

# Synthesis and Reactivity of *N*-Allenyl Cyanamides

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# 1. General Information

Unless stated otherwise, all reactions were performed in oven-dried glassware sealed with rubber septa under a nitrogen atmosphere and were stirred with teflon-coated magnetic stirrer bars. Dry tetrahydrofuran (THF), acetonitrile, toluene, hexanes and diethyl ether were obtained after passing these previously degassed solvents through activated alumina columns (Mbraun, SPS-800). All other solvents and commercial reagents were used as supplied without further purification unless stated otherwise.

Room temperature (rt) refers to 20-25 °C. Temperatures of 0 °C and -15 °C were obtained using ice/water and ice/water/NaCl baths respectively. All reactions involving heating were carried out using DrySyn blocks and a contact thermometer. *In vacuo* refers to the use of a rotary evaporator under reduced pressure.

Analytical thin layer chromatography was carried out using aluminium plates coated with silica (Kieselgel 60 F<sub>254</sub> silica) and visualization was achieved using ultraviolet light (254 nm), followed by staining with a 1% aqueous KMnO<sub>4</sub> solution. Flash chromatography used Kieselgel 60 silica in the solvent system stated.

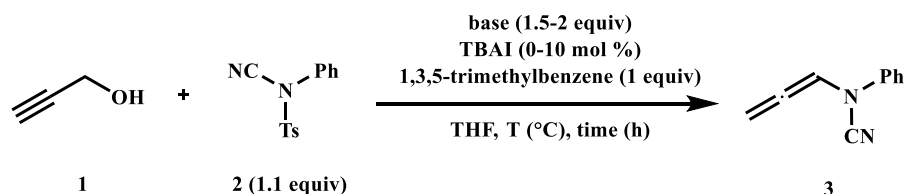
Melting points were recorded on an Electrothermal 100 apparatus and are corrected using benzophenone and benzoic acid as calibration standards. Dec refers to decomposition.

Infra red spectra were recorded on a Shimadzu IRAffinity-1 Fourier Transform ATIR spectrometer as thin films using a pike miracle ATR accessory. Characteristic peaks are quoted ( $\nu_{\max}$  / cm<sup>-1</sup>).

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>19</sup>F{<sup>1</sup>H} NMR spectra were obtained on either a Bruker Avance 300 (300 MHz <sup>1</sup>H, 76 MHz <sup>13</sup>C, 282 MHz <sup>19</sup>F), Bruker Avance 400 (400 MHz <sup>1</sup>H, 101 MHz <sup>13</sup>C, 377 MHz <sup>19</sup>F) or a Bruker Avance 500 (500 MHz <sup>1</sup>H, 126 MHz <sup>13</sup>C, 471 MHz <sup>19</sup>F) spectrometer at 25 °C in the solvent stated. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent signal. All coupling constants, *J*, are quoted in Hz. Multiplicities are reported with the following symbols: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and multiples thereof. The abbreviation Ar is used to denote aromatic, Ph to denote phenyl, Bn to denote benzyl, br to denote broad and app to denote apparent.

High resolution mass spectrometry (HRMS, *m/z*) data was acquired either at Cardiff University on a Micromass LCT spectrometer or at the EPSRC UK National Mass Spectrometry Facility at Swansea University.

## 2. Reaction optimization



### General procedure 1

To a reaction vial was added propargyl alcohol **1** (58  $\mu\text{L}$ , 1 mmol, 1 equiv) followed by THF ([propargyl alcohol] = 0.2 mol dm<sup>-3</sup>) base (1.5-2 equiv), 1,3,5-trimethylbenzene (139  $\mu\text{L}$ , 1 mmol, 1 equiv) as internal standard, NCTS **2** (300 mg, 1.1 mmol, 1.1 equiv) and TBAI (0-10 mol %) as an additive, the reactions were stirred at constant temperature. The reaction was monitored taking aliquots at specified times (T1= 1 h, T2= 3 h, T3= 6 h, T4 = 23 h) *via* <sup>1</sup>H NMR analysis. Each <sup>1</sup>H NMR was analysed to determine the amount of product present within the reaction mixture.

Entry	Base (eq.)	Solvent	NCTS (eq.)	Additive (mol %)	[SM] /mol dm-3	T / °C	T1 = 1h Product	T2 = 3 h Product	T3 = 6 h Product	T4 = 23 h Product
1	NaH (2)	THF	1.1	TBAI (10)	0.2	20	30	74	76	56
2	NaOt Am (2)	THF	1.1	TBAI (10)	0.2	20	35	63	61	58
3	KOt Bu (2)	THF	1.1	TBAI (10)	0.2	20	7	17	18	19
4	DBU (2)	THF	1.1	TBAI (10)	0.2	20	0	0	0	5
5	LHMDS (2)	THF	1.1	TBAI (10)	0.2	20	0	0	0	0
6	DBN (2)	THF	1.1	TBAI (10)	0.2	20	0	0	0	0
7	NaH (2)	THF	1.1	-	0.2	20	8	26	36	40
8	NaOt Am (2)	THF	1.1	-	0.2	20	20	30	33	40
9	NaOt Am (2)	DME	1.1	TBAI (10)	0.2	20	47	59	73	73

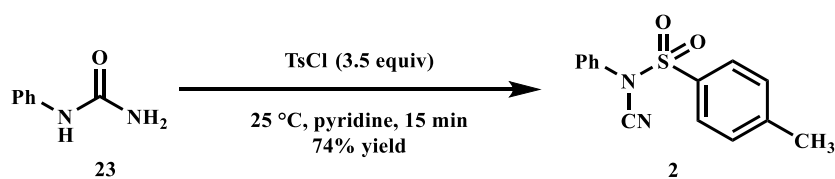
### General procedure 2

To a reaction vial was added propargyl alcohol **1** (58  $\mu\text{L}$ , 1 mmol, 1 equiv) followed by THF ([propargyl alcohol] = 0.2 mol dm<sup>-3</sup>), 1,3,5-trimethylbenzene (139  $\mu\text{L}$ , 1 mmol, 1 equiv) as internal standard, NCTS **2** (300 mg, 1.1 mmol, 1.1 equiv) and TBAI (0-10 mol %) as an additive and stirred for 5 min. Base (1.5-2 equiv) is then added and the reactions were stirred at constant temperature. The reaction was monitored taking aliquots at specified times (T1= 1 h, T2= 3 h, T3= 6 h, T4 = 23 h) *via* <sup>1</sup>H NMR analysis. Each <sup>1</sup>H NMR was analysed to determine the amount of product present within the reaction mixture.

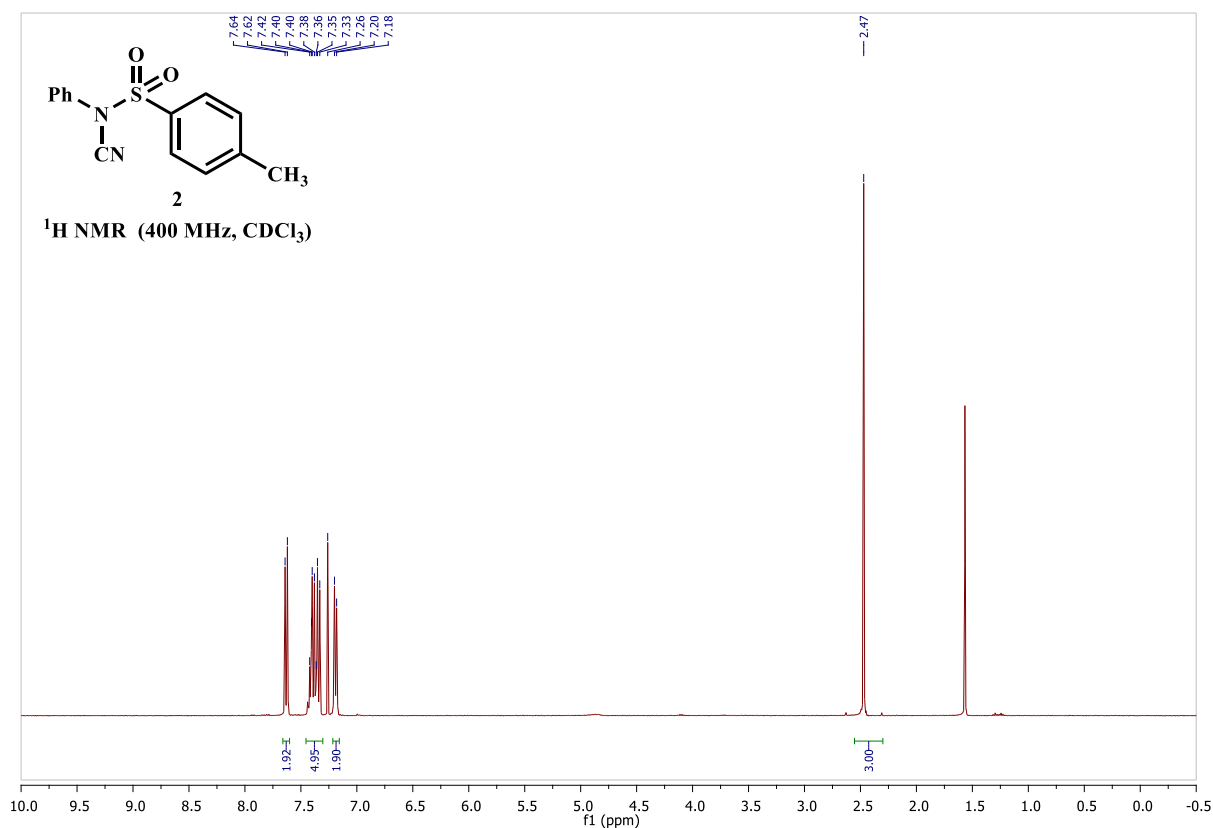
Entry	Base (eq.)	Solvent	NCTS (eq.)	Additive (mol %)	[SM] /mol dm-3	T / °C	T1 = 1h Product	T2 = 3 h Product	T3 = 6 h Product	T4 = 23 h Product
1	NaOt Am (2)	DME	1.1	TBAI (10)	0.2	20	55	61	73	75
2	<b>NaH (2)</b>	<b>THF</b>	<b>1.1</b>	<b>TBAI (10)</b>	<b>0.2</b>	<b>20</b>	<b>38</b>	<b>73</b>	<b>73</b>	<b>76</b>
3	NaH (2)	DME	1.1	TBAI (10)	0.2	20	40	75	75	74
4	NaOt Am (1.5)	THF	1.1	TBAI (10)	0.2	20	24	27	46	42
5	NaH (1.5)	THF	1.1	TBAI (10)	0.2	20	31	44	52	56

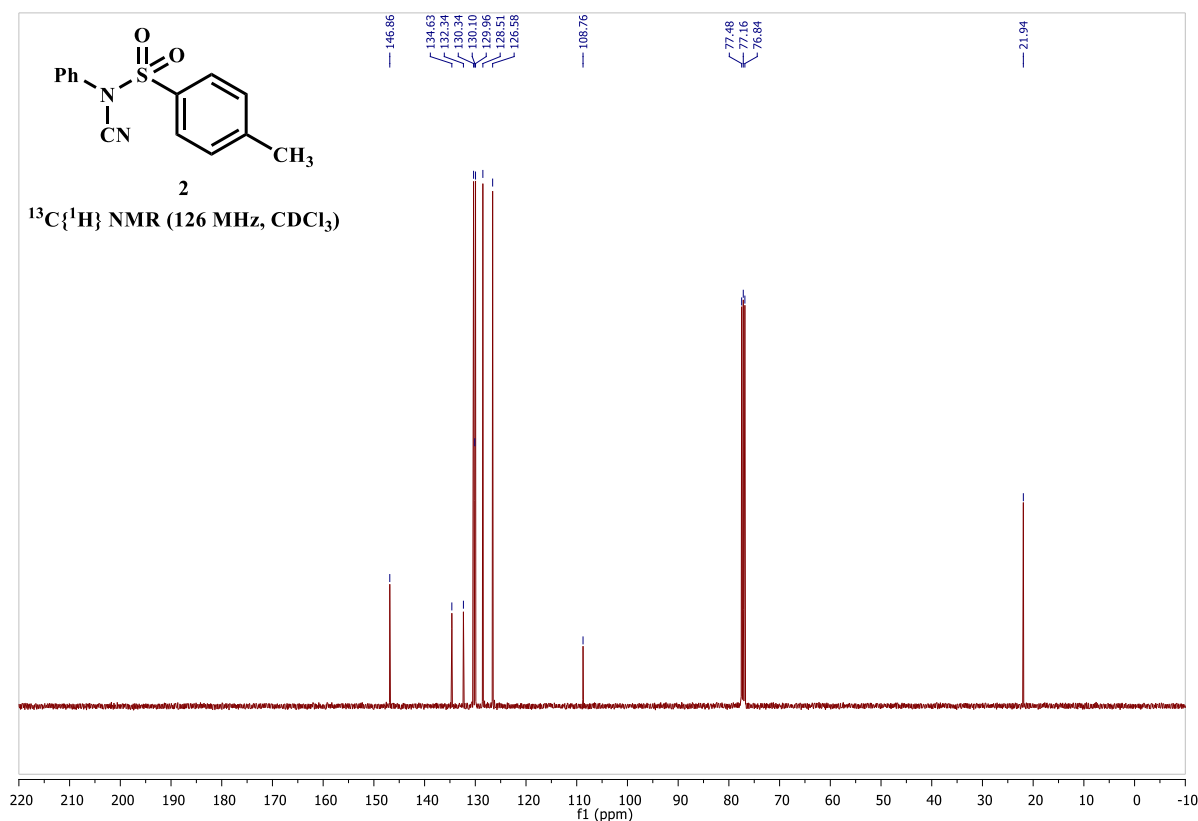
### 3. Sulfonamide synthesis

#### *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide

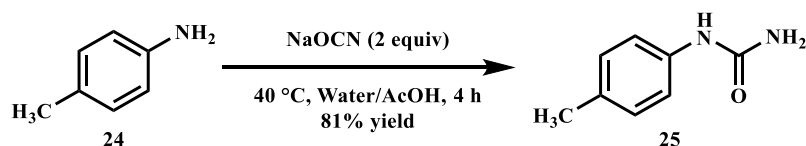


To a 1 L round-bottom flask containing a magnetic follower was charged phenylurea **23** (21.8 g, 160 mmol, 1 equiv) and pyridine (108 mL). The flask was immersed in a 25 °C water bath before *p*-toluenesulfonyl chloride (106 g, 554 mmol, 3.5 equiv) was added portionwise over 5 minutes. The reaction mixture was stirred at 25 °C for 15 min. The reaction was quenched with ice-cooled water (800 mL) and left to stir for an additional 15 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure titled compound **2** (32.1 g, 118 mmol, 74%) was isolated as a white crystalline solid with physical properties and spectroscopic data in accordance with the literature;<sup>1</sup> mp 85-86 °C (EtOH) (lit. 86-88 °C)<sup>1</sup>;  $R_f = 0.55$  (eluent = 30% EtOAc in hexanes); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$ : 2.47 (3H, s), 7.19 (2H, d,  $J$  7.7), 7.33-7.44 (5H, m), 7.64 (2H, d,  $J$  8.3); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_C$ : 21.9, 108.8, 126.6, 128.5, 130.0, 130.1, 130.3, 132.3, 134.6, 146.9.

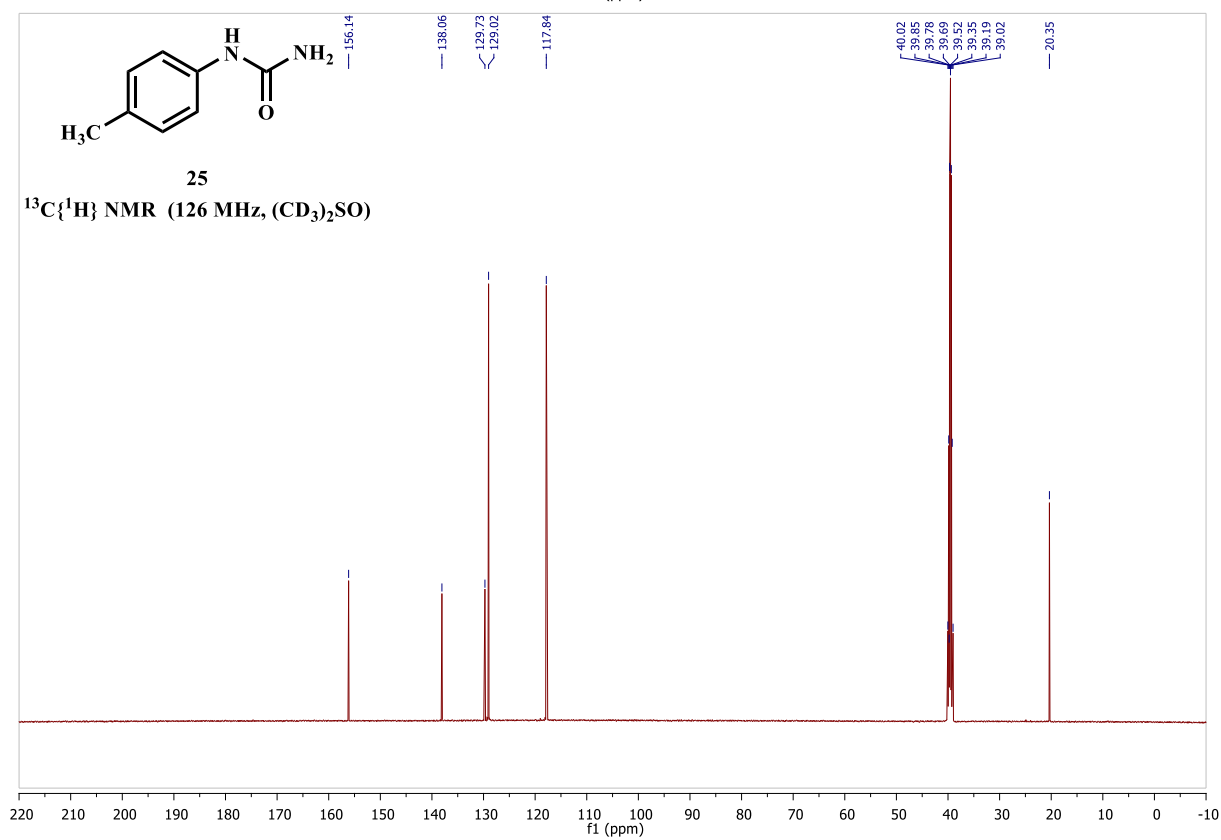
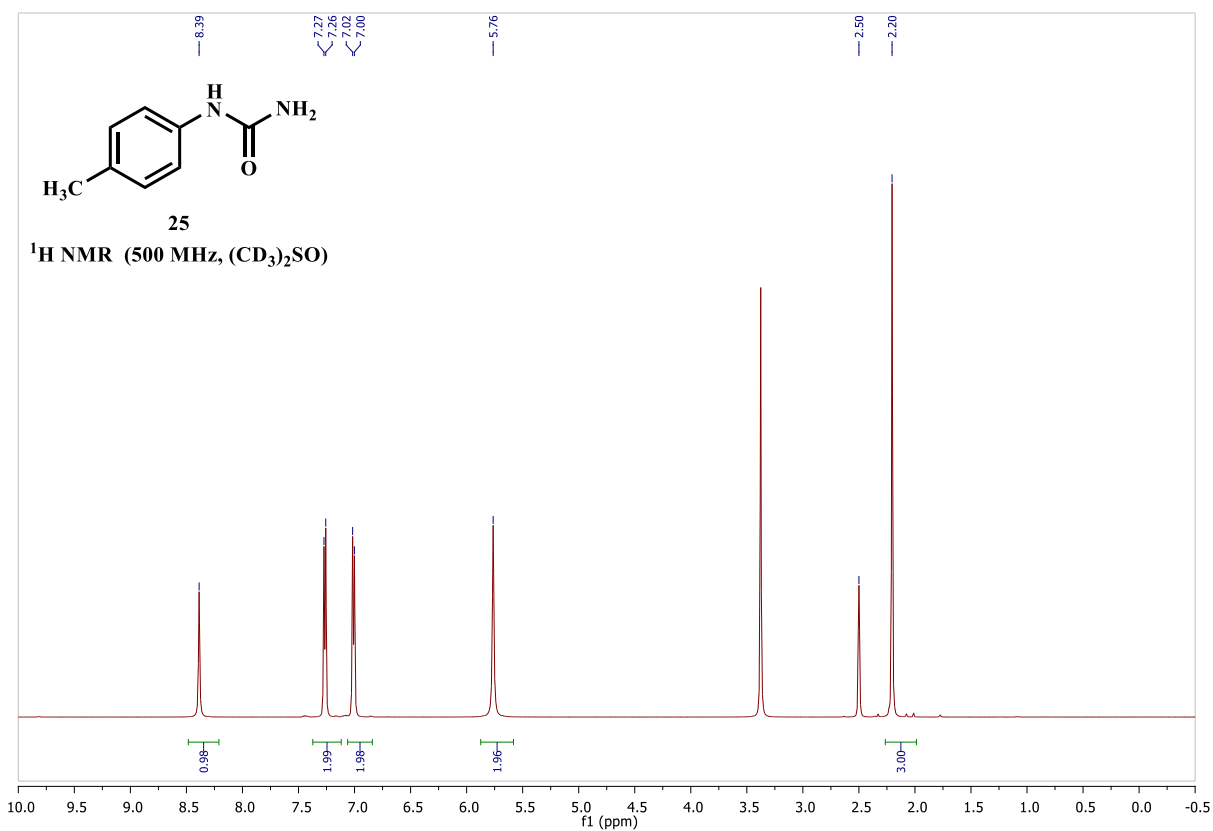




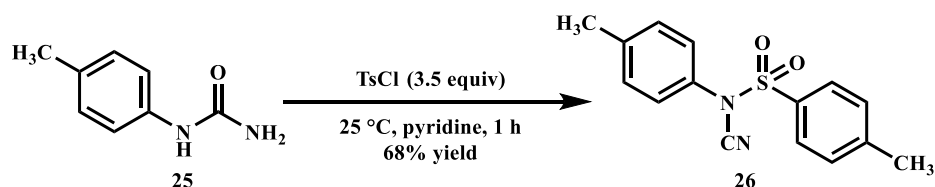
### 1-(*p*-tolyl)urea



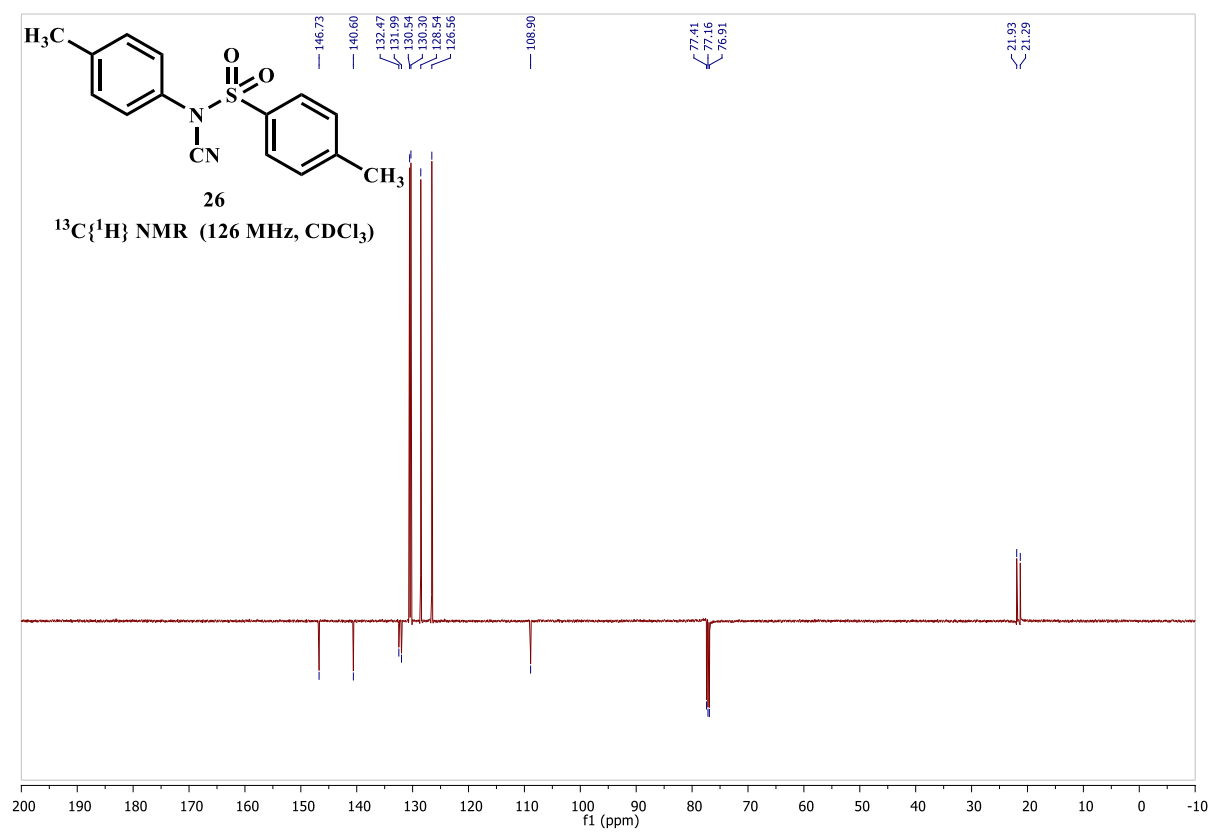
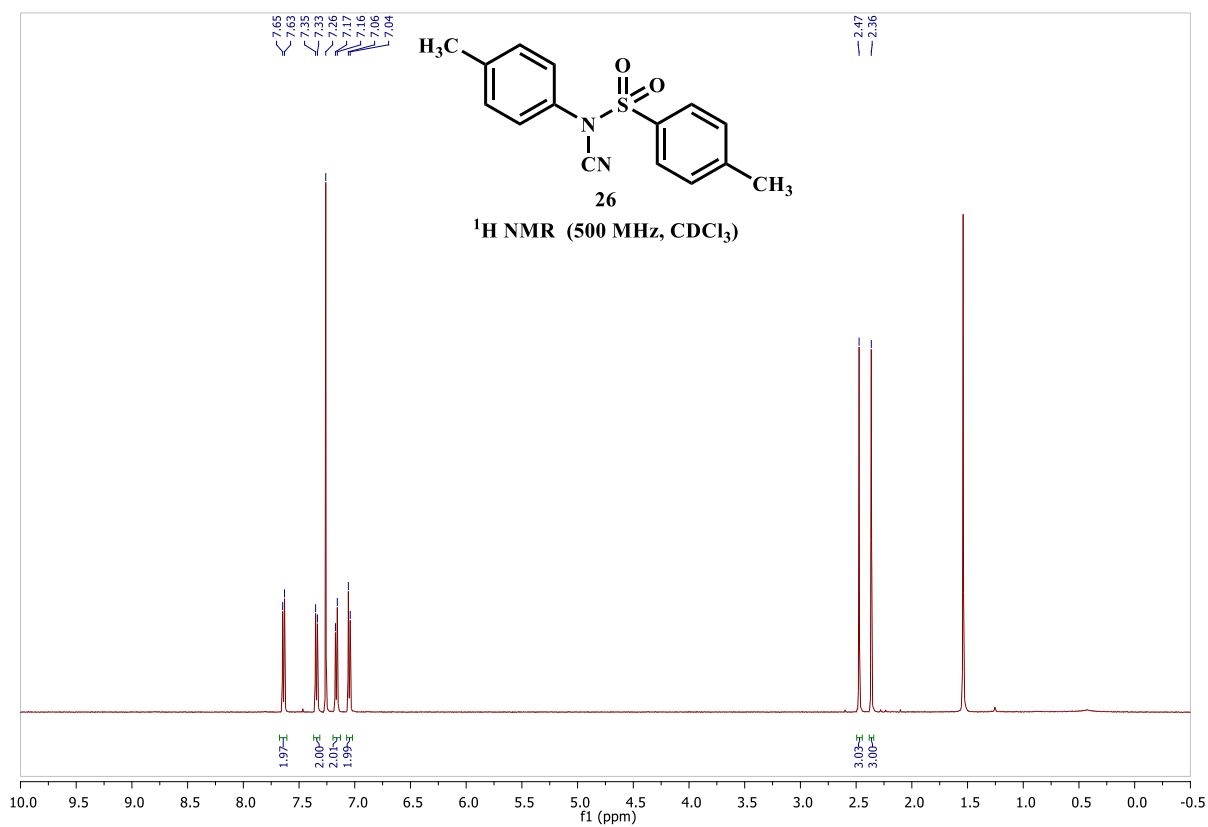
To a 250 mL round-bottom flask containing a magnetic stirrer bar was charged in order *p*-toluidine **24** (10 g, 93 mmol, 1 equiv), acetic acid (25 mL), water (25 mL) and sodium cyanate (12.1 g, 187 mmol, 2 equiv). The reaction was stirred at 40 °C for 4 h. Water (50 mL) was added to the mixture and was stirred at 25 °C for an additional 30 min. The precipitate formed was filtered, washed with water and dried *in vacuo*. The crude product was recrystallised from  $\text{Et}_2\text{O}$  and gave the pure titled compound **25** (14 g, 93 mmol, 81%) as a white crystalline solid with physical properties and spectroscopic data in accordance with the literature;<sup>2</sup> mp 176-178 °C ( $\text{Et}_2\text{O}$ ) (lit. 186-188 °C)<sup>2</sup>;  $R_f = 0.10$  (eluent = 50%  $\text{EtOAc}$  in hexanes);  $^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta_{\text{H}}$ : 2.20 (3H, s), 5.76 (2H, s), 7.01 (2H, d,  $J$  7.9), 7.26 (2H, d,  $J$  8.0), 8.39 (1H, s).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta_{\text{C}}$ : 20.4, 117.8, 129.0, 129.7, 138.1, 156.1.



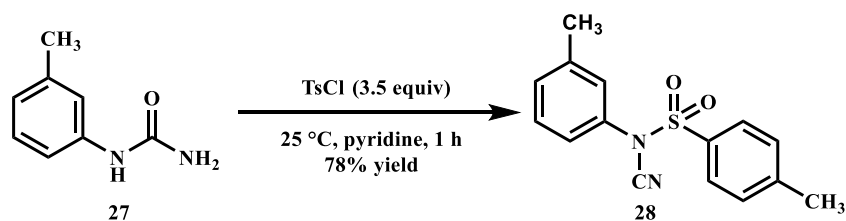
***N*-cyano-*p*-methyl-*N*-(*p*-tolyl)benzenesulfonamide**



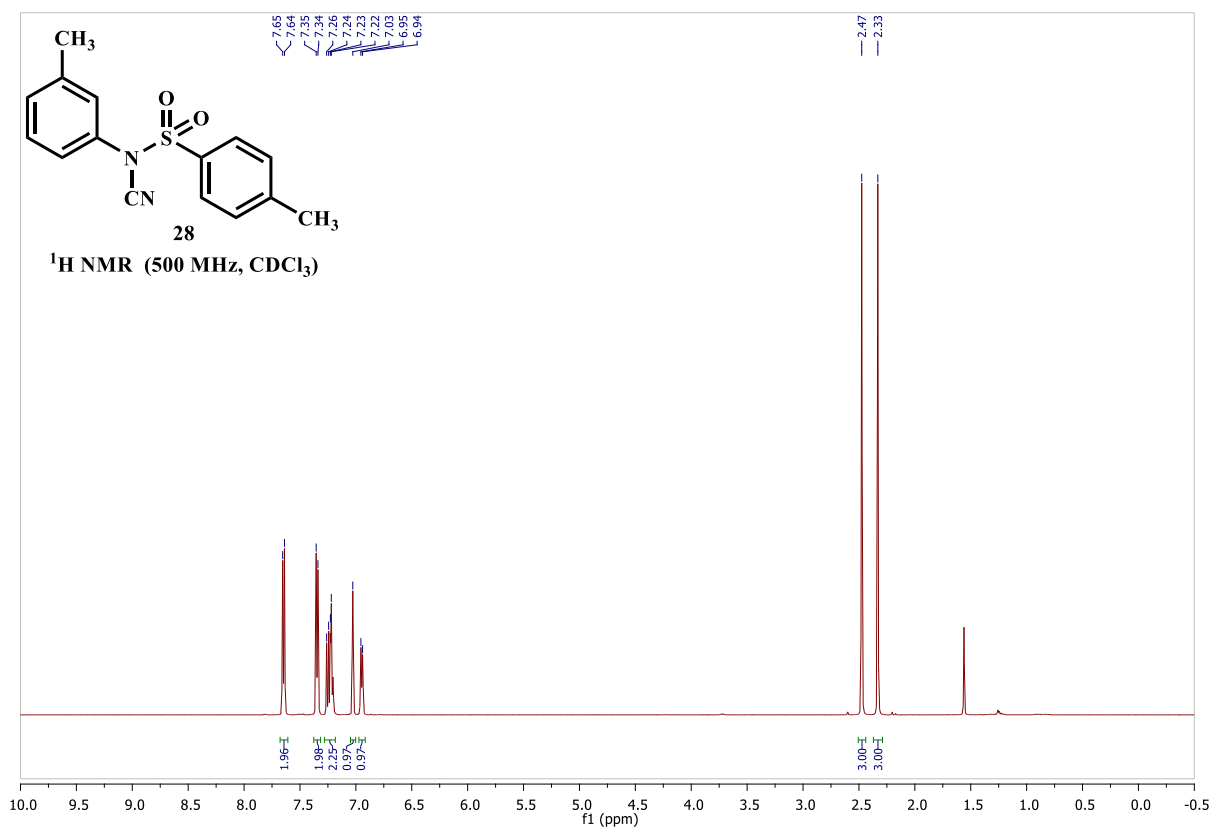
To a 500 mL round-bottom flask containing a magnetic stirrer bar was charged *p*-tolylurea **25** (4.00 g, 26.6 mmol, 1 equiv) and pyridine (186 mL). The flask was immersed in a 25 °C water bath before *p*-toluenesulfonyl chloride (17.8 g, 93.2 mmol, 3.5 equiv) was added portionwise over 5 minutes. The reaction mixture was stirred at 25 °C for 1 h. The reaction was quenched with ice-cooled water (1.02 L) and left to stir for an additional 15 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure titled compound **26** (4.91 g, 18.0 mmol, 68%) was isolated as a white crystalline solid; mp 120-121 °C (EtOH);  $R_f = 0.47$  (eluent = EtOAc 30% in hexanes);  $\nu_{\max} / \text{cm}^{-1}$  (film): 2232 (C≡N), 1595, 1504, 1385, 1175, 1086, 887, 806, 704, 667, 619, 579, 557, 532; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 2.36 (3H, s), 2.47 (3H, s), 7.04 (2H, d,  $J$  8.1), 7.16 (2H, d,  $J$  8.0), 7.34 (2H, d,  $J$  8.0), 7.63 (2H, d,  $J$  8.1); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$ : 21.3, 21.9, 108.9, 126.6, 128.5, 130.3, 130.5, 132.0, 132.5, 140.6, 146.7; HRMS (NSI<sup>+</sup>) calculated for [C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>S]<sup>+</sup> (M+H)<sup>+</sup> :  $m/z$  287.0849 found 287.0852, (+1.1 ppm).

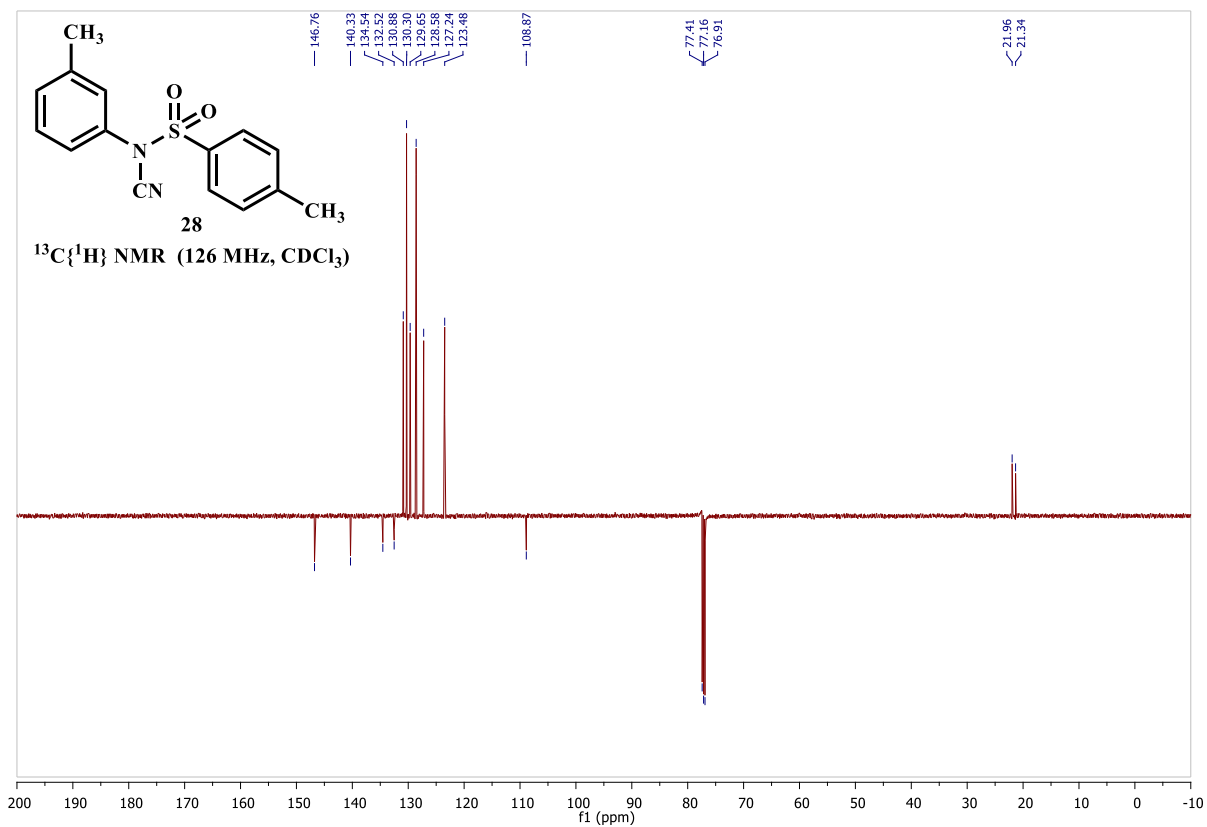


### *N*-cyano-*p*-methyl-*N*-(*m*-tolyl)benzenesulfonamide

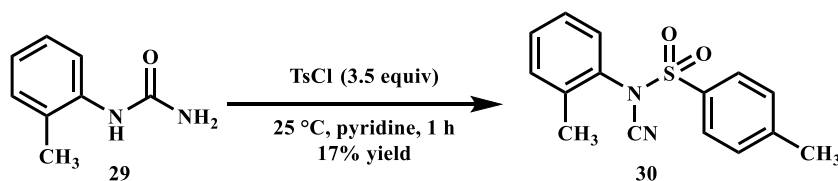


To a 500 mL round-bottom flask containing a magnetic stirrer bar was charged *m*-tolylurea **27** (4.42 g, 29.4 mmol, 1 equiv) and pyridine (206 mL). The flask was immersed in a 25 °C water bath before *p*-toluenesulfonyl chloride (19.6 g, 103 mmol, 3.5 equiv) was added portionwise over 5 minutes. The reaction mixture was stirred at 25 °C for 1 h. The reaction was quenched with ice-cooled water (1.13 L) and left to stir for an additional 15 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure titled compound **28** (6.27 g, 22.9 mmol, 78%) was isolated as a white crystalline solid; mp 98-100 °C (EtOH);  $R_f = 0.52$  (eluent = 30% EtOAc in hexanes);  $\nu_{\max} / \text{cm}^{-1}$  (film): 2228 (C≡N), 1593, 1487, 1385, 1190, 1167, 1082, 945, 814, 681, 654, 586, 548;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.33 (3H, s), 2.47 (3H, s), 6.95 (1H, d,  $J$  7.4), 7.03 (1H, s), 7.22-7.26 (2H, m), 7.35 (2H, d,  $J$  7.9), 7.65 (2H, d,  $J$  7.9);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 21.3, 22.0, 108.9, 123.5, 127.2, 128.6, 129.7, 130.3, 130.9, 132.5, 134.5, 140.3, 146.8; HRMS (NSI $^+$ ) calculated for  $[\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2\text{S}]^+$  ( $\text{M}+\text{H}$ ) $^+$ :  $m/z$  287.0849, found 287.0851 (+0.8 ppm).

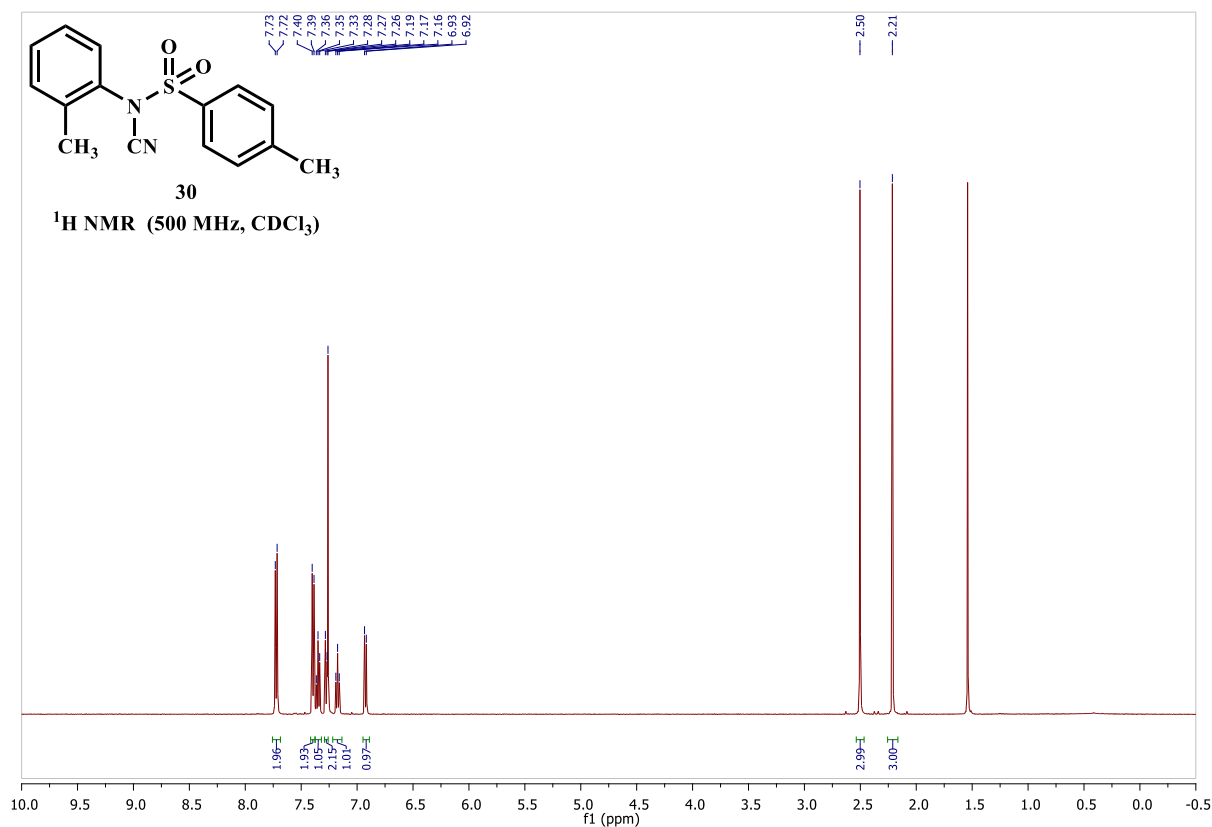


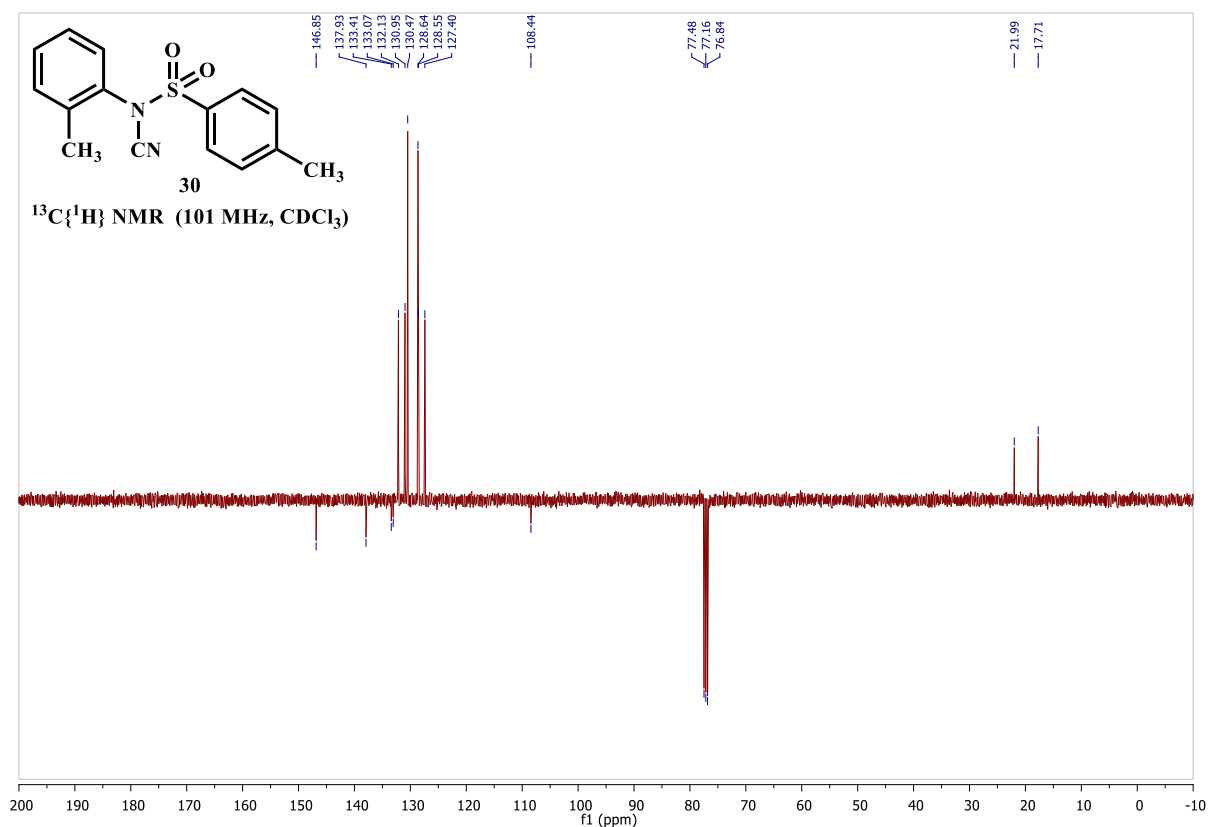


### *N*-cyano-*p*-methyl-*N*-(*o*-tolyl)benzenesulfonamide

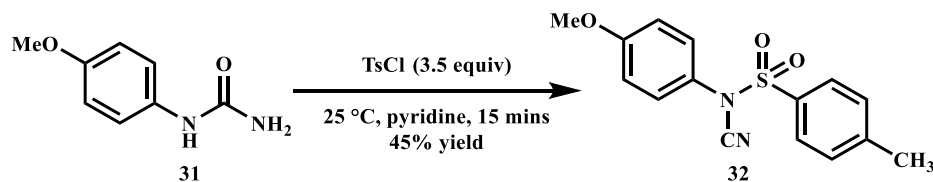


To a 500 mL round-bottom flask containing a magnetic stirrer bar was charged *o*-tolylurea **29** (5.73 g, 38.15 mmol, 1 equiv) and pyridine (206 mL). The flask was immersed in a 25 °C water bath before *p*-toluenesulfonyl chloride (25.5 g, 138 mmol, 3.5 equiv) was added portionwise over 5 minutes. The reaction mixture was stirred at 25 °C for 1 h. The reaction was quenched with ice-cooled water (1.13 L) and left to stir for an additional 15 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure titled compound **30** (3.48 g, 12.2 mmol, 17%) was isolated as a white crystalline solid; mp 104-106 °C (EtOH);  $R_f = 0.52$  (eluent = 30% EtOAc in hexanes);  $\nu_{\max} / \text{cm}^{-1}$  (film): 3007, 2228 (C≡N), 1595, 1489, 1379, 1165, 1082, 905, 814, 762, 675, 652, 575, 538;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.21 (3H, s), 2.50 (3H, s), 6.92 (1H, d,  $J$  8.0), 7.17 (1H, t,  $J$  7.4), 7.28-7.35 (2H, m), 7.39 (2H, d,  $J$  8.0), 7.72 (2H, d,  $J$  7.0);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 17.7, 22.0, 108.4, 127.4, 128.6, 128.6, 130.5, 131.0, 132.1, 133.3, 133.4, 137.9, 146.9; HRMS (NSI $^+$ ) calculated for  $[\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2\text{S}]^+$  ( $\text{M}+\text{H}$ ) $^+$ :  $m/z$  287.0849, found 287.0852 (+1.1 ppm).



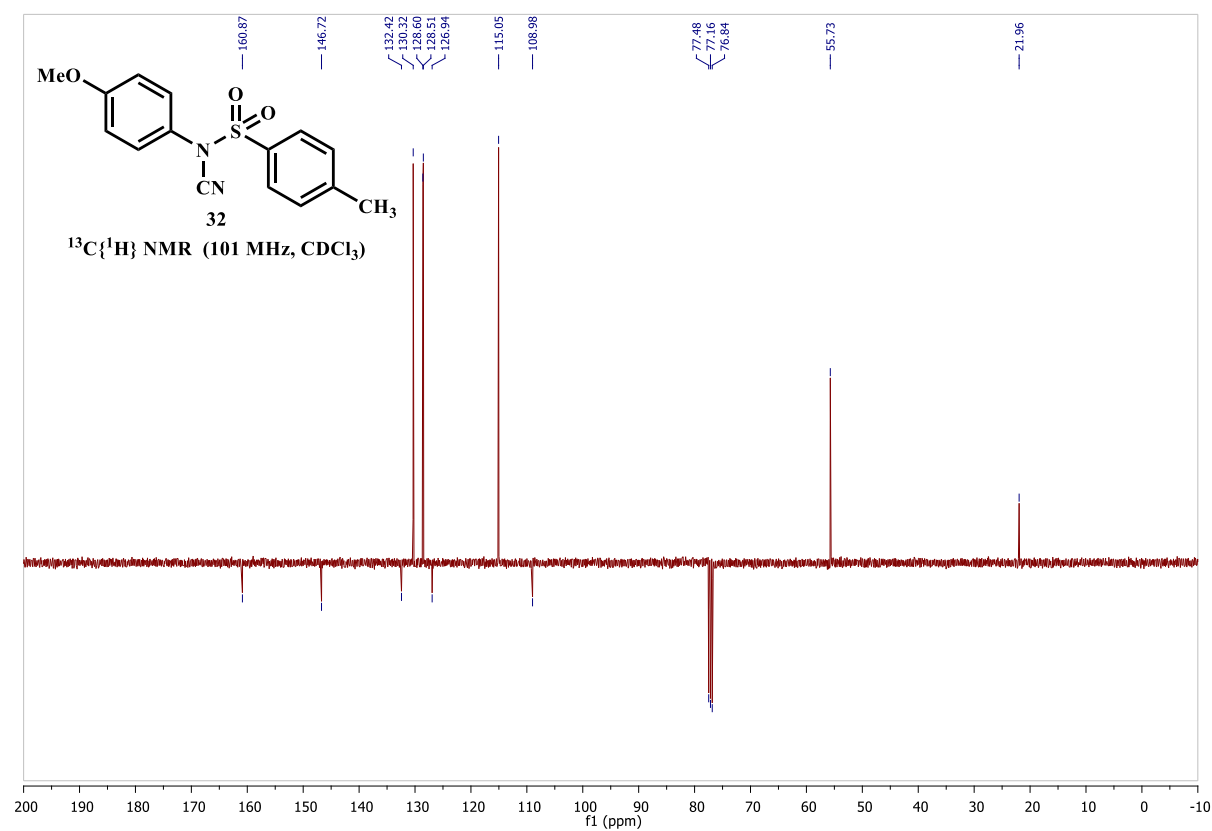
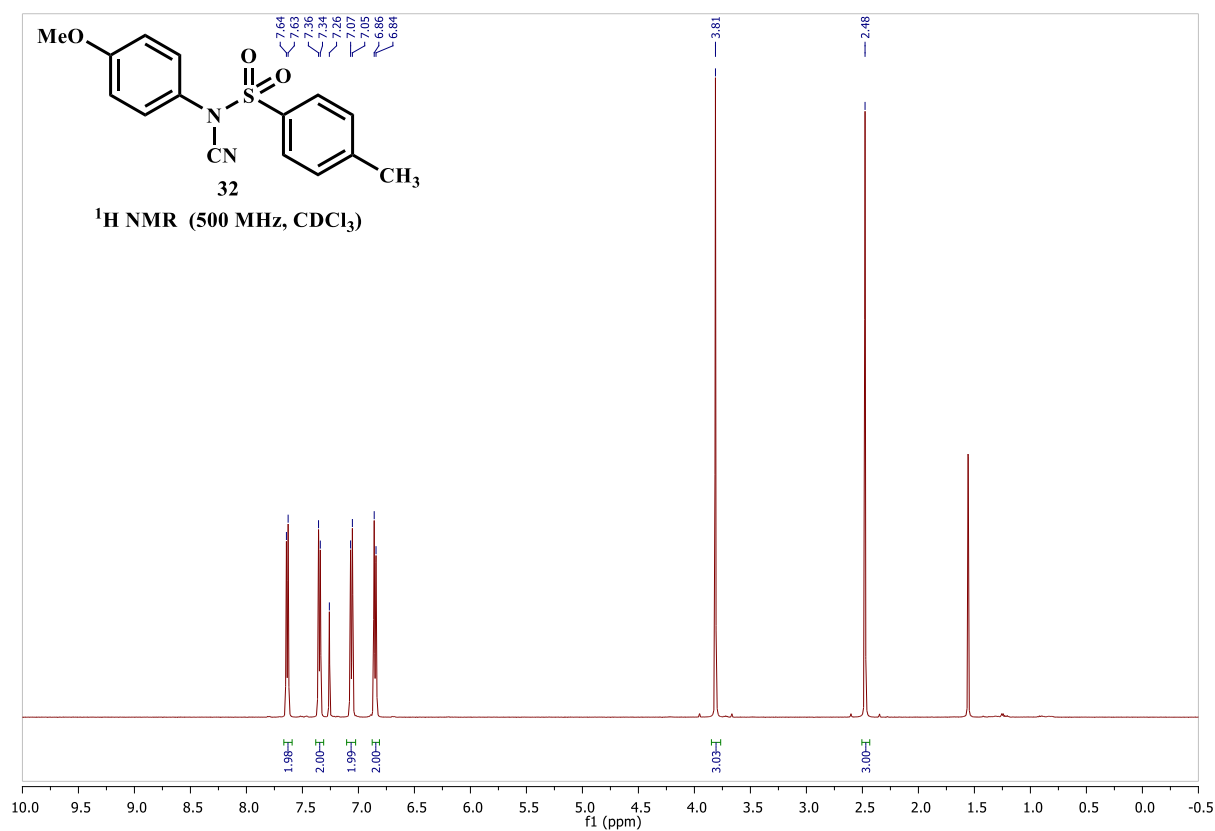


### *N*-cyano-*N*-(*p*-methoxyphenyl)-*p*-methylbenzenesulfonamide

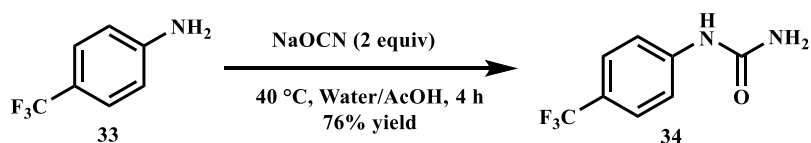


To a 250 mL round-bottom flask containing a magnetic stirrer bar was charged 4-methoxyphenylurea **31** (2.16 g, 13.0 mmol, 1 equiv) and pyridine (88 mL). The flask was immersed in a  $25\text{ }^\circ\text{C}$  water bath before *p*-toluenesulfonyl chloride (8.61 g, 45.2 mmol, 3.5 equiv) was added portionwise over 5 minutes. The reaction mixture was stirred at  $25\text{ }^\circ\text{C}$  for 15 min. The reaction was quenched with ice-cooled water (500 mL) and left to stir for an additional 15 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure titled compound **32** (2.03 g, 5.85 mmol, 45%) was isolated as a white crystalline solid; mp  $119\text{--}120\text{ }^\circ\text{C}$  (EtOH);  $R_f = 0.43$  (eluent = EtOAc 30% in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2978, 2363, 2232 ( $\text{C}\equiv\text{N}$ ), 1504, 1381, 1258, 1175, 1084, 1032, 893, 833, 808, 671, 579, 559, 538, 521;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.48 (3H, s), 3.81 (3H, s), 6.85 (2H, t,  $J$  8.1), 7.06 (2H, d,  $J$  8.1), 7.35 (2H, d,  $J$  7.9), 7.64 (2H, d,  $J$  7.6);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )

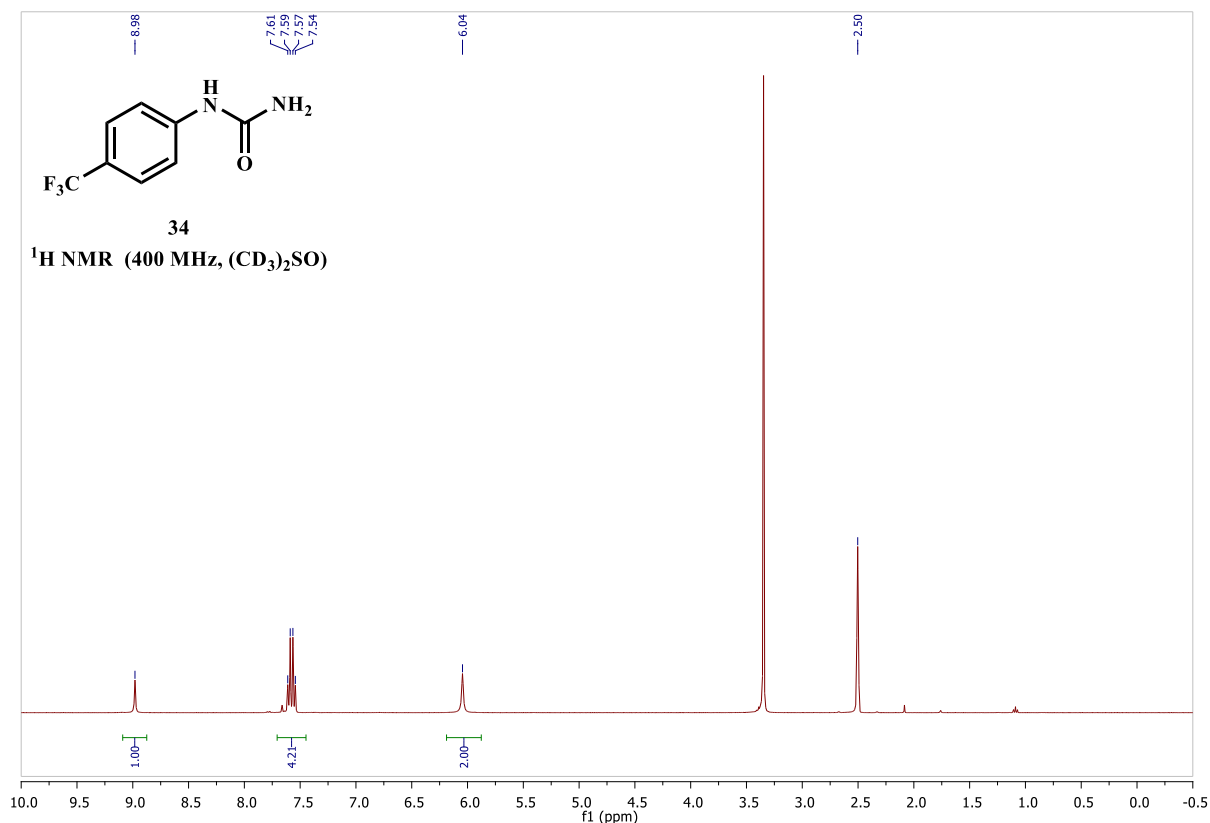
$\delta_c$ : 22.0, 55.7, 109.0, 115.1, 126.9, 128.5, 128.6, 130.3, 132.4, 146.7, 160.9; HRMS (NSI<sup>+</sup>) calculated for [C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>S]<sup>+</sup> (M+H)<sup>+</sup> m/z : 303.0798, found 303.0802 (+1.4 ppm).

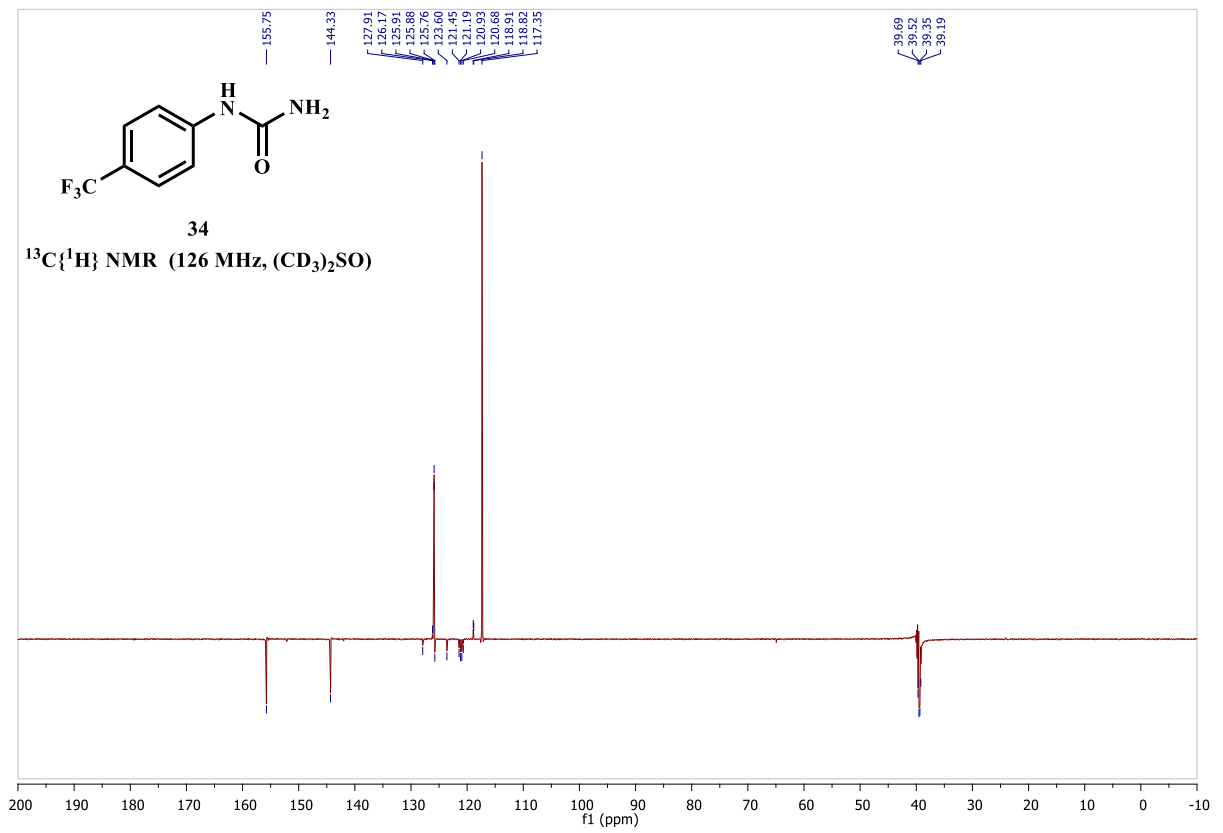
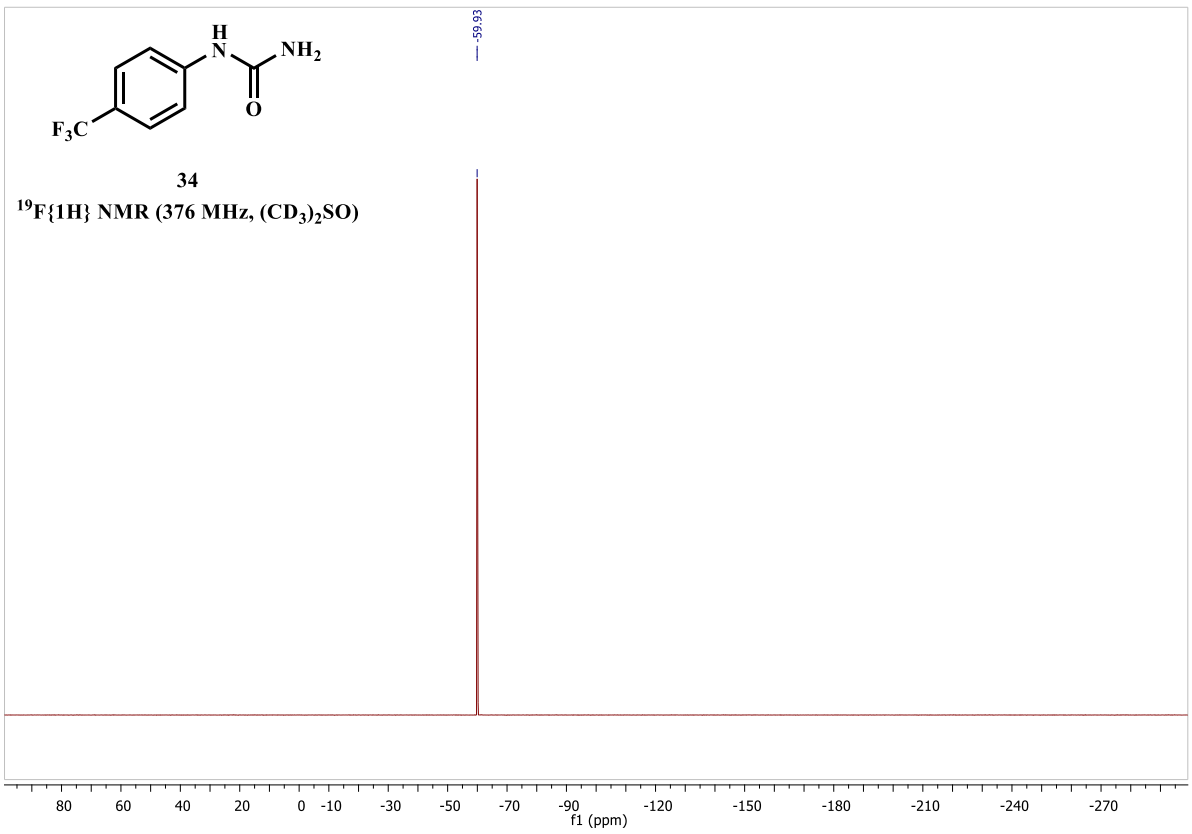


## 1-(4-(trifluoromethyl)phenyl)urea

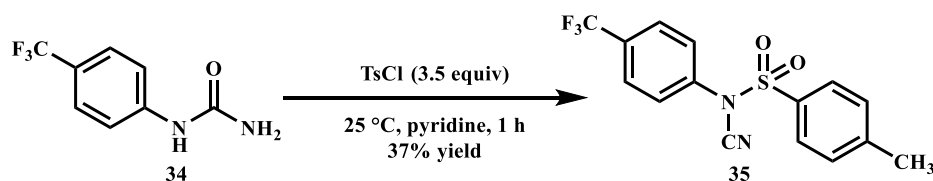


To a 250 mL round-bottom flask containing a magnetic stirrer bar was charged in order 4-(trifluoromethyl)aniline **33** (3.14 mL, 25 mmol, 1 equiv), acetic acid (7 mL), water (7 mL) and sodium cyanate (3.25 g, 50 mmol, 2 equiv). The reaction was stirred at 40 °C for 4 h. Water (30 mL) was added to the mixture and was stirred at 25 °C for an additional 30 min. The precipitate formed was filtered, washed with water and dried *in vacuo*. The crude product was recrystallised from hexanes and gave the pure titled compound **34** (4.18 g, 20.5 mmol, 76% yield) as a white crystalline solid; mp 142-145 °C (hexanes);  $R_f = 0.18$  (eluent = 50% EtOAc in hexanes);  $\nu_{\max} / \text{cm}^{-1}$  (film): 3428, 3316, 2968, 1744, 1649, 1543, 1364, 1323, 1233, 1217, 1157, 1125, 1103, 1069, 1018, 831, 773, 689, 590, 453;  $^1\text{H NMR}$  (400 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta_{\text{H}}$ : 6.04 (2H, s), 7.57 (4H, q,  $J$  8.9), 8.98 (1H, s);  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta_{\text{F}}$ : -60.0;  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta_{\text{C}}$ : 117.4, 121.1 (q,  $J$  32.2), 124.7 (q,  $J$  270.9), 125.9 (q,  $J$  3.5), 144.3, 155.8; HRMS (NSI $^+$ )  $\text{C}_8\text{H}_8\text{ON}_2\text{F}_3$  ( $\text{M}+\text{H}$ ) $^+$   $m/z$  205.0583, found 205.0583 (-0.1 ppm).

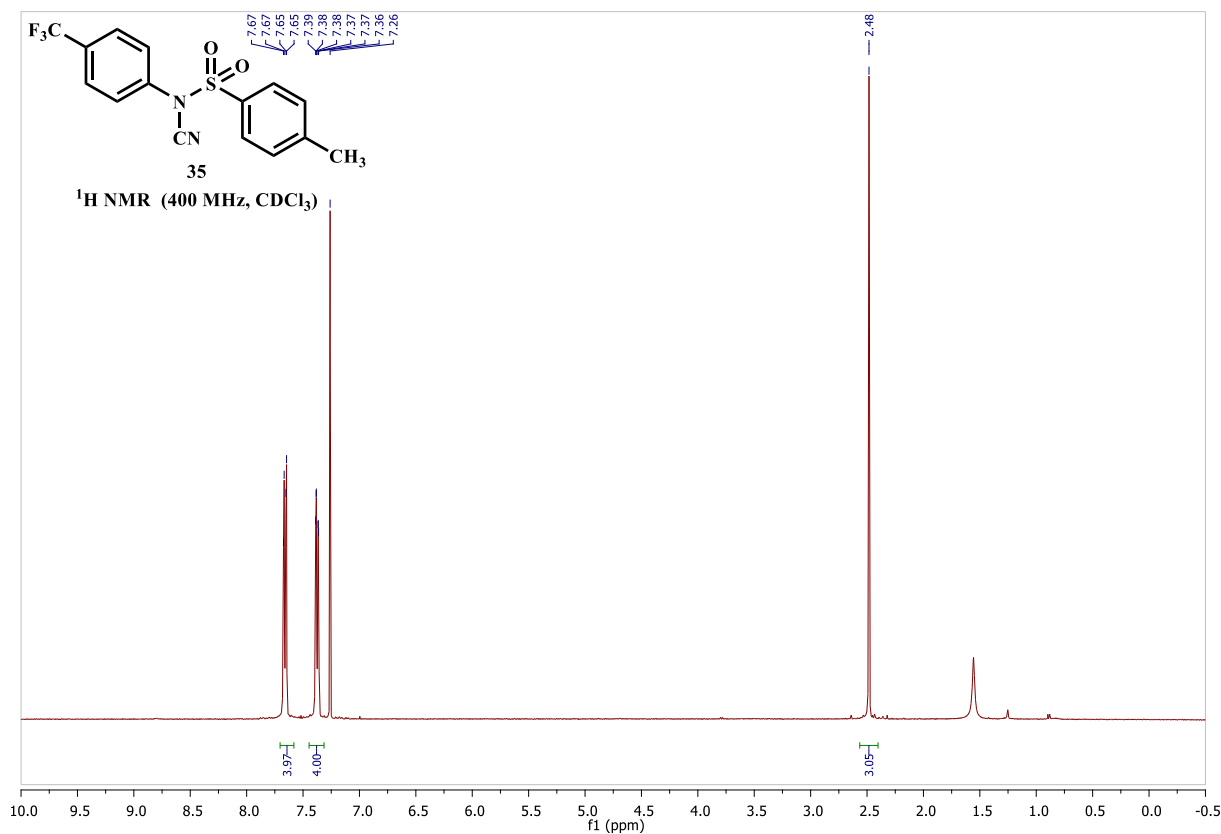


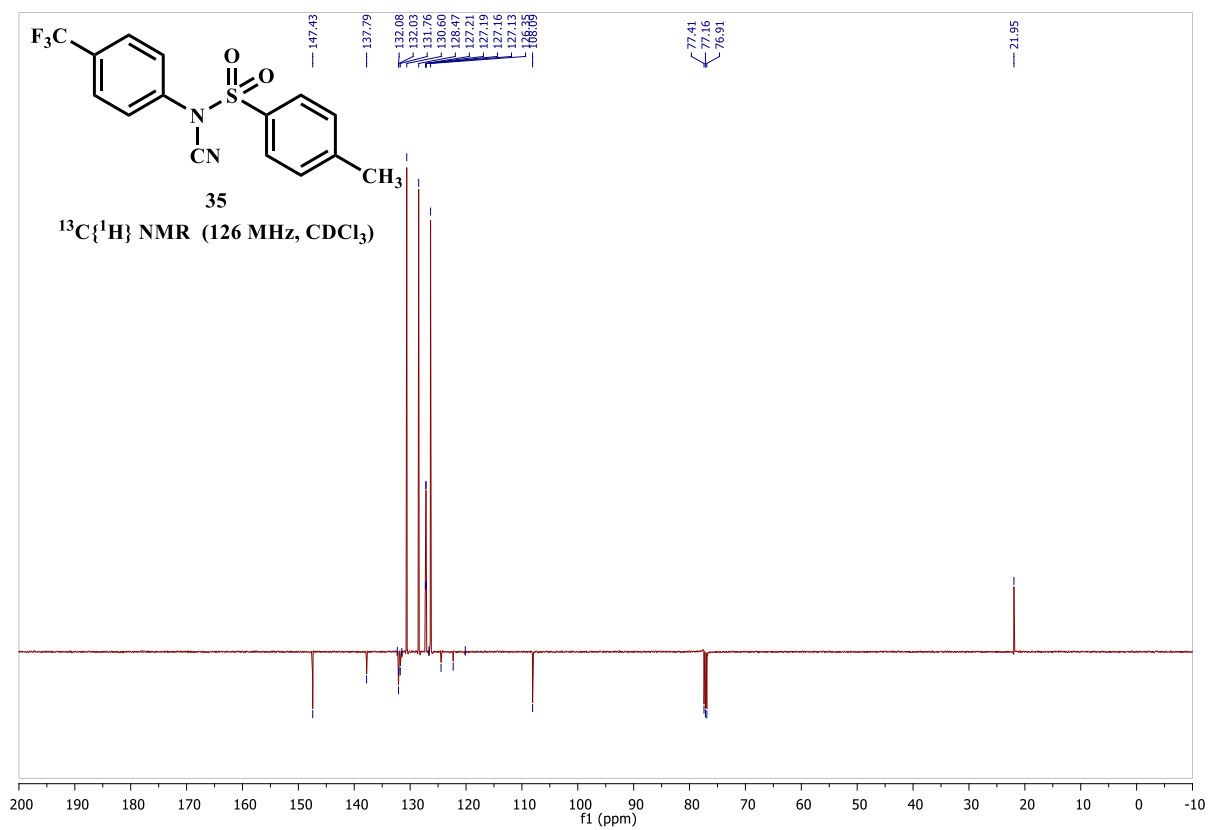
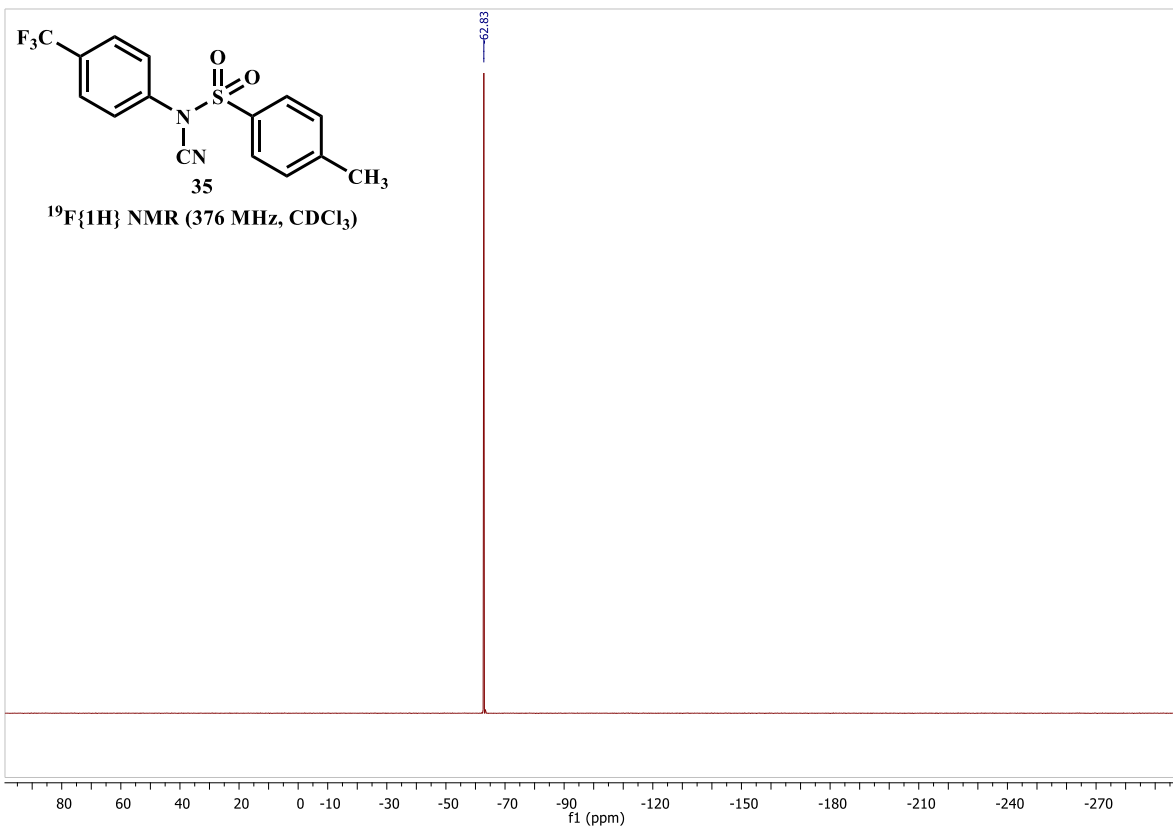


### *N*-cyano-*p*-methyl-*N*-(*p*-(trifluoromethyl)phenyl)benzenesulfonamide

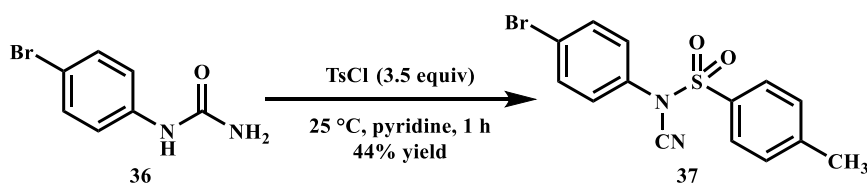


To a 500 mL round-bottom flask containing a magnetic stirrer bar was charged 1-(4-(trifluoromethyl)phenyl)urea **34** (2.93 g, 14.4 mmol, 1 equiv) and pyridine (101 mL). The flask was immersed in a 25 °C water bath before *p*-toluenesulfonyl chloride (9.60 g, 50.3 mmol, 3.5 equiv) was added portionwise over 5 minutes. The reaction mixture was stirred at 25 °C for 1 h. The reaction was quenched with ice-cooled water (536 mL) and left to stir for an additional 15 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure titled compound **35** (1.83 g, 5.38 mmol, 37%) was isolated as a white crystalline solid; mp 98-99 °C (EtOH);  $R_f = 0.55$  (eluent = EtOAc 30% in hexanes);  $\nu_{\max} / \text{cm}^{-1}$  (film): 2241 (C≡N), 1595, 1389, 1323, 1258, 1163, 1109, 1067, 1018, 912, 845, 818, 702, 691, 662, 584, 552, 534;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.48 (3H, s), 7.37 (4H, d,  $J$  7.4), 7.66 (4H, d,  $J$  7.2);  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$ : -62.8;  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 22.0, 108.3, 123.4 (q,  $J$  272.6), 126.4, 127.2 (q,  $J$  3.6), 128.7, 130.6, 131.9 (q,  $J$  33.3), 132.1, 137.8, 147.4; HRMS (NSI<sup>+</sup>) calculated for  $[\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}_3\text{O}_2\text{S}]^+$  ( $\text{M}+\text{NH}_4$ )<sup>+</sup>  $m/z$  358.0832, found 358.0835 (+1.0 ppm).

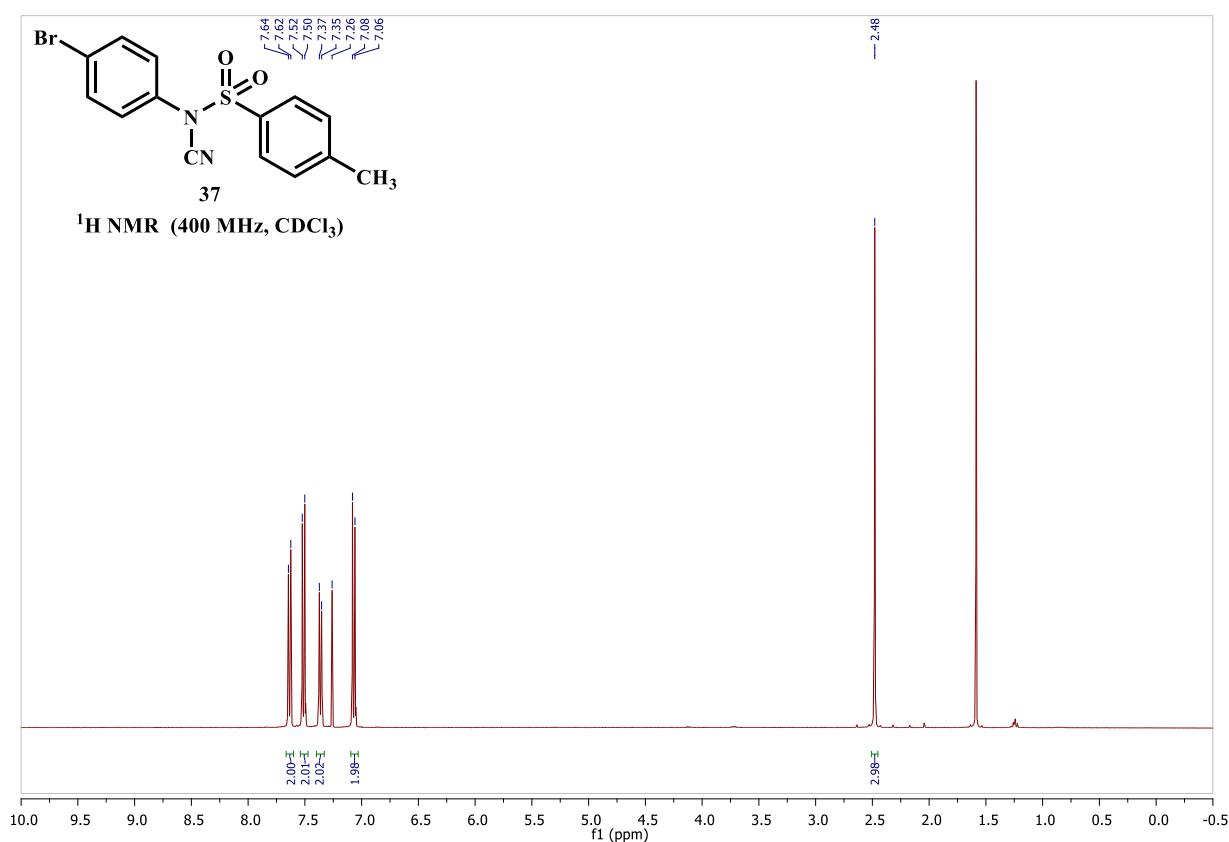


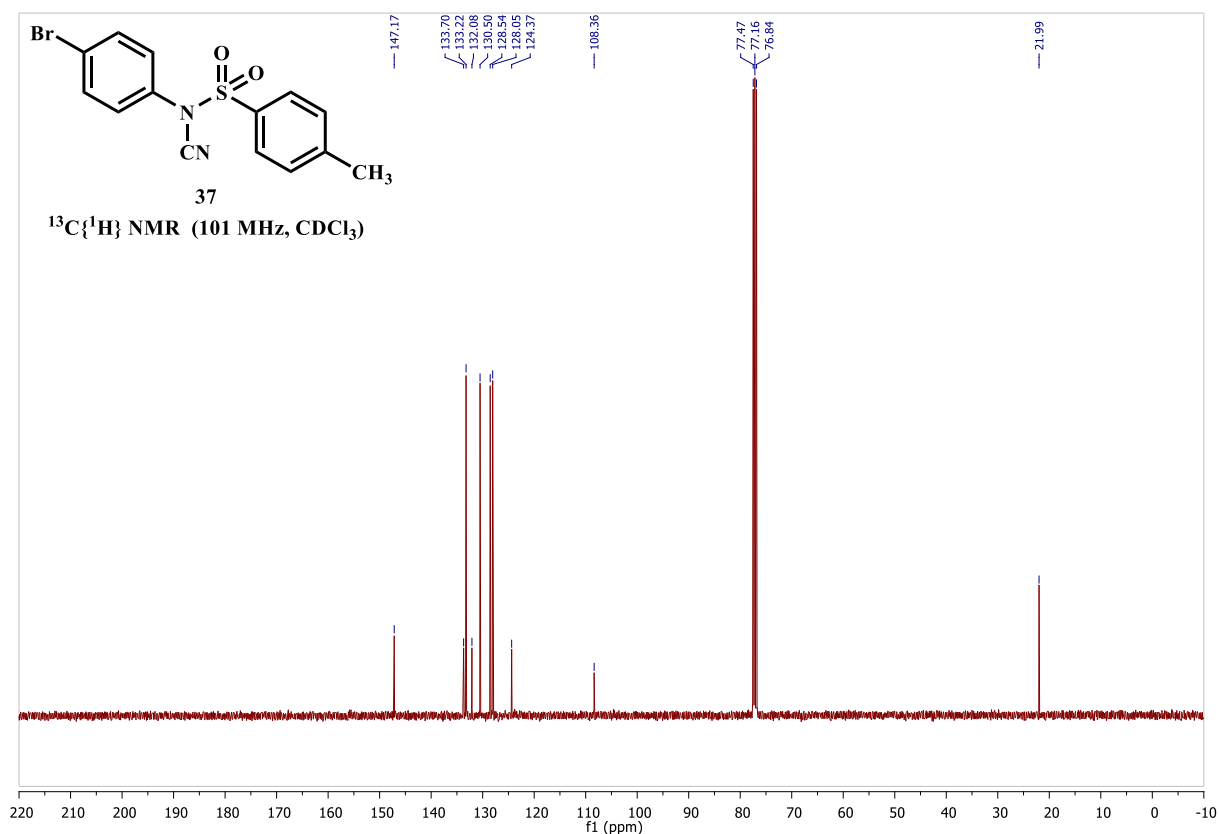


### *N*-(*p*-bromophenyl)-*N*-cyano-*p*-methylbenzenesulfonamide

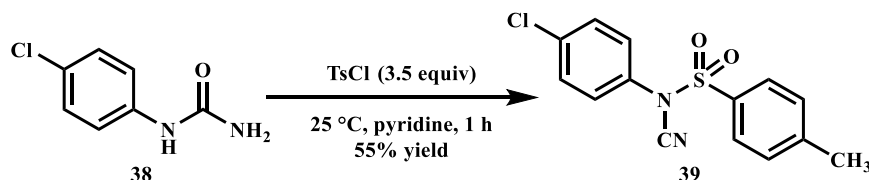


To a 500 mL round-bottom flask containing a magnetic stirrer bar was charged 1-(4-bromophenyl)urea **36** (3.01 g, 14 mmol, 1 equiv) and pyridine (101 mL). The flask was immersed in a 25 °C water bath before *p*-toluenesulfonyl chloride (9.34 g, 49 mmol, 3.5 equiv) was added portionwise over 5 minutes. The reaction mixture was stirred at 25 °C for 1 h. The reaction was quenched with ice-cooled water (536 mL) and left to stir for an additional 15 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure titled compound **37** (2.16 g, 6.15 mmol, 44%) was isolated as a white crystalline solid; mp 132-134 °C (EtOH);  $R_f = 0.77$  (eluent = EtOAc 30% in hexanes);  $\nu_{\max} / \text{cm}^{-1}$  (film): 2984, 2236 (C≡N), 1477, 1385, 1180, 1069, 1013, 893, 812, 718, 700, 662, 583, 554, 536;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.48 (3H, s), 7.07 (2H, d,  $J$  8.8), 7.36 (2H, d,  $J$  8.3), 7.51 (2H, d,  $J$  8.9), 7.63 (2H, d,  $J$  8.3);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 22.0, 108.4, 124.4, 128.1, 128.5, 130.5, 132.1, 133.2, 133.7, 147.2; HRMS (NSI+) calculated for  $[\text{C}_{14}\text{H}_{12}\text{BrN}_2\text{O}_2\text{S}]^+$ :  $m/z$  350.9797 found 350.9804 (+1.9 ppm).

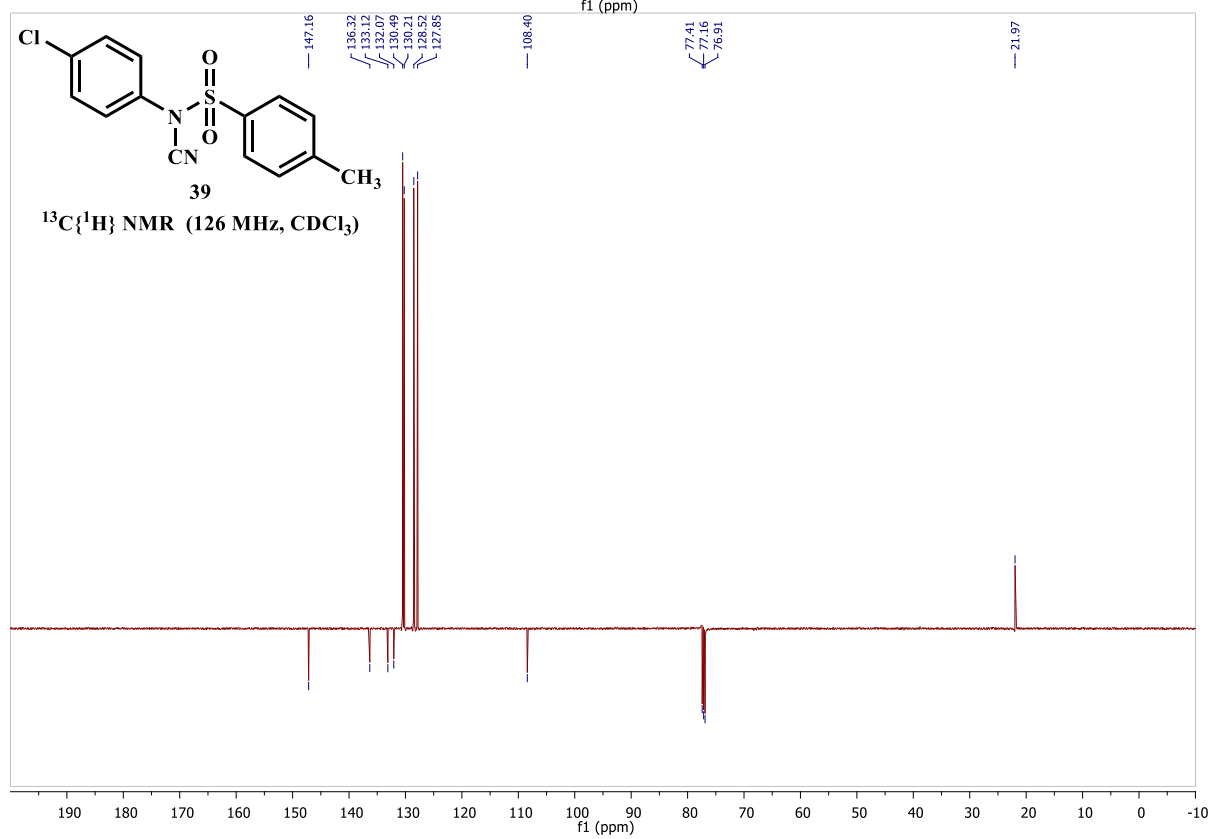
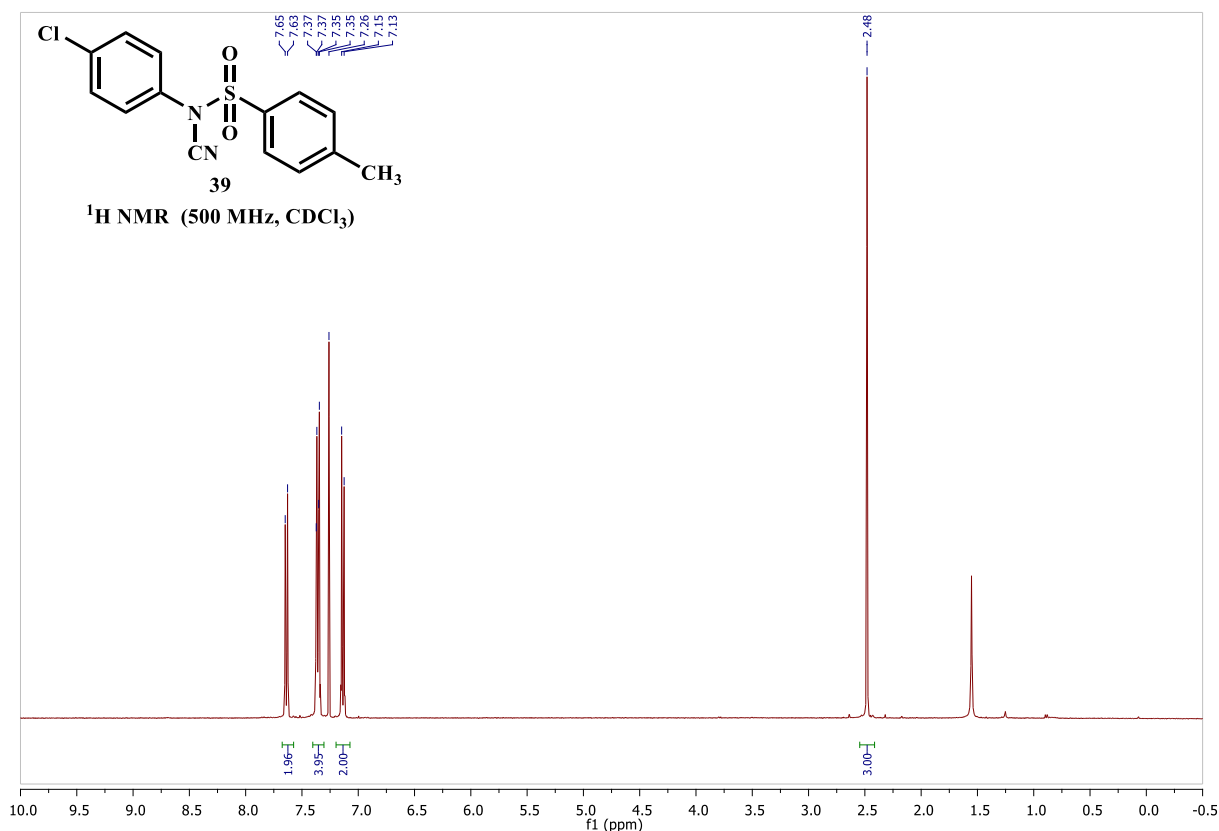




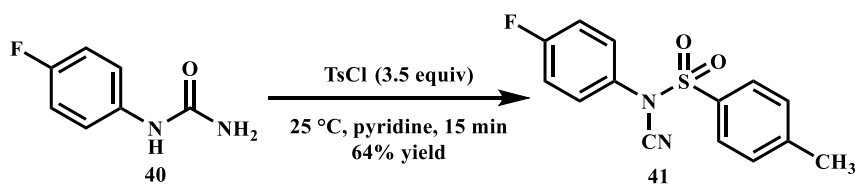
### *N*-(*p*-chlorophenyl)-*N*-cyano-*p*-methylbenzenesulfonamide



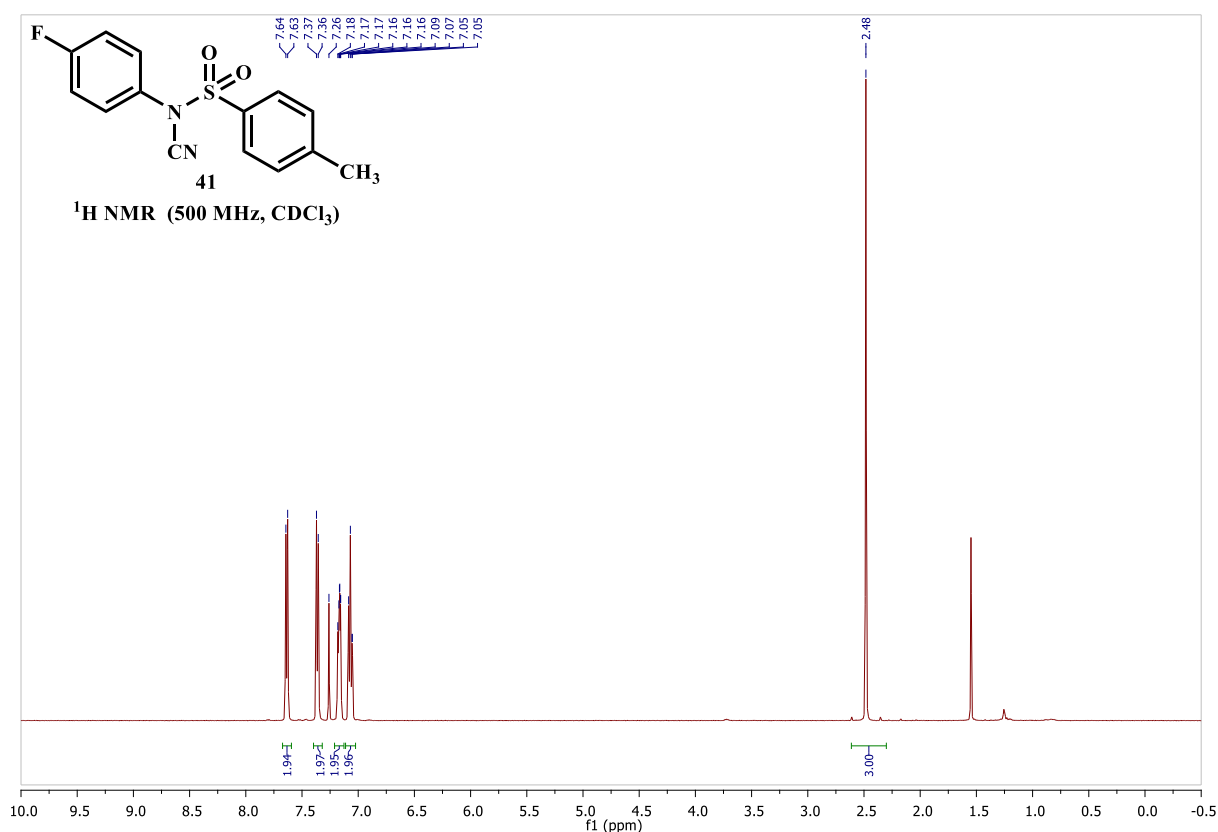
To a 500 mL round-bottom flask containing a magnetic stirrer bar was charged 4-chlorophenylurea **38** (1.49 g, 8.79 mmol, 1 equiv) and pyridine (206 mL). The flask was immersed in a  $25\text{ }^\circ\text{C}$  water bath before *p*-toluenesulfonyl chloride (5.86 g, 26.4 mmol, 3.5 equiv) was added portionwise over 5 minutes. The reaction mixture was stirred at  $25\text{ }^\circ\text{C}$  for 1 h. The reaction was quenched with ice-cooled water (0.5 l) and left to stir for an additional 15 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure titled compound **39** (1.49 g, 4.86 mmol, 55%) was isolated as a white crystalline solid; mp  $137\text{--}138\text{ }^\circ\text{C}$  (EtOH);  $R_f = 0.58$  (eluent = 30% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2974, 2359, 2228 ( $\text{C}\equiv\text{N}$ ), 1591, 1481, 1387, 1171, 1084, 891, 812, 737, 660, 584, 561, 538, 517;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.48 (3H, s), 7.14 (2H, d,  $J$  8.3), 7.36 (4H, dd,  $J$  8.4, 2.9), 7.64 (2H, d,  $J$  7.9);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 22.0, 108.4, 127.9, 128.5, 130.2, 130.5, 132.1, 133.1, 136.3, 147.2; HRMS ( $\text{NSI}^+$ ) calculated for  $[\text{C}_{14}\text{H}_{12}\text{ClN}_2\text{O}_2\text{S}]^+$  ( $\text{M}+\text{H}$ ) $^+$   $m/z$  307.0303, found 307.0309 (+2.1 ppm).

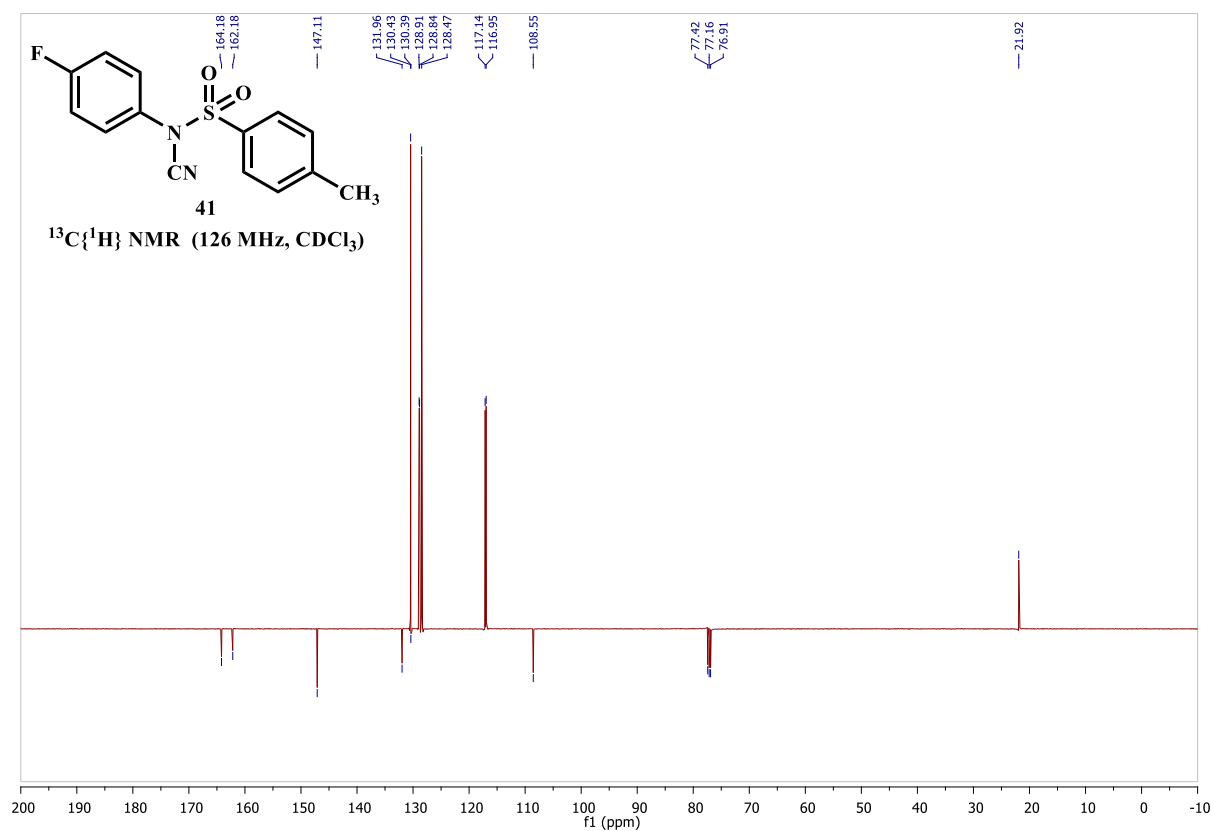
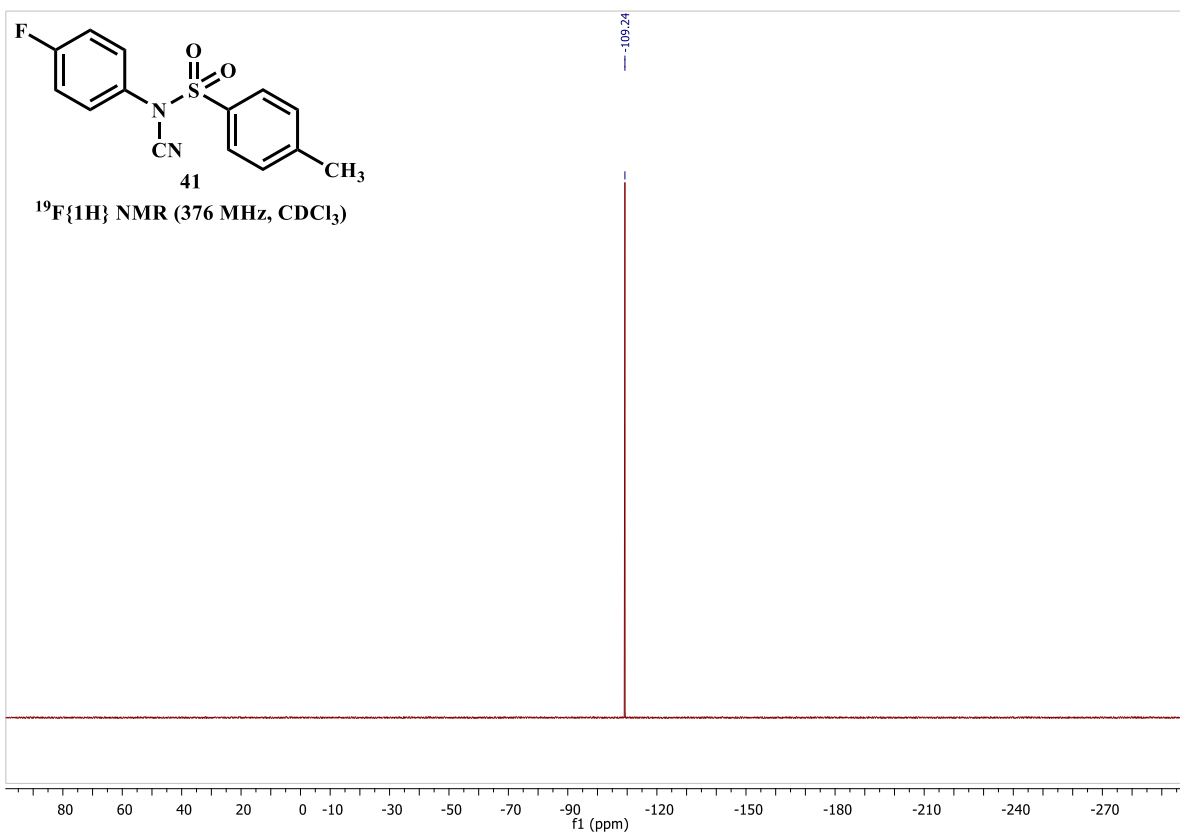


### *N*-cyano-*N*-(*p*-fluorophenyl)-*p*-methylbenzenesulfonamide

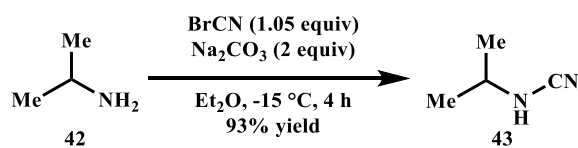


To a 500 mL round-bottom flask containing a magnetic stirrer bar was charged 4-fluorophenylurea **40** (4.25 g, 27.6 mmol, 1 equiv) and pyridine (187 mL). The flask was immersed in a 25 °C water bath before *p*-toluenesulfonyl chloride (18.4 g, 96.5 mmol, 3.5 equiv) was added portionwise over 5 minutes. The reaction mixture was stirred at 25 °C for 15 min. The reaction was quenched with ice-cooled water (1.06 L) and left to stir for an additional 15 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure titled compound **41** (5.15 g, 17.7 mmol, 64%) was isolated as a white crystalline solid; mp 98-100 °C (EtOH);  $R_f = 0.67$  (eluent = 30% EtOAc in hexanes);  $\nu_{\max} / \text{cm}^{-1}$  (film): 2974, 2232 (C≡N), 1595, 1503, 1389, 1182, 1157, 1086, 887, 839, 812, 702, 667, 617, 575, 554, 538;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.48 (3H, s), 7.07 (2H, t,  $J$  8.1), 7.16-7.18 (2H, m), 7.36 (2H, d,  $J$  7.9), 7.64 (2H, d,  $J$  7.8);  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$ : -109.2;  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 21.9, 108.6, 117.1 (d,  $J$  22.7), 128.5, 128.9 (d,  $J$  8.8), 130.4, 130.4, 132.0, 147.1, 163.2 (d, 252.0); HRMS (NSI<sup>+</sup>) calculated for  $[\text{C}_{14}\text{H}_{15}\text{FN}_3\text{O}_2\text{S}]^+$  ( $\text{M}+\text{NH}_4$ )<sup>+</sup>  $m/z$  308.0864, found 308.0865 (+0.5 ppm).

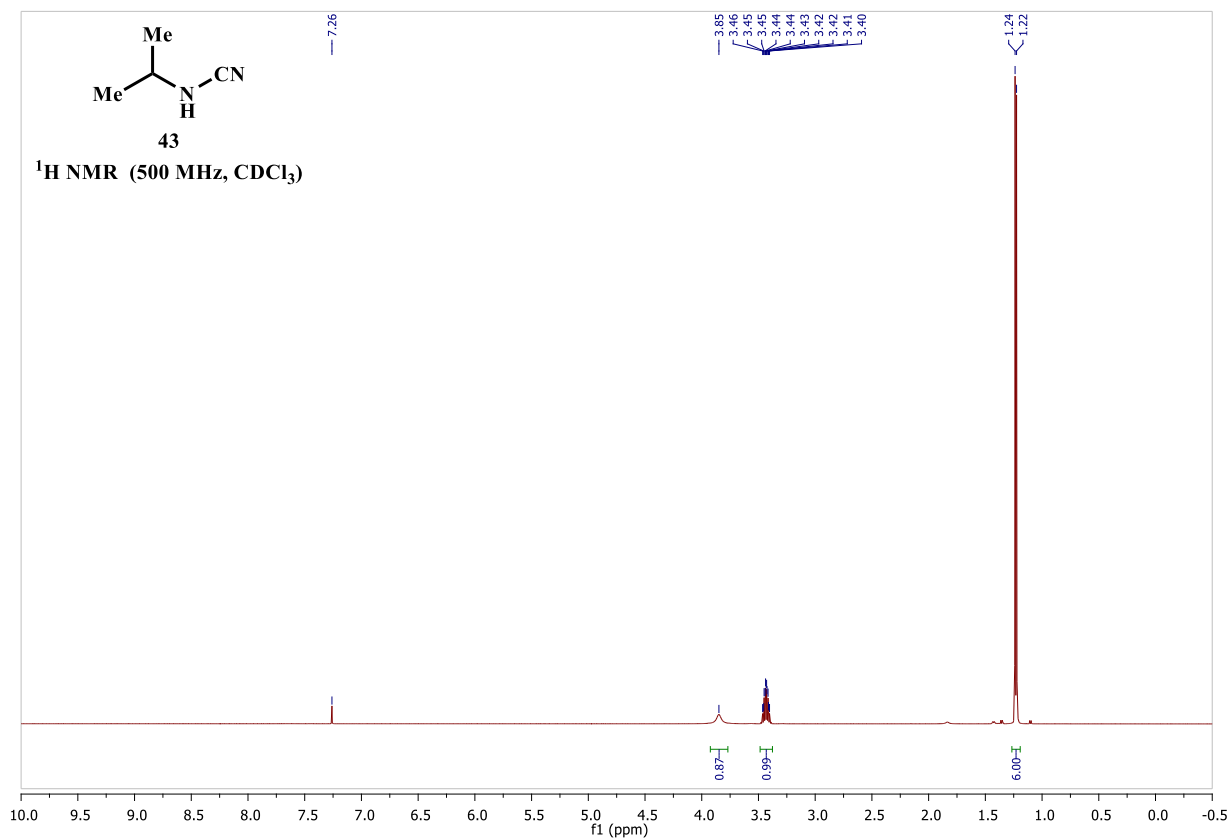


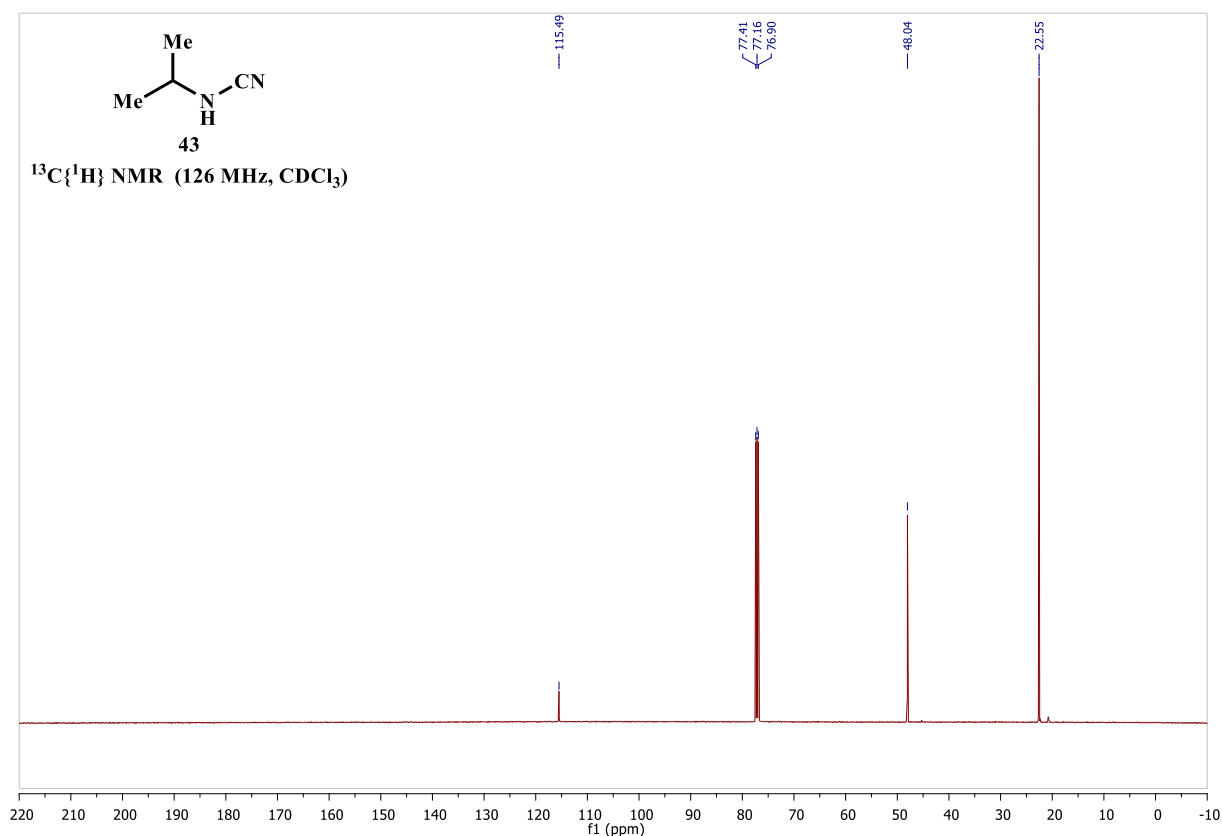


## N-isopropylcyanamide

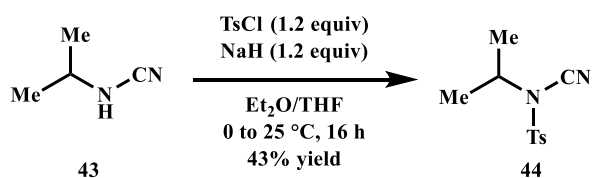


To a 100 mL round bottomed flask equipped with a magnetic stirrer bar was charged sodium carbonate (4.24 g, 40 mmol, 2 equiv), cyanogen bromide (2.22 g, 21 mmol, 1.05 equiv) and diethyl ether (30 mL). The mixture was cooled to -15 °C, before the slow addition of isopropylamine **42** (1.7 mL, 20 mmol, 1 equiv) over 5 min. The resultant reaction mixture was then stirred at -15 °C until completion, as determined by thin-layer chromatography (TLC) monitoring. After completion, the crude reaction mixture was filtered and the filtrate was concentrated *in vacuo* to give the desired cyanamide, without the need for further purification to give the titled compound **43** as a pale yellow oil (1.56 g, 18.54 mmol, 93%) with physical properties and spectroscopic data in accordance with the literature;<sup>3</sup>  $R_f = 0.29$  (eluent = 30% EtOAc in hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta_H$ : 1.23 (6H, d,  $J$  6.5), 3.43 (1H, septet of doublets,  $J$  6.4, 4.6), 3.85 (1H, br s); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>)  $\delta_C$ : 22.5, 48.0, 115.5.



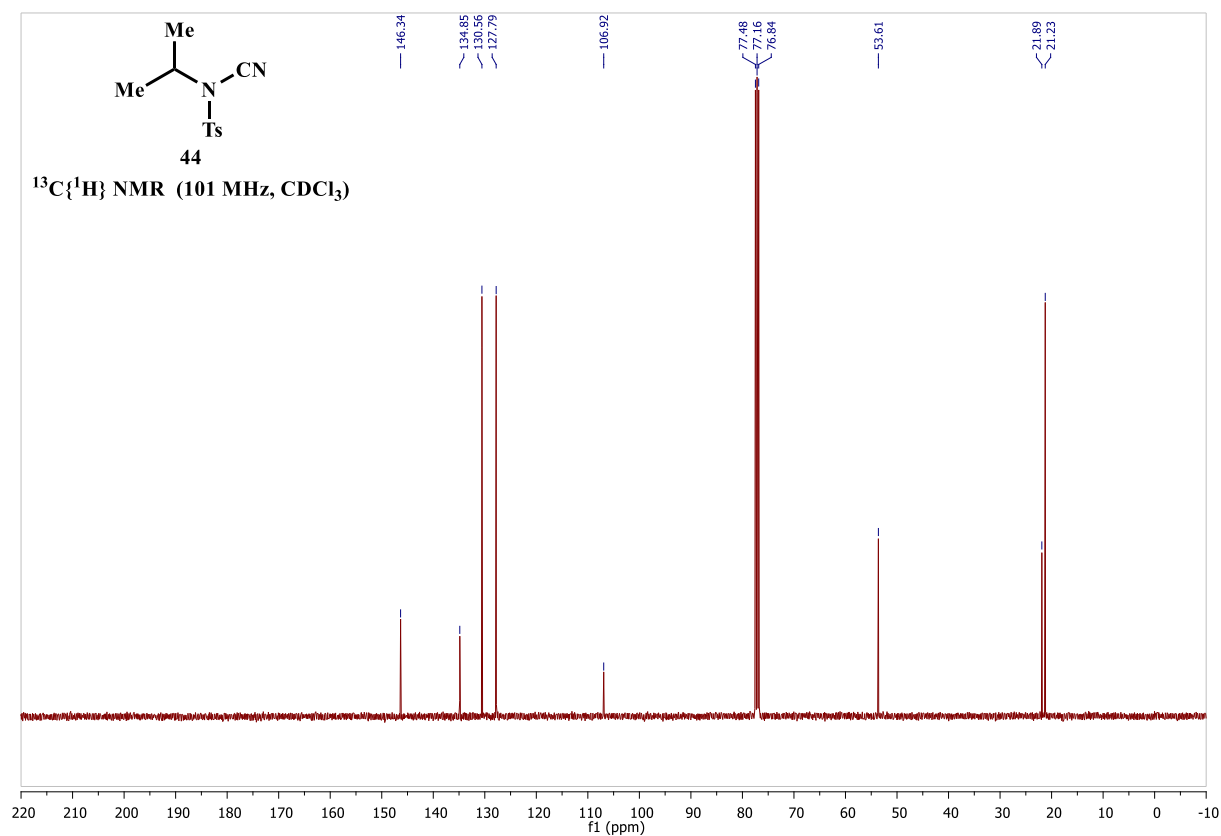
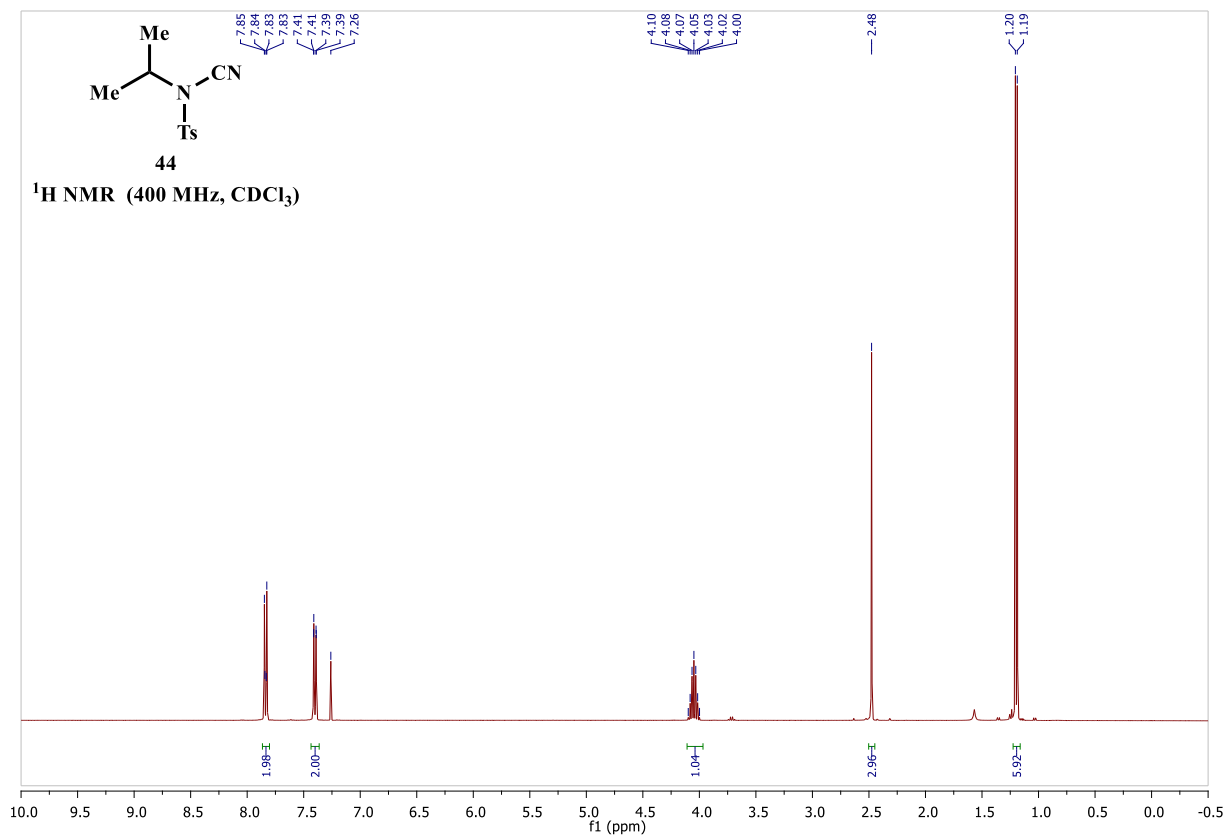


### *N*-cyano-*N*-isopropyl-*p*-methylbenzenesulfonamide

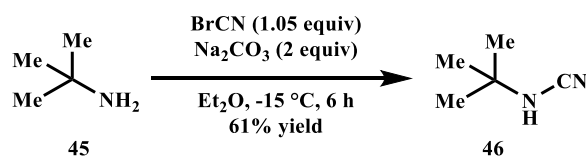


To a 100 mL round-bottom flask equipped with a magnetic stirrer bar was charged sodium hydride (60% in paraffin oil) (480 mg, 12 mmol, 1.2 equiv) and THF (50 mL). The flask was cooled to 0 °C before the addition of *N*-isopropylcyanamide **43** (1 g, 12.3 mmol, 1.0 equiv) in diethyl ether (5 mL) and tosyl chloride (2.8 g, 14.8 mmol, 1.2 equiv) in THF (5 mL). The reaction mixture was then stirred at 25 °C for 16 h. The reaction was then quenched with water (1 mL) and diluted with diethyl ether (10 mL). Brine solution (50 mL) was added, and the product was extracted with ethyl acetate (3 × 15 mL). The combined organic fraction was dried ( $\text{MgSO}_4$ ), filtered and concentrated *in vacuo* and recrystallised from ethanol to give the titled compound **44** as a white crystalline solid (1.26 g, 5.29 mmol, 43%); mp 56–60 °C (EtOH);  $R_f = 0.46$  (eluent = 30% EtOAc in hexanes);  $\nu_{\text{max}}/\text{cm}^{-1}$  (film): 2216 ( $\text{C}\equiv\text{N}$ ), 1589, 1454, 1373, 1346, 1298, 1157, 1126, 970, 866, 812, 706, 677, 644, 586, 542, 422;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 1.20 (6H, d,  $J$  8.2), 2.48 (3H, s), 4.05 (1H, septet,  $J$  6.7), 7.40 (2H, d,  $J$  8.2), 7.84 (2H, d,  $J$

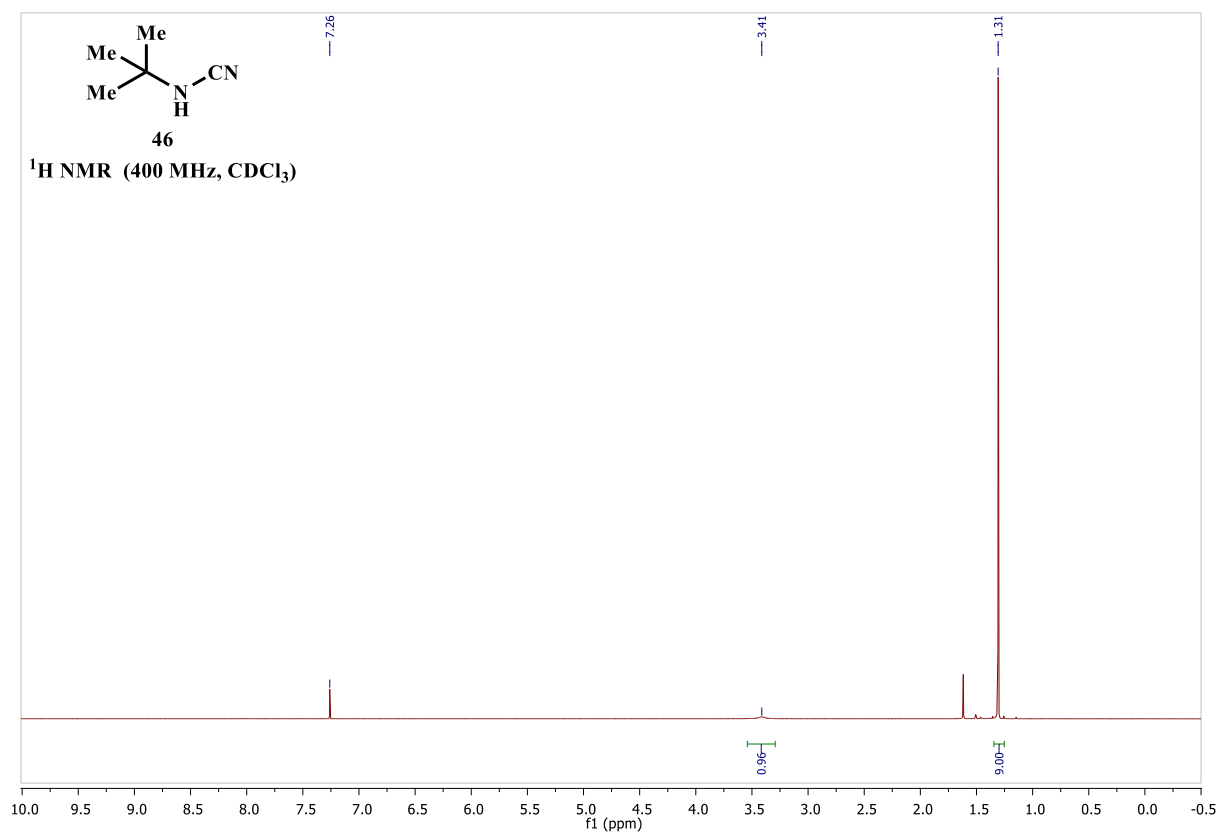
8.5);  $^{13}\text{C}$  { $^1\text{H}$ } NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 21.2, 21.9, 53.6, 106.9, 127.8, 130.6, 134.9, 146.3; HRMS (NSI $^+$ ) calculated for  $[\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_2\text{S}]^+$ :  $m/z$  239.0849 found 239.0851 (+0.9 ppm).

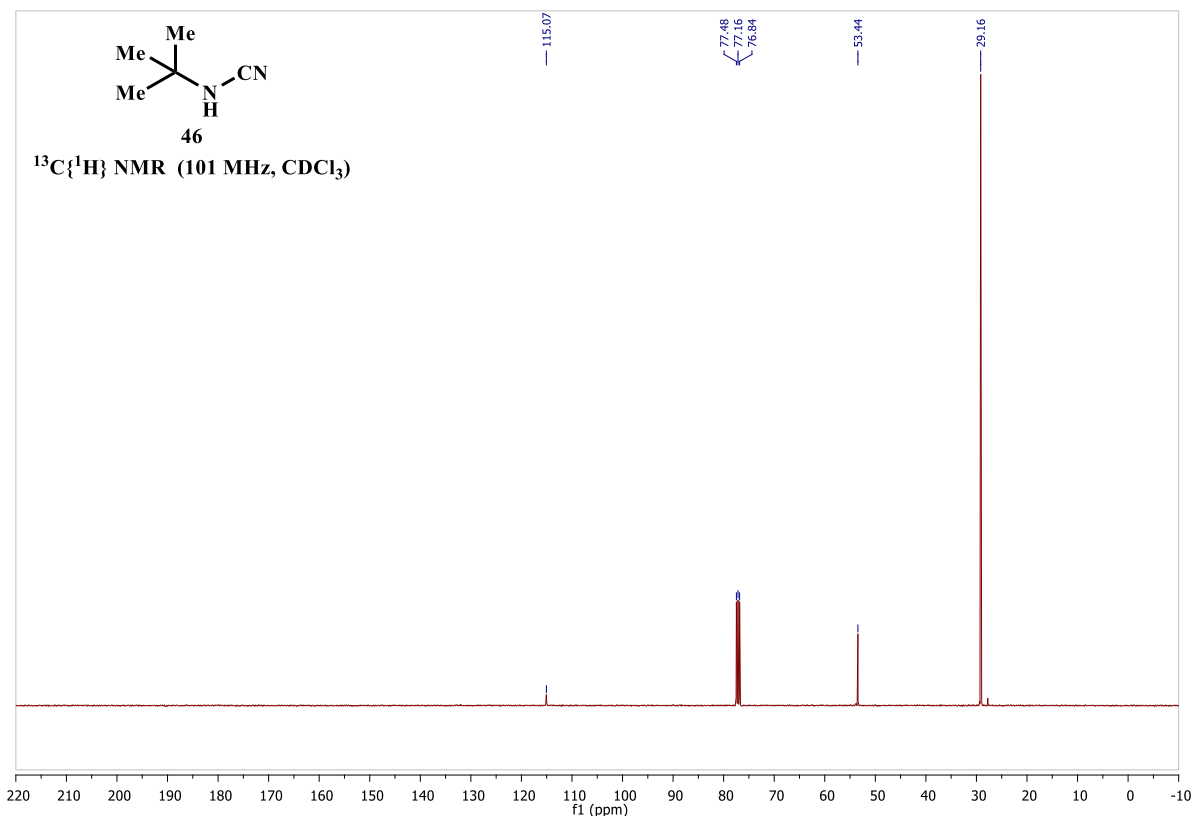


## *N*-(*tert*-butyl)cyanamide

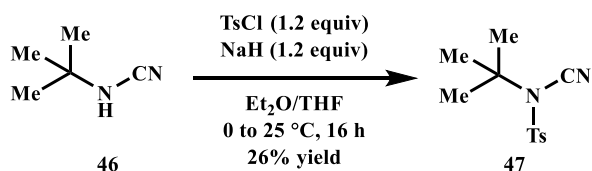


To a 100 mL round bottomed flask equipped with a magnetic stirrer bar was charged sodium carbonate (4.24 g, 40 mmol, 2 equiv), cyanogen bromide (2.22 g, 21 mmol, 1.05 equiv) and diethyl ether (30 mL). The mixture was cooled to  $-15\text{ }^\circ\text{C}$ , before the slow addition of the *tert*-butylamine **45** (2.1 mL, 20 mmol, 1 equiv) over 5 min. The resultant reaction mixture was then stirred at  $-15\text{ }^\circ\text{C}$  until completion, as determined by thin-layer chromatography (TLC) monitoring. After completion, the crude reaction mixture was filtered and the filtrate was concentrated *in vacuo* to give the desired cyanamide, without the need for further purification to give the titled compound **46** as a pale orange oil (1.20 g, 12.23 mmol, 61%);  $R_f = 0.53$  (eluent = 30% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 3184, 2972, 2212 ( $\text{C}\equiv\text{N}$ ), 1443, 1396, 1368, 1207, 893, 775, 638, 552;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 1.31 (9H, s), 3.41 (1H, s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 29.2, 53.4, 115.1; HRMS (NSI+) calculated for  $[\text{C}_5\text{H}_{11}\text{N}_2]^+$ :  $m/z$  99.0917 found 99.0917 (+0.3 ppm).



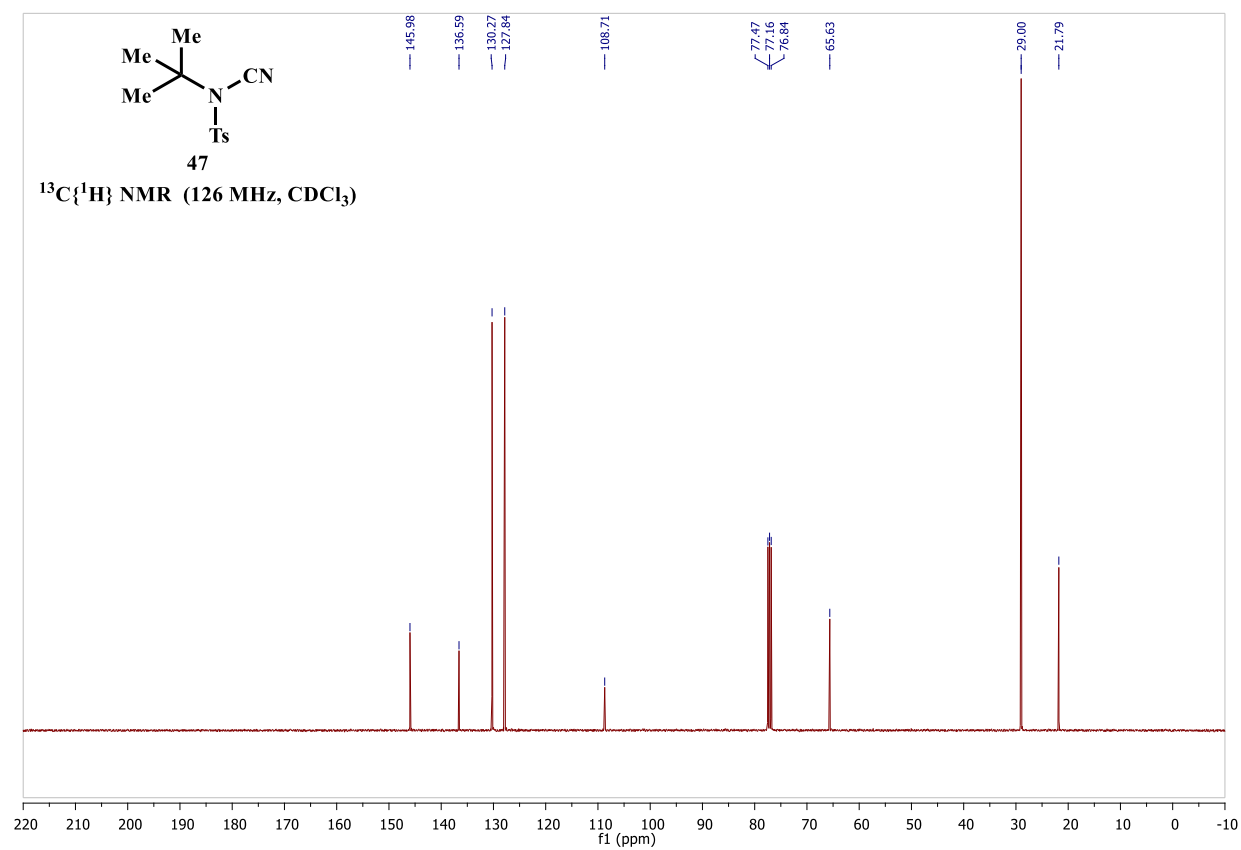
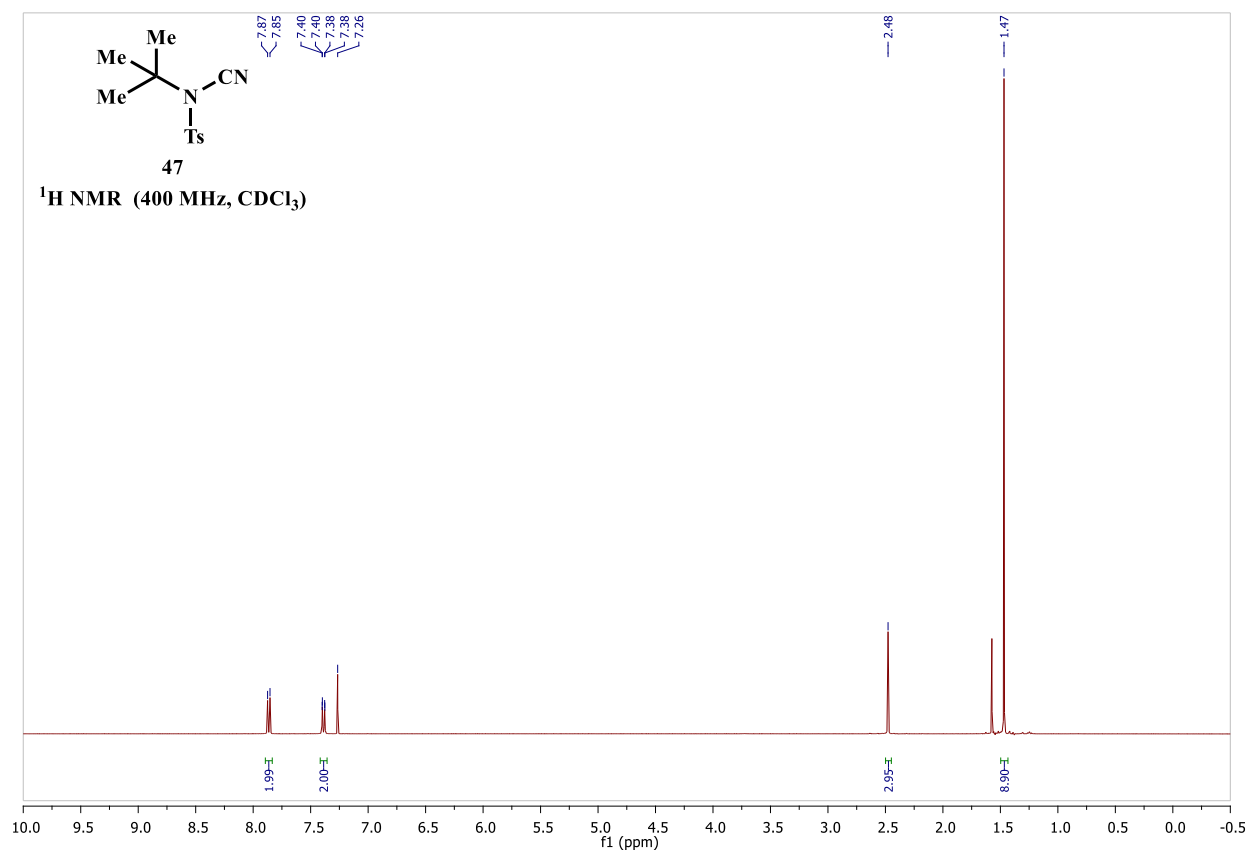


### *N*-(*t*-butyl)-*N*-cyano-*p*-toluenesulfonamide



To a 100 mL round-bottom flask equipped with a magnetic stirrer bar was charged sodium hydride (60% in paraffin oil) (480 mg, 12 mmol, 1.2 equiv) and THF (50 mL). The flask was cooled to 0 °C before the addition of *N*-(*tert*-butyl)cyanimide **46** (981 mg, 10 mmol, 1.0 equiv) in diethyl ether (5 mL) and tosyl chloride (2.3 g, 12 mmol, 1.2 equiv) in THF (5 mL). The reaction mixture was then stirred at 25 °C for 16 h. The reaction was then quenched with water (1 mL) and diluted with diethyl ether (10 mL). Brine solution (50 mL) was added, and the product was extracted with ethyl acetate (3 × 15 mL). The combined organic fraction was dried ( $\text{MgSO}_4$ ), filtered and concentrated *in vacuo* and recrystallised from ethanol to give the titled compound **47** as a white crystalline solid (651 mg, 2.58 mmol, 26%); mp 58-62 °C (EtOH);  $R_f = 0.60$  (eluent = 30% EtOAc in hexanes);  $\nu_{\text{max}}/\text{cm}^{-1}$  (film): 2988, 2216 ( $\text{C}\equiv\text{N}$ ), 1593, 1464, 1362, 1152, 1080, 918, 806, 667, 608, 548, 511;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 1.47 (9H, s), 2.48 (3H, s), 7.39 (2H, d,  $J$  8.2), 7.86 (2H, d,  $J$  8.4);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 21.8,

29.0, 65.6, 108.7, 127.8, 130.3, 136.6, 146.0; HRMS (NSI<sup>+</sup>) calculated for [C<sub>12</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S]<sup>+</sup>: m/z 253.1005 found 253.1009 (+1.5 ppm).



## 4. Substrate scope

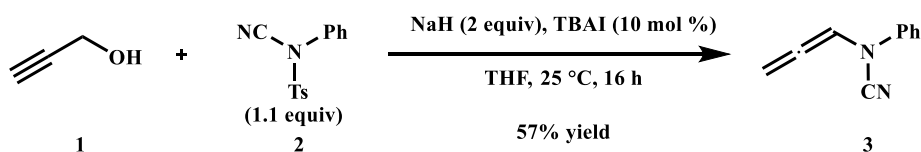
### General procedure 3

To an oven dried reaction vial was added propargyl alcohol (1 equiv) followed by THF ([propargyl alcohol] = 0.2 mol dm<sup>-3</sup>), the requisite sulfonamide (1.1 equiv) and TBAI (10 mol %). The reaction was stirred and NaH (2 equiv) was added. The reaction was stirred for 16 h at rt. After 16 h the reaction was quenched with sat. aq. NH<sub>4</sub>Cl and diluted with H<sub>2</sub>O. The product was extracted with EtOAc (× 3). The combined organic phase was washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated *in vacuo*. The crude product was purified by flash silica column chromatography.

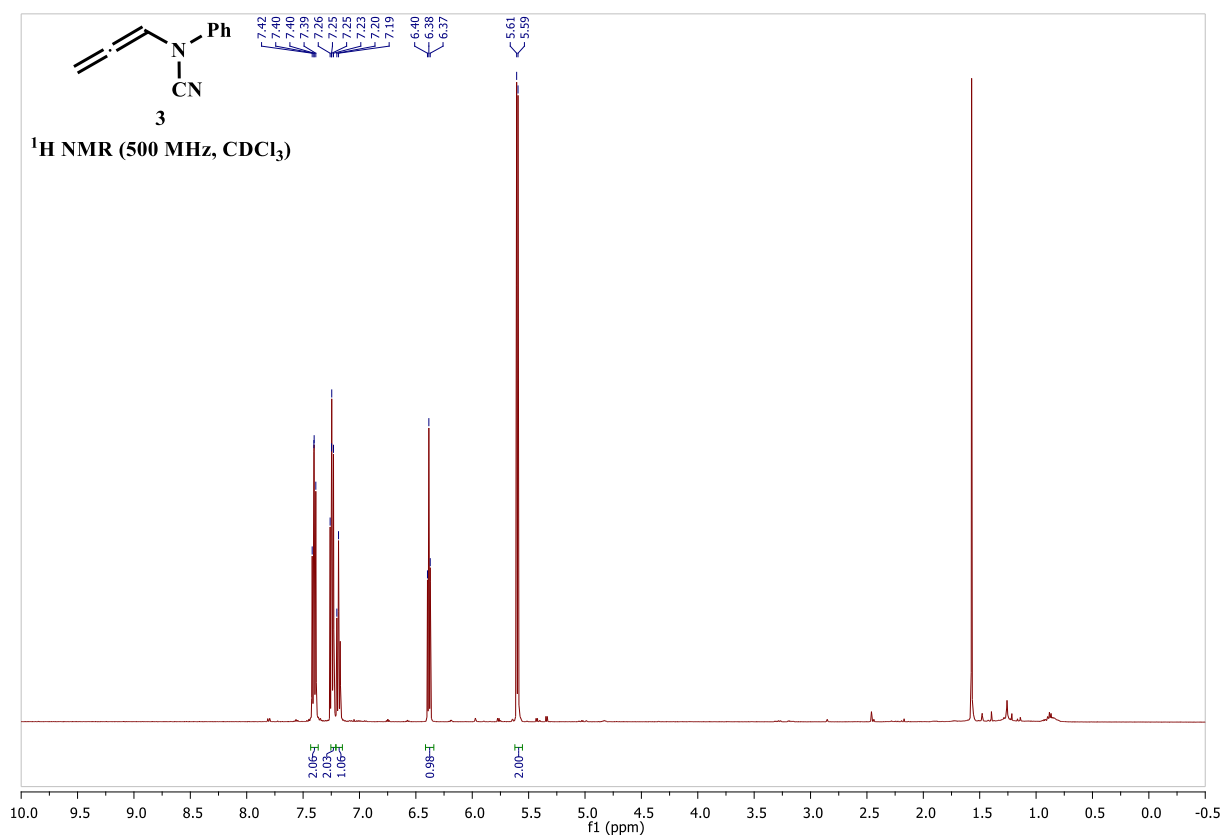
### General procedure 4

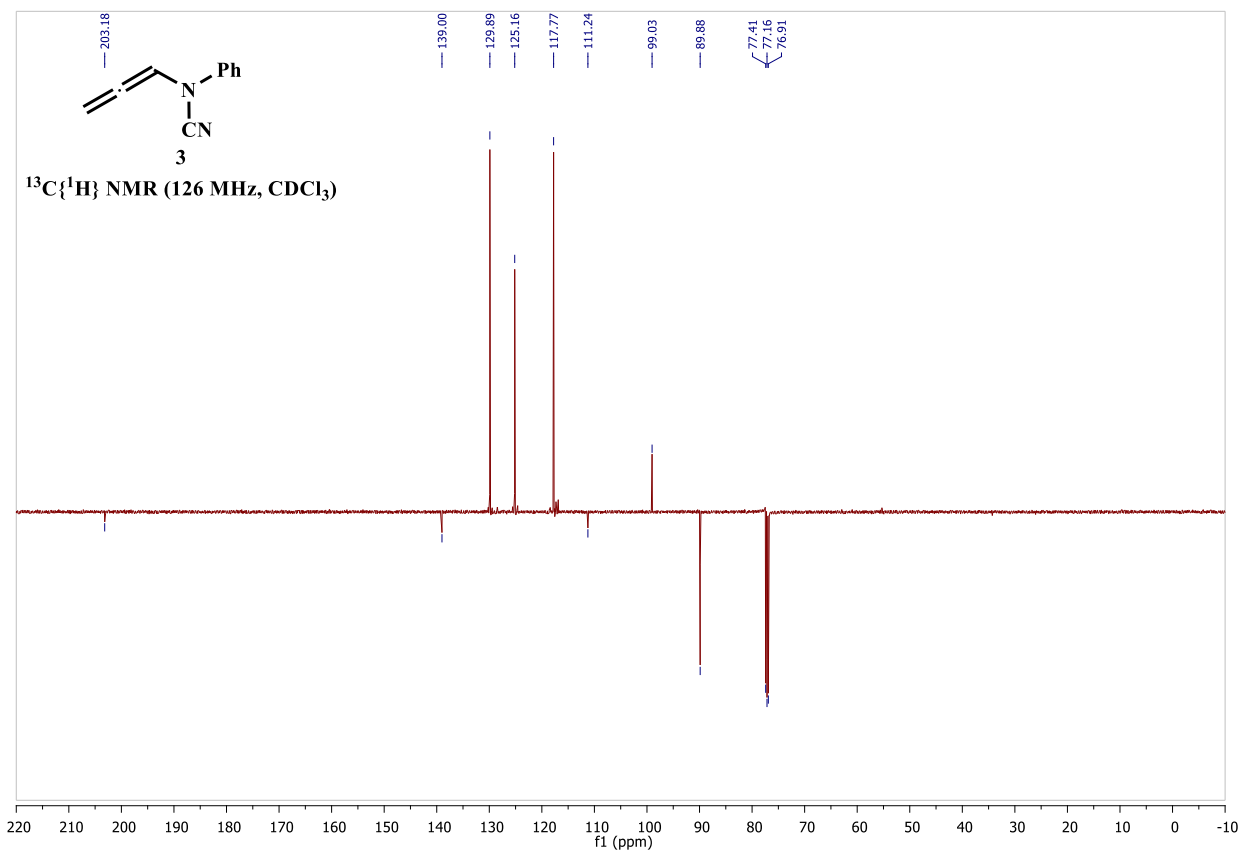
To an oven dried reaction vial was added propargyl alcohol (1 equiv) followed by THF ([propargyl alcohol] = 0.2 mol dm<sup>-3</sup>), the requisite sulfonamide (1.1 equiv) and TBAI (10 mol %). The reaction was stirred and NaH (2 equiv) was added. The reaction was stirred for 16 h at rt. After 16 h the reaction was quenched and diluted with H<sub>2</sub>O. The product was extracted with EtOAc (× 3). The combined organic phase was washed with brine, dried (MgSO<sub>4</sub>), filtered and concentrated *in vacuo*. The crude product was purified by flash silica column chromatography.

### *N*-phenyl-*N*-(1,2-propdienyl)cyanamide

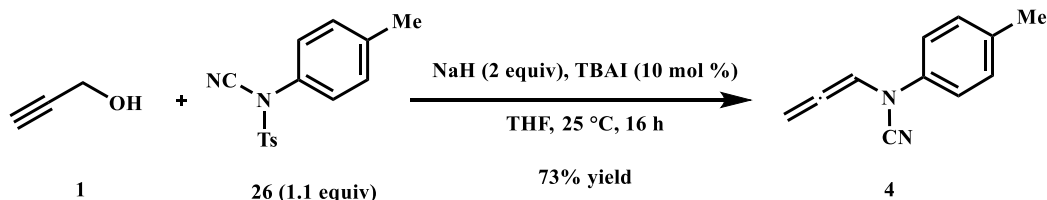


Following general procedure **3**, propargyl alcohol **1** (58  $\mu$ L, 1 mmol, 1 equiv), THF (5 mL), NCTS **2** (300 mg, 1.1 mmol, 1.1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes, 30  $\times$  120 mm silica) the titled compound **3** (89 mg, 0.57 mmol, 57% yield) as a clear oil.  $R_f$  = 0.59 (eluent = 20% EtOAc in hexanes);  $\nu_{\max}$  /  $\text{cm}^{-1}$ : 2223 ( $\text{C}\equiv\text{N}$ ), 1593, 1494, 1436, 1352, 1238, 838, 734, 673, 486;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 5.60 (2H, d,  $J$  6.1), 6.38 (1H, t,  $J$  6.1), 7.19 (1H, t,  $J$  7.4), 7.24 (2H, d,  $J$  7.8), 7.39-7.42 (2H, m);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 89.9, 99.0, 111.3, 117.8, 125.2, 129.9, 139.0, 203.2; HRMS (NSI+) calculated for  $[\text{C}_{10}\text{H}_9\text{N}_2]^+(\text{M}+\text{H})^+$ :  $m/z$  157.0760, found 157.0757 (-2.1 ppm).

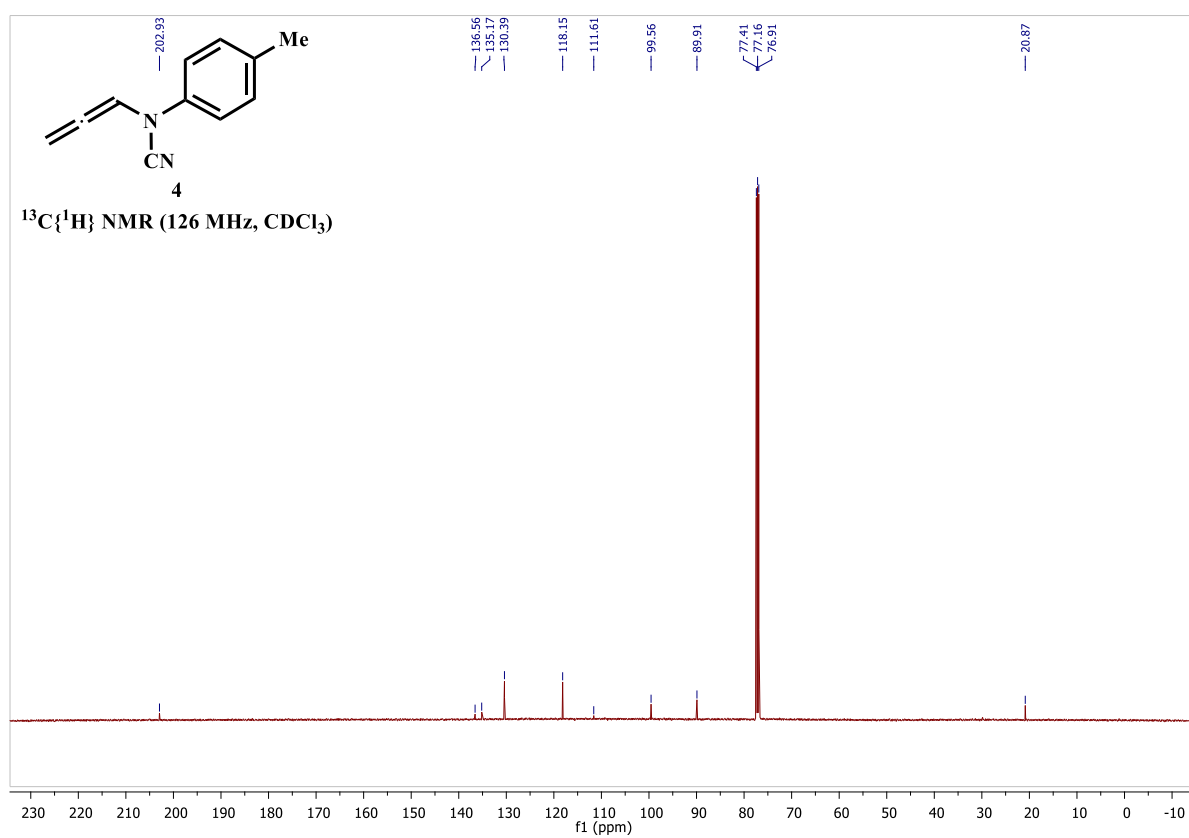
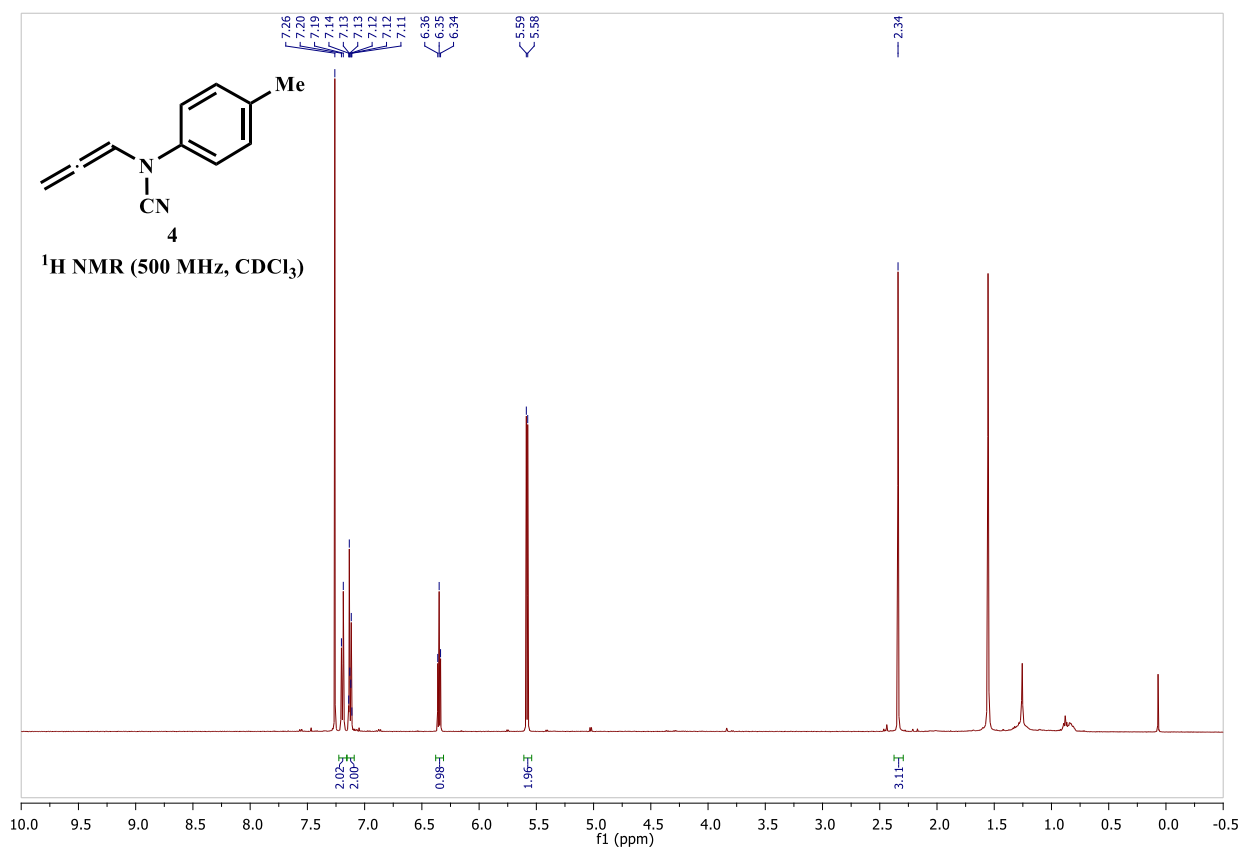




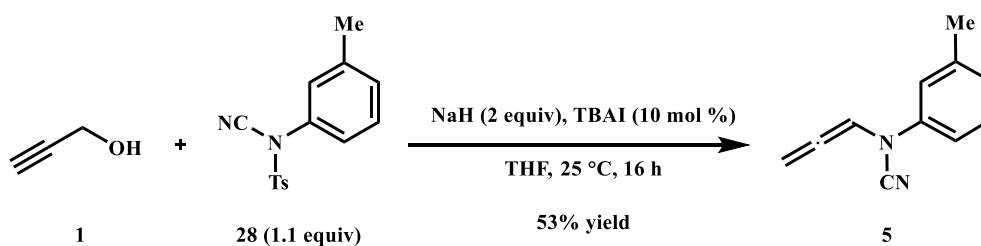
### *N*-(1,2-propdienyl)-*N*-(*p*-tolyl)cyanamide



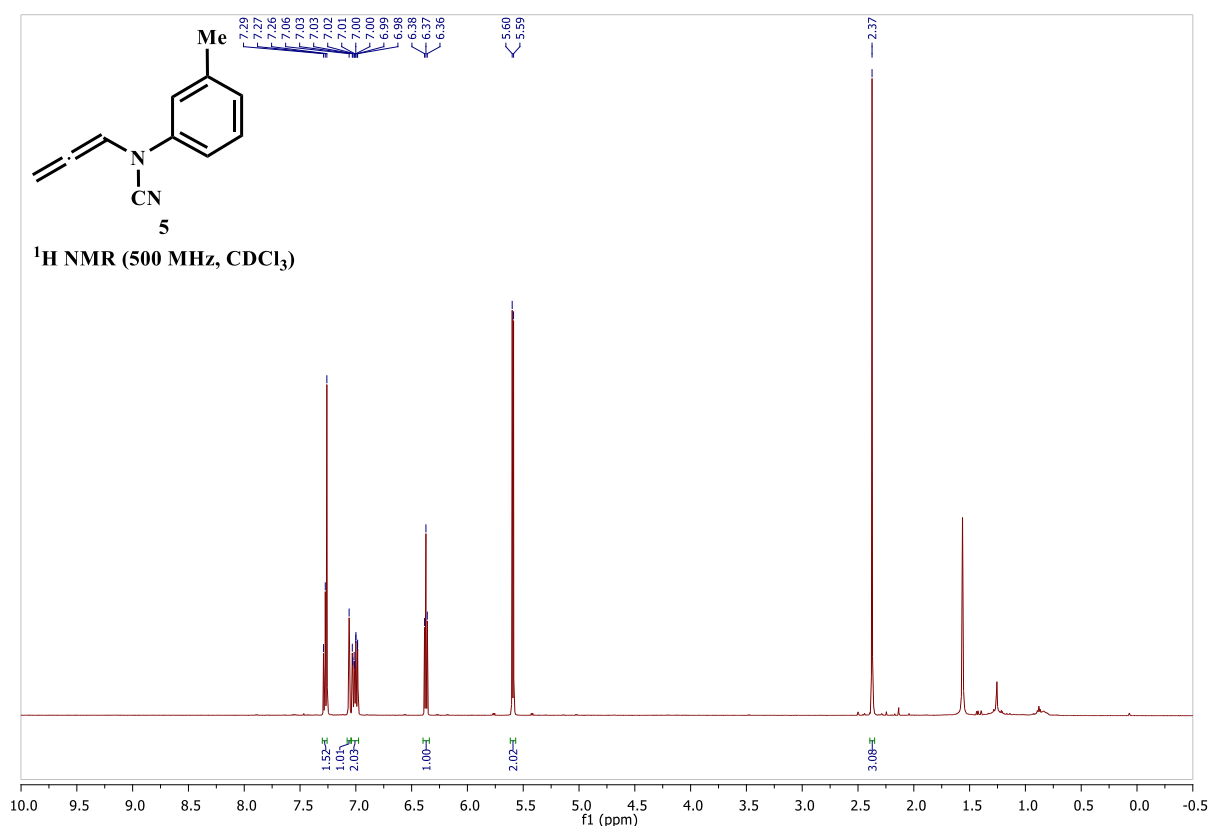
Following general procedure **3**, propargyl alcohol **1** (795  $\mu\text{L}$ , 13.7 mmol, 1 equiv), THF (70 mL), *N*-cyano-*p*-methyl-*N*-(*p*-tolyl)benzenesulfonamide **26** (4.3 g, 15.0 mmol, 1.1 equiv), TBAI (506 mg, 1.37 mmol, 0.1 equiv) and NaH (60%) (1.09 g, 27.3 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes,  $30 \times 120$  mm silica) the titled compound **4** (1.69 mg, 9.93  $\mu\text{mol}$ , 73% yield) as a white solid; mp 48-50  $^\circ\text{C}$ ;  $R_f = 0.76$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2223 ( $\text{C}\equiv\text{N}$ ), 1510, 1438, 1359, 1128, 893, 796, 615, 484;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.34 (3H, s), 5.58 (2H, d,  $J$  6.1), 6.35 (1H, t,  $J$  6.1), 7.11-7.14 (2H, m), 7.19 (2H, d,  $J$  8.1);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 20.9, 89.9, 99.6, 111.6, 118.2, 130.4, 135.2, 136.6, 202.9; HRMS (NSI+) calculated for  $[\text{C}_{11}\text{H}_{11}\text{N}_2]^+(\text{M}+\text{H})^+$ :  $m/z$  171.0917, found 171.0915 (-1.0 ppm).

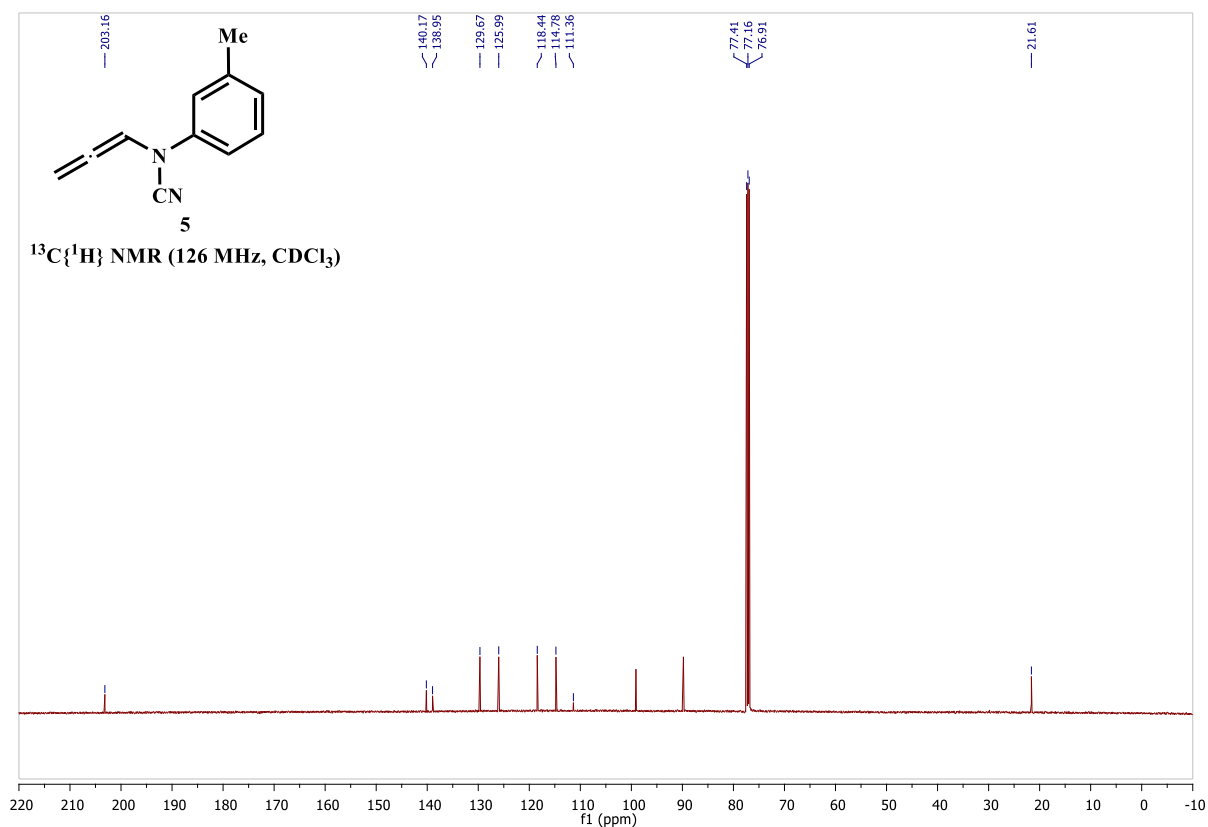


### *N*-(1,2-propdienyl)-*N*-(*m*-tolyl)cyanamide

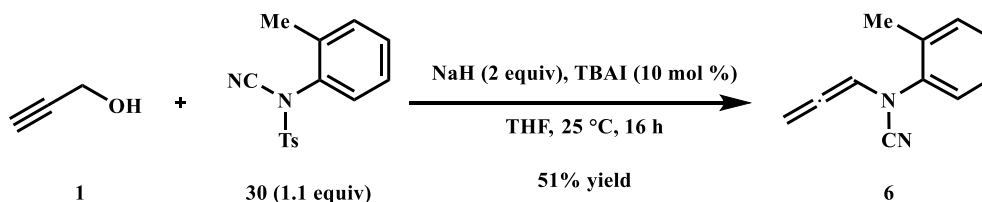


Following general procedure **3**, propargyl alcohol **1** (58  $\mu$ L, 1 mmol, 1 equiv), THF (5 mL), *N*-cyano-*p*-methyl-*N*-(*m*-tolyl)benzenesulfonamide **28** (315 mg, 1.1 mmol, 1.1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes, 30  $\times$  120 mm silica) the titled compound **5** (96 mg, 0.53 mmol, 53% yield) as a clear oil.  $R_f$  = 0.74 (eluent = 20% EtOAc in hexanes);  $\nu_{\max}$  /  $\text{cm}^{-1}$  (film): 2223 (C $\equiv$ N), 1606, 1494, 1357, 1273, 1184, 887, 686, 497;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.37 (3H, s), 5.59 (2H, d,  $J$  6.1), 6.37 (1H, t,  $J$  6.1), 6.98-7.03 (2H, m), 7.06 (1H, s), 7.27-7.29 (1H, m);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 21.6, 89.8, 99.1, 111.4, 114.8, 118.4, 126.0, 129.7, 139.0, 140.2, 203.2; HRMS (NSI+) calculated for  $[\text{C}_{11}\text{H}_{11}\text{N}_2]^+(\text{M}+\text{H})^+$ :  $m/z$  171.0917, found 171.0914 (-1.6 ppm).

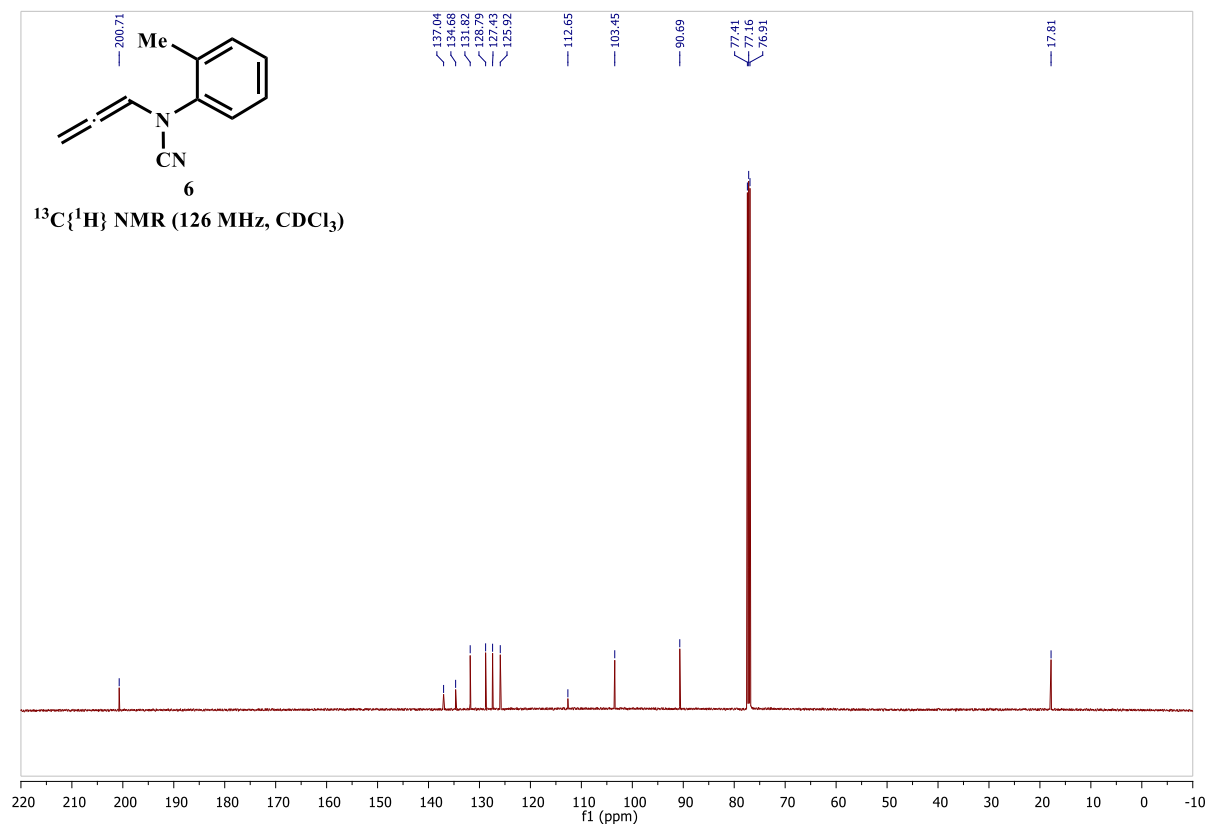
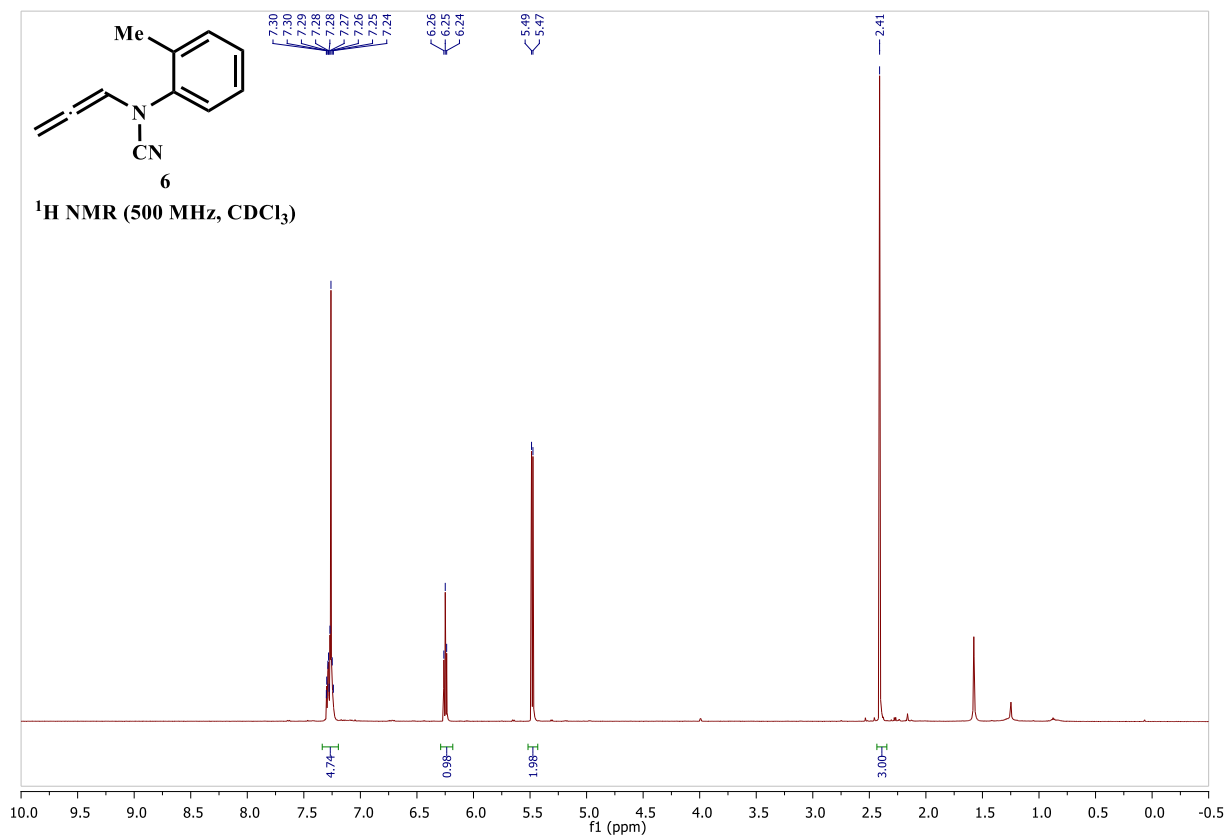




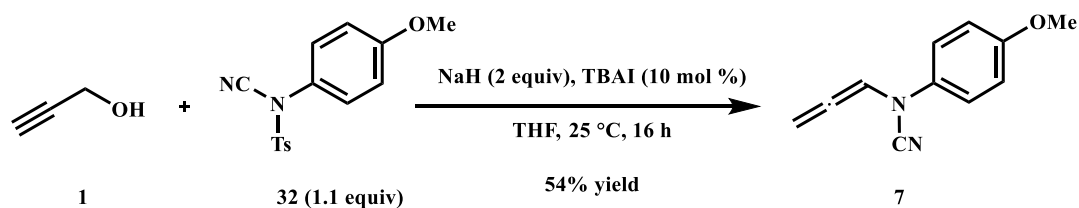
### *N*-(1,2-propadienyl)-*N*-(*o*-tolyl)cyanamide



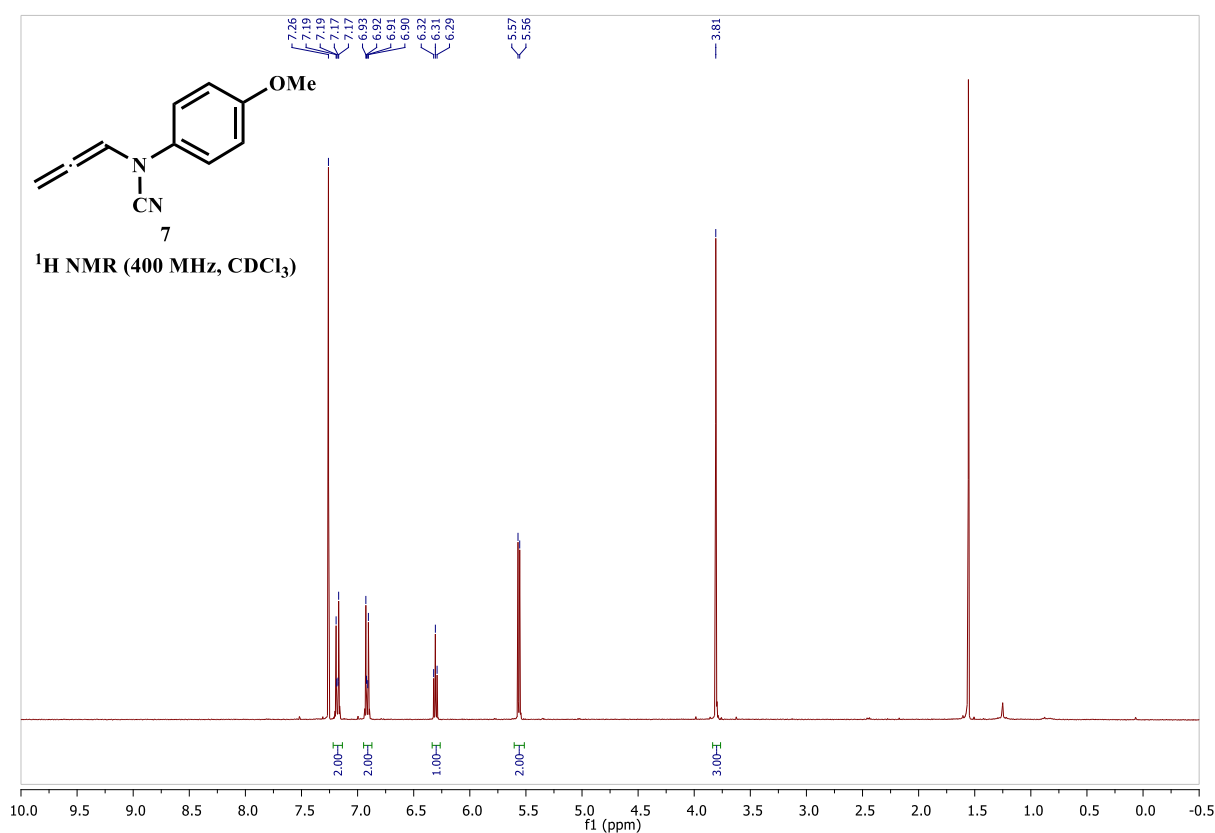
Following general procedure **3**, propargyl alcohol **1** (58  $\mu\text{L}$ , 1 mmol, 1 equiv), THF (5 mL), *N*-cyano-*p*-methyl-*N*-(*o*-tolyl)benzenesulfonamide **30** (315 mg, 1.1 mmol, 1.1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes, 30  $\times$  120 mm silica) the titled compound **6** (87 mg, 0.51 mmol, 51% yield) as a clear oil.  $R_f = 0.56$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2223 (C $\equiv$ N), 1492, 1363, 1259, 1230, 1122, 1109, 891, 761, 501;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.41 (3H, s), 5.48 (2H, d,  $J$  6.2), 6.25 (1H, t,  $J$  6.2), 7.24-7.30 (4H, m);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 17.8, 90.7, 103.5, 112.7, 125.9, 127.4, 128.8, 131.8, 134.7, 137.0, 200.7; HRMS (NSI+) calculated for  $[\text{C}_{11}\text{H}_{11}\text{N}_2]^+(\text{M}+\text{H})^+$ :  $m/z$  171.0917, found 171.0915 (-1.0 ppm).

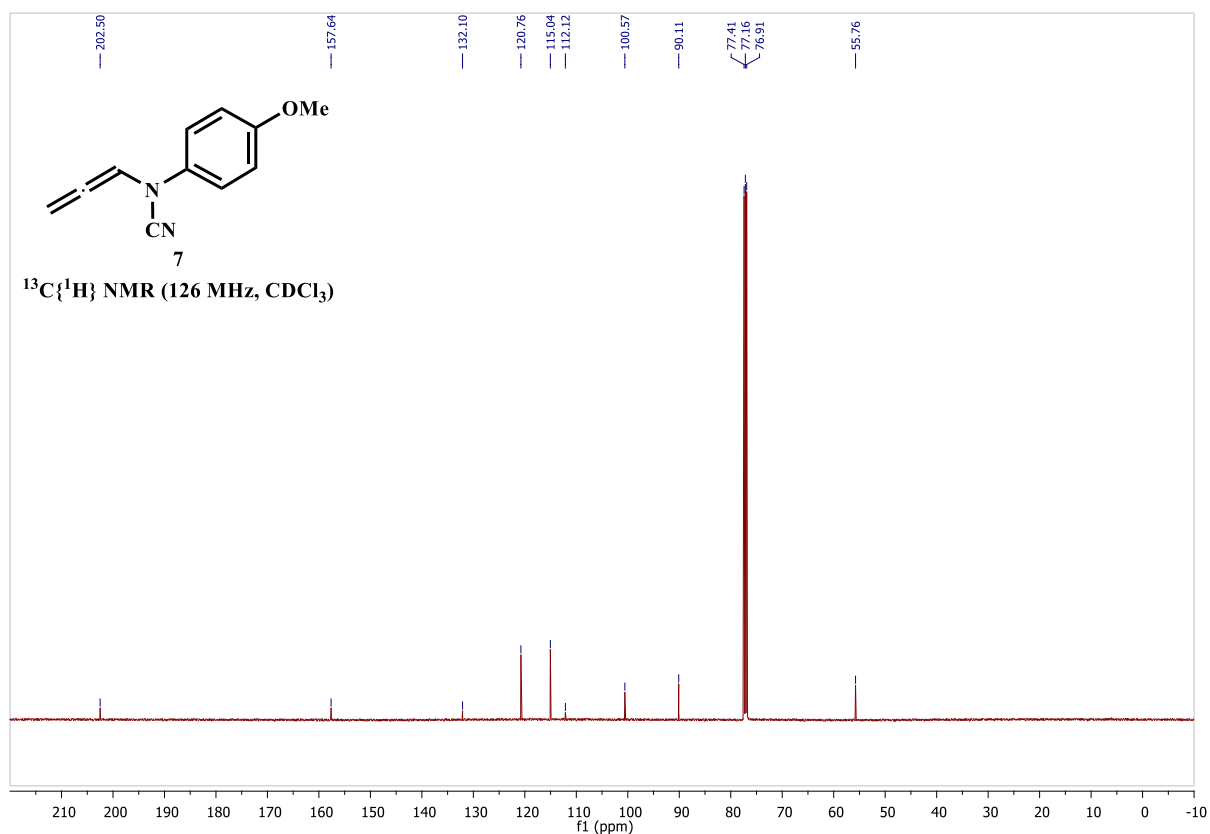


### *N*-(*p*-methoxyphenyl)-*N*-(1,2-propdienyl)cyanamide

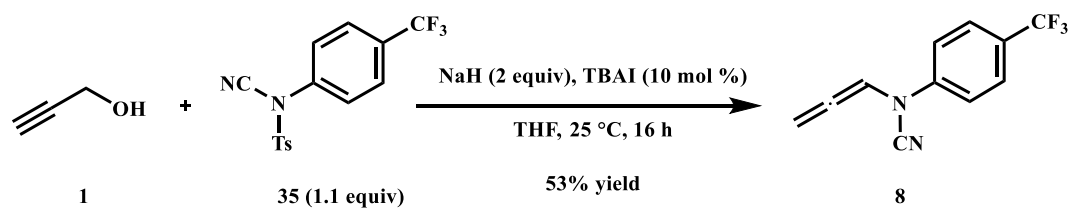


Following general procedure **3**, propargyl alcohol **1** (58  $\mu$ L, 1 mmol, 1 equiv), THF (5 mL), *N*-cyano-*N*-(*p*-methoxyphenyl)-*p*-methylbenzenesulfonamide **32** (333 mg, 1.1 mmol, 1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes, 30  $\times$  120 mm silica) the titled compound **7** (100 mg, 0.54 mmol, 54% yield) as a white solid; mp 60-64 °C;  $R_f$  = 0.45 (eluent = 20% EtOAc in hexanes);  $\nu_{\max}$  /  $\text{cm}^{-1}$  (film): 2223 (C $\equiv$ N), 1508, 1249, 1184, 1031, 926, 889, 825, 773, 613;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 3.81 (3H, s) 5.56 (2H, d,  $J$  6.1), 6.31 (1H, t,  $J$  6.1), 6.90-6.93 (2H, m), 7.17-7.19 (2H, m);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 55.8, 90.1, 100.57, 112.12, 115.04, 120.76, 132.1, 157.6, 202.5; HRMS (NSI+) calculated for  $[\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_1]^+(\text{M}+\text{H})^+$ :  $m/z$  187.0866, found 187.0864 (-1.0 ppm).

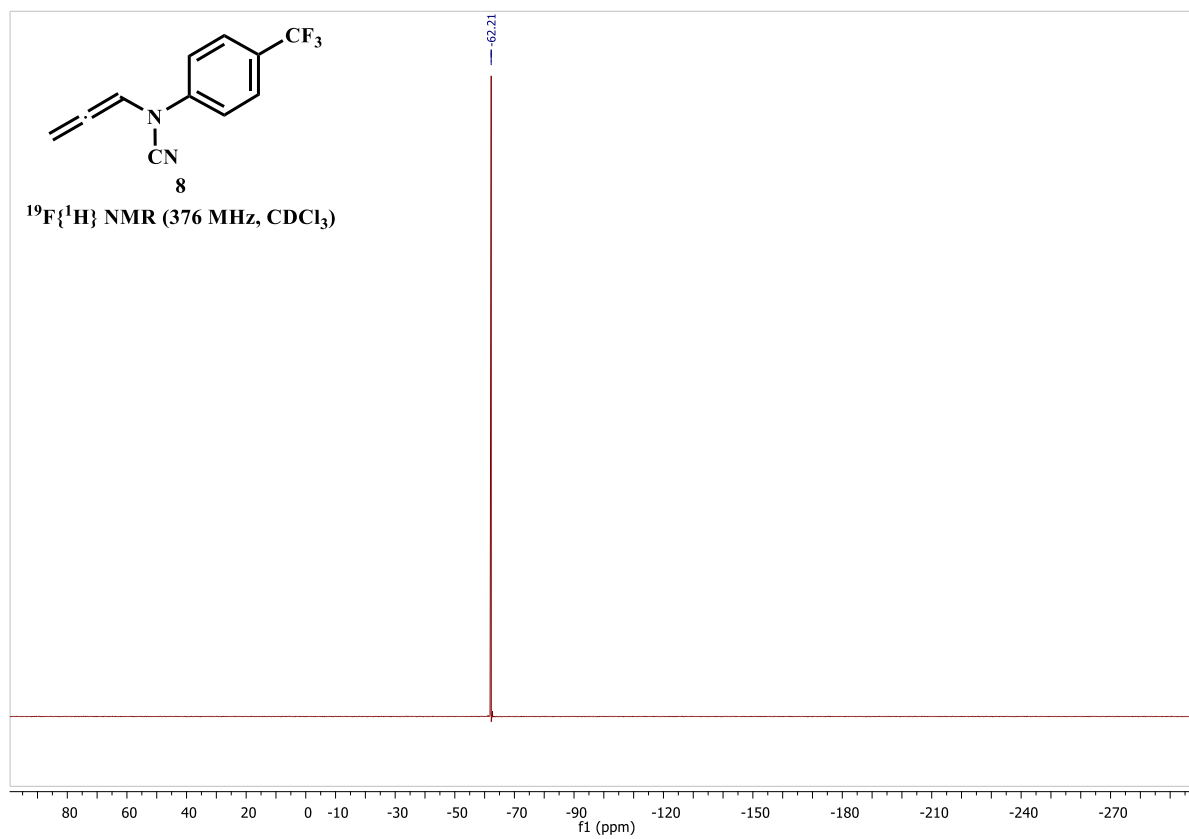
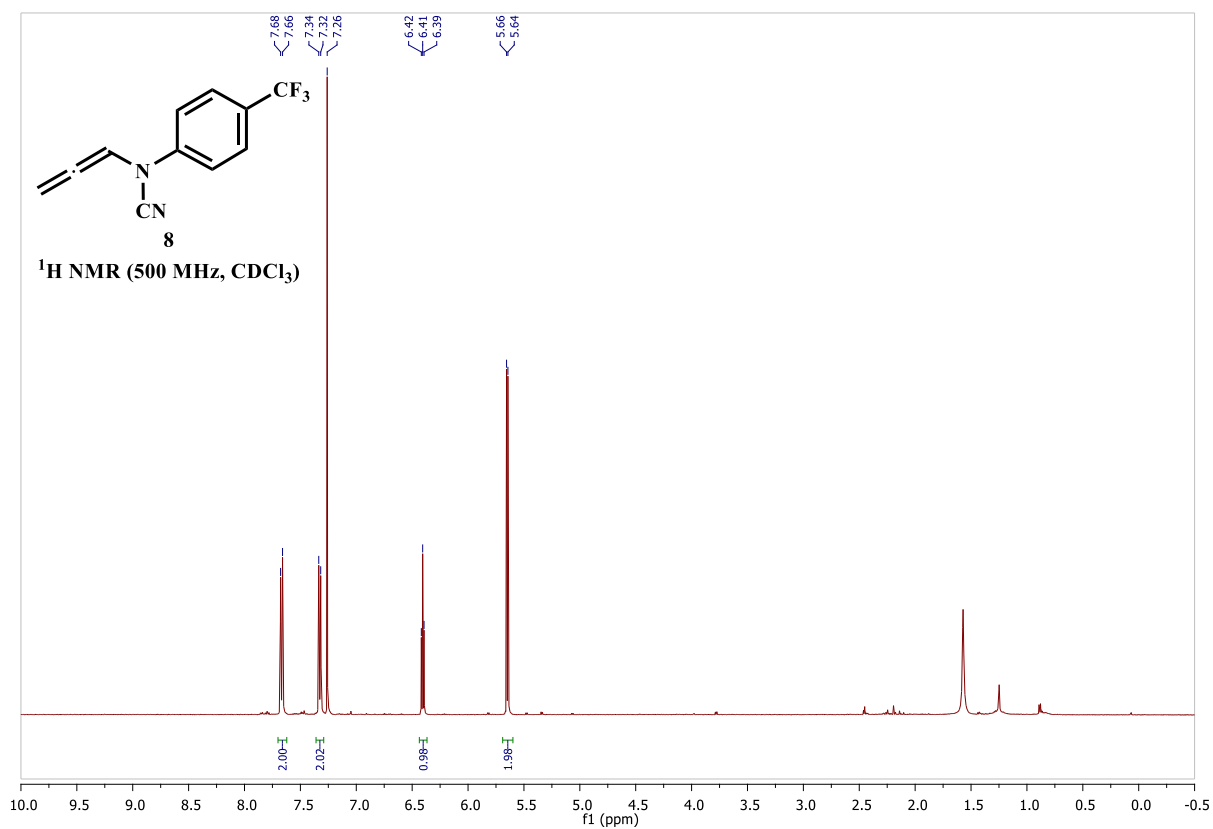


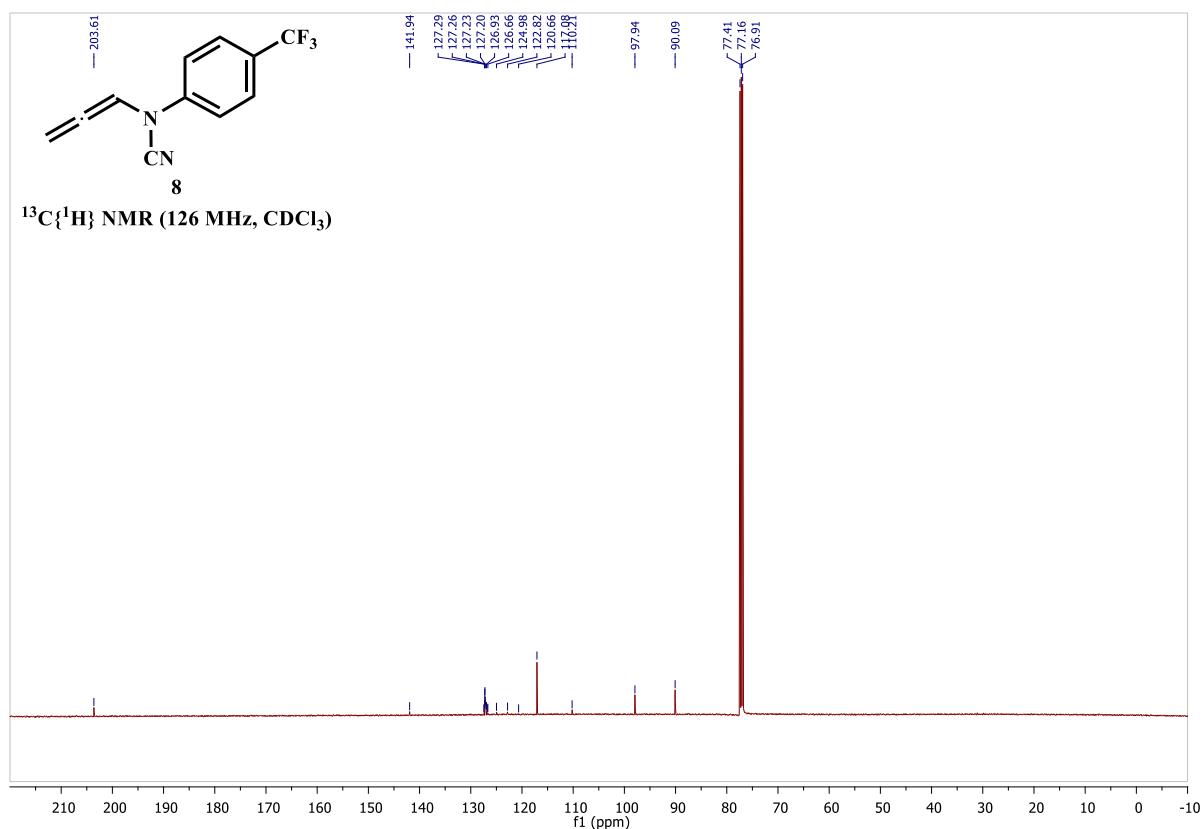


### *N*-(1,2-propadienyl)-*N*-(*p*-(trifluoromethyl)phenyl)cyanamide

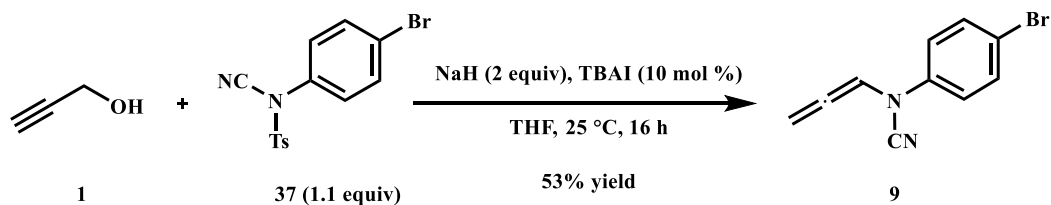


Following general procedure **4**, propargyl alcohol **1** (58  $\mu\text{L}$ , 1 mmol, 1 equiv), THF (5 mL), *N*-cyano-*p*-methyl-*N*-(*p*-(trifluoromethyl)phenyl)benzenesulfonamide **35** (374 mg, 1.1 mmol, 1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 5% EtOAc in hexanes,  $30 \times 120$  mm silica) the titled compound **8** (122 mg, 0.55 mmol, 53% yield) as a white solid; mp 32-34  $^\circ\text{C}$ ;  $R_f = 0.52$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2227 ( $\text{C}\equiv\text{N}$ ), 1612, 1325, 1271, 1166, 1114, 1063, 829;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 5.65 (2H, d,  $J$  6.1), 6.41 (1H, t,  $J$  6.1), 7.33 (2H, d,  $J$  8.7), 7.67 (2H, d,  $J$  8.7);  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$ : -62.2;  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 90.1, 98.0, 110.2, 117.1, 123.9 (q,  $J$  272.2), 127.1 (q,  $J$  66.8), 127.3 (q,  $J$  3.8), 141.9, 203.6; HRMS (ASAP+) calculated for  $[\text{C}_{11}\text{H}_8\text{N}_2\text{F}_3]^+(\text{M}+\text{H})^+$ :  $m/z$  225.0640, found 225.0643 (+1.0 ppm).

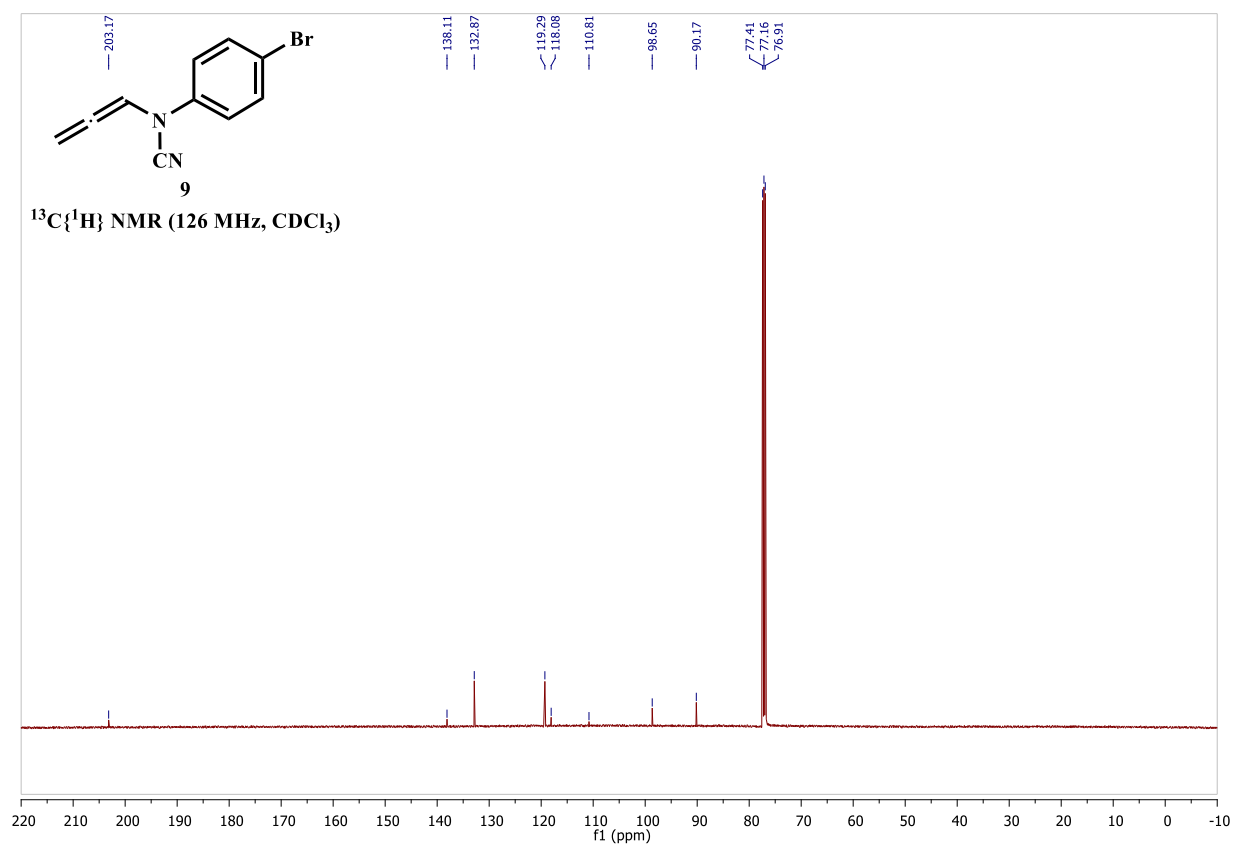
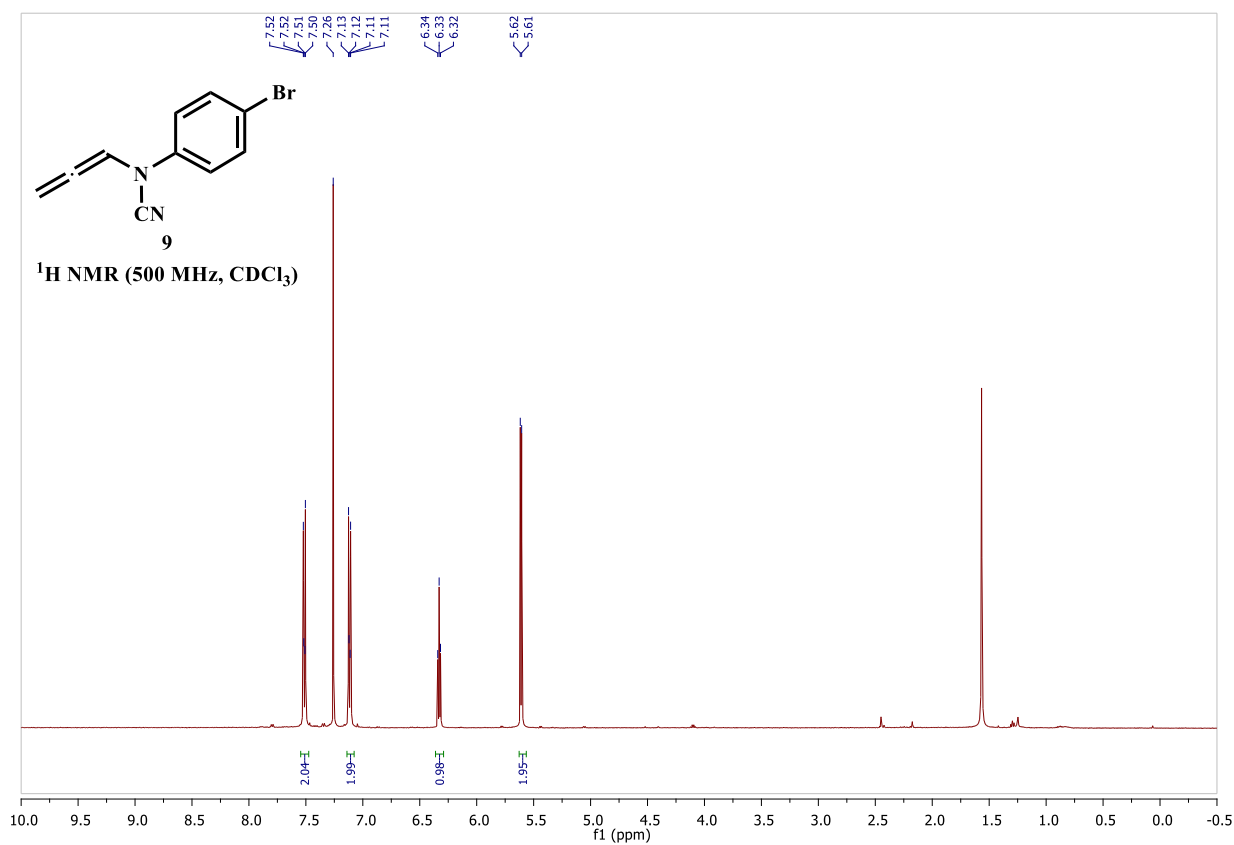




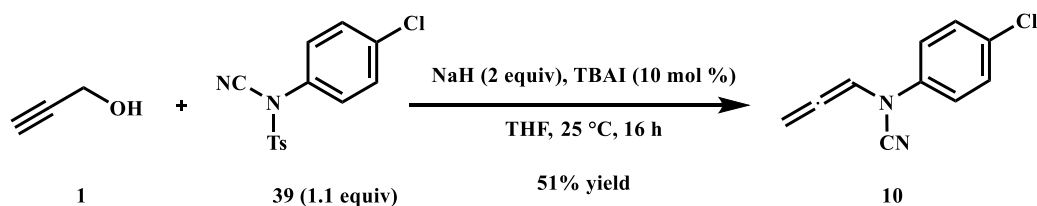
### *N*-(*p*-bromophenyl)-*N*-(1,2-propdienyl)cyanamide



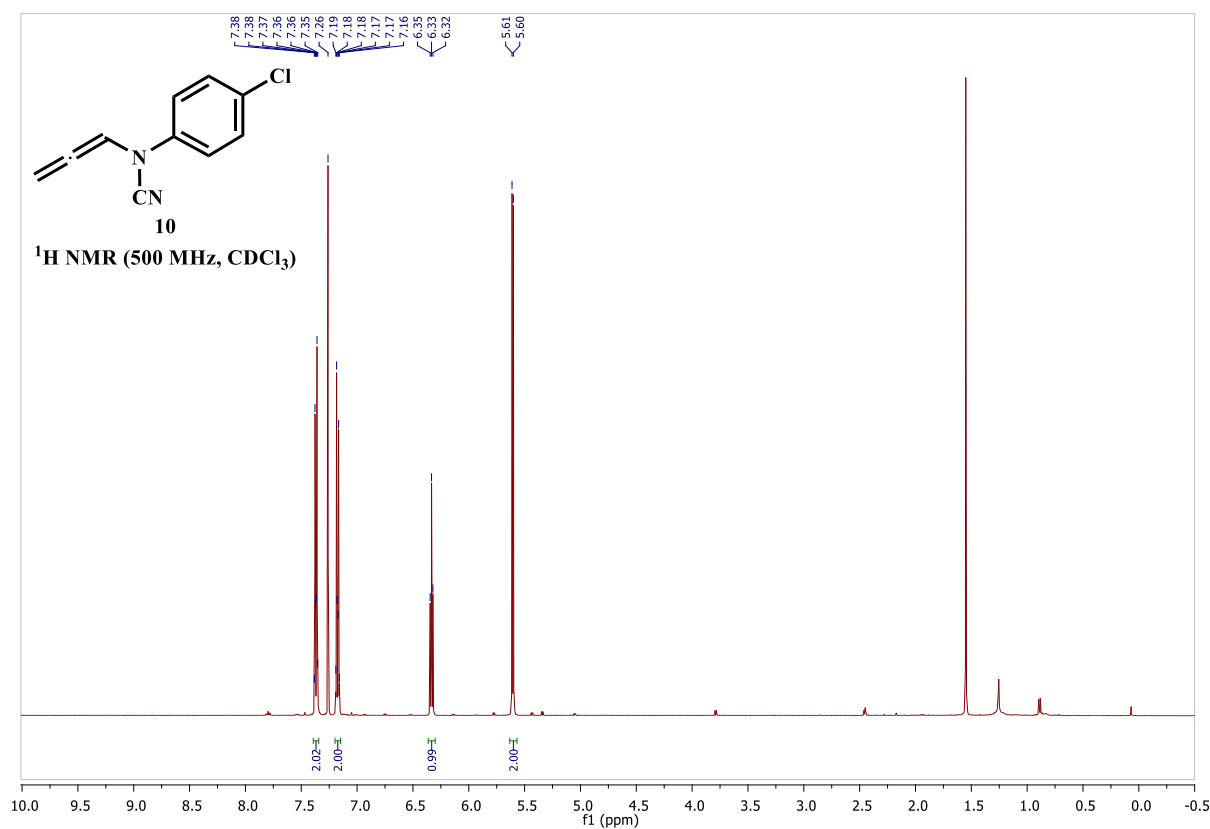
Following general procedure **3**, propargyl alcohol **1** (58  $\mu\text{L}$ , 1 mmol, 1 equiv), THF (5 mL), *N*-(*p*-bromophenyl)-*N*-cyano-*p*-methylbenzenesulfonamide **37** (386 mg, 1.1 mmol, 1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes,  $30 \times 120$  mm silica) the titled compound **9** (125 mg, 0.53 mmol, 53% yield) as a white solid; mp 42-44  $^\circ\text{C}$ ;  $R_f = 0.54$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2220 ( $\text{C}\equiv\text{N}$ ), 1485, 1379, 1265, 1236, 1155, 1078, 950, 813;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 5.61 (2H, d,  $J$  6.1), 6.33 (1H, t,  $J$  6.1), 7.05 (2H, d,  $J$  9.0), 7.45 (2H, d,  $J$  9.0);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 90.2, 98.7, 110.8, 118.1, 119.3, 132.9, 138.1, 203.2; HRMS (ASAP+) calculated for  $[\text{C}_{10}\text{H}_8\text{N}_2\text{Br}_1]^+(\text{M}^+)$ :  $m/z$  234.9871, found 234.9869 (-0.9 ppm).

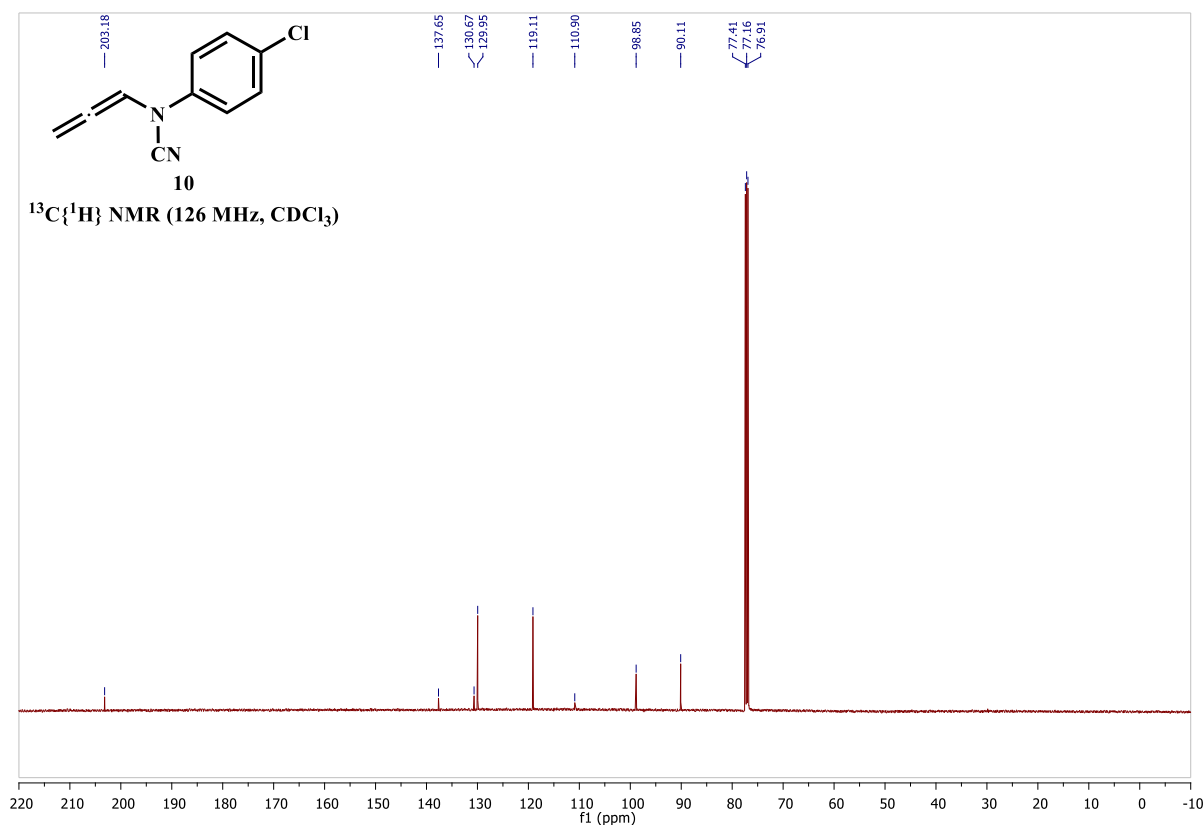


### *N*-(*p*-chlorophenyl)-*N*-(1,2-propadienyl)cyanamide

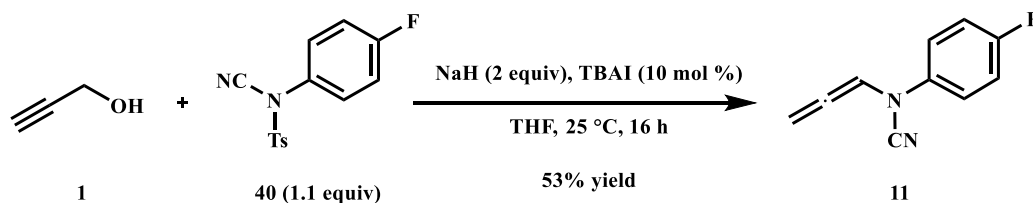


Following general procedure **3**, propargyl alcohol **1** (58  $\mu\text{L}$ , 1 mmol, 1 equiv), THF (5 mL), *N*-(*p*-chlorophenyl)-*N*-cyano-*p*-methylbenzenesulfonamide **39** (337 mg, 1.1 mmol, 1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes, 30  $\times$  120 mm silica) the titled compound **10** (98 mg, 0.51 mmol, 51% yield) as a white solid; mp 35-37  $^\circ\text{C}$ ;  $R_f = 0.50$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2231 (C $\equiv$ N), 1593, 1490, 1357, 1267, 1095, 962, 887, 810, 551;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 5.61 (2H, d,  $J$  6.1), 6.33 (1H, t,  $J$  6.1), 7.16-7.19 (2H, m), 7.35-7.28 (2H, m);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 90.1, 98.9, 110.9, 119.1, 130.0, 130.7, 137.7, 203.2; HRMS (NSI+) calculated for  $[\text{C}_{10}\text{H}_8\text{N}_2\text{Cl}_1]^+(\text{M}+\text{H})^+$ :  $m/z$  191.0371, found 191.0370 (-0.3 ppm)

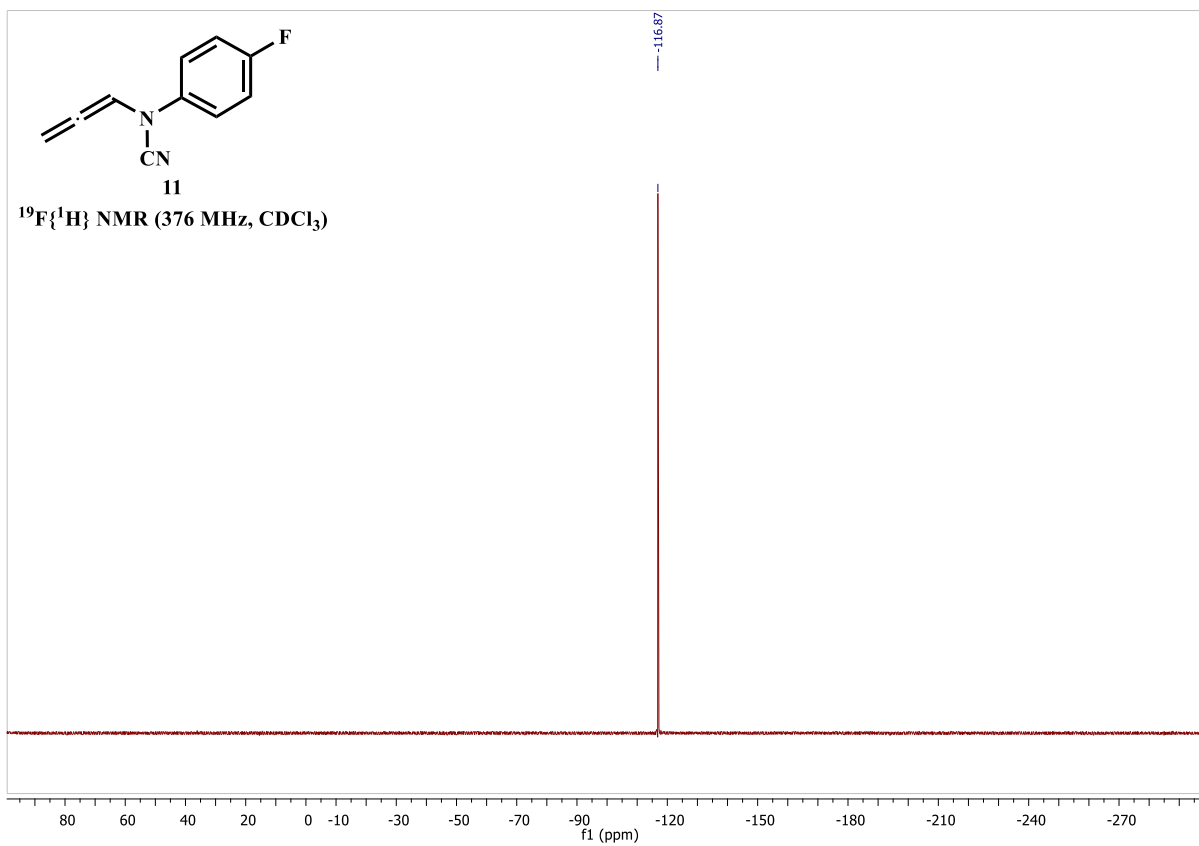
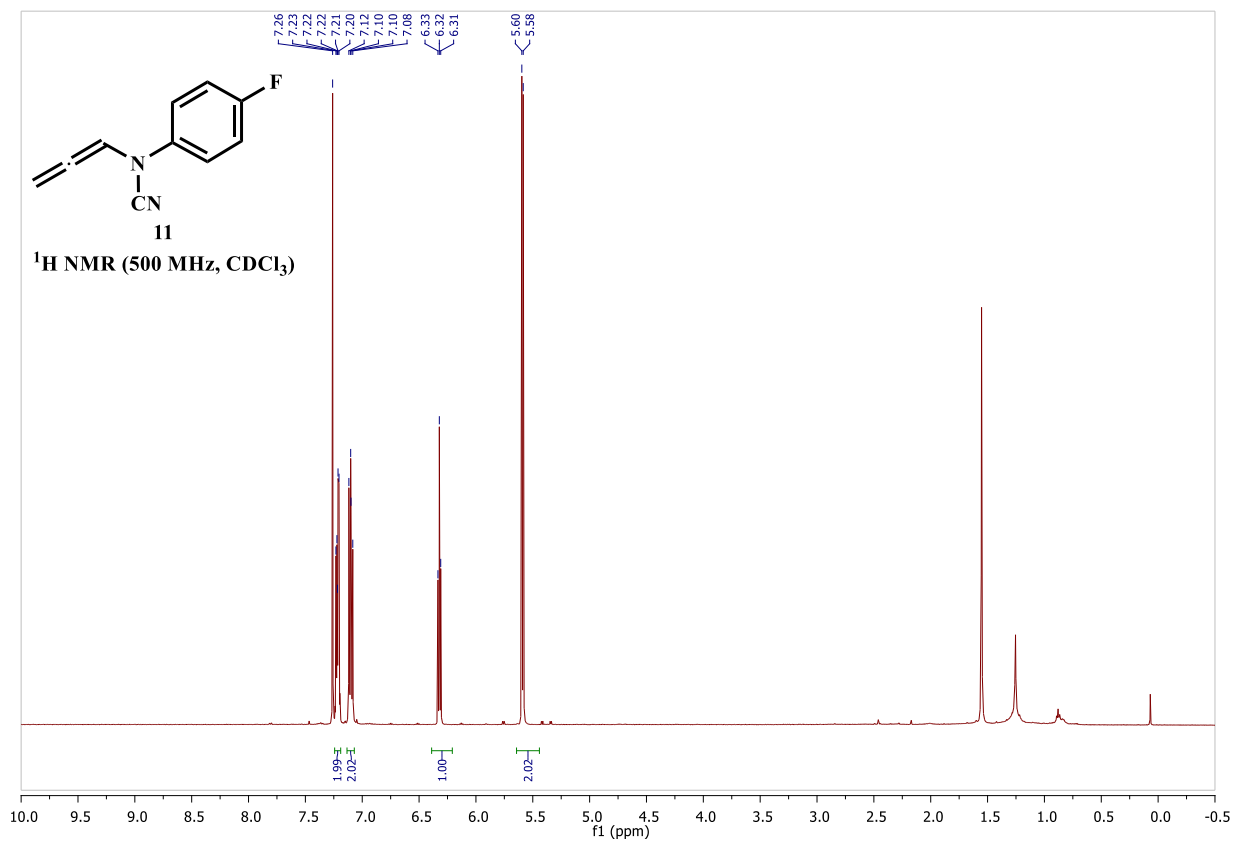


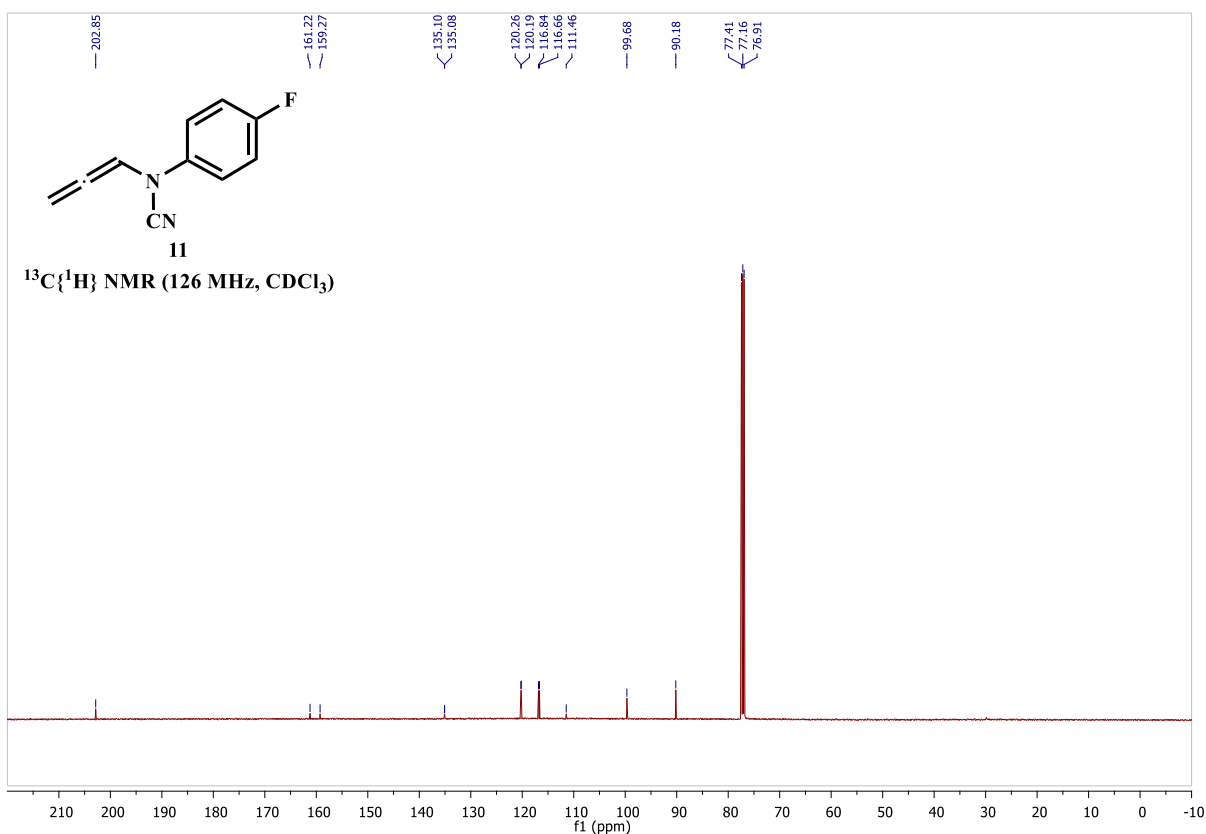


### *N*-(*p*-fluorophenyl)-*N*-(1,2-propdienyl)cyanamide

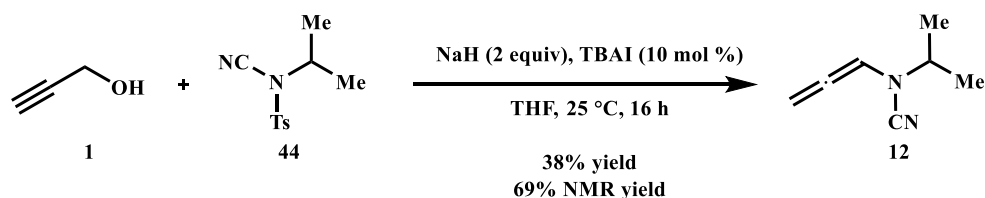


Following general procedure **3**, propargyl alcohol **1** (58  $\mu\text{L}$ , 1 mmol, 1 equiv), THF (5 mL), *N*-cyano-*N*-(*p*-fluorophenyl)-*p*-methylbenzenesulfonamide **40** (319 mg, 1.1 mmol, 1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes,  $30 \times 120$  mm silica) the titled compound **11** (92 mg, 0.53 mmol, 53% yield) as a white solid; mp 40-44  $^\circ\text{C}$ ;  $R_f = 0.50$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2223 ( $\text{C}\equiv\text{N}$ ), 1508, 1442, 1363, 1232, 1103, 889, 775, 619;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 5.59 (2H, d,  $J$  6.1), 6.32 (1H, t,  $J$  6.1), 7.08-7.12 (2H, m), 7.20-7.23 (2H, m);  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{F}}$ : -116.9;  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 90.2, 99.7, 111.5, 116.8 (d,  $J$  23.3), 120.2 (d,  $J$  8.3), 135.1 (d,  $J$  2.8), 160.24 (d,  $J$  245.6), 202.9; HRMS (NSI+) calculated for  $[\text{C}_{10}\text{H}_8\text{N}_2\text{F}_1]^+(\text{M}+\text{H})^+$  :  $m/z$  175.0662, found 175.0666 (-1.7 ppm).

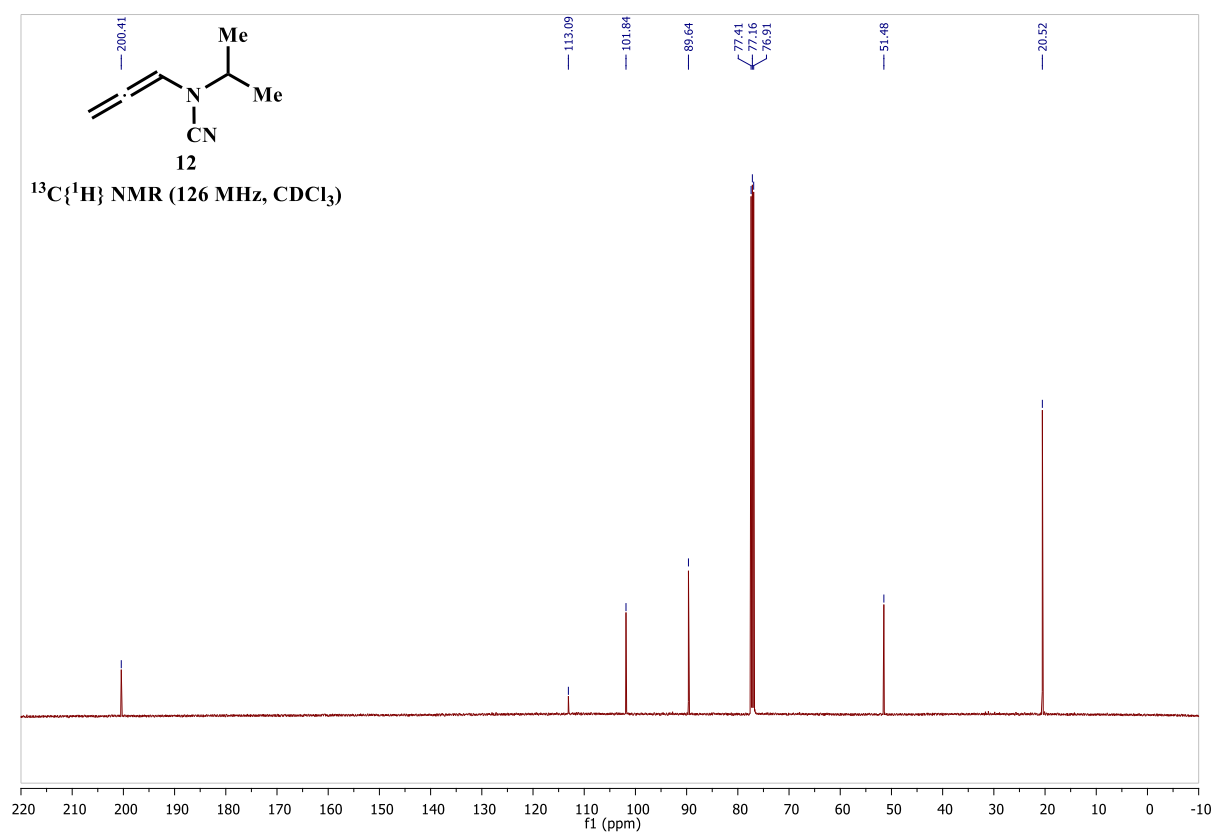
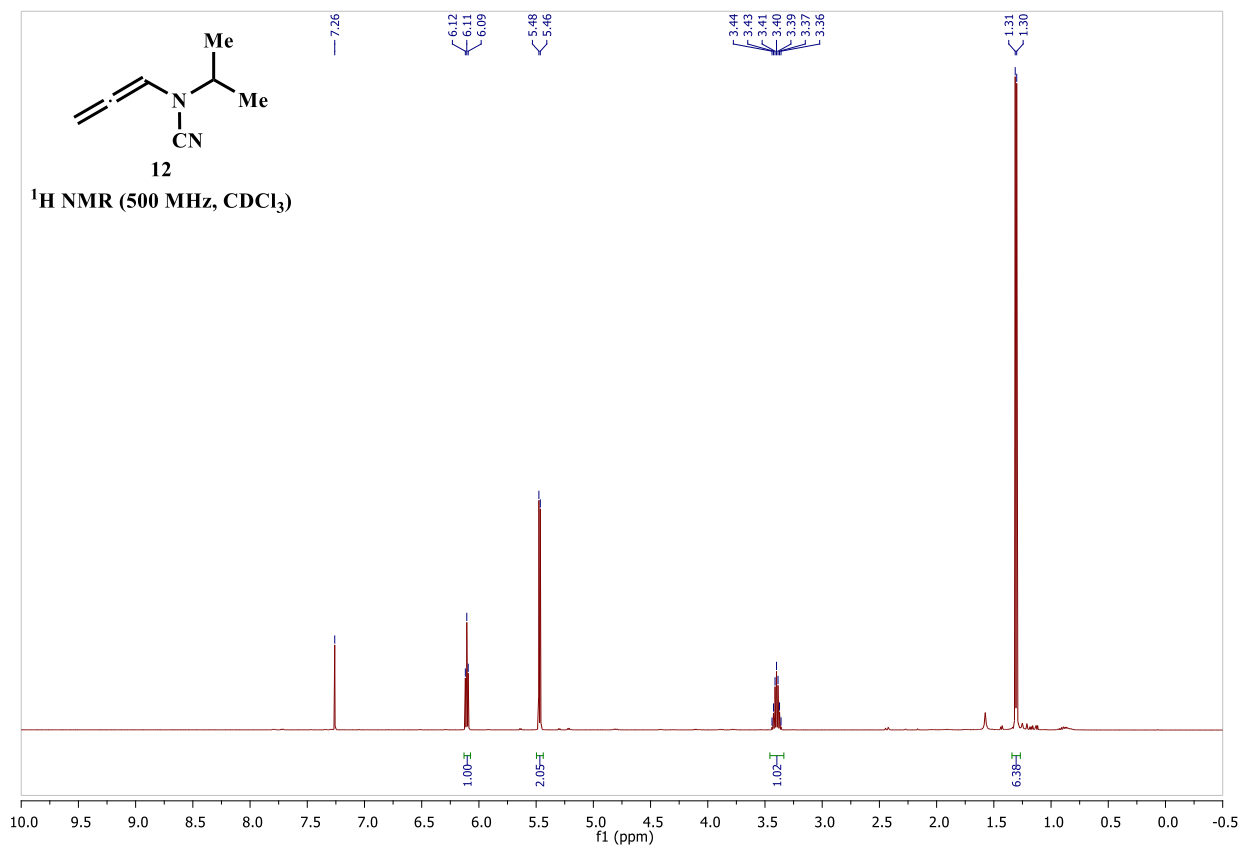




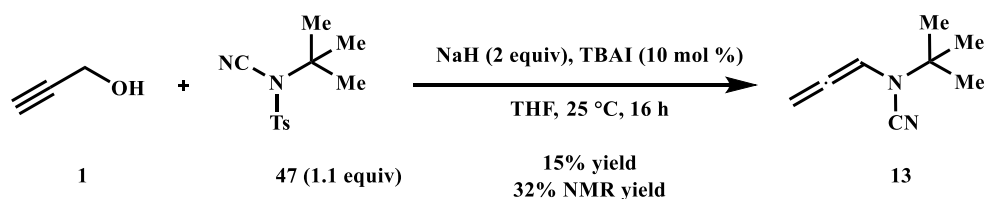
### *N*-isopropyl-*N*-(1,2-propdienyl)cyanamide



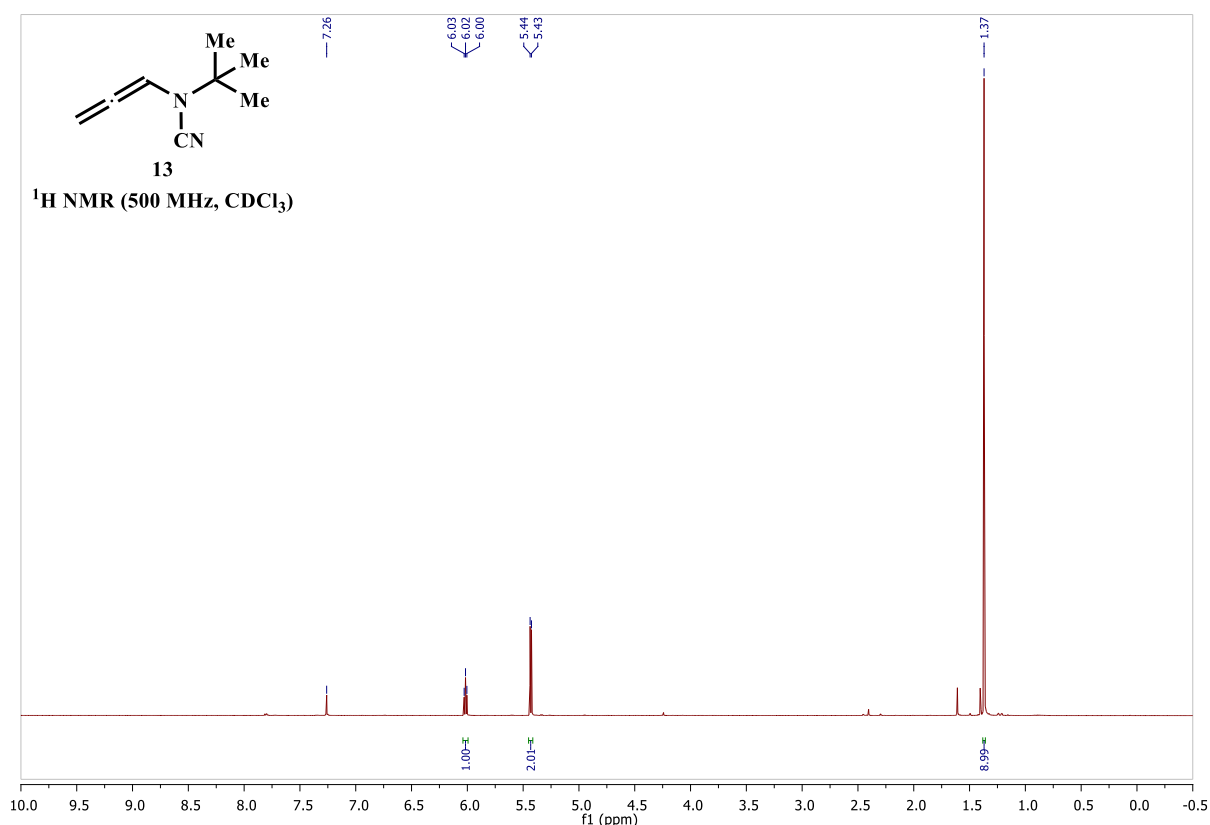
Following general procedure **3**, propargyl alcohol **1** (58  $\mu\text{L}$ , 1 mmol, 1 equiv), THF (5 mL), *N*-cyano-*N*-isopropyl-*p*-methylbenzenesulfonamide **44** (262 mg, 1.1 mmol, 1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes,  $30 \times 120$  mm silica) the titled compound **12** (46 mg, 0.38 mmol, 38% yield) as a volatile colourless oil;  $R_f = 0.42$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2216 ( $\text{C}\equiv\text{N}$ ), 1454, 1398, 1332, 1234, 1178, 1126, 1064, 887, 792, 717, 514;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 1.31 (6H, d,  $J$  6.6), 3.40 (1H, hept,  $J$  6.6), 5.47 (2H, d,  $J$  6.3), 6.11 (1H, t,  $J$  6.3);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 20.5, 51.5, 89.6, 101.8, 113.1, 200.4; HRMS (ASAP+) calculated for  $[\text{C}_7\text{H}_{11}\text{N}_2]^+(\text{M}+\text{H})^+$ :  $m/z$  123.0922, found 123.0912 (-8.1 ppm).

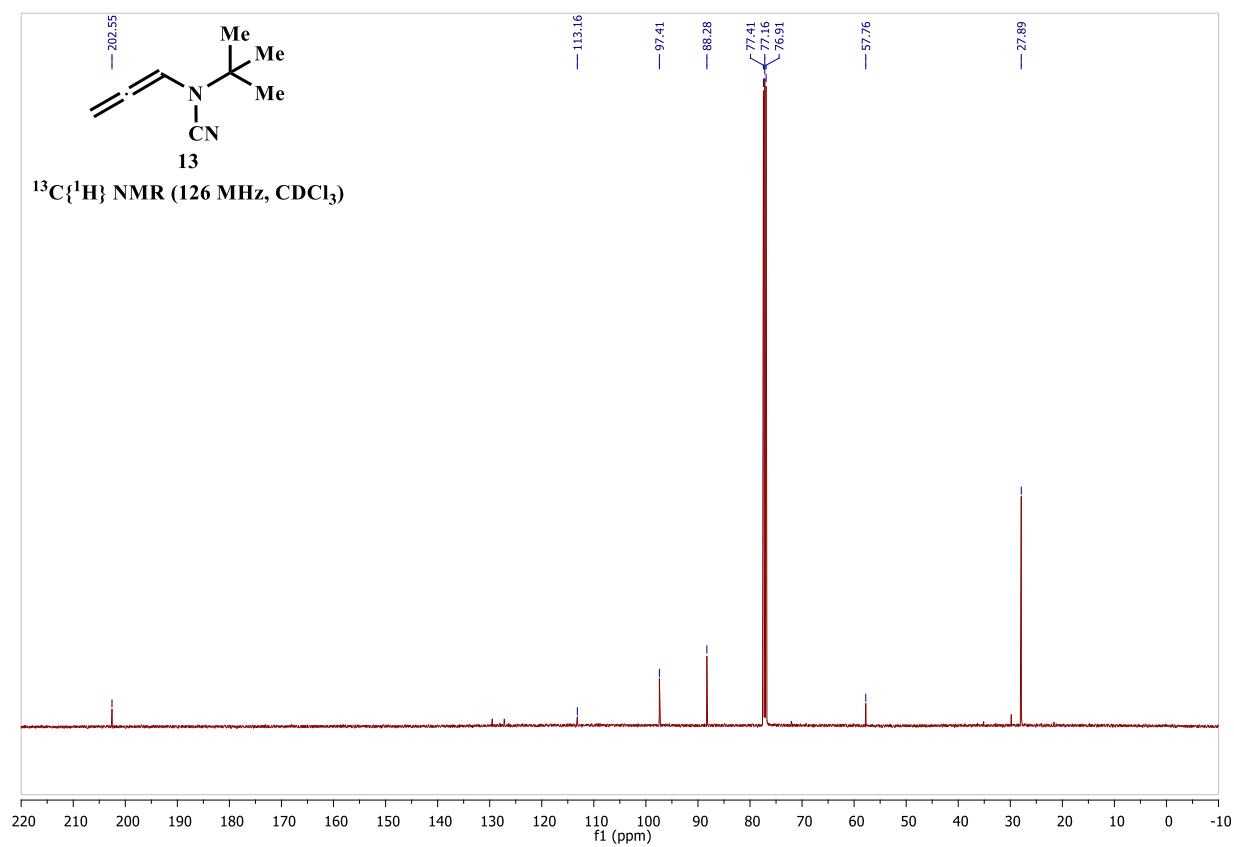


### *N*-(*tert*-butyl)-*N*-(1,2-propdienyl)cyanamide



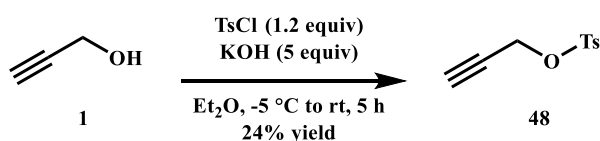
Following general procedure **3**, propargyl alcohol **1** (58  $\mu$ L, 1 mmol, 1 equiv), THF (5 mL), *N*-(*t*-butyl)-*N*-cyano-*p*-methylbenzenesulfonamide **47** (277 mg, 1.1 mmol, 1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 15-30% Et<sub>2</sub>O/Petrol 40-60, 30  $\times$  120 mm silica) the titled compound **13** (20 mg, 0.15 mmol, 15% yield) as a volatile colourless oil;  $R_f$  = 0.30 (eluent = 30% Et<sub>2</sub>O/Petrol 40-60);  $\nu_{\max}$  / cm<sup>-1</sup> (film): 2976, 2208 (C $\equiv$ N), 1444, 1373, 1300, 1197, 1004, 881; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta_H$ : 1.37 (9H, s), 5.43 (2H, d, *J* 6.1), 6.02 (1H, t, *J* 6.1); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>)  $\delta_C$ : 27.9, 57.8, 88.3, 97.4, 113.2, 202.6; HRMS (EI+) calculated for [C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>]<sup>+</sup>(M)<sup>+</sup>: *m/z* 136.1000, found 136.1001 (+0.7 ppm).



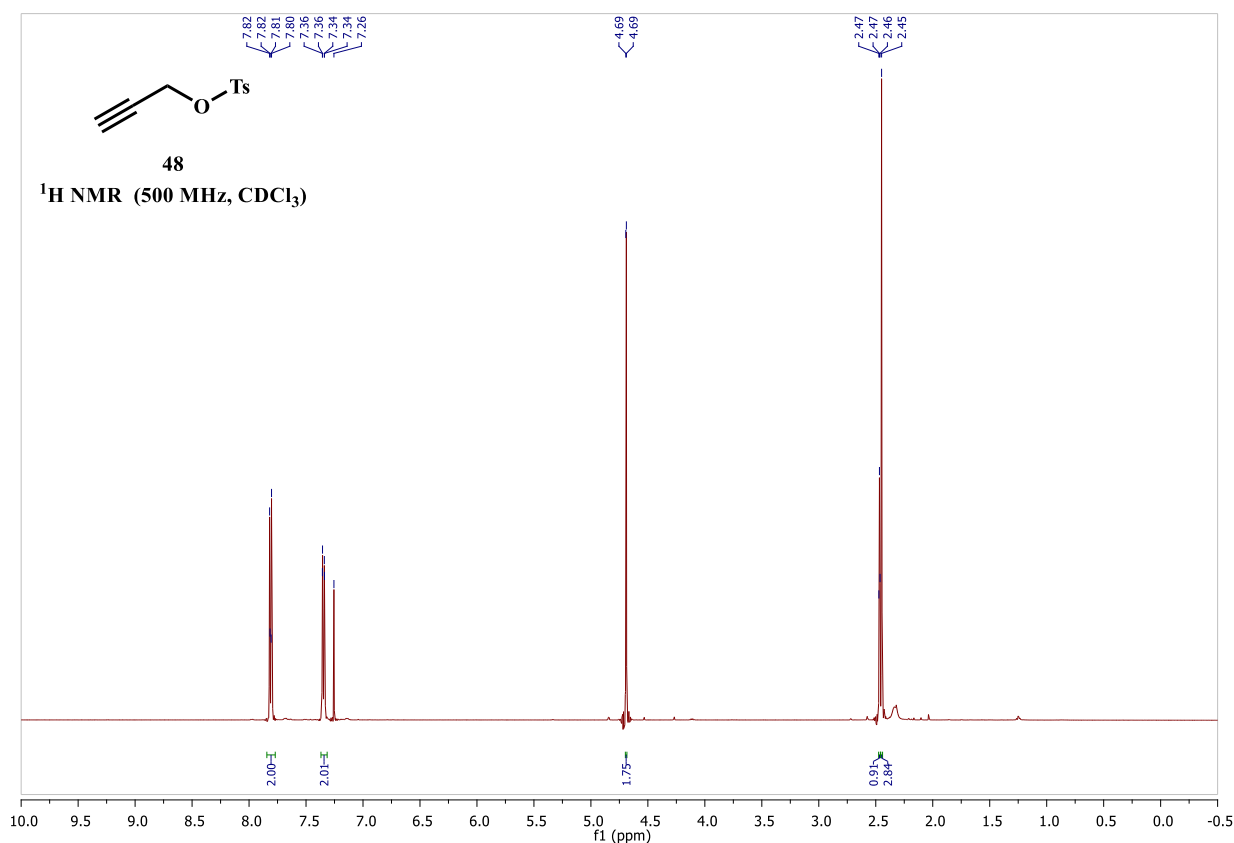


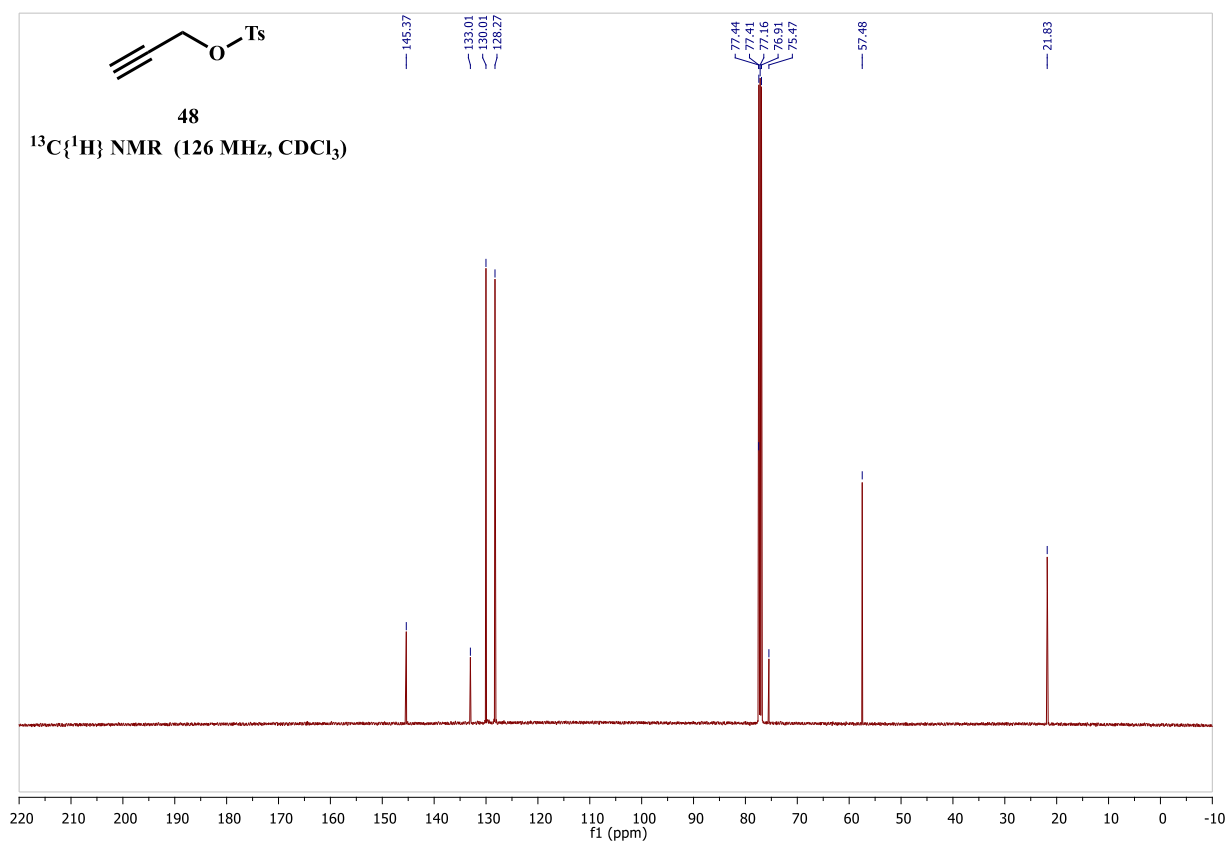
## 5. Mechanistic studies

### prop-2-yn-1-yl 4-methylbenzenesulfonate

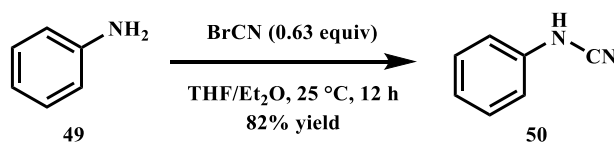


Following a modified literature procedure,<sup>4</sup> to a 100 mL round bottomed flask was added propargyl alcohol **1** (1.75 mL, 30 mmol, 1 equiv) followed by Et<sub>2</sub>O (30 mL) and tosyl chloride (6.9 g, 36 mmol, 1.2 equiv). The solution was cooled to -5 °C in an ice/water/NaCl bath before powdered KOH (8.4 g, 150 mmol, 5 equiv) was added portionwise. The reaction was stirred for 1 h at -5 °C before gradually warming to rt over 4 hours. The mixture was poured onto cold water (25 mL) and the layers separated. The aqueous layer was extracted with Et<sub>2</sub>O (× 3) and the combined ether extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solution was concentrated *in vacuo* and the resulting oil was purified by column chromatography (140 × 30mm silica, EtOAc 5%/hexanes) to yield the titled product **48** as clear brown oil with physical properties and spectroscopic data in accordance with the literature (1.48 g, 7.0 mmol, 24%);<sup>4</sup> R<sub>f</sub> = 0.40 (eluent = 20% EtOAc in hexanes); ν<sub>max</sub>/cm<sup>-1</sup> (film): 3284, 1598, 1352, 1170, 1091, 975, 921, 802, 661, 547; ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 2.45 (3H, s), 2.47 (1H, t, *J* 2.5), 4.69 (2H, d, *J* 2.5), 7.35 (2H, d, *J* 8.0), 7.81 (2H, d, *J* 8.4); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 21.8, 57.5, 75.47, 77.4, 128.3, 130.0, 133.0, 145.4; MS (ASAP+) [C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>S]<sup>+</sup> 211.04.

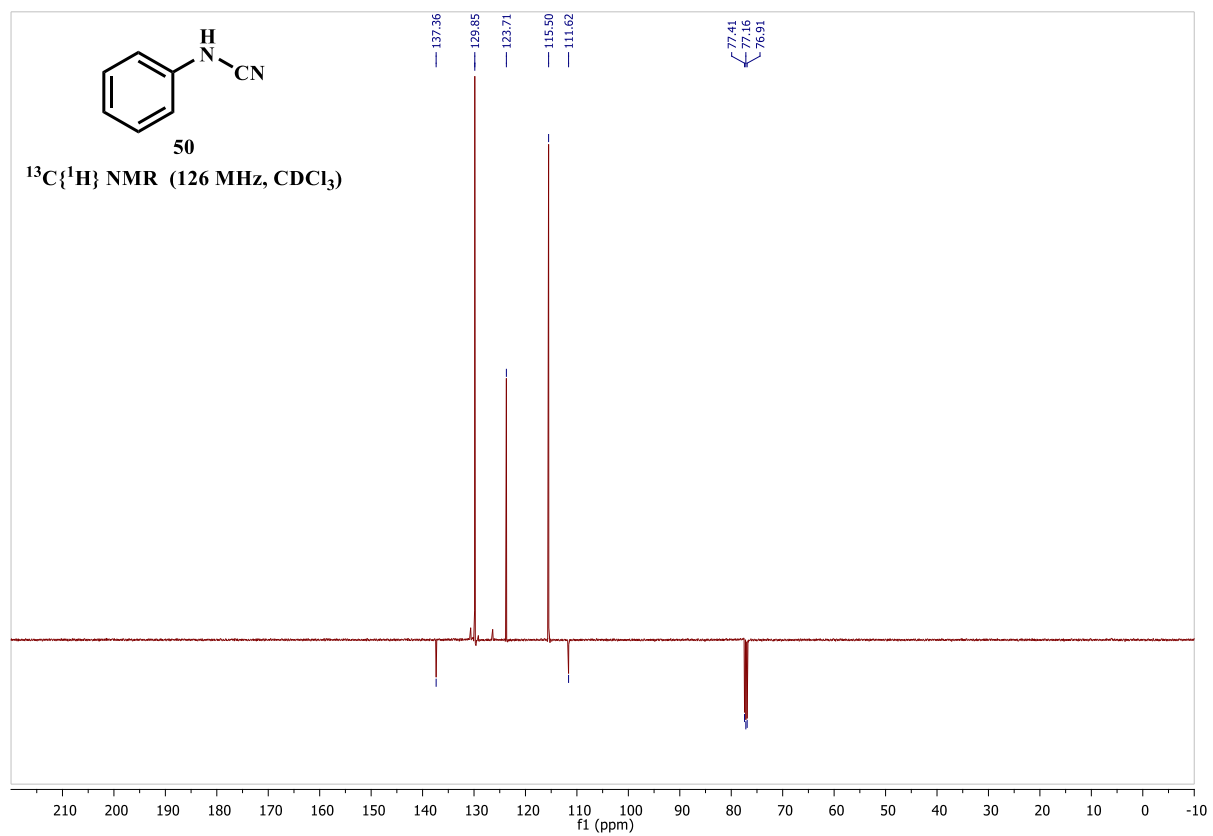
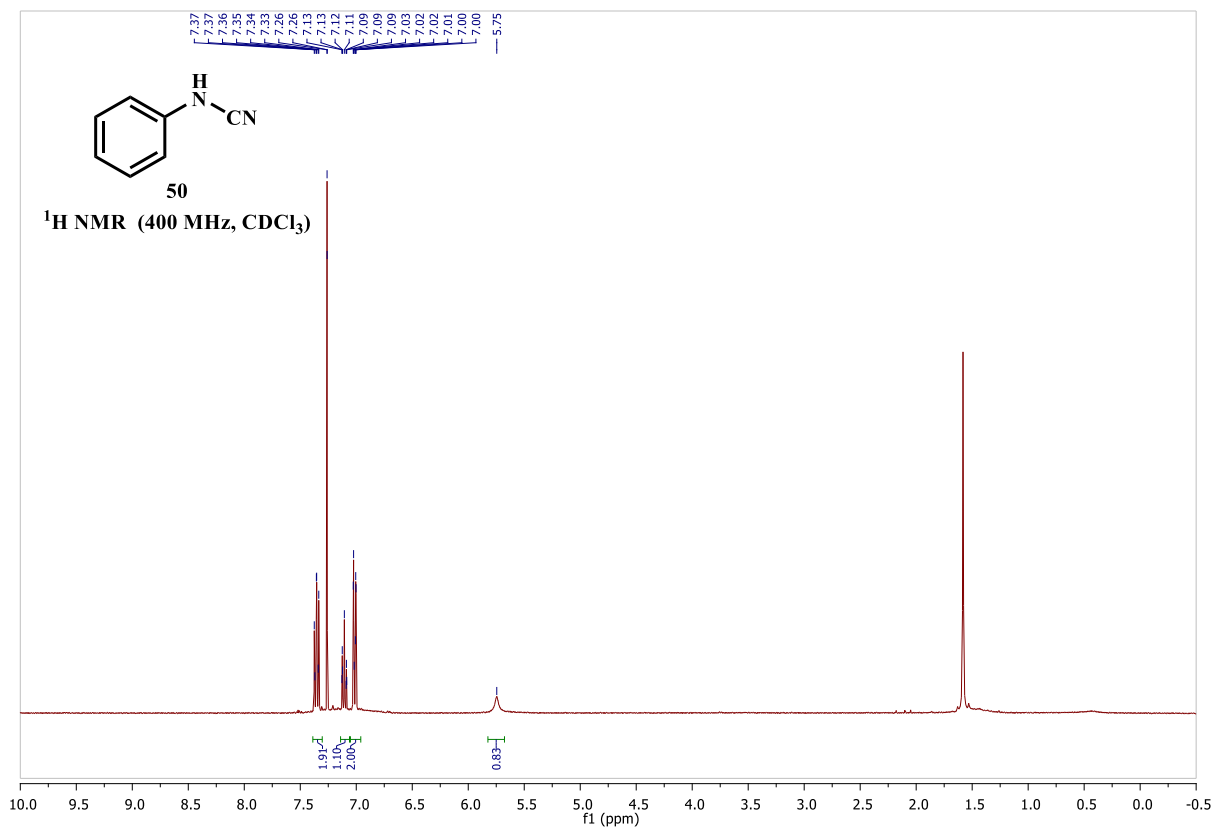




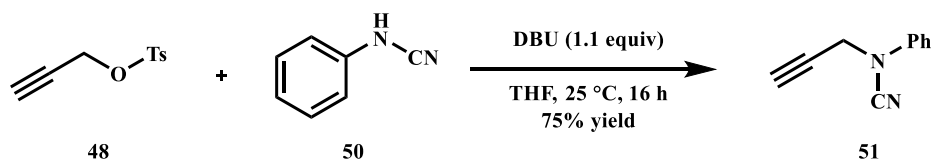
### *N*-phenylcyanamide



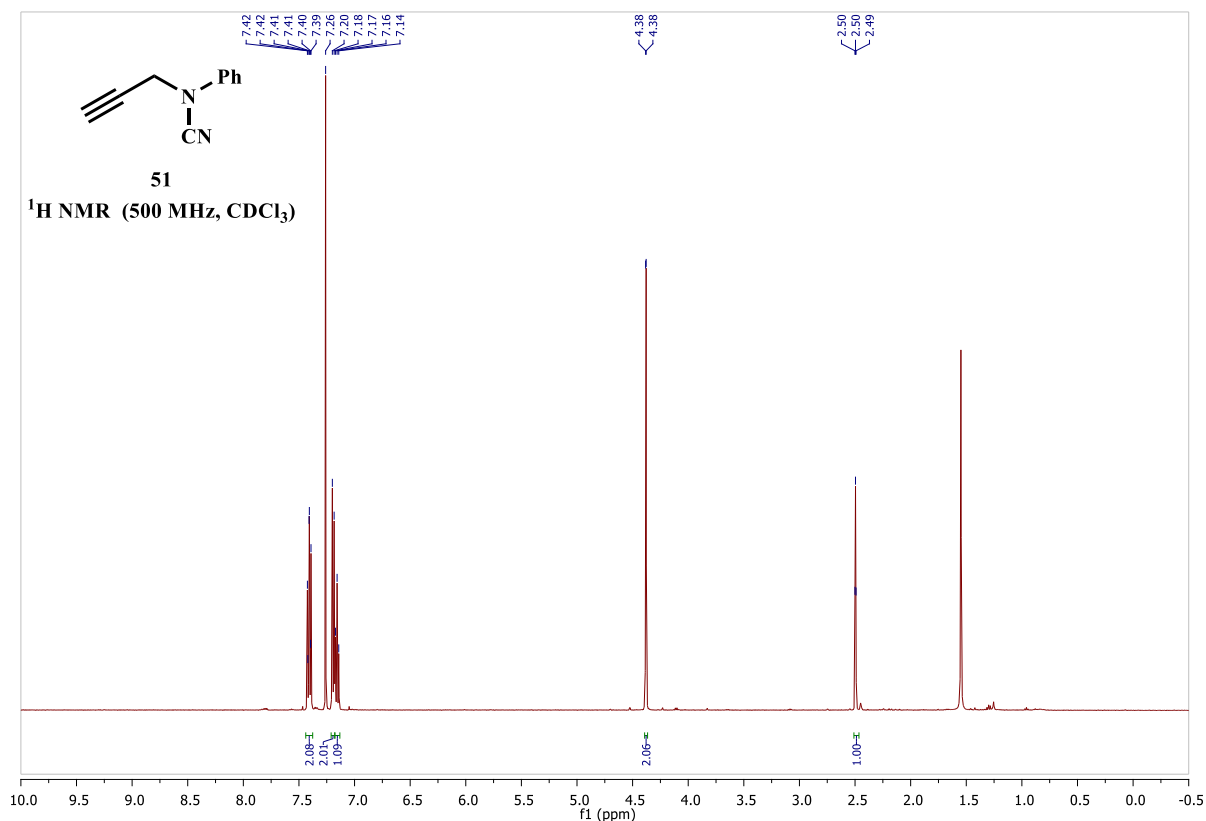
To a 100 mL round-bottom flask containing a magnetic stirrer bar was charged cyanogen bromide (1.82 g, 17 mmol, 0.63 equiv), THF (18 mL) and diethyl ether (6 mL). The solution was cooled to 0 °C before addition of aniline **49** (2.48 mL, 27 mmol, 1 equiv). The reaction mixture was then stirred for 12 h at 25 °C. The mixture was then concentrated in vacuo to give a crude solid. The solid was dissolved in water, and a precipitate was formed. The mixture was then filtered and washed with hexanes to give the titled product **50** (1.64 g, 14 mmol, 82% yield) as a brown solid with physical properties and spectroscopic data in accordance with the literature;<sup>5</sup> mp 37-38 °C (Lit. 44-46 °C)<sup>5</sup>; R<sub>f</sub> = 0.3 (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}}$  /  $\text{cm}^{-1}$  (film): 3387, 3150, 3098, 2986, 2909, 2224 (C≡N), 1599, 1497, 1435, 1252, 735, 681, 484;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 5.75 (1H, s), 7.00-7.03 (2H, m), 7.09-7.13 (1H, m), 7.33-7.37 (2H, m);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 111.6, 115.5, 123.7, 129.9, 137.4.

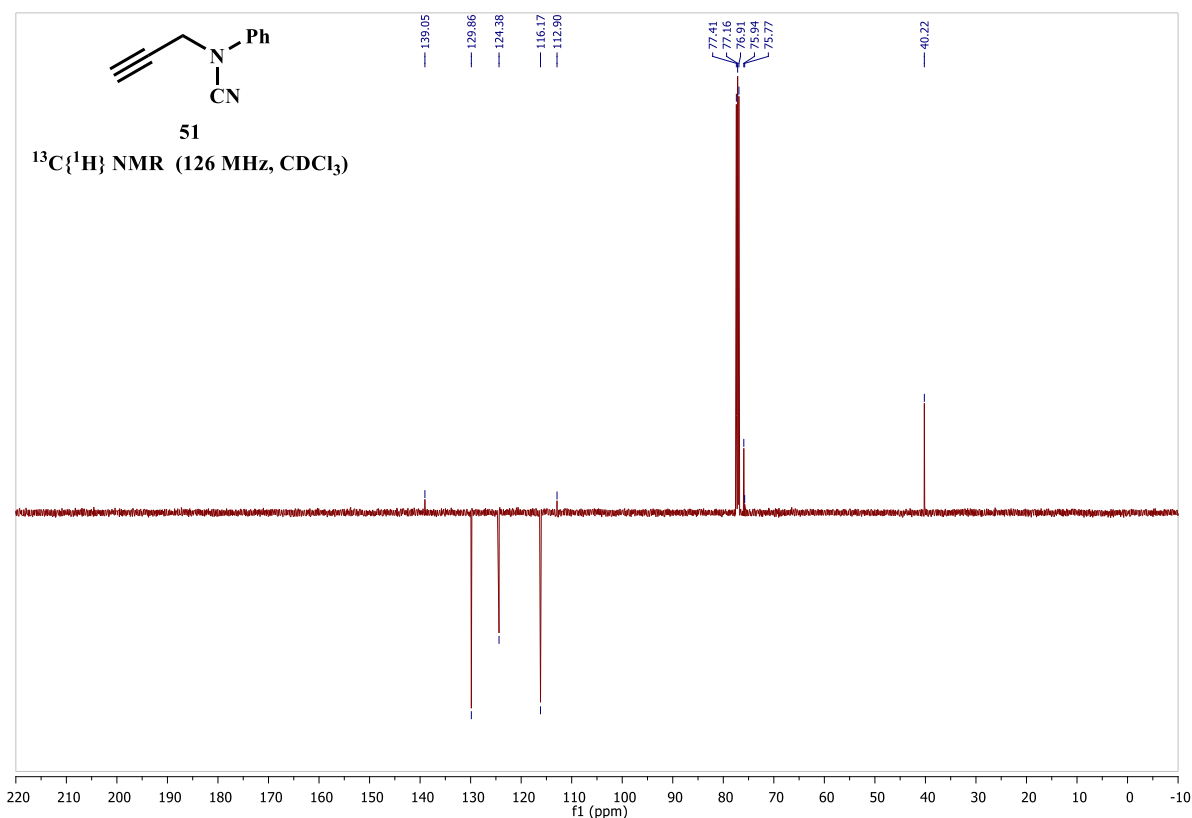


### *N*-phenyl-*N*-(prop-2-yn-1-yl)cyanamide

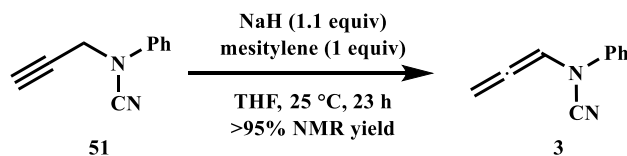


To a reaction vial was added prop-2-yn-1-yl 4-methylbenzenesulfonate **48** (547 mg, 2.73 mmol, 1 equiv) followed by *N*-phenylcyanamide **50** (322 mg, 2.37 mmol, 1 equiv) and THF (10 mL). The solution was stirred before DBU (512  $\mu$ L, 3.0 mmol, 1.1 equiv) was added. The reaction was stirred for 16 h at rt. The reaction was quenched with sat. aq.  $\text{NH}_4\text{Cl}$  and extracted with EtOAc ( $\times 3$ ). The combined organic phase was then washed with brine and dried over  $\text{MgSO}_4$  filtered. The solution was concentrated *in vacuo* before purification by silica gel column chromatography (120  $\times$  30 mm, EtOAc 10%/hexanes) to yield the titled compound **51** as off white crystals (320.3 mg, 2.05 mmol, 75%); mp 33-35  $^\circ\text{C}$ ;  $R_f = 0.36$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 3284, 2960, 2221 ( $\text{C}\equiv\text{N}$ ), 1598, 1498, 1373, 1330, 1188, 1043, 923, 740, 680, 486;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.50 (1H, t,  $J$  2.5), 4.38 (2H, d,  $J$  2.5), 7.16 (1H, t,  $J$  7.4), 7.19 (2H, d,  $J$  8.0), 7.41 (2H, dd,  $J$  8.7, 7.5);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 40.2, 75.8, 75.9, 112.9, 116.2, 124.4, 129.9, 139.1; HRMS ( $\text{EI}^+$ ) calculated for  $[\text{C}_{10}\text{H}_8\text{N}_2]^+$ :  $m/z$  156.0687 found 156.0681 (-3.8 ppm).



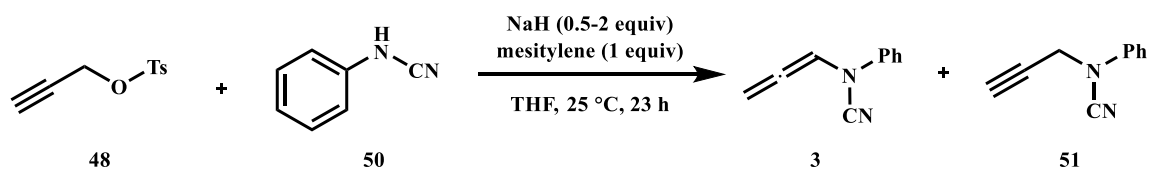


### *N*-phenyl-*N*-(1,2-propadienyl)cyanamide



To a reaction vial was added *N*-phenyl-*N*-(prop-2-yn-1-yl)cyanamide **51** (31 mg, 0.2, 1 equiv) followed by THF (1 mL) and mesitylene (28  $\mu\text{L}$ , 0.2 mmol, 1 equiv). The solution was stirred before NaH (9 mg, 0.22 mmol, 1.1 equiv) was added. The reaction was stirred for 23 h at rt before an aliquot was taken and added to an NMR tube with  $\text{CDCl}_3$ . The reaction was analysed by  $^1\text{H}$  NMR to determine the conversion to the allene with mesitylene as internal standard. The titled compound **3** was observed in >95% NMR yield with all spectroscopic data in accordance with those previously obtained.

### *N*-phenyl-*N*-(1,2-propdienyl)cyanamide

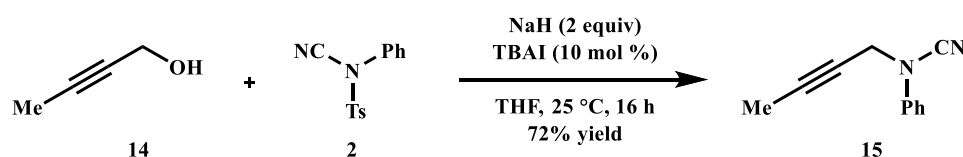


To a reaction vial was added prop-2-yn-1-yl 4-methylbenzenesulfonate **48** (53 mg, 0.25 mmol, 1 equiv), *N*-phenylcyanamide **50** (29 mg, 0.25 mmol, 1 equiv), mesitylene and THF (1 mL). The requisite amount of NaH (0.5-2 equiv) was then added and the reaction was stirred for 23 h at rt. Aliquots were then taken and added to an NMR tube with CDCl<sub>3</sub>. The reactions were analysed by <sup>1</sup>H NMR with mesitylene as internal standard to determine the composition of the reaction mixture of **3** to **51**.

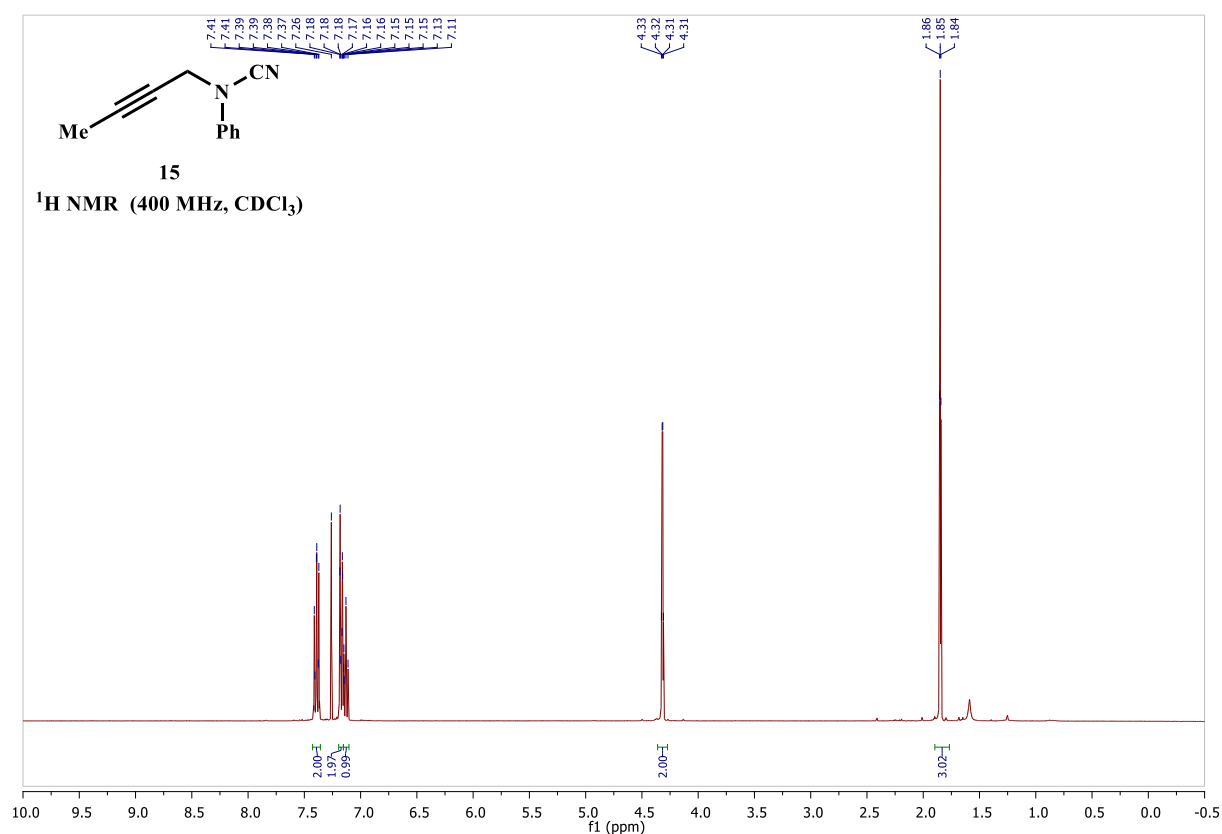
NaH used (equiv)	0.5	1	1.5	2
Propargyl tosylate remaining (%)	51	27	25	<5
Conversion to <i>N</i> -propargy cyanamide (%)	49	30	19	<5
Conversion to <i>N</i> -allenyl cyanamide (%)	0	31	46	90

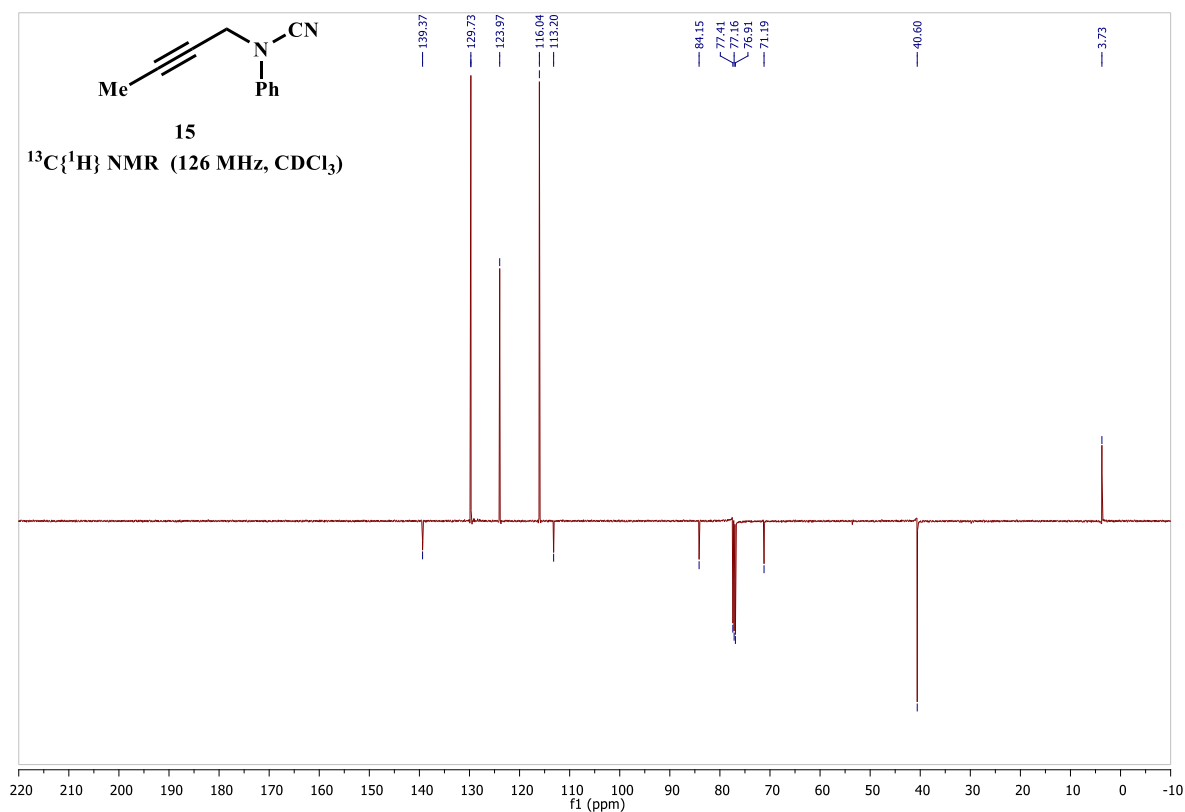
## 6. Employing substituted propargyl alcohols

### *N*-(but-2-yn-1-yl)-*N*-phenylcyanamide

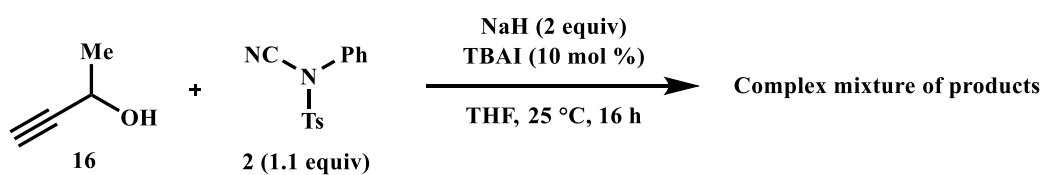


Following general procedure **4**, but-2-yn-1-ol **14** (75  $\mu$ L, 1 mmol, 1 equiv), THF (5 mL), *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide **2** (299 mg, 1.1 mmol, 1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave after flash column chromatography (eluent = 10% EtOAc in hexanes, 30  $\times$  120 mm silica) the titled compound **15** (122 mg, 0.72 mmol, 72% yield) as a white solid; mp 50-52 °C;  $R_f$  = 0.54 (eluent = 20% EtOAc in hexanes);  $\nu_{\max}$  /  $\text{cm}^{-1}$  (film): 2216 ( $\text{C}\equiv\text{N}$ ), 1603, 1495, 1362, 1223, 1184, 907, 731, 687, 648, 496;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 1.85 (3H, t,  $J$  2.4), 4.32 (2H, q,  $J$  2.4), 7.11-7.19 (3H, m), 7.36-7.42 (2H, m);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 3.7, 40.6, 71.2, 84.2, 113.2, 116.0, 124.0, 129.7, 139.4; HRMS (ASAP+) calculated for  $[\text{C}_{11}\text{H}_{11}\text{N}_2]^+$ :  $m/z$  171.0917 found 171.0914 (-1.6 ppm).





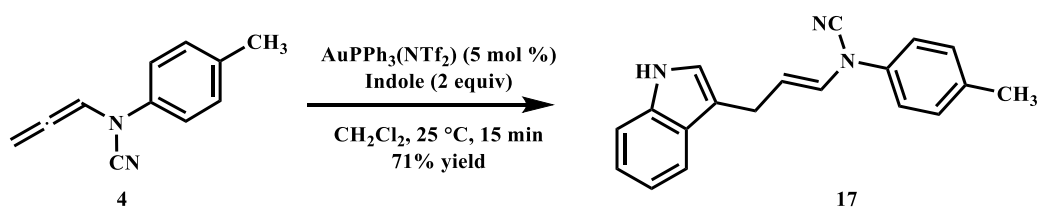
### Reaction of but-3-yn-2-ol



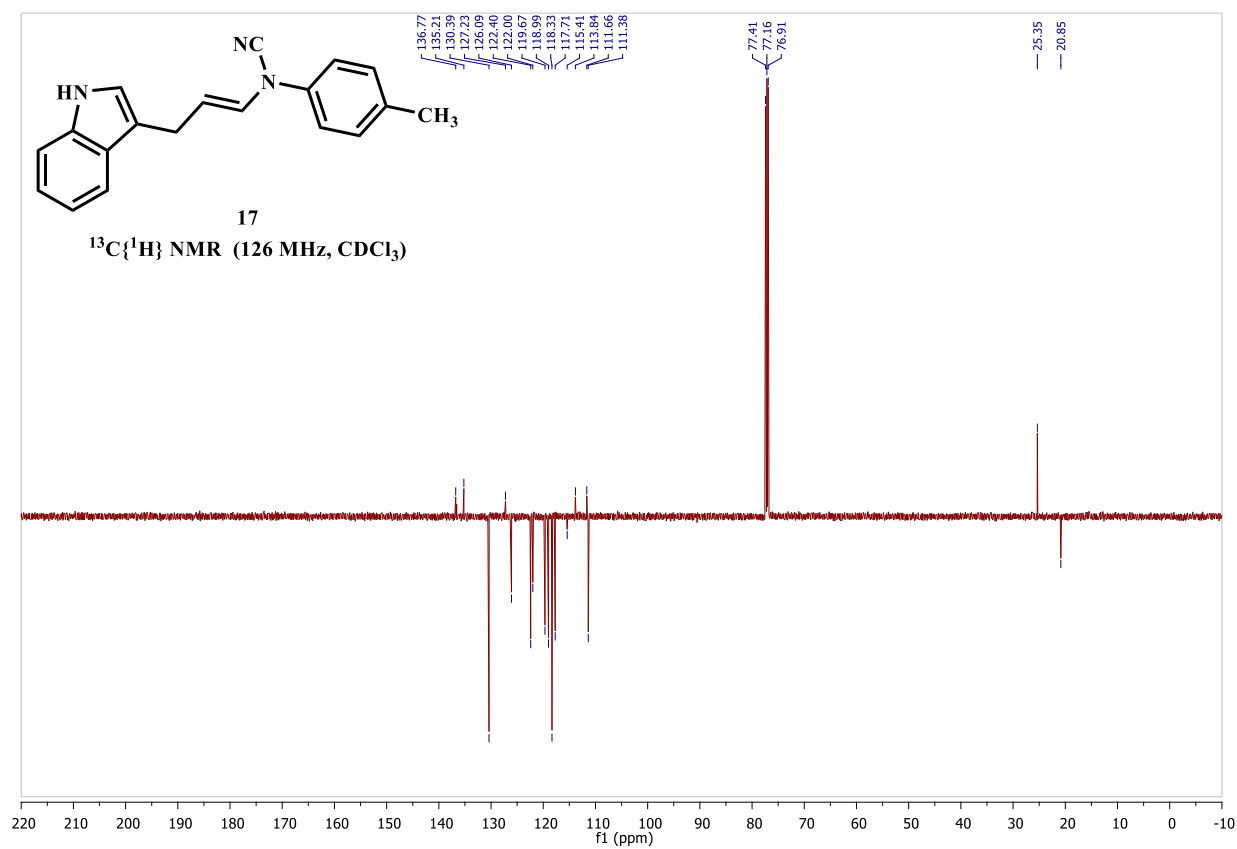
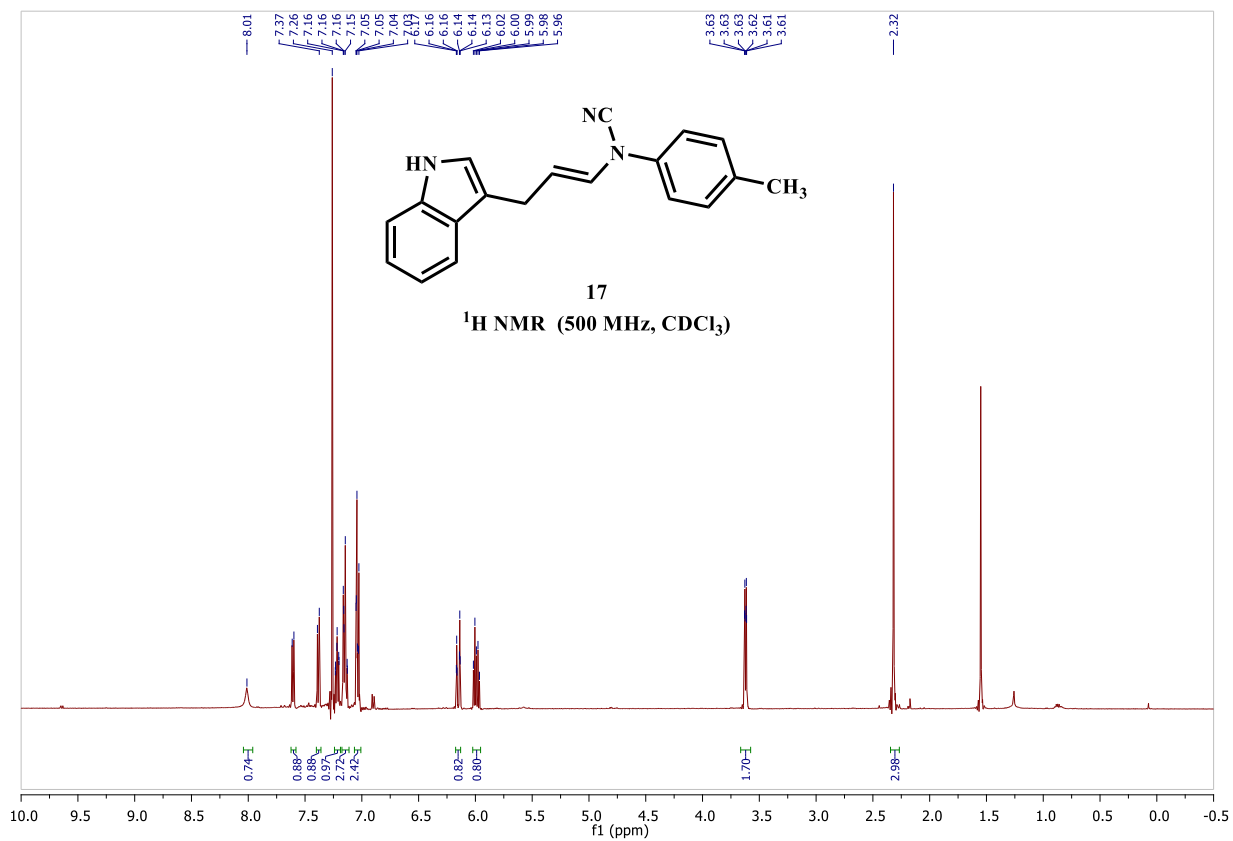
Following general procedure **2**, but-3-yn-2-ol **16** (75  $\mu\text{L}$ , 1 mmol, 1 equiv), THF (5 mL), *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide **2** (299 mg, 1.1 mmol, 1 equiv), TBAI (37 mg, 0.1 mmol, 0.1 equiv) and NaH (60%) (80 mg, 2 mmol, 2 equiv) gave a complex mixture of products.

## 7. Derivatization of *N*-cyano allenamides

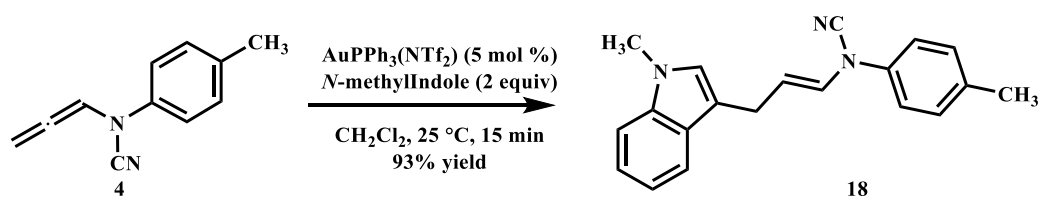
### (*E*)-*N*-(3-(indolin-3-yl)prop-1-en-1-yl)-*N*-(*p*-tolyl)cyanamide



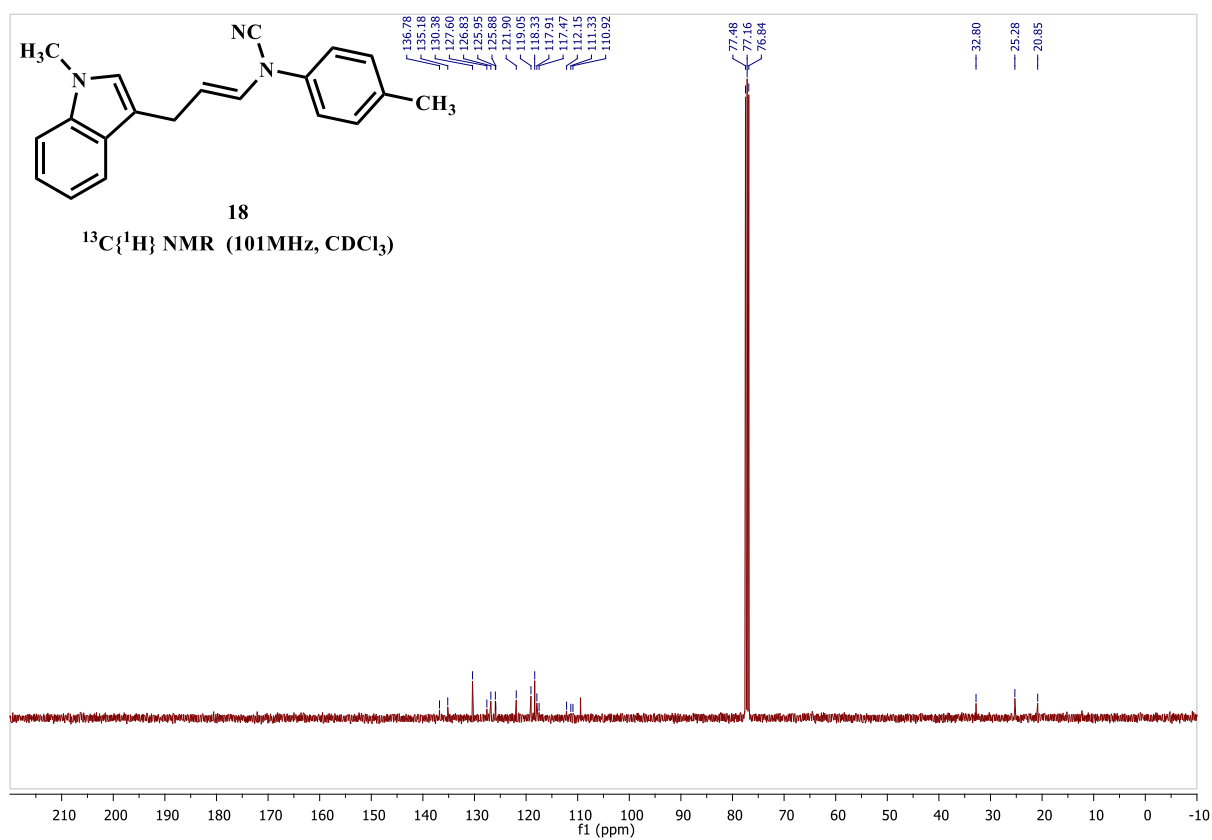
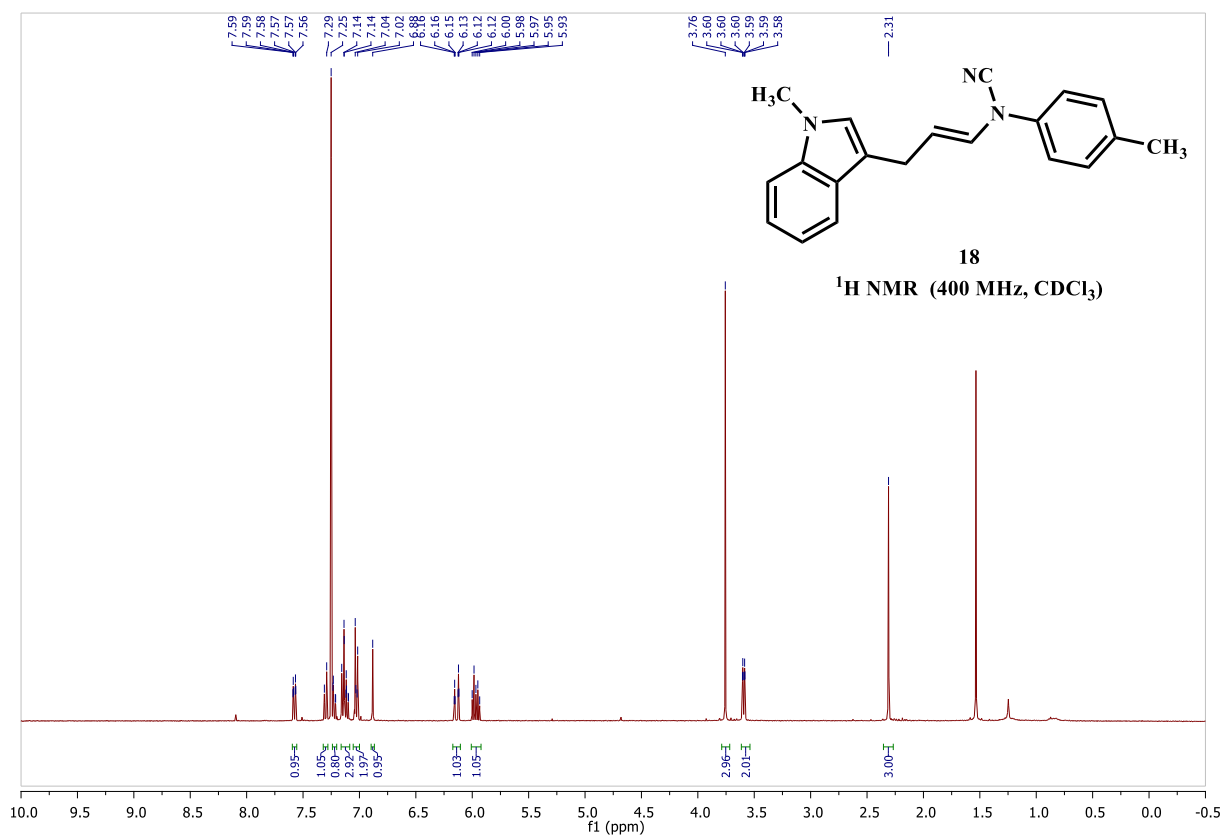
Following a modified literature procedure,<sup>6</sup> to a reaction vial was added *N*-(1,2-propadienyl)-*N*-(*p*-tolyl)cyanamide **4** (54 mg, 0.32 mmol, 1 equiv), CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and indole (75 mg, 0.64 mmol, 2 equiv). The solution was stirred and AuPPh<sub>3</sub>(NTf<sub>2</sub>) (25 mg, 0.016 mmol, 0.05 equiv) was added. The reaction was stirred at rt and monitored by TLC. After completion (15 min) the reaction mixture was filtered through celite and the crude mixture purified by silica gel column chromatography (eluent = 5-15% EtOAc in hexanes, 25 × 120 mm silica) the titled compound **17** (65 mg, 0.23 mmol, 71% yield) as a white solid; mp 74-76 °C; R<sub>f</sub> = 0.26 (eluent = 20% EtOAc in hexanes); ν<sub>max</sub> / cm<sup>-1</sup> (film): 2357, 2330, 2231 (C≡N), 1662, 1514, 1452, 1334, 1230, 1087, 810, 740, 497; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 2.32 (3H, s), 3.61-3.63 (2H, m), 5.99 (1H, dt, *J* 13.4, 6.5), 6.15 (1H, dt, *J* 13.6, 1.5), 7.03-7.05 (3H, m), 7.13-7.16 (3H, m), 7.20, 7.23 (1H, m), 7.38 (1H, d, *J* 8.1), 7.61 (1H, d, *J* 7.5), 8.01 (1H, s); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 20.9, 25.4, 111.4, 111.7, 113.8, 115.4, 117.7, 118.3, 119.0, 119.7, 122.0, 122.4, 126.1, 127.2, 130.4, 135.2, 136.8; HRMS (NSI<sup>+</sup>) calculated for [C<sub>19</sub>H<sub>18</sub>N<sub>3</sub>]<sup>+</sup>(M)<sup>+</sup>: m/z 288.1495, found 288.1498 (+1.0 ppm).



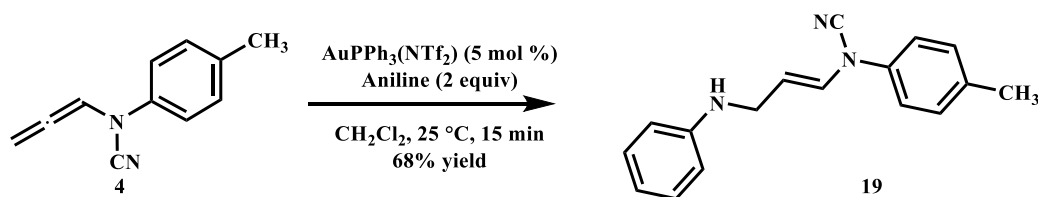
**(E)-N-(3-(1-methylindolin-3-yl)prop-1-en-1-yl)-N-(p-tolyl)cyanamide**



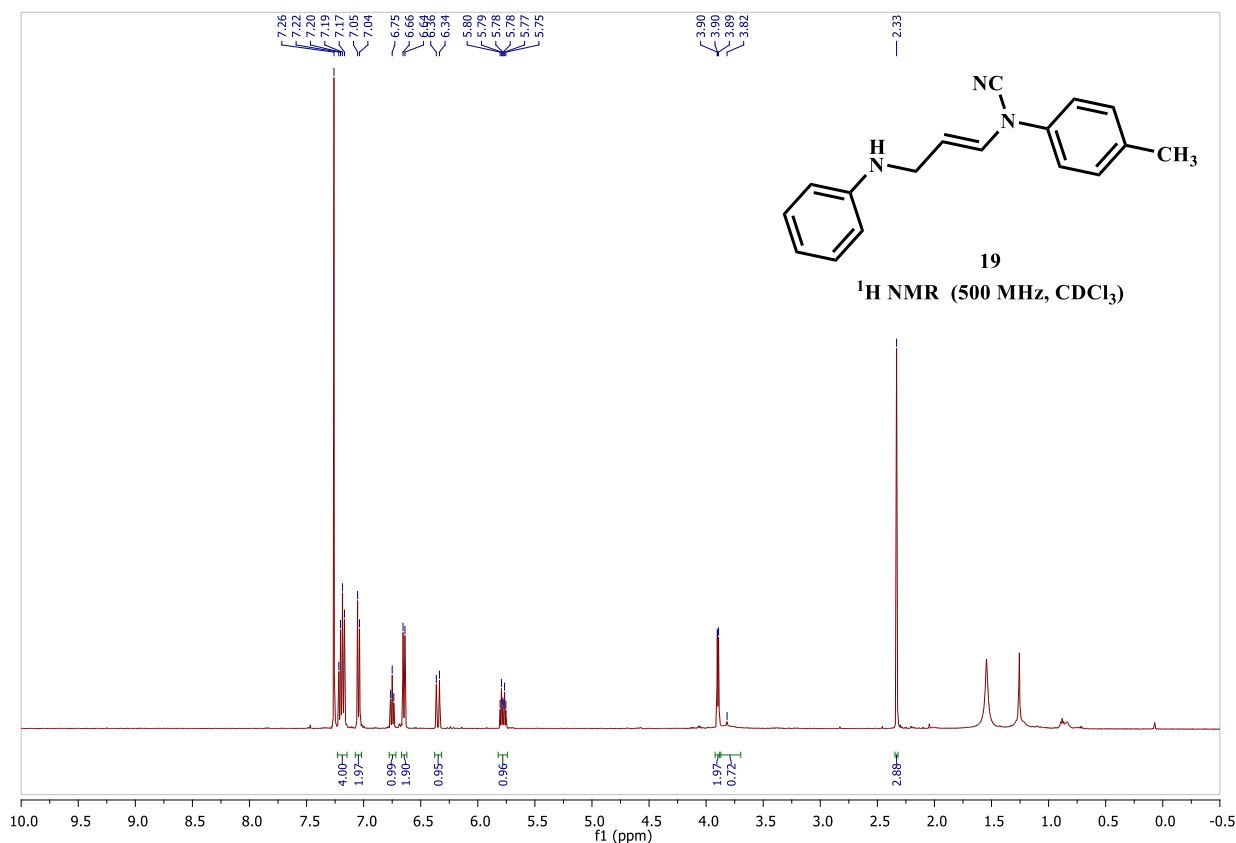
Following a modified literature procedure,<sup>6</sup> to a reaction vial was added *N*-(1,2-propdienyl)-*N*-(*p*-tolyl)cyanamide **4** (54 mg, 0.32 mmol, 1 equiv), CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and *N*-methylindole (84 mg, 0.64 mmol, 2 equiv). The solution was stirred and AuPPh<sub>3</sub>(NTf<sub>2</sub>) (25 mg, 0.016 mmol, 0.05 equiv) was added. The reaction was stirred at rt and monitored by TLC. After completion (15 min) the reaction mixture was filtered through celite and the crude mixture purified by silica gel column chromatography (eluent = 5-15% EtOAc in hexanes, 25 × 120 mm silica) the titled compound **18** (90 mg, 0.30 mmol, 93% yield) as a white solid; mp 91-94 °C; R<sub>f</sub> = 0.45 (eluent = 20% EtOAc in hexanes); ν<sub>max</sub> / cm<sup>-1</sup> (film): 2214 (C≡N), 1662, 1610, 1512, 1469, 1377, 1327, 1232, 1006, 935, 813, 738; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 2.31 (3H, s), 3.58-3.60 (2H, m) 3.76 (3H, s), 5.93-6.00 (1H, m), 6.14 (1H, dt *J* 13.6, 1.5), 6.88 (1H, s), 7.02-7.04 (2H, m), 7.12-7.16 (3H, m), 7.22 (1H, dd, *J* 8.2, 1.2), 7.30 (1H, d *J* 8.2), 7.56-7.59 (1H, m); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 20.9, 25.3, 32.8, 110.9, 111.3, 112.2, 117.4, 117.9, 118.3, 119.1, 119.1, 121.9, 125.9, 125.9, 126.8, 130.4, 135.2, 136.8; HRMS (NSI+) calculated for [C<sub>20</sub>H<sub>20</sub>N<sub>3</sub>]<sup>+</sup>(M)<sup>+</sup> : m/z 302.1656, found 302.1652 (+1.4 ppm).

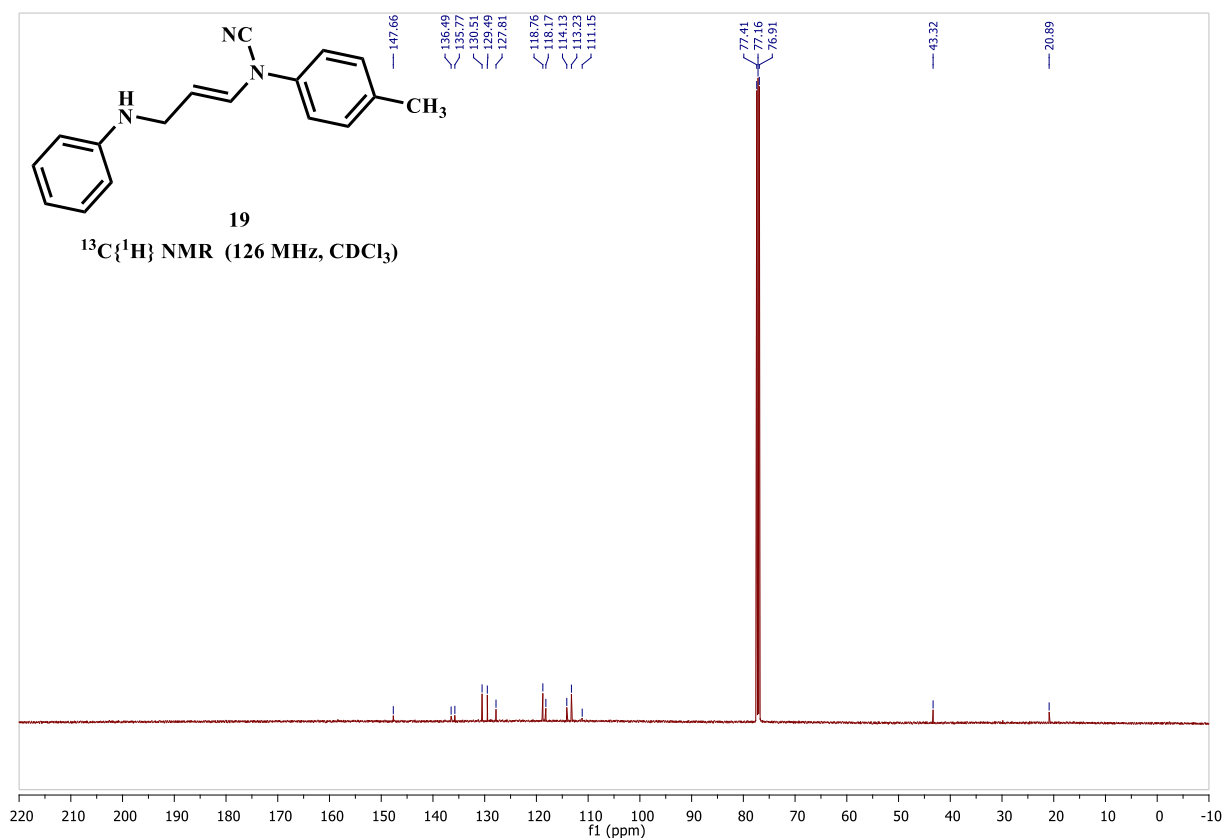


**(E)-N-(3-(phenylamino)prop-1-en-1-yl)-N-(p-tolyl)cyanamide**

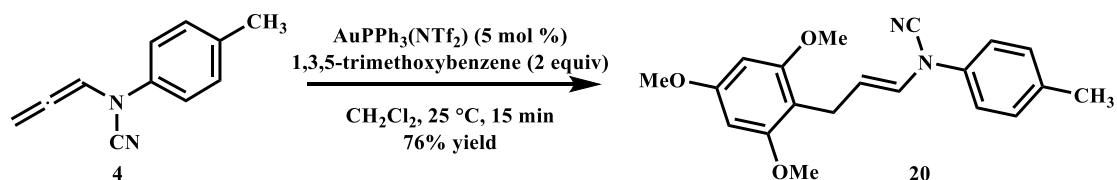


Following a modified literature procedure,<sup>7</sup> to a reaction vial was added *N*-(1,2-propadienyl)-*N*-(*p*-tolyl)cyanamide **4** (54 mg, 0.32 mmol, 1 equiv),  $\text{CH}_2\text{Cl}_2$  (1 mL) and aniline (31 mg, 0.34 mmol, 1.05 equiv). The solution was stirred and  $\text{AuPPh}_3(\text{NTf}_2)$  (25 mg, 0.016 mmol, 0.05 equiv) was added. The reaction was stirred at rt and monitored by TLC. After completion the reaction mixture was filtered through celite and the crude mixture purified by silica gel column chromatography (eluent = 10% EtOAc in hexanes,  $25 \times 120$  mm silica) the titled compound **19** (57 mg, 0.22 mmol, 68% yield) as a white solid; mp 95-97 °C;  $R_f = 0.40$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2218 ( $\text{C}\equiv\text{N}$ ) 1602, 1508, 1236, 931, 810, 752, 690;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.33 (3H, s), 3.82 (1H, br s), 3.89-3.90 (2H, m), 5.78 (1H, dt,  $J$  13.6, 5.7), 6.35 (1H, d,  $J$  13.7), 6.65 (2H, d,  $J$  8.4), 6.75 (1H, t,  $J$  7.2), 7.04 (2H, d,  $J$  8.4), 7.17-7.22 (4H, m);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 20.9, 43.3, 111.2, 113.2, 114.1, 118.2, 118.8, 127.8, 129.5, 130.5, 135.8, 136.5, 147.7; HRMS (NSI+) calculated for  $[\text{C}_{17}\text{H}_{17}\text{N}_3]^+(\text{M}+\text{H})^+$ :  $m/z$  264.1495, found 264.1399 (+1.4 ppm).

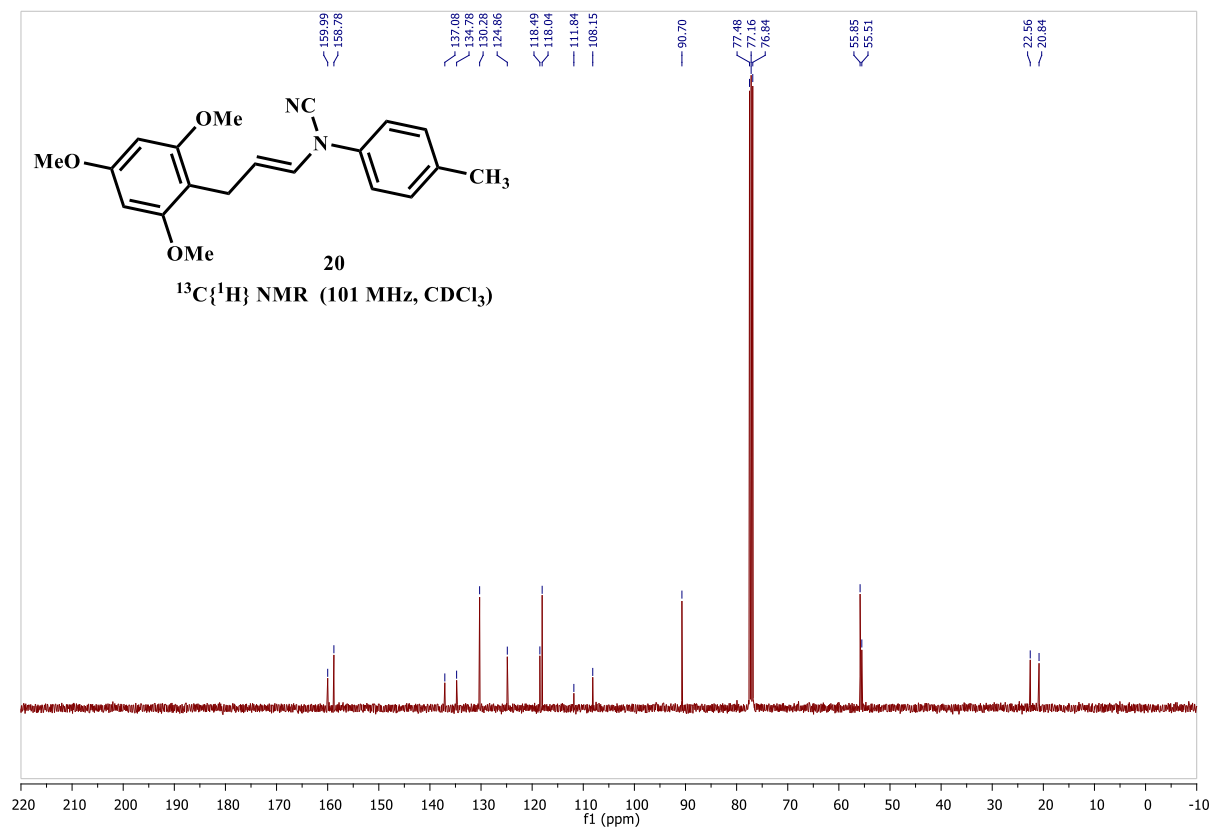
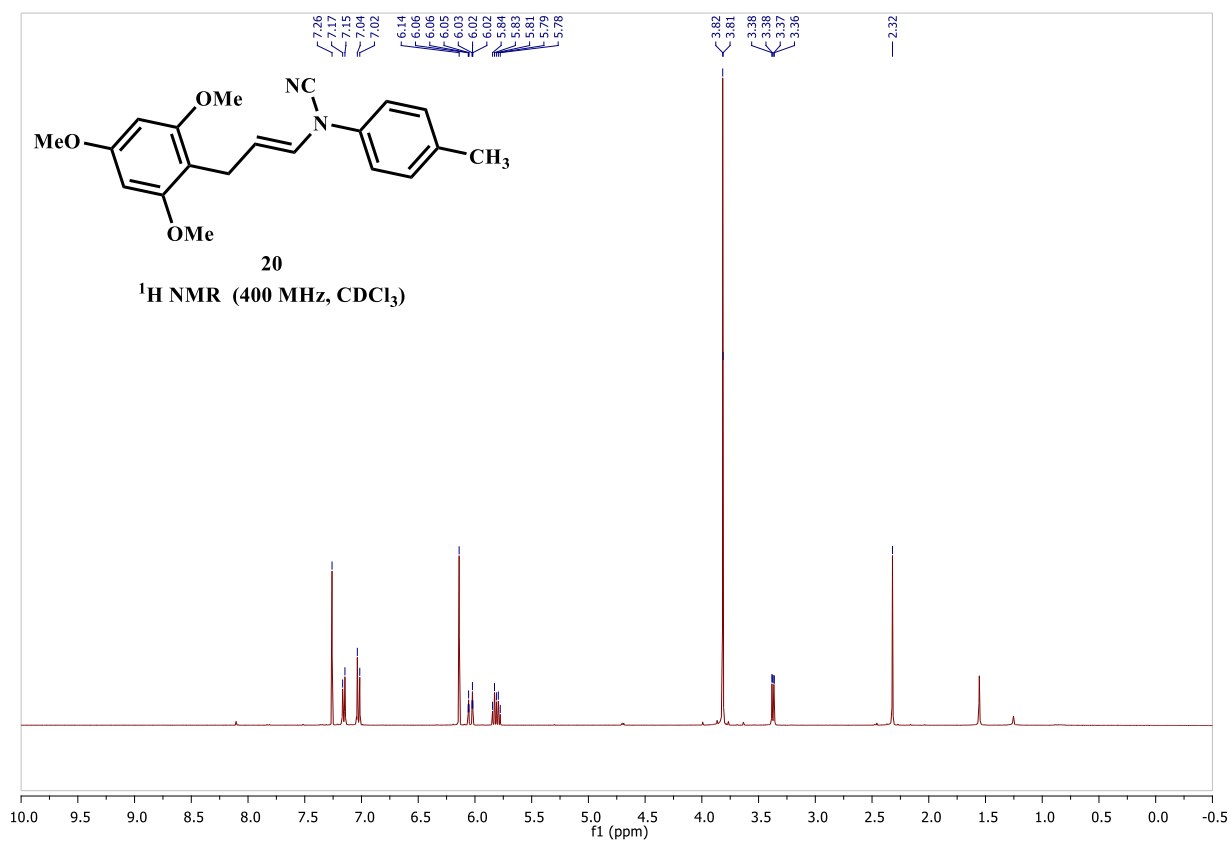




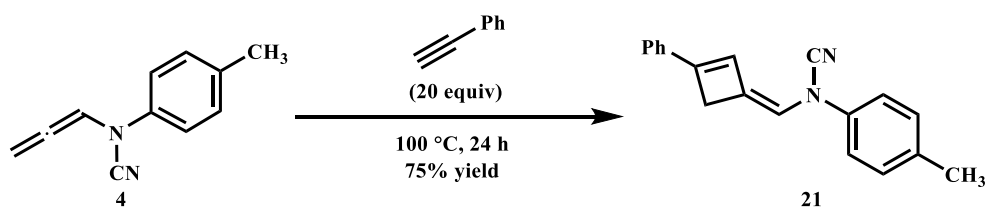
**(E)-N-(p-tolyl)-N-(3-(2,4,6-trimethoxyphenyl)prop-1-en-1-yl)cyanamide**



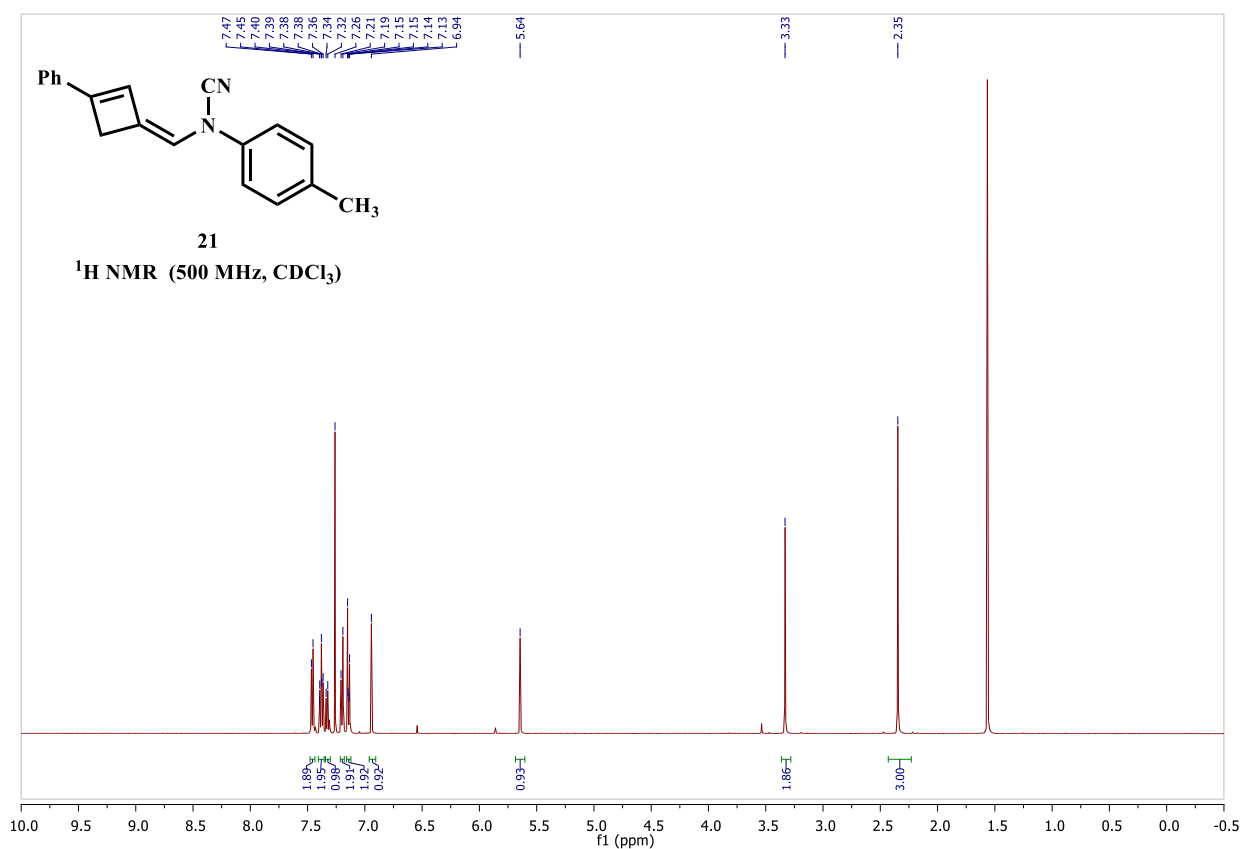
Following a modified literature procedure,<sup>6</sup> to a reaction vial was added *N*-(1,2-propadienyl)-*N*-(*p*-tolyl)cyanamide **4** (54 mg, 0.32 mmol, 1 equiv),  $\text{CH}_2\text{Cl}_2$  (1 mL) and 1,3,5-trimethoxybenzene (108 mg, 0.64 mmol, 2 equiv). The solution was stirred and  $\text{AuPPh}_3(\text{NTf}_2)$  (25 mg, 0.016 mmol, 0.05 equiv) was added. The reaction was stirred at rt and monitored by TLC. After completion (1 h) the reaction mixture was filtered through celite and the crude mixture purified by silica gel column chromatography (eluent = 10% EtOAc in hexanes,  $25 \times 120$  mm silica) the titled compound **20** (82.3 mg, 0.24 mmol, 76% yield) as a white solid; mp 77-79 °C;  $R_f = 0.36$  (eluent = 20% EtOAc in hexanes);  $\nu_{\text{max}} / \text{cm}^{-1}$  (film): 2222 ( $\text{C}\equiv\text{N}$ ), 1608, 1593, 1510, 1454, 1228, 1207, 1188, 1147, 1058, 950, 810;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.32 (3H, s), 3.37 (2H, dd,  $J$  6.8, 1.3), 3.81 (9H, s), 5.81 (1H, dt,  $J$  13.6, 6.8), 6.04 (1H, dt,  $J$  13.5, 1.4), 6.14 (2H, s), 7.03 (2H, d,  $J$  8.6), 7.16 (2H, d,  $J$  8.7);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 20.8, 22.6, 55.5, 55.9, 90.7, 108.2, 111.8, 118.0, 118.5, 124.9, 130.3, 134.8, 137.1, 158.8, 160.0; HRMS (NSI+) calculated for  $[\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_3]^+(\text{M}+\text{H})^+$ :  $m/z$  339.1703, found 339.1708 (+1.4 ppm).

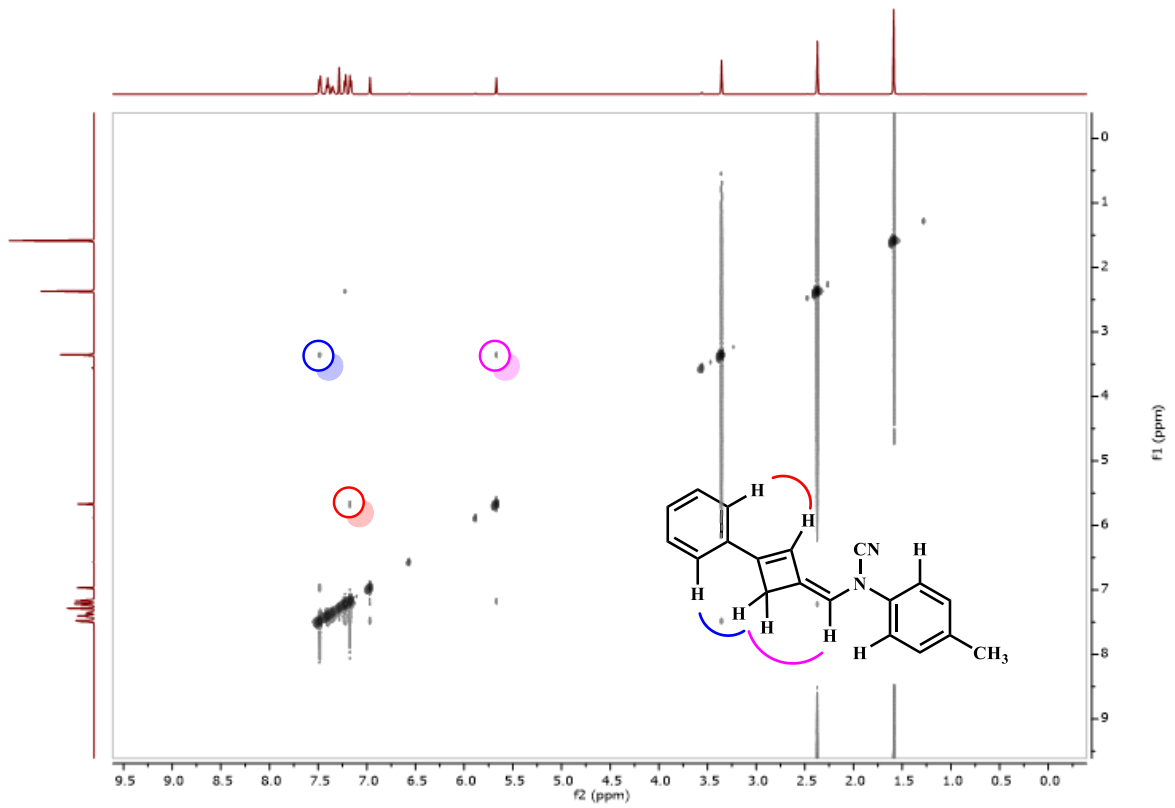
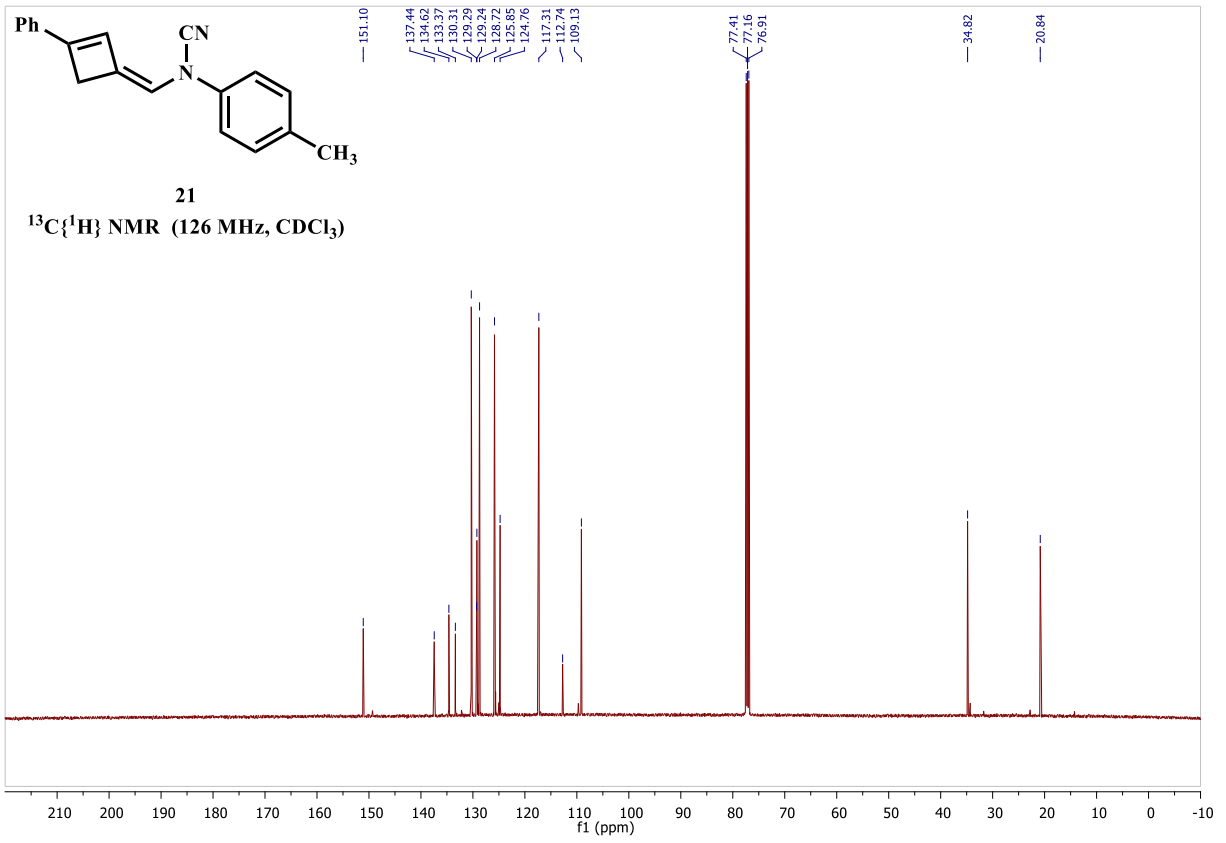


**(Z)-N-((3-phenylcyclobut-2-en-1-ylidene)methyl)-N-(p-tolyl)cyanamide**

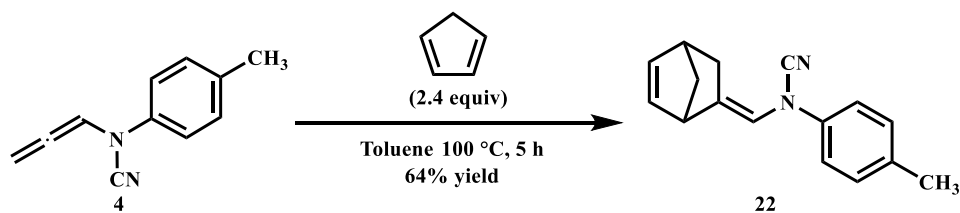


Following a modified literature procedure,<sup>8</sup> to a reaction vial was added *N*-(1,2-propadienyl)-*N*-(*p*-tolyl)cyanamide **4** (50 mg, 0.29 mmol, 1 equiv) and phenylacetylene (640  $\mu$ L, 5.8 mmol, 20 equiv) and the reaction stirred at 100 °C for 24 h. After 24 h the reaction was concentrated *in vacuo* and purified by silica gel column chromatography (eluent = 10% EtOAc in hexanes, 25  $\times$  120 mm silica) the titled compound **21** (59 mg, 0.22 mmol, 75% yield) as a white solid; mp 110-112 °C;  $R_f$  = 0.58 (eluent = 20% EtOAc in hexanes);  $\nu_{\max}$  /  $\text{cm}^{-1}$  (film): 2218 (C $\equiv$ N), 1685, 1514, 1274, 1247, 802, 752, 686, 497;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.35 (3H, s), 3.33 (2H, s), 5.64 (1H, s), 6.94 (1H, s), 7.13-7.15 (2H, m), 7.20 (2H, d,  $J$  7.2), 7.33 (1H, d,  $J$  7.2), 7.36-7.40 (2H, m), 7.46 (2H, d,  $J$  7.0);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 20.8, 34.8, 109.1, 112.7, 117.3, 124.8, 125.9, 128.7, 129.2, 129.3, 130.3, 133.4, 134.6, 137.4, 151.1; HRMS (ASAP+) calculated for  $[\text{C}_{19}\text{H}_{17}\text{N}_2]^+(\text{M}+\text{H})^+$ :  $m/z$  273.1386, found 273.1388 (+0.6 ppm).

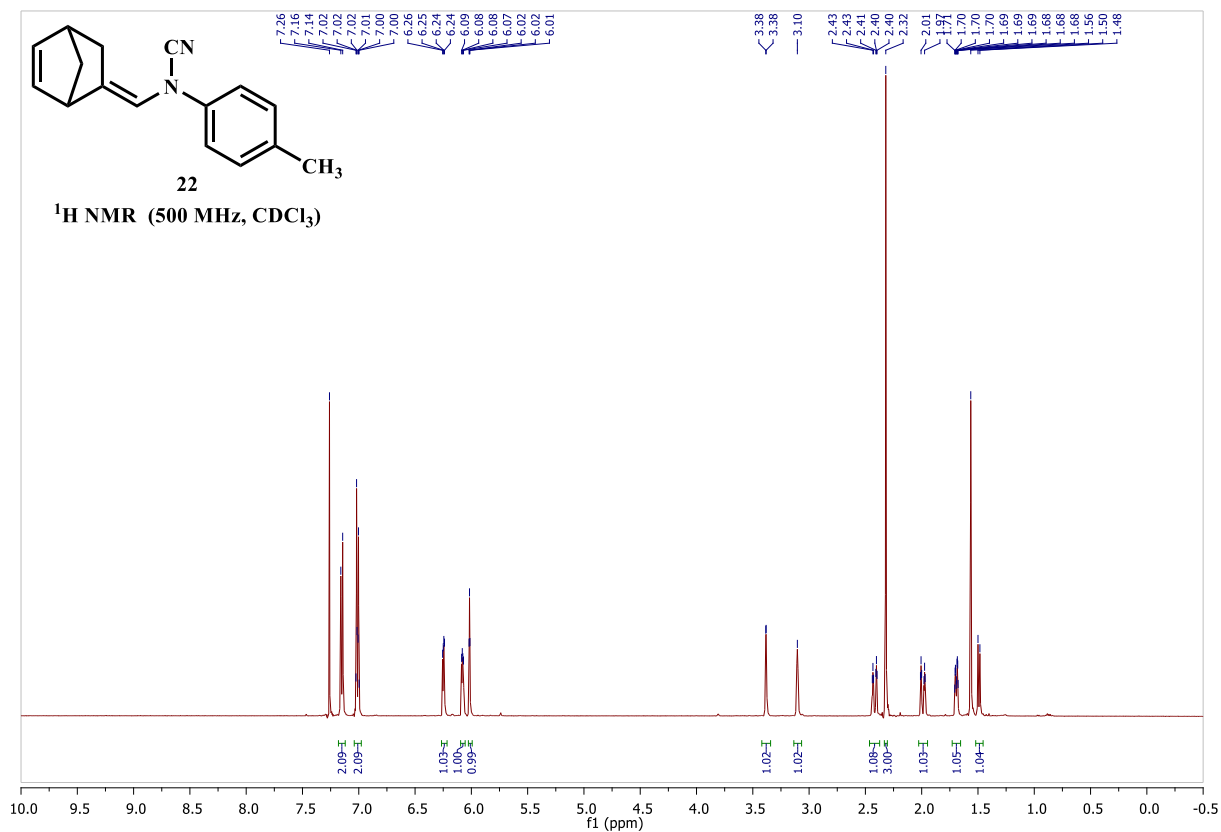


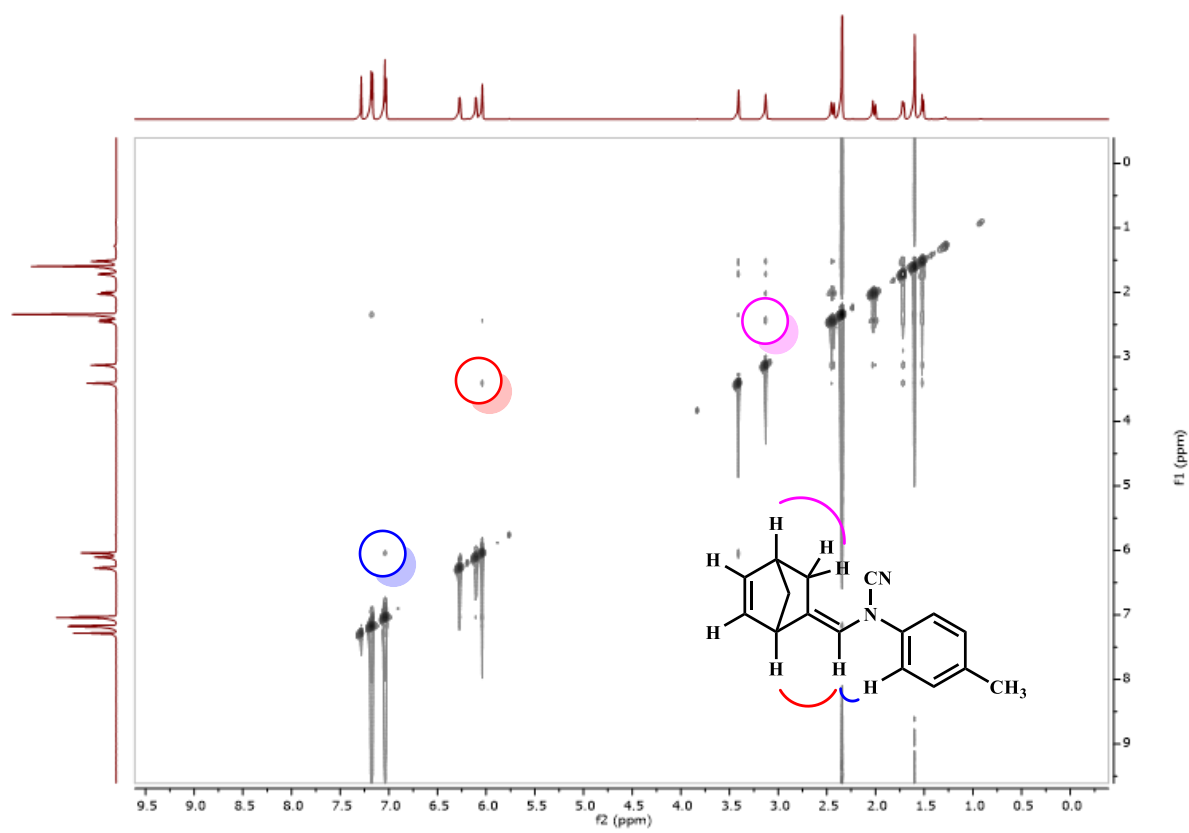
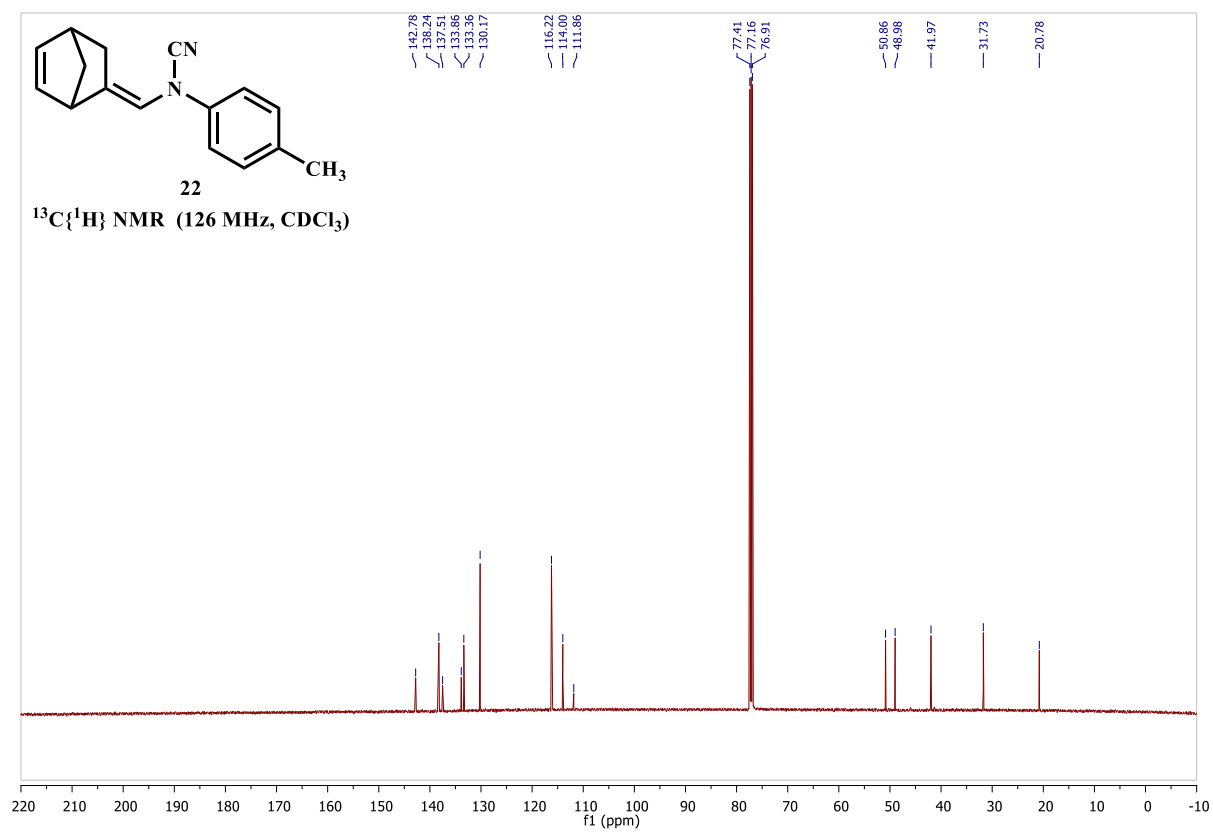


**(E)-N-(bicyclo[2.2.1]hept-5-en-2-ylidene-methyl)-N-(p-tolyl)cyanamide**



Following a modified literature procedure,<sup>9</sup> to a reaction vial was added *N*-(1,2-propadienyl)-*N*-(*p*-tolyl)cyanamide **4** (50 mg, 0.29 mmol, 1 equiv) and freshly distilled cyclopentadiene (59  $\mu$ L, 0.70 mmol, 2.4 equiv) and toluene (0.5 mL) the reaction stirred at 100 °C for 5 h. After 5 h the reaction was concentrated *in vacuo* and purified by silica gel column chromatography (eluent = 10% EtOAc in hexanes, 30  $\times$  120 mm silica) the titled compound **22** (45 mg, 0.19 mmol, 64% yield) as a white solid; mp 71-73 °C;  $R_f$  = 0.65 (eluent = 20% EtOAc in hexanes);  $\nu_{\max}$  /  $\text{cm}^{-1}$  (film): 2980, 2360, 2212 ( $\text{C}\equiv\text{N}$ ), 1510, 1276, 1224, 810, 715, 497;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 1.49 (1H, d,  $J$  8.4), 1.69 (1H, ddt,  $J$  8.4, 3.2, 1.6), 1.97-2.01 (1H, m), 2.32 (3H, s), 2.40-2.42 (1H, m), 3.10 (1H, s), 3.38 (1H, d,  $J$  1.4), 6.02 (1H, t,  $J$  1.8), 6.08 (1H, dd,  $J$  5.4, 3.1), 6.25 (1H, dd,  $J$  5.5, 3.0), 7.00-7.02 (2H, m), 7.15 (2H, d,  $J$  8.2);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 20.8, 31.7, 42.0, 49.0, 50.9, 111.9, 114.0, 116.2, 130.2, 133.4, 133.9, 137.5, 138.3, 142.8; HRMS (NSI+) calculated for  $[\text{C}_{16}\text{H}_{17}\text{N}_2]^+(\text{M}+\text{H})^+$  :  $m/z$  237.1386, found 273.1389 (+1.2 ppm).



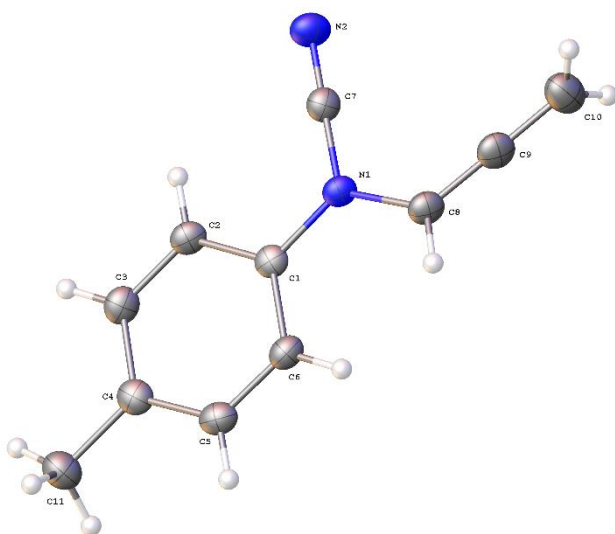


Submitted by: **Louis C. Morrill**  
Cardiff University

Solved by: **Graham J. Tizzard**

Sample ID: **JNA3-404P**

## Crystal Data and Experimental



**Experimental.** Single colourless block-shaped crystals of (**2018ncs0271z**) were recrystallised from hexane by slow evaporation. A suitable crystal (0.10×0.10×0.03) mm<sup>3</sup> was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector diffractometer. The crystal was kept at  $T = 100(2)$  K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

**Crystal Data.** C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>,  $M_r = 170.21$ , triclinic,  $P-1$  (No. 2),  $a = 6.5626(3)$  Å,  $b = 6.8800(3)$  Å,  $c = 10.9964(4)$  Å,  $\alpha = 90.367(3)^\circ$ ,  $\beta = 102.217(4)^\circ$ ,  $\gamma = 108.740(4)^\circ$ ,  $V = 458.04(4)$  Å<sup>3</sup>,  $T = 100(2)$  K,  $Z = 2$ ,  $Z' = 1$ ,  $\mu(\text{MoK}\alpha) = 0.075$ , 10157 reflections measured, 2089 unique ( $R_{int} = 0.0407$ ) which were used in all calculations. The final  $wR_2$  was 0.1759 (all data) and  $R_1$  was 0.0608 ( $I > 2(I)$ ).

Compound	2018ncs0271z
Formula	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub>
$D_{calc.}/\text{g cm}^{-3}$	1.234
$\mu/\text{mm}^{-1}$	0.075
Formula Weight	170.21
Colour	colourless
Shape	block
Size/mm <sup>3</sup>	0.10×0.10×0.03
$T/\text{K}$	100(2)
Crystal System	triclinic
Space Group	$P-1$
$a/\text{Å}$	6.5626(3)
$b/\text{Å}$	6.8800(3)
$c/\text{Å}$	10.9964(4)
$\alpha/^\circ$	90.367(3)
$\beta/^\circ$	102.217(4)
$\gamma/^\circ$	108.740(4)
$V/\text{Å}^3$	458.04(4)
$Z$	2
$Z'$	1
Wavelength/Å	0.71075
Radiation type	MoK $\alpha$
$\theta_{min}/^\circ$	1.901
$\theta_{max}/^\circ$	27.481
Measured Refl.	10157
Independent Refl.	2089
Reflections Used	1834
$R_{int}$	0.0407
Parameters	125
Restraints	2
Largest Peak	0.733
Deepest Hole	-0.267
GooF	1.047
$wR_2$ (all data)	0.1759
$wR_2$	0.1703
$R_1$ (all data)	0.0672
$R_1$	0.0608

## Structure Quality Indicators

<b>Reflections:</b>	d min (Mo) 0.77	I/ $\sigma$ 36.7	Rint 4.07%	complete 100% (IUCr) 100%
<b>Refinement:</b>	Shift 0.000	Max Peak 0.7	Min Peak -0.3	Goof 1.047

A colourless block-shaped crystal with dimensions 0.10×0.10×0.03 mm<sup>3</sup> was mounted on a MITIGEN holder in perfluoroether oil. X-ray diffraction data were collected using a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector equipped with an Oxford Cryosystems low-temperature device, operating at  $T = 100(2)$  K.

Data were measured using profile data from  $\omega$ -scans of 0.5° per frame for 9.0 s using MoK $\alpha$  radiation (Rotating Anode, 45.0 kV, 55.0 mA). The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.46, 2018). The maximum resolution achieved was  $\theta = 27.481^\circ$ .

Cell parameters were retrieved using the **CrysAlisPro** (Rigaku, V1.171.39.46, 2018) software and refined using **CrysAlisPro** (Rigaku, V1.171.39.46, 2018) on 4393 reflections, 43 % of the observed reflections. Data reduction was performed using the **CrysAlisPro** (Rigaku, V1.171.39.46, 2018) software which corrects for Lorentz polarisation. The final completeness is 100.00 % out to 27.481° in  $\theta$ .

A multi-scan absorption correction was performed using CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient  $\mu$  of this material is 0.075 mm<sup>-1</sup> at this wavelength ( $\lambda = 0.71075\text{\AA}$ ) and the minimum and maximum transmissions are 0.50093 and 1.00000..

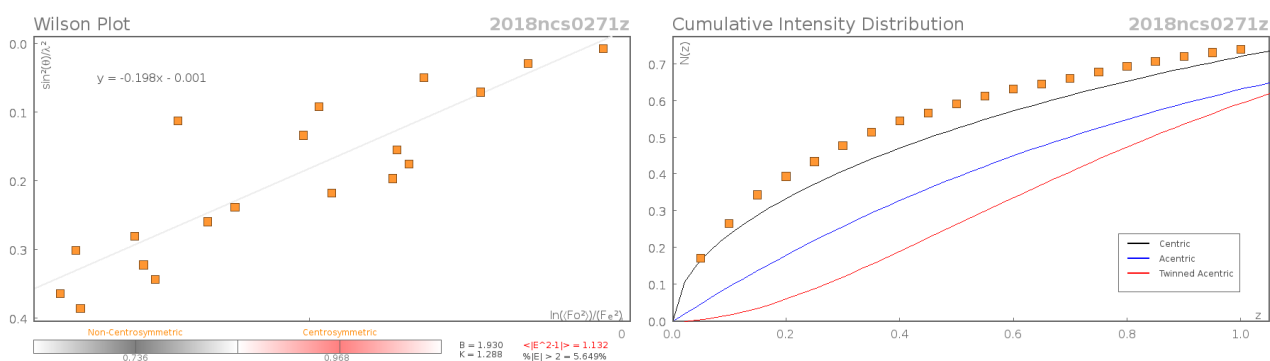
The structure was solved in the space group  $P-1$  (# 2) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

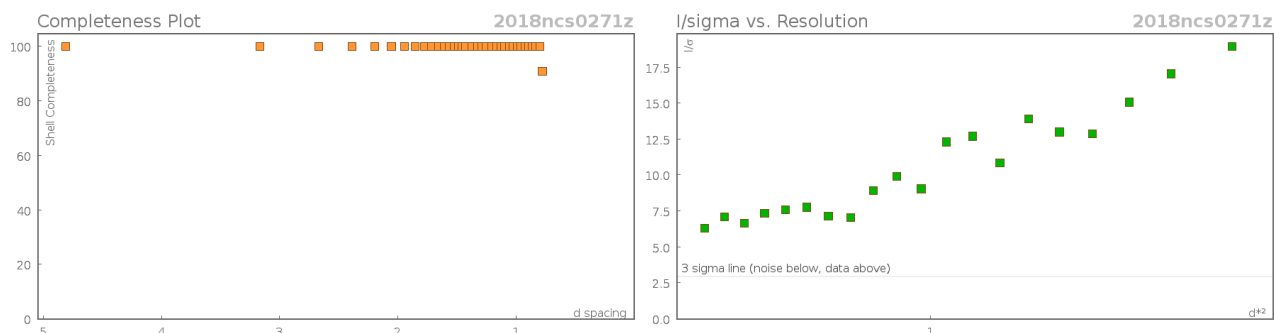
*\_refine\_special\_details:* H-atoms bonded to C10 were located in the difference map and refined with a riding model and a geometric restraint (0.86\text{Å})

*\_exptl\_absorpt\_process\_details:* CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

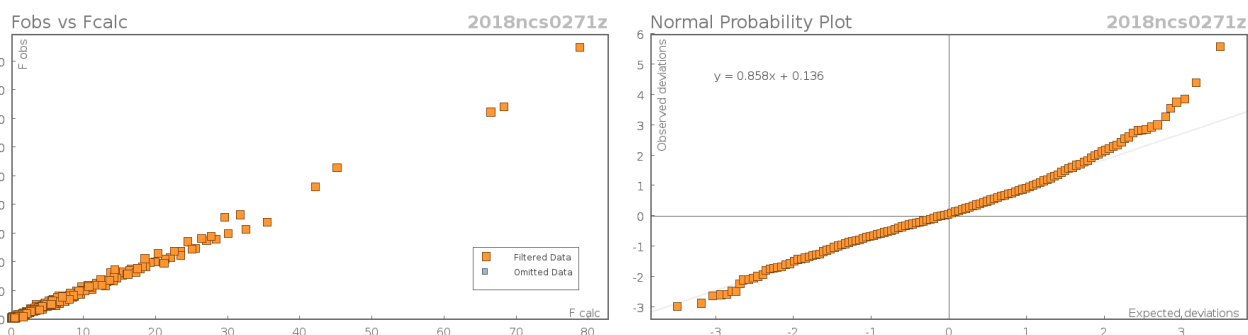
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

## Data Plots: Diffraction Data





## Data Plots: Refinement and Data



## Reflection Statistics

Total reflections (after filtering)	10157	Unique reflections	2089
Completeness	0.998	Mean $I/\sigma$	21.36
hkl <sub>max</sub> collected	(8, 8, 14)	hkl <sub>min</sub> collected	(-8, -8, -14)
hkl <sub>max</sub> used	(8, 8, 14)	hkl <sub>min</sub> used	(-8, -8, 0)
Lim d <sub>max</sub> collected	100.0	Lim d <sub>min</sub> collected	0.36
d <sub>max</sub> used	10.71	d <sub>min</sub> used	0.77
Friedel pairs	1807	Friedel pairs merged	1
Inconsistent equivalents	1	R <sub>int</sub>	0.0407
R <sub>sigma</sub>	0.0272	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(767, 1288, 911, 622, 260, 43, 5)	Maximum multiplicity	11
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

**Table 1:** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **2018ncs0271z**.  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$ .

Atom	x	y	z	$U_{eq}$
N1	6017.1(18)	3016.7(17)	6690.0(11)	21.2(3)
N2	10083(2)	3823(2)	7287.8(12)	30.5(3)
C1	4910(2)	2587.3(19)	5406.2(13)	19.8(3)
C7	8204(2)	3440(2)	7004.6(13)	22.7(3)
C6	2630(2)	2096(2)	5041.8(14)	23.2(3)
C2	6124(2)	2680(2)	4504.0(14)	22.7(3)
C4	2792(2)	1780(2)	2872.5(14)	24.4(3)
C8	4918(2)	2988(2)	7679.9(14)	24.5(3)
C5	1615(2)	1709(2)	3788.0(14)	25.0(4)
C3	5070(2)	2278(2)	3258.5(14)	25.4(4)
C9	5821(2)	2940(2)	8844.3(14)	27.7(4)
C11	1638(3)	1364(3)	1512.0(15)	31.8(4)
C10	6713(3)	2987(3)	10014.3(16)	37.2(4)

**Table 2:** Anisotropic Displacement Parameters ( $\times 10^4$ ) **2018ncs0271z**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
N1	19.5(6)	20.2(6)	26.9(6)	0.7(5)	6.4(5)	10.0(5)
N2	23.4(6)	35.8(7)	34.3(7)	-1.6(5)	6.1(5)	13.2(5)
C1	24.0(7)	12.0(6)	26.6(7)	1.6(5)	6.2(5)	9.9(5)
C7	25.7(7)	20.4(7)	25.5(7)	0.0(5)	7.5(5)	11.1(5)
C6	23.2(7)	18.8(6)	30.6(7)	2.4(5)	9.8(5)	8.7(5)
C2	22.0(7)	19.3(7)	30.9(7)	0.9(5)	7.2(5)	11.6(5)
C4	29.4(7)	16.8(6)	29.1(7)	1.2(5)	5.5(6)	11.3(5)
C8	21.8(7)	25.8(7)	29.7(7)	0.0(6)	7.9(5)	11.7(5)
C5	23.5(7)	18.5(7)	34.2(8)	1.6(5)	5.0(6)	9.5(5)
C3	29.1(8)	22.2(7)	30.9(8)	1.8(6)	11.0(6)	14.0(6)
C9	24.8(7)	31.0(8)	33.4(8)	0.3(6)	10.8(6)	14.8(6)
C11	34.6(8)	33.4(8)	29.3(8)	0.0(6)	4.3(6)	15.6(7)
C10	35.1(9)	50.3(10)	31.6(9)	0.4(7)	8.2(7)	20.9(8)

**Table 3:** Bond Lengths in Å for **2018ncs0271z**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.4251(18)	C2	C3	1.379(2)
N1	C7	1.3356(17)	C4	C5	1.385(2)
N1	C8	1.4243(18)	C4	C3	1.390(2)
N2	C7	1.1470(19)	C4	C11	1.506(2)
C1	C6	1.391(2)	C8	C9	1.298(2)
C1	C2	1.388(2)	C9	C10	1.291(2)
C6	C5	1.381(2)			

**Table 4:** Bond Angles in ° for **2018ncs0271z**.

Atom	Atom	Atom	Angle/°
C7	N1	C1	119.17(11)
C7	N1	C8	117.12(12)
C8	N1	C1	123.70(12)
C6	C1	N1	120.96(12)
C2	C1	N1	119.63(12)
C2	C1	C6	119.41(13)
N2	C7	N1	179.04(15)
C5	C6	C1	119.37(13)
C3	C2	C1	120.08(13)
C5	C4	C3	117.42(14)
C5	C4	C11	120.94(14)
C3	C4	C11	121.63(14)
C9	C8	N1	123.59(13)
C6	C5	C4	122.20(13)
C2	C3	C4	121.52(13)
C10	C9	C8	176.97(16)

**Table 5:** Hydrogen Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **2018ncs0271z**.  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$ .

Atom	x	y	z	$U_{eq}$
H6	1795.92	2029.36	5636.53	28
H2	7650.22	3012.57	4739.59	27
H8	3474.62	3005.3	7480.74	29
H5	90.2	1389.33	3550.79	30
H3	5901.62	2341.52	2663.22	30
H11A	345.34	163.74	1403.83	48
H11B	2618.94	1135.79	1034.27	48
H11C	1215.57	2526.16	1230.8	48
H10A	7470(30)	4118(17)	10464(16)	45
H10B	6620(30)	1863(17)	10371(17)	45

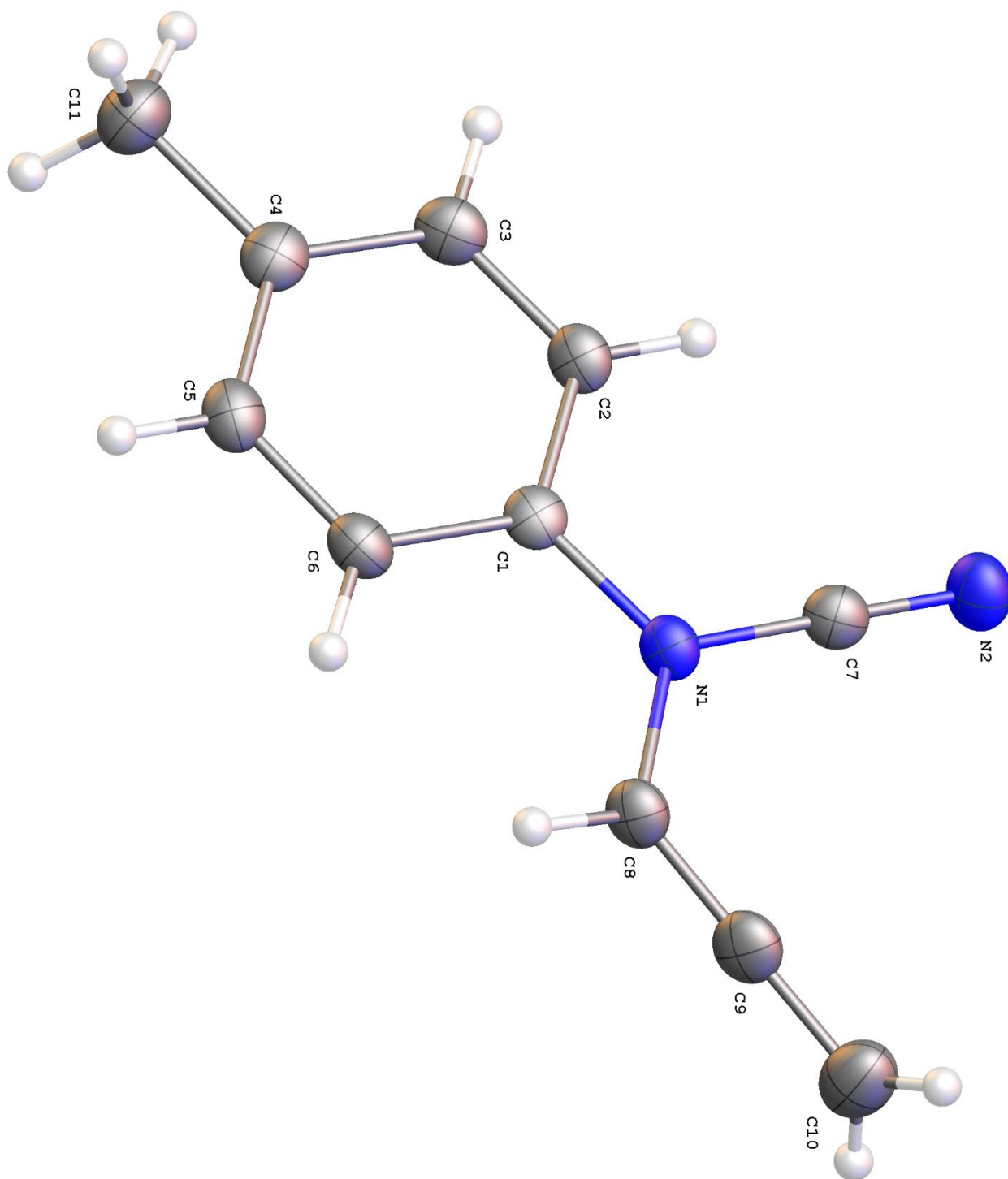
### Citations

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