Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Photoinduced Decarboxylative Azidation

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2 General Experimental Details

All required fine chemicals were used directly without purification unless stated otherwise. All air and moisture sensitive reactions were carried out under nitrogen atmosphere using standard Schlenk manifold technique. THF was distilled from sodium/benzophenone, CH_2Cl_2 and was distilled from CaH_2, CH_3CN was distilled from activated 4Å molecular sieves, Et_3N was distilled over KOH. ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were acquired at various field strengths as indicated and were referenced to $CHCl_3$ (7.27 and 77.0 ppm for ^1H and ^{13}C respectively). ^1H NMR coupling constants are reported in Hertz and refer to apparent multiplicities and not true coupling constants. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, qi = quintet, sx = sextet, sp = septet, m = multiplet, dd = doublet of doublets, etc.), proton assignment (determined by 2D NMR experiments: COSY, HSQC and HMBC) where possible. High-resolution mass spectra were obtained using a JEOL JMS-700 spectrometer or a Fissions VG Trio 2000 quadrupole mass spectrometer. Spectra were obtained using electron impact ionization (EI) and chemical ionization (CI) techniques, or positive electrospray (ES). Infra-red spectra were recorded using a JASCO FT/IR 410 spectrometer or using an ATI Mattson Genesis Seris FTIR spectrometer as evaporated films or liquid films. Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60 F254. Compounds were visualized by exposure to UV-light or by dipping the plates in permanganate ($KMnO_4$) stain followed by heating. Flash column chromatography was performed using Merck Silica Gel 60 (40–63 μm). All mixed solvent eluents are reported as v/v solutions. UV/Vis spectra were obtained using an Agilent 6453 spectrometer and 1 mm High Precision Cell made of quartz from Hellma Analytics.

The LEDs used are Aquapet Ceramic 220-240V~50/60 Hz for green light and Kessil H150-blue for blue light. In the case of diastereomeric mixtures, the signals corresponding to the different diastereomers have been labeled with ^{M} = major and ^{m} = minor, where possible. We have also used this legend to label the ^{13}C NMRs of compounds having rotameric mixtures.

All the reactions were conducted in CEM 10 mL glass microwave tubes.

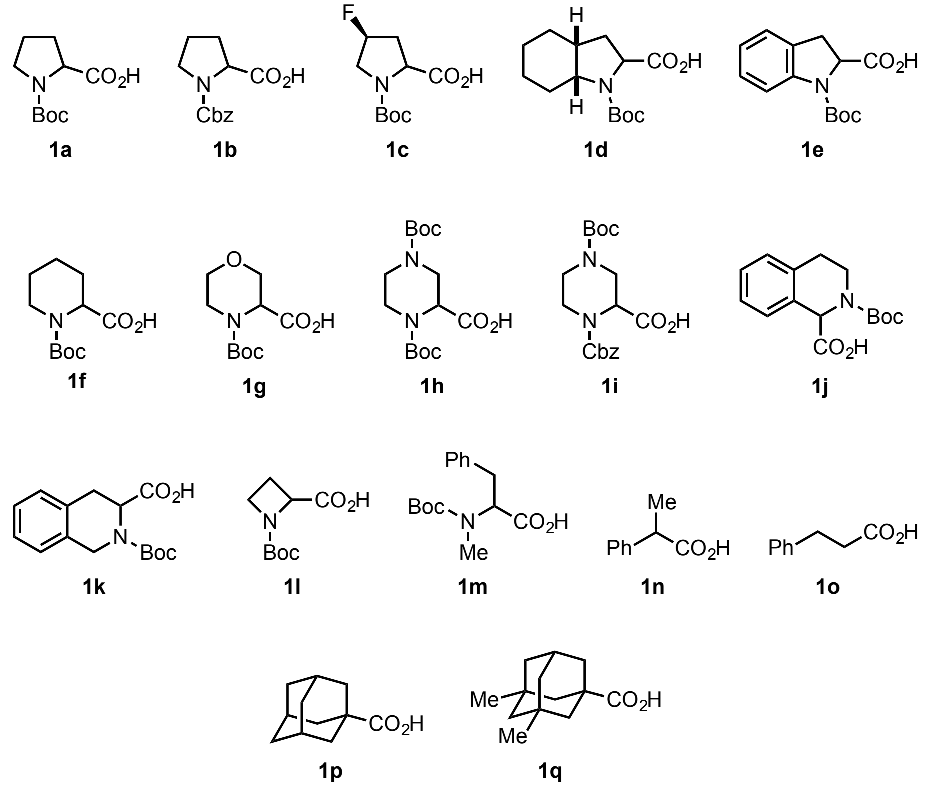
3 Safety

Low molecular weight organic azides are potential explosives and should not be isolated on scale without an assessment of the energetic properties. The long term stability of the products X-X has not been assessed. Long term storage of compounds with the potential to degrade with the generation of azide is not advised without an assessment of stability. Care must be taken to ensure the reaction and work up are basified to prevent the possible formation of hydrozoic acid (HN_3), which is both highly toxic and explosive. A full safety protocol has been observed all the time.[1]

Compound **2** and **13** are not stable in acidic condition purification on silica gel should be avoided.

4 Commercially Available Starting Materials

All the starting materials **1a–q** are commercially available.



Scheme SI-1.

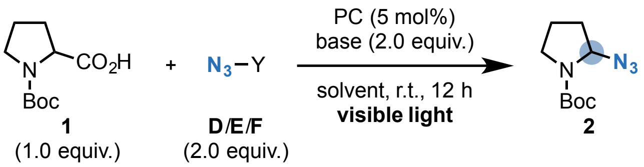
5 Decarboxylative Azidations

5.1 Reaction optimization with 1a

General Procedure for the Optimization

A dry tube equipped with a stirring bar was charged with **1a** (12 mg, 0.05 mmol, 1.0 equiv.), the base (0.1 mmol, 2.0 equiv.), the photocatalyst (5.0 µmol, 5 mol%) and the azide SOMOphile (0.1 mmol, 2.0 equiv.). The tube was sealed with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (x 3). The degassed and dry solvent (0.1M) was added, the cap was secured with Parafilm and the light was switched on. The mixture was stirred in front of the appropriate LEDs source (distance = 4 cm), cooled by a fan (see Figure SI-1) for 12 h. 1,3,5-Trimethoxybenzene (5.5 mg, 33.0 µmol, 0.3 equiv.) was added and the mixture was filtered through a pad of Celite/$MgSO_4$ washing with EtOAc and evaporated. The crude was dissolved in $CDCl_3$ (0.6 mL) and analysed by ^1H NMR spectroscopy to determine the NMR yield.

Table SI-1

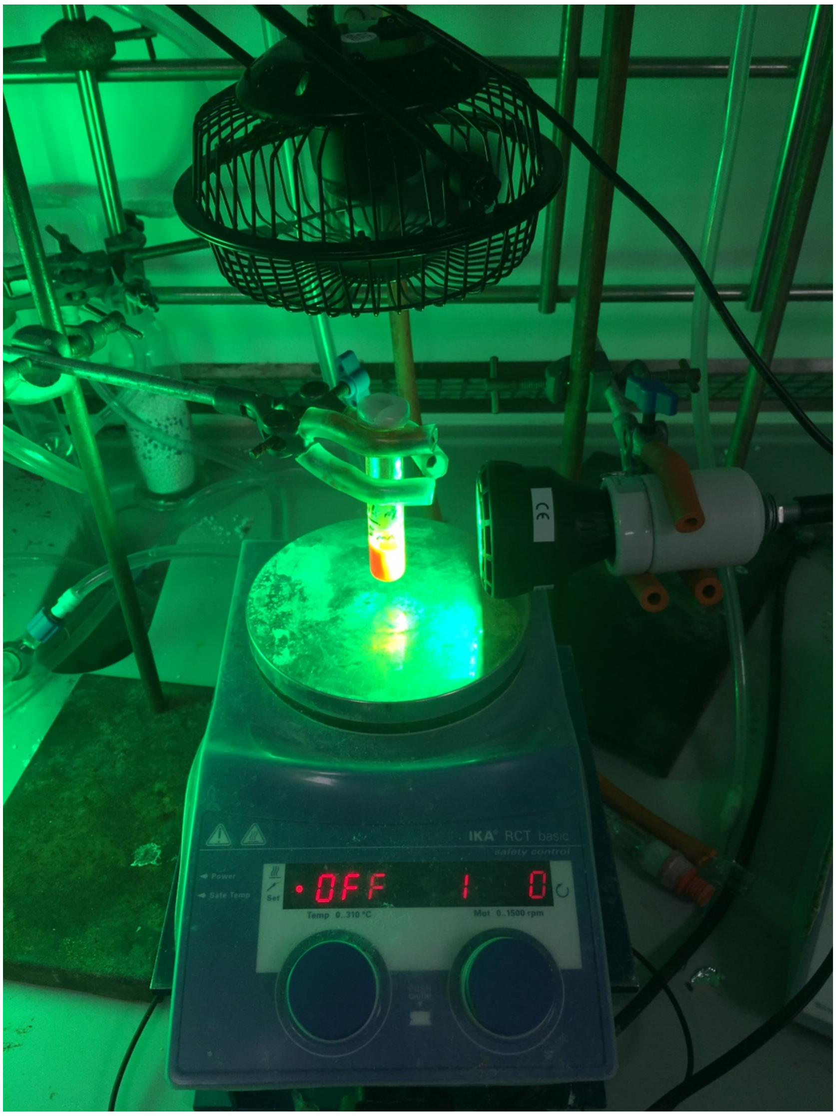


Entry	PC	Base	N_3–Y	Solvent	Light	Yield (%)
1	Ir(ppy)$_3$	CsOBz	**E**	DCE	**Blue LEDs**	0
2	Ru(bpy)$_3$Cl$_2$	CsOBz	**E**	DCE	**Blue LEDs**	5
3	4CzIPN	CsOBz	**E**	DCE	**Blue LEDs**	34
4	MesAcr•HClO$_4$	CsOBz	**E**	DCE	**Blue LEDs**	11
5	EY	CsOBz	**E**	DCE	**Green LED**	15
6	Riboflavin	CsOBz	**E**	DCE	**Blue LED**	39
7	Methylene Blue	CsOBz	**E**	DCE	**Blue LED**	32
8	Rhodamine 6G	CsOBz	**E**	DCE	**Green LED**	90
9	Rhodamine 6G	CsOBz	**E**	CH_2Cl_2	**Green LED**	51
10	Rhodamine 6G	CsOBz	**E**	CH_3CN	**Green LED**	54
11	Rhodamine 6G	CsOBz	**E**	THF	**Green LED**	72
12	Rhodamine 6G	CsOBz	**E**	DMF	**Green LED**	30
13	Rhodamine 6G	K_2CO_3	**E**	DCE	**Green LED**	36
14	Rhodamine 6G	CsOAc	**E**	DCE	**Green LED**	44
15	Rhodamine 6G	$CsHCO_3$	**E**	DCE	**Green LED**	55
16	Rhodamine 6G	$NaHCO_3$	**E**	DCE	**Green LED**	51
17	Rhodamine 6G	TMG	**E**	DCE	**Green LED**	85

Entry	**PC**	**Base**	**N_3–Y**	**Solvent**	**Light**	**Yield (%)**
18[a]	Rhodamine 6G	CsOBz	**E**	DCE	**Green LED**	30
19[b]	Rhodamine 6G	CsOBz	**E**	DCE	**Green LED**	51
20	–	CsOBz	**E**	DCE	**Green LED**	0
21	Rhodamine 6G	–	**E**	DCE	**Green LED**	0
22	Rhodamine 6G	CsOBz	**E**	DCE	–	2
23[d]	Rhodamine 6G	CsOBz	**E**	DCE	**Green LED**	5

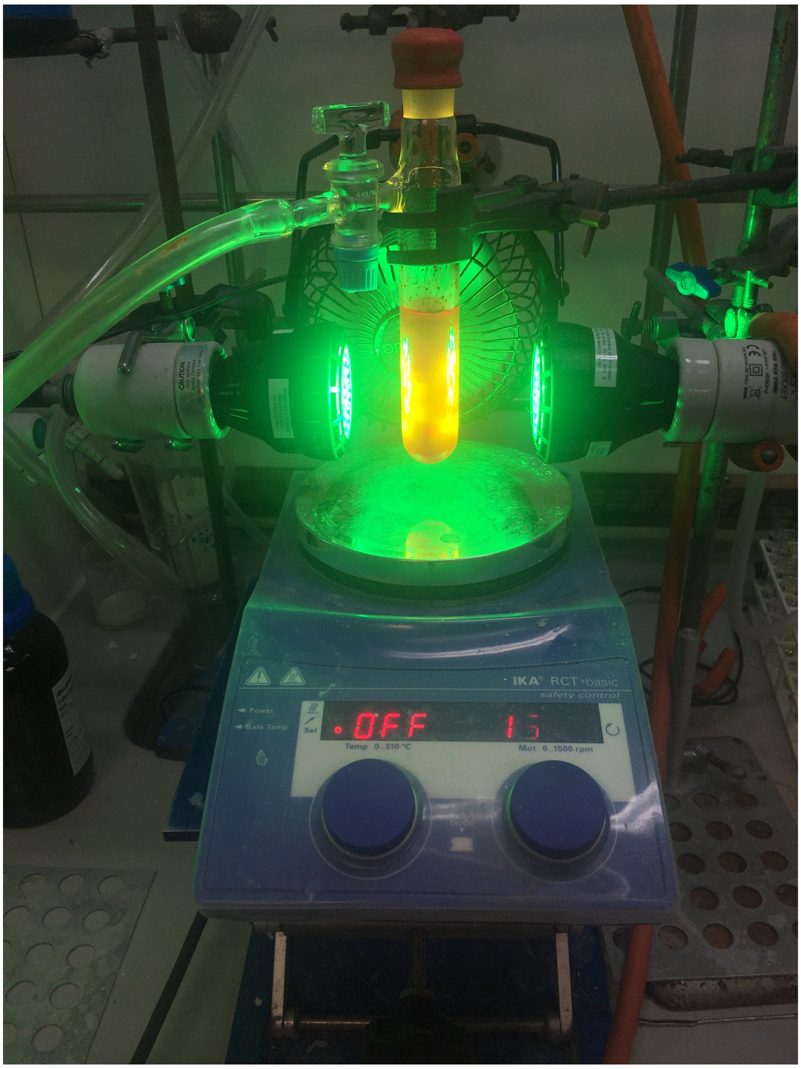
[a] Reaction time 1 h; [b] Reaction time 4 h; [c] CuOAc; [d] reaction run under oxygen atmosphere.

5.2 Picture of Reaction Set-up



0.1 mmol scale reaction

Figure SI-1.



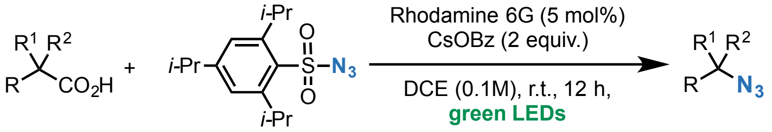
gram-scale reaction

Figure SI-2. 2.0 mmol. scale reaction set-up

5.3 General Procedures for the Substrate Scope

General Procedures for the Decarboxylative Azidation

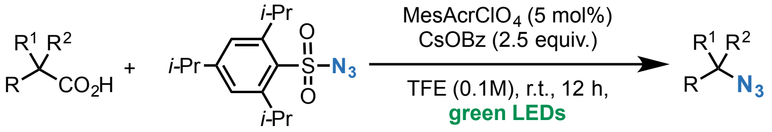
GP1



1 (1.0 equiv.) **E** (2.0 equiv.) **2–20**

A dry tube equipped with a stirring bar was charged with the carboxylic acid, (0.10 mmol, 1.0 equiv.), CsOBz (51 mg, 0.2 mmol, 2.0 equiv.), rhodamine 6G (2.5 mg, 5.0 µmol, 5 mol%) and 2,4,6-triisopropylbenzenesulfonyl azide (73 mg, 0.2 mmol, 2.0 equiv., 10% water). The tube was sealed with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (x 3). Degassed and dry DCE (0.1M) was added, the cap was secured with Parafilm and the green LEDs were switched on. The mixture was stirred in front of the green LEDs (distance = 4 cm), cooled by a fan for 12 h, (see figure 1SI). $NaHCO_3$sat. (4 mL) and CH_2Cl_2 (4 mL) were added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 4 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. Purification by flash chromatography on basic aluminium oxide eluting with petrol:EtOAc (30:1 → 1:1) gave the pure products.

GP2

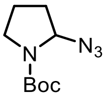


1 (1.0 equiv.) **E** (2.0 equiv.) **2–20**

A dry tube equipped with a stirring bar was charged with **1n-q,** (0.10 mmol, 1.0 equiv.), CsOBz (63.5 mg, 0.25 mmol, 2.5 equiv.), 9-mesityl-10-metylacridinium perchlorate (2.1 mg, 5.0 µmol, 5 mol%) and 2,4,6-Triisopropylbenzenesulfonyl azide (72.8 mg, 0.2 mmol, 2.0 equiv. 10% water). The tube was sealed with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (x 3). Degassed dry TFE (0.5M) was added, the cap was secured with Parafilm and the green LEDs were switched on. The mixture was stirred in front of the green LEDs (distance = 4 cm), cooled by a fan for 26 h, (see figure 1SI). $NaHCO_3$sat. (4 mL) and CH_2Cl_2 (4 mL) were added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 4 mL). The combined organic layer were dried ($MgSO_4$), filtered and evaporated. Purification by flash chromatography on basic aluminium oxide eluting with petrol:EtOAc (30:1 → 1:1) gave the pure products.

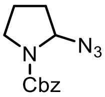
5.4 Products Characterization[a]

***tert*-Butyl 2-Azidopyrrolidine-1-carboxylate (2)**



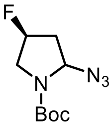
Following **GP1**, **1a** (22 mg, 0.1 mmol) gave **2** (19 mg, 87%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 5.60–5.43 (1H, m), 3.58–3.40 (1H, m), 3.31–3.25 (1H, m), 1.90–1.85 (4H, m), 1.51 & 1.48 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$, rotamers) δ 154.7^M, 153.6^m, 81.2^M, 80.4^m, 74.5^M, 74.4^m, 45.9^M, 45.8^m, 33.3^M, 32.4^m, 28.3^M, 28.2^m, 22.9^m, 22.0^M; HRMS (ESI) Found MNa^+ 235.1174, $C_9H_{16}N_4O_2Na$ requires 235.1171. Data in accordance with the literature.[1]

Benzyl 2-Azidopyrrolidine-1-carboxylate (3)



Following **GP1**, but using TMG as the base, **1b** (25 mg, 0.1 mmol) gave **3** (16 mg, 64%) as an oil. FT-IR ν_{max} (film)/cm^{-1} 2957, 2104, 1705, 1404, 1356, 1185; ^{1}H NMR (500 MHz, CD_3CN, rotamers) δ 7.44–7.31 (5H, m), 5.52 (0.6H, d, J = 5.5 Hz), 5.49 (0.4H, d, J = 5.9 Hz), 5.15 (2H, s), 3.55–3.47 (1H, m), 3.36–3.31 (1H, m), 2.06–1.78 (4H, m); ^{13}C NMR (126 MHz, CD_3CN, rotamers) δ 156.2^M, 155.0^m, 137.9 ^{M}, 137.7^m, 129.45^M, 129.4^m, 129.0^M, 128.9^m, 128.75^M, 128.7^m, 76.5^M, 75.7^m, 67.9^M, 67.7^m, 47.3^M, 47.0^m, 33.9^M, 33.0^m, 23.7^M, 22.7^m; HRMS (ESI) Found MNa^+ 269.1003, $C_{12}H_{14}N_4O_2Na$ requires 269.1009.

***tert*-Butyl (2*S*,4*S*)-2-Azido-4-fluoropyrrolidine-1-carboxylate (4) and *tert*-Butyl (2*R*,4*S*)-2-Azido-4-fluoropyrrolidine-1-carboxylate (4')**

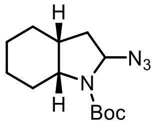


Following **GP1**, but purifying the product by flash chromatography of the crude reaction mixture after evaporation of DCE, **1c** (23 mg, 0.1 mmol) gave of **4** and **4'** (16 mg, 68%) as an oil. **4**:**4'** = 1.3:1.

4: FT-IR ν_{max} (film)/cm^{-1} 2106, 1699, 1384, 1366, 1160; ^{1}H NMR (500 MHz, CD_3CN, rotamers) δ 5.50–5.49 (1H, m), 5.22 (1H, dt, J = 53.2, 4.16 Hz), 3.70–3.51 (2H, m), 2.35–2.23 (1H, m), 2.19–2.11 (1H, m), 1.49 (5H, s), 1.47 (4H, s); ^{13}C NMR (126 MHz, CD_3CN, rotamers) δ 155.2^M, 154.2^m, 93.3 ^{m} (d, J = 175.4 Hz), 92.4 ^{M} (d, J = 175.0 Hz), 81.8^M, 81.4^m, 74.6^m, 74.5^M, 54.7 ^{m} (d, J = 23.7 Hz), 54.3 ^{M} (d, J = 23.8 Hz), 40.3 ^{M} (d, J = 20.8 Hz), 39.3 ^{m} (d, J = 20.7 Hz), 28.4; ^{19}F NMR (161 MHz, CD_3CN) δ –174.5, –174.7; HRMS (ESI) Found MNa^+ 253.1067, $C_9H_{15}N_4O_2FNa$ requires 253.1071.

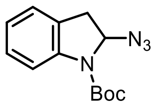
4': FT-IR ν_{max} (film)/cm^{-1} 2132, 1785, 1323, 1209, 1121; ^{1}H NMR (500 MHz, CD_3CN, rotamers) δ 5.67–5.60 (1H, m), 5.18 (1H, d, J = 53.2 Hz), 3.81–3.70 (1H, m), 3.57–3.42 (1H, m), 2.62–2.49 (1H, m), 2.06–1.98 (1H, m), 1.50 (5H, s), 1.47 (4H, s); ^{13}C NMR (126 MHz, CD$_3$CN, rotamers and diastereomers) δ 153.5, 92.2 (d, *J* = 125.0 Hz), 82.1, 75.1, 74.8, 53.3 (d, *J* = 22.7 Hz), 52.6 (d, *J* = 22.5 Hz), 41.1 (d, *J* = 22.5 Hz), 39.9 (d, *J* = 20.6 Hz), 28.4; ^{19}F NMR (161 MHz, CD$_3$CN) δ –178.8, –179.2; HRMS (ESI) Found MNa$^+$ 253.1068, C$_9$H$_{15}$N$_4$O$_2$FNa requires 253.1071.

tert-Butyl 2-Azidooctahydro-1H-indole-1-carboxylate (5) and *tert*-Butyl 2-Azidooctahydro-1H-indole-1-carboxylate (5')



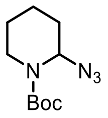
Following **GP1**, but purifying the product by flash chromatography of the crude reaction mixture after evaporation of DCE **1d** (27 mg, 0.1 mmol) gave **5** and **5'** (21 mg, 80%) as an oil; **5**:**5'** = 1.2:1. FT-IR ν$_{max}$ (film)/cm^{-1} 2928, 2106, 1699, 1382, 1365, 1248, 1163; ^{1}H NMR (400 MHz, CD$_3$CN, rotamers and diastereomers) δ 5.37 (0.6H, d, *J* = 6.2 Hz), 5.35 (0.4, d, *J* = 5.9 Hz), 3.77–3.61 (1H, m), 2.48–2.31 (1H, m), 2.22–2.10 (2H, m), 1.69–1.58 (4H, m), 1.48–1.43 (9H, m), 1.35–0.96 (4H, m); ^{13}C NMR (126 MHz, CD$_3$CN) (diastereoisomer) δ 153.9^{m}, 155.3^{M}, 81.1^{M}, 80.7^{m}, 75.6 (x 2), 57.9^{m}, 57.6^{M}, 36.3^{M}, 35.7^{m}, 35.6^{M}, 34.6^{m}, 28.9^{M}, 28.5 (x 2)^{m}, 28.4 (x 2)^{M}, 28.1^{m}, 26.5^{m}, 26.2^{M}, 26.1^{m}, 24.2 (x 2), 24.0^{M}, 21.4^{M}, 21.2^{m}; HRMS (ESI) Found MNa$^+$ 289.1631, C$_{13}$H$_{22}$N$_4$O$_2$Na requires 289.1635.

tert-Butyl 2-Azidoindoline-1-carboxylate (6)



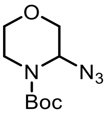
Following **GP1**, **1e** (26 mg, 0.1 mmol) gave **6** (21 mg, 80%) as an oil. FT-IR ν$_{max}$ (film)/cm^{-1} 2978, 2113, 1711, 1482, 1386, 1282; ^{1}H NMR (500 MHz, CD$_3$CN, rotamers) δ 7.87–7.49 (1H, m), 7.24–7.19 (2H, m), 7.01 (1H, t, *J* = 7.5), 6.02 (1H, dd, *J* = 7.9 1.2 Hz), 3.39 (1H, dd, *J*= 17.2, 7.9 Hz), 2.85 (1H, d, *J*= 17.2 Hz), 1.58 (9H, s); ^{13}C NMR (126 MHz, CD$_3$CN) δ 152.5, 141.9, 129.7, 128.5, 125.8, 124.0, 115.6, 83.2, 77.2, 36.5, 28.4; HRMS (ESI) Found MNa$^+$ 283.1161, C$_{13}$H$_{16}$N$_4$O$_2$Na requires 283.1165.

tert-Butyl 2-Azidopiperidine-1-carboxylate (7)



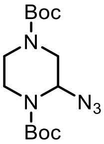
Following **GP1**, but using as TMG the base, **1f** (22 mg, 0.1 mmol) gave **7** (19 mg, 86%) as an oil. ^{1}H NMR (500 MHz, CDCl$_3$, rotamers) δ 6.07–5.89 (1H, m), 4.03–3.90 (2H, m), 3.71–3.63 (2H, m) 2.99–2.81 (1H, m), 1.76–1.41 (6H, m), 1.52 (9H, s); ^{13}C NMR (126 MHz, CD$_3$CN, rotamers) δ 158.7, 81.0, 71.4, 41.5, 28.4, 24.5, 21.5, 18.1; HRMS (ESI) Found MNa$^+$ 249.1325, $C_{10}H_{18}N_4O_2Na$ requires 249.1327. Data in accordance with the literature.[2]

tert-Butyl 3-Azidomorpholine-4-carboxylate (8)



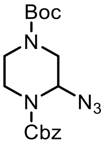
Following **GP1**, **1g** (23 mg, 0.1 mmol) gave **8** (17 mg, 76%) as an oil. FT-IR ν_{max} (film)/cm^{-1} 2106, 1703, 1393, 1300, 1231, 1160; ^{1}H NMR (500 MHz, CDCl$_3$, rotamers) δ 5.76–5.41 (1H, m), 3.98–3.93 (1H, m), 3.85 (1H, d, *J* = 12.0 Hz), 3.70–3.66 (1H, m), 3.55 (1H, dd, *J* = 12.0, 2.4 Hz), 3.50 (1H, dt, *J* = 12.0, 3.0 Hz), 3.29 (1H, bs), 1.50 (9H, s); ^{13}C NMR (126 MHz, CDCl$_3$, rotamers) δ 154.9^m, 154.1^M, 82.1^M, 81.5^m, 68.95^M, 68.9^m, 68.15^M, 68.1^m, 66.55^M, 66.5^m, 40.5^m, 39.1^M, 28.25^M, 28.2^m; HRMS (ESI) Found MNa$^+$ 251.1117, $C_9H_{16}N_4O_3Na$ requires 251.1120.

Di-*tert*-butyl 2-Azidopiperazine-1,4-dicarboxylate (9)



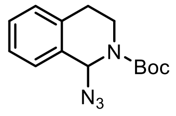
Following **GP1**, **1h** (33 mg, 0.1 mmol) gave **9** (28 mg, 85%) as an oil. FT-IR ν_{max} (film)/cm^{-1} 2997, 2108, 1699, 1366, 1232, 1162; ^{1}H NMR (500 MHz, CD$_3$CN, rotamers) δ 5.76 (1H, s), 3.98 (1H, d, *J* = 13.6 Hz), 3.93 (1H, bs), 3.75 (1H, d, *J* = 13.1 Hz), 3.04 (2H, bs), 2.86 (2H, bs), 1.46 (9H, s), 1.43 (9H, s); ^{13}C NMR (126 MHz, CDCl$_3$, rotamers) δ 155.4 (x 2), 82.1, 80.6, 69.3^M, 68.3^m, 47.5^M, 46.3^m, 43.8^M, 42.7^m, 40.7^m, 39.5^M, 28.4, 28.2; HRMS (ESI) Found MNa$^+$ 350.1793, $C_{14}H_{25}N_5O_4Na$ requires 350.1799.

1-Benzyl 4-(*tert*-Butyl) 2-Azidopiperazine-1,4-dicarboxylate (10)



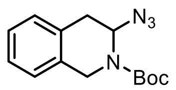
Following **GP1**, **1i** (36 mg, 0.1 mmol) gave **10** (21 mg, 59%) as an oil. FT-IR ν_{max} (film)/cm^{-1} 2110, 1698, 1406, 1365, 1224; ^{1}H NMR (400 MHz, CD$_3$CN, rotamers) δ 7.43–7.31 (5H, m), 5.79 (1H, s), 5.17 (2H, s), 4.04 (1H, d, *J* = 14.1 Hz), 3.94 (1H, bs), 3.81 (1H, dt, *J* = 13.3, 3.4 Hz), 3.30–2.98 (2H, m), 2.91 (1H, bs), 1.43 (9H, s); ^{13}C NMR (101 MHz, CD$_3$CN, rotamers) δ 155.3, 137.4, 129.5 (x 2), 129.2, 128.9 (x 2), 80.7, 68.8, 68.5, 46.5, 42.9, 40.4, 28.4; HRMS (ESI) Found MNa$^+$ 384.1649, $C_{17}H_{23}N_5O_4Na$ requires 384.1648.

tert-Butyl 1-Azido-3,4-dihydroisoquinoline-2(1H)-carboxylate (11)



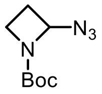
Following **GP1**, **1j** (27.7 mg, 0.1 mmol) gave **11** (19 mg, 70%) as colourless oil. FT-IR ν_{max} (film)/cm^{-1} 3648, 3001, 2253, 1627, 1442, 1375; ^{1}H NMR (400 MHz, CD_3CN, rotamers) δ 7.39 (0.5H, br s), 7.37 (1H, br s), 7.21–7.17 (2H, m), 6.90 (0.5H, br s), 5.86 (1H, br s), 4.08–3.99 (0.6H, m), 3.84–3.72 (1.3H, m), 3.22–3.13 (0.6H, m), 2.98–2.84 (1.4H, m), 1.32–1.22 (9H, m); ^{13}C NMR (101 MHz, CD_3CN) δ 156.8^{m}, 151.5^{M}, 147.5^{M}, 140.9^{m}, 136.6^{m}, 135.8^{M}, 130.3 (x 2)^{m}, 129.4 (x 2)^{M}, 127.8^{M}, 127.2^{m}, 126.0^{M},125.8^{m}, 80.1^{mM}, 57.9^{M}, 50.1^{m},42.4^{M}, 34.8^{m}, 30.3^{M}, 28.4^{M}, 28.1^{m}, 24.7^{m}; HRMS (ESI) Found MNa^{+} 297.1322, $C_{14}H_{18}N_4O_2Na$ requires 297.1327.

tert-Butyl 3-Azido-3,4-dihydroisoquinoline-2(1H)-carboxylate (12)



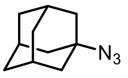
Following **GP1**, **1k** (28 mg, 0.1 mmol) gave **12** (21 mg, 76%) as colourless oil; FT-IR ν_{max} (film)/cm^{-1} 2973, 2104, 1703, 1457, 1390, 1229, 1162; ^{1}H NMR (400 MHz, CD_3CN, rotamers) δ 7.25–7.17 (4H, m), 6.13 (1H, bs), 4.57–4.44 (2H, m), 3.07 (1H, dd, *J* = 15.9, 4.1 Hz), 2.88 (1H, d, *J* = 15.9 Hz), 1.51 (9H, s); ^{13}C NMR (101 MHz, CD_3CN, rotamers) δ 151.9^{M}, 151.7 ^{m}, 133.8 ^{m}, 132.4 ^{M}, 129.5, 125.4^{m}, 128.0, 127.7, 127.1, 125.9^{M}, 82.1^{M}, 81.9^{m}, 69.8^{M}, 68.9^{m}, 44.7 ^{M}, 44.3^{m}, 35.2^{m}, 34.9^{M}, 28.3; HRMS (ESI) Found MNa^{+} 297.1321, $C_{14}H_{18}N_4O_2Na$ requires 297.1327.

tert-Butyl 2-Azidoazetidine-1-carboxylate (13)



Following **GP1**, but purifying the product by flash chromatography of the crude reaction mixture after evaporation of DCE, **1l** (20 mg, 0.1 mmol) gave **13** (10 mg, 48%) as an oil. FT-IR ν_{max} (film)/cm^{-1} 2110, 1708, 1381, 1246, 1134; ^{1}H NMR (500 MHz, CD_3CN) δ 5.38 (1H, s), 3.72–3.61 (2H, m), 2.51–2.41 (1H, m), 2.08–2.00 (1H, m), 1.44 (9H, s); ^{13}C NMR (126 MHz, CD_3CN) δ 152.4, 81.0, 76.9, 45.3, 28.4, 24.5; HRMS (ESI) Found MNa^{+} 221.1007, $C_8H_{14}N_4O_2Na$ requires 221.1009.

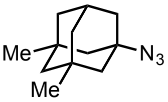
1-Azidoadamantane (17)



Following **GP1**, but using $MesAcrBF_4$ as the photocatalyst, **1p** (18 mg, 0.1 mmol) gave **17** (16 mg, 90%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.17 (3H, bs), 1.83 (6H, bs), 1.73−1.65 (6H, m); ^{13}C

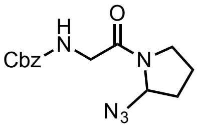
NMR (126 MHz, CD_3CN) δ 58.4, 41.2, 35.2, 29.6; HRMS (ESI) Found MNa^+ 200.1156, $C_{10}H_{15}N_3Na$ Na requires 200.1161. Data in accordance with the literature.[3]

1-Azido-3,5-dimethyladamantane (18)



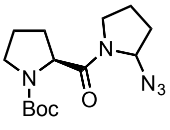
Following **GP1**, but using $MesAcrBF_4$ as the photocatalyst, **1q** (21 mg, 0.1 mmol) gave **18** (10 mg, 46%) as colourless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 2.20–2.17 (1H, m), 1.61–1.60 (2H, m), 1.45–1.22 (8H, m), 1.12 (2H, bs), 0.86 (6H, s); ^{13}C NMR (126 MHz, CD_3CN) δ 60.1, 49.9, 47.2, 42.0, 39.8, 32.8, 30.1, 29.6; HRMS (ESI) Found MNa^+ 228.1470, $C_{12}H_{19}N_3Na$ requires 228.1477. Data in accordance with the literature.[3]

Benzyl (2-(2-Azidopyrrolidin-1-yl)-2-oxoethyl)carbamate (19)



Following **GP1**, **1r** (28 mg, 0.1 mmol) gave **19** (16 mg, 54%) as an oil. FT-IR ν_{max} (film)/cm^{-1} 2923, 2131, 1698, 1456, 1329, 1199, 1143; ^1H NMR (400 MHz, CD_3CN, rotamers) δ 7.39–7.30 (5H, m), 5.84 (0.85H, bs), 5.67 (0.85H, dd, J = 5.8, 1.5 Hz), 5.50 (0.15H, bs), 5.36–5.35 (0.15H, m), 5.09 (2H, s), 4.03 (0.3H, ABq, J_{AB} = 14.3, 5.7 Hz), 3.91 (1.7H, dd, J= 5.6, 1.5 Hz), 3.60–3.51 (1H, m), 3.41–3.31 (1H, m), 2.02–1.96 (2H, m), 1.93–1.87 (1H, m), 1.79 (1H, dt, J = 12.5, 3.7 Hz); ^{13}C NMR (126 MHz, CD_3CN, rotamers) δ 169.9, 157.5, 138.2, 129.4, 128.9, 128.7, 75.1^M, 74.1^m, 67.1, 47.2^m, 46.3, 43.9^M, 33.9^m, 32.3^M, 24.1^M, 21.8^m; HRMS (ESI) Found MNa^+ 326.1216, $C_{14}H_{17}N_5O_3Na$ requires 326.1224.

***tert*-Butyl (*S*)-2-((*R*)-2-Azidopyrrolidine-1-carbonyl)pyrrolidine-1-carboxylate (20)**
and *tert*-Butyl (*S*)-2-((*S*)-2-Azidopyrrolidine-1-carbonyl)pyrrolidine-1-carboxylate (20')



Following **GP1**, **1s** (31 mg, 0.1 mmol) gave **20** and **20'** (21 mg, 68%) an inseparable mixture as an oil. dr = 1.5:1.0. FT-IR ν_{max} (film)/cm^{-1} 2899, 2187, 1714, 1412, 1399, 1231, 1171; ^1H NMR (400 MHz, CD_3CN) δ 5.72 (1H, dd, J = 5.4, 1.3 Hz), 5.68 (0.7H, d, J = 5.4 Hz), 5.35 (0.2H, d, J = 5.7 Hz), 5.30 (0.1H, d, J = 4 .9 Hz), 4.57 (0.1H, dd, J = 8.7, 3.6 Hz), 4.52 (0.2H, dd, J = 8.5, 3.7 Hz), 4.41 (0.2H, dd, J = 8.7, 3.7 Hz), 4.39 (1.8H, dd, J = 8.3.6, 4.3 Hz), 3.66–3.60 (1.8H, m), 3.55 (1H, q, J = 9.3), 3.49 (1.4H, q, J = 9.7 Hz), 3.44–3.35(4H, m,), 2.33–2.27 (2.2H, m), 2.06–1.99 (4H, m), 1.97–

1.90 (2H, m), 1.89–1.76 (8H, m), 1.42 (6H, s), 1.32 (0.6H, s), 1.29 (1.2H, s), 1.26 (9H, s); ^{13}C NMR (126 MHz, CD_3CN, major diastereomer) δ 174.4, 154.5, 79.8, 74.2, 58.8, 47.5, 47.2, 32.3, 31.6, 28.5, 24.4, 24.3; ^{13}C NMR (126 MHz, CD_3CN, minor diastereomer) δ 173.9, 155.1, 79.9, 74.2, 58.7, 47.8, 47.1, 32.2, 30.8, 28.7, 24.9, 24.3; HRMS (ESI) Found MNa^+ 332.1685, $C_{14}H_{23}N_5O_3Na$ requires 332.1693.

6 Emission Quenching Experiments

Stern-Volmer experiments for *N*-Boc-Proline Cesium salt **1-Cs** and triisopropylbenzenesulfonyl azide **E** were carried out monitoring the emission intensity of argon-degassed solution of rhodamine 6G (0.1 mM, 2.2 mL) containing variable amounts of the quencher in dry DCE. All The rhodamine 6G solutions were excited at 528 nm and the emission intensity was collected at 548 nm.

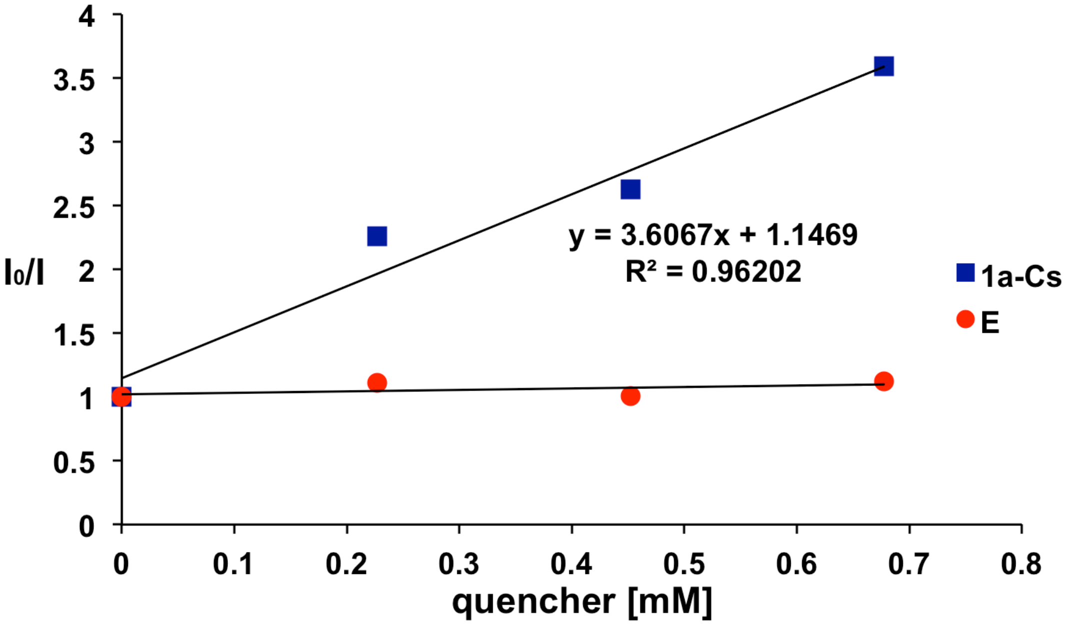


Figure SI-3.

The quenching constants k_q were obtained using the Stern-Volmer relationship and the reported excited-state lifetime for rhodamine 6G in MeOH (0.00413 μs).[4]

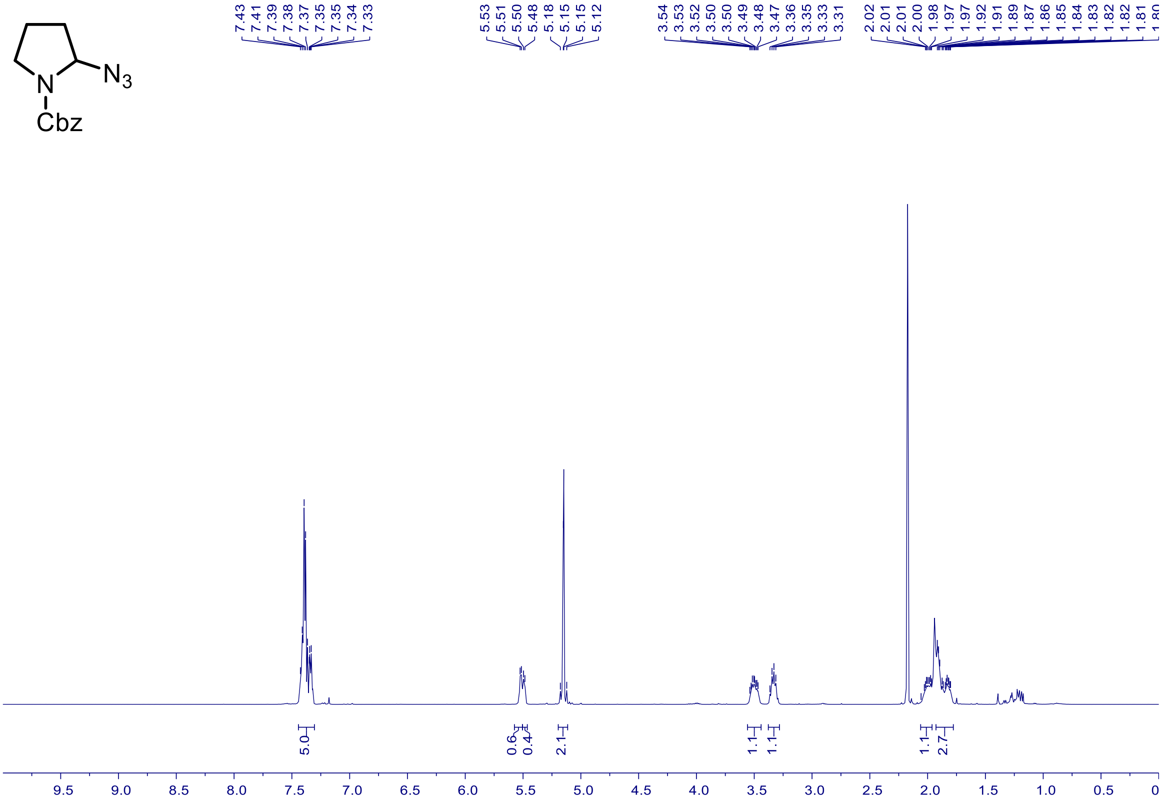
$$\frac{I_o}{I} = 1 + k_{q\tau_0}[Quencher]$$

Table SI-2.

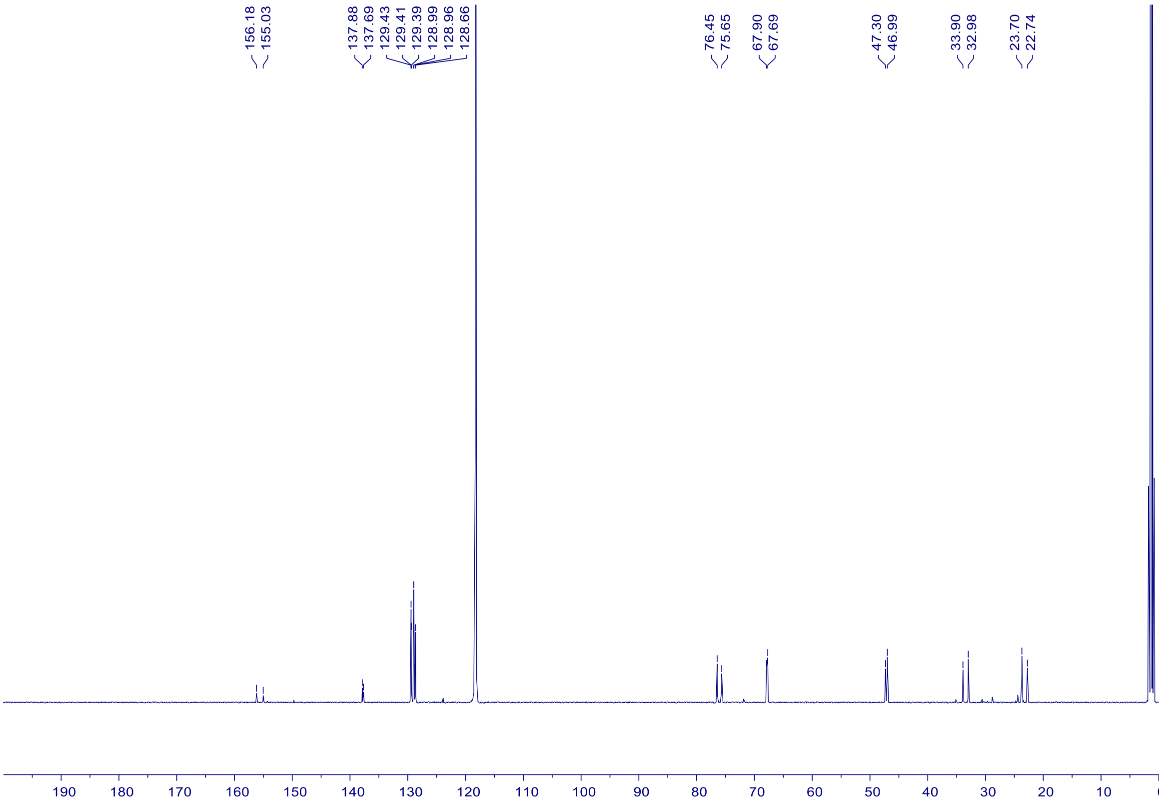
Quencher	k_q (M^{-1} s^{-1})
1a-Cs	2.1×10^9
E	–

7 ^{1}H and ^{13}C NMR Spectra

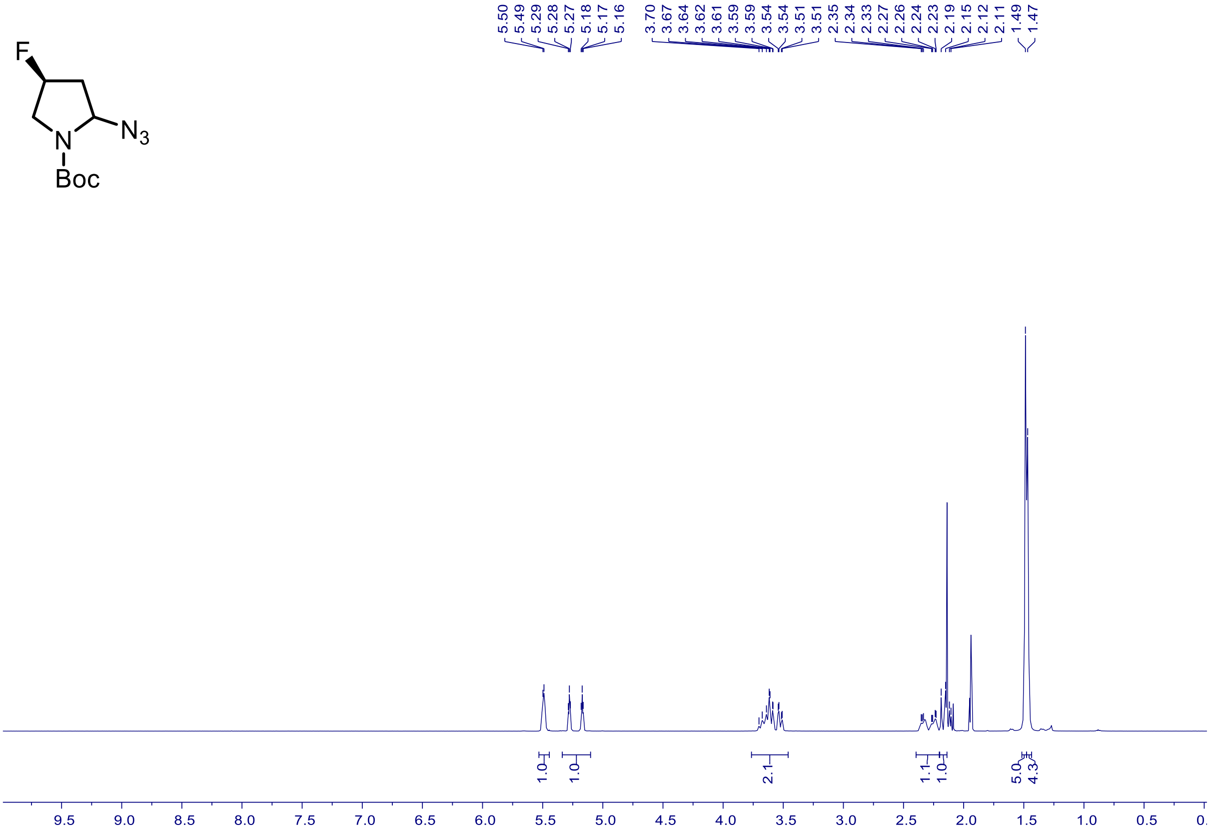
3 – ^{1}H NMR (500 MHz, CD$_3$CN)



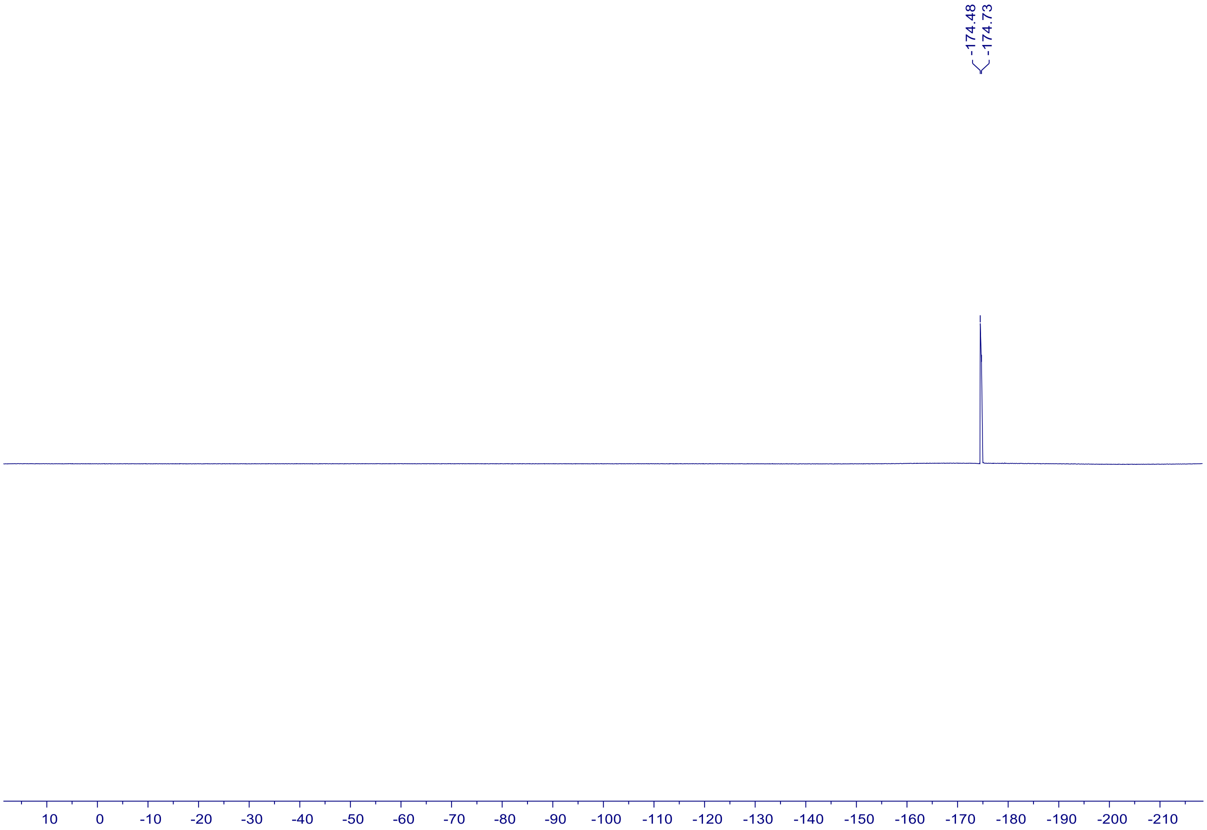
3 – ^{13}C NMR (126 MHz, CD$_3$CN)



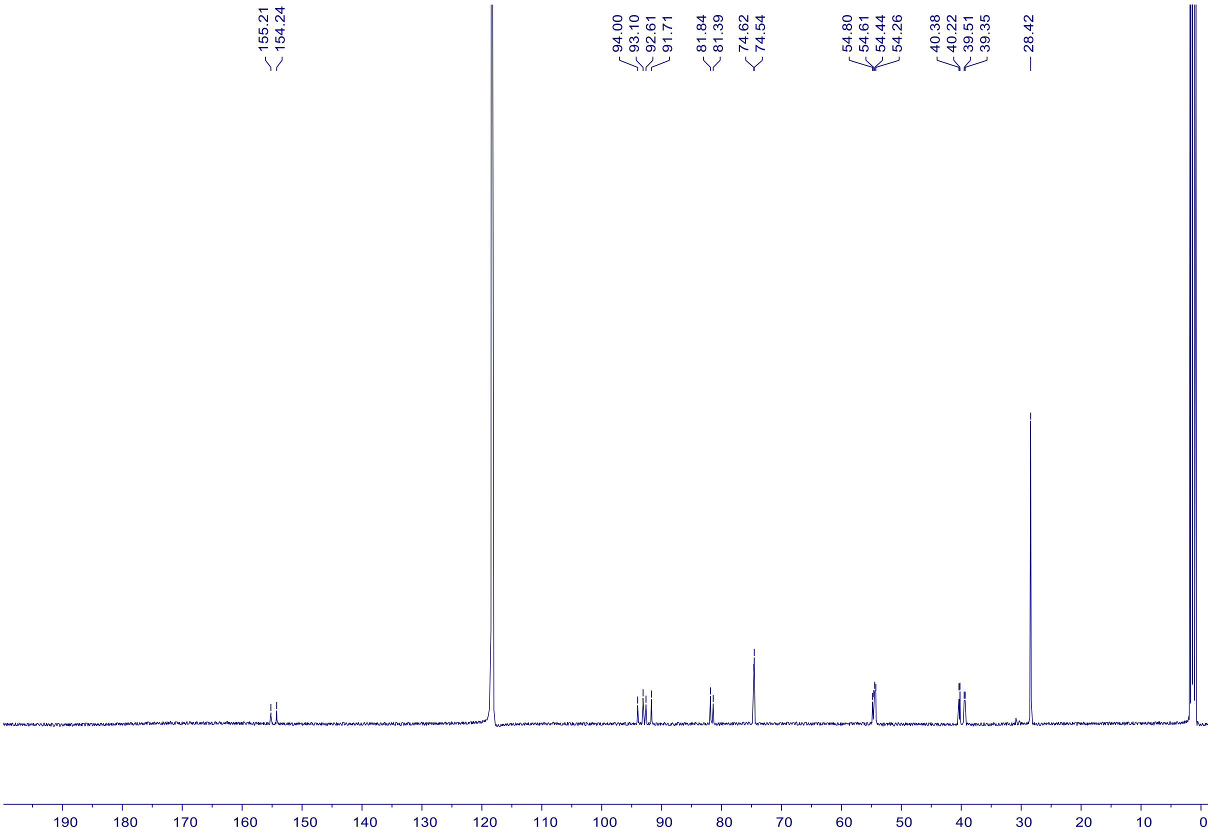
4 – ^{1}H NMR (500 MHz, CD$_3$CN)



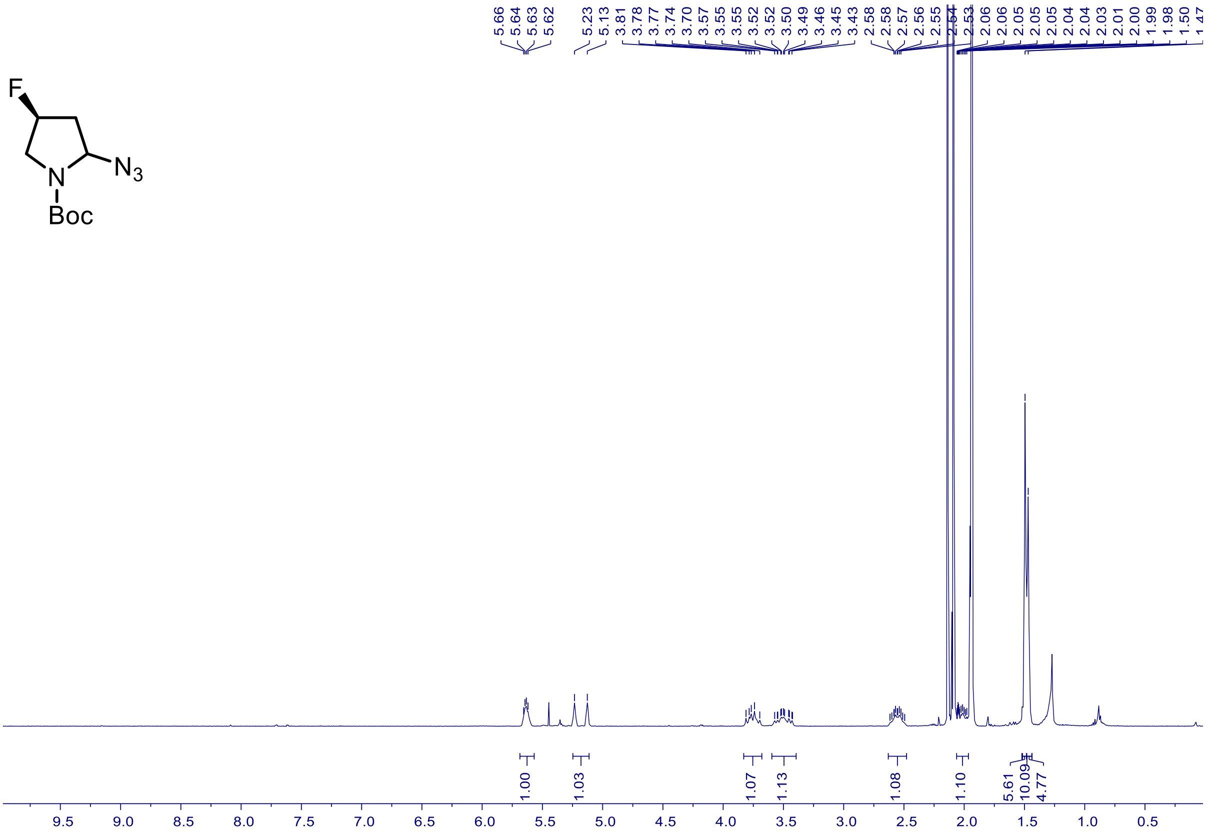
4 – ^{19}F NMR (161 MHz, CD$_3$CN)



4 – ^{13}C NMR (126 MHz, CD$_3$CN)

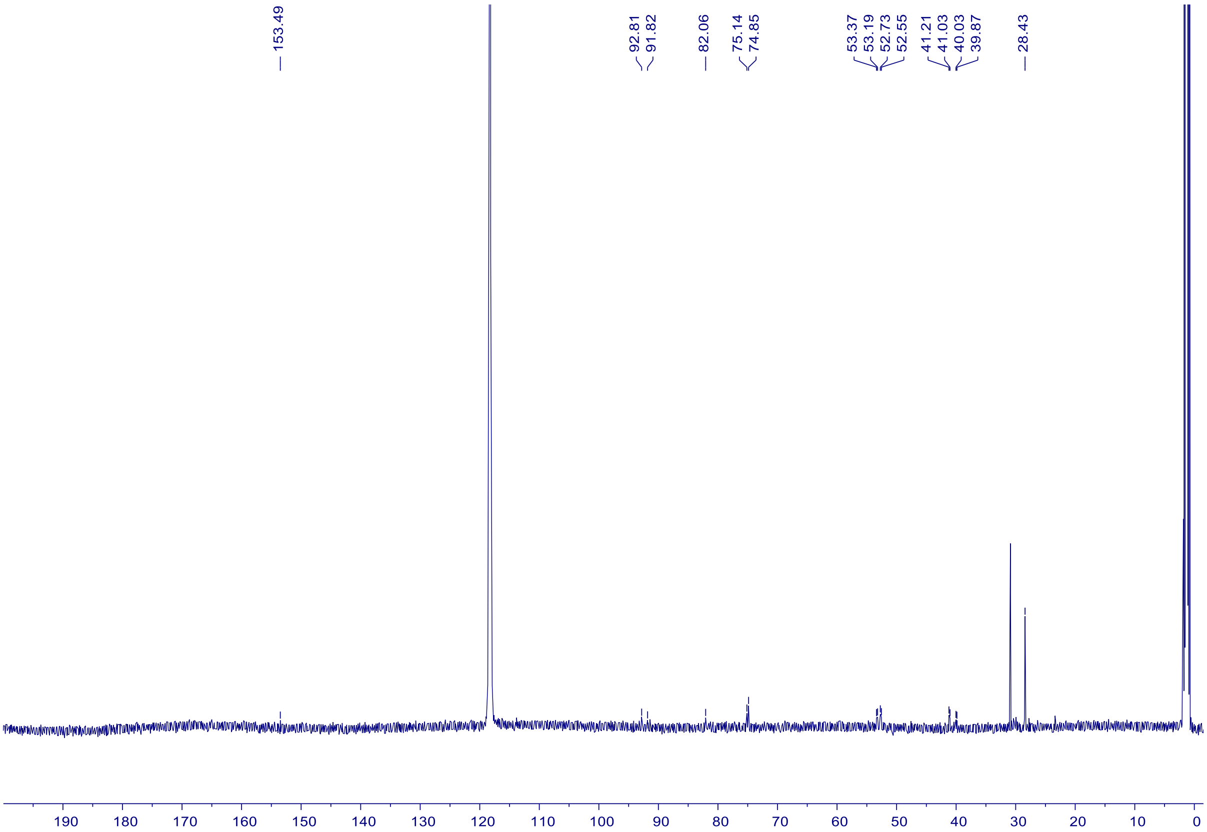


4’ – ^{1}H NMR (500 MHz, CD_3CN)

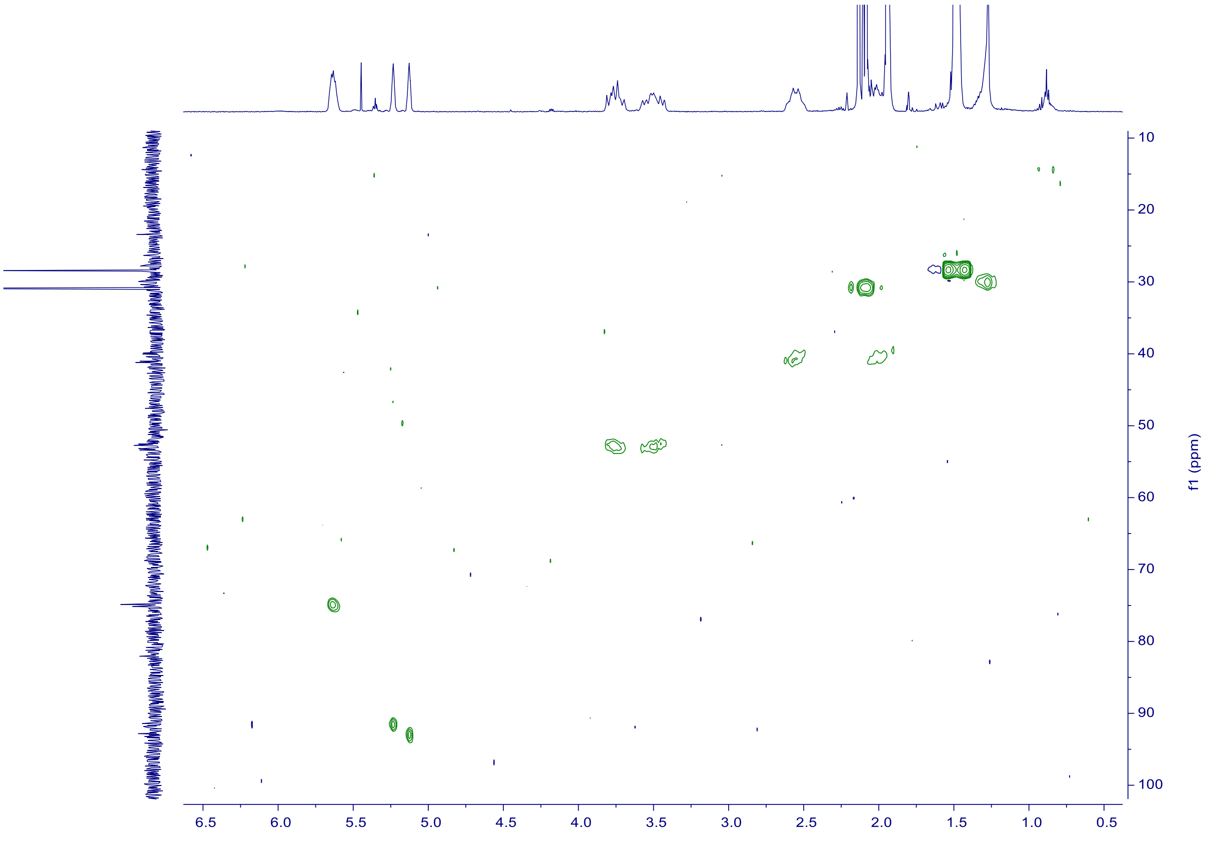


4’ – ^{19}F NMR (161 MHz, CD_3CN)

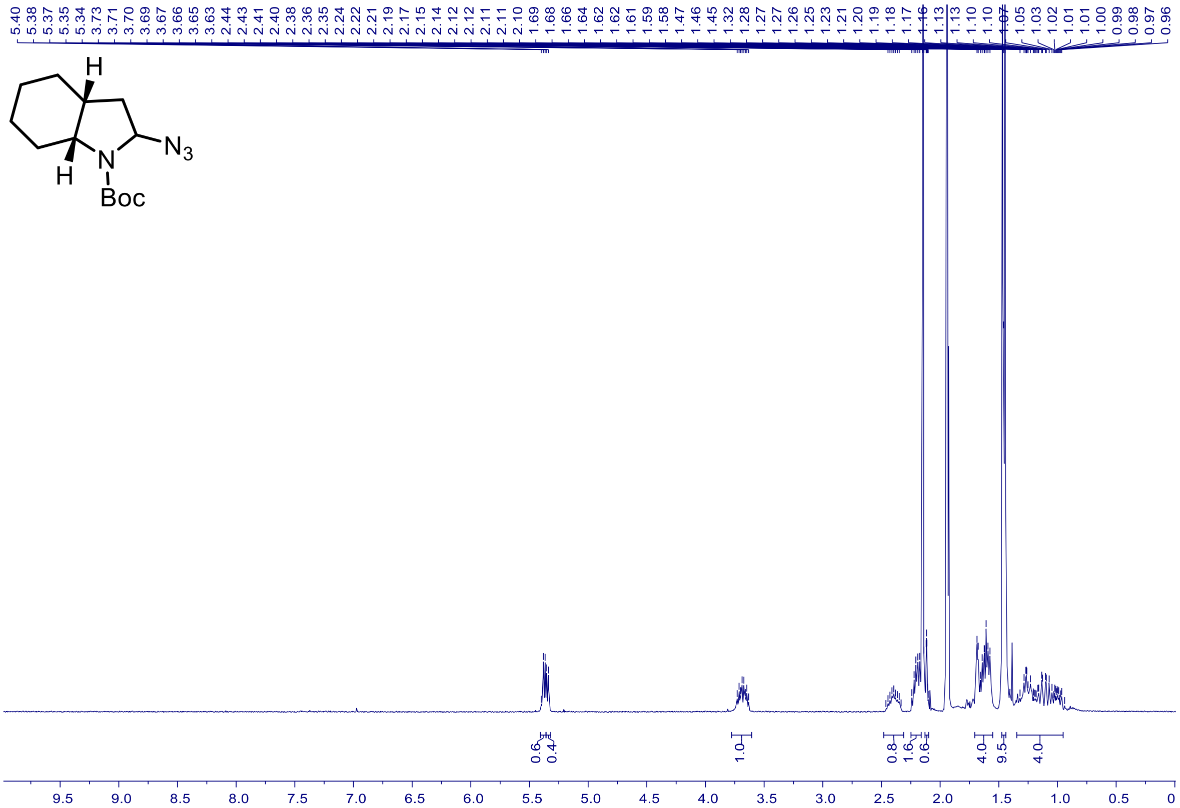
4’ – ^{13}C NMR (126 MHz, CD$_3$CN)



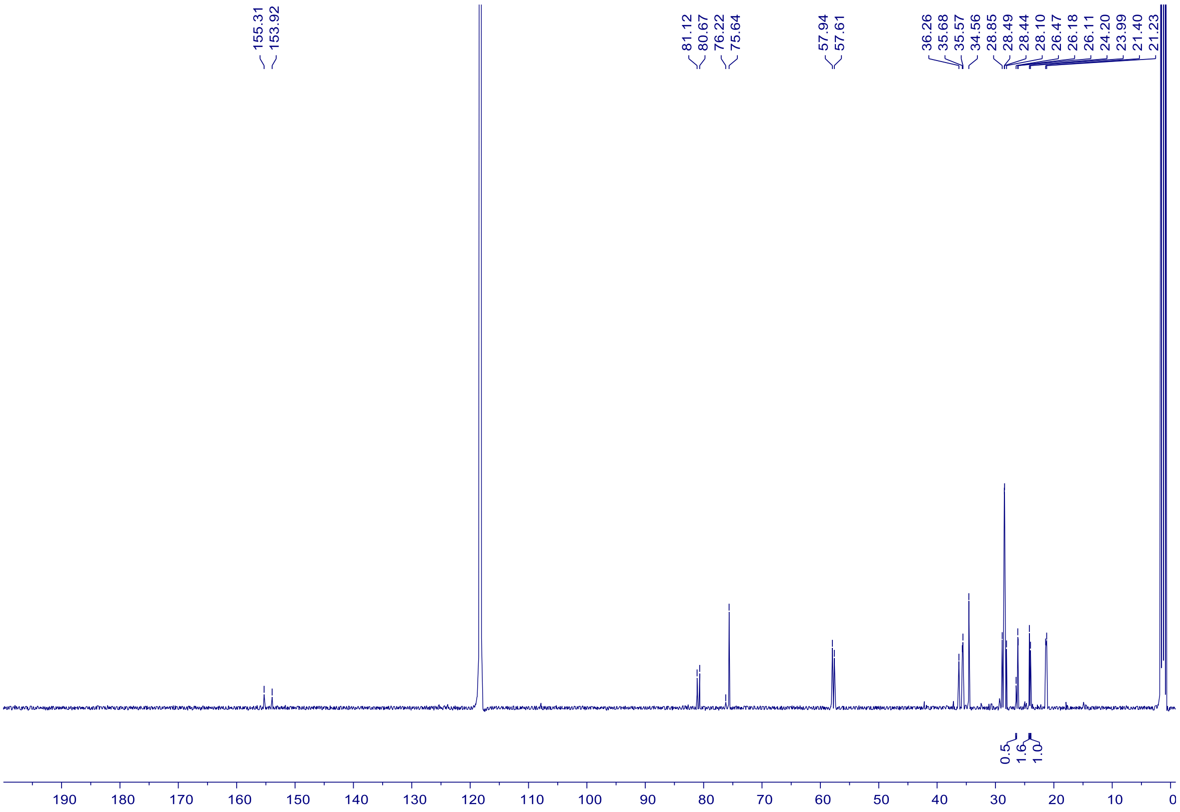
4’ – ^{1}H–^{13}C HSQC (500 MHz, CD$_3$CN)



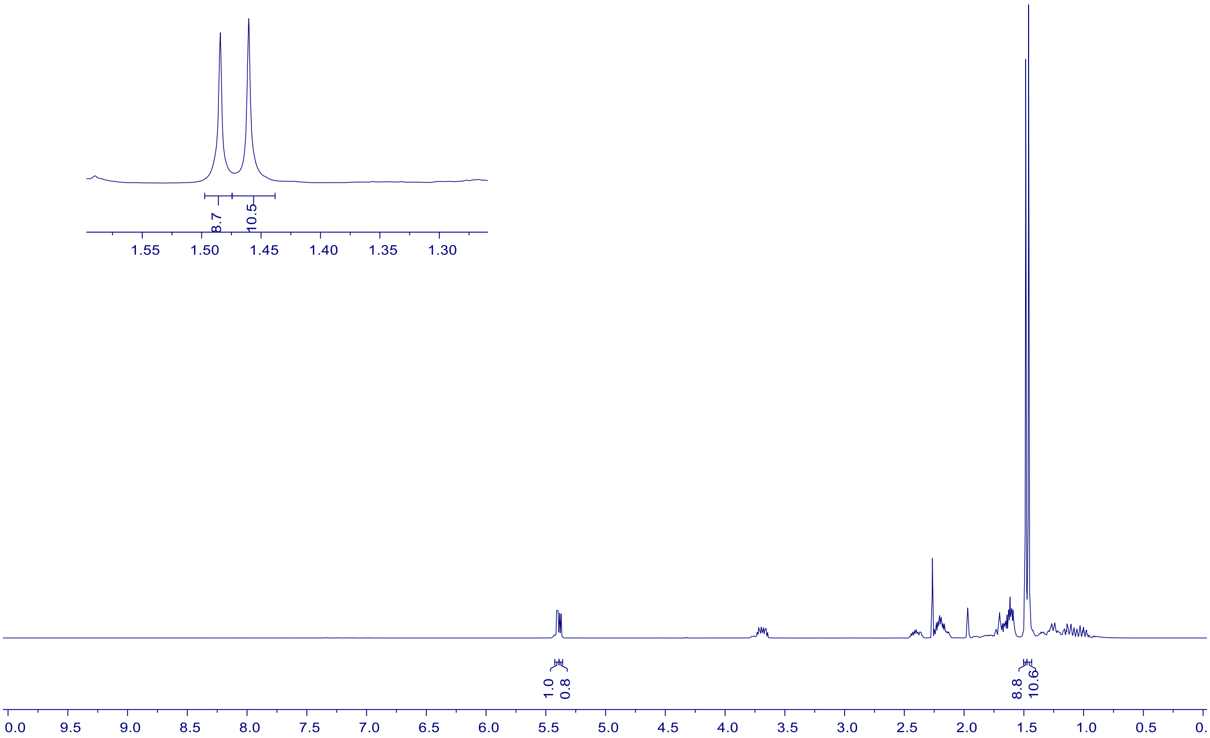
5 – ^{1}H NMR (400 MHz, CD_3CN)



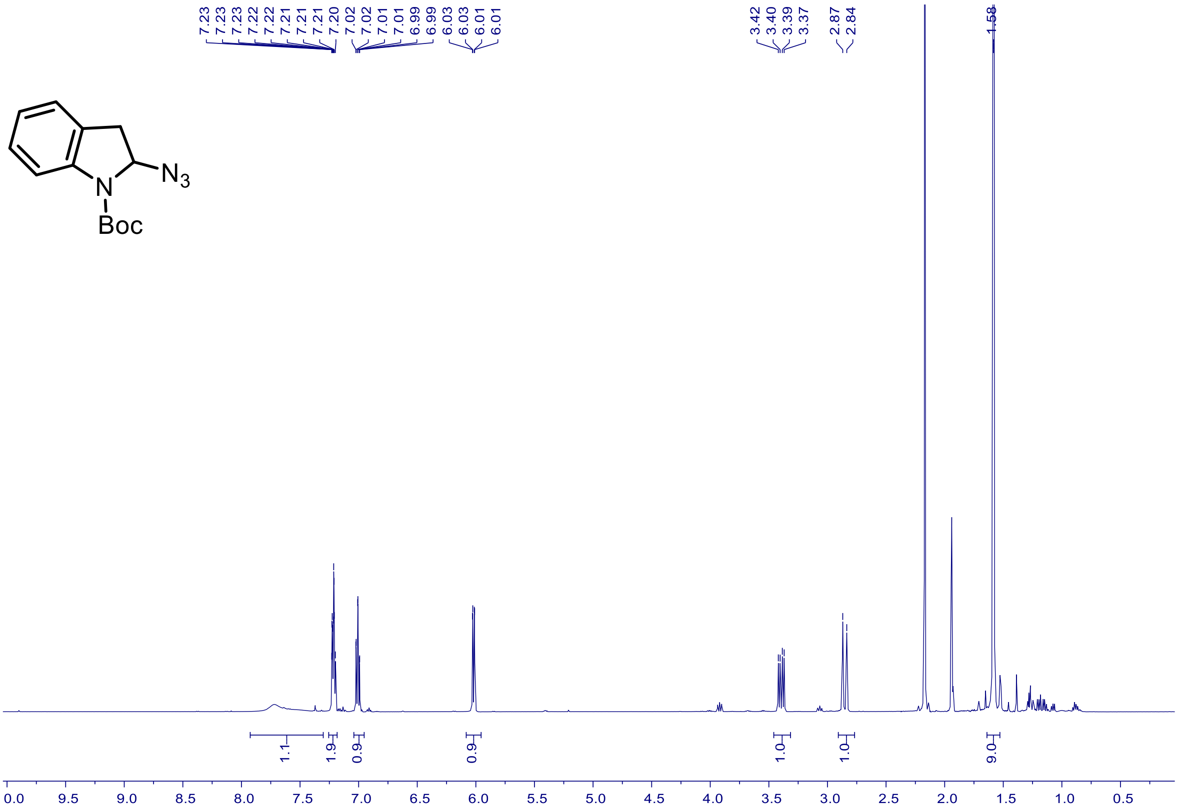
5 – ^{13}C NMR (126 MHz, CD_3CN)



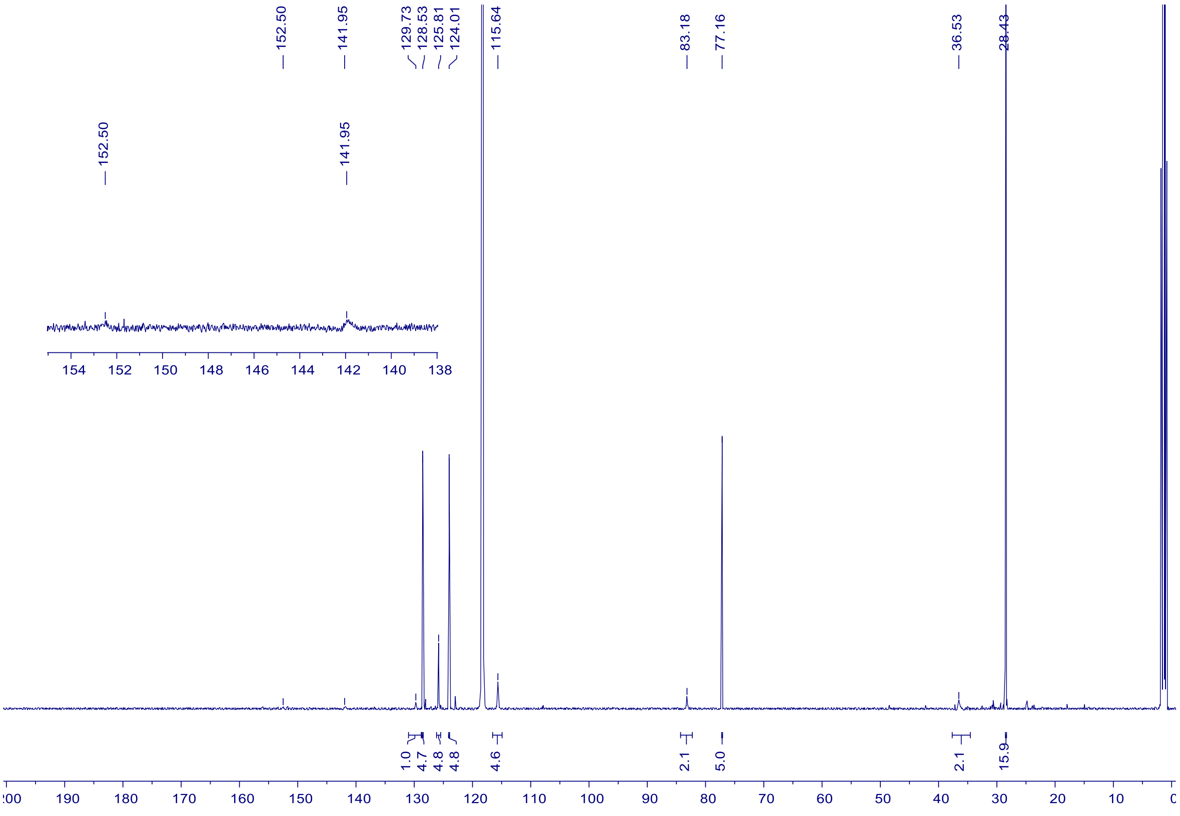
5 – VT ^{1}H NMR (400 MHz, CD_3CN, 70 °C)



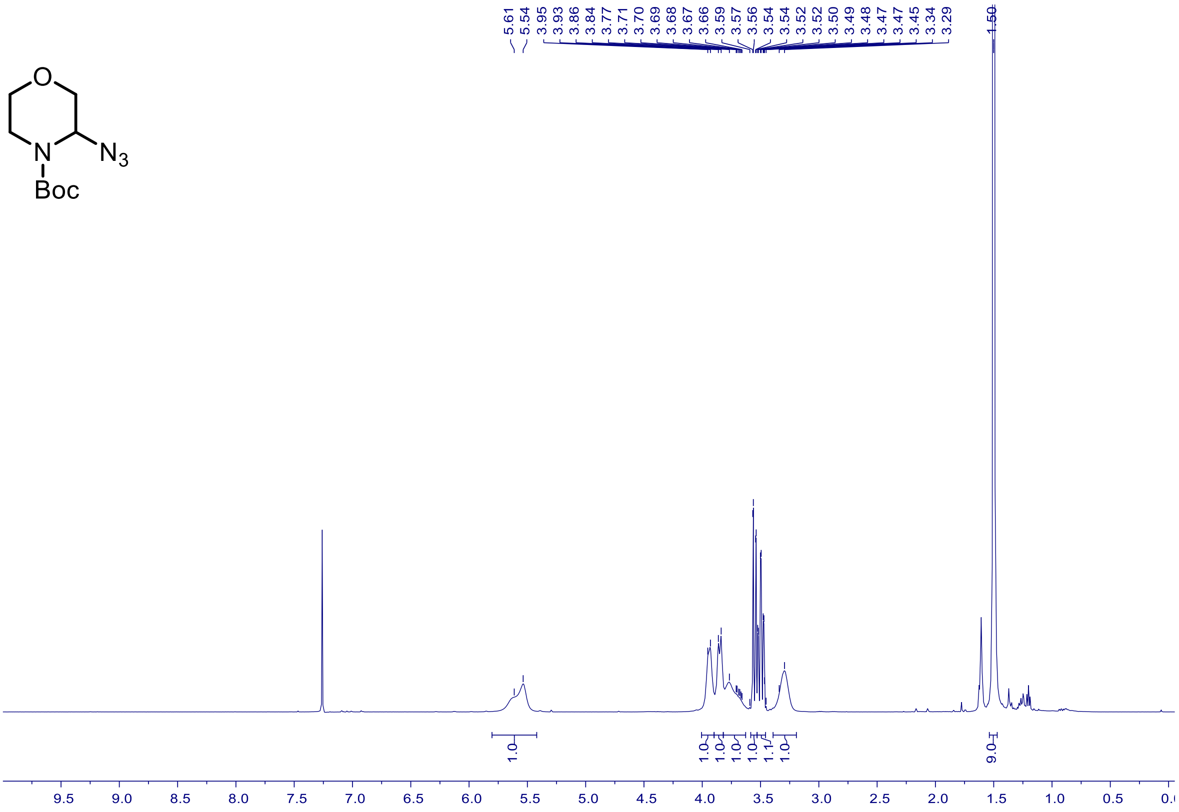
6 – ^{1}H NMR (500 MHz, CD$_3$CN)



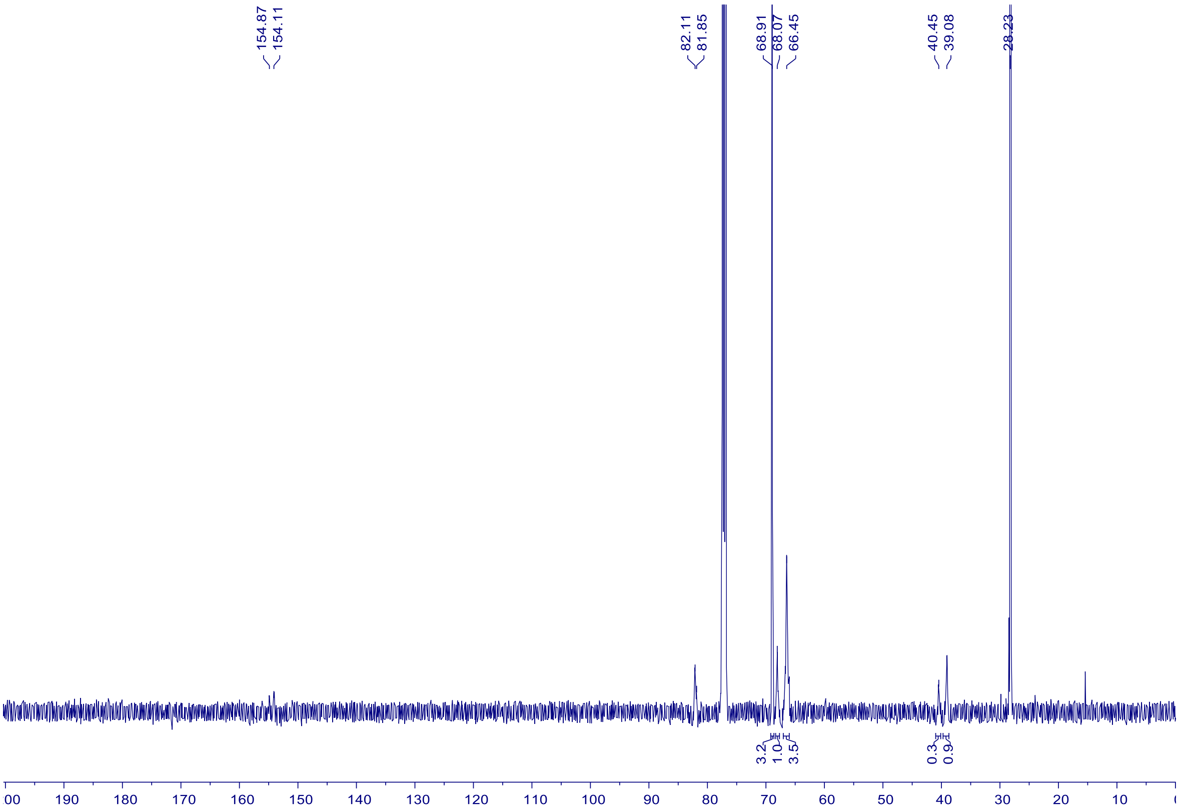
6 – ^{13}C NMR (126 MHz, CD$_3$CN)



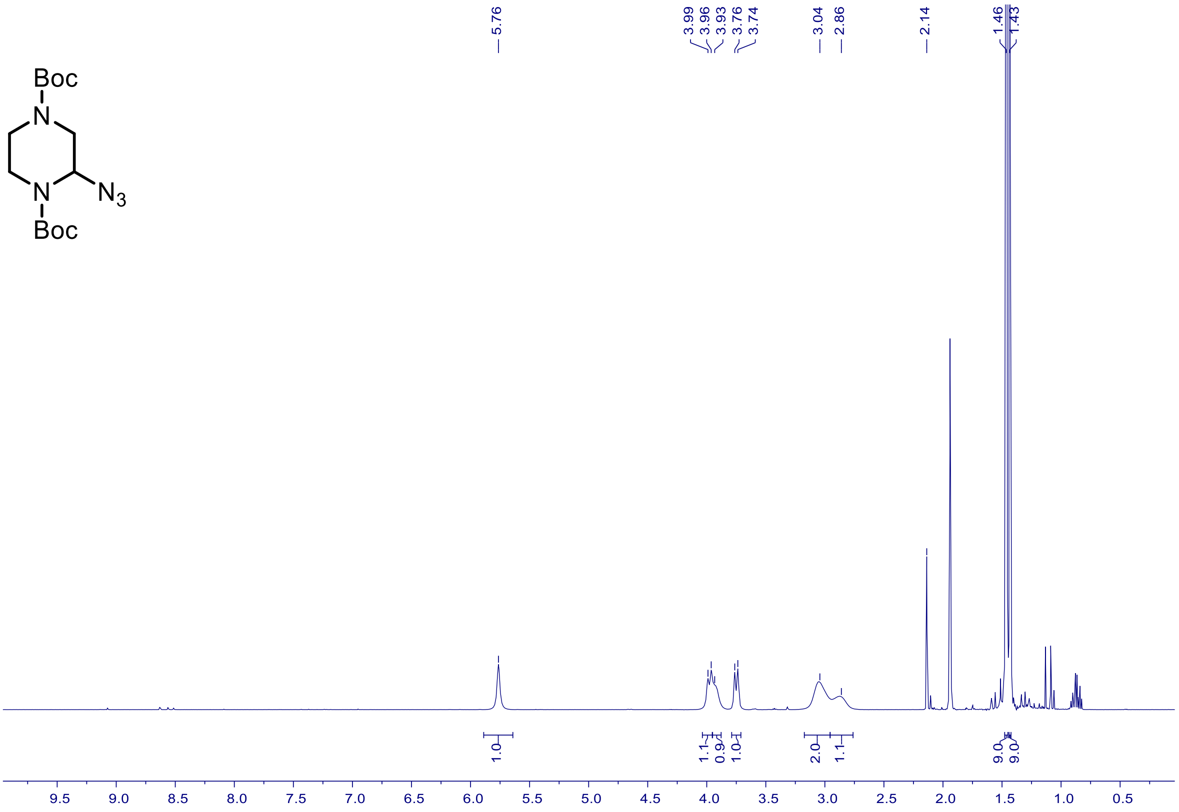
8 – ^{1}H NMR (500 MHz, CDCl$_3$)



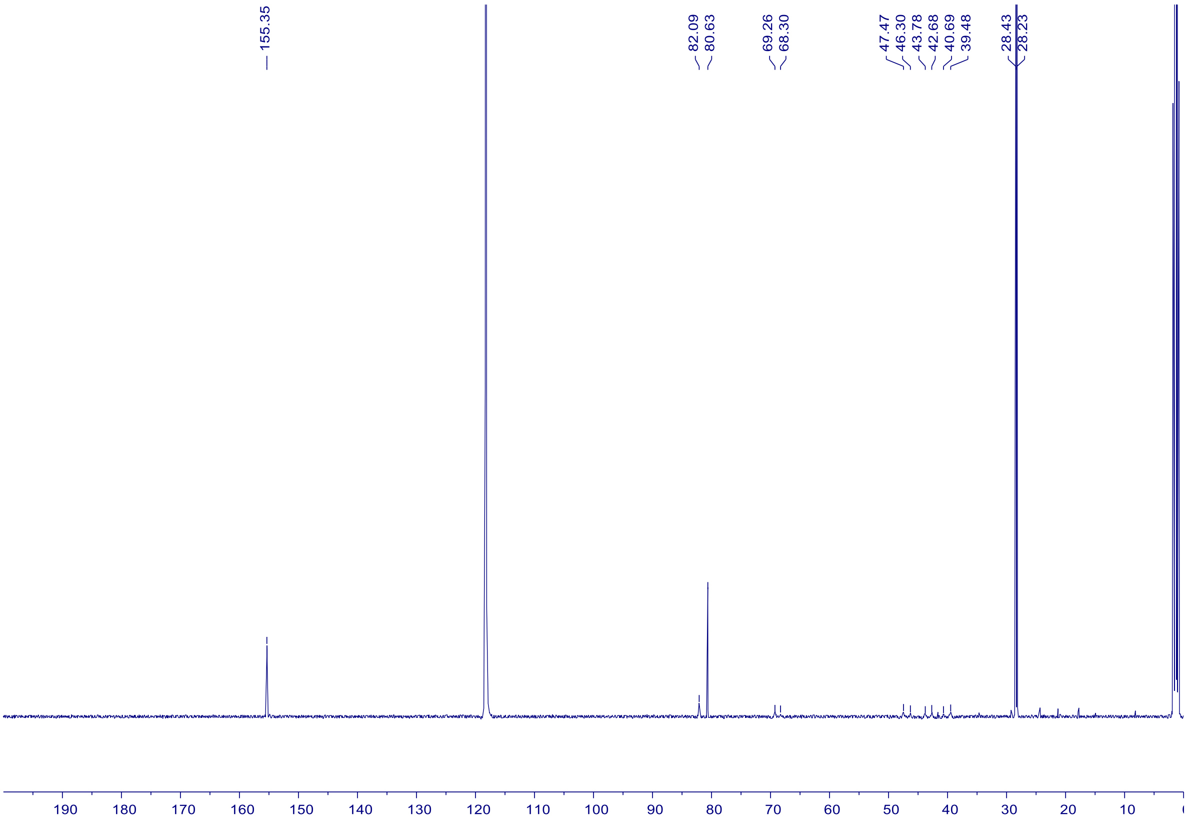
8 – ^{13}C NMR (126 MHz, CDCl$_3$)



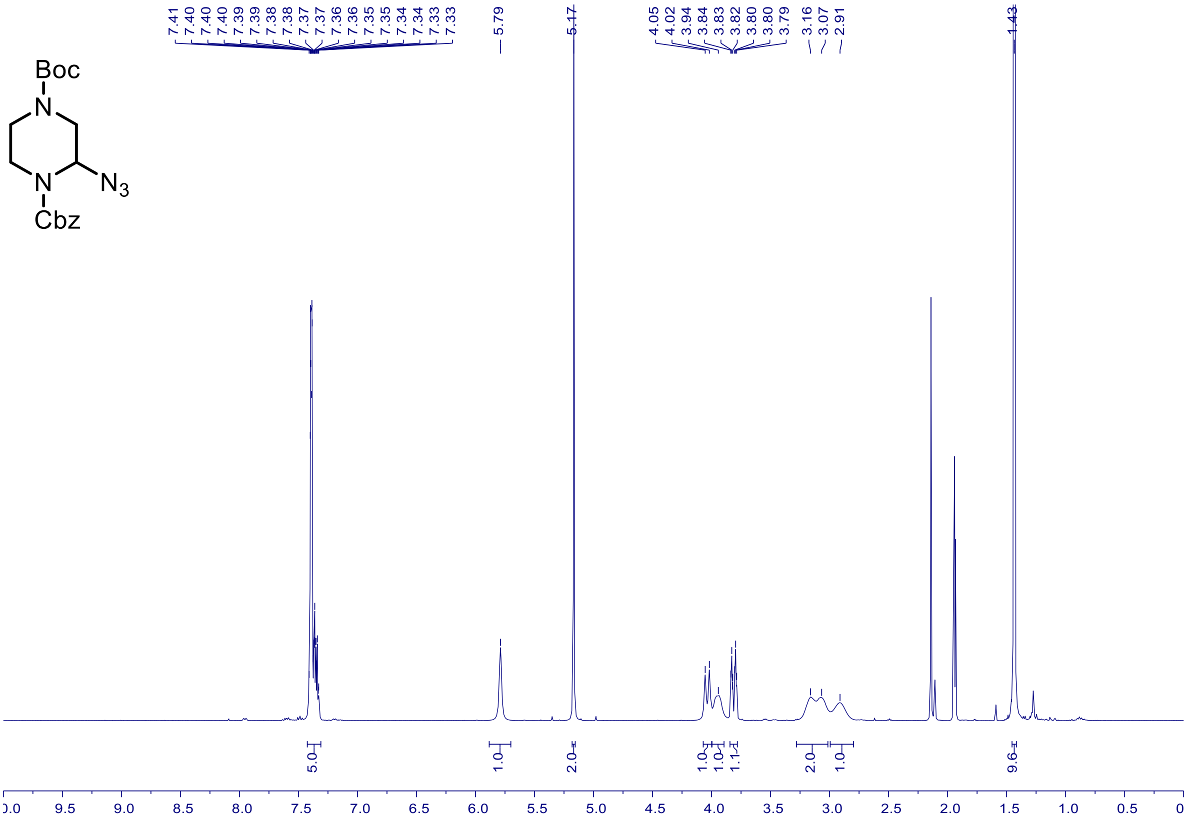
9 – ^{1}H NMR (500 MHz, CD$_3$CN)



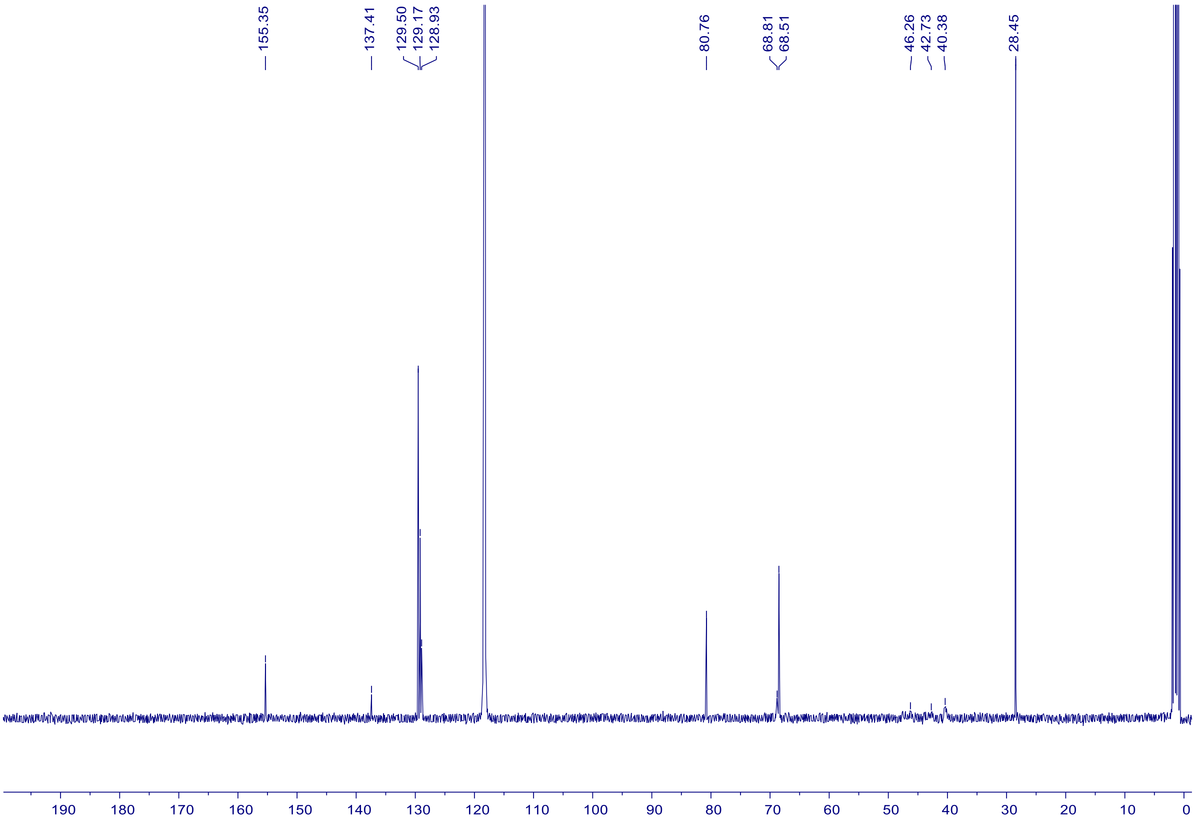
9 – ^{13}C NMR (126 MHz, CD$_3$CN)



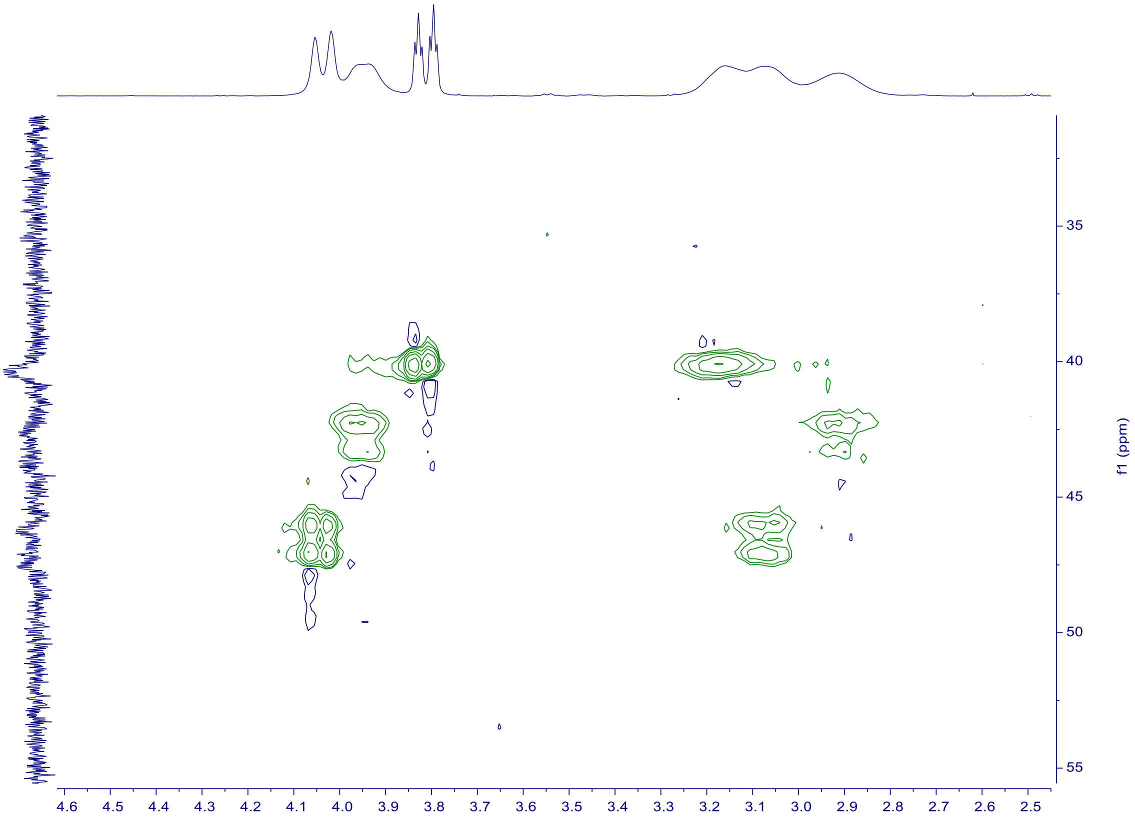
10 – ^{1}H NMR (400 MHz, CD_3CN)



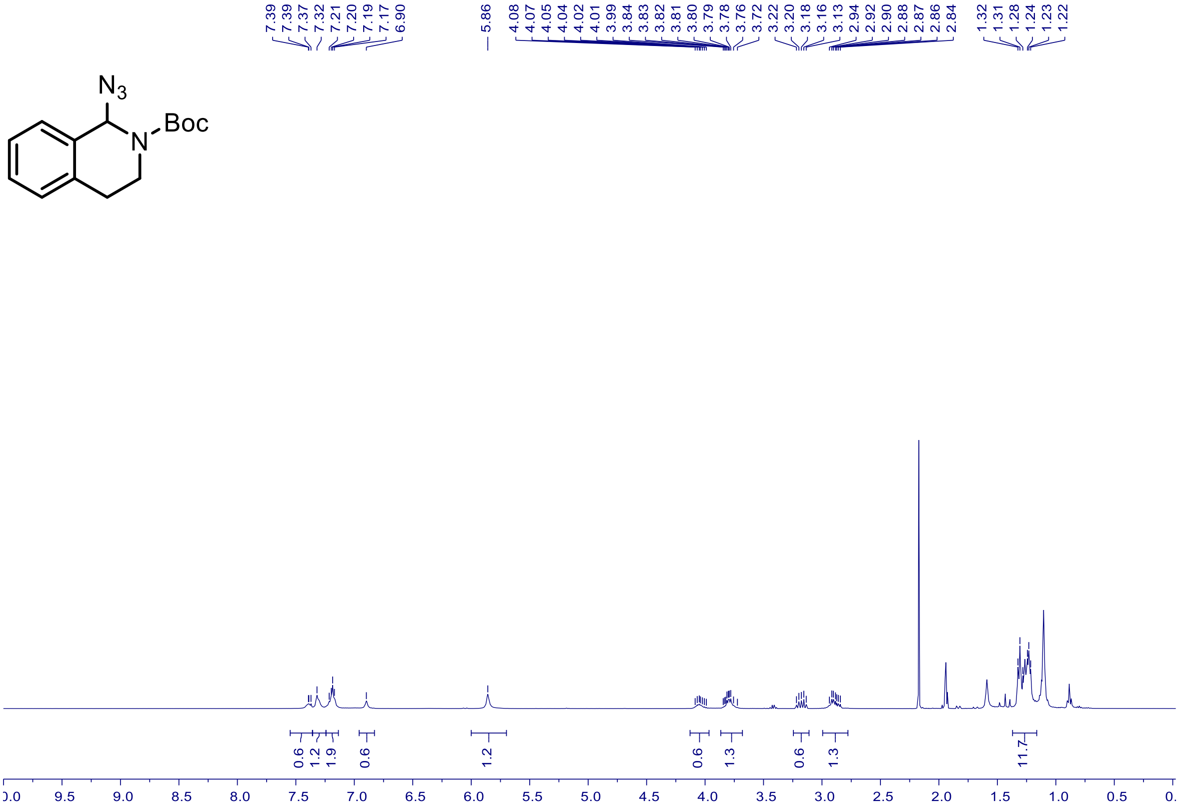
10 – ^{13}C NMR (101 MHz, CD_3CN)



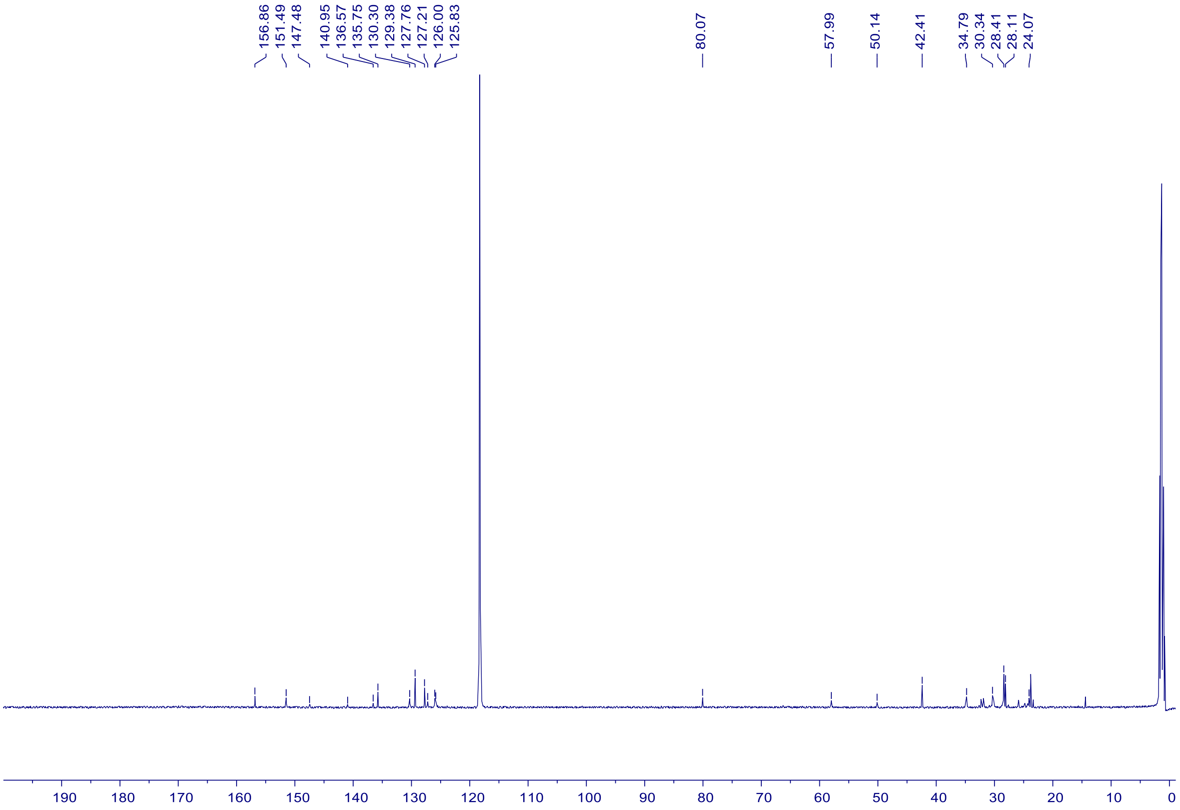
10 – ^{1}H–^{13}C HSQC (500 MHz, CD_3CN)



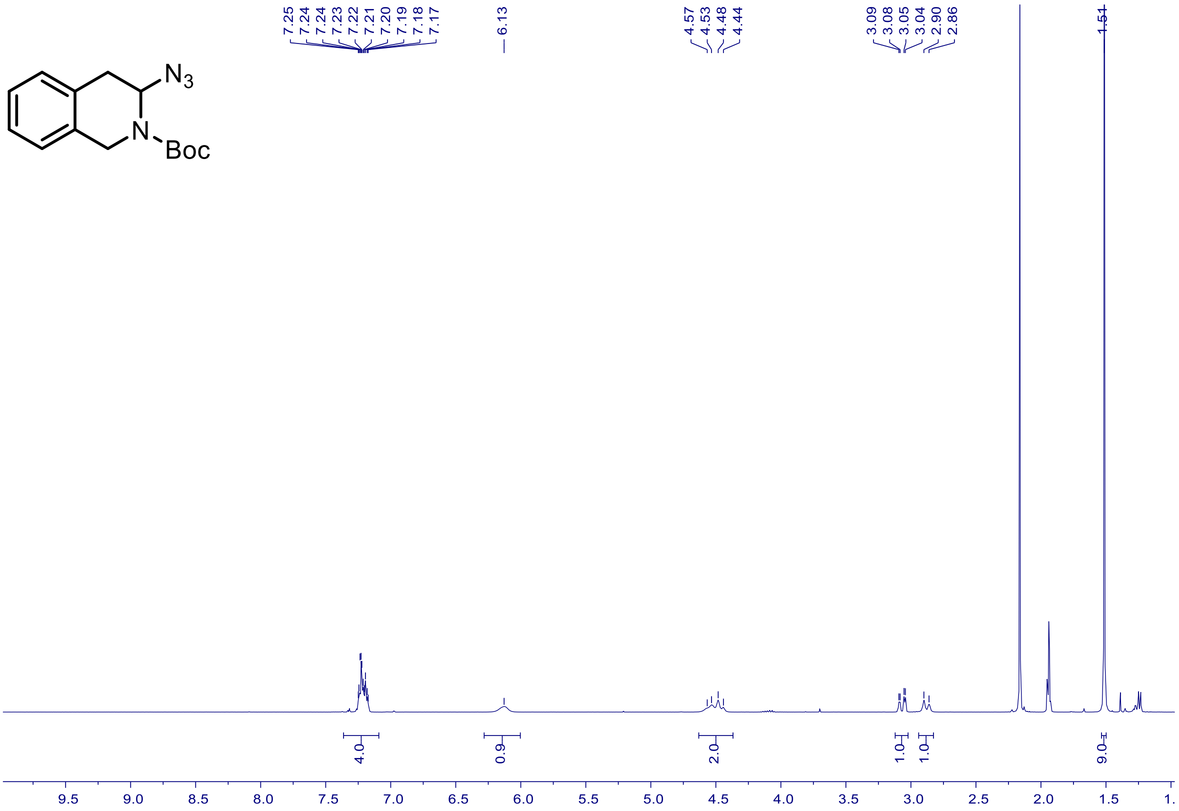
11 – ^{1}H NMR (400 MHz, $CDCl_3$)



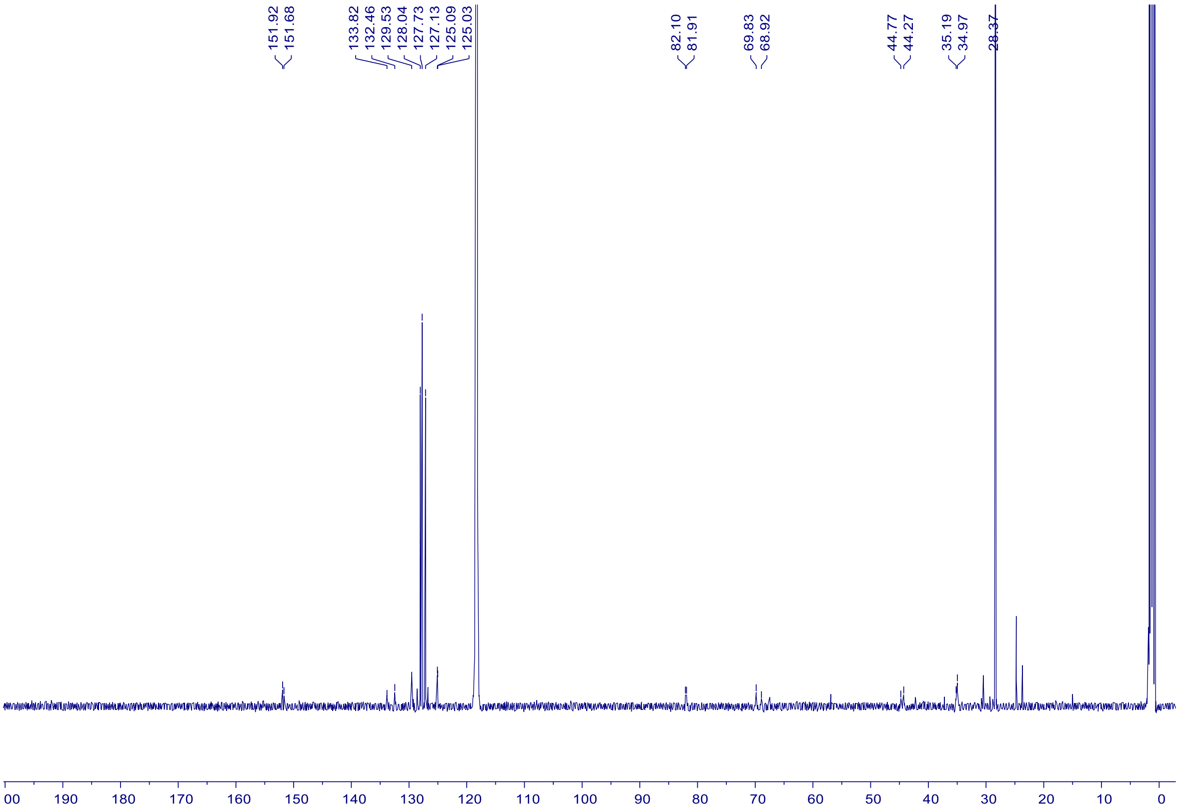
11 – ^{13}C NMR (101 MHz, $CDCl_3$)



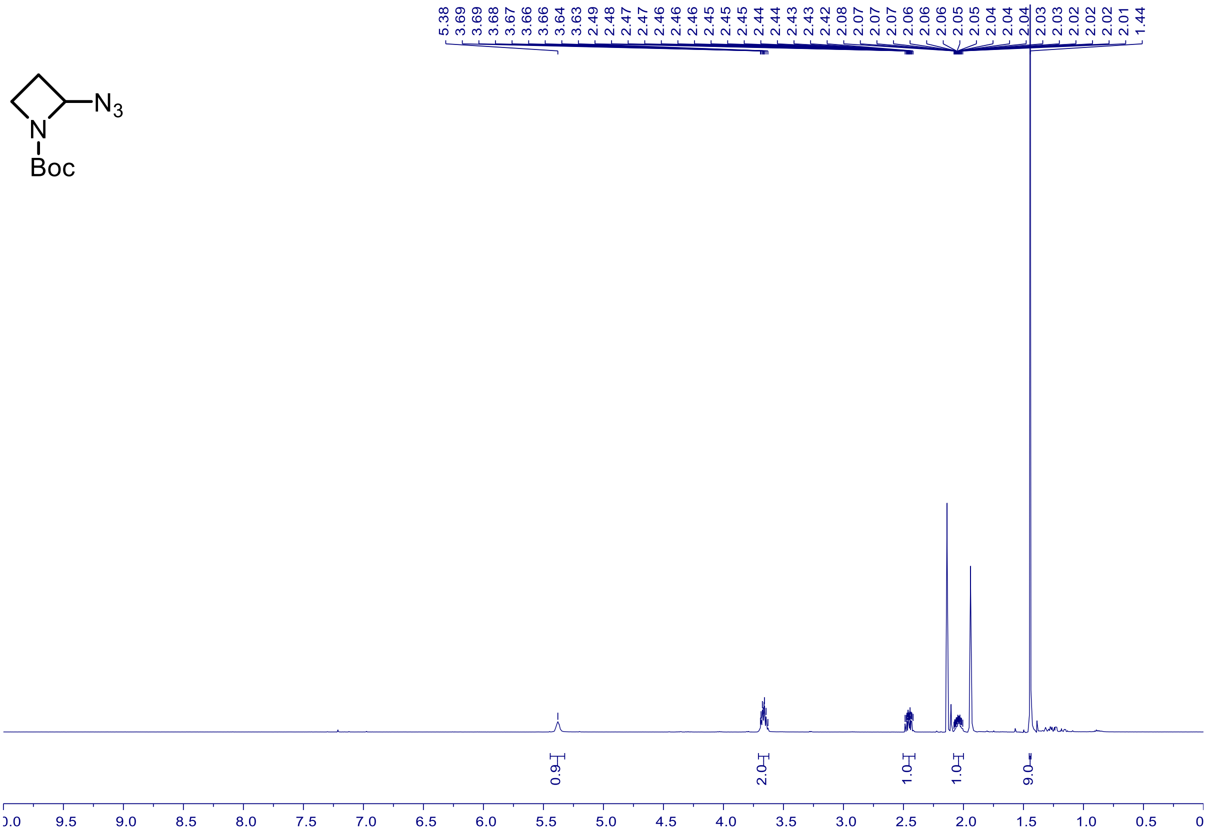
12 – ^{1}H NMR (400 MHz, $CDCl_3$)



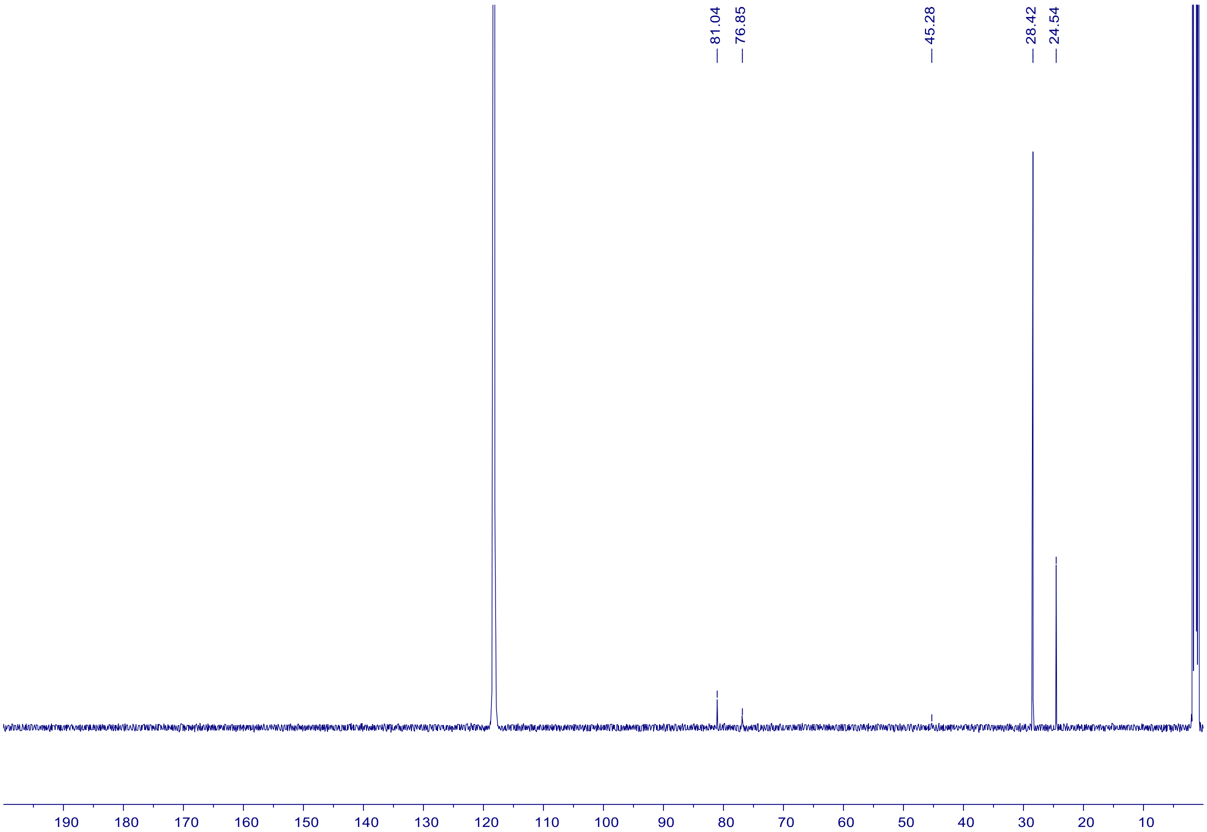
12 – ^{13}C NMR (101 MHz, $CDCl_3$)



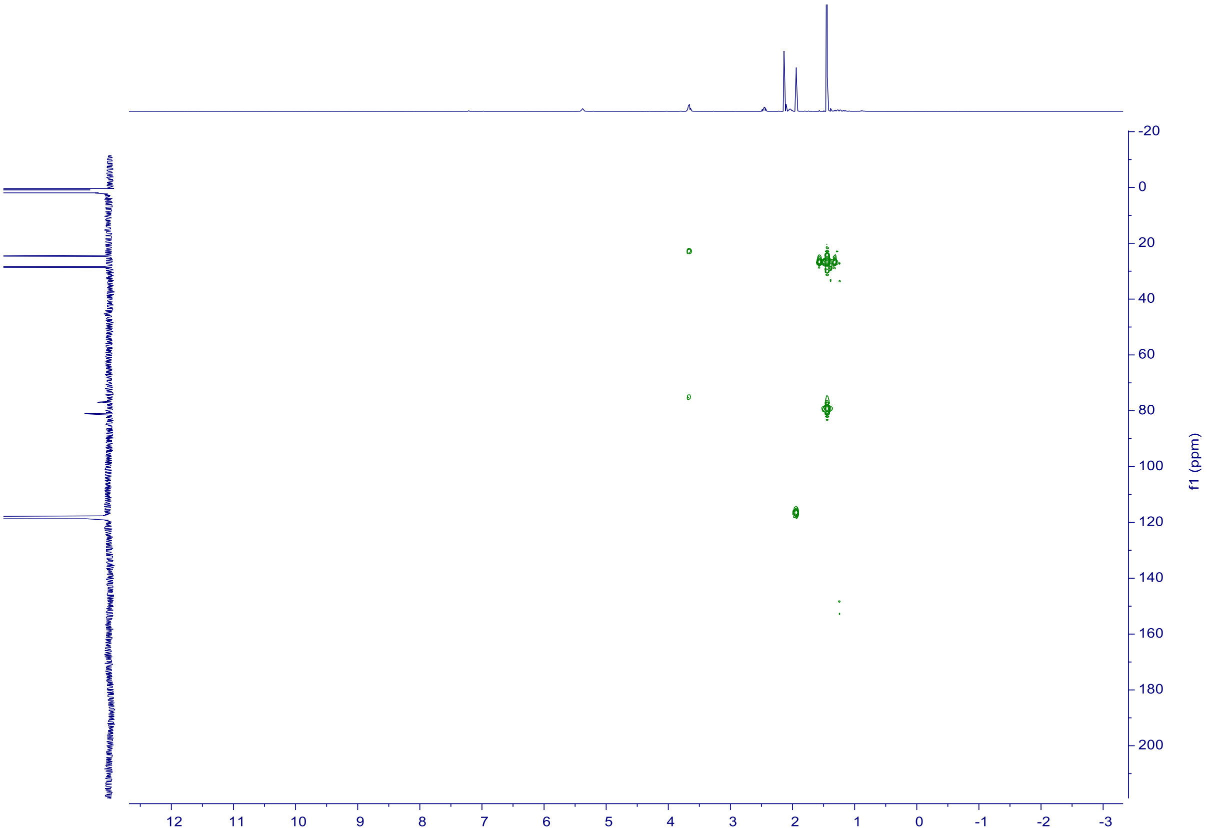
13 – ^{1}H NMR (500 MHz, CD_3CN)



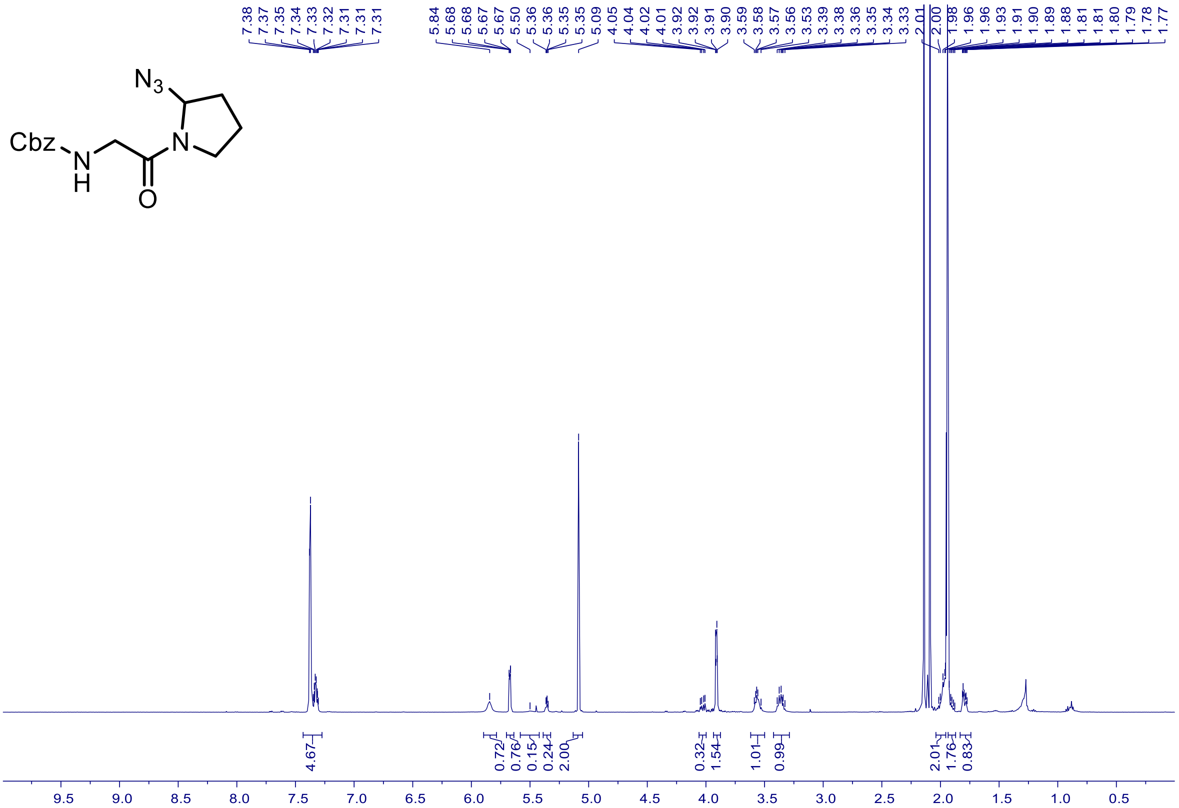
13 – ^{13}C NMR (126 MHz, CD_3CN)



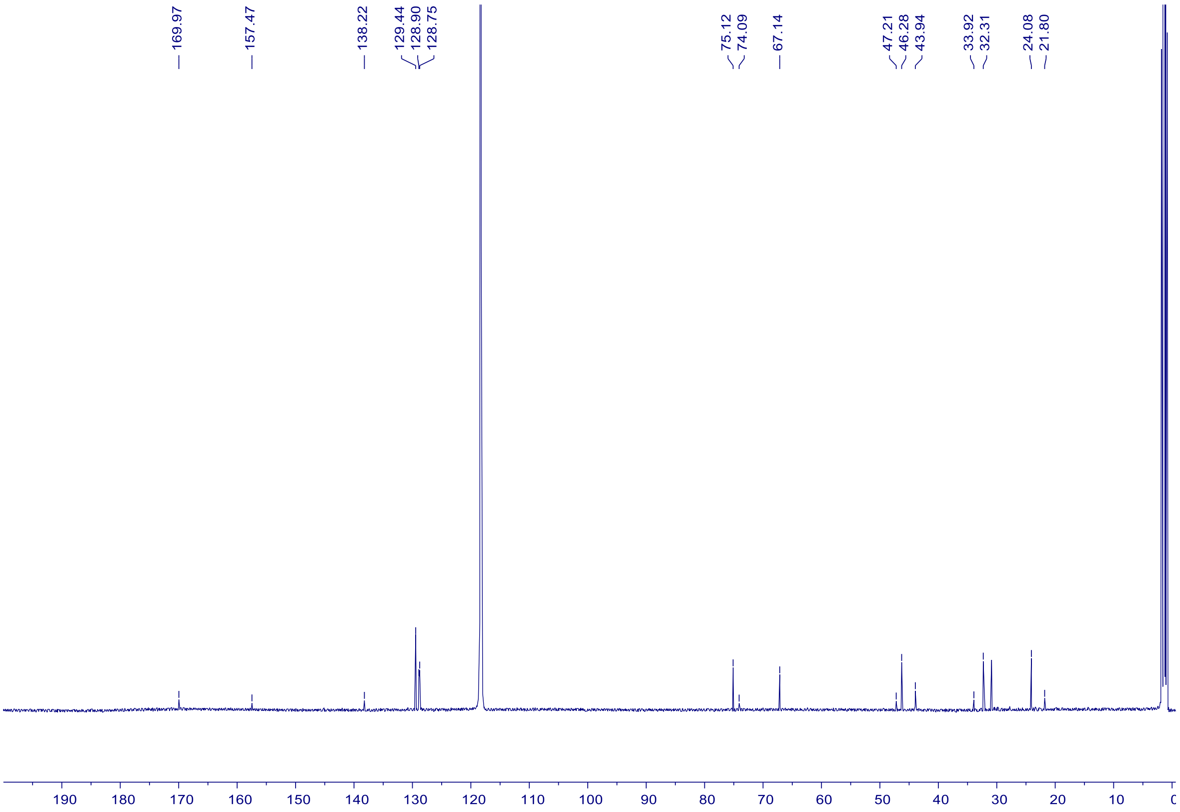
13 – ^{1}H–^{13}C HMBC(500 MHz, CD_3CN)



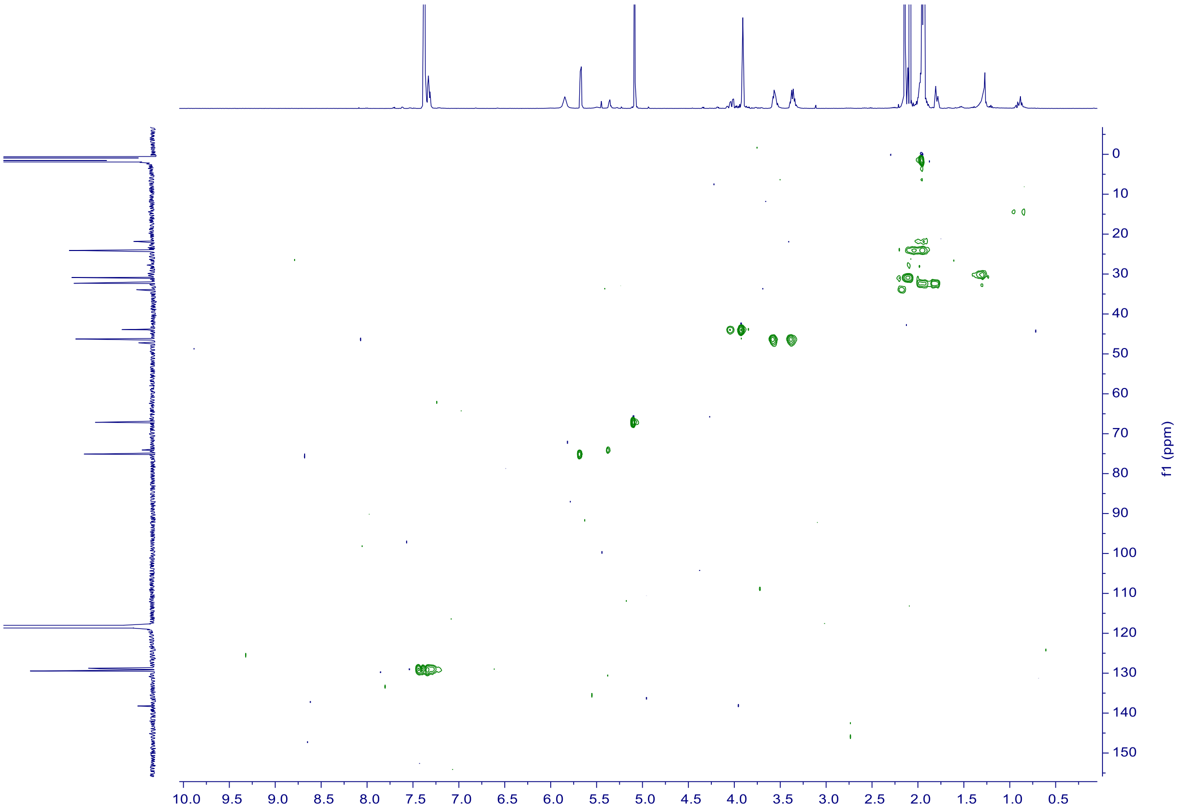
19 – ^{1}H NMR (400 MHz, CDCl$_3$)



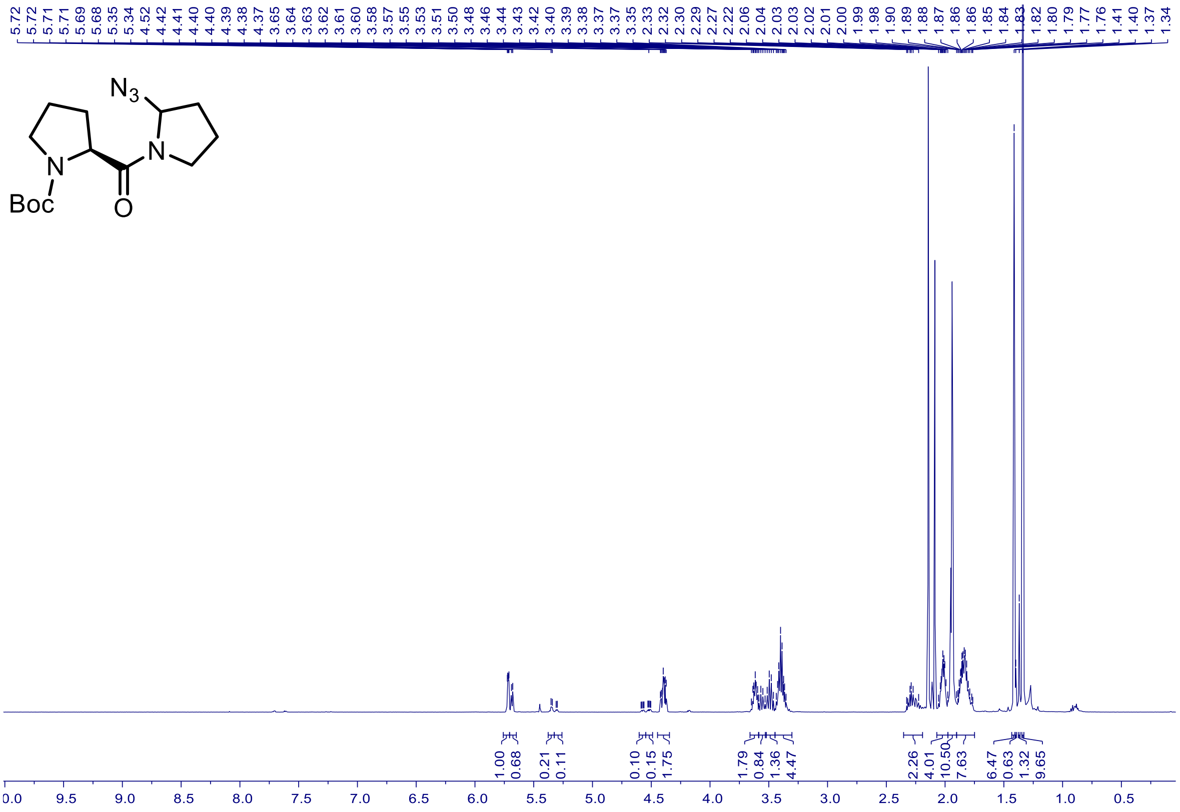
19 – ^{13}C NMR (101 MHz, CDCl$_3$)



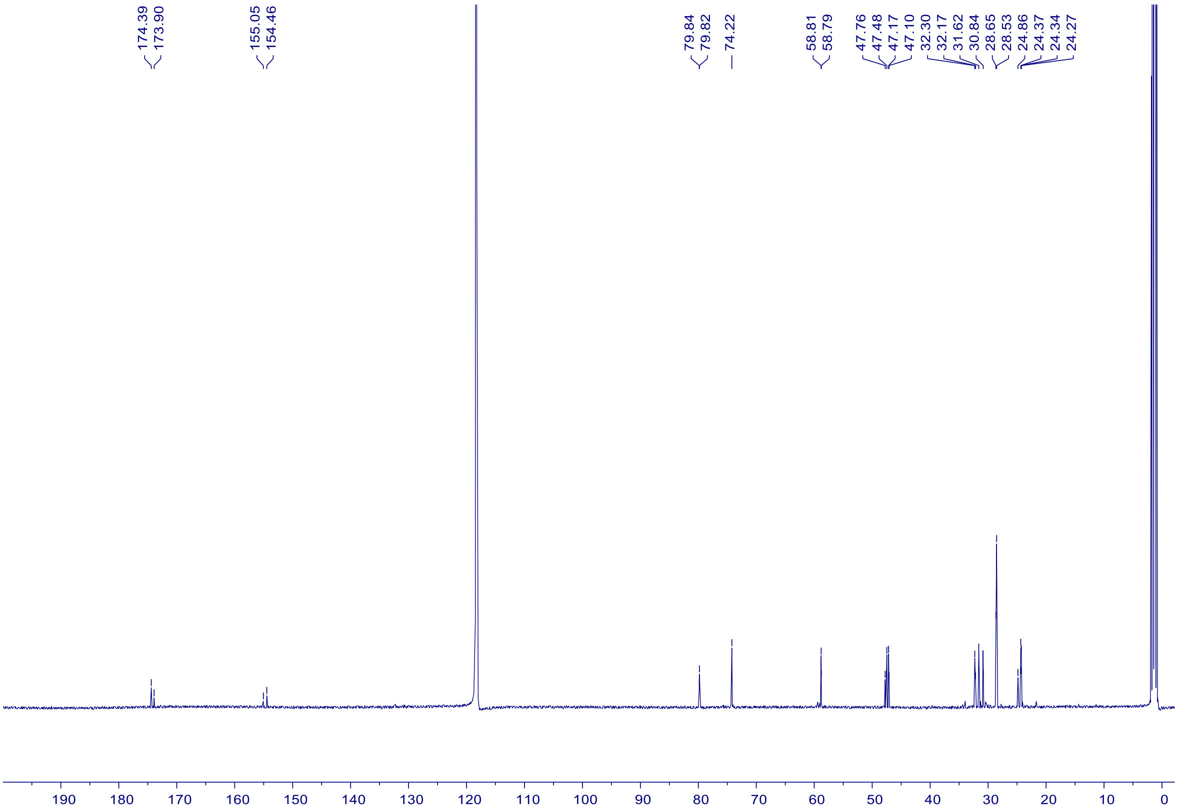
19 – ^{1}H–^{13}C HSQC500 MHz, CD$_3$CN)



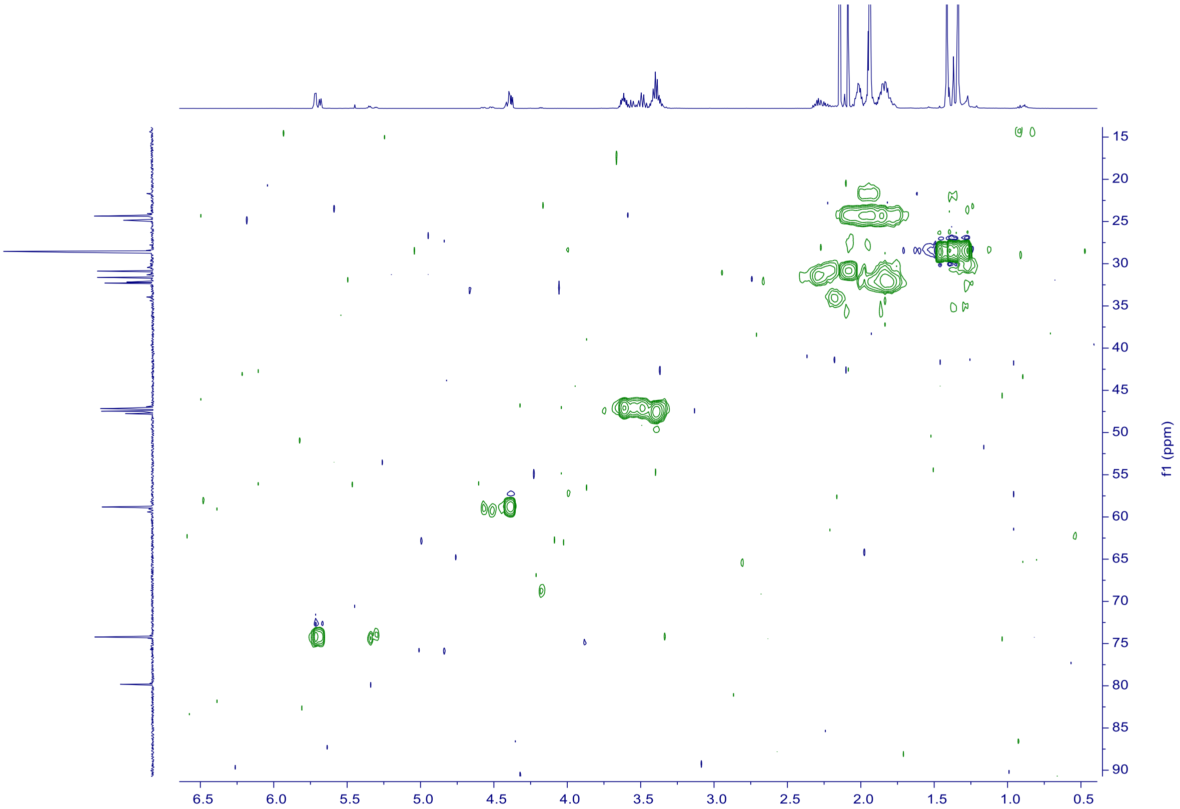
20 – ^{1}H NMR (400 MHz, CDCl$_3$)



20 – ^{13}C NMR (101 MHz, CDCl$_3$)



20 – ^{1}H–^{13}C HSQC500 MHz, CD$_3$CN)



8 References

(1) S. Bräse, C. Gil, K. Knepper, V. Zimmerman, *Angew. Chem. Int. Ed.*, 2005, **44**, 5188.

(2) E. Nyfeler, P . Renaud, *Org. Lett.* 2008, **10**, 985.

(3) P. Magnus, C. Hulme, W. Weber, *J. Am. Chem. Soc.* 1994, **116**, 4501.

(4) Z. Yuchao, L. Xinyao, W. Xiaoyang, H. Xiaoqiang, S. Tao, Z. Yiqun, S. Xiang, Z. Miancheng, S. Spmg, J. Ning, *Org. Lett.* 2015, **17**, 4702.

(5) D. Magde, G. E. Rojas, P.G. Seybold, *Photochem. and Photobiol.* 1999, **70**, 737.