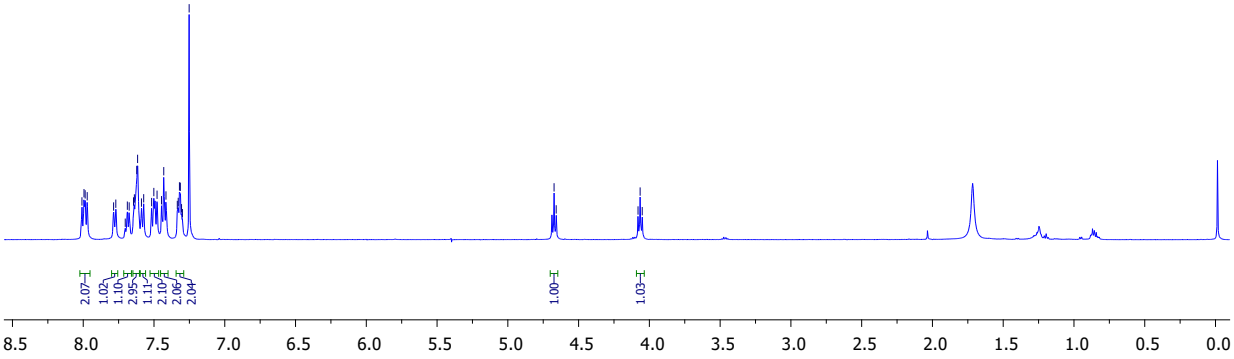
16



^{1}H NMR (500 MHz, $CDCl_3$)

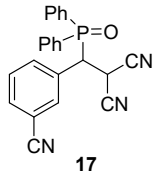


17

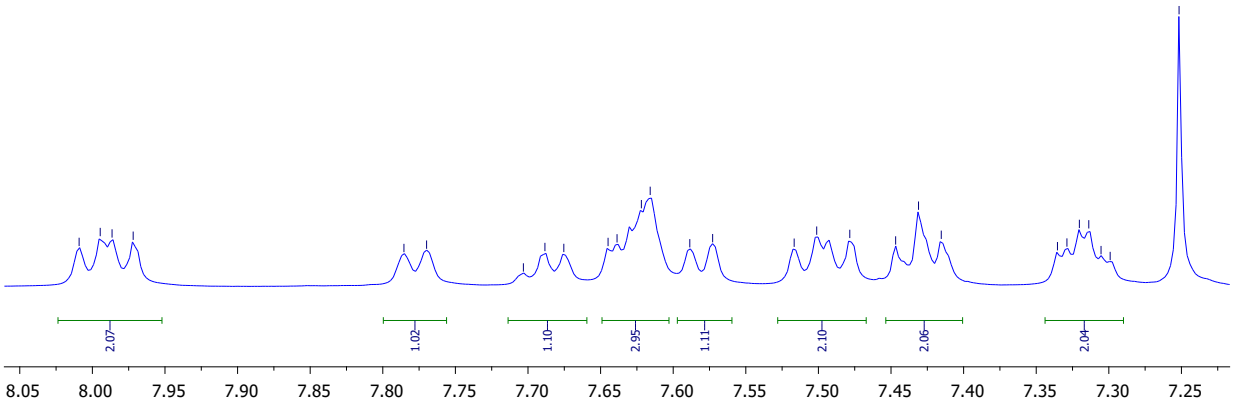


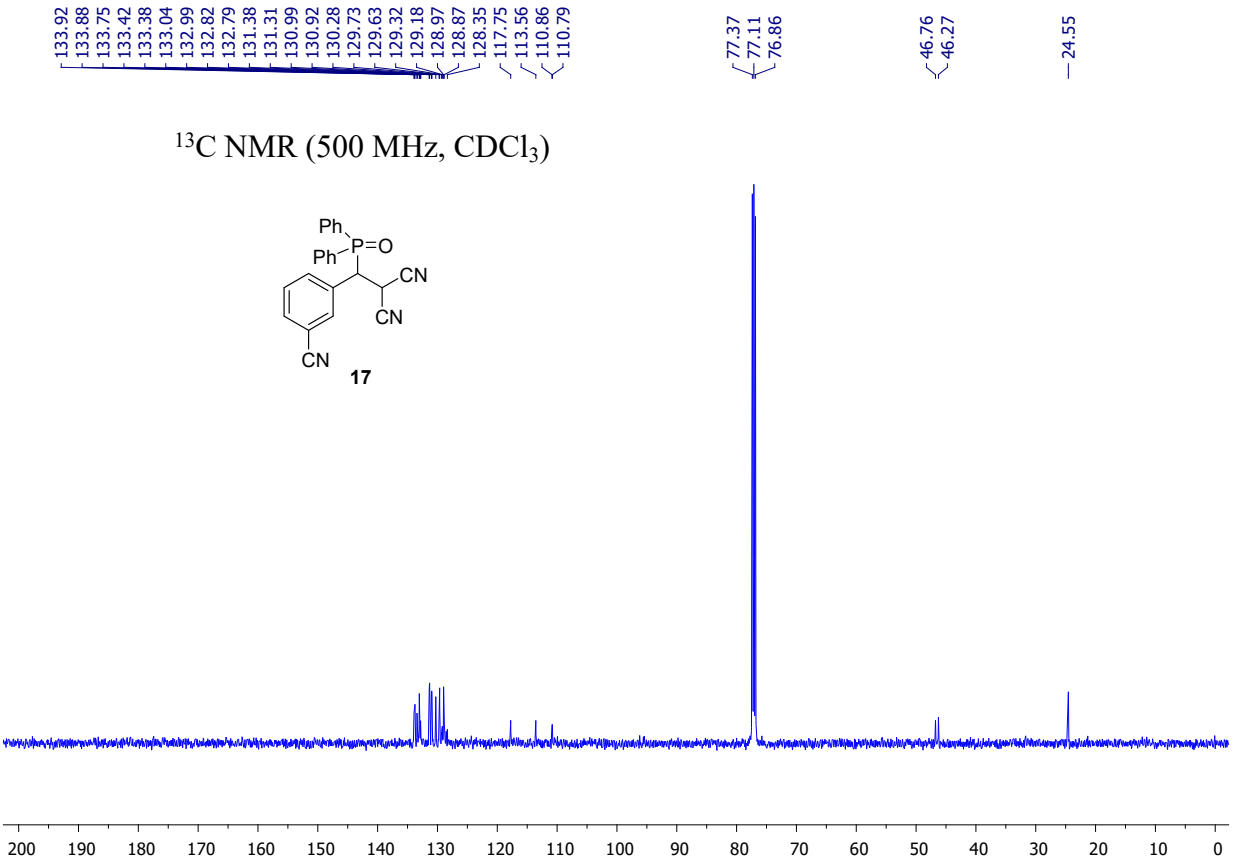
8.01
7.99
7.99
7.97
7.79
7.77
7.70
7.69
7.68
7.64
7.64
7.62
7.62
7.59
7.57
7.52
7.50
7.48
7.45
7.43
7.42
7.34
7.33
7.32
7.31
7.31
7.30
7.25

^{1}H NMR (500 MHz, $CDCl_3$)



17

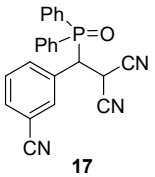




^{13}C NMR (500 MHz, $CDCl_3$)

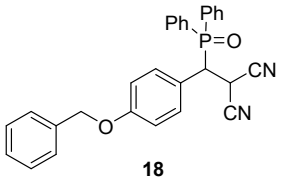
17

^{31}P NMR (500 MHz, $CDCl_3$)

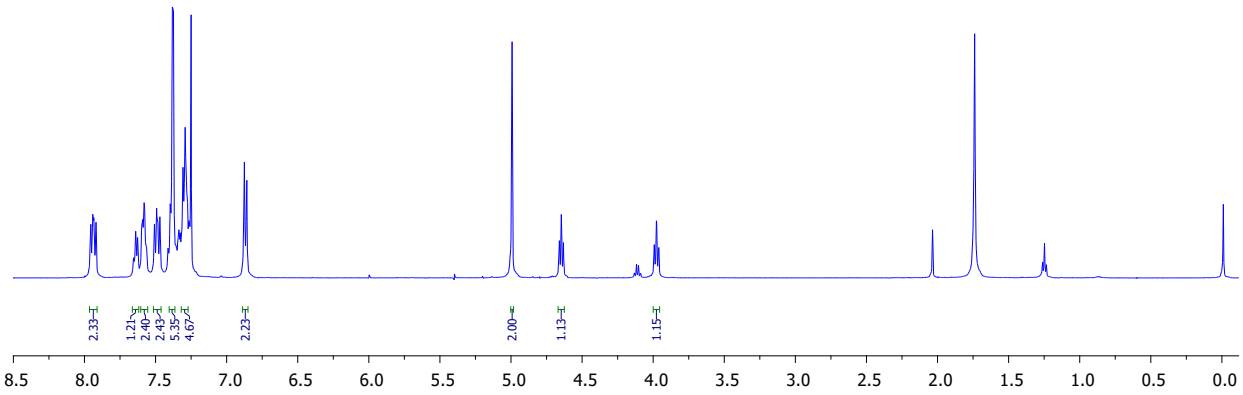


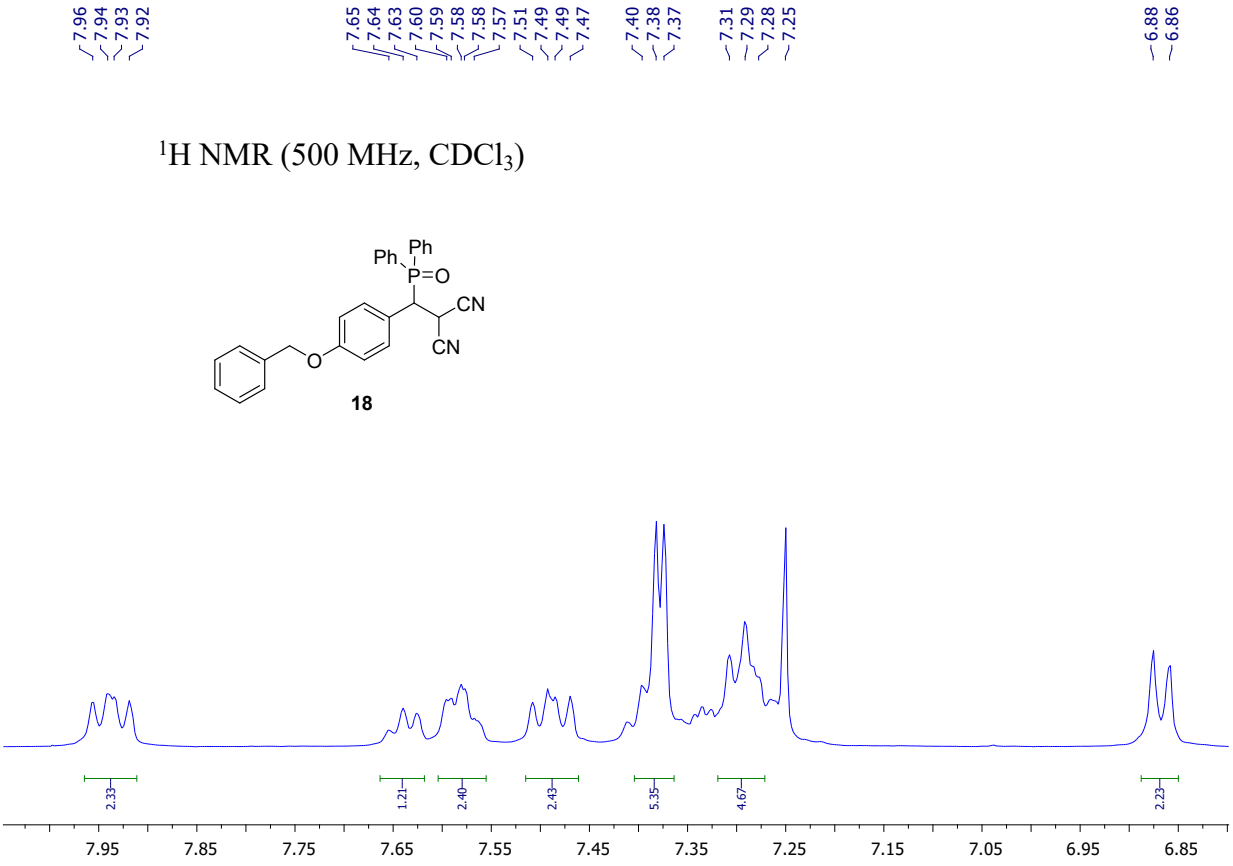
17

^{1}H NMR (500 MHz, $CDCl_3$)



18

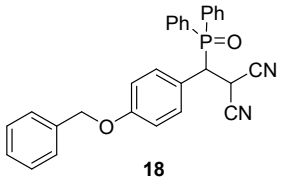




^{1}H NMR (500 MHz, $CDCl_3$)

159.53
131.41
131.34
131.18
131.14
129.44
129.34
128.71
128.59
128.49
128.23
127.63
115.67
111.51
111.44
111.37
111.30
77.37
77.12
76.86
70.10
46.73
46.22
25.11

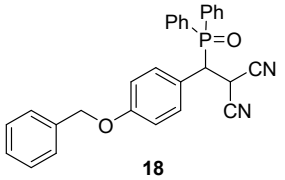
^{13}C NMR (500 MHz, $CDCl_3$)



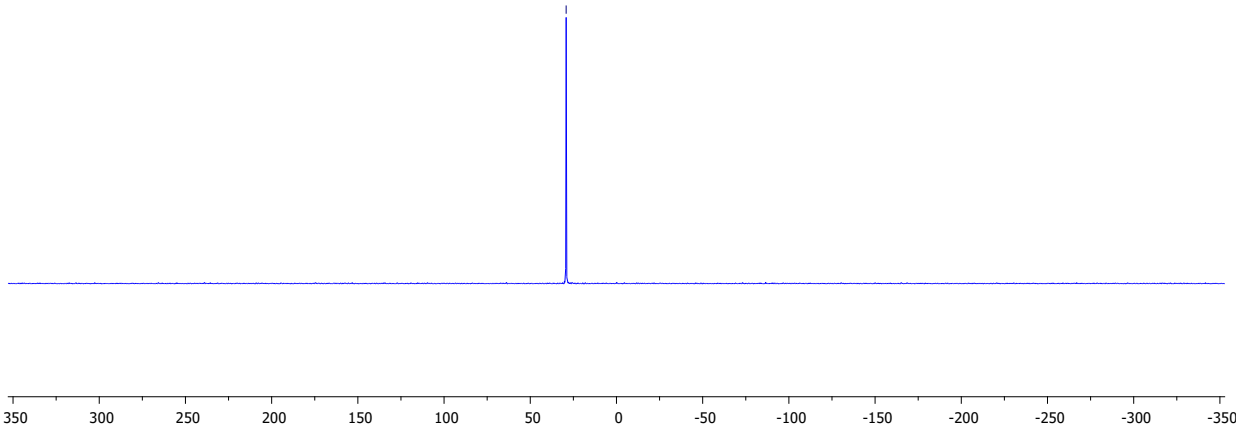
18

29.19

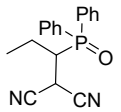
^{31}P NMR (500 MHz, $CDCl_3$)



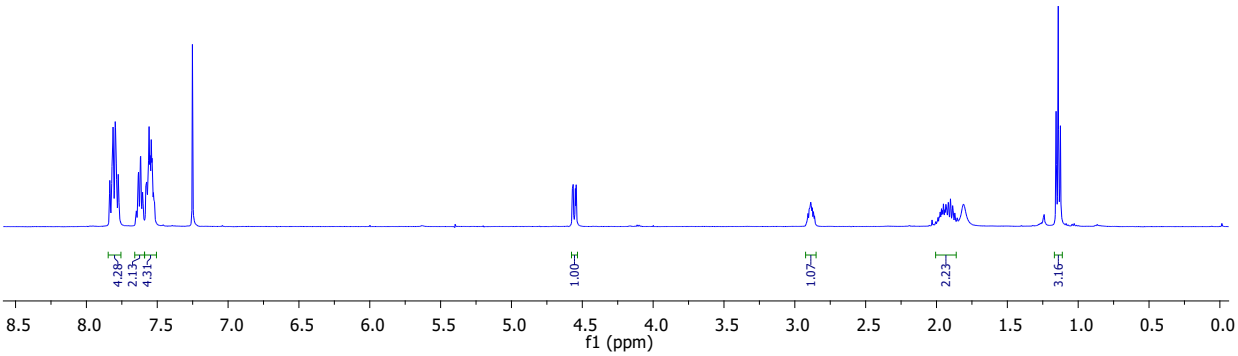
18



^{1}H NMR (500 MHz, $CDCl_3$)

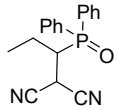


19

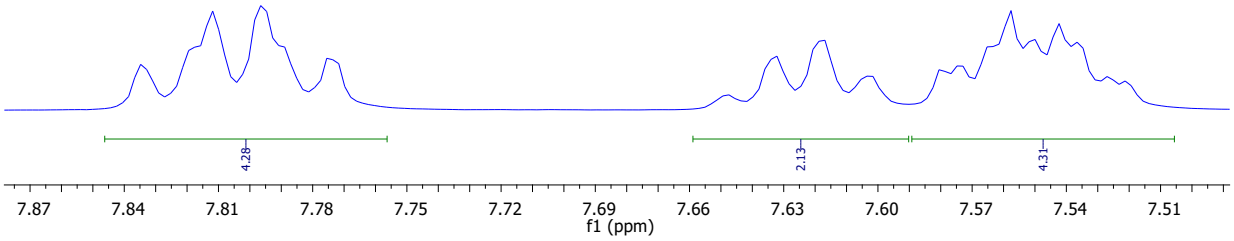


7.83 7.81 7.80 7.77 7.65 7.63 7.62 7.60 7.58 7.57 7.56 7.55 7.54 7.54 7.53 7.52

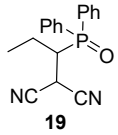
^{1}H NMR (500 MHz, $CDCl_3$)



19



^{13}C NMR (500 MHz, $CDCl_3$)



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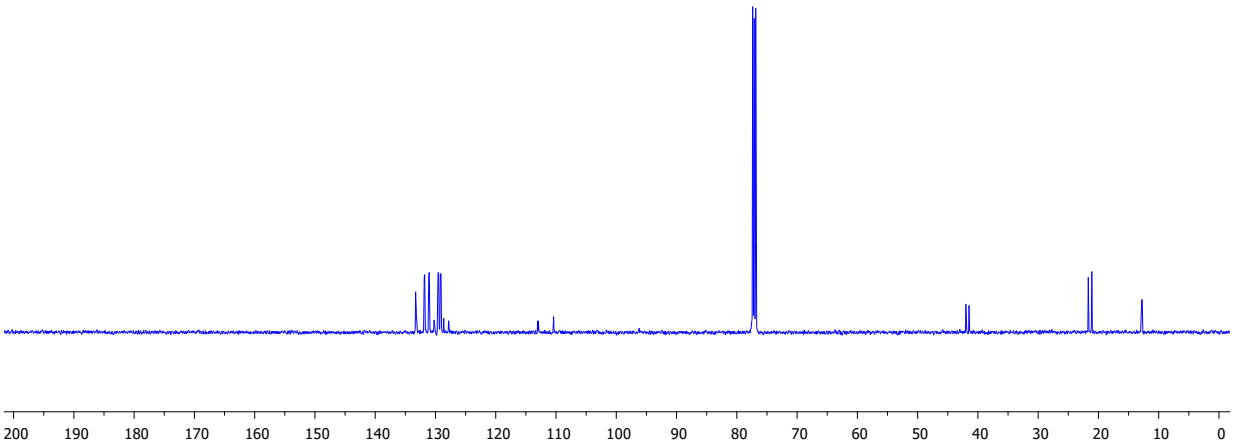
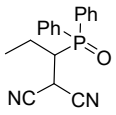


^{31}P NMR (202.4 MHz, $CDCl_3$)



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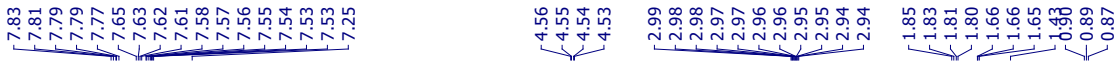
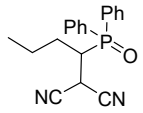


^{1}H NMR (500 MHz, $CDCl_3$)



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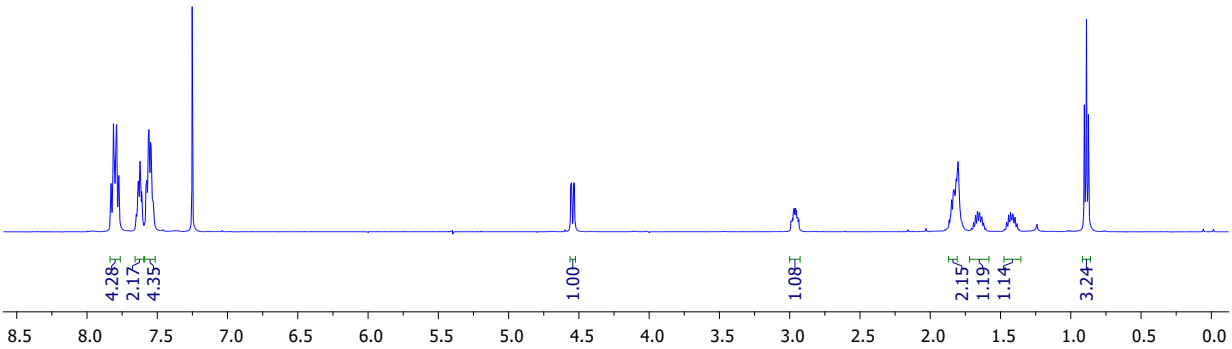
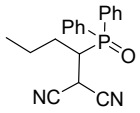


7.83
7.81
7.79
7.79
7.77
7.65
7.63
7.62
7.61
7.58
7.57
7.56
7.55
7.54
7.53
7.53
7.25

^{1}H NMR (500 MHz, $CDCl_3$)



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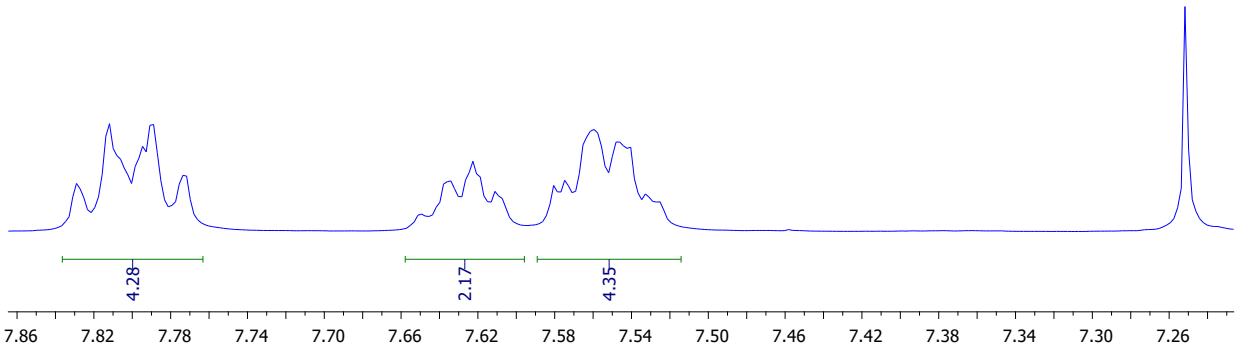
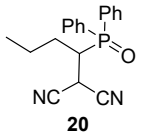


^{1}H NMR (500 MHz, $CDCl_3$)



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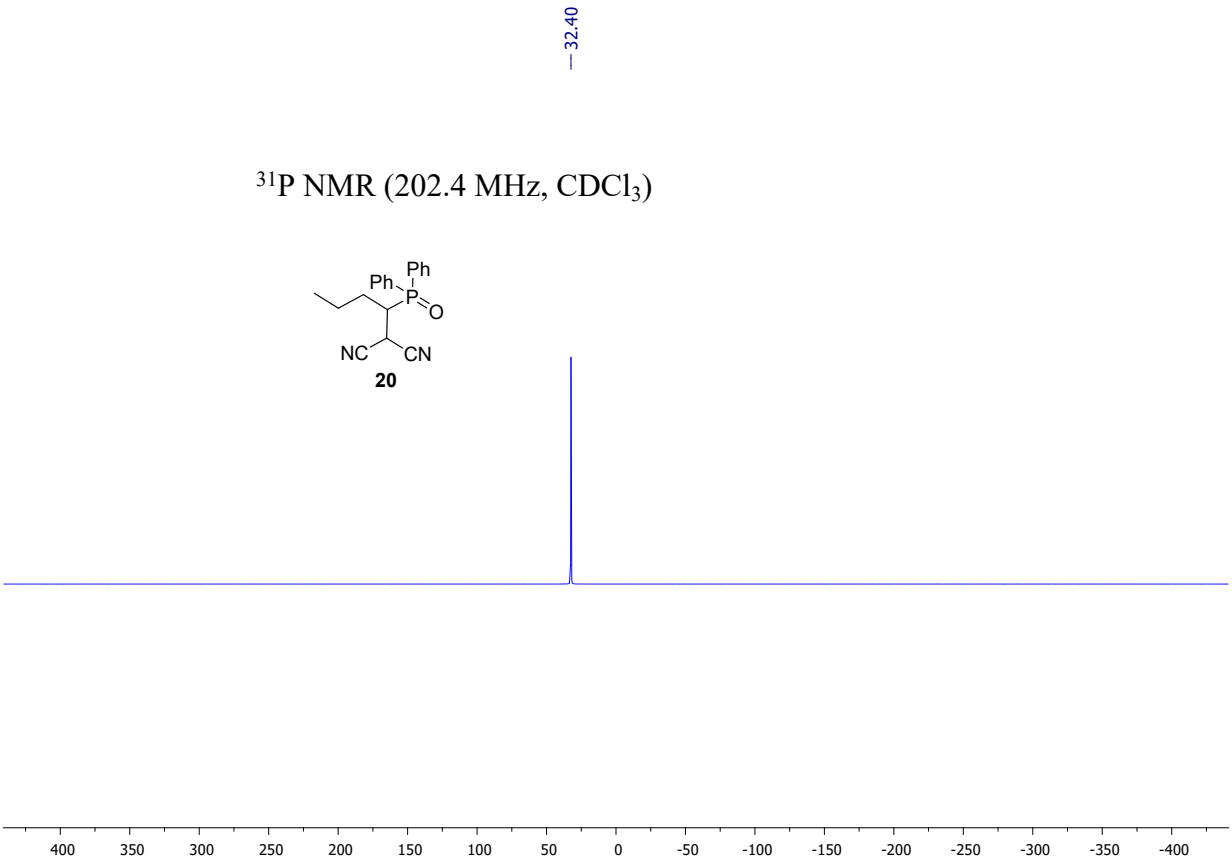
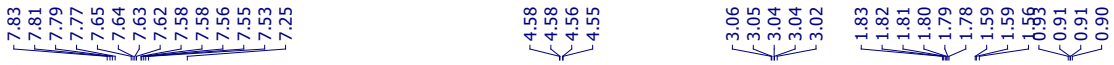
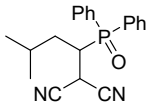


^{31}P NMR (202.4 MHz, $CDCl_3$)

20



^{1}H NMR (500 MHz, $CDCl_3$)



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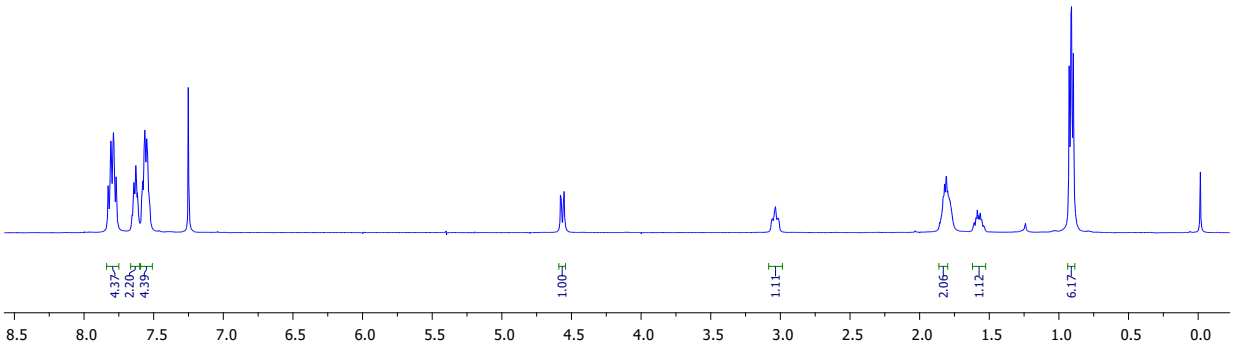
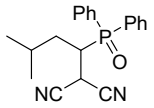
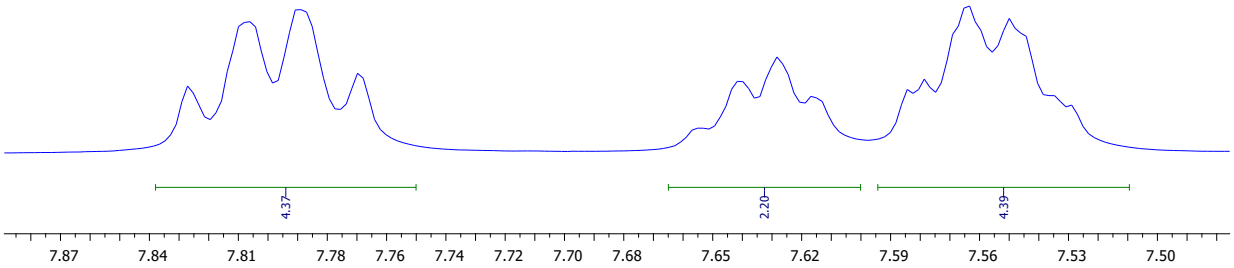
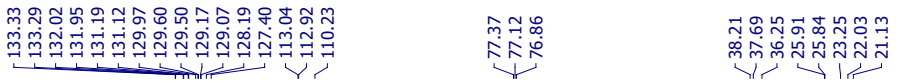


^{1}H NMR (500 MHz, $CDCl_3$)

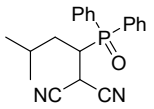


21

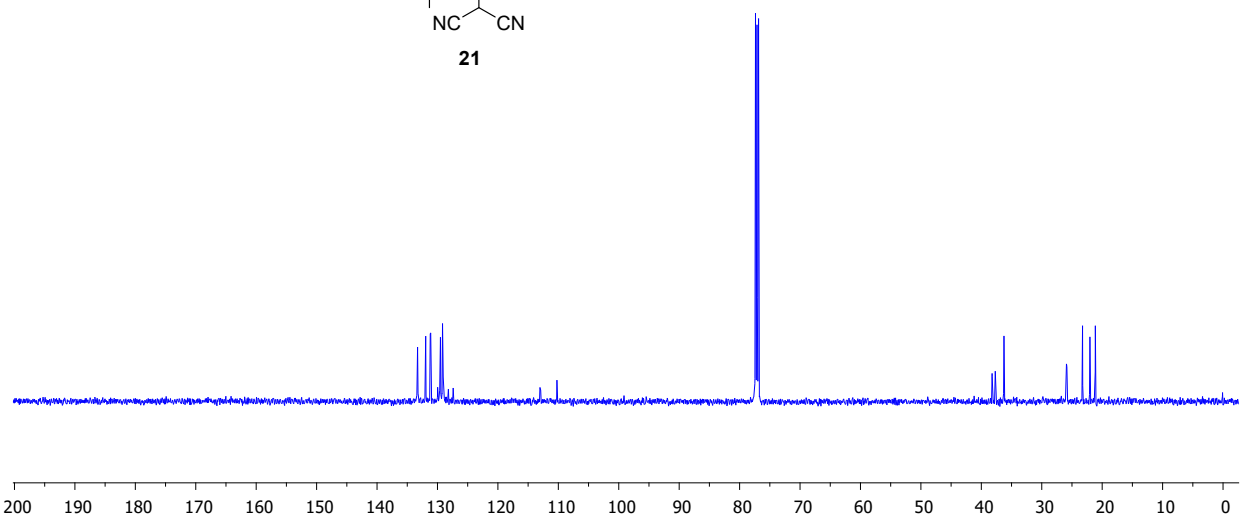




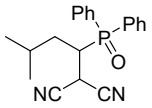
^{13}C NMR (500 MHz, $CDCl_3$)



21

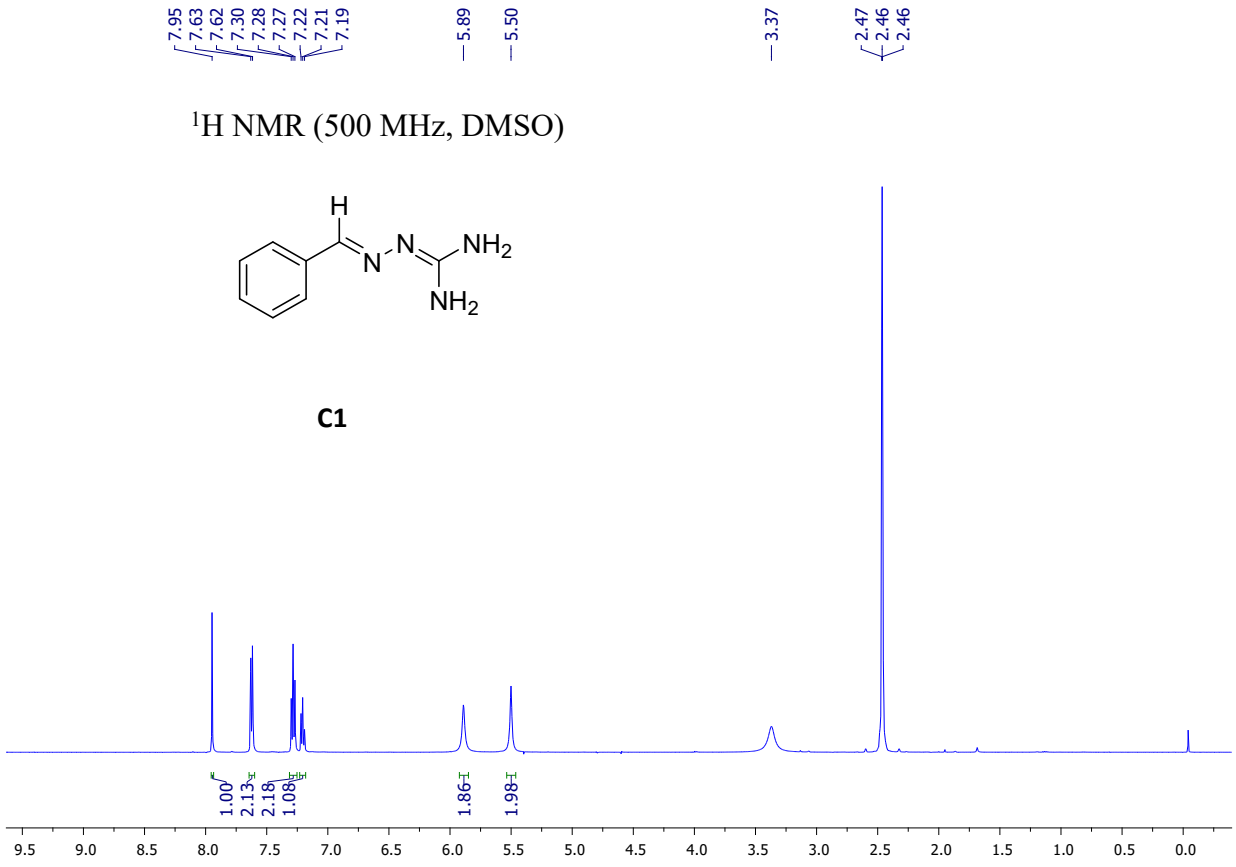


^{31}P NMR (500 MHz, $CDCl_3$)



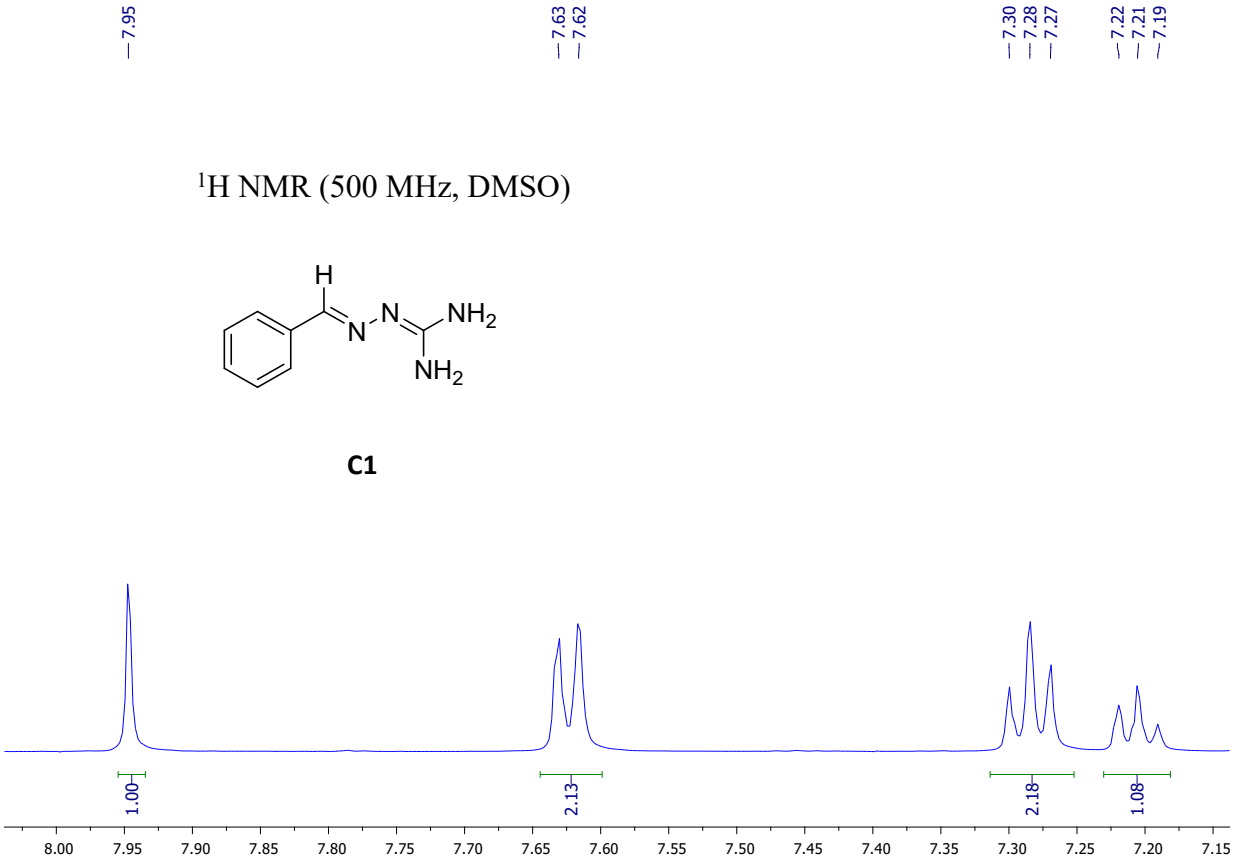
21

8 1H and ^{13}C NMR spectra of catalysts:



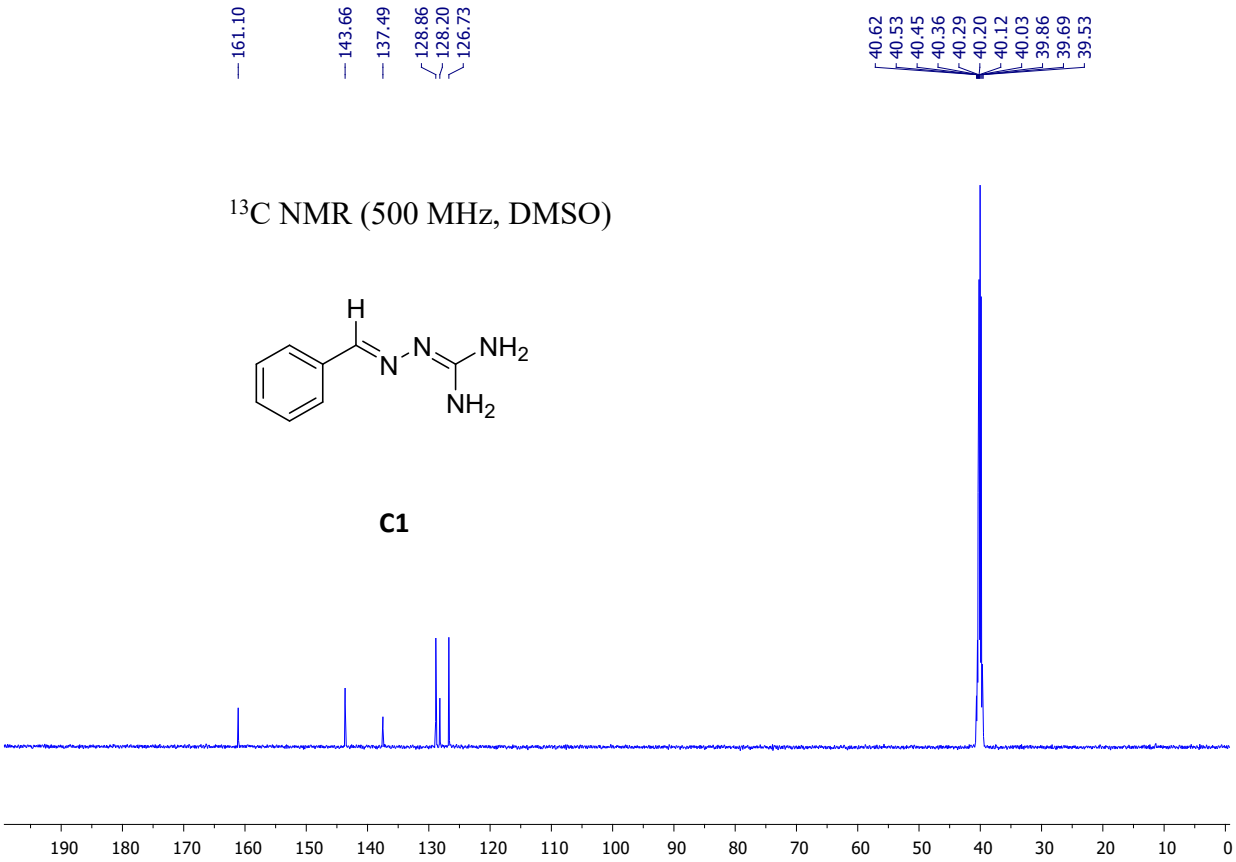
^{1}H NMR (500 MHz, DMSO)

C1



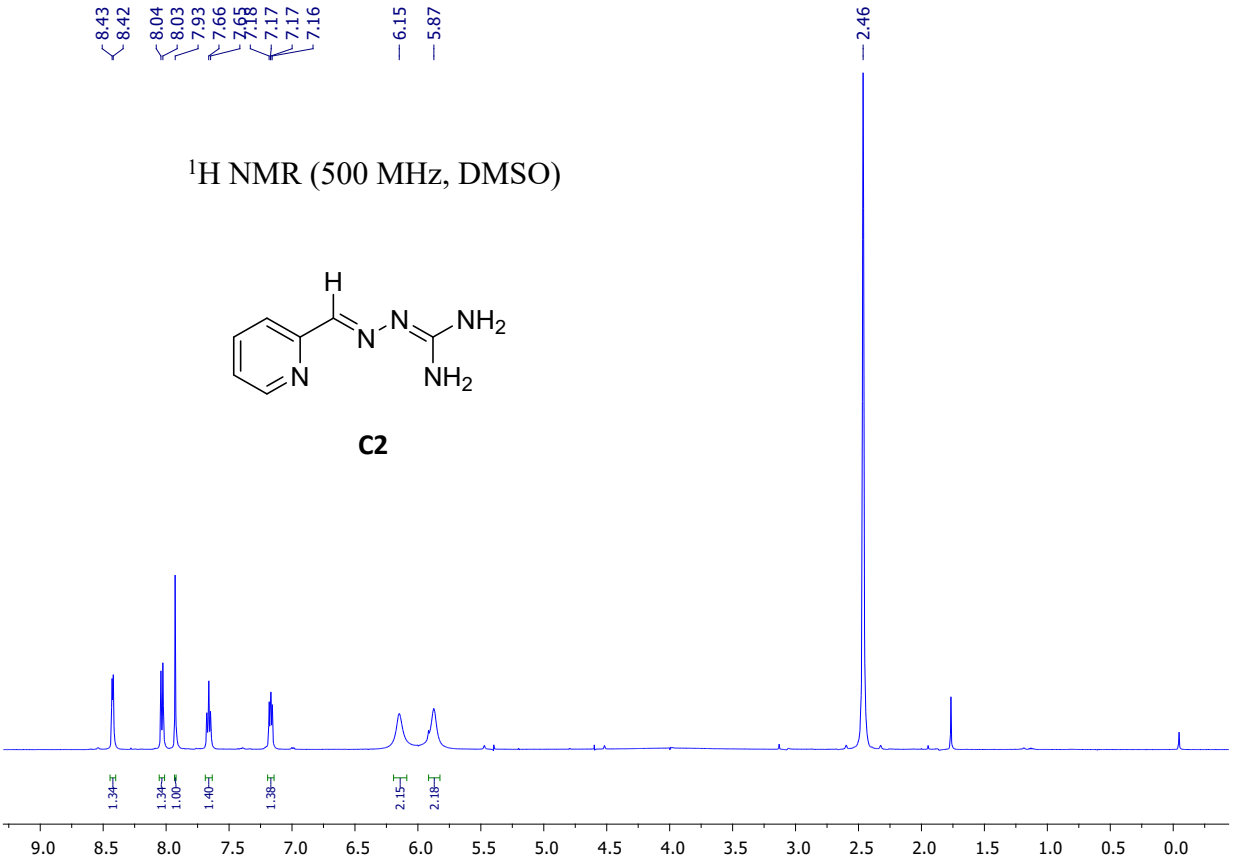
^{1}H NMR (500 MHz, DMSO)

C1



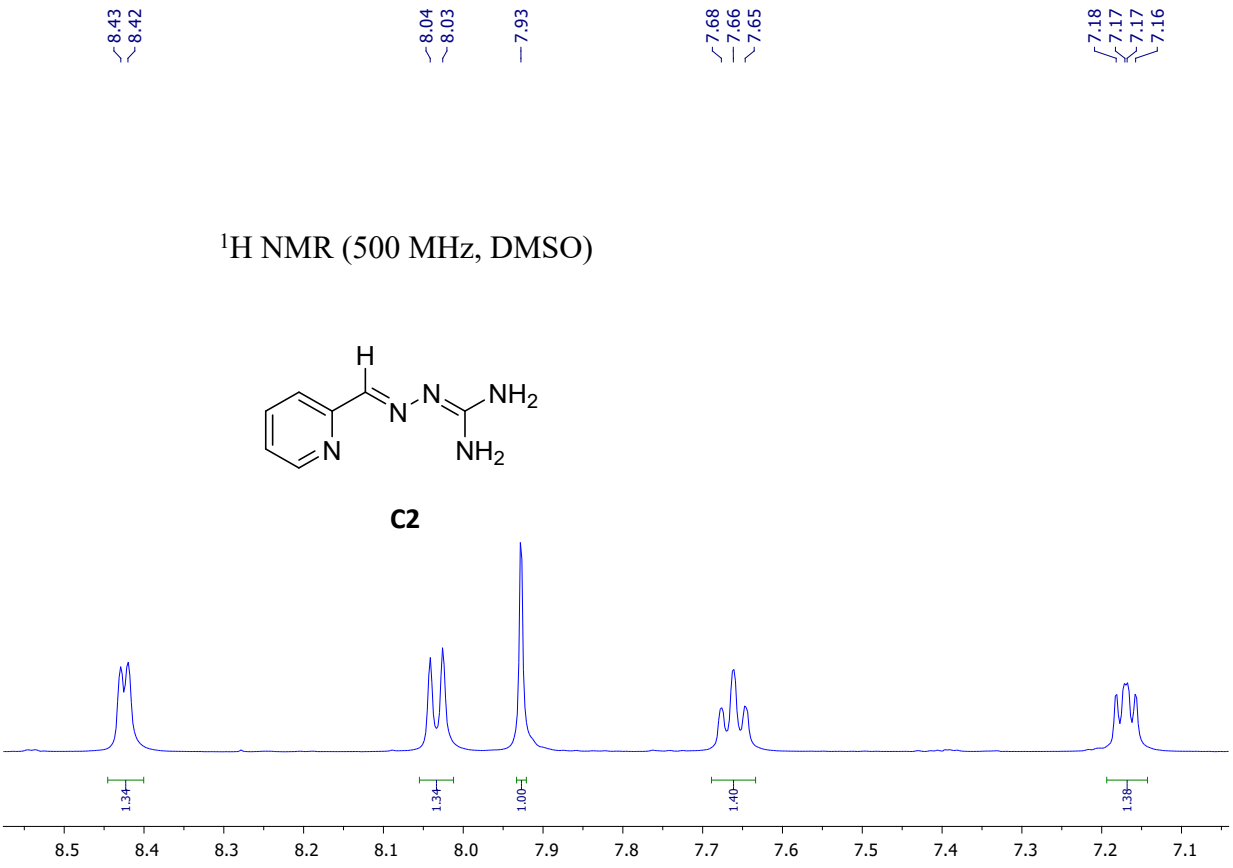
^{13}C NMR (500 MHz, DMSO)

C1



^{1}H NMR (500 MHz, DMSO)

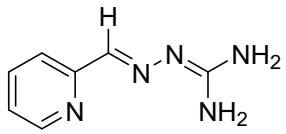
C2



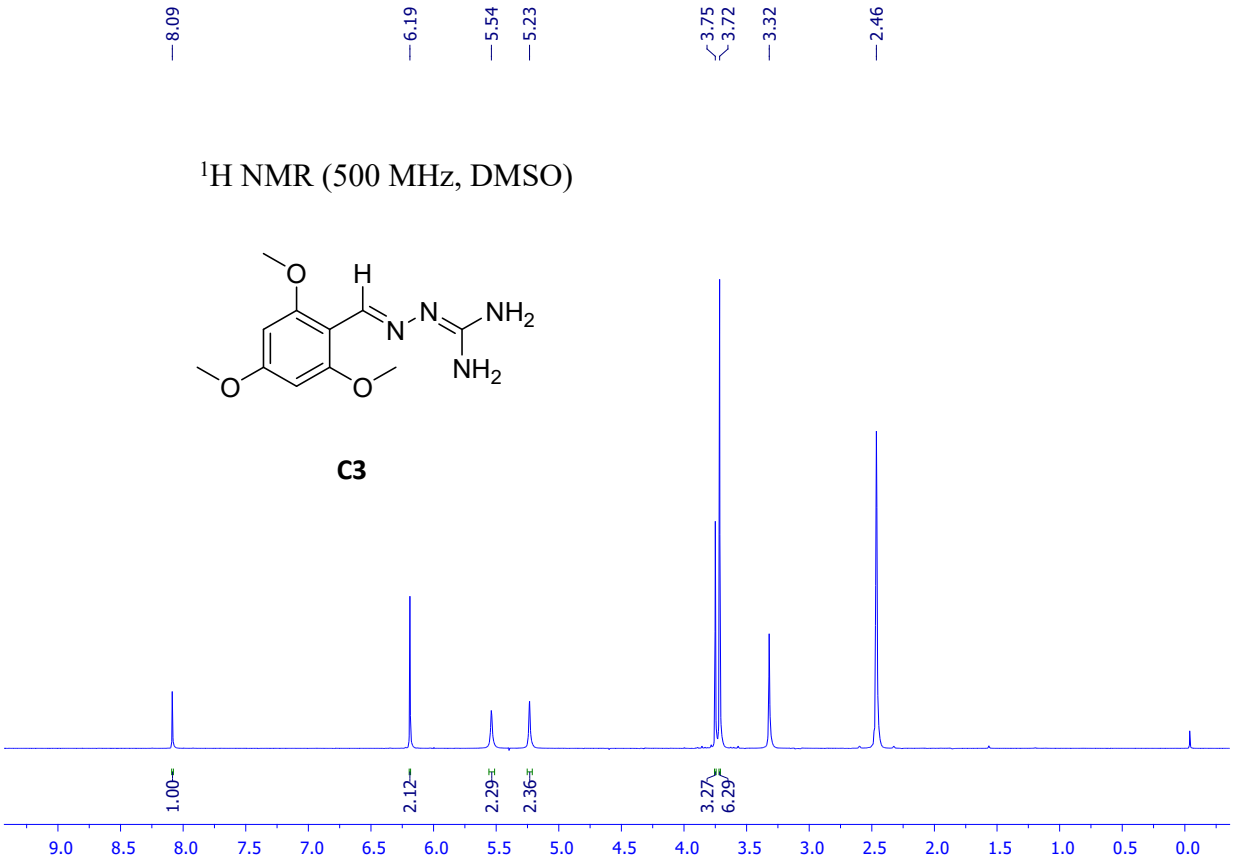
^{1}H NMR (500 MHz, DMSO)

C2

^{13}C NMR (500 MHz, DMSO)

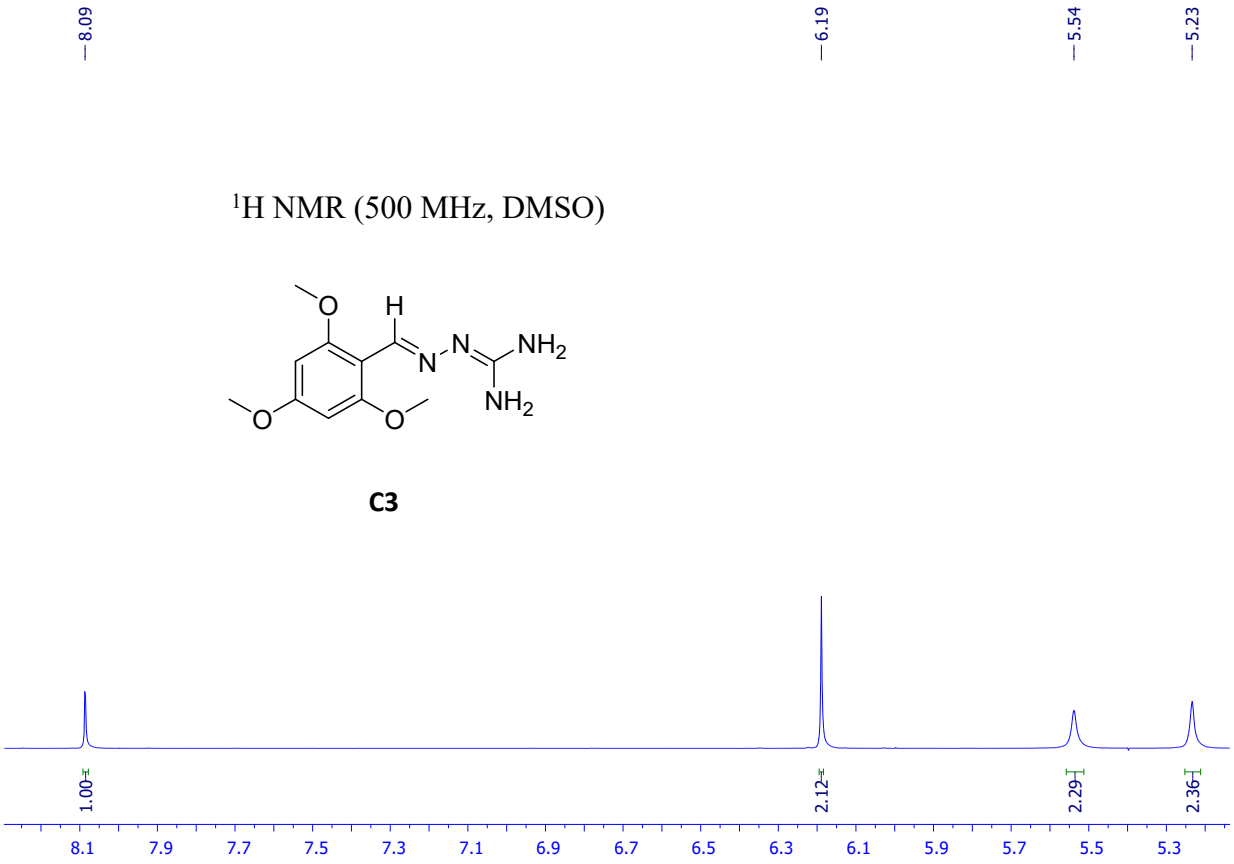


C2



^{1}H NMR (500 MHz, DMSO)

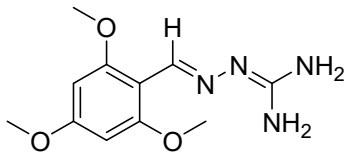
C3



^{1}H NMR (500 MHz, DMSO)

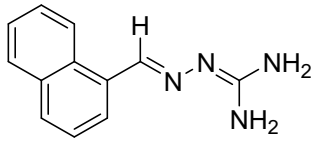
C3

^{13}C NMR (500 MHz, DMSO)

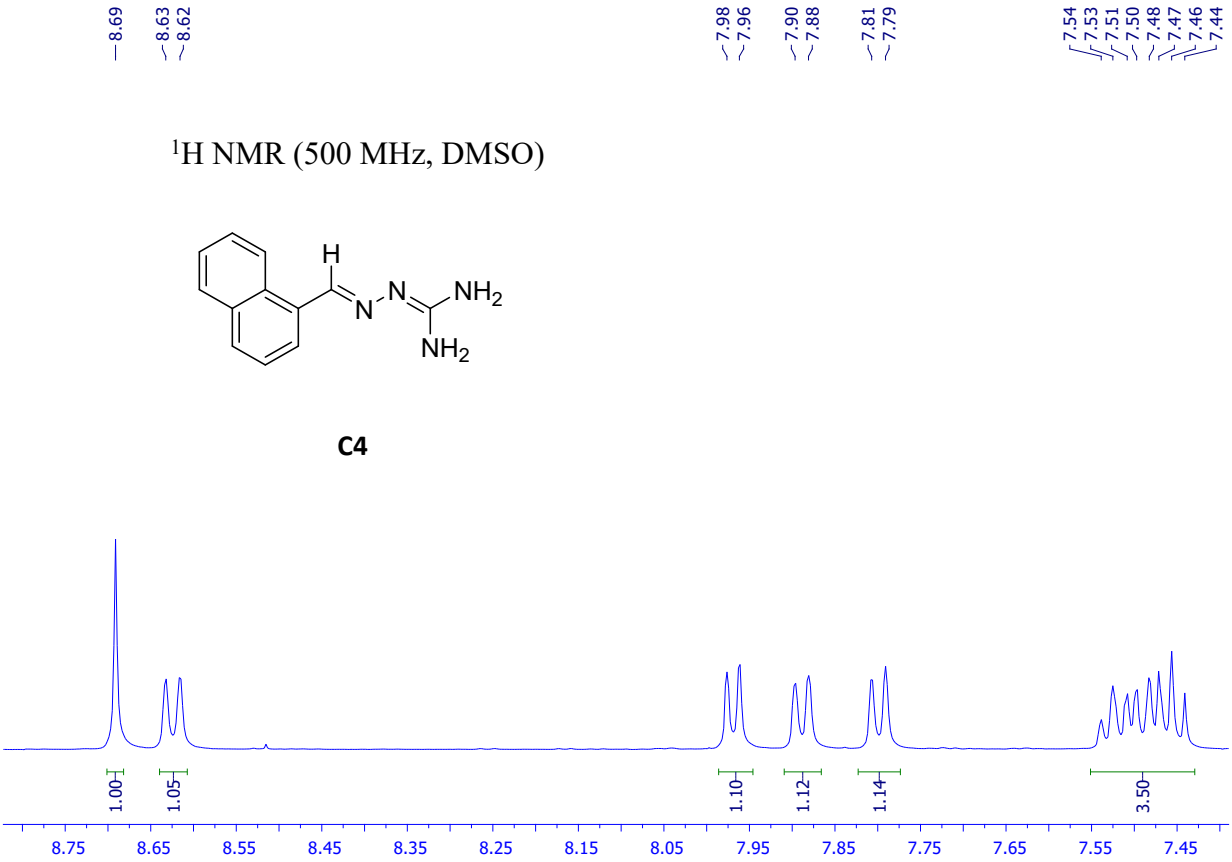


C3

^{1}H NMR (500 MHz, DMSO)

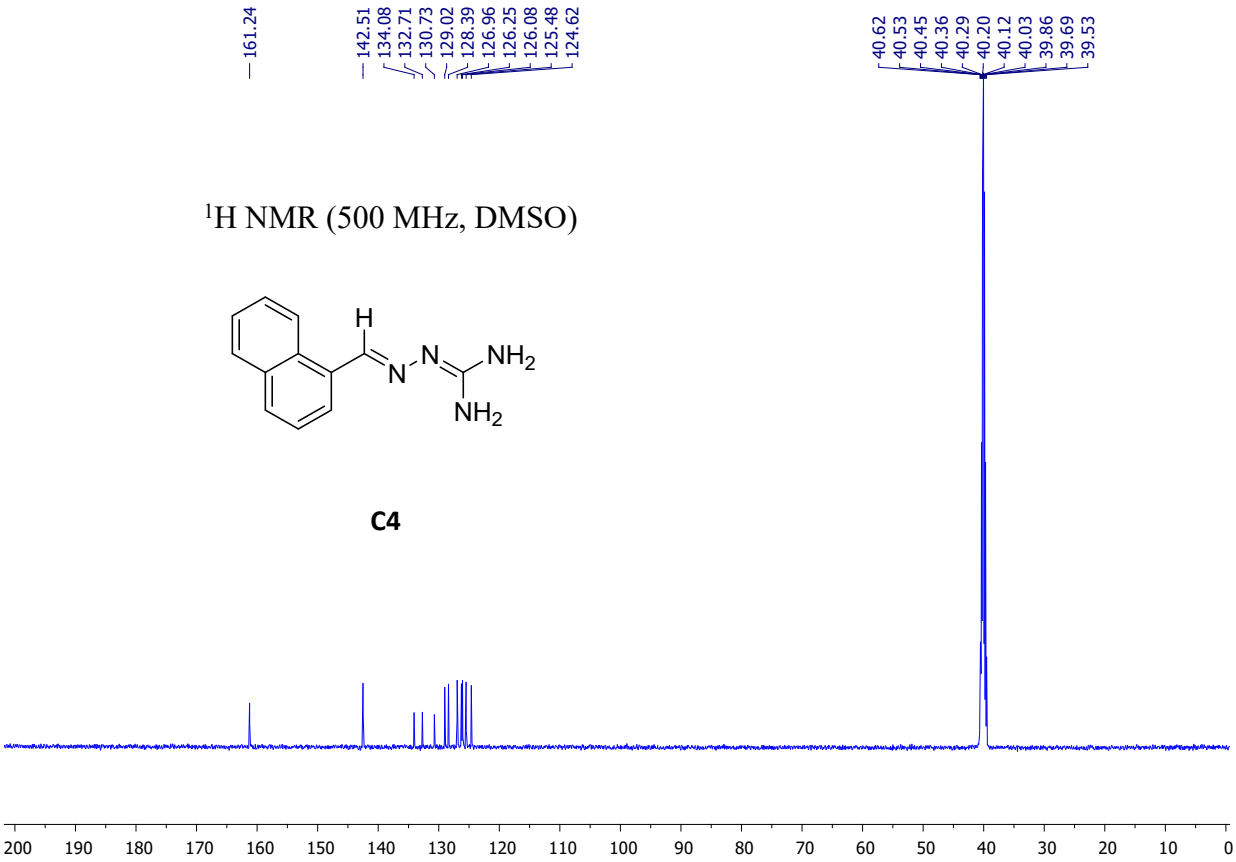


C4



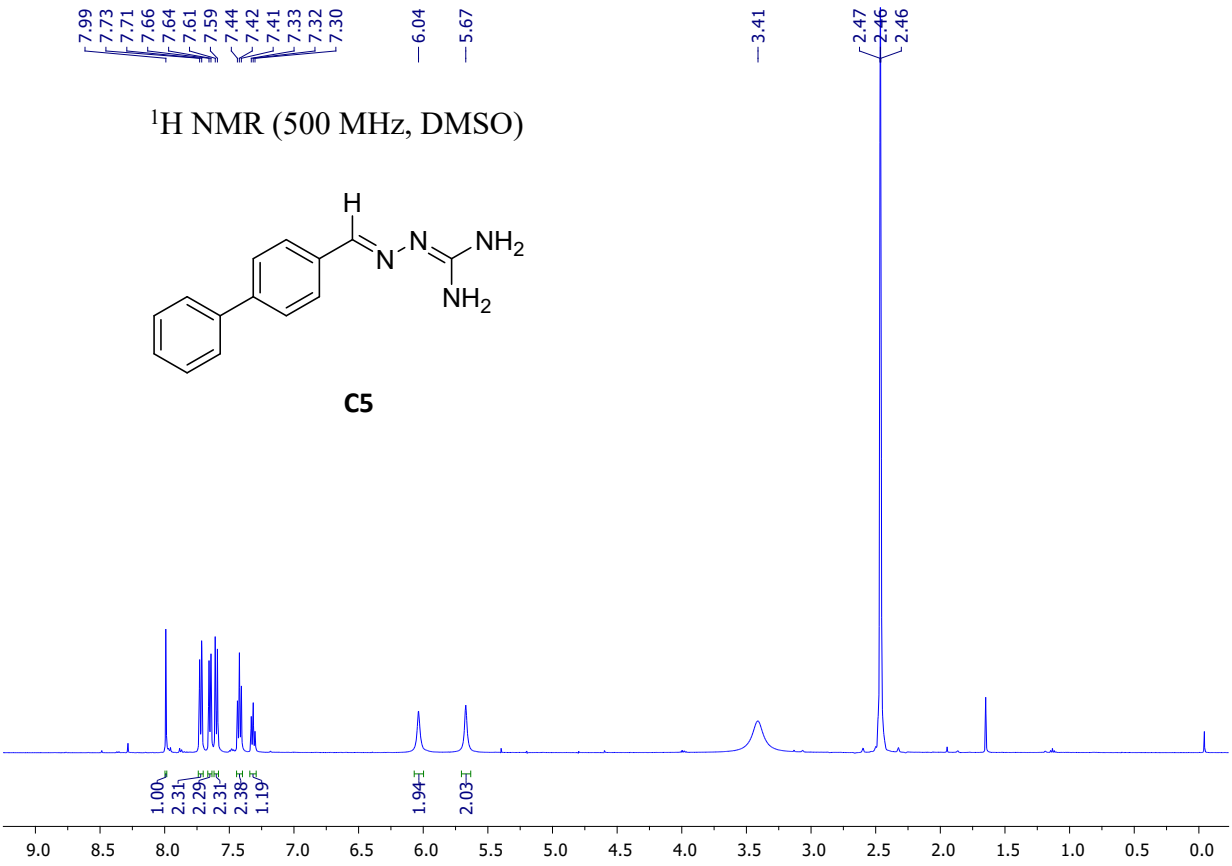
^{1}H NMR (500 MHz, DMSO)

C4



^{1}H NMR (500 MHz, DMSO)

C4

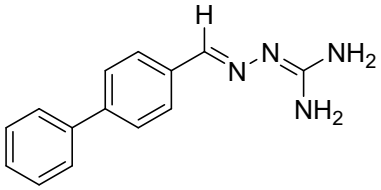


^{1}H NMR (500 MHz, DMSO)

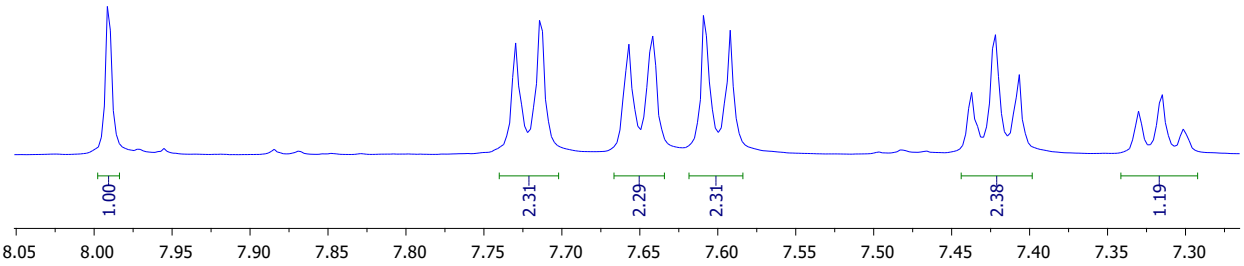
C5

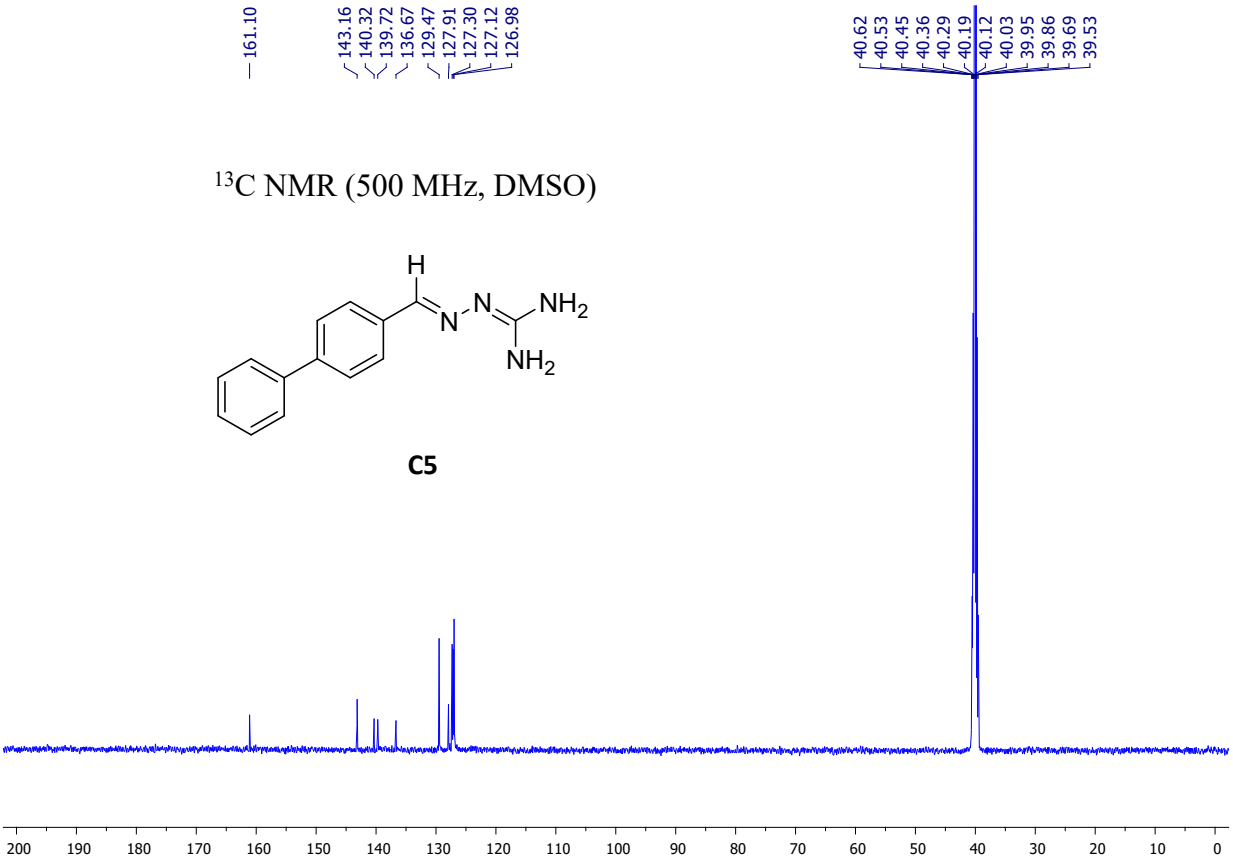
7.99 7.73 7.71 7.66 7.64 7.61 7.59 7.44 7.42 7.41 7.33 7.32 7.30

^{1}H NMR (500 MHz, DMSO)



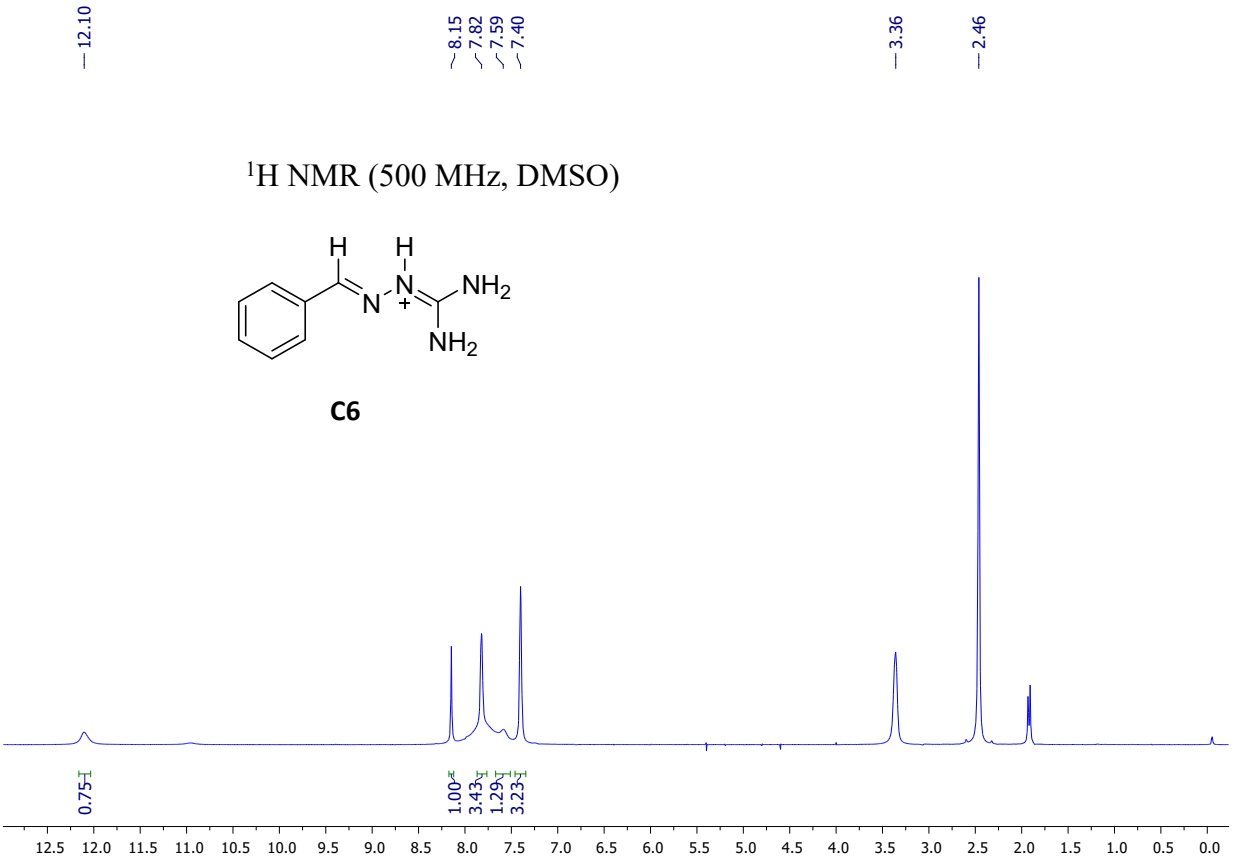
C5





^{13}C NMR (500 MHz, DMSO)

C5

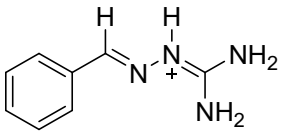


^{1}H NMR (500 MHz, DMSO)

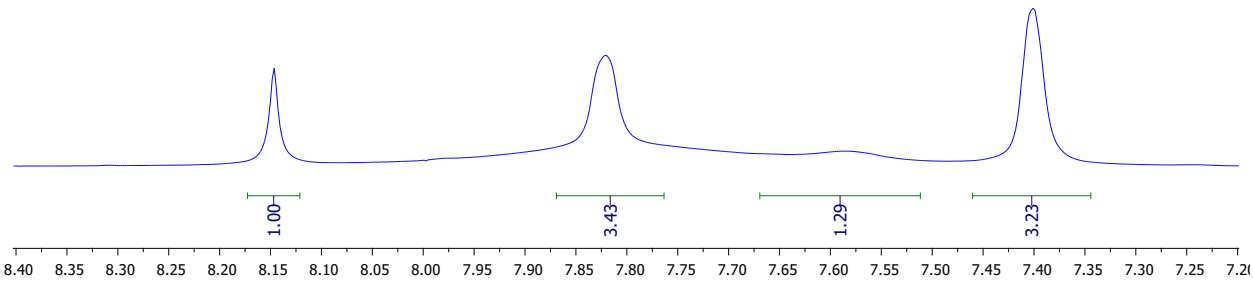
C6

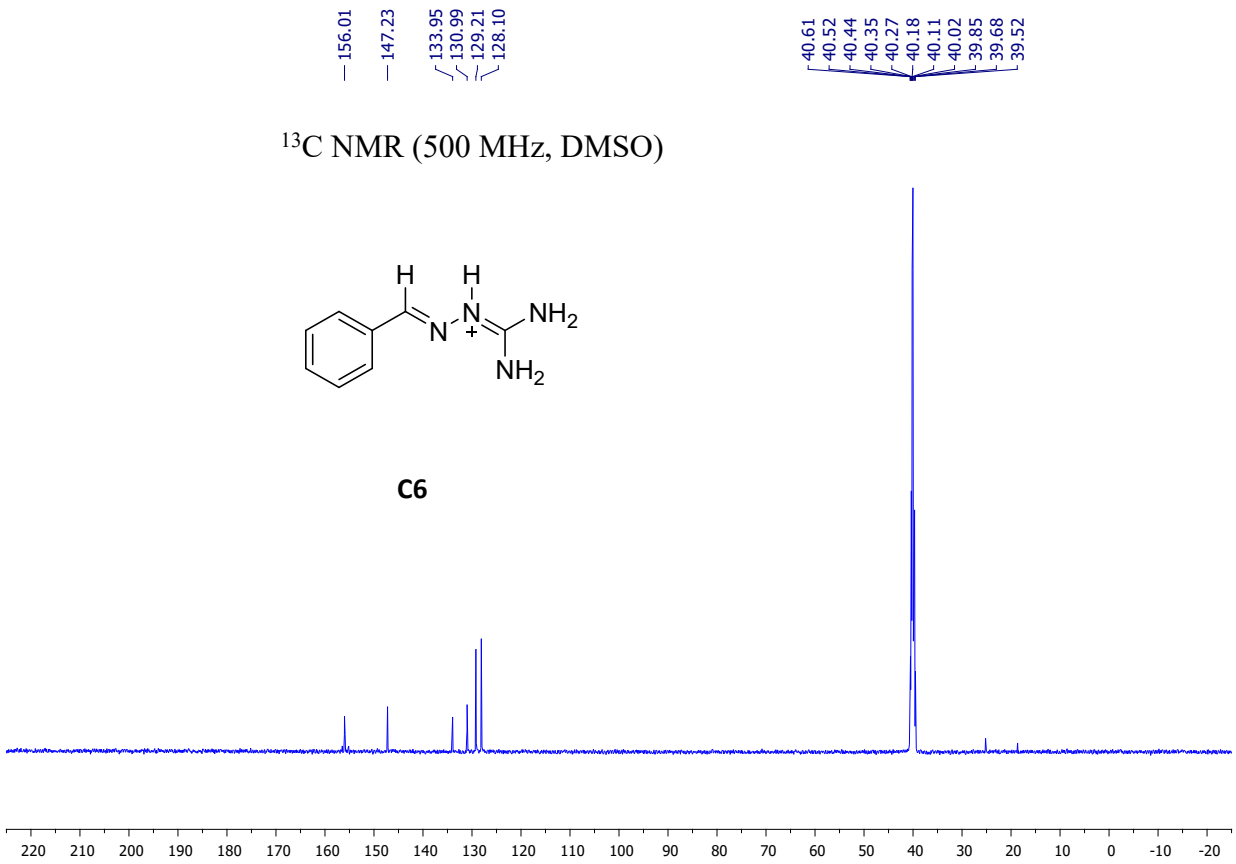
— 8.15 — 7.82 — 7.59 — 7.40

^{1}H NMR (500 MHz, DMSO)



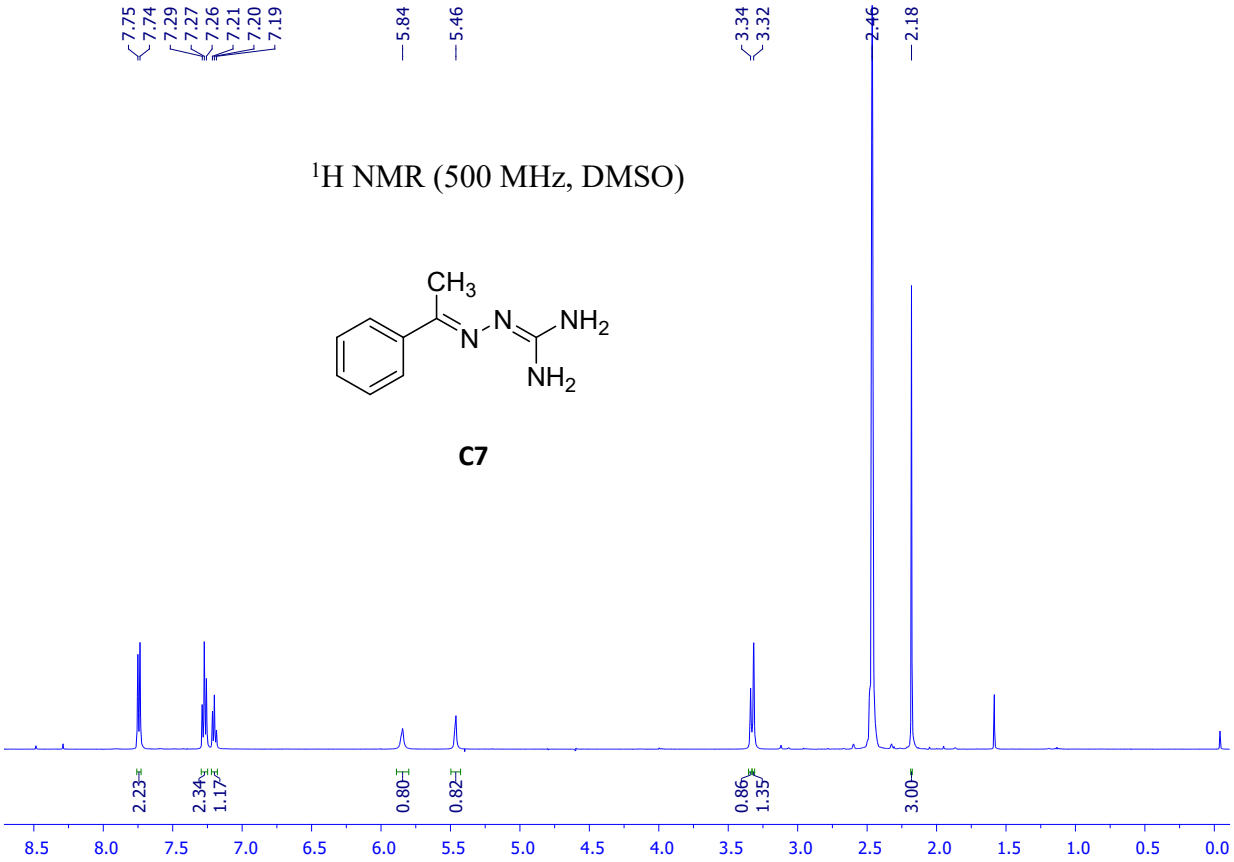
C6





^{13}C NMR (500 MHz, DMSO)

C6

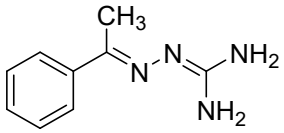


^{1}H NMR (500 MHz, DMSO)

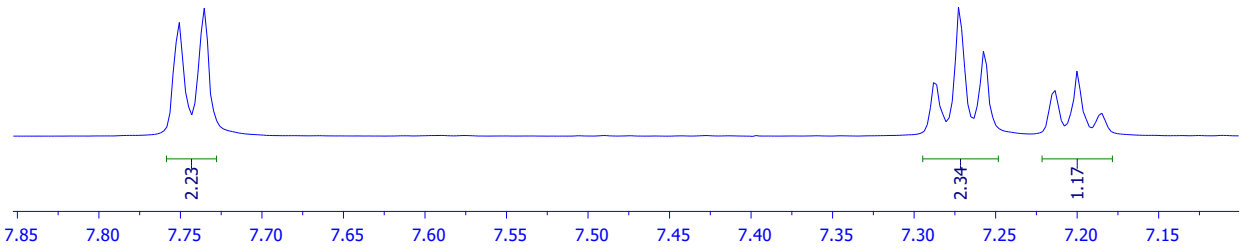
C7

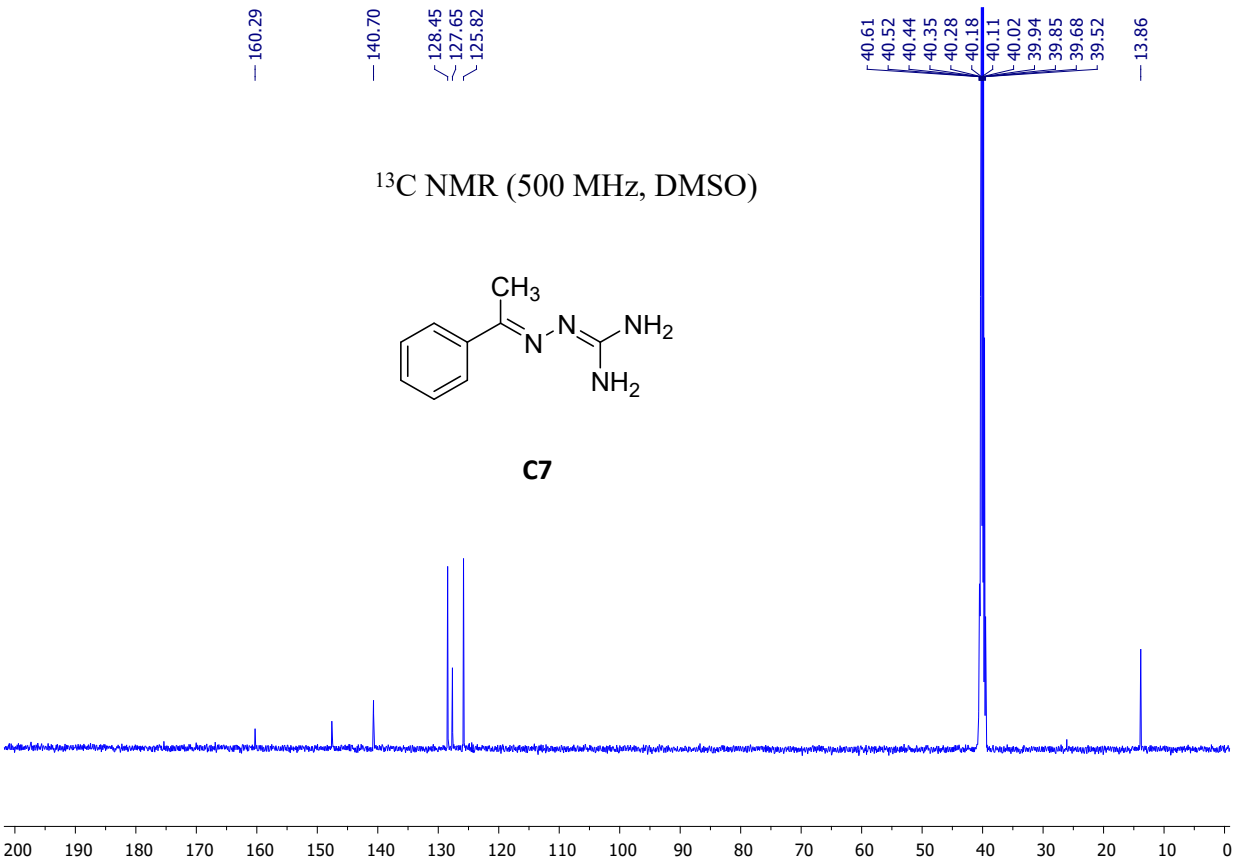
7.75
7.74
7.29
7.27
7.26
7.21
7.20
7.19

^{1}H NMR (500 MHz, DMSO)



C7





^{13}C NMR (500 MHz, DMSO)

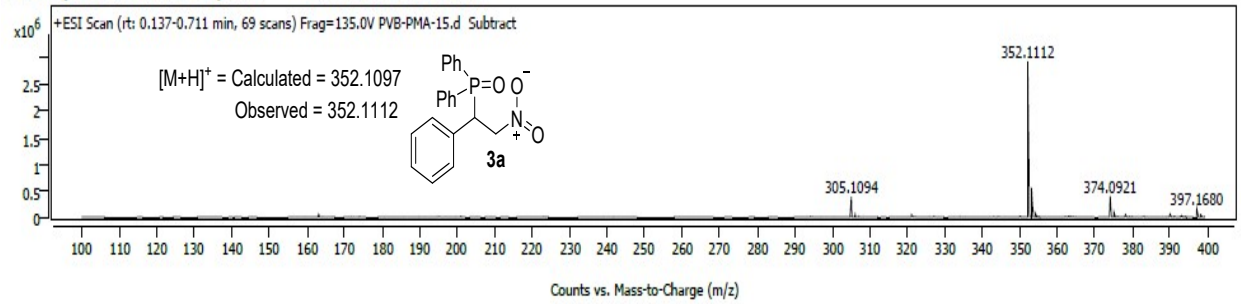
C7

9. HRMS Spectra of 3a, 3b, 3c, 3d and 6-21

HRMS of 3a

Sample Spectra

+ Scan (rt: 0.137-0.711 min) Sub Peak 1 from + TIC Scan

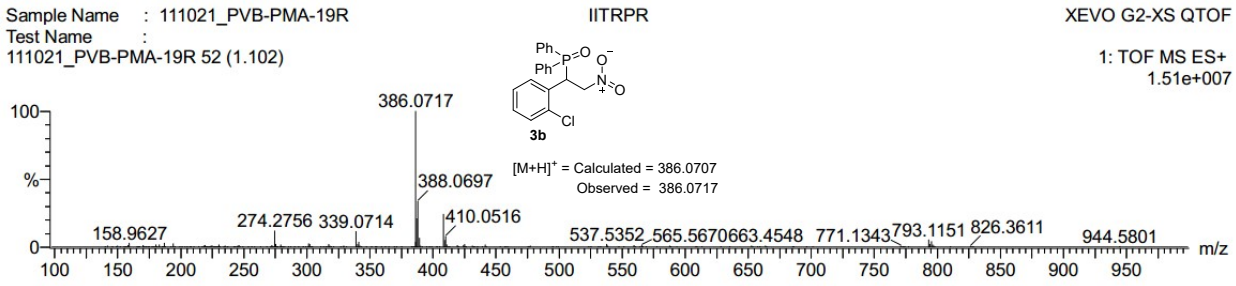


Spectrum Peaks

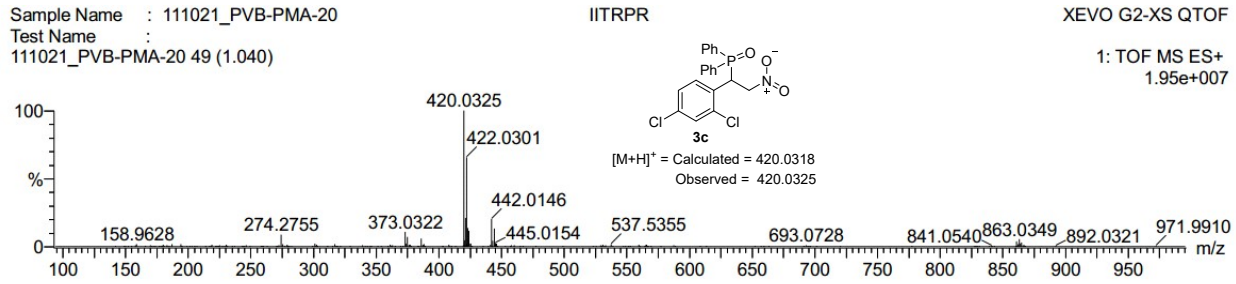
m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
305.1094		390410	12.73					
352.1112	1	3067378	100.00					
353.1136	1	554956	18.09					
374.0921		401182	13.08					
397.1680		160761	5.24					

MassHunter Qual 10.0
(End of Report)

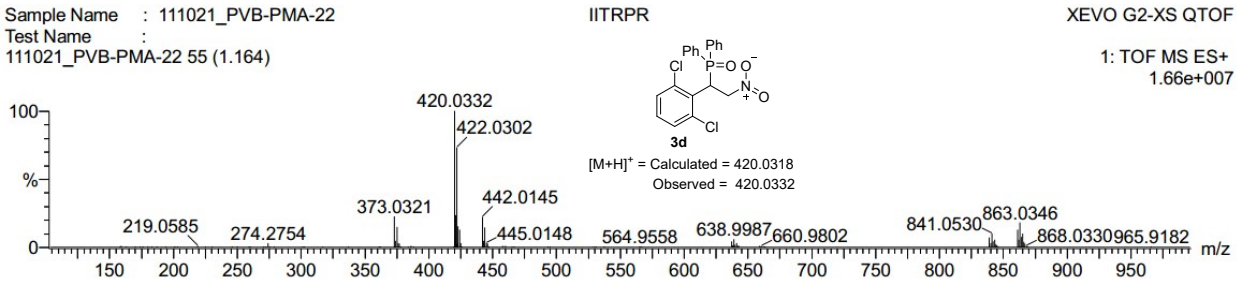
HRMS of 3b



HRMS of 3c



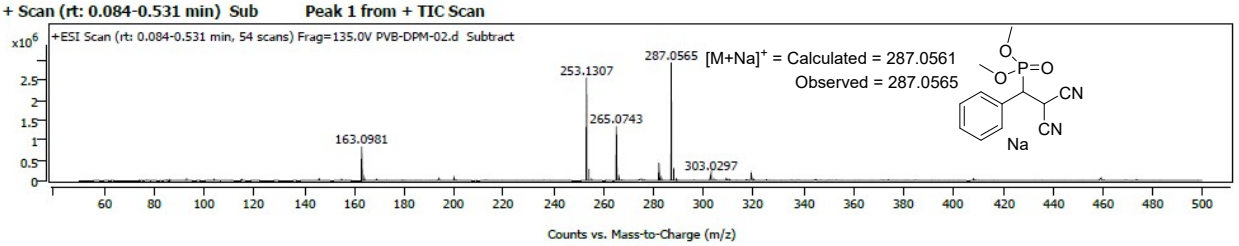
HRMS of 3d



HRMS of 6

Sample Spectra

+ Scan (rt: 0.084-0.531 min) Sub Peak 1 from + TIC Scan



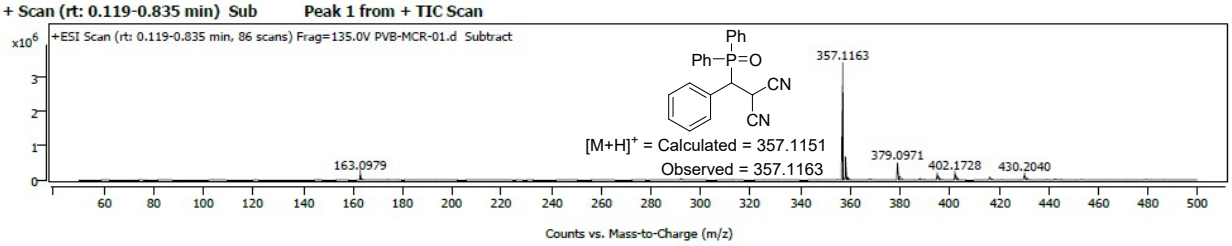
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
163.0981		845082	28.65					
253.1307	1	2569780	87.11					
254.1330	1	279009	9.46					
265.0743		1381580	46.83					
282.1006		461862	15.66					
287.0565	1	2949908	100.00					
288.0591	1	307118	10.41					
303.0297		190757	6.47					
319.0821		158437	5.37					

HRMS of 7

Sample Spectra

+ Scan (rt: 0.119-0.835 min) Sub Peak 1 from + TIC Scan



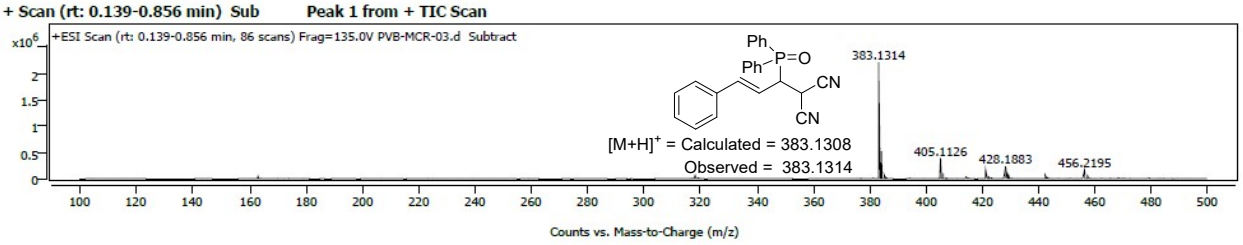
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
163.0979		221244	6.43					
357.1163	1	3440425	100.00					
358.1186	1	716900	20.84					
379.0971		504055	14.65					
395.0708		180971	5.26					
402.1728		218013	6.34					
430.2040		179460	5.22					

HRMS of 8

Sample Spectra

+ Scan (rt: 0.139-0.856 min) Sub Peak 1 from + TIC Scan



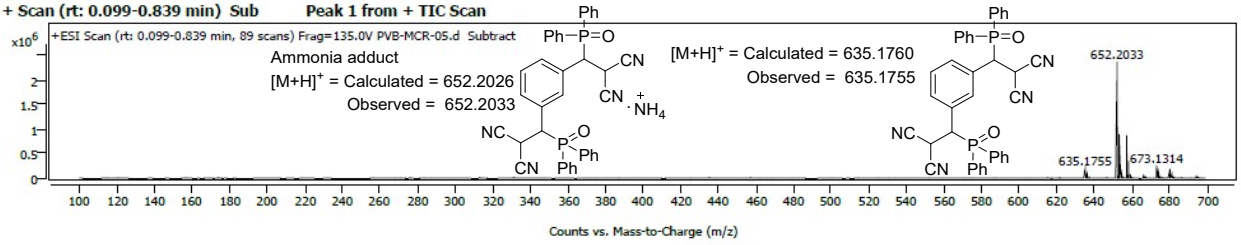
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
383.1314	1	2271951	100.00					
384.1340	1	521938	22.97					
405.1126		393844	17.34					
421.0863		173878	7.65					
428.1883		236408	10.41					
456.2195		170113	7.49					

HRMS of 9

Sample Spectra

+ Scan (rt: 0.099-0.839 min) Sub Peak 1 from + TIC Scan



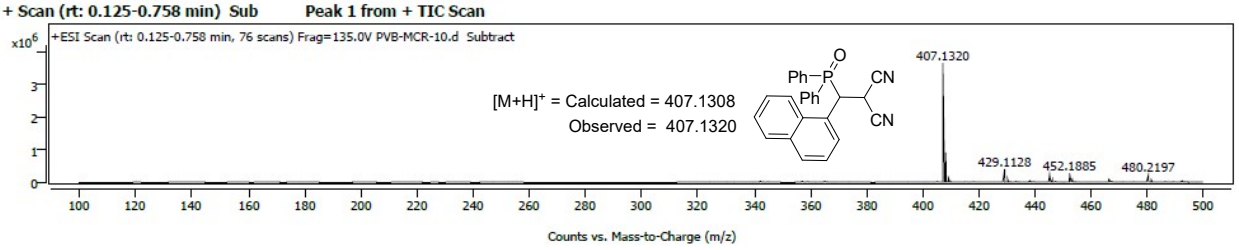
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
635.1755		199236	8.42					
652.2033	1	2367377	100.00					
653.2058	1	917034	38.74					
654.2084	1	180733	7.63					
657.1579	1	878579	37.11					
658.1608	1	345168	14.58					
673.1314		265683	11.22					
680.2334		189162	7.99					

HRMS of 10

Sample Spectra

+ Scan (rt: 0.125-0.758 min) Sub Peak 1 from + TIC Scan

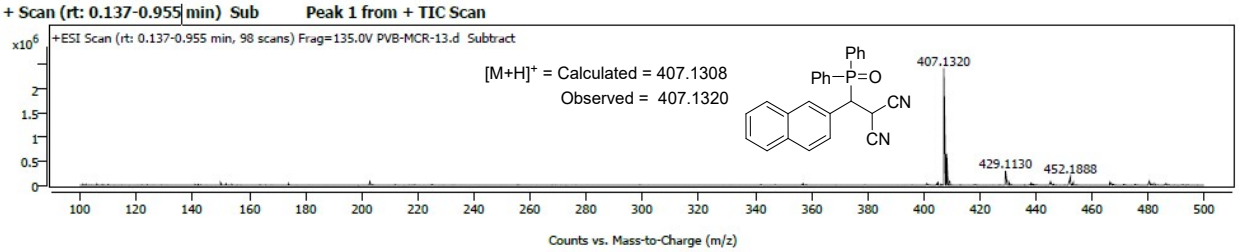


Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
407.1320	1	3659161	100.00					
408.1343	1	928052	25.36					
429.1128		397940	10.88					
445.0866		247726	6.77					
452.1885		272682	7.45					
480.2197		218077	5.96					

HRMS of 11

+ Scan (rt: 0.137-0.955 min) Sub Peak 1 from + TIC Scan



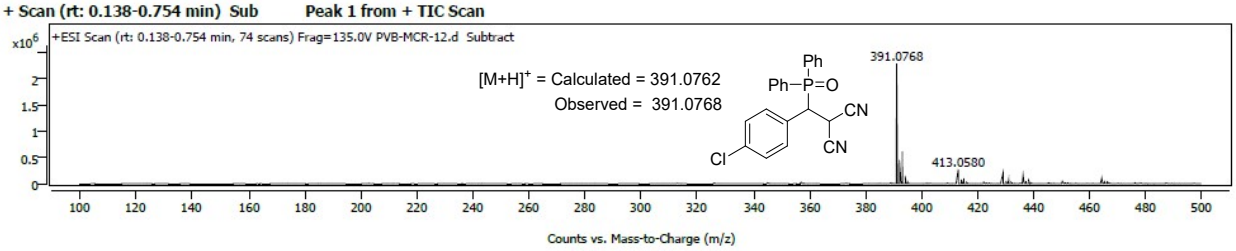
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
407.1320	1	2526970	100.00					
408.1345	1	650093	25.73					
429.1130		299223	11.84					
452.1888		176470	6.98					

HRMS of 12

Sample Spectra

+ Scan (rt: 0.138-0.754 min) Sub **Peak 1 from + TIC Scan**



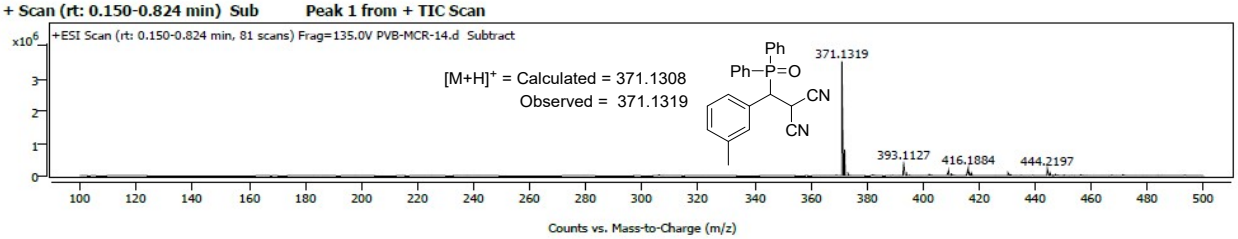
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
391.0768	1	2281856	100.00					
392.0794	1	452788	19.84					
393.0736	1	611463	26.80					
394.0764		150158	6.58					
413.0580		278675	12.21					
429.0318		207345	9.09					
436.1338		170314	7.46					

HRMS of 13

Sample Spectra

+ Scan (rt: 0.150-0.824 min) Sub **Peak 1 from + TIC Scan**



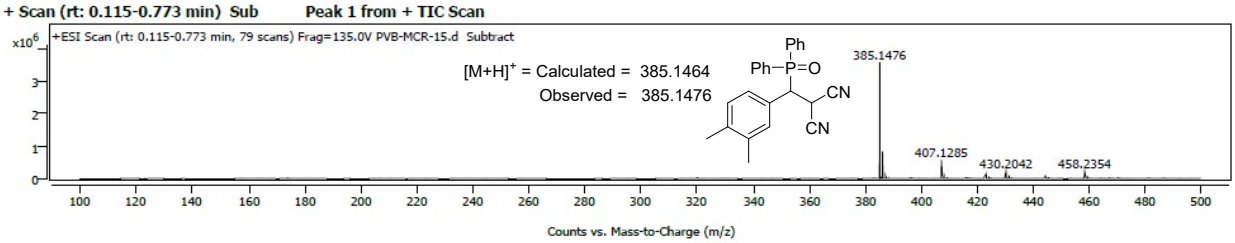
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
371.1319	1	3634589	100.00					
372.1342	1	809925	22.28					
393.1127		446950	12.30					
416.1884		268659	7.39					
444.2197		245047	6.74					

HRMS of 14

Sample Spectra

+ Scan (rt: 0.115-0.773 min) Sub Peak 1 from + TIC Scan



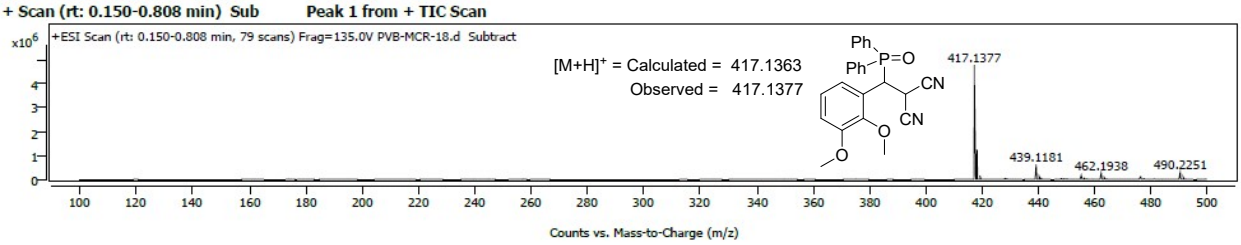
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
385.1476	1	3629732	100.00					
386.1500	1	837868	23.08					
407.1285		584051	16.09					
430.2042		244721	6.74					
458.2354		240044	6.61					

HRMS of 15

Sample Spectra

+ Scan (rt: 0.150-0.808 min) Sub Peak 1 from + TIC Scan



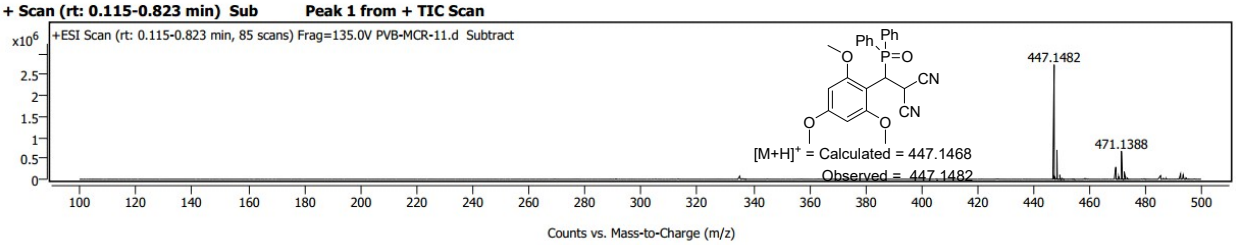
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
417.1377	1	4993331	100.00					
418.1397	1	1249660	25.03					
439.1181		648523	12.99					
462.1938		282685	5.66					
490.2251		309979	6.21					

HRMS of 16

Sample Spectra

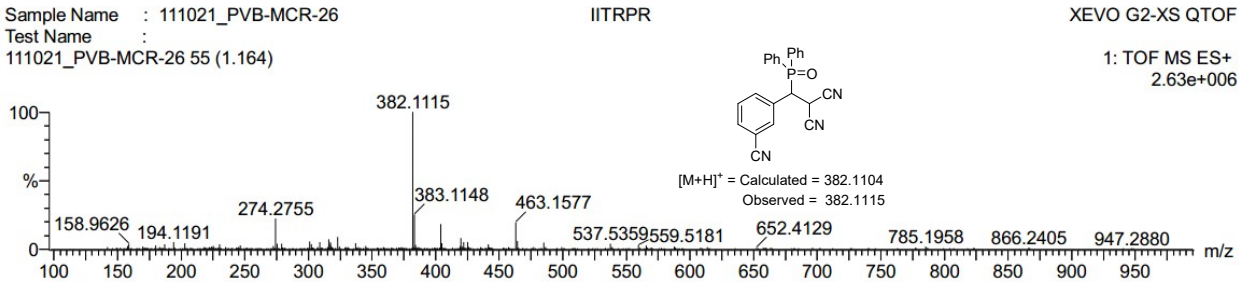
+ Scan (rt: 0.115-0.823 min) Sub Peak 1 from + TIC Scan



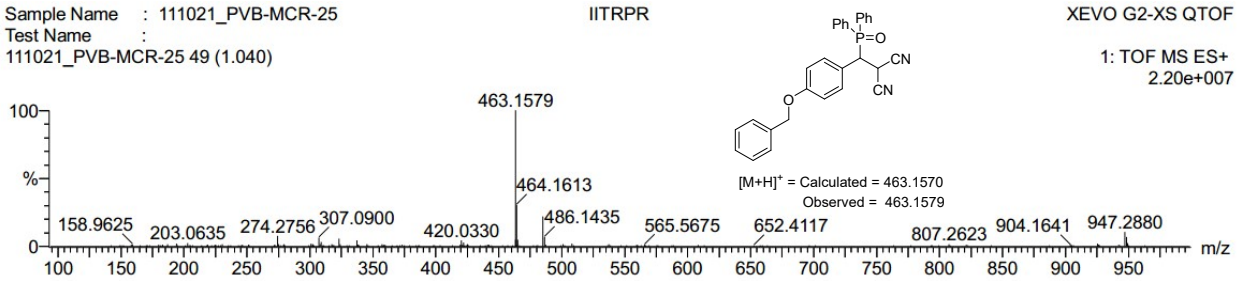
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
447.1482	1	2882462	100.00					
448.1504	1	691925	24.00					
469.1289		302542	10.50					
471.1388	1	681762	23.65					
472.1418	1	180071	6.25					

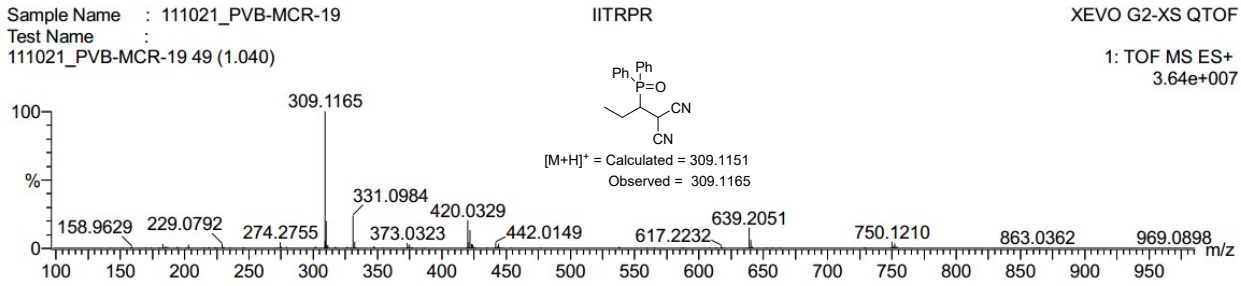
HRMS of 17



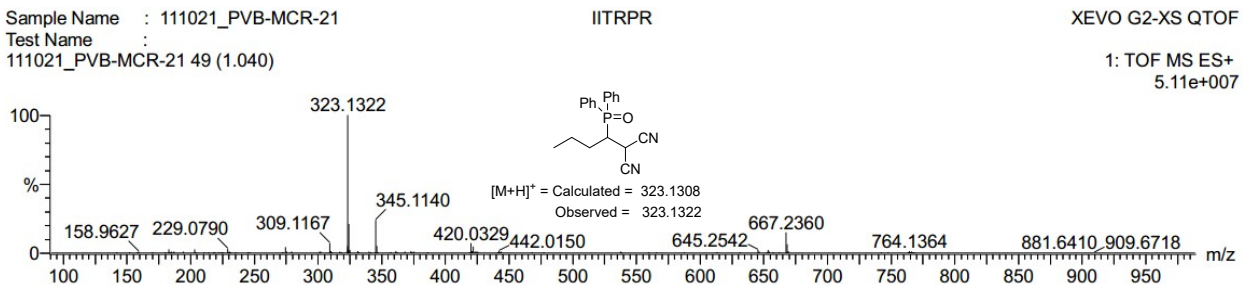
HRMS of 18



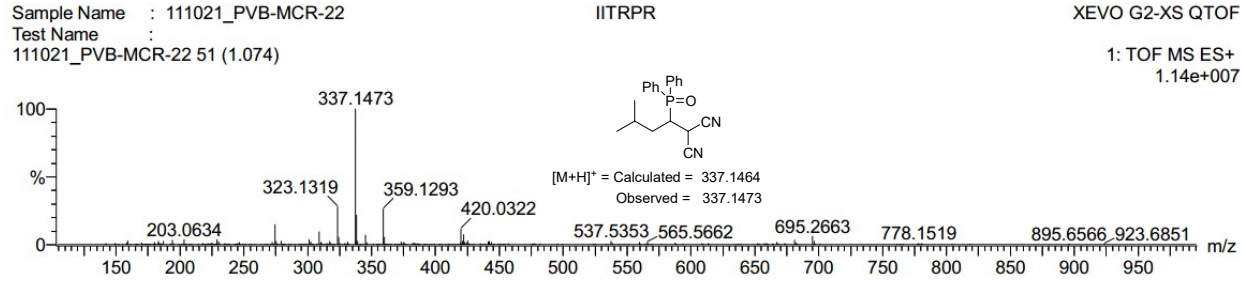
HRMS of 19



HRMS of 20

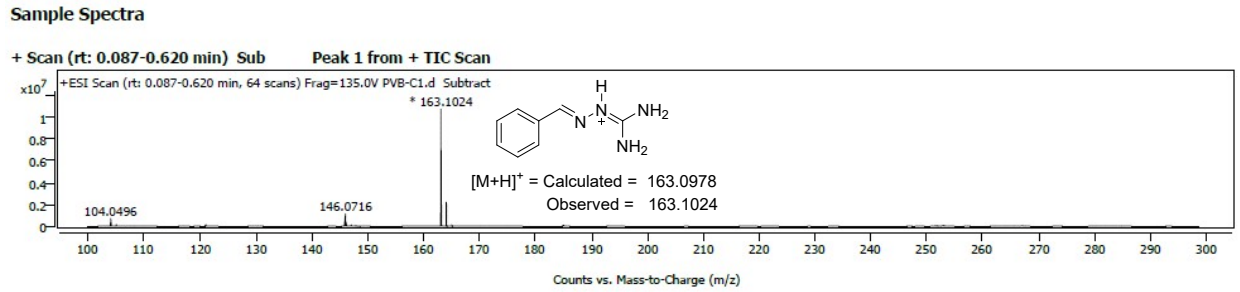


HRMS of 21



10. HRMS Spectra of catalysts:

HRMS Spectra of C1

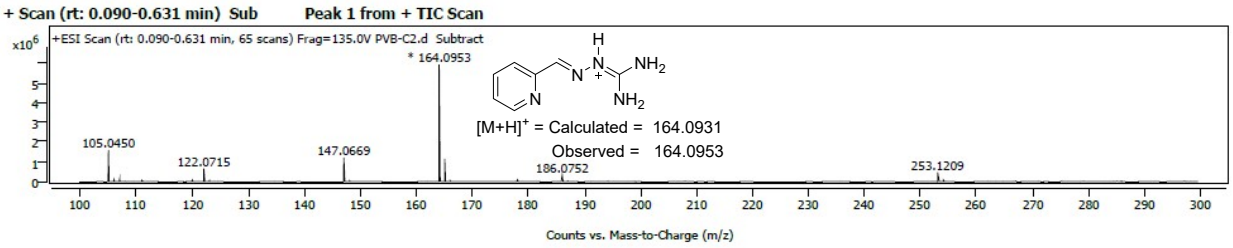


Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
104.0496		745528	6.78					
146.0716		1181067	10.74					
163.0966		8084771	73.51					
163.1024	1	10998011	100.00					
164.1016	1	2308196	20.99					

HRMS Spectra of C2

Sample Spectra

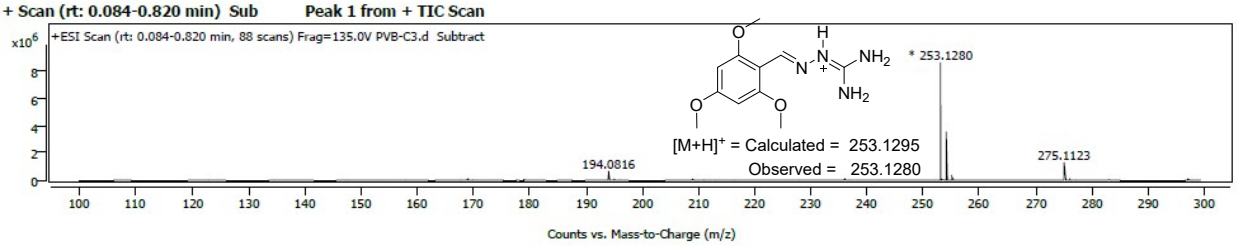


Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
105.0450		1675332	28.22					
122.0715		690875	11.64					
147.0669		1254967	21.14					
164.0953	1	5936662	100.00					
165.0965	1	1186302	19.98					
186.0752		348006	5.86					
253.1209		471528	7.94					

HRMS Spectra of C3

Sample Spectra

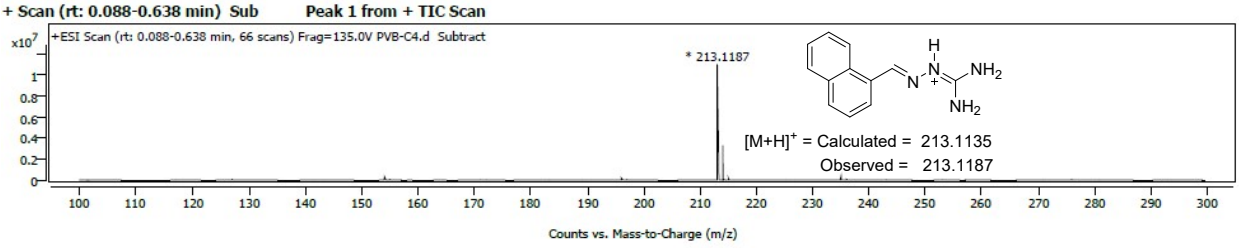


Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
194.0816		683367	7.92					
253.1280		8630835	100.00					
253.1356		3877259	44.92					
254.1343		3599335	41.70					
275.1123		1313030	15.21					

HRMS Spectra of C4

Sample Spectra



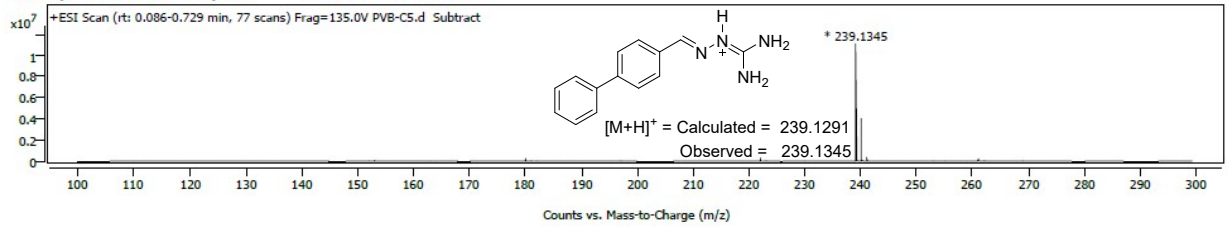
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
213.1120		8629589	75.56					
213.1187		11420416	100.00					
214.1179		3336225	29.21					

HRMS Spectra of C5

Sample Spectra

+ Scan (rt: 0.086-0.729 min) Sub Peak 1 from + TIC Scan



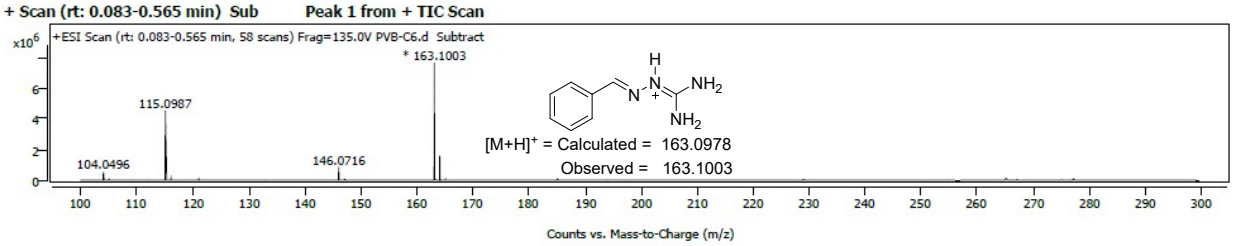
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
239.1274		7981910	71.61					
239.1345		11145638	100.00					
240.1339		4302387	38.60					

HRMS Spectra of C6

Sample Spectra

+ Scan (rt: 0.083-0.565 min) Sub Peak 1 from + TIC Scan



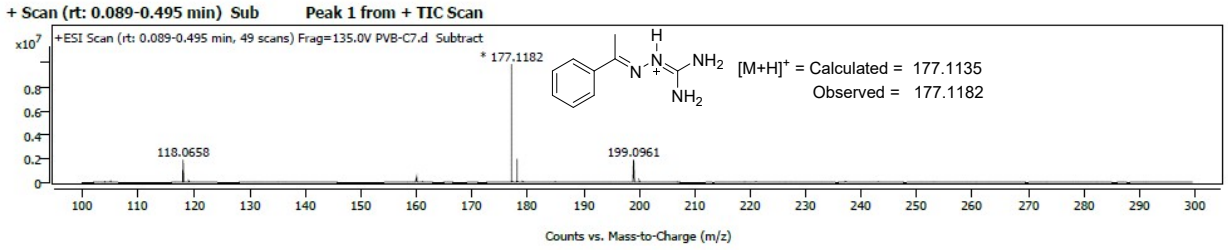
Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
104.0496		554216	7.20					
115.0987		4670656	60.66					
146.0716		852050	11.07					
163.1003	1	7700189	100.00					
164.1016	1	1640567	21.31					

HRMS Spectra of C7

Sample Spectra

+ Scan (rt: 0.089-0.495 min) Sub Peak 1 from + TIC Scan



Spectrum Peaks

m/z	Z	Abund	Abund %	m/z (Calc)	Diff (ppm)	Ion Species	Formula	Ion Type
118.0658		1918189	19.34					
177.1122		6388936	64.42					
177.1182	1	9916993	100.00					
178.1176	1	1961497	19.78					
199.0961		1889313	19.05					

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