Electronic Supplementary Information

Electrochemical Multicomponent Reaction toward C−H Tetrazolation of Alkyl Arenes and Vicinal Azidotetrazolation of Alkenes

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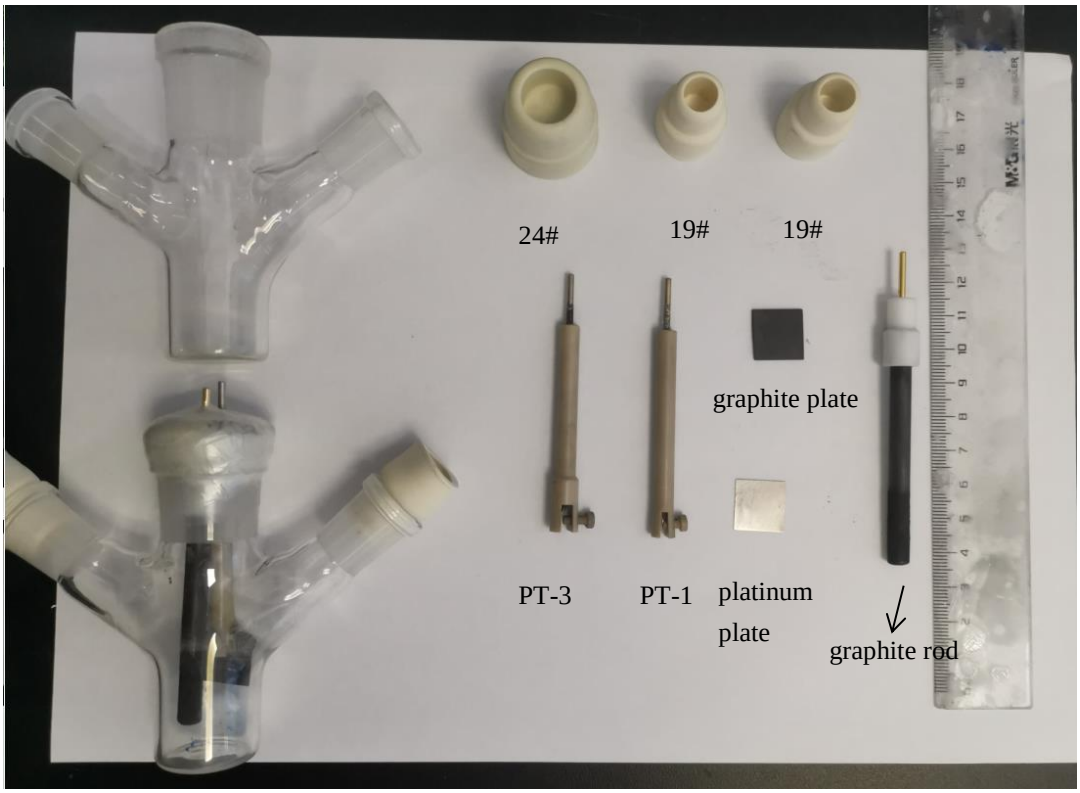
1 General information

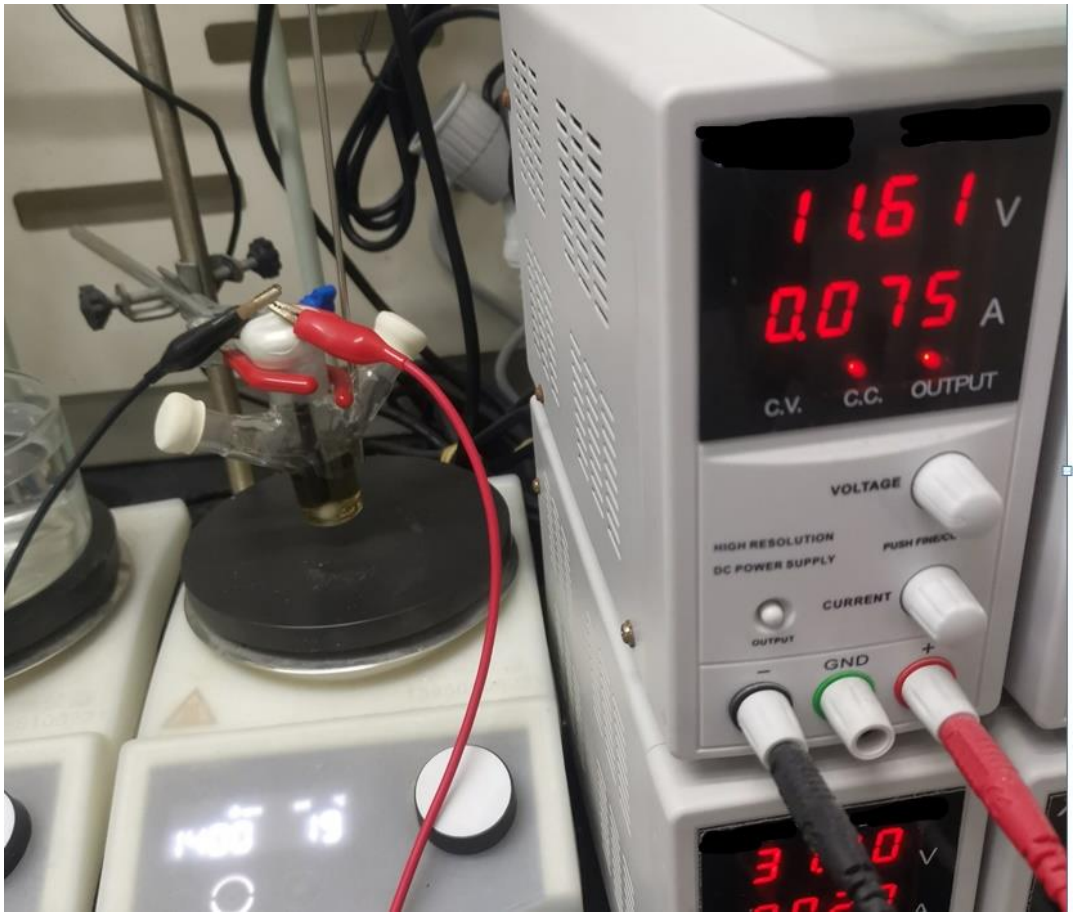
All reactions were performed under an atmosphere of nitrogen using standard undivided three-necked glassware, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light and stained with potassium permanganate. Yields refer to products isolated after purification by column chromatography, unless otherwise stated. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) were recorded on Bruker AV-400 (400 MHz), JEOL-500 (500 MHz), and JEOL ECZ600S (600 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances. IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR. HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer and Aglient 1290-6545xt with the use of quadrupole analyzer. All chemcials were purchased from *TCI Shanghai* or *Energy Chemical* and used as received.

Electrolysis experiments were performed using MESTEK DC power supply. graphite rod (ϕ 6 mm, >99.99%), electrode clips (PT-1 or PT-3) and platinum plate (99.99%, 15*15*1 mm) was purchased from Gaoss Union. The graphite plate (>99.99%) was cut into 15 x 15 x 0.3 mm pieces before use, and was clamped between electrode clips.

CAUTION: Organic azides are known to be potentially explosive compounds. While we did not encounter any issues during their synthesis, proper precautions were taken. All azidation reactions and subsequent workups should be performed behind a blast shield. Once isolated, organic azides should be stored below room temperature and away from sources of heat, light, pressure and shock.

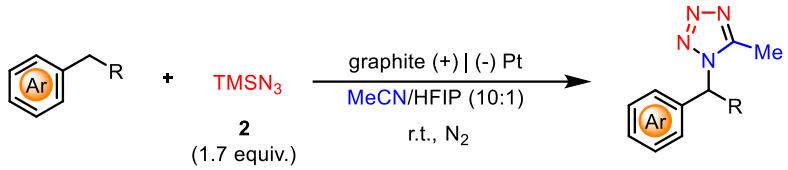
Figure S1. Electrolysis setup





2. General procedures

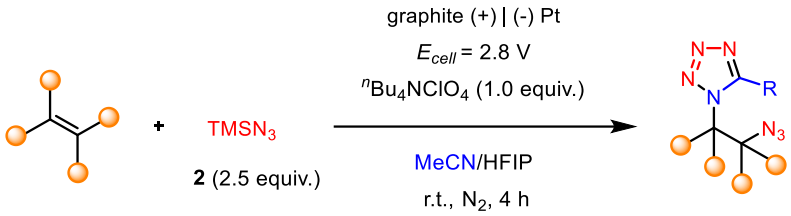
General procedure for the electrochemical C–H tetrazolation



Method A: In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, $^{n}Bu_4NClO_4$ (0.3 mmol) was added. The glassware was equipped with a graphite rod (ϕ 6 mm, about 20±1 mm immersion depth in solution) as the anode and a platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N_2, alkyl arenes (0.3 mmol), $TMSN_3$ (1.7 equiv.), CH_3CN (10 mL), and HFIP (1 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 75 mA at room temperature for 20 minutes. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.

Method B: In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, $LiClO_4$ (0.3 mmol) was added. The glassware was equipped with a graphite rod (ϕ 6 mm, about 20±1 mm immersion depth in solution) as the anode and a platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N_2, alkyl arenes (0.3 mmol), $TMSN_3$ (1.7 equiv.), CH_3CN (10 mL), and HFIP (1 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 75 mA at room temperature for 23 minutes. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.

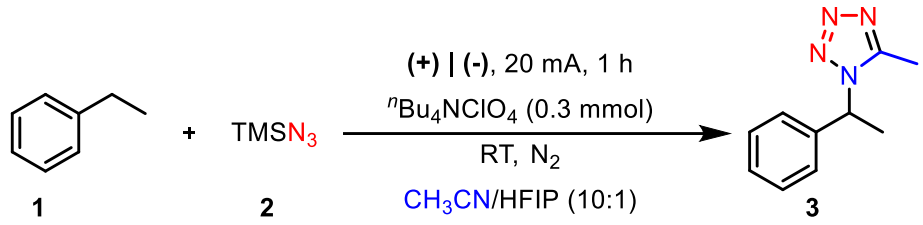
Method C: General procedure for the electrochemical synthesis of vicinal azidotetrazoles (constant cell-potential electrolysis)



In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, $^{n}Bu_4NClO_4$ (0.3 mmol) was added. The glassware was equipped with a graphite plate (15 mm × 15 mm × 1 mm) as the anode and a platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N_2, olefin substrates (0.3 mmol), $TMSN_3$ (2.5 equiv.), CH_3CN (10 mL), and HFIP (0.8 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant cell potential of 2.8 V at room temperature for 4 h. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.

3. Optimization of reaction conditions

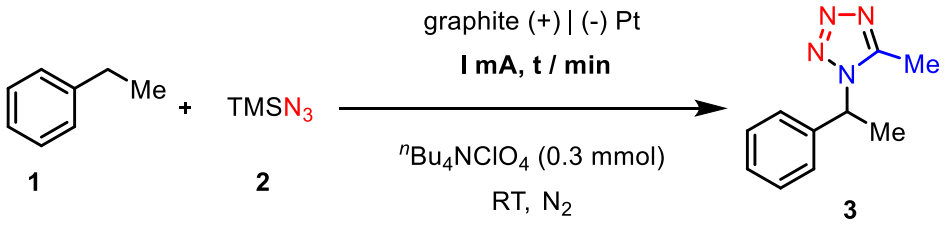
Table S1. Screening of electrode materials



Entry	**(+) | (-)**	Yield[a] / %
1	**C_{rod} | Pt**	**57/61[b]**
2	C_{felt} | Pt	11
3	C_{block} | Pt	47/54[b]
4	C_{rod} | Ni	52
5	C_{rod} | Fe	34
6	C_{rod} | C_{block}	43

[a] Yield was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as the internal standard; [b] isolated yield.

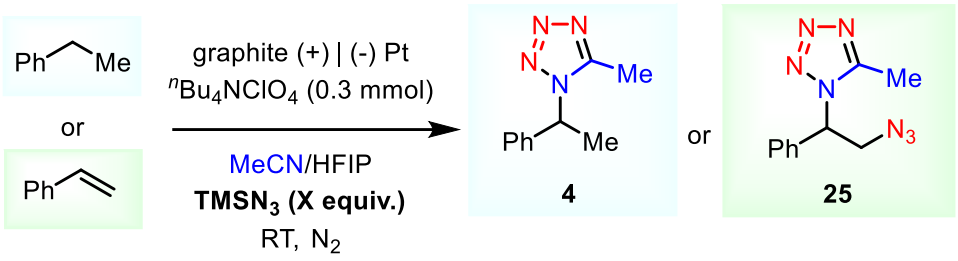
Table S2. Screening of current



Entry	**I mA, t / min**	Yield[a] / %
1	20, 70	62
2	25, 60	62
3	50, 30	62/68[b]
4	**75, 20**	**62/68[b]**
5	150, 10	48

[a] Yield was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as the internal standard; [b] isolated yield.

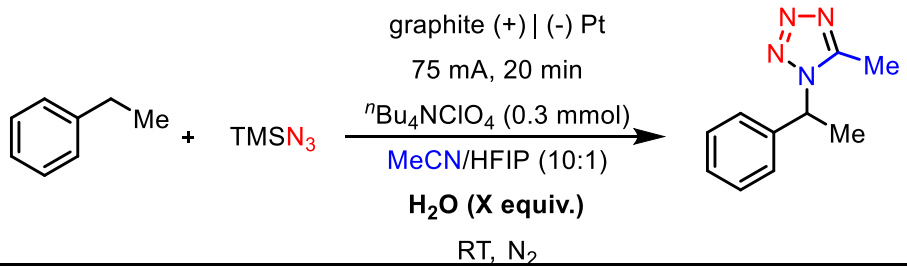
Table S3. Screening of the amount of $TMSN_3$



Entry	**$TMSN_3$ (X equiv.)**	**4**, Yield[a]	**25**, Yield[a]
1	1.3	49	--
2	1.5	57	--
3	**1.7**	**63**	--
4	2	57	60
5	2.2	55	64
6	**2.5**	--	**68**
7	2.7	--	56
8	3.5	--	46

[a] Yield was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as the internal standard.

Table S4. Screening of the amount of H_2O

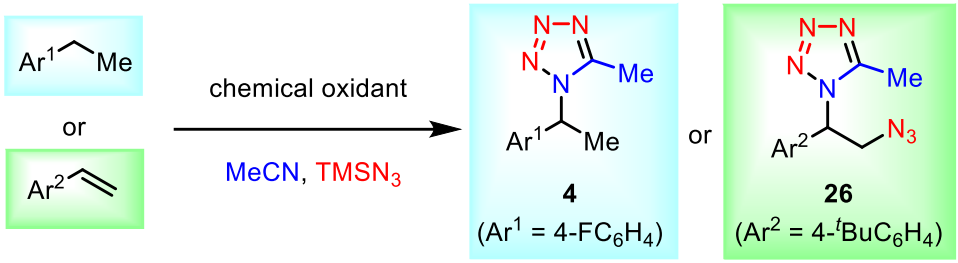


Entry	**H_2O (X equiv.)**	Yield (%)[a]
1	0	63[b]
2	0	33
3	3	18
4	10	2

[a] Yield was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as the internal standard, undehydrated acetonitrile; [b] dry acetonitrile.

4. Procedure for control experiments using chemical oxidants

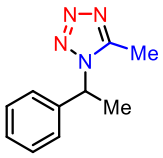
In an oven-dried schlenk (10 mL) equipped with a stirring bar, $^{n}Bu_4NClO_4$ (0.1 mmol) was added. Under the protection of N_2, 4-ethylfluorobenzene or 4-tert-butylstyrene (0.1 mmol), $TMSN_3$ (1.7 or 2.5 equiv.), oxidant (1 equiv.), CH_3CN/HFIP (1:0.1) were injected respectively into the glassware via syringes. The reaction mixture was stirred at room temperature for 4 h. Following concentration in vacuo, the yield and conversion were determined by NMR of the crude reaction mixture with $PhOCF_3$ or CH_2Br_2 as the internal standard.



Entry	Oxidant	**4**, Yield (Conv, %)[a]	**26**, Yield (Conv, %)[a]
1	anode	68 (>95)	70 (>95)
2	NFSI	n.d. (11)	n.d. (51)
3	TBHP	n.d. (20)	n.d. (73)
4	CAN	n.d. (36)	n.d. (35)
5	*m*-CPBA	n.d. (14)	n.d. (22)
6	DDQ	n.d. (15)	n.d. (91)
7	$PhI(OAc)_2$	n.d. (30)	n.d. (>95)
8	$Mn(OAc)_3$	n.d. (69)	n.d. (>95)
9	$AgNO_3$	n.d. (>95)	n.d. (>95)

[a] Yield and conversion were determined by NMR of the crude reaction mixture with $PhOCF_3$ or CH_2Br_2 as the internal standard; n.d. = not detected.

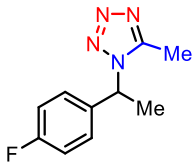
5 Characterization of products



5-Methyl-1-(1-phenylethyl)-1H-tetrazole (3)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 38.4 mg (68% yield) of **3** as a yellow oil.

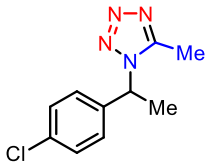
IR (neat, cm^{-1}): 3055(w), 1733(w), 1402(w), 1264(m), 731(s), 704(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.29 (m, 3H), 7.25 – 7.13 (m, 2H), 5.56 (q, *J* = 7.1 Hz, 1H), 2.38 (s, 3H), 2.05 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.2, 138.9, 129.2, 128.7, 126.0, 58.2, 21.8, 9.2. HRMS (ESI) calculated for $C_{10}H_{12}N_4Na^+$ $[M+Na]^+$: 211.0954; found: 211.0952.



1-(1-(4-Fluorophenyl)ethyl)-5-methyl-1H-tetrazole (4)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 33.3 mg (54% yield) of **4** as a white solid.

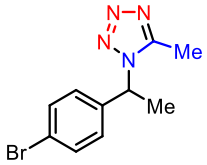
IR (neat, cm^{-1}): 3055(w), 1513(w), 1422(w), 1264(m), 896(s), 731(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.26 – 7.19 (m, 2H), 7.12 – 6.90 (m, 2H), 5.56 (q, *J* = 7.1 Hz, 1H), 2.41 (s, 3H), 2.04 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ162.6 (d, *J* = 248.3 Hz), 151.1, 134.7 (d, *J* = 3.4 Hz), 127.9 (d, *J* = 8.4 Hz), 116.2 (d, *J* = 21.8 Hz), 57.5, 21.9, 9.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -112.5 (td, *J* = 8.5, 8.1, 4.5 Hz). HRMS (ESI) calculated for $C_{10}H_{11}FN_4Na^+$ $[M+Na]^+$: 229.0860; found: 229.0862.



1-(1-(4-Chlorophenyl)ethyl)-5-methyl-1H-tetrazole (5)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 41.6 mg (62% yield) of **5** as a white solid.

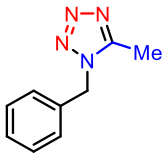
IR (neat, cm^{-1}): 3055(w), 1493(w), 1264(m), 1091(w), 733(s), 543(w). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.19 – 7.13 (m, 2H), 5.55 (q, *J* = 7.0 Hz, 1H), 2.41 (s, 3H), 2.03 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.2, 137.3, 134.7, 129.4, 127.5, 57.5, 21.8, 9.2. HRMS (ESI) calculated for $C_{10}H_{11}ClN_4Na^+$ $[M+Na]^+$: 245.0564; found: 245.0566.



1-(1-(4-Bromophenyl)ethyl)-5-methyl-1H-tetrazole (6)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 45.1 mg (57% yield) of **6** as a white solid.

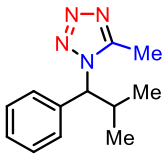
IR (neat, cm^{-1}): 3054(w), 1405(w), 1264(m), 1074(w), 731(s), 706(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.44 (m, 2H), 7.14 – 7.05 (m, 2H), 5.54 (q, *J* = 7.0 Hz, 1H), 2.41 (s, 3H), 2.03 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.2, 137.9, 132.3, 127.7, 122.7, 57.5, 21.7, 9.1. HRMS (ESI) calculated for $C_{10}H_{11}BrN_4Na^+$ $[M+Na]^+$: 289.0059; found: 289.0057.



1-Benzyl-5-methyl-1H-tetrazole (7)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 23.7mg (45% yield) of **7** as a yellow oil.

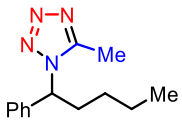
IR (neat, cm^{-1}): 2930(w), 1528 (m), 1408(m), 1246(w), 726(s), 698(s), 580(w). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.32 (m, 3H), 7.23 – 7.16 (m, 2H), 5.51 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.6, 133.0, 129.2, 128.9, 127.4, 50.8, 9.0. HRMS (ESI) calculated for $C_9H_{11}N_4^+$ $[M+H]^+$: 175.0978; found: 175.0988.



5-Methyl-1-(2-methyl-1-phenylpropyl)-1H-tetrazole (8)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 46.7 mg (72% yield) of **8** as a yellow oil.

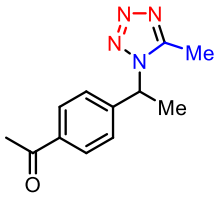
IR (neat, cm^{-1}): 3055(w), 1422(w), 1264(m), 896(w), 731(s), 524(w). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 2H), 7.38 – 7.31 (m, 3H), 4.75 (d, *J* = 10.5 Hz, 1H), 2.99 (ddt, *J* = 13.2, 10.7, 6.6 Hz, 1H), 2.51 (s, 3H), 0.90 (dd, *J* = 9.1, 6.6 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.5, 136.8, 129.0, 128.7, 127.6, 70.0, 33.2, 20.1, 20.0, 9.1. HRMS (ESI) calculated for $C_{12}H_{16}N_4Na^+$ $[M+Na]^+$: 239.1267; found: 239.1272.



5-Methyl-1-(1-phenylpentyl)-1H-tetrazole (9)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 47.1 mg (68% yield) of **9** as a yellow oil.

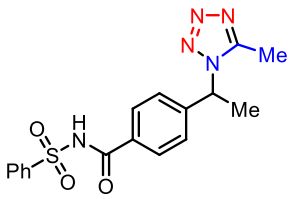
IR (neat, cm^{-1}): 3055(w), 1423(w), 1264(m), 896(w), 731(s), 706(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 3H), 7.32 – 7.23 (m, 2H), 5.26 (dd, *J* = 8.7, 6.7 Hz, 1H), 2.58 (dq, *J* = 15.5, 8.3 Hz, 1H), 2.44 (s, 3H), 2.32 (dq, *J* = 14.3, 7.4 Hz, 1H), 1.37 (dq, *J* = 14.6, 7.0 Hz, 2H), 1.25 (h, *J* = 6.7 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.4, 137.9, 129.0, 128.6, 126.6, 63.0, 35.2, 28.5, 22.1, 13.7, 9.1. HRMS (ESI) calculated for $C_{13}H_{18}N_4Na^+$ $[M+Na]^+$: 253.1424; found: 253.1423.



1-(4-(1-(5-Methyl-1H-tetrazol-1-yl)ethyl)phenyl)ethan-1-one (10)

Followed **Method B**, F = 3.58 F/mol the desired pure product was purified using silica gel chromatography (EA) to give 43.7 mg (63% yield) of **10** as a yellow oil.

IR (neat, cm^{-1}): 2991(w), 1683(s), 1406(m), 1267(s), 1077(m), 840(m). ^{1}H NMR (500 MHz, Methanol-d_1) δ 6.46 – 6.40 (m, 2H), 5.87 – 5.81 (m, 2H), 4.39 (q, *J* = 7.0 Hz, 1H), 1.03 (s, 3H), 0.91 (s, 3H), 0.46 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Methanol-d_1) δ 197.0, 150.7, 143.0, 135.3, 127.4, 124.8, 55.9, 23.9, 19.0, 6.0. HRMS (ESI) calculated for $C_{12}H_{14}N_4NaO^+$ $[M+Na]^+$: 253.1060; found: 253.1064.

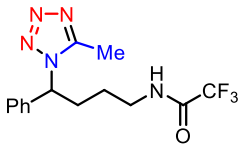


4-(1-(5-Methyl-1H-tetrazol-1-yl)ethyl)-N-(phenylsulfonyl)benzamide (11)

Followed **Method B**, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (DCM : CH_3OH = 20:1) to give 58.1 mg (53% yield) of **11** as a yellow oil.

IR (neat, cm^{-1}): 3318(m), 2942(w), 2831(w), 1495(w), 1021(s), 625(w). ^{1}H NMR (600 MHz, Methanol-d_4) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.63 (t, *J* =

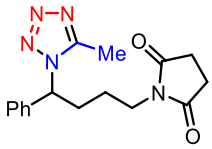
7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 5.87 (q, *J* = 7.0 Hz, 1H), 2.41 (s, 3H), 1.98 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 172.3, 151.5, 143.5, 141.3, 137.6, 130.1, 128.6, 127.2, 126.2, 124.7, 57.1, 20.0, 6.8. HRMS (ESI) calculated for $C_{17}H_{17}N_5NaO_3S^+$ $[M+Na]^+$: 394.0944; found: 394.0947.



2,2,2-Trifluoro-N-(4-(5-methyl-1H-tetrazol-1-yl)-4-phenylbutyl)acetamide (12)

Followed **Method A**, 20 mA, 90 min, F = 3.73 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1.5) to give 50.5 mg (52% yield) of **12** as a yellow oil.

IR (neat, cm^{-1}): 3056(w), 1716(w), 1556(w), 1264(m), 1210(w), 731(s), 706(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (t, *J* = 4.7 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.26 – 7.21 (m, 2H), 5.38 (dd, *J* = 8.7, 6.6 Hz, 1H), 3.50 –3.39 (m, 2H), 2.68 – 2.58 (m, 1H), 2.43 (s, 3H), 2.36 (ddt, *J* = 14.1, 9.9, 6.1 Hz, 1H), 1.71 – 1.51 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.7 (q, *J* = 37.0 Hz), 151.9, 137.2, 129.3, 129.0, 126.5, 115.8 (q, *J* = 287.7 Hz), 62.3, 38.9, 32.4, 25.7, 9.0. HRMS (ESI) calculated for $C_{14}H_{16}F_3N_5NaO^+$ $[M+Na]^+$: 350.1199; found: 350.1202.

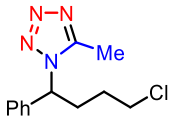


1-(4-(5-Methyl-1H-tetrazol-1-yl)-4-phenylbutyl)pyrrolidine-2,5-dione (13)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (EA) to give 52.7 mg (56% yield) of **13** as a yellow oil.

IR (neat, cm^{-1}): 3055(w), 1704(w), 1420(w), 1264(m), 897(w), 731(s), 706(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.27 (m, 3H), 7.29 – 7.25 (m, 2H), 5.41 (dd, *J* = 8.5, 6.9 Hz, 1H), 3.56 (t, *J* = 6.9 Hz, 2H), 2.72 (s, 4H), 2.60 – 2.49 (m, 1H), 2.46 (s, 3H), 2.38 – 2.21 (m, 1H), 1.65 – 1.49 (m, 2H). ^{13}C NMR (126 MHz,

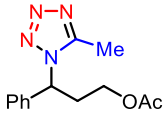
Chloroform-*d*) δ 177.3, 151.6, 137.3, 129.2, 128.8, 126.6, 61.7, 37.2, 32.2, 28.1, 24.2, 9.0. HRMS (ESI) calculated for $C_{16}H_{19}N_5O_2^+$ $[M]^+$: 313.1539; found: 313.1547.



1-(4-Chloro-1-phenylbutyl)-5-methyl-1H-tetrazole (14)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 41.0 mg (55% yield) of **14** as a yellow oil.

IR (neat, cm^{-1}): 3055(w), 1443(w), 1264(m), 895(w), 731(s), 704(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 5.36 (dd, *J* = 8.7, 6.7 Hz, 1H), 3.57 (dtd, *J* = 7.0, 3.8, 1.5 Hz, 2H), 2.79 – 2.65 (m, 1H), 2.60 – 2.49 (m, 1H), 2.44 (s, 3H), 1.87 – 1.69 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.6, 137.3, 129.2, 128.9, 126.5, 62.3, 44.0, 32.9, 29.1, 9.1. HRMS (ESI) calculated for $C_{12}H_{15}ClN_4^+$ $[M]^+$: 250.0983; found: 250.0985.

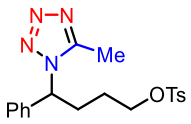


3-(5-Methyl-1H-tetrazol-1-yl)-3-phenylpropyl acetate (15)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 35.9 mg (46% yield) of **15** as a yellow oil.

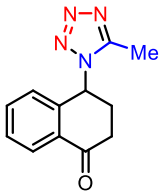
IR (neat, cm^{-1}): 3056(w), 1738(m), 1524(w), 1399(w), 1261(m), 1040(w), 731(s), 704(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 3H), 7.27 (dt, *J* = 7.5, 1.7 Hz, 2H), 5.45 (dd, *J* = 8.7, 6.5 Hz, 1H), 4.10 (ddd, *J* = 11.6, 6.7, 4.9 Hz, 1 H), 4.03 (ddd, *J* = 11.8, 7.4, 4.6 Hz, 1 H), 2.97 (dddd, *J* = 15.4, 8.7, 6.8, 4.6 Hz, 1H), 2.69 – 2.61 (m, 1H), 2.45 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.6,

151.7, 136.9, 129.3, 129.1, 126.6, 60.5, 59.6, 34.6, 20.7, 9.0. HRMS (ESI) calculated for $C_{13}H_{17}N_4O_2^+$ $[M+H]^+$: 261.1346; found: 261.1353.



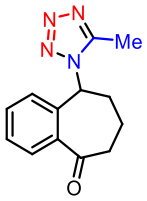
4-(5-Methyl-1H-tetrazol-1-yl)-4-phenylbutyl 4-methylbenzenesulfonate (16)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (EA) to give 60.6 mg (52% yield) of **16** as a colourless oil. IR (neat, cm^{-1}): 2958(w), 1355(m), 1174(s), 1096(w), 927(m), 734(s), 702(m), 555(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.79 – 7.72 (m, 2H), 7.38 – 7.31 (m, 5H), 7.25 – 7.19 (m, 2H), 5.34 (dd, *J* = 8.9, 6.5 Hz, 1H), 4.05 (t, *J* = 6.0 Hz, 2H), 2.67 – 2.56 (m, 1H), 2.45 (s, 3H), 2.44 – 2.35 (m, 4H), 1.67 (dt, *J* = 8.1, 6.2 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.7, 145.1, 137.2, 132.5, 129.9, 129.2, 128.9, 127.8, 126.5, 69.6, 62.0, 31.9, 25.6, 21.6, 9.0. HRMS (ESI) calculated for $C_{19}H_{22}N_4O_3SNa^+$ $[M+Na]^+$: 409.1305; found: 409.1307.



4-(5-Methyl-1H-tetrazol-1-yl)-3,4-dihydronaphthalen-1(2H)-one (17)

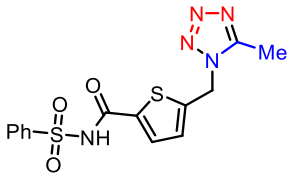
Followed **Method B**, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (EA) to give 37.9 mg (56% yield) of **17** as a white solid. IR (neat, cm^{-1}): 3055(w), 1693(w), 1422(w), 1264(m), 895(w), 731(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.19 – 8.15 (m, 1H), 7.58 – 7.48 (m, 2H), 6.63 (dt, *J* = 6.1, 1.2 Hz, 1H), 5.99 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.03 (ddd, *J* = 16.1, 5.8, 3.5 Hz, 1H), 2.87 – 2.71 (m, 2H), 2.68 – 2.61 (m, 1H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 194.8, 151.5, 138.5, 134.4, 132.0, 129.5, 128.1, 126.1, 56.5, 36.0, 29.5, 9.6. HRMS (ESI) calculated for $C_{12}H_{12}N_4NaO^+$ $[M+Na]^+$: 251.0903; found: 251.0903.



9-(5-Methyl-1H-tetrazol-1-yl)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (18)

Followed **Method B**, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (PE :EA = 1:2) to give 28.7 mg (40% yield) of **18** as a white solid.

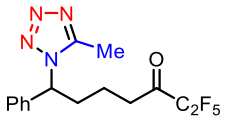
IR (neat, cm^{-1}): 3055(w), 2158(w), 1683(w), 1422(w), 1264(m), 860(w), 731(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.75 – 7.69 (m, 1H), 7.49 – 7.38 (m, 2H), 6.29 – 6.21 (m, 1H), 5.75 (dd, *J* = 11.7, 5.3 Hz, 1H), 3.03 – 2.89 (m, 2H), 2.77 (ddd, *J* = 18.3, 12.7, 2.9 Hz, 1H), 2.55 – 2.43 (m, 1H), 2.35 (s, 3H), 2.19 (dtd, *J* = 18.5, 6.4, 3.9 Hz, 1H), 1.94 – 1.81 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 204.8, 152.0, 137.0, 135.6, 133.0, 129.1, 129.0, 123.9, 58.8, 40.3, 30.6, 19.0, 9.1. HRMS (ESI) calculated for $C_{13}H_{14}N_4NaO^+$ $[M+Na]^+$: 265.1060; found: 265.1065.



5-((5-Methyl-1H-tetrazol-1-yl)methyl)-N-(phenylsulfonyl)thiophene-2-carboxamide (19)

Followed **Method B**, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (DCM : CH_3OH = 10:1) to give 57.7 mg (53% yield) of **19** as a white solid.

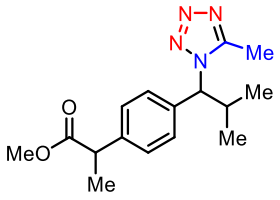
IR (neat, cm^{-1}): 3336(m), 2944(w), 2832(w), 1450(w), 1267(m), 1024(s), 734(s). ^1H NMR (500 MHz, Methanol-d_4) δ 7.98 – 7.90 (m, 2H), 7.51 – 7.39 (m, 4H), 7.02 (d, *J* = 3.8 Hz, 1H), 5.77 (s, 2H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 167.2, 151.6, 144.5, 143.3, 139.0, 130.2, 129.0, 127.2, 127.2, 126.2, 44.7, 6.7. HRMS (ESI) calculated for $C_{14}H_{14}N_5NaO_3S_2^+$ $[M+Na]^+$: 386.0352; found:386.0357.



1,1,1,2,2-Pentafluoro-7-(5-methyl-1H-tetrazol-1-yl)-7-phenylheptan-3-one (20)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (EA) to give 37.5 mg (35% yield) of **20** as a white solid.

IR (neat, cm^{-1}): 3056(w), 1754(w), 1401(w), 1264(w), 1201(w), 733(s) 703(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 3H), 7.26 – 7.21 (m, 2H), 5.34 – 5.21 (m, 1H), 2.84 (q, *J* = 6.8 Hz, 2H), 2.71 – 2.52 (m, 1H), 2.43 (s, 3H), 2.41 – 2.33 (m, 1H), 1.67 (dt, *J* = 15.3, 7.0 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.7 (t, *J* = 26.7 Hz), 151.6, 137.2, 129.3, 129.1, 126.5, 117.7 (dt, *J* = 286.6, 34.0 Hz), 106.7 (tq, *J* = 266.8, 37.9 Hz), 62.9, 36.7, 34.4, 19.3, 9.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -81.8, -123.2 . HRMS (ESI) calculated for $C_{15}H_{15}F_5N_4ONa^+$ $[M+Na]^+$: 385.1058; found: 385.1057.

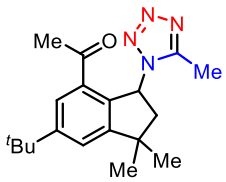


Methyl 2-(4-(2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)phenyl)propanoate (21)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 50.0 mg (55% yield) of **21** as a yellow oil.

IR (neat, cm^{-1}): 2972(w), 1734(s), 1519(w), 1209(w), 1167(m), 1073(m), 794(w). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 2H), 7.30 – 7.26 (m, 2H), 4.74 (d, *J* = 10.5 Hz, 1H), 3.71 (q, *J* = 7.1 Hz, 1H), 3.65 (d, *J* = 0.9 Hz, 3H), 3.03 – 2.90 (m, 1H), 2.52 (d, *J* = 0.6 Hz, 3H), 1.47 (dd, *J* = 7.2, 1.4 Hz, 3H), 0.89 (dd, *J* = 6.6, 1.7 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.5, 151.5, 141.1, 135.7, 128.1, 127.9,

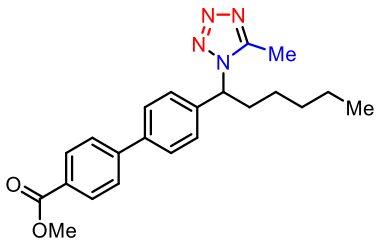
69.6, 52.0, 44.9, 33.2, 20.0, 18.4, 9.1. HRMS (ESI) calculated for $C_{16}H_{23}N_4O_2^+$ $[M+H]^+$: 303.1816; found: 303.1815.



1-(6-(Tert-butyl)-1,1-dimethyl-3-(5-methyl-1H-tetrazol-1-yl)-2,3-dihydro-1H-inden-4-yl)ethan-1-one (22)

Followed **Method B**, F = 3.58 F/mol, the desired pure product was purified using silica gel chromatography (PE : EA = 1:1) to give 34.7 mg (36% yield) of **22** as a yellow oil.

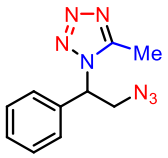
IR (neat, cm^{-1}): 2959(s), 2869(w), 1680(s), 1361(m), 1237(s), 734(s), 657(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 1.7 Hz, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 6.32 (dd, *J* = 8.9, 4.6 Hz, 1H), 2.79 (s, 3H), 2.59 (dd, *J* = 13.7, 8.9 Hz, 1H), 2.39 (s, 3H), 2.12 (dd, *J* = 13.7, 4.6 Hz, 1H), 1.46 (s, 3H), 1.40 (s, 9H), 1.36 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.4, 154.7, 153.8, 152.0, 133.9, 133.3, 126.5, 123.9, 59.8, 48.5, 42.9, 35.0, 31.3, 30.4, 29.7, 27.4, 9.1. HRMS (ESI) calculated for $C_{19}H_{26}N_4ONa^+$ $[M+Na]^+$: 349.1999; found: 349.2008.



Methyl -4'-(1-(5-methyl-1H-tetrazol-1-yl)hexyl)-[1,1'-biphenyl]-4-carboxylate (23)

Followed **Method A**, F = 3.11 F/mol, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 46.5 mg (41% yield) of **23** as a yellow oil.

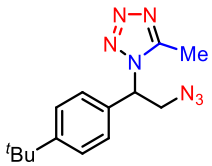
IR (neat, cm^{-1}): 3055(w), 1720(w), 1264(m), 1112(w), 732(s), 706(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 – 8.04 (m, 2H), 7.67 – 7.55 (m, 4H), 7.42 – 7.33 (m, 2H), 5.31 (dd, *J* = 8.6, 6.6 Hz, 1H), 3.94 (s, 3H), 2.61 (dt, *J* = 14.9, 7.3 Hz, 1H), 2.48 (s, 3H), 2.36 (dt, *J* = 14.8, 7.0 Hz, 1H), 1.41 – 1.21 (m, 6H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.8, 151.5, 144.4, 140.4, 137.8, 130.1, 129.3, 127.9, 127.3, 126.9, 62.7, 52.1, 35.5, 31.1, 26.1, 22.3, 13.9, 9.2. HRMS (ESI) calculated for $C_{22}H_{27}N_4O_2^+$ $[M+H]^+$:379.2129; found:379.2119.



1-(2-Azido-1-phenylethyl)-5-methyl-1H-tetrazole (25)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 46.7 mg (68% yield) of **25** as a yellow solid.

IR (neat, cm^{-1}): 2934(w), 2103(s), 1402(m), 1272(m), 732(w), 701(m). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.34 (m, 3H), 7.33 – 7.26 (m, 2H), 5.50 (dd, *J* = 9.6, 5.1 Hz, 1H), 4.47 (dd, *J* = 12.9, 9.6 Hz, 1H), 4.02 (dd, *J* = 12.9, 5.1 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.1, 134.2, 129.4, 129.2, 126.7, 61.8, 54.2, 8.7. HRMS (ESI) calculated for $C_{10}H_{12}N_7^+$ $[M+H]^+$: 230.1149; found: 230.1147.

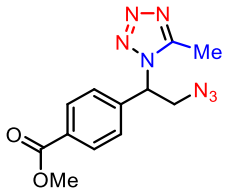


1-(2-Azido-1-(4-(tert-butyl)phenyl)ethyl)-5-methyl-1H-tetrazole (27)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 60 mg (70% yield) of **27** as a yellow solid.

IR (neat, cm^{-1}): 3693(m), 2104(s), 1525(m), 1401(m), 1270(m), 835(m), 568(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.24 – 7.19 (m, 2H), 5.38 (dd, *J* = 9.8, 4.9 Hz, 1H), 4.49 (dd, *J* = 12.9, 9.8 Hz, 1H), 3.98 (dd, *J* = 12.9, 4.9 Hz, 1H), 2.49 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.9, 152.0, 131.3,

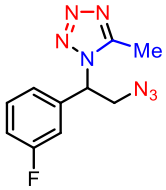
126.5, 126.3, 61.8, 54.5, 34.6, 31.1, 9.0. HRMS (ESI) calculated for $C_{14}H_{19}N_7Na^+$ $[M+Na]^+$: 308.1594; found: 308.1596.



Methyl 4-(2-azido-1-(5-methyl-1H-tetrazol-1-yl)ethyl)benzoate (28)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 38.8 mg (45% yield) of **28** as a yellow oil.

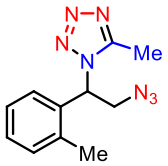
IR (neat, cm^{-1}): 2953(w), 2106(s), 1722(s), 1436(m), 1281(s), 1113(m), 707(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.11 – 8.01 (m, 2H), 7.42 – 7.33 (m, 2H), 5.45 (dd, *J* = 9.4, 5.2 Hz, 1H), 4.50 (dd, *J* = 12.9, 9.4 Hz, 1H), 4.04 (dd, *J* = 12.9, 5.2 Hz, 1H), 3.93 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.0, 152.1, 138.9, 131.5, 130.7, 127.0, 61.7, 54.3, 52.4, 8.9. HRMS (ESI) calculated for $C_{12}H_{14}N_7O_2^+$ $[M+H]^+$: 288.1203; found: 288.1201.



1-(2-Azido-1-(3-fluorophenyl)ethyl)-5-methyl-1H-tetrazole (29)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 32.6 mg (44% yield) of **29** as a yellow oil.

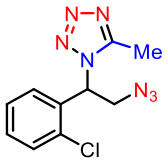
IR (neat, cm^{-1}): 2939(w), 2105(s), 1594(m), 1491(m), 1267(m), 701(s), 522(m). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 (q, *J* = 7.1 Hz, 1H), 7.15-7.06 (m, 3H), 5.39 (dd, *J* = 9.0, 5.3 Hz, 1H), 4.53 – 4.41 (m, 1H), 4.02 (dd, *J* = 12.6, 4.7 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0 (d, *J* = 249.1 Hz), 152.1, 136.6 (d, *J* = 7.0 Hz), 131.3 (d, *J* = 8.3 Hz), 122.6 (d, *J* = 3.2 Hz), 116.8 (d, *J* = 21.1 Hz), 114.1 (d, *J* = 23.0 Hz), 61.4, 54.4, 9.0. HRMS (ESI) calculated for $C_{10}H_{11}FN_7^+$ $[M+H]^+$: 248.1054; found: 248.1052.



1-(2-Azido-1-(o-tolyl)ethyl)-5-methyl-1H-tetrazole (30)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 40.9 mg (56% yield) of **30** as a yellow oil.

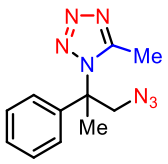
IR (neat, cm^{-1}): 2935(w), 2103(s), 1525(m), 1402(m), 1270(m), 735(s), 544(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 2H), 7.23 – 7.17 (m, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 5.64 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.48 (dd, *J* = 13.0, 9.5 Hz, 1H), 3.93 (dd, *J* = 13.0, 4.8 Hz, 1H), 2.47 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.9, 134.8, 132.6, 131.1, 129.4, 127.4, 126.4, 58.3, 53.9, 19.2, 8.9. HRMS (ESI) calculated for $C_{11}H_{13}N_7Na^+$ $[M+Na]^+$: 266.1125; found: 266.1124.



1-(2-Azido-1-(2-chlorophenyl)ethyl)-5-methyl-1H-tetrazole (31)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 45.9 mg (58% yield) of **31** as a yellow oil.

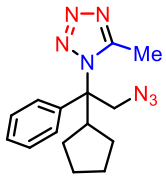
IR (neat, cm^{-1}): 2941(w), 2103(s), 1525(m), 1401(m), 1273(m), 1038(m), 747(m). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.32 – 7.28 (m, 2H), 5.98 (dd, *J* = 9.9, 4.5 Hz, 1H), 4.44 (dd, *J* = 12.9, 9.9 Hz, 1H), 4.00 (dd, *J* = 12.9, 4.5 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.3, 132.6, 131.9, 130.9, 130.1, 128.3, 128.1, 57.8, 53.5, 8.8. HRMS (ESI) calculated for $C_{10}H_{10}ClN_7Na^+$ $[M+Na]^+$: 286.0578; found: 286.0586.



1-(1-Azido-2-phenylpropan-2-yl)-5-methyl-1H-tetrazole (32)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 54.7 mg (75% yield) of **32** as a yellow oil.

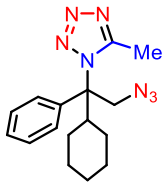
IR (neat, cm^{-1}): 2996(w), 2105(s), 1515(m), 1449(m), 1380(m), 1093(m), 699(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 3H), 7.12 – 7.07 (m, 2H), 4.38 (d, *J* = 12.7 Hz, 1H), 4.09 (d, *J* = 12.7 Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.8, 138.7, 129.3, 129.2, 125.6, 66.4, 60.2, 23.8, 10.9. HRMS (ESI) calculated for $C_{11}H_{13}N_7Na^+$ $[M+Na]^+$: 266.1125; found: 266.1132.



1-(2-Azido-1-cyclopentyl-1-phenylethyl)-5-methyl-1H-tetrazole (33)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 48.2 mg (54% yield) of **33** as a yellow oil.

IR (neat, cm^{-1}): 2958(w), 2102(s), 1512(m), 1448(m), 1288(m), 734(m), 703(s). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.40 (m, 3H), 7.18 – 7.07 (m, 2H), 4.36 (d, *J* = 12.7 Hz, 1H), 4.17 (d, *J* = 12.8 Hz, 1H), 3.32 (p, *J* = 8.1, 7.7 Hz, 1H), 1.99 (d, *J* = 9.1 Hz, 1H), 1.96 (s, 3H), 1.91 – 1.77 (m, 1H), 1.59 (dq, *J* = 13.2, 8.0 Hz, 2H), 1.53 – 1.32 (m, 3H), 1.19 – 1.02 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.7, 136.3, 129.0, 128.8, 127.2, 71.8, 57.9, 45.3, 27.8, 27.6, 24.4, 24.2, 12.1. HRMS (ESI) calculated for $C_{15}H_{19}N_7Na^+$ $[M+Na]^+$: 320.1594; found: 320.1599.

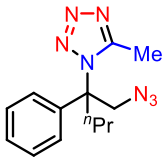


1-(2-Azido-1-cyclohexyl-1-phenylethyl)-5-methyl-1H-tetrazole (34)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 59.8 mg (64% yield) of **34** as a yellow oil.

IR (neat, cm^{-1}): 2934(m), 2856(w), 2102(s), 1447(m), 1372(m), 734(m), 703(s). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 4.9 Hz, 3H), 7.11 (d, *J* = 4.9 Hz, 2H),

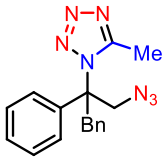
4.40 (d, *J* = 12.9 Hz, 1H), 4.14 (d, *J* = 12.9 Hz, 1H), 2.87 (t, *J* = 11.9 Hz, 1H), 2.00-1.98 (m, 1H), 1.97 (s, 3H), 1.89 – 1.63 (m, 4H), 1.43 – 1.43 (m, 2H), 1.05 – 0.95 (m, 1H), 0.88 – 0.72 (m, 2H), ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.9, 135.6, 128.9, 128.7, 127.2, 72.8, 56.9, 42.8, 28.2, 28.1, 26.5, 26.2, 25.9, 12.4. HRMS (ESI) calculated for $C_{16}H_{21}N_7K^+$ $[M+K]^+$: 350.1490; found: 350.1498.



1-(1-Azido-2-phenylpentan-2-yl)-5-methyl-1H-tetrazole (35)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 61.1 mg (75% yield) of **35** as a yellow oil.

IR (neat, cm^{-1}): 2964(m), 2875(w), 2105(s), 1515(m), 1449(m), 1282(m), 700(s). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 3H), 7.12 (dt, *J* = 6.6, 1.7 Hz, 2H), 4.39 (d, *J* = 12.7 Hz, 1H), 4.23 (d, *J* = 12.6 Hz, 1H), 2.61 (td, *J* = 13.6, 4.7 Hz, 1H), 2.36 (td, *J* = 14.0, 13.4, 4.5 Hz, 1H), 1.99 (s, 3H), 1.43 – 1.19 (m, 1H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.85 – 0.60 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.9, 138.7, 129.3, 129.2, 126.1, 68.7, 57.2, 36.8, 16.4, 14.0, 10.9. HRMS (ESI) calculated for $C_{13}H_{17}N_7Na^+$ $[M+Na]^+$: 294.1438; found: 294.1437.

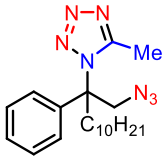


1-(1-Azido-2,3-diphenylpropan-2-yl)-5-methyl-1H-tetrazole (36)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 59.4 mg (62% yield) of **36** as a yellow oil.

IR (neat, cm^{-1}): 3031(w), 2106(s), 1497(m), 1449(m), 1289(m), 735(m), 699(s). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.36 (m, 3H), 7.25 – 7.15 (m, 3H), 7.15 – 7.09 (m, 2H), 6.62 (d, *J* = 7.5 Hz, 2H), 4.21 (d, *J* = 12.5 Hz, 1H), 4.09 (d, *J* = 12.5 Hz, 1H), 3.87 (d, *J* = 13.7 Hz, 1H), 3.76 (d, *J* = 13.7 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.0, 138.0, 133.0, 129.9, 129.4, 129.3, 128.5, 127.7, 126.4,

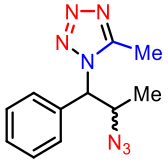
68.7, 56.1, 40.6, 11.2. HRMS (ESI) calculated for $C_{17}H_{18}N_7^+$ $[M+H]^+$: 320.1618; found: 320.1598.



1-(1-Azido-2-phenyldodecan-2-yl)-5-methyl-1H-tetrazole (37)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 79.8 mg (72% yield) of **37** as a yellow oil.

IR (neat, cm^{-1}): 2924(s), 2853(m), 2105(s), 1449(m), 1379(m), 1283(m), 700(s). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.36 (m, 3H), 7.17 – 7.07 (m, 2H), 4.39 (d, *J* = 12.5 Hz, 1H), 4.23 (d, *J* = 12.6 Hz, 1H), 2.62 (t, *J* = 13.3 Hz, 1H), 2.38 (t, *J* = 12.5 Hz, 1H), 1.99 (s, 3H), 1.31 – 1.23 (m, 15H), 0.87 (t, *J* = 6.1 Hz, 3H), 0.70 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.9, 138.7, 129.2, 129.1, 126.1, 68.7, 57.1, 34.6, 31.8, 29.4, 29.3, 29.2, 22.8, 22.6, 14.0, 10.8. HRMS (ESI) calculated for $C_{20}H_{31}N_7Na^+$ $[M+Na]^+$: 392.2533; found: 392.2539.



1-(2-Azido-1-phenylpropyl)-5-methyl-1H-tetrazole (38)

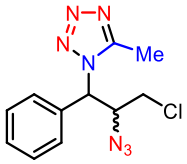
Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 57.7 mg (79%, dr = 1.5:1) of **38** as a yellow oil.

diastereoisomer 1:

IR (neat, cm^{-1}): 2983(w), 2112(s), 1524(m), 1261(m), 749(m), 701(s), 519(w). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 2H), 7.42 – 7.36 (m, 3H), 4.94 (d, *J* = 10.0 Hz, 1H), 4.77 (dq, *J* = 10.0, 6.6 Hz, 1H), 2.53 (s, 3H), 1.23 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.9, 134.0, 129.7, 129.4, 127.8, 67.4, 60.4, 17.6, 9.0. HRMS (ESI) calculated for $C_{11}H_{13}N_7Na^+$ $[M+Na]^+$: 266.1125; found: 266.1143.

diastereoisomer 2:

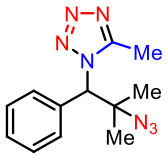
IR (neat, cm^{-1}): 2936(w), 2105(s), 1523(m), 1267(m), 750(m), 702(s), 523(w). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 5H), 5.03 (d, *J* = 9.0 Hz, 1H), 4.66 (dq, *J* = 8.9, 6.4 Hz, 1H), 2.50 (s, 3H), 1.29 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.9, 134.5, 129.6, 129.3, 127.8, 66.6, 60.4, 17.5, 9.1. HRMS (ESI) calculated for $C_{11}H_{13}N_7Na^+$ $[M+Na]^+$: 266.1125; found: 266.1126 .



1-(2-Azido-3-chloro-1-phenylpropyl)-5-methyl-1H-tetrazole (39)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 53.2 mg (64%, dr= 1:1) of **39** as a yellow oil.

IR (neat, cm^{-1}): 2953(w), 2127(s), 1605(m), 1525(m), 1001(m), 700(s), 547(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.52 – 4.47 (m, 4H), 4.45 – 4.41 (m, 6H), 5.52 (d, *J* = 9.1 Hz, 1H), 5.33 (d, *J* = 10.2 Hz, 1H), 4.99 (ddd, *J* = 10.2, 4.6, 3.0 Hz, 1H), 4.91 (dt, *J* = 9.1, 3.6 Hz, 1H), 3.81 (dd, *J* = 12.3, 3.1 Hz, 1H), 3.75 (dd, *J* = 12.1, 3.0 Hz, 1H), 3.51 (dd, *J* = 12.3, 3.9 Hz, 1H), 3.39 (dd, *J* = 12.2, 4.6 Hz, 1H), 2.55 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.1, 133.4, 132.7, 130.2, 130.0, 129.7, 129.5, 128.0, 127.7, 64.5, 64.0, 63.6, 61.6, 44.7, 44.4, 8.9. HRMS (ESI) calculated for $C_{11}H_{13}ClN_7^+$ $[M+H]^+$: 278.0915; found: 278.0913.

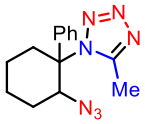


1-(2-Azido-2-methyl-1-phenylpropyl)-5-methyl-1H-tetrazole (40)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 57.1 mg (74% yield) of **40** as a yellow oil.

IR (neat, cm^{-1}): 2981(w), 2107(s), 1584(m), 1373(m), 1108(m), 707(s), 538(m). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.42 – 7.36 (m, 3H), 5.17 (s, 1H), 2.56 (s, 3H), 1.50 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ

152.6, 132.9, 129.3, 128.7, 69.6, 64.2, 24.4, 23.0, 9.4. HRMS (ESI) calculated for $C_{12}H_{15}N_7Na^+$ $[M+Na]^+$: 280.1281; found: 280.1285.



1-(2-Azido-1-phenylcyclohexyl)-5-methyl-1H-tetrazole (41)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 5:1) to give 58.9 mg (69%, dr = 1.1:1) of **41** as a yellow oil.

diastereoisomer 1:

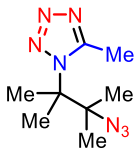
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.32 (m, 3H), 7.19 – 7.10 (m, 2H), 4.90 – 4.81 (m, 1H), 2.73 (ddd, *J* = 15.1, 12.0, 3.2 Hz, 1H), 2.64 – 2.47 (m, 2H), 2.13 – 2.04 (m, 4H), 1.80 – 1.53 (m, 4H), 1.25 – 0.75 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.1, 139.5, 129.1, 128.9, 126.4, 68.6, 65.6, 29.3, 27.7, 20.6, 20.2, 11.3.

diastereoisomer 2:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.33 (m, 3H), 7.23 – 7.15 (m, 2H), 4.43 (dd, *J* = 9.0, 3.9 Hz, 1H), 2.76 (ddt, *J* = 14.4, 3.8, 2.5 Hz, 1H), 2.41 (ddd, *J* = 14.0, 9.9, 3.7 Hz, 1H), 2.25 – 2.09 (m, 3H), 2.09 (s, 3H), 2.00 – 1.77 (m, 2H), 1.65 – 1.53 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.5, 139.3, 129.1, 128.8, 126.2, 68.9, 64.0, 36.0, 26.9, 22.6, 21.5, 11.7.

IR (neat, cm^{-1}): 2931(w), 2108(s), 1513(w), 1448(w), 1376(w), 759(m), 703(m).

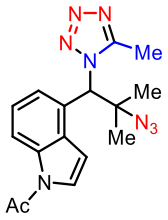
HRMS (ESI) calculated for $C_{14}H_{17}N_7Na^+$ $[M+Na]^+$: 306.1438; found: 306.1443.



1-(3-Azido-2,3-dimethylbutan-2-yl)-5-methyl-1H-tetrazole (42)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 47.1 mg (75% yield) of **42** as a colorless solid.

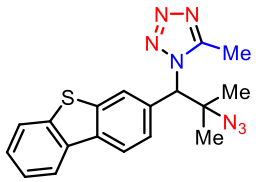
IR (neat, cm^{-1}): 2998(w), 2110(s), 2085(m), 1509(m), 1376(m), 1267(m), 1137(m). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.81 (s, 3H), 1.82 (s, 6H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.9, 68.2, 67.6, 24.4, 22.2, 13.0. HRMS (ESI) calculated for $C_8H_{16}N_7^+$ $[M+H]^+$: 210.1462; found: 210.1460.



1-(4-(2-Azido-2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)-1H-indol-1-yl)ethan-1-one (43)

Followed **Method C**, 2.5 V, 4.5 h. The desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 27.4 mg (27%) of **43** as a black oil.

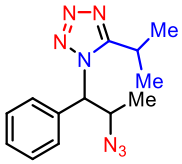
IR (neat, cm^{-1}): 2926(w), 2108(s), 1710(s), 1430(s), 1325(s), 1271(m), 764(m). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 3.9 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 3.9 Hz, 1H), 5.65 (s, 1H), 2.67 (s, 3H), 2.48 (s, 3H), 1.60 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.6, 152.6, 135.5, 129.9, 126.6, 125.4, 124.9, 124.7, 117.5, 105.9, 66.0, 64.7, 24.6, 23.9, 23.5, 9.4. HRMS (ESI) calculated for $C_{16}H_{18}N_8NaO^+$ $[M+Na]^+$: 361.1496; found: 361.1498.



1-(2-Azido-1-(dibenzo[b,d]thiophen-3-yl)-2-methylpropyl)-5-methyl-1H-tetrazole (44)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 43.2 mg (40%) of **44** as a yellow oil.

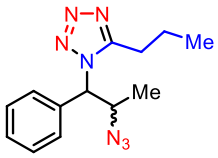
IR (neat, cm^{-1}): 3055(w), 2111(m), 1398(w), 1264(m), 731(s), 705(w). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 – 8.13 (m, 2H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.93 – 7.84 (m, 1H), 7.58 – 7.47 (m, 3H), 5.57 (s, 1H), 2.63 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.8, 140.2, 137.9, 136.3, 135.7, 128.1, 128.0, 127.5, 125.3, 125.2, 122.7, 122.5, 122.0, 67.5, 65.0, 24.8, 23.1, 9.5. HRMS (ESI) calculated for $C_{18}H_{17}N_7NaS^+$ $[M+Na]^+$: 386.1164; found: 386.1161.



1-(2-Azido-1-phenylpropyl)-5-isopropyl-1H-tetrazole (45)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 56.2 mg (69%, dr = 1.2:1) of **45** as a yellow oil.

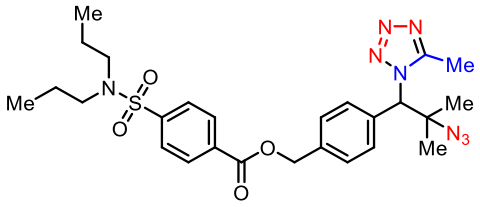
IR (neat, cm^{-1}): 2977(w), 2931(w), 2109(s), 1456(m), 1261(m), 1100(m), 748(m), 699(s). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 4H), 7.43 – 7.35 (m, 6H), 5.10 (d, *J* = 9.1 Hz, 1H), 4.98 (d, *J* = 10.0 Hz, 1H), 4.78 (p, *J* = 6.6 Hz, 1H), 4.65 (p, *J* = 6.7 Hz, 1H), 3.19 – 3.10 (m, 2H), 1.49 – 1.44 (m, 6H), 1.25 – 1.18 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 159.7, 135.1, 134.4, 129.6, 129.4, 129.3, 129.2, 127.9, 127.8, 67.2, 66.2, 60.8, 60.7, 24.10, 24.09, 21.1, 21.02, 20.96, 20.93, 17.6, 17.4. HRMS (ESI) calculated for $C_{13}H_{17}N_7Na^+$ $[M+Na]^+$: 294.1438; found: 294.1437.



1-(2-Azido-1-phenylpropyl)-5-propyl-1H-tetrazole (46)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 68.4 mg (84%, dr = 1.5:1) of **46** as a yellow oil.

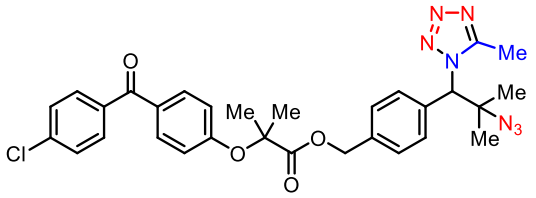
IR (neat, cm^{-1}): 2967(w), 2935(w), 2110(s), 1512(m), 1457(m), 1262(m), 749(m), 701(s). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.37 (m, 10H), 5.03 (d, *J* = 9.5 Hz, 1H), 4.92 (d, *J* = 10.0 Hz, 1H), 4.84 – 4.71 (m, 1H), 4.65 (p, *J* = 7.3 Hz, 1H), 2.68 – 2.88 (m, 4H), 1.85 – 1.71 (m, 4H), 1.27 – 1.21 (m, 6H), 1.00 – 0.93 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.2, 155.1, 134.8, 134.2, 129.5, 129.4, 129.3, 129.1, 127.8, 127.7, 67.2, 66.2, 60.54, 60.49, 25.0, 20.4, 20.3, 17.5, 17.3, 13.49, 13.46. HRMS (ESI) calculated for $C_{13}H_{18}N_7^+$ $[M+H]^+$: 272.1618; found: 272.1614.



4-(2-Azido-2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)benzyl 4-(N,N-dipropylsulfamoyl)benzoate (47)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 114.3 mg (69%) of **47** as a yellow oil.

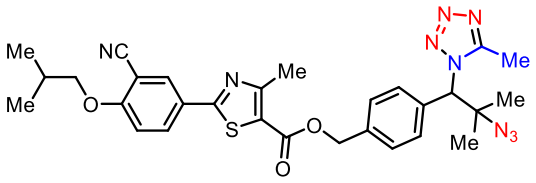
IR (neat, cm^{-1}): 2972(w), 2111(w), 1724(w), 1265(m), 1105(w), 731(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.22 – 8.12 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 2H), 5.39 (s, 2H), 5.20 (d, *J* = 1.7 Hz, 1H), 3.14 – 3.05 (m, 4H), 2.57 (s, 3H), 1.55 (q, *J* = 7.4 Hz, 4H), 1.49 (s, 3H), 1.47 (s, 3H), 0.87 (td, *J* = 7.3, 1.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.9, 152.6, 144.4, 136.7, 133.2, 133.0, 130.3, 129.8, 128.4, 127.0, 69.2, 66.3, 64.2, 49.8, 24.2, 23.1, 21.8, 11.0, 9.3. HRMS (ESI) calculated for $C_{26}H_{34}N_8NaO_4S^+$ $[M+Na]^+$: 577.2321; found: 577.2323.



4-(2-Azido-2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)benzyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (48)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 79.9 mg (45%) of **48** as a white solid.

IR (neat, cm^{-1}): 2987(w), 2110(m), 1739(w), 1596(m), 1263(m), 1135(w), 732(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (ddt, *J* = 11.7, 9.6, 2.5 Hz, 4H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.87 – 6.76 (m, 2H), 5.19 (d, *J* = 2.7 Hz, 2H), 5.14 (s, 1H), 2.55 (s, 3H), 1.68 (d, *J* = 3.3 Hz, 6H), 1.44 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 194.1, 173.4, 159.4, 138.4, 136.4, 136.2, 133.1, 131.9, 131.1, 130.4, 129.7, 128.5, 128.2, 117.2, 79.3, 69.2, 66.4, 64.2, 25.5, 25.2, 24.2, 23.1, 9.4. HRMS (ESI) calculated for $C_{30}H_{30}ClN_7NaO_4^+$ $[M+Na]^+$: 610.1945; found: 610.1946.

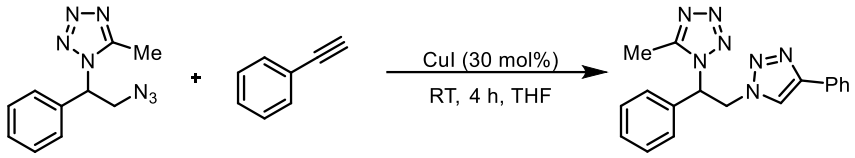


4-(2-Azido-2-methyl-1-(5-methyl-1H-tetrazol-1-yl)propyl)benzyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (49)

Followed **Method C**, MeCN/DCM (7:3, 10mL) as co-solvent. The desired pure product was purified using silica gel chromatography (PE:EA = 1:1) to give 63.5 mg (36%) of **49** as a white solid.

IR (neat, cm^{-1}): 2966(w), 2109(m), 1711(w), 1375(w), 1261(s), 1088(w), 732(s). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 2.2 Hz, 1H), 8.08 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 1H), 5.33 (s, 2H), 5.18 (s, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.76 (s, 3H), 2.57 (s, 3H), 2.20 (dp, *J* = 13.3, 6.6 Hz, 1H), 1.49 (d, *J* = 6.5 Hz, 6H), 1.10 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 162.5, 161.8, 161.6, 152.6, 136.9, 133.0, 132.5, 132.0, 129.8, 128.2, 125.7, 121.0, 115.3, 112.6, 102.9, 75.6, 69.2, 65.9, 64.2, 28.1, 24.3, 23.1, 19.0, 17.5, 9.4. HRMS (ESI) calculated for $C_{29}H_{32}N_9NaO_3S^+$ $[M+H]^+$: 586.2343; found: 586.2334.

6. Derivatization of products

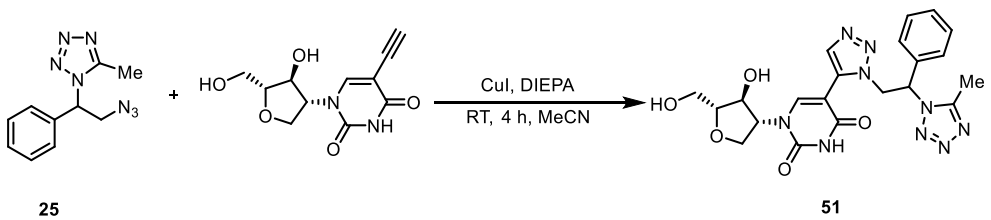


25 50

The mixture solution of 1-(2-azido-1-phenylethyl)-5-methyl-1H-tetrazole (**25**, 41 mg, 0.18 mmol, 1.0 equiv.) , phenylacetylene (3 equiv.) and CuI (30 mol%) in THF (2 mL) was stirred at temperature for 4 h. The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (PE/EA=1:2) to give product 5-methyl-1-(1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)-1H-tetrazole (**50**, 55.5 mg, 93% yield) as a white solid.

5-Methyl-1-(1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)-1H-tetrazole (50).

IR (neat, cm^{-1}): 2925(w), 1524(w), 1458(w), 1265(w), 1077(w), 765(m), 733(s), 696(s). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.62 (s, 1H), 7.46 – 7.35 (m, 7H), 7.35 – 7.28 (m, 1H), 6.10 (dd, *J* = 10.0, 4.9 Hz, 1H), 5.51 (dd, *J* = 14.2, 10.0 Hz, 1H), 5.13 (dd, *J* = 14.2, 4.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.3, 147.7, 133.7, 130.0, 129.8, 129.7, 128.8, 128.4, 126.8, 125.7, 121.2, 62.0, 53.5, 8.7. HRMS (ESI) calculated for $C_{18}H_{18}N_7^+$ $[M+H]^+$: 332.1618; found: 332.1611.



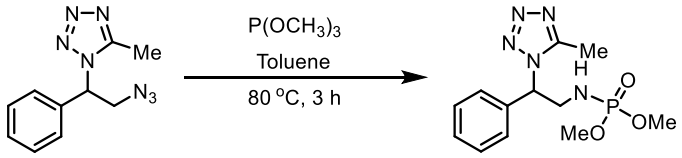
25 51

The mixture solution of 1-(2-Azido-1-phenylethyl)-5-methyl-1H-tetrazole (**25**, 23 mg, 0.1 mmol, 1.0 equiv.) , alkyne (1.1 equiv.), CuI (2 equiv.) and DIPEA (3 equiv.) in MeCN (2 mL) was stirred at temperature for 4 h. The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column

chromatography on silica gel (DCM/CH_3OH=10:1) to give product 5-methyl-1-(1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)-1H-tetrazole (**51**, 36.1mg, 73% yield) as a white solid.

1-((3R,4S,5R)-4-Hydroxy-5-(hydroxymethyl)tetrahydrofuran-3-yl)-5-(1-(2-(5-methyl-1H-tetrazol-1-yl)-2-phenylethyl)-1H-1,2,3-triazol-5-yl)pyrimidine-2,4(1H,3H)-dione (51).

IR (neat, cm^{-1}): 3385(s), 2490(s), 2071(m), 1686(m), 1120(m), 972(s). ^1H NMR (500 MHz, Methanol-d_4) δ 8.57 (s, 1H), 8.31 (s, 1H), 7.57 – 7.45 (m, 2H), 7.43 (q, *J* = 5.7 Hz, 3H), 6.43 – 6.35 (m, 1H), 6.32 (t, *J* = 6.7 Hz, 1H), 5.59 (dd, *J* = 14.2, 9.6 Hz, 1H), 5.29 (dd, *J* = 14.2, 5.7 Hz, 1H), 4.42 (dq, *J* = 6.4, 3.2 Hz, 1H), 3.95 (q, *J* = 3.2 Hz, 1H), 3.82 (dt, *J* = 12.0, 2.8 Hz, 1H), 3.75 (dd, *J* = 12.0, 4.1 Hz, 1H), 2.40 (s, 3H), 2.33 (ddt, *J* = 12.0, 5.9, 3.0 Hz, 1H), 2.26 (dtd, *J* = 13.6, 6.8, 4.0 Hz, 1H), 1.90 (s, 1H), 1.36 (d, *J* = 6.6 Hz, 1H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 163.0, 154.1, 151.5, 140.8, 138.0, 135.6, 130.8, 130.5, 128.6, 124.8, 106.4, 89.1, 86.9, 72.3, 62.9, 62.5, 54.2, 41.5, 8.6. HRMS (ESI) calculated for $C_{21}H_{26}N_9O_5^+$ $[M+H]^+$: 484.2051; found: 484.2050.



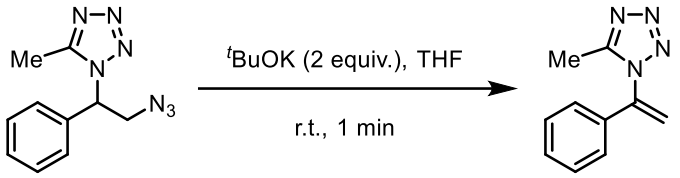
25 **52**

The mixture solution of **25** (0.2 mmol, 1.0 equiv) , $P(OMe)_3$ (1.5 equiv) in toluene (1.2 mL) was stirred at 80 °C for 3 h. The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (DCM/CH_3OH=10:1) to give the desired products (**52**, 52.1 mg, 84% yield).

Dimethyl (2-(5-methyl-1H-tetrazol-1-yl)-2-phenylethyl)phosphoramidate (52).

IR (neat, cm^{-1}): 3216(w), 2952(w), 1455(w), 1240(w), 1034(s), 834(m), 525(w). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.32 (m, 3H), 7.24 (dd, *J* = 7.3, 1.9 Hz, 2H), 5.57 (dd, *J* = 9.7, 4.7 Hz, 1H), 4.02 (dddd, *J* = 16.9, 14.7, 9.7, 6.9 Hz, 1H), 3.76 – 3.69 (m, 1H), 3.67 (d, *J* = 11.2 Hz, 3H), 3.60 (d, *J* = 11.2 Hz, 3H), 2.45 (s, 3H). ^{13}C

NMR (126 MHz, Chloroform-*d*) δ 152.5, 135.1, 129.23, 129.16, 126.7, 53.2 (d, *J* = 5.8 Hz), 53.3 (d, *J* = 6.0 Hz), 53.2 (d, *J* = 5.8 Hz), 45.8, 8.9. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 10.7 (m). HRMS (ESI) calculated for $C_{12}H_{19}N_5O_3P^+$ $[M+H]^+$: 312.1220; found: 312.1216.



25 **53**

The mixture solution of 1-(2-azido-1-phenylethyl)-5-methyl-1H-tetrazole (**25**, 23 mg, 0.1 mmol, 1.0 equiv.), ^{t}BuOK (2 equiv.) in THF (1 mL) was stirred at temperature for 1 min. The mixture was then filtered and washed with DCM, and the organic solvent evaporates under reduced pressure to give the pure compound **53** as colorless oil (18.6 mg, 99% yield).

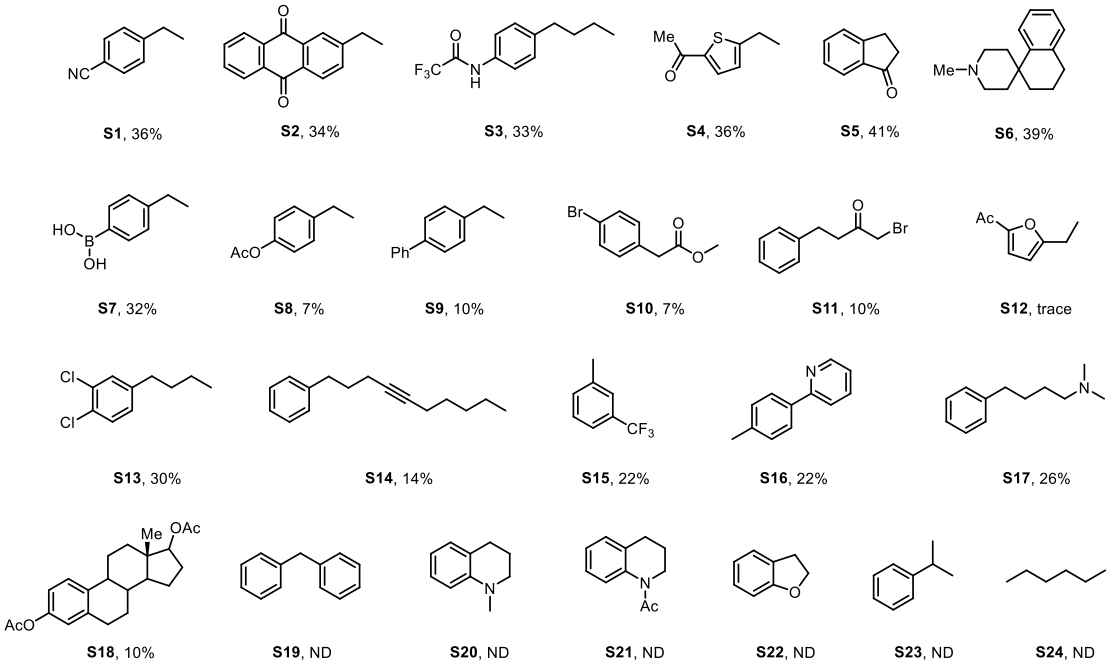
5-Methyl-1-(1-phenylvinyl)-1H-tetrazole (53)

IR (neat, cm^{-1}): 3924(w), 1518(m), 1407(m), 1266(m), 918(w), 775(m), 732(s), 701(s). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.34 (m, 3H), 7.21 – 7.12 (m, 2H), 6.00 (d, *J* = 1.5 Hz, 1H), 5.61 (d, *J* = 1.5 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.1, 140.2, 133.4, 130.3, 129.2, 125.7, 115.0, 9.4. HRMS (ESI) calculated for $C_{10}H_{11}N_4^+$ $[M+H]^+$: 187.0978; found: 187.0977.

7. Unsuccessful substrates

Unsuccessful substrates of C–H tetrazolation are shown in Table S5. For **S1-S5**, **S13-S15**, these reaction systems were clean but the yields were generally low. For **S7**, the desired tetrazole cannot be separated from the C-H acetylation byproduct. For **S8-S12**, **S20-S22**, these reactions only afforded complex reaction mixtures. For **S6**, **S16-S18**, low conversions were obtained as there were a lot of raw materials recovered. For **S19**, the desired C-H tetrazolization reaction did not occur at all. For **S23** and **S24**, no formation of C-H tetrazolization products was detected.

Table S5. Unsuccessful substrates of C–H tetrazolation.



S1, 36% **S2**, 34% **S3**, 33% **S4**, 36% **S5**, 41% **S6**, 39%

S7, 32% **S8**, 7% **S9**, 10% **S10**, 7% **S11**, 10% **S12**, trace

S13, 30% **S14**, 14% **S15**, 22% **S16**, 22% **S17**, 26%

S18, 10% **S19**, ND **S20**, ND **S21**, ND **S22**, ND **S23**, ND **S24**, ND

Unsuccessful substrates of vicinal azidotetrazolation are shown in Table S6. **F6-F8**, **F10-F16**, **F31-F36** these reactions only afforded complex reaction mixtures. For **F9**, **F42-F44**, the yields of these reactions were generally low and the desired products were difficult to purifiy. For **F21-F26**, **F29**, **F37-F39**, **F40** and **F41**, low conversions were obtained as there were a lot of raw materials recovered. For F**1**-F**5**, **F17-F20**, **F27**, **F28, F30, F45-F47**, these reaction systems were clean but the yields were generally low.

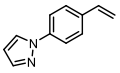
Table S6. Unsuccessful substrates of vicinal azidotetrazolation.

F1, R= CH_3, 53%*b*
F2, R= CH_2Cl, 56%
F3, R= F, 44%
F4, R= Cl, 50%
F5, R= Br, 34%
F6, R= 4-Ph 28%
F7, R= OMe, 11%
F8, R= SMe, 10%
F9, R= OCOMe, 25%

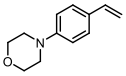
F10, R= OH trace
F11, R= CF_3 trace
F12, R= CHO ND
F13, R= CN ND
F14, R= COOH ND
F15, R= $B(OH)_2$ ND
F16, R= NO_2 ND

F17, 45%

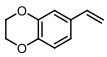
F18, R= CH_3, 34%
F19, R= Cl, 36%
F20, R= Br, 39%



F21, 22%

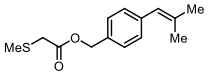


F22, trace



F23, trcae

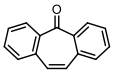
F24, trace



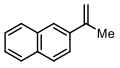
F25, 37%

F26, ND

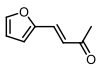
F27, n=0, 36%, > 20:1 dr
F28, n=1, 27%, > 20:1 dr



F29, 10%



F30, 48%



F31, trace

F32, ND

F33, trace

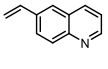
F34, 9%

F35, 26%

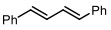
F36, ND

F37, ND

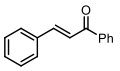
F38, ND



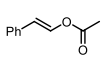
F39, ND



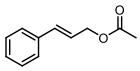
F40, 10%, 1.1:1



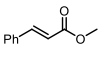
F41, 13%, 1.1:1 dr



F42, 17%, 1.1:1 dr



F43, 24%, 1:1 dr



F44, trace

F45, 24%, > 20:1 dr

F46, 23%

F47, 31%

8. Mechanistic experiments

8.1 Cyclic voltammetry studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter), a platinum wire auxiliary electrode and submerged in saturated aqueous KCl solution Ag/AgCl reference electrode. Current was reported in mA, while all potentials were reported in V.

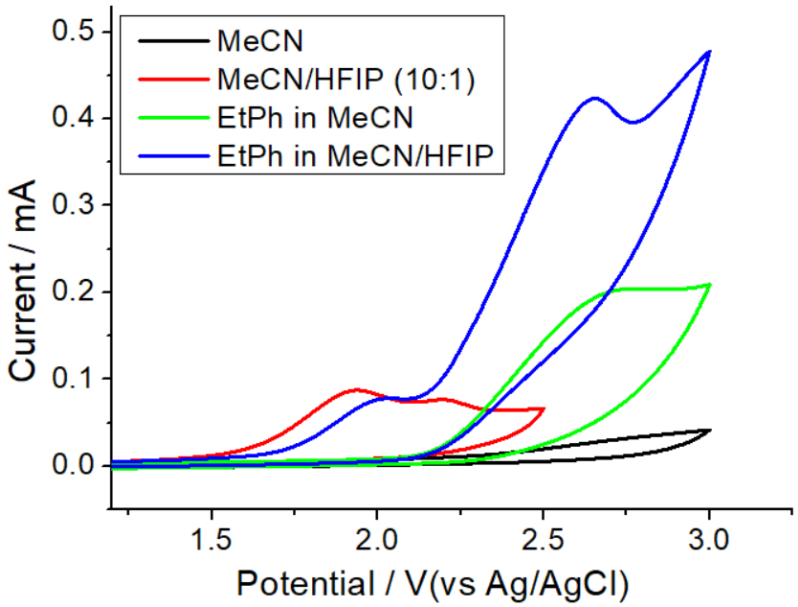


Figure S2. Cyclic voltammogram with $^{n}Bu_4NClO_4$ (10 mM) as electrolyte. Scan rate: 0.1 V/s.

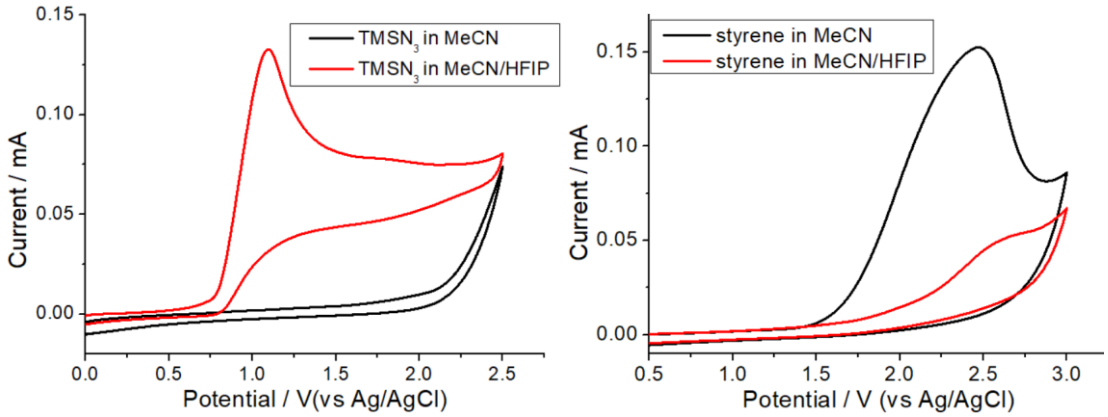
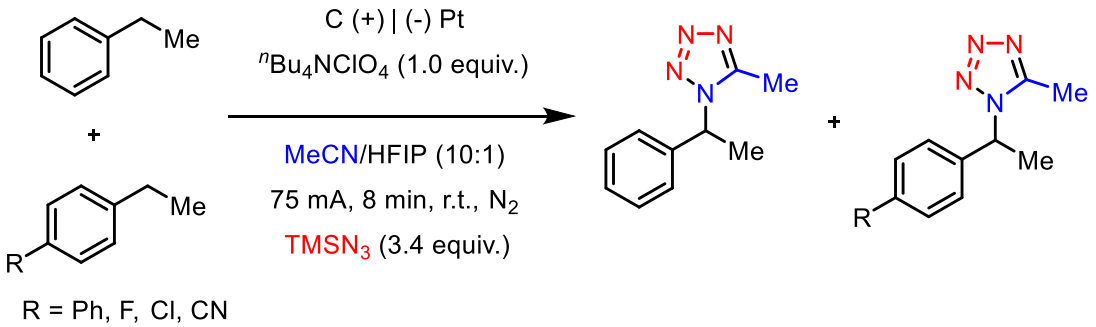


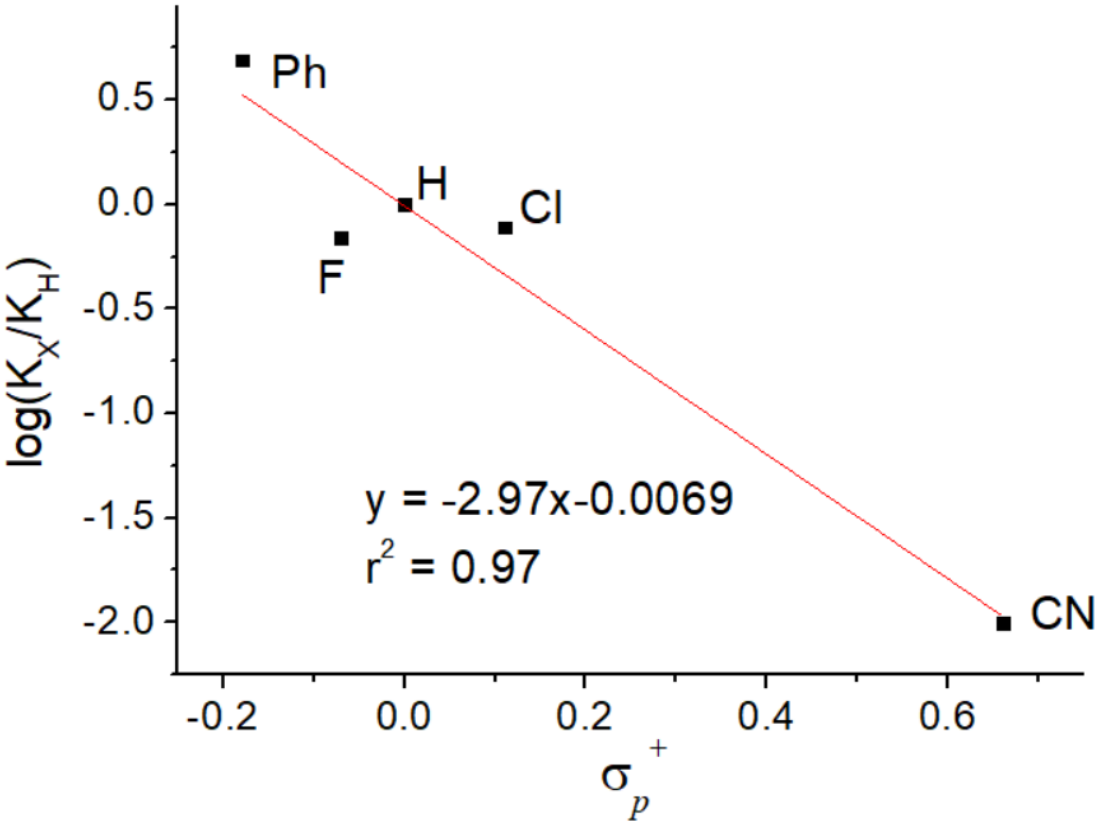
Figure S3. Cyclic voltammogram with $^{n}Bu_4NClO_4$ (10 mM) as electrolyte. Scan rate: 0.1 V/s.

8.2 Hammett plot experiment

To a solution of ethylbenzene (0.3 mmol, 1.0 equiv.), *p*-substituted ethylbenzene (0.3 mmol, 1.0 equiv.), $TMSN_3$ (0.4 mmol, 3.4 equiv.), in MeCN/HFIP (10/1, ml) reacted at 75 mA for 8 min. The crude mixture was monitored by ^{1}H NMR (figure S5-S8). As

shown in figure S3, the electronic effect on the aromatic ring of ethylbenzene is significant, and a much negative ρ value (-2.97) in Hammett plot was given in below.





	H	Ph	F	Cl	CN
σ_p^+	0	-0.18	-0.07	0.11	0.66
$\log(K_X/K_H)$	0	0.687	-0.161	-0.114	-2

Figure S4. Hammett plot of tetrazolation of ethylbenzene

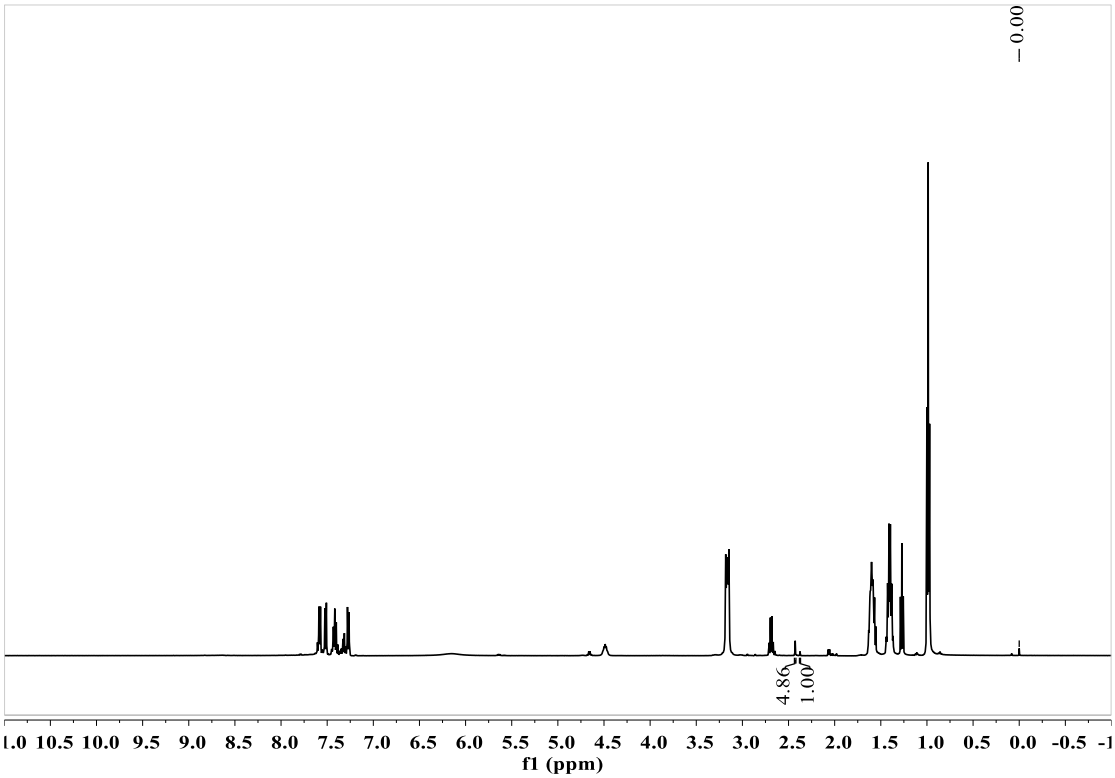


Figure S5. [1]H NMR Spectrum of ethylbenzene and *p*-Ph ethylbenzene reaction mixture

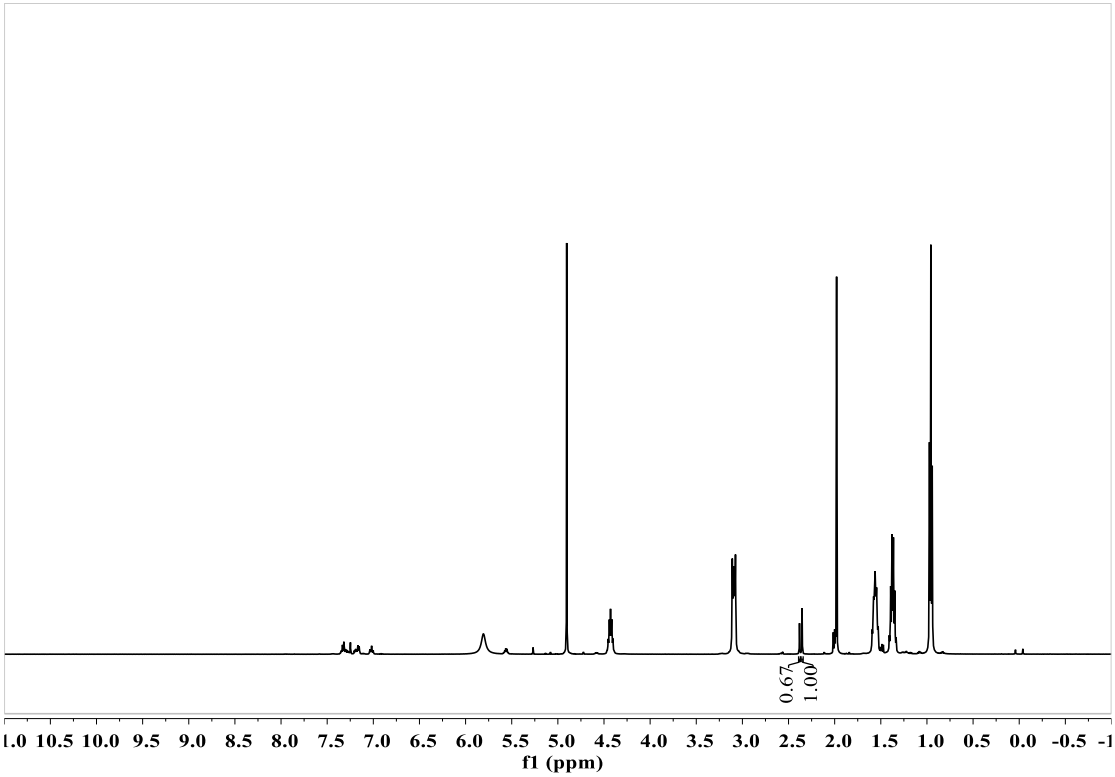


Figure S6. [1]H NMR Spectrum of ethylbenzene and *p*-F ethylbenzene reaction mixture

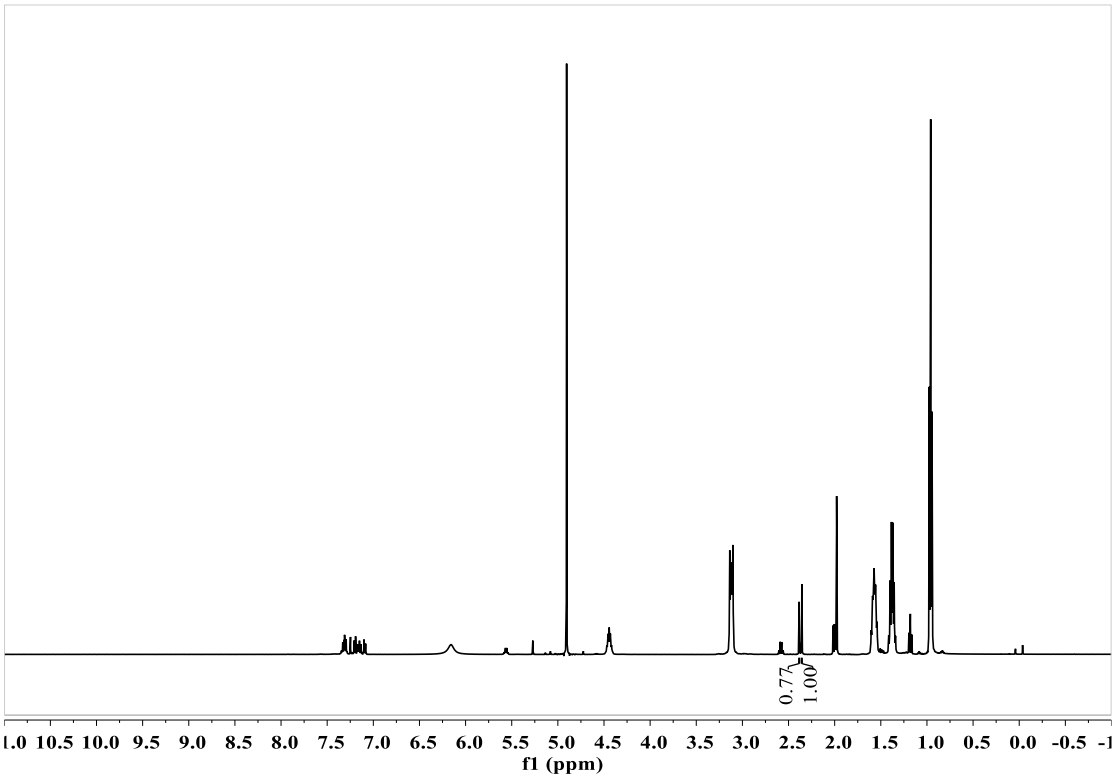


Figure S7. ^{1}H NMR Spectrum of ethylbenzene and *p*-Cl ethylbenzene reaction mixture

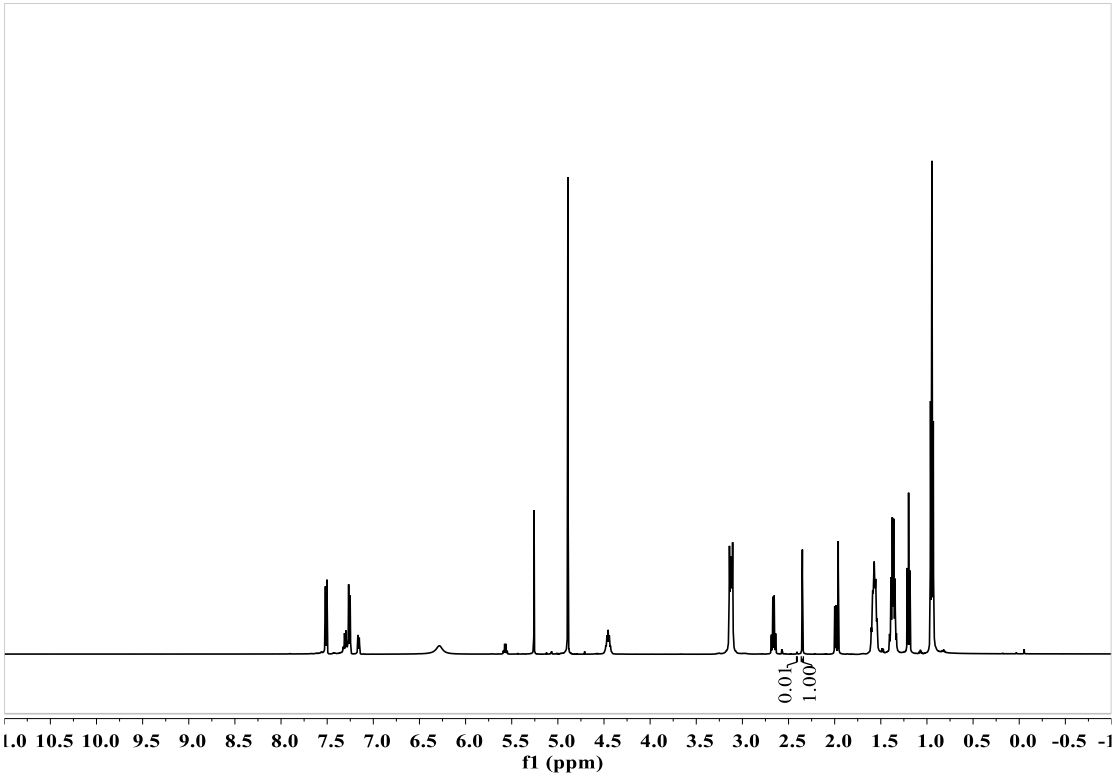


Figure S8. ^{1}H NMR Spectrum of ethylbenzene and *p*-CN ethylbenzene reaction mixture

8.3 Radical clock experiment

54 **55**, 21%, 7.5:1 dr

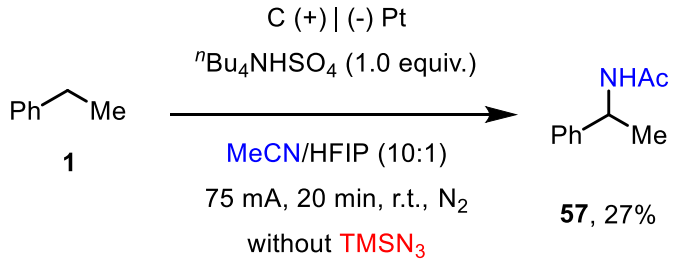
Following the standard procedure for the synthesis of vicinal azidotetrazoles and azidoacetamides using 1- (2-phenylcyclopropyl)vinyl)benzene (0.3 mmol) as the starting material. After work-up, the crude mixture was purified using column chromatography to afford **55**.

1-(4-Azido-1,4-diphenylbut-3-en-1-yl)-5-methyl-1H-tetrazole (55)

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 22.1 mg (21%, dr = 7.5:1) of **55** as a yellow oil.

IR (neat, cm^{-1}): 2926(w), 2099(s), 1523(m), 1402(m), 1247(m), 702(s). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 9H), 7.24 (s, 1H), 5.86 (t, *J* = 7.6 Hz, 1H), 5.38 (dd, *J* = 8.6, 6.7 Hz, 1H), 4.28 (d, *J* = 13.7 Hz, 1H), 4.12 (d, *J* = 13.7 Hz, 1H), 3.60 (dt, *J* = 16.4, 8.3 Hz, 1H), 3.28 (dt, *J* = 14.5, 6.9 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.7, 140.0, 138.0, 137.1, 129.4, 129.2, 128.6, 128.0, 127.4, 126.6, 126.1, 63.0, 49.2, 35.3, 9.1. HRMS (ESI) calculated for $C_{19}H_{20}N_7^+$ $[M+H]^+$: 346.1775; found: 346.1769.

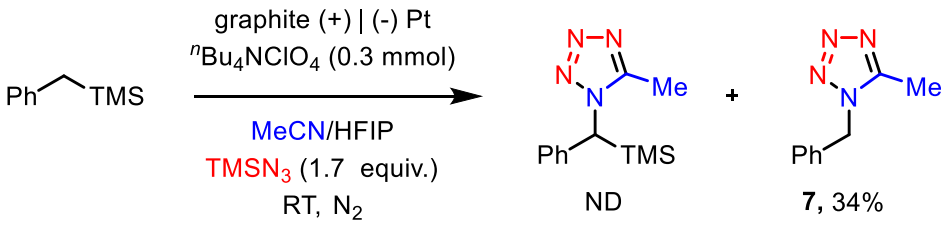
8.4 Trapping the carbocation intermediate



N-(1-phenylethyl)acetamide (**57**).[1] ^1H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 5.76 (brs, 1H), 5.13 (p, *J* = 7.0 Hz, 1H), 1.98 (s, 3H), 1.49 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.2, 143.1, 128.7, 127.4, 126.2, 48.8, 23.5, 21.7.

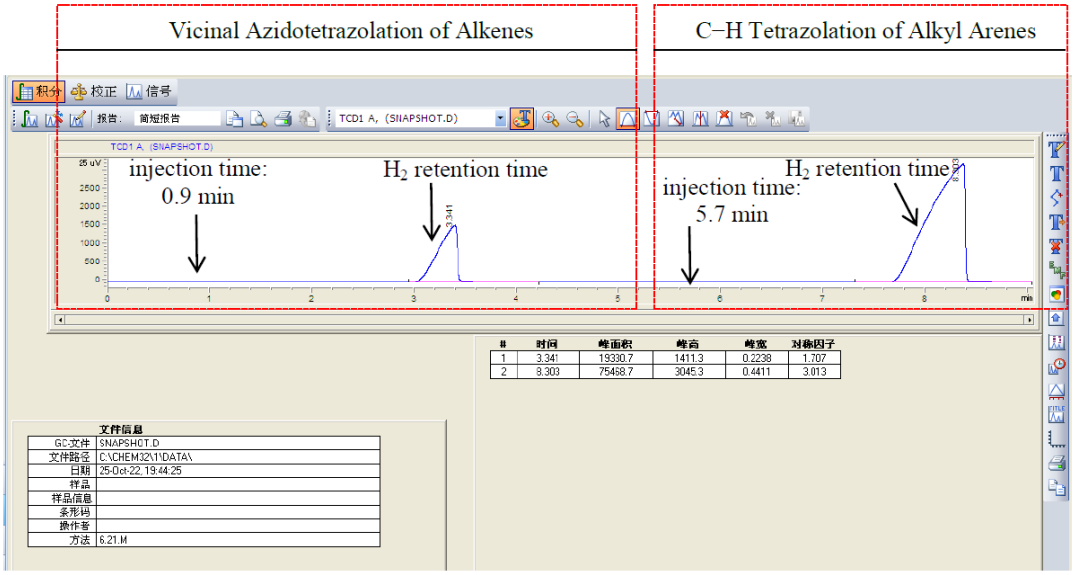
8.5 Probing arene radical cations

The procedure is the same as **Method A**



8.6 H_2 detection experiment

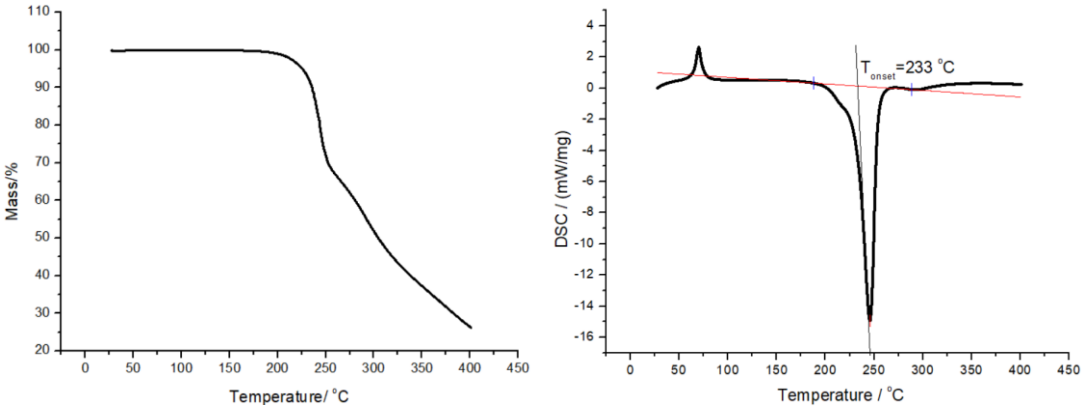
We have carried out the headspace GC analysis of the reaction mixture and confirmed the formation of H_2 both in the tetrazolation and azidotetrazolation.



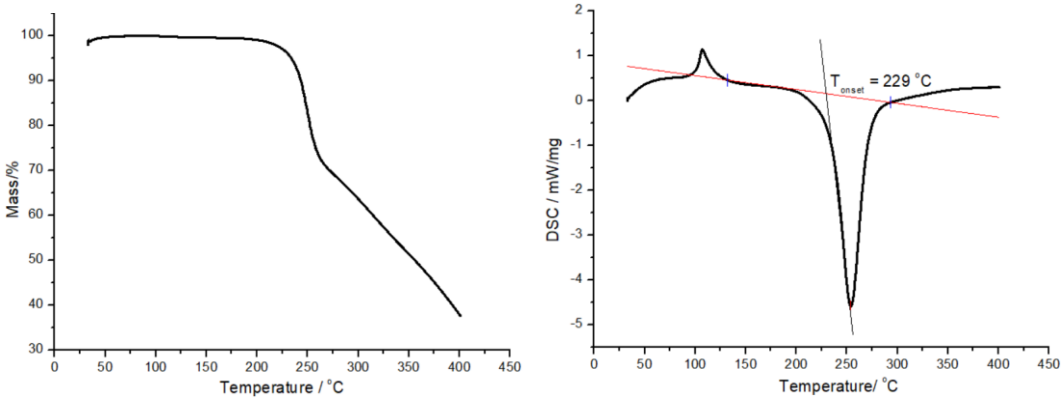
9. TG-DSC experiments

The TG-DSC curves of compound **25, 27, 42** were measured at N_2 flow rate of 20 mL•min^{-1}, heating rate of 10.0 ℃• min^{-1} and temperature range of RT to 400 ℃. Crucible with aluminum lid was used as the sample tank.

Compound **25** (6.78 mg was used, ΔH = –1270 J g^{-1})



Compound **27** (5.48 mg was used, ΔH = –1330 J g^{-1})



Compound **42** (6.5 mg was used, ΔH = –1330 J g^{-1})

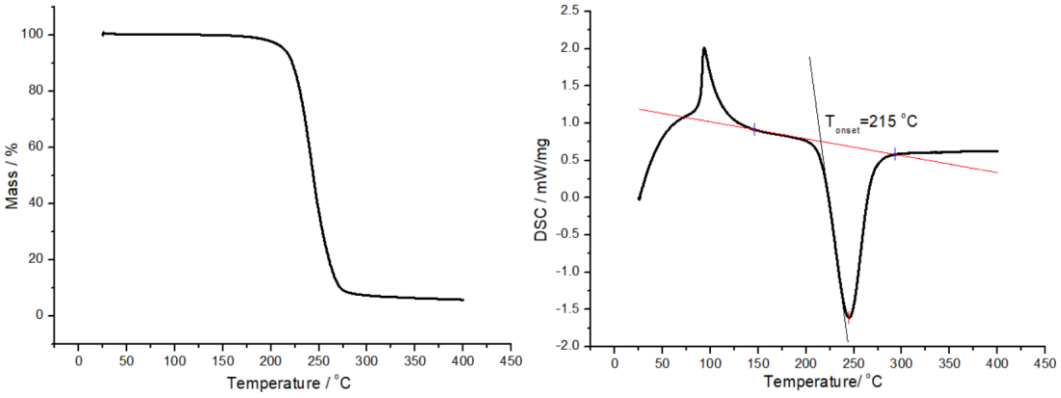


Table S7. Onset Temperatures and Decomposition Enthalpies Calculated from DSC.

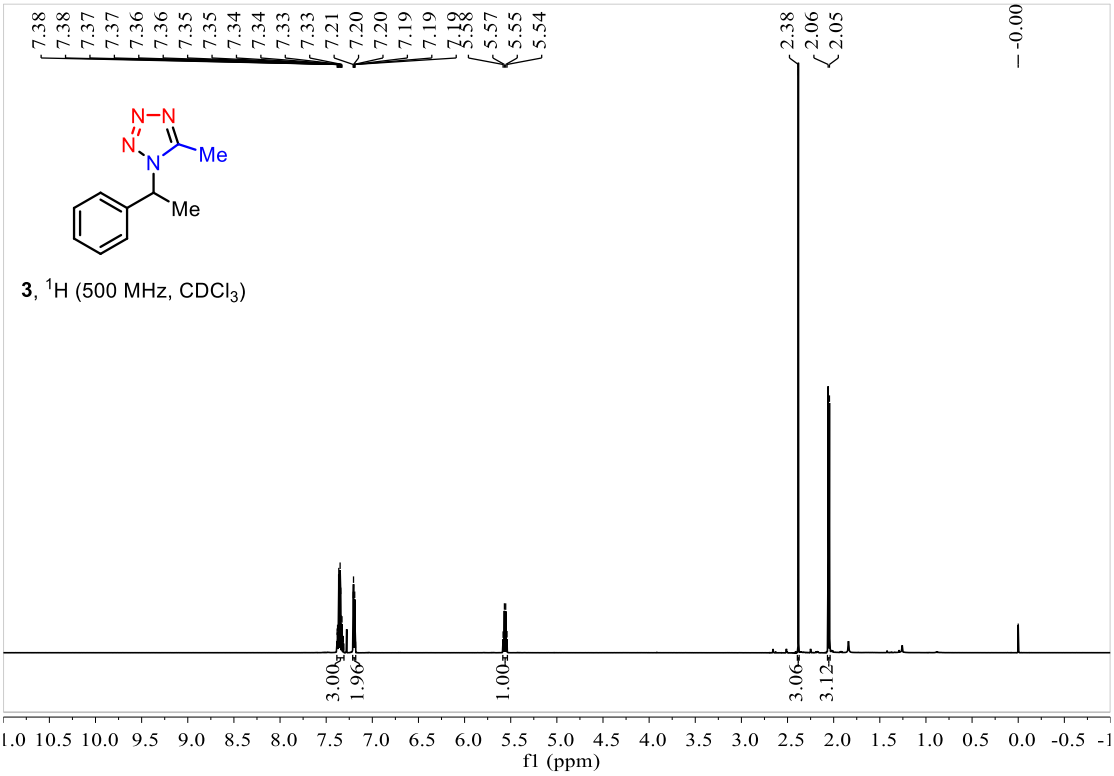
Compound	T_{onset} (°C)	T_m[a] (°C)	TD_{24}[b] (°C)	ΔH (J g^{-1})	ΔH (kJ mol^{-1})
25	233	246	117.1	-1270	-291
27	229	253	114.3	-1330	-379
42	215	246	104.5	-1330	-278

[a] Temperature of maximum in the DSC curve. [b] Temperature in which the time of maximum rate is 24 h.

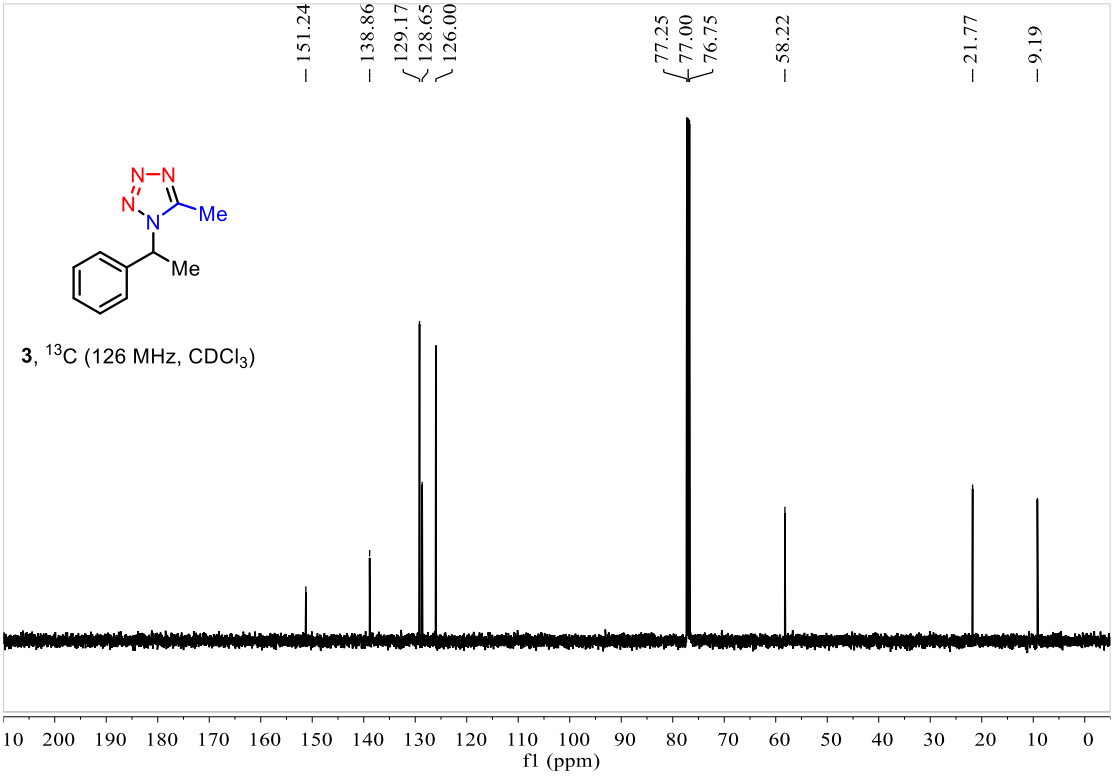
10 Reference

1. Y. Chen, X. Yi, Y. Cheng, A. Huang, Z. Yang, X. Zhao, F. Ling and W. Zhong, *J. Org. Chem.*, 2022, **87**, 7864-7874.

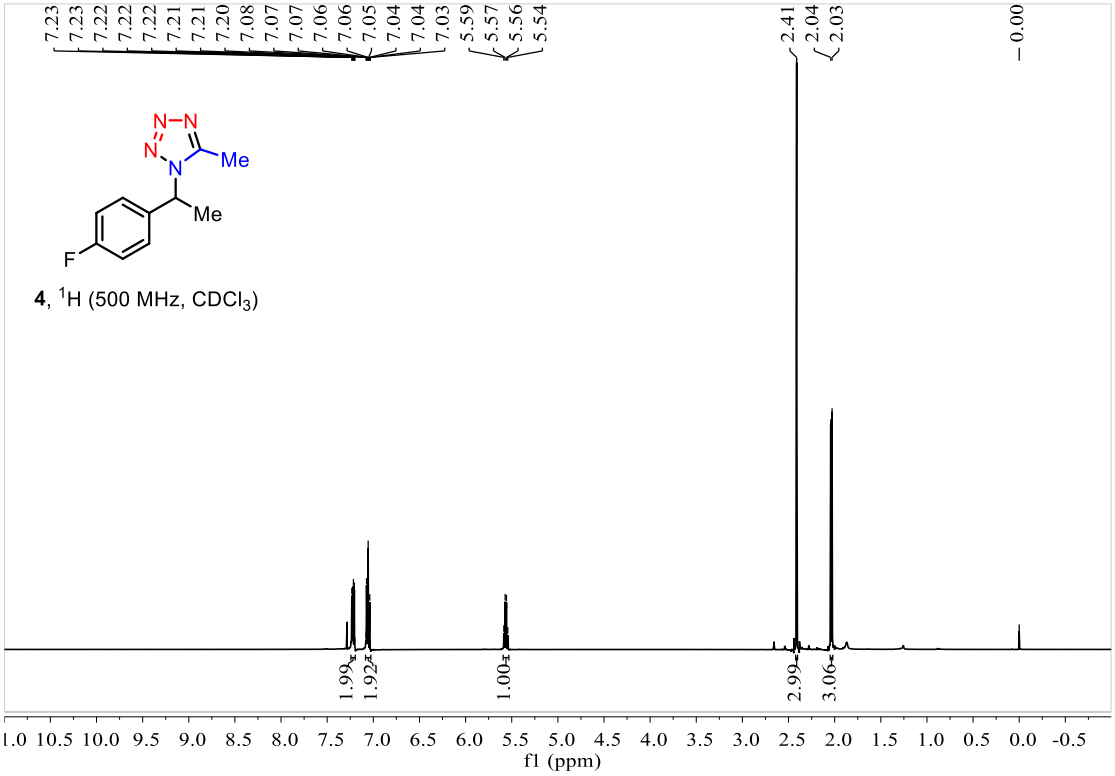
11. Spectral data (^{1}H, ^{13}C, ^{19}F) of products



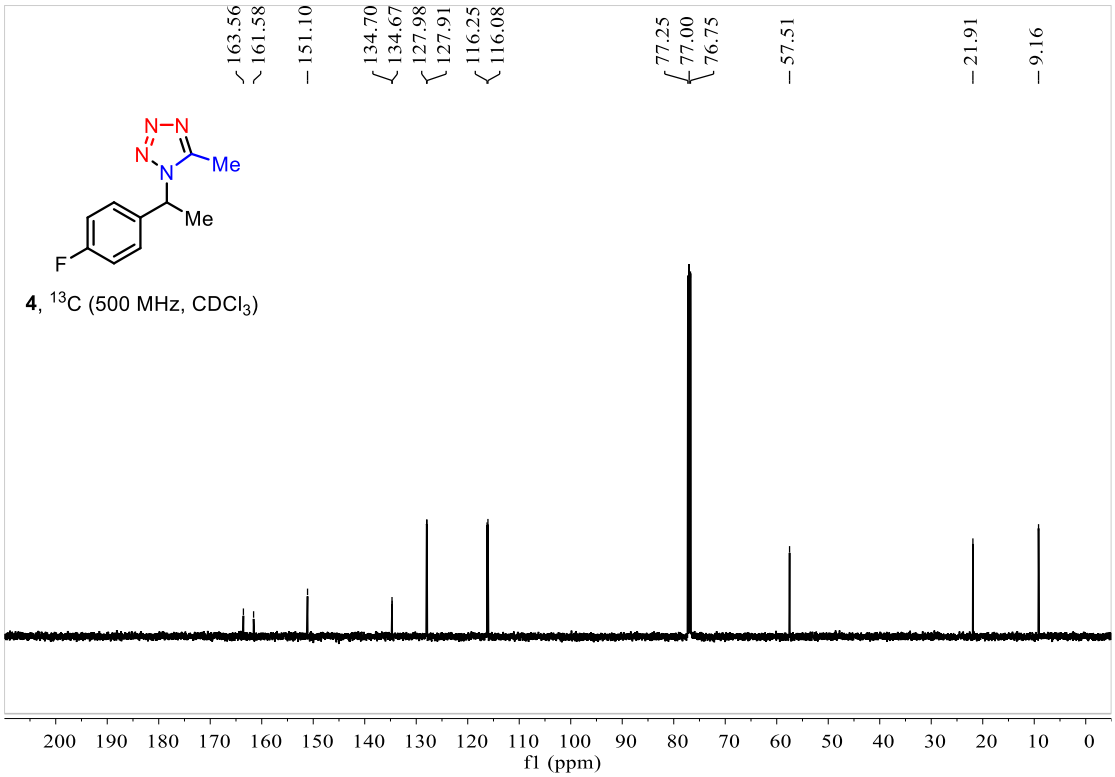
3, ^{1}H (500 MHz, $CDCl_3$)



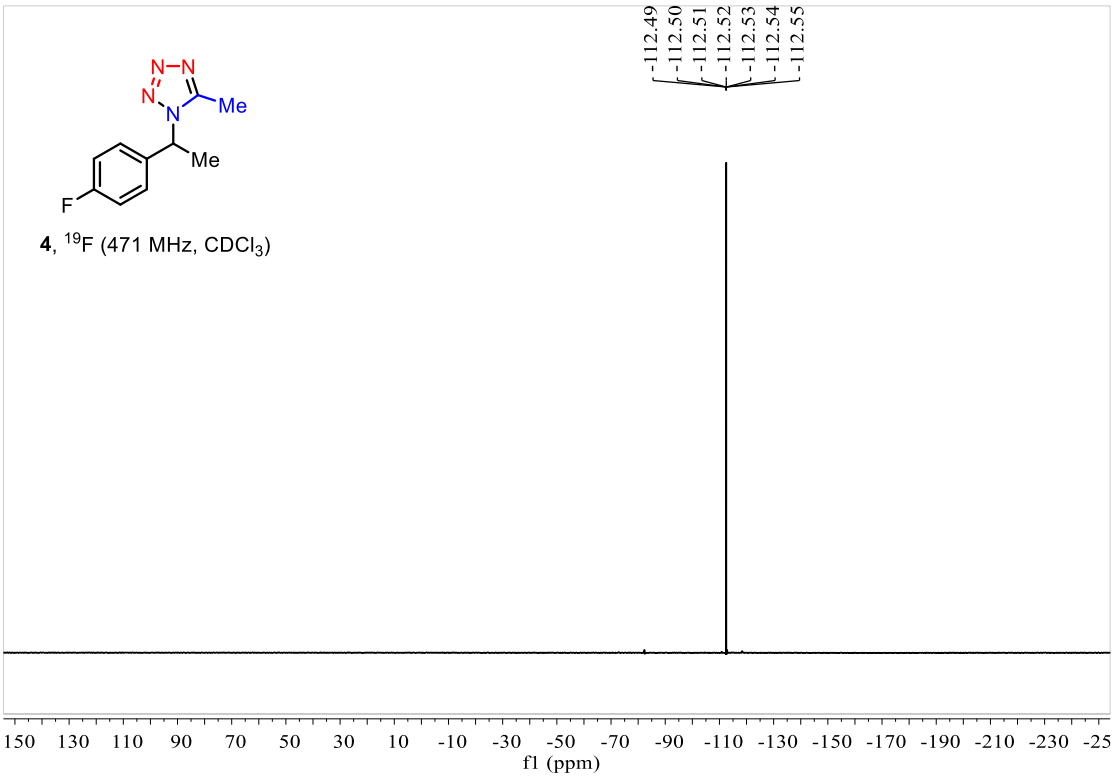
3, ^{13}C (126 MHz, $CDCl_3$)



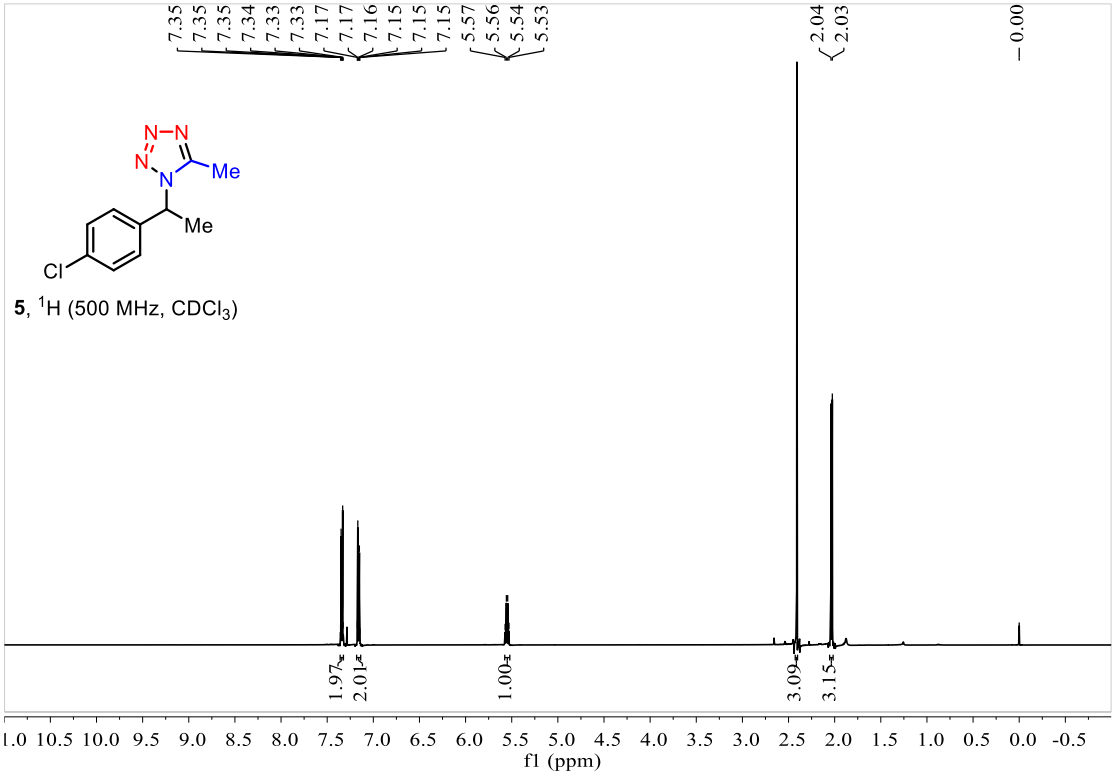
4, ^{1}H (500 MHz, $CDCl_3$)



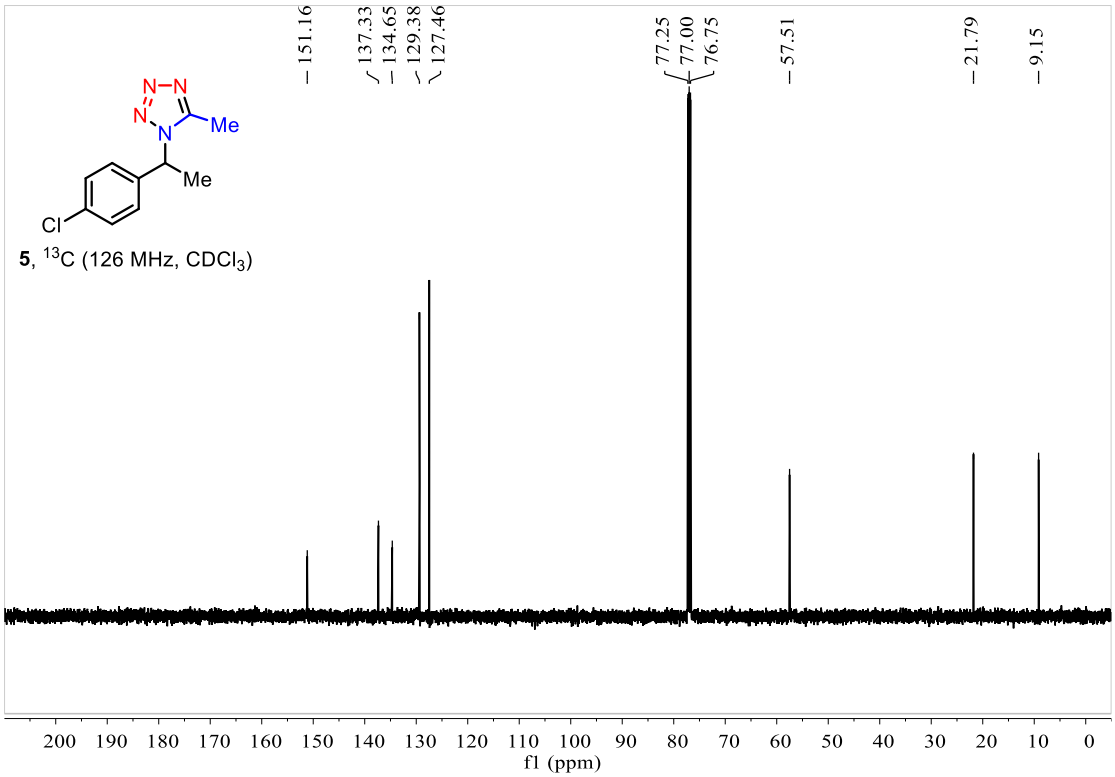
4, ^{13}C (500 MHz, $CDCl_3$)



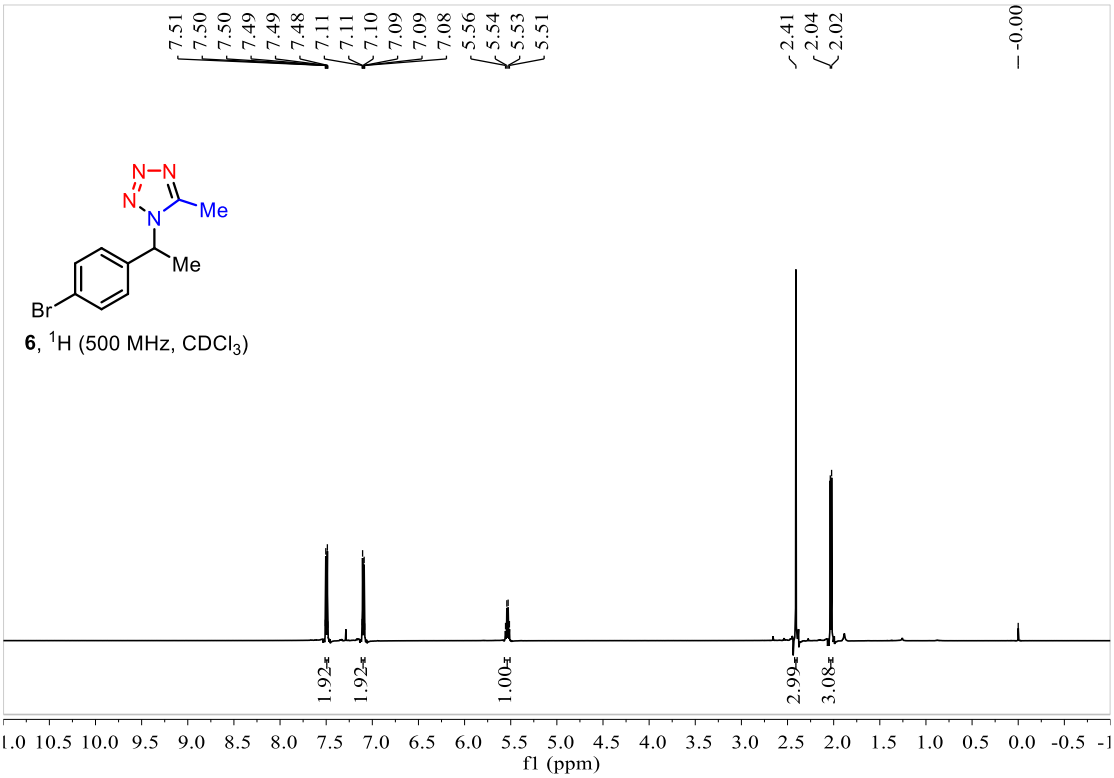
4, ^{19}F (471 MHz, $CDCl_3$)



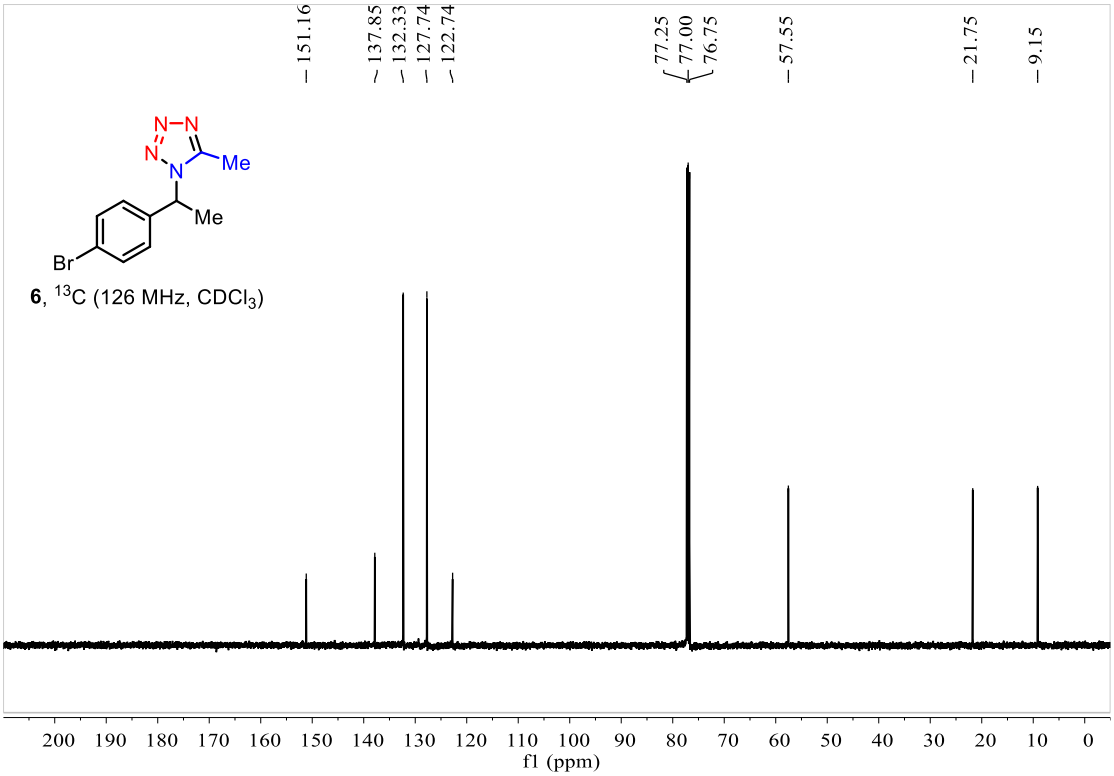
5, ^{1}H (500 MHz, $CDCl_3$)



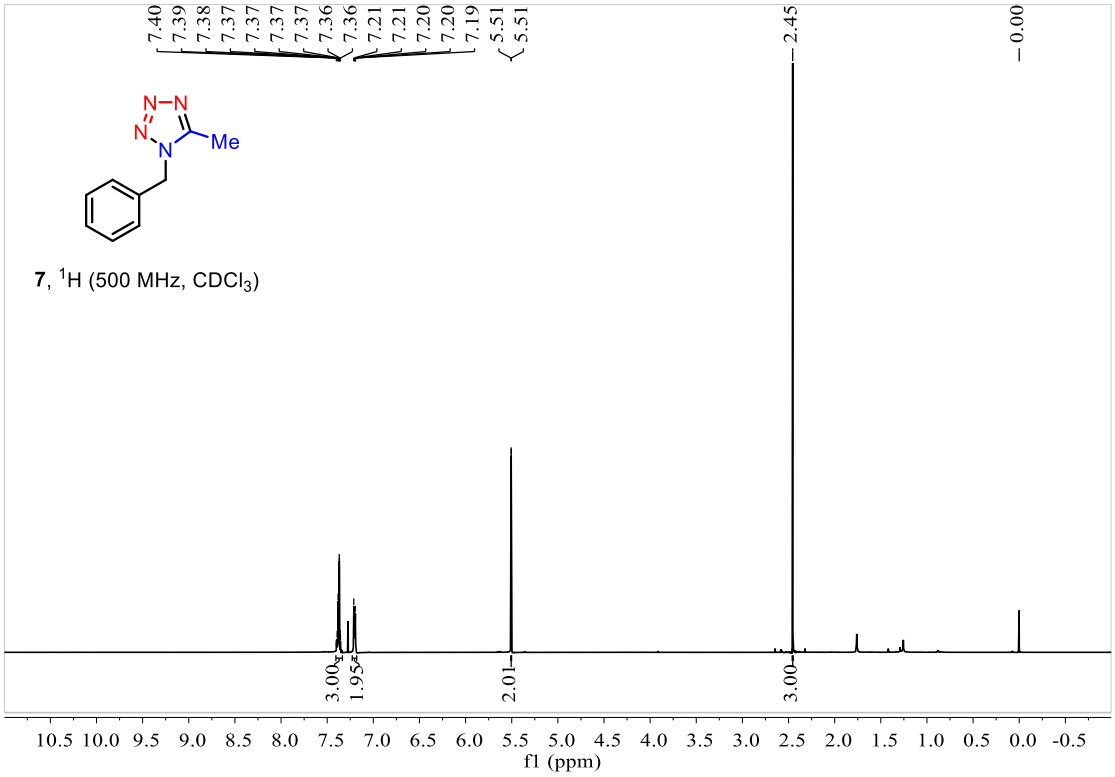
5, ^{13}C (126 MHz, $CDCl_3$)



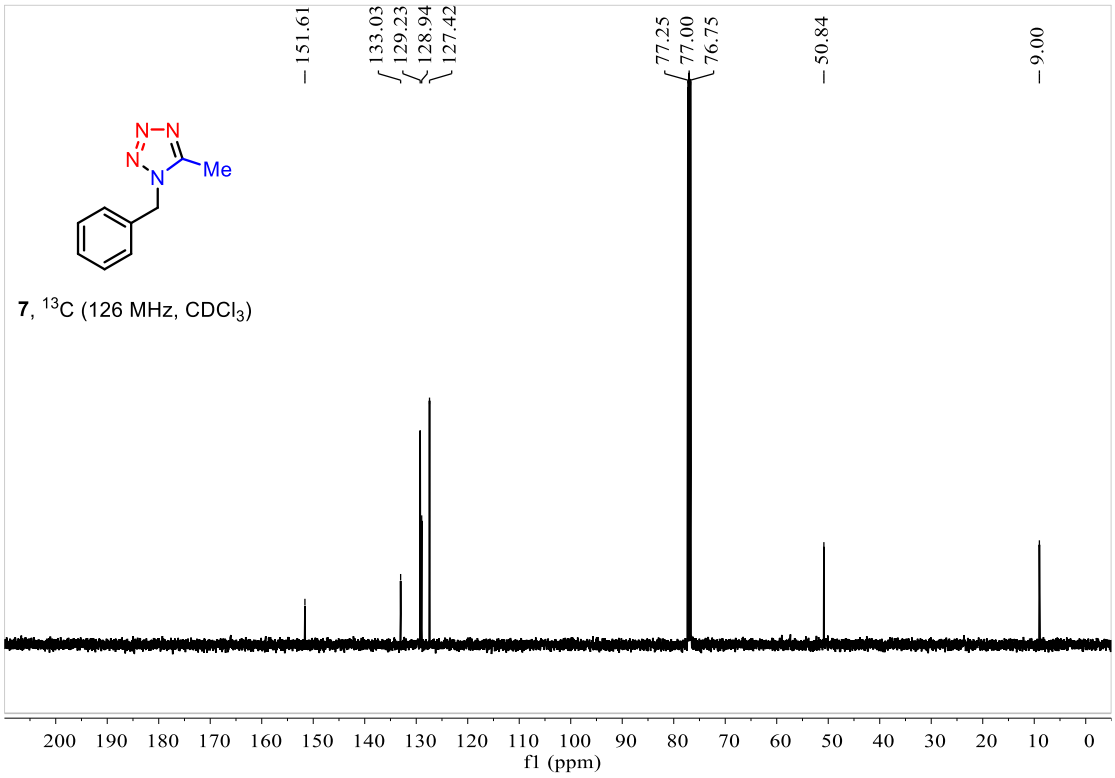
6, ^{1}H (500 MHz, $CDCl_3$)



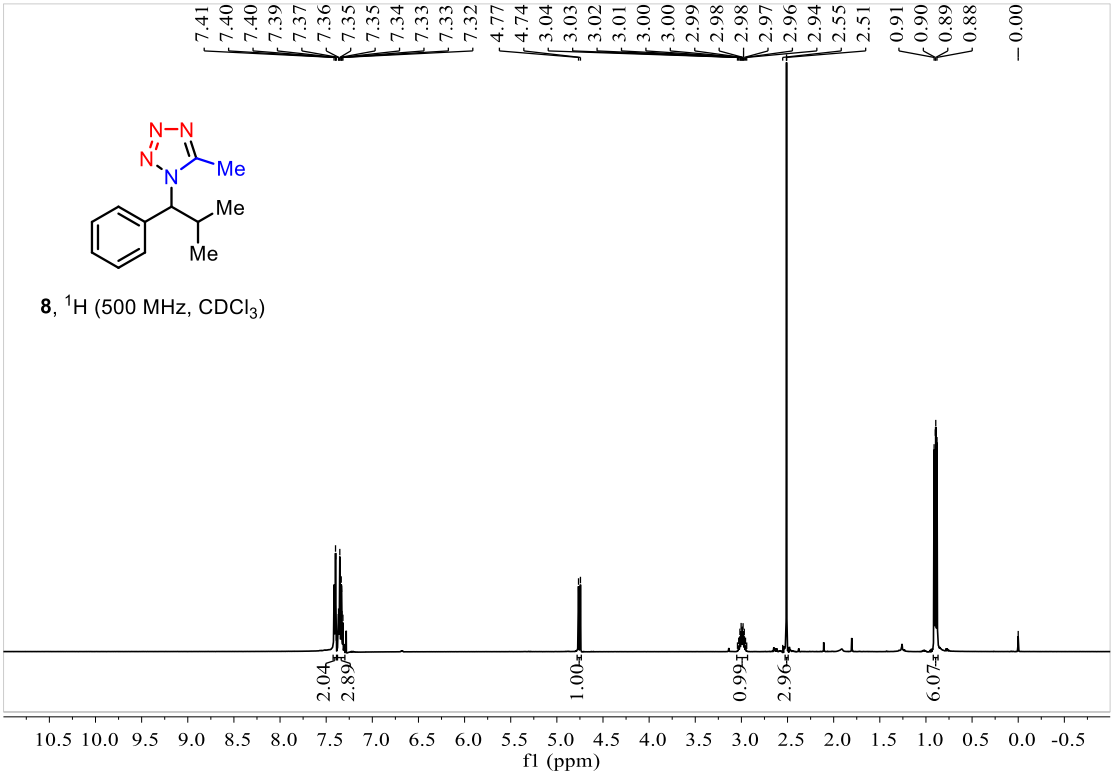
6, ^{13}C (126 MHz, $CDCl_3$)



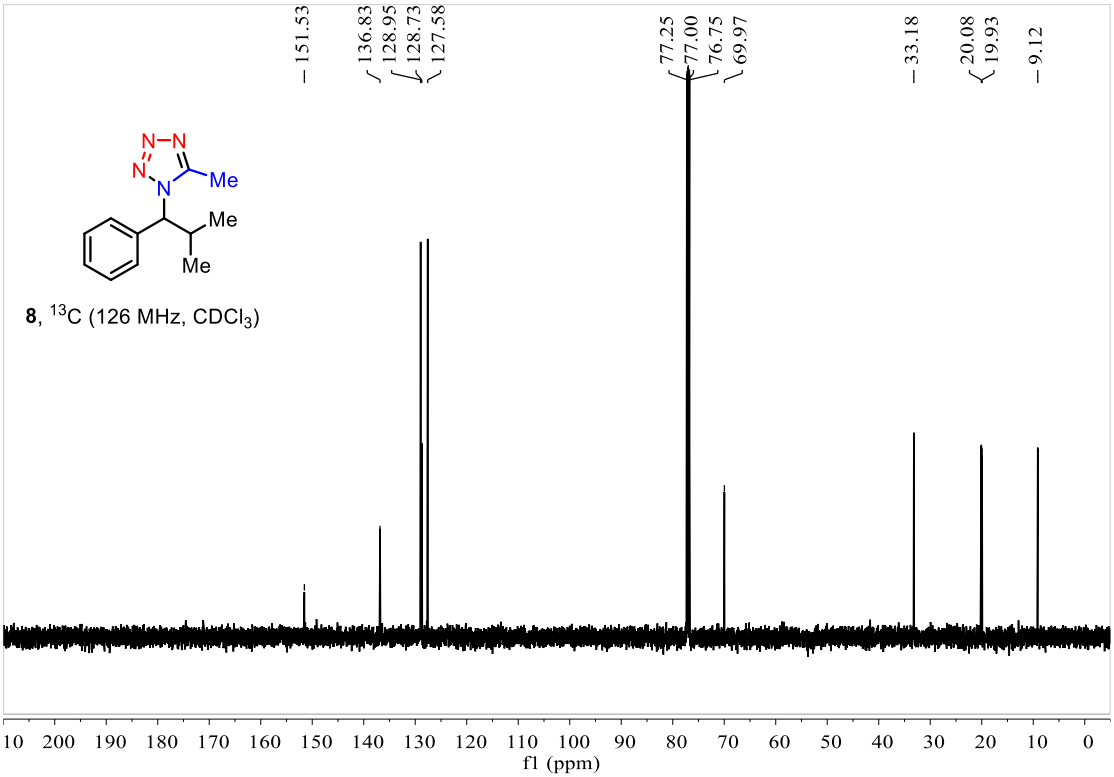
7, ^{1}H (500 MHz, $CDCl_3$)



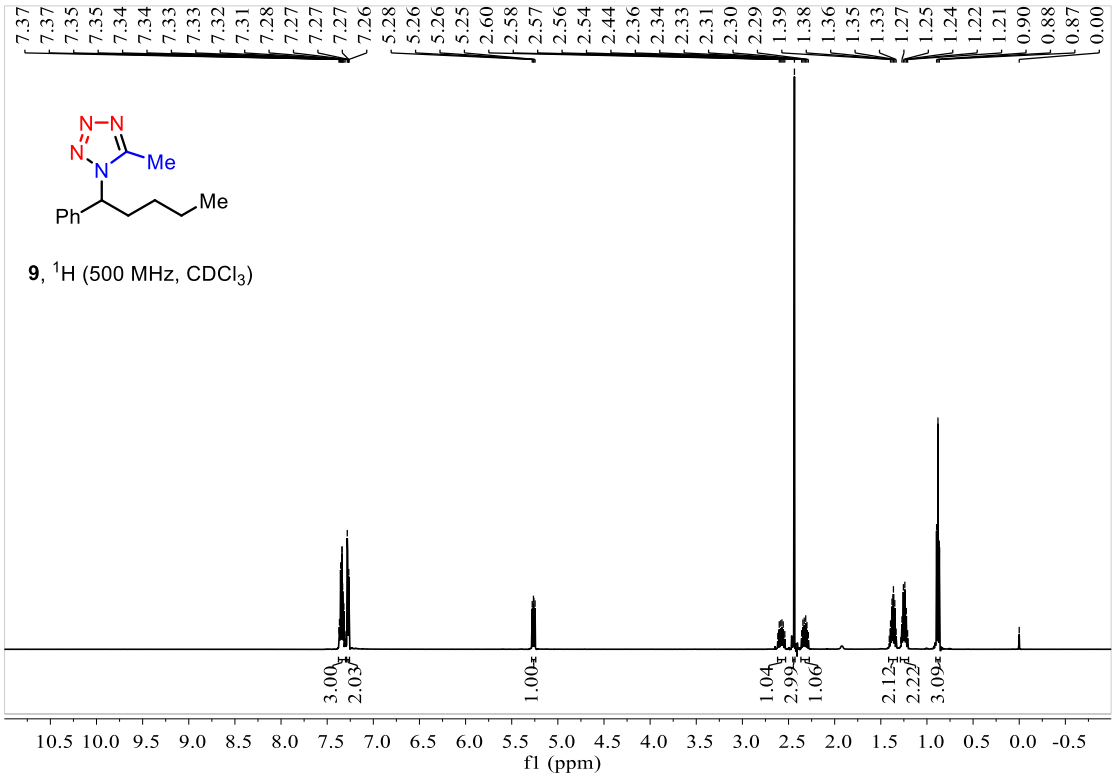
7, ^{13}C (126 MHz, $CDCl_3$)

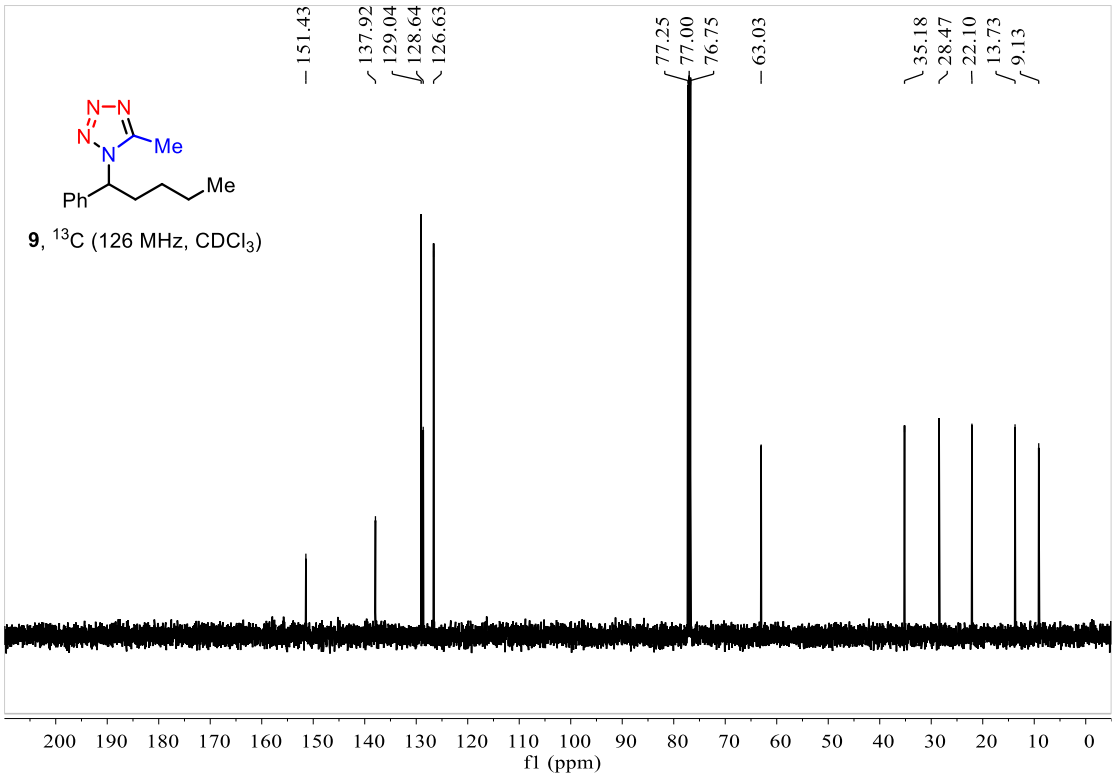


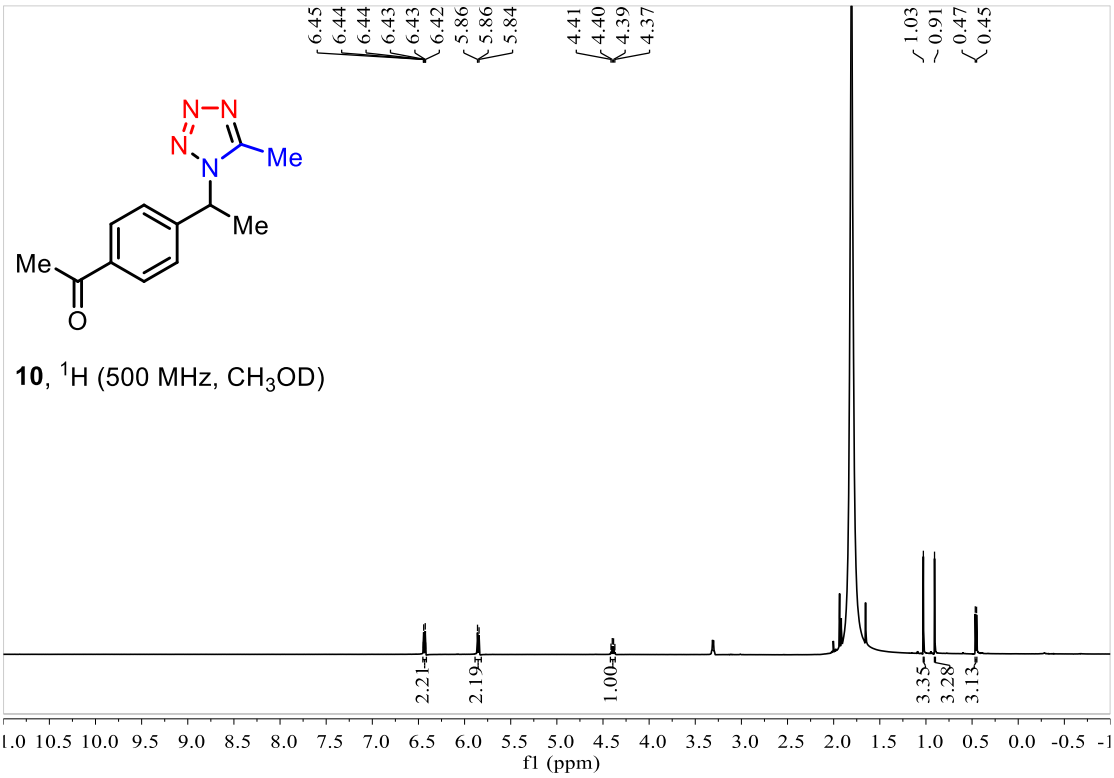
8, ^{1}H (500 MHz, $CDCl_3$)



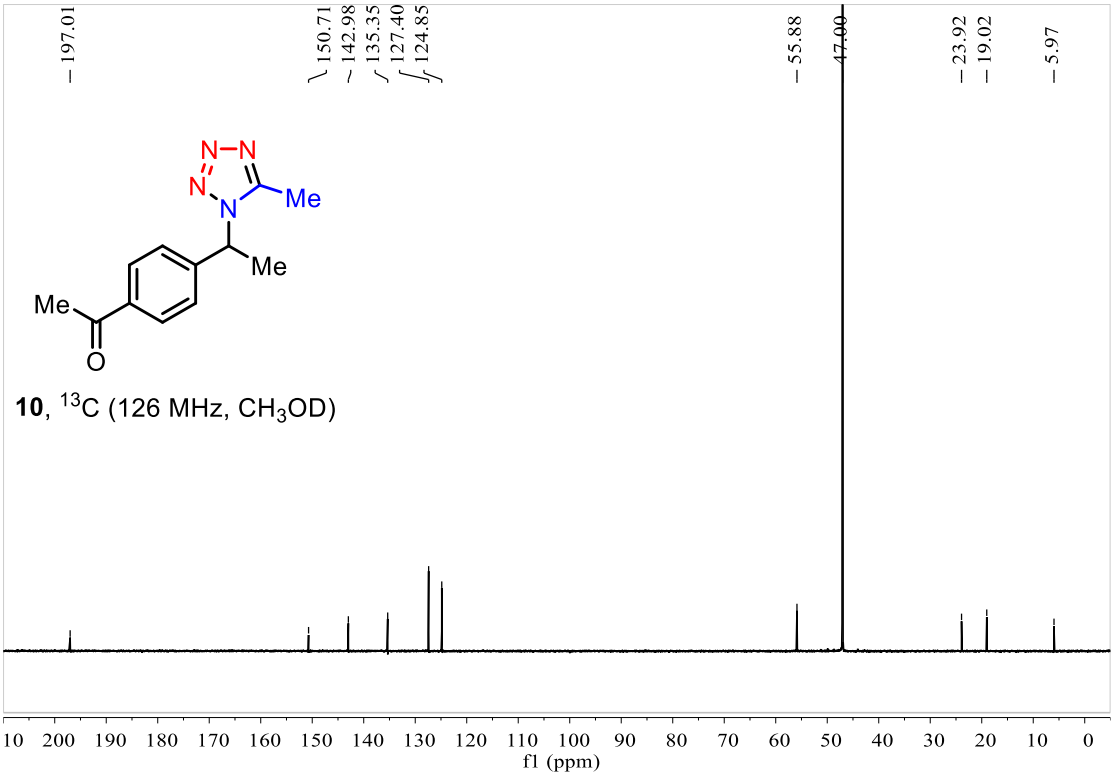
8, ^{13}C (126 MHz, $CDCl_3$)


7.37 7.37 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.28 7.27 7.27 7.27 7.26 5.28 5.26 5.26 5.25 2.60 2.58 2.57 2.56 2.54 2.44 2.36 2.34 2.33 2.31 2.30 2.29 1.39 1.38 1.36 1.35 1.33 1.27 1.25 1.24 1.22 1.21 0.90 0.88 0.87 0.00
N–N
N
N
Me
Ph
Me
9, 1H (500 MHz, CDCl3)
3.00 2.03 1.00 1.04 2.99 1.06 2.12 2.22 3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

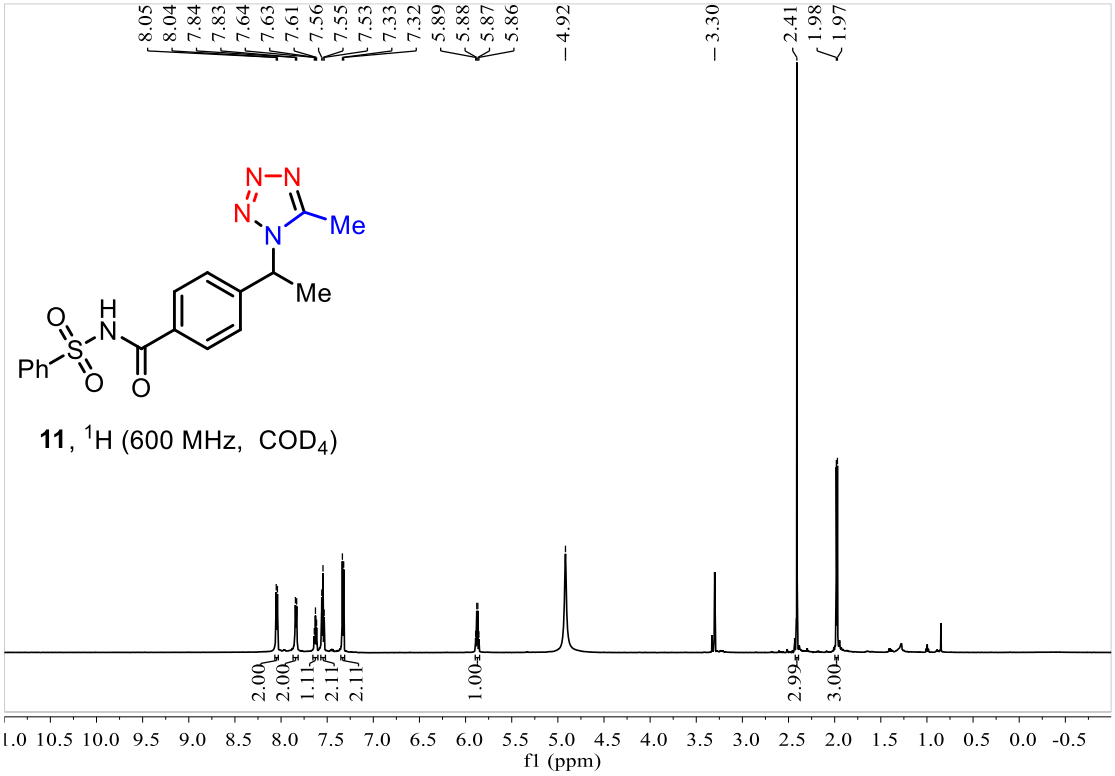

151.43 137.92 129.04 128.64 126.63 77.25 77.00 76.75 63.03 35.18 28.47 22.10 13.73 9.13
N–N
N
N
Me
Ph
Me
9, 13C (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

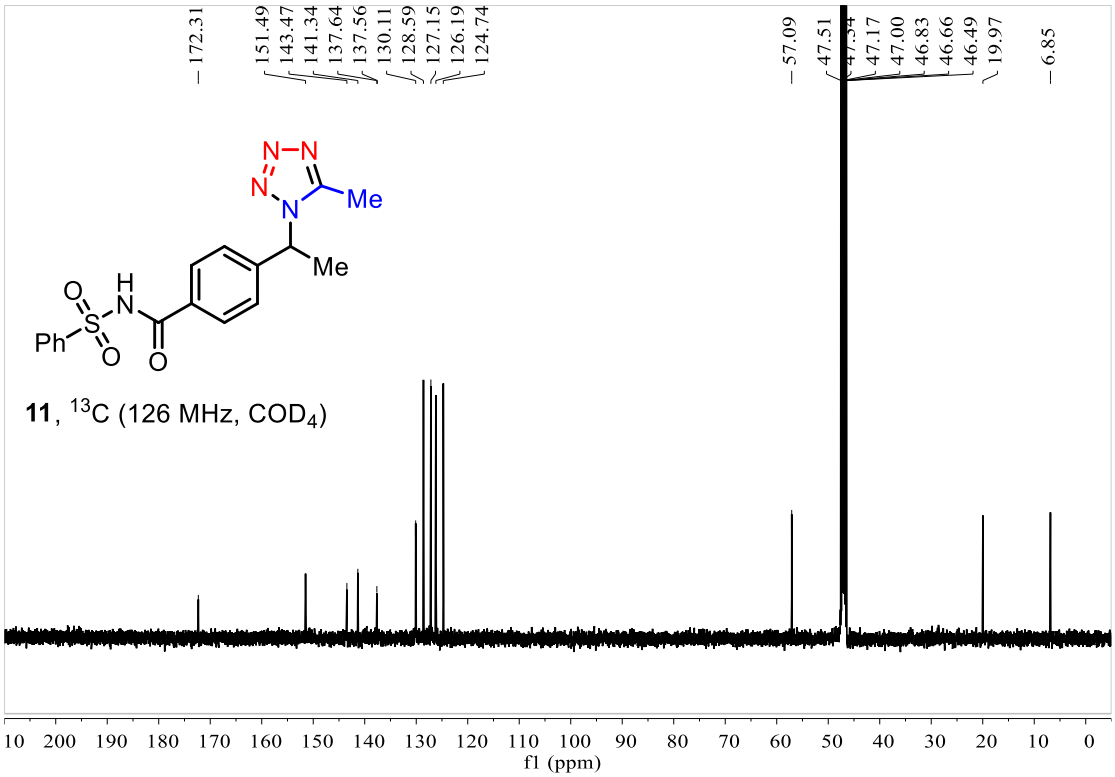


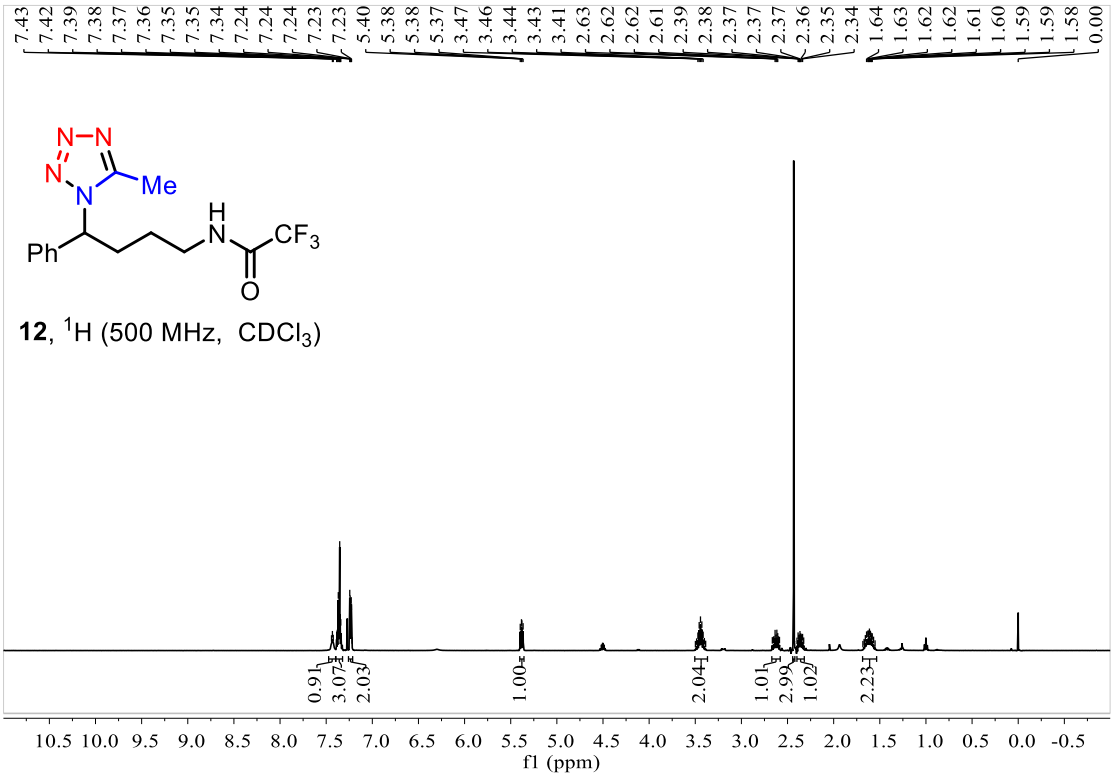
10, ^{1}H (500 MHz, CH_3OD)



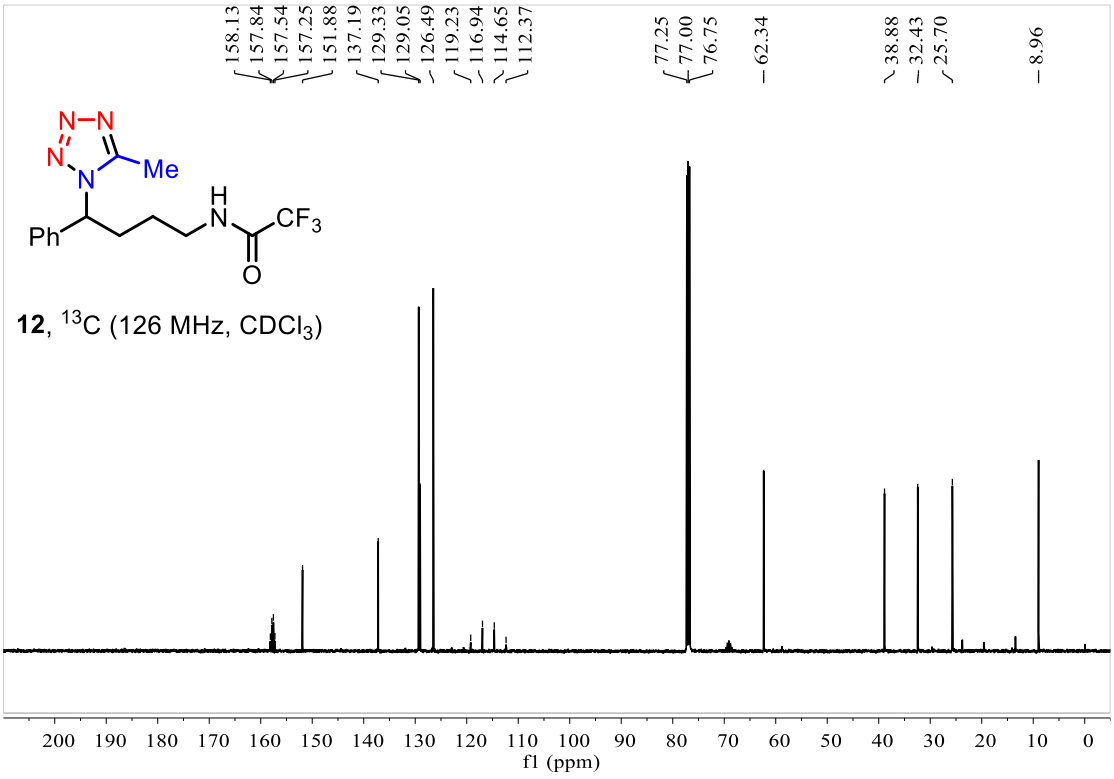
10, ^{13}C (126 MHz, CH_3OD)


8.05
8.04
7.84
7.83
7.64
7.63
7.61
7.56
7.55
7.53
7.33
7.32
5.89
5.88
5.87
5.86
4.92
3.30
2.41
1.98
1.97
N–N
N
N
Me
Me
H
N
O
S
O
Ph
O
O
11, 1H (600 MHz, COD4)
2.00
2.00
1.11
2.11
2.11
1.00
2.99
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

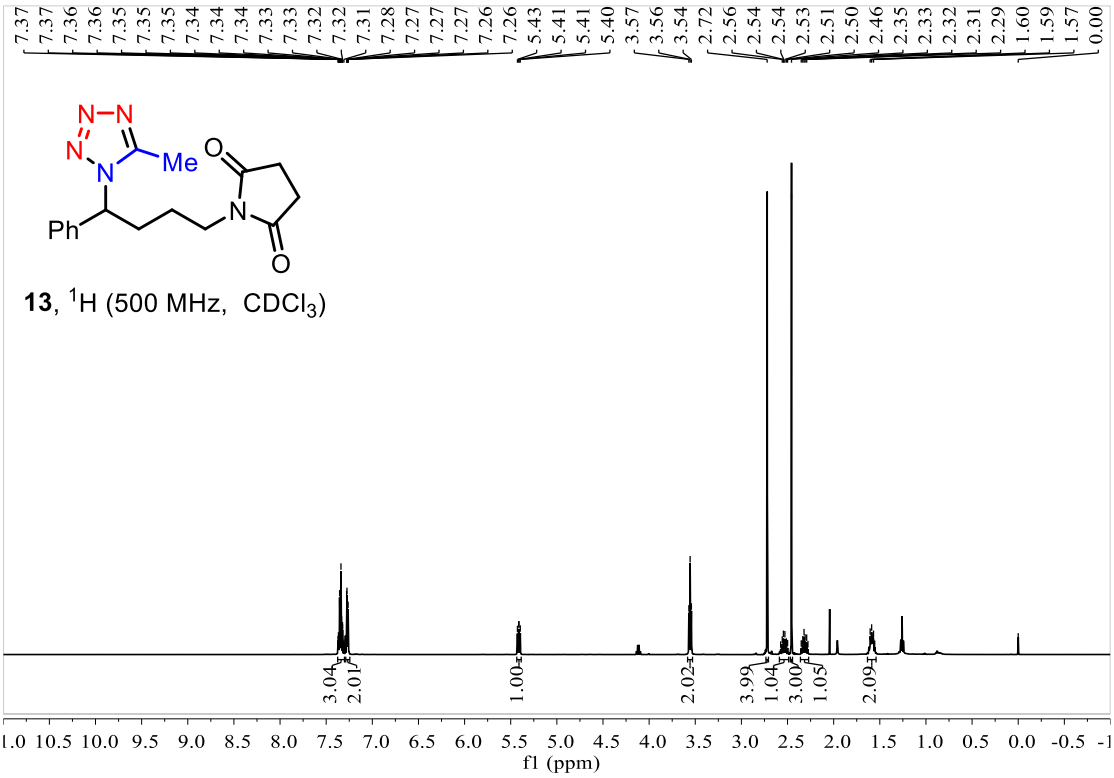

172.31
151.49
143.47
141.34
137.64
137.56
130.11
128.59
127.15
126.19
124.74
57.09
47.51
47.34
47.17
47.00
46.83
46.66
46.49
19.97
6.85
N–N
N
N
Me
Me
H
N
O
S
O
Ph
O
O
11, 13C (126 MHz, COD4)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



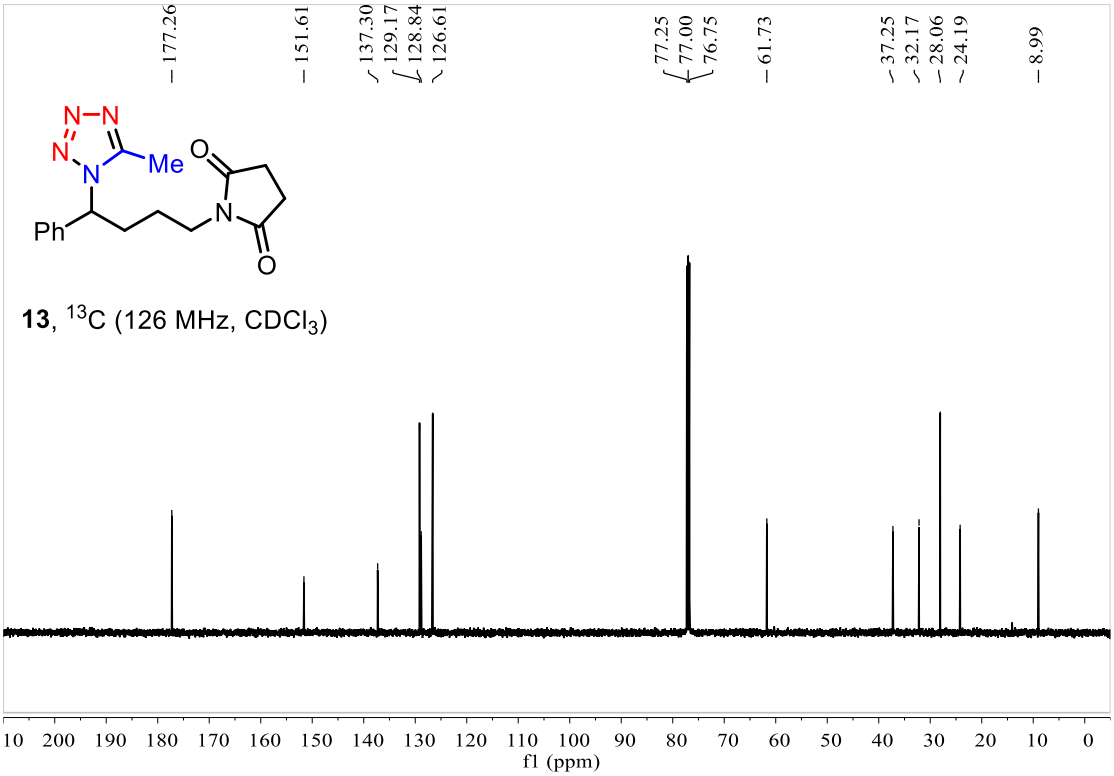
12, ^{1}H (500 MHz, $CDCl_3$)



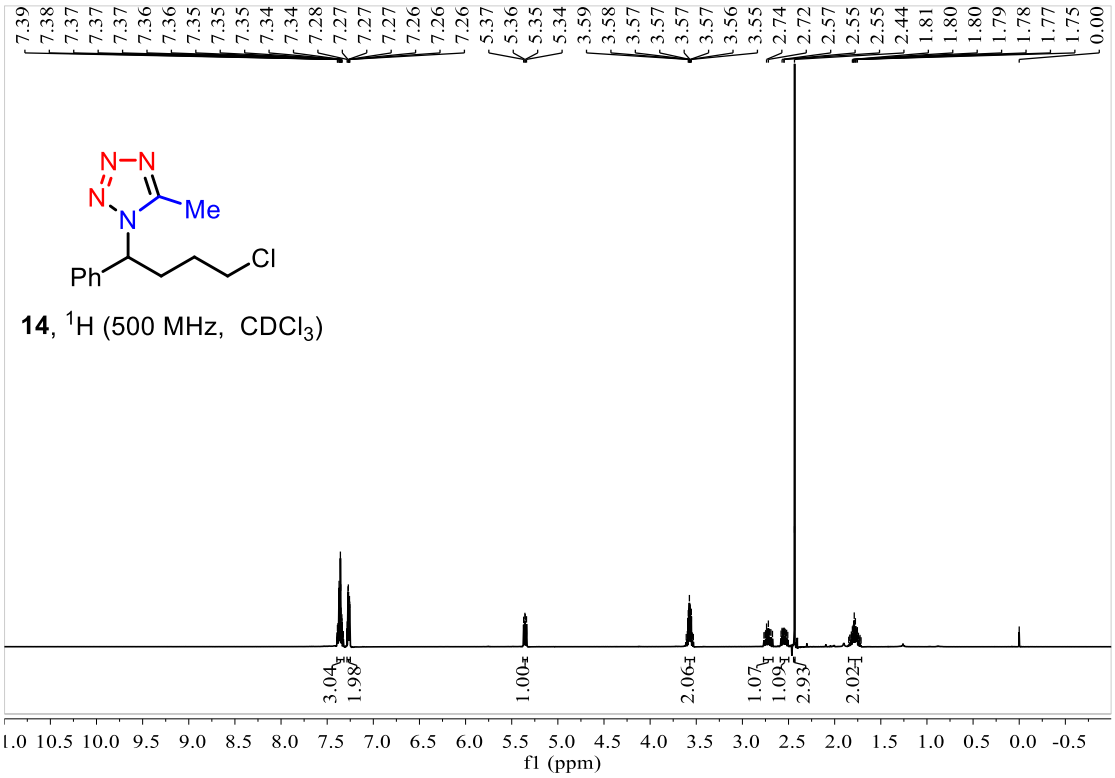
12, ^{13}C (126 MHz, $CDCl_3$)

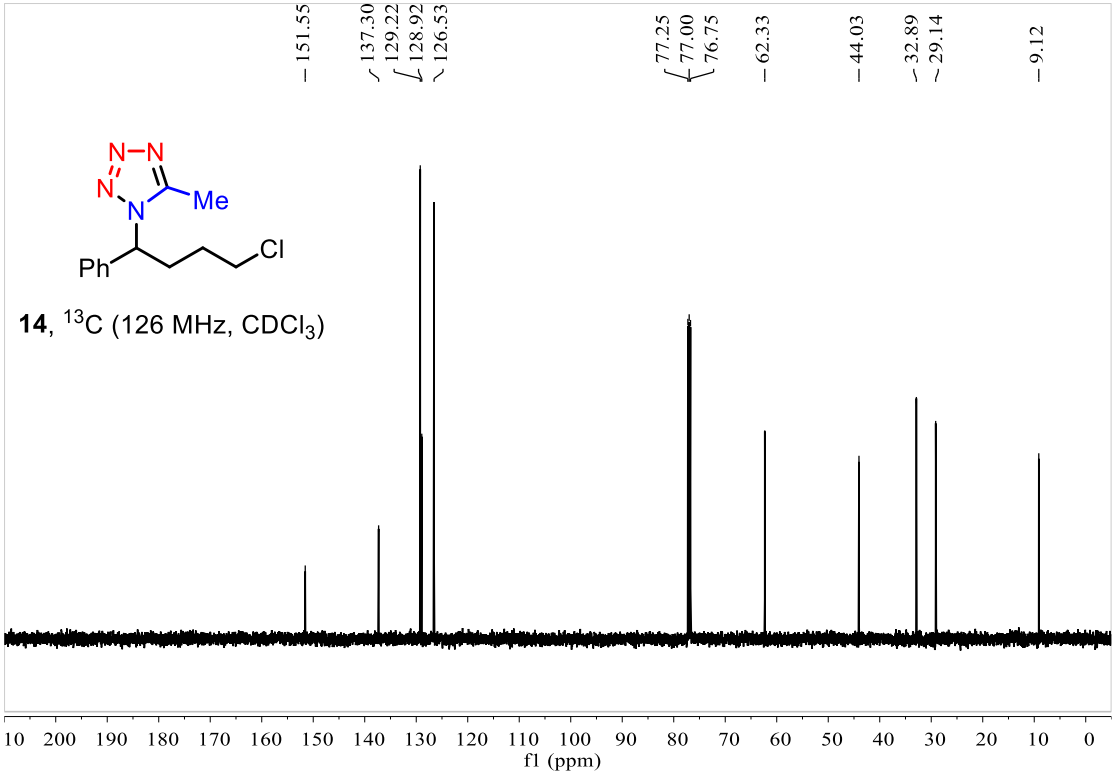


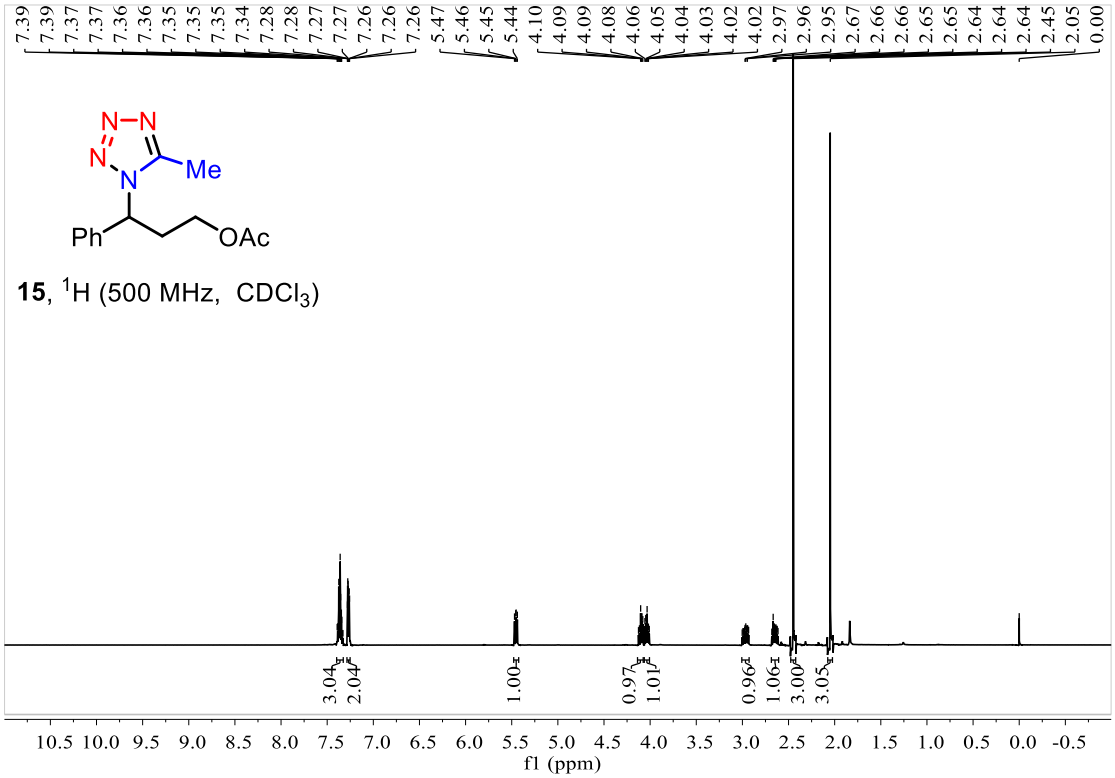
13, ^{1}H (500 MHz, $CDCl_3$)



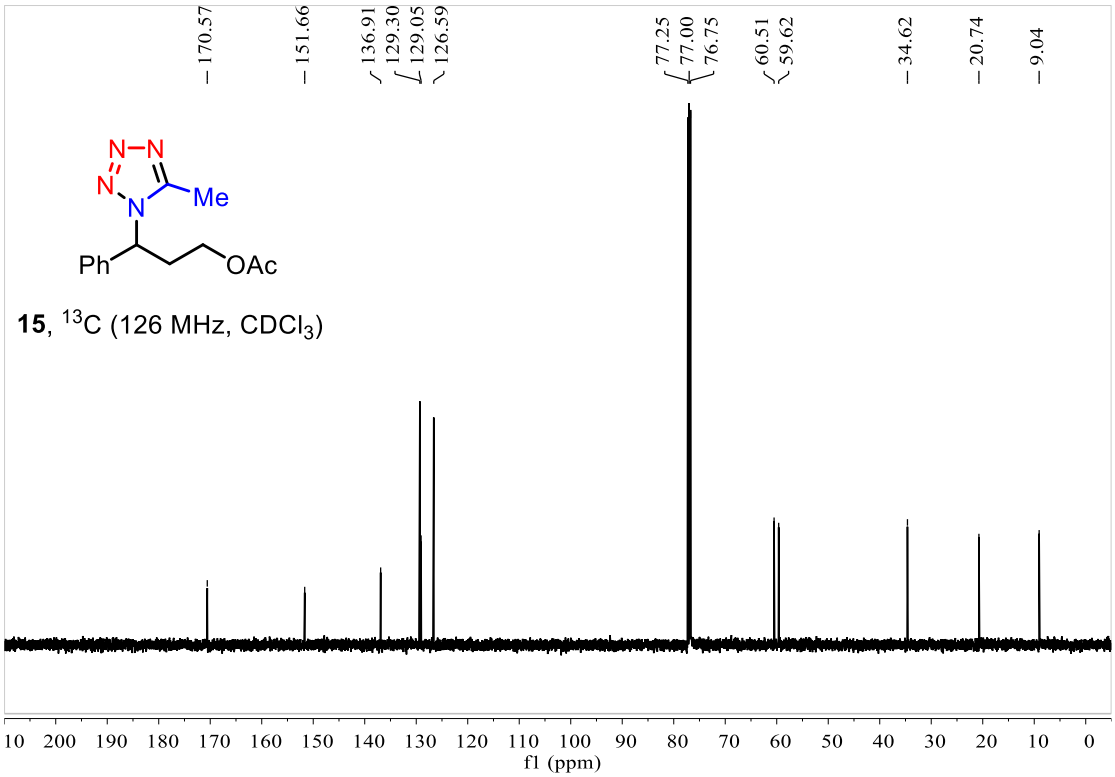
13, ^{13}C (126 MHz, $CDCl_3$)


7.39 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.28 7.27 7.27 7.27 7.26 7.26 7.26
5.37 5.36 5.35 5.34
3.59 3.58 3.57 3.57 3.57 3.57 3.56 3.55
2.74 2.72 2.57 2.55 2.55 2.44
1.81 1.80 1.80 1.79 1.78 1.77 1.75
0.00
N–N
N
N
Me
Ph
Cl
14, 1H (500 MHz, CDCl3)
3.04 1.98 1.00 2.06 1.07 1.09 2.93 2.02
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

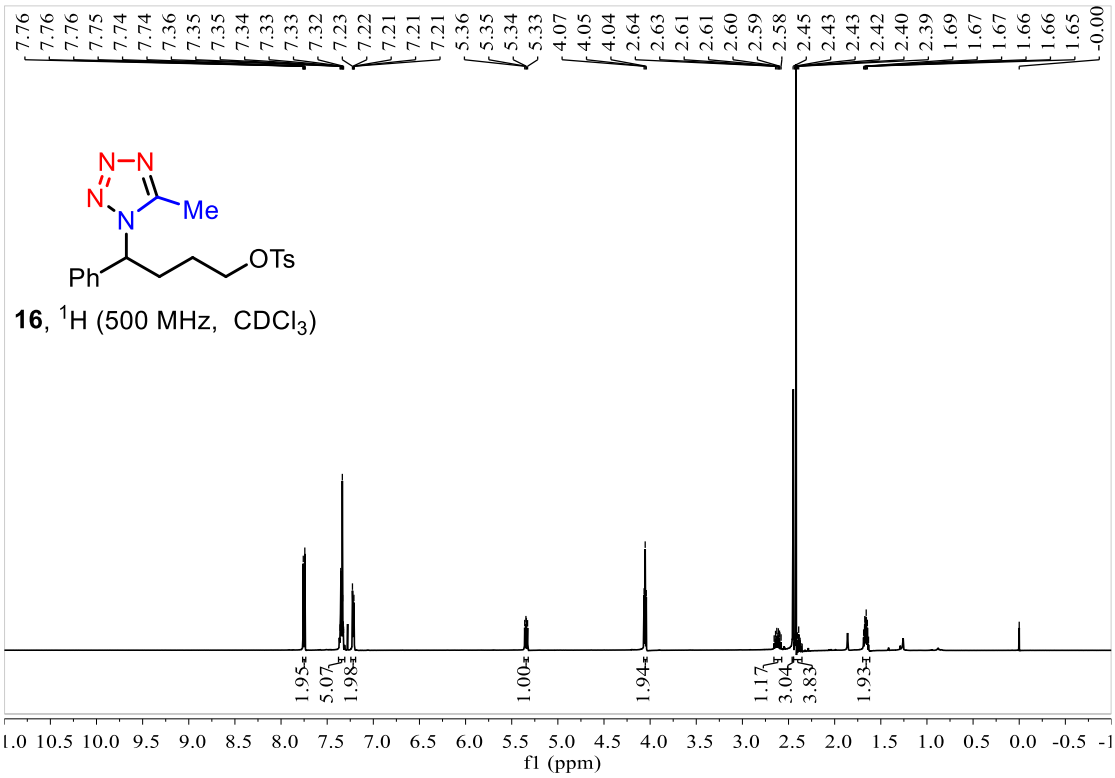

151.55
137.30
129.22
128.92
126.53
77.25
77.00
76.75
62.33
44.03
32.89
29.14
9.12
N–N
N
N
Me
Ph
Cl
14, 13C (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

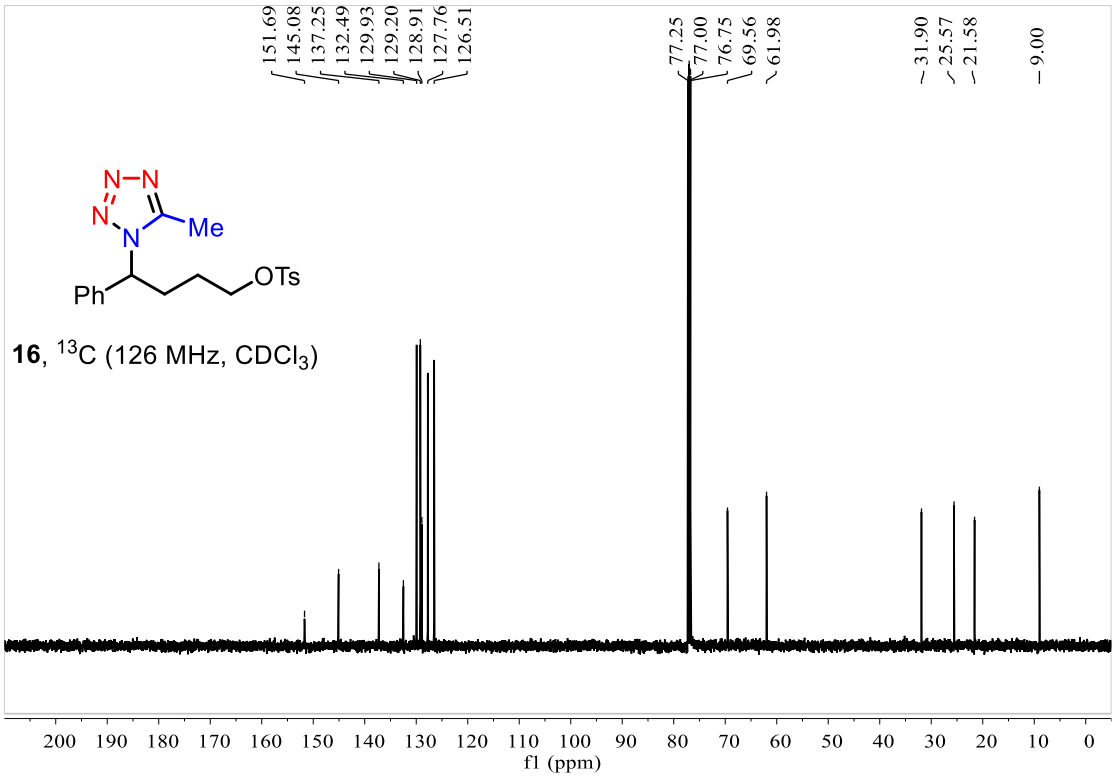


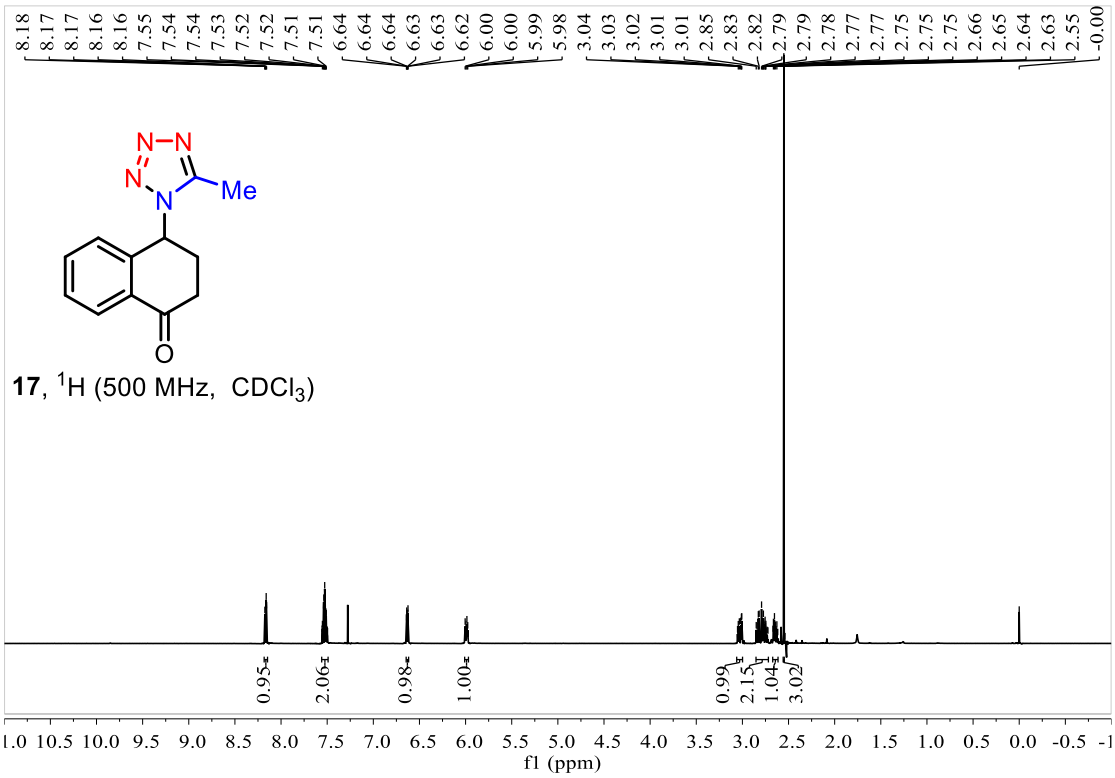
15, ^{1}H (500 MHz, $CDCl_3$)



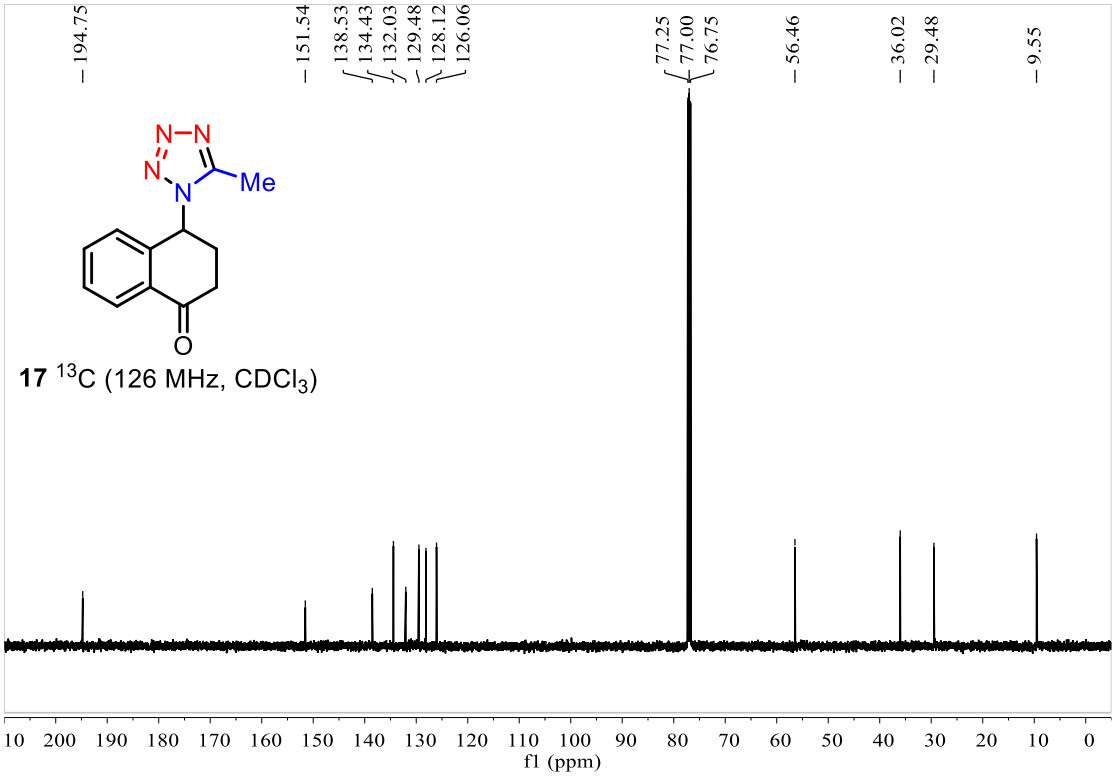
15, ^{13}C (126 MHz, $CDCl_3$)


7.76 7.76 7.76 7.75 7.74 7.74 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.23 7.22 7.21 7.21 7.21 5.36 5.35 5.34 5.33 4.07 4.05 4.04 2.64 2.63 2.61 2.61 2.60 2.59 2.58 2.45 2.43 2.43 2.42 2.40 2.39 1.69 1.67 1.67 1.66 1.66 1.65 -0.00
N–N
N
N
Me
Ph
OTs
16, 1H (500 MHz, CDCl3)
1.95 5.07 1.98 1.00 1.94 1.17 3.04 3.83 1.93
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

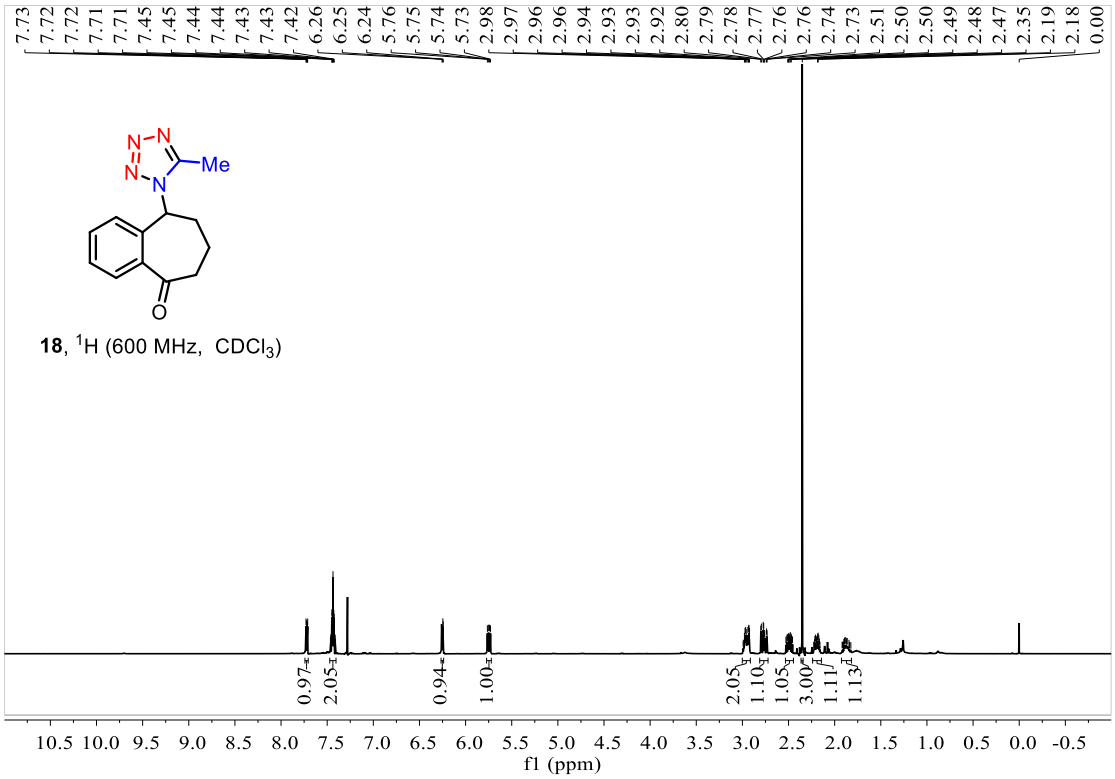

151.69 145.08 137.25 132.49 129.93 129.20 128.91 127.76 126.51
77.25 77.00 76.75 69.56 61.98
31.90 25.57 21.58 9.00
N–N
N
N
Me
Ph
OTs
16, 13C (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



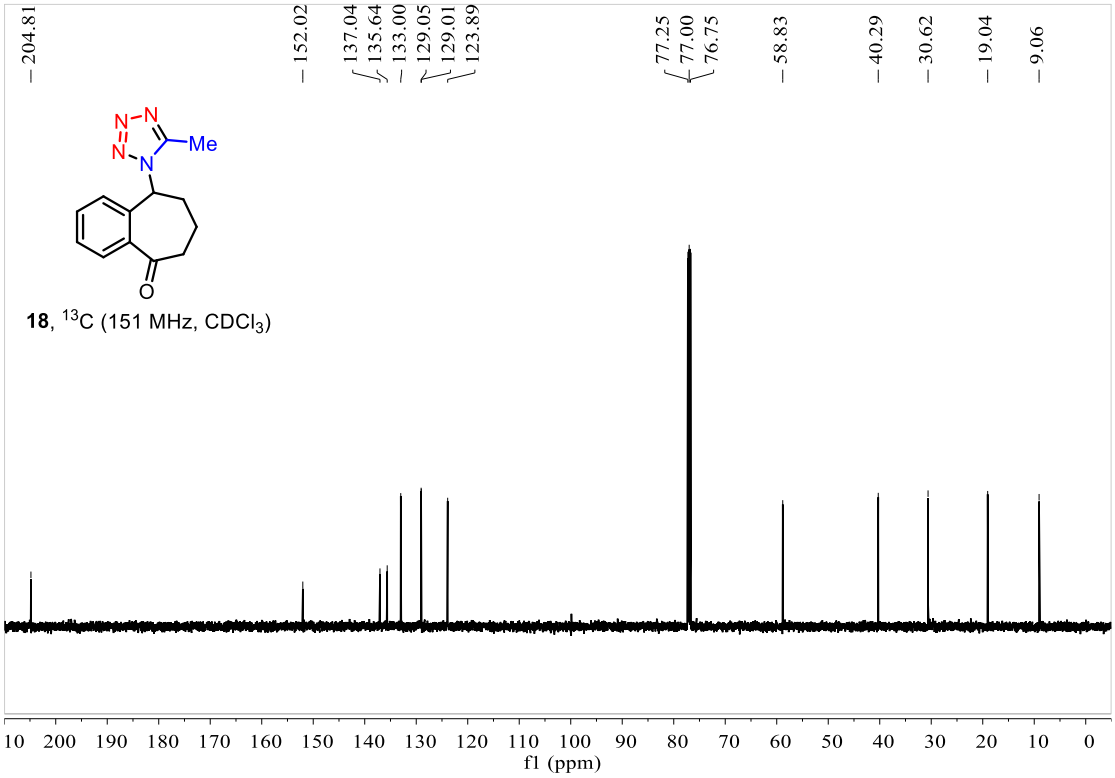
17, ^{1}H (500 MHz, $CDCl_3$)



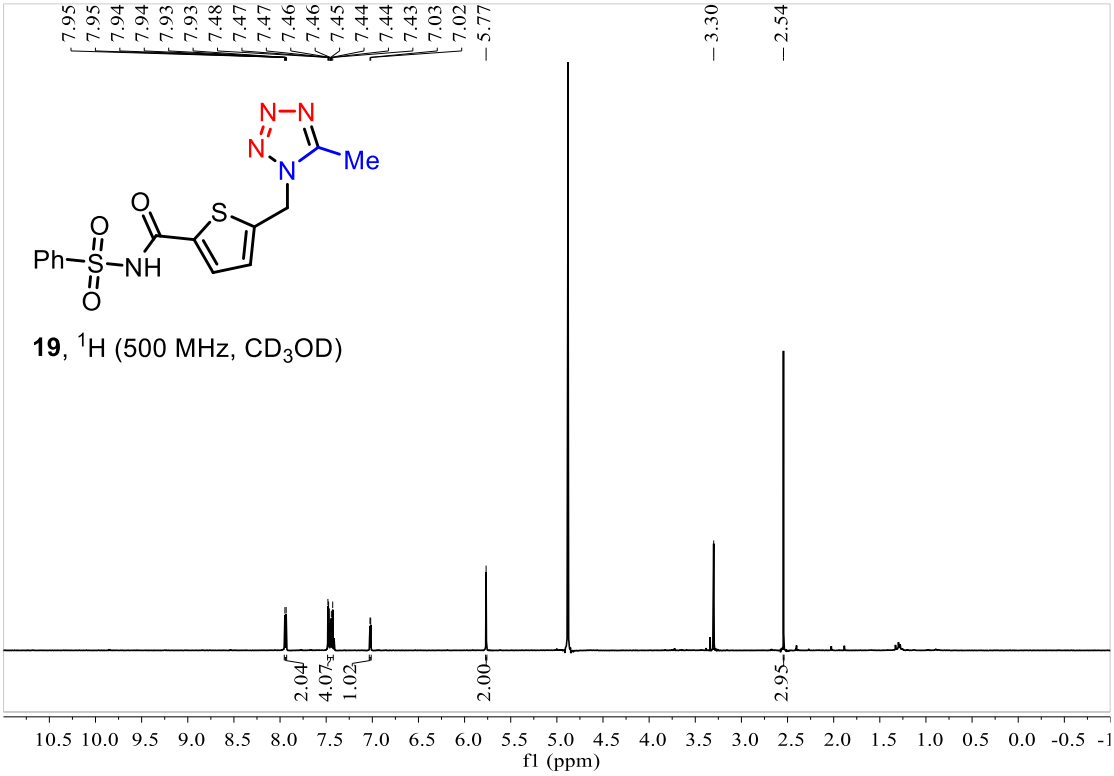
17 ^{13}C (126 MHz, $CDCl_3$)



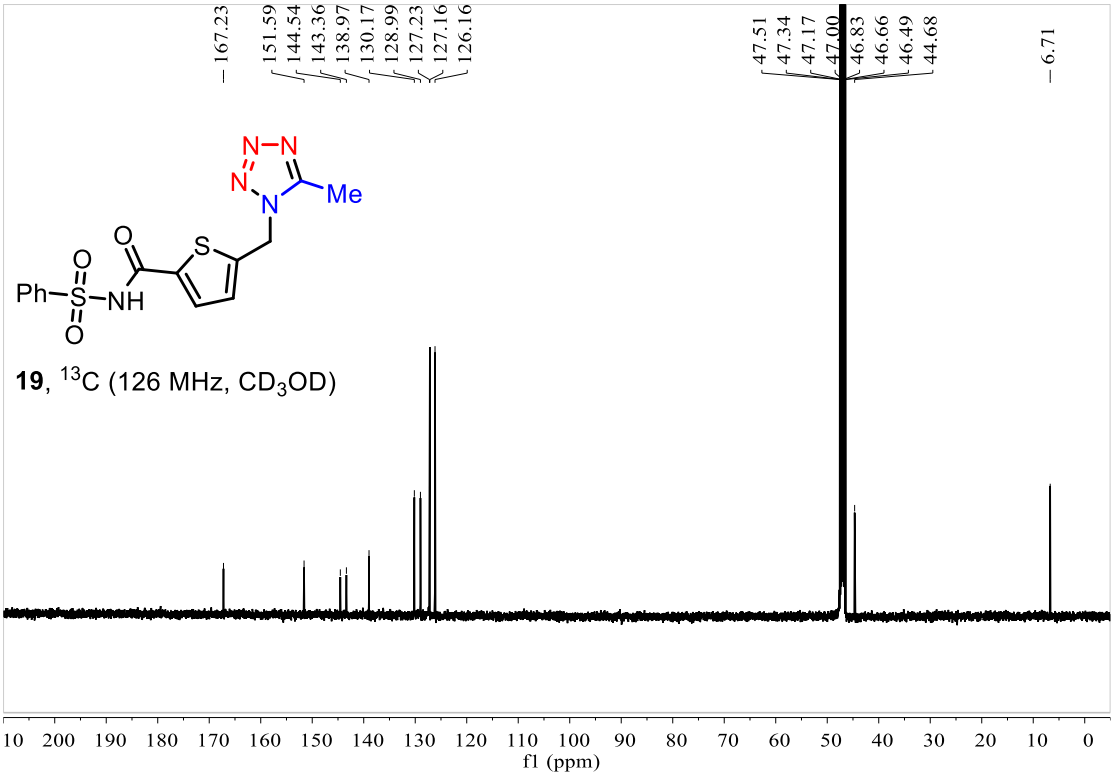
18, ^{1}H (600 MHz, $CDCl_3$)



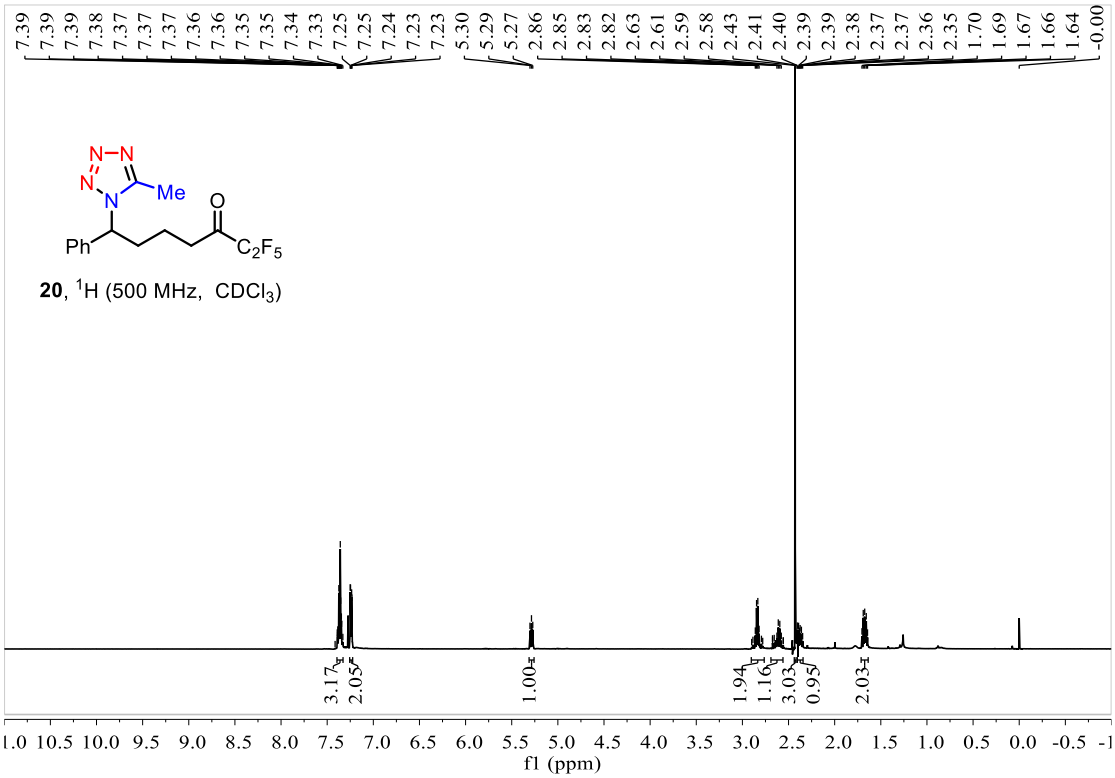
18, ^{13}C (151 MHz, $CDCl_3$)



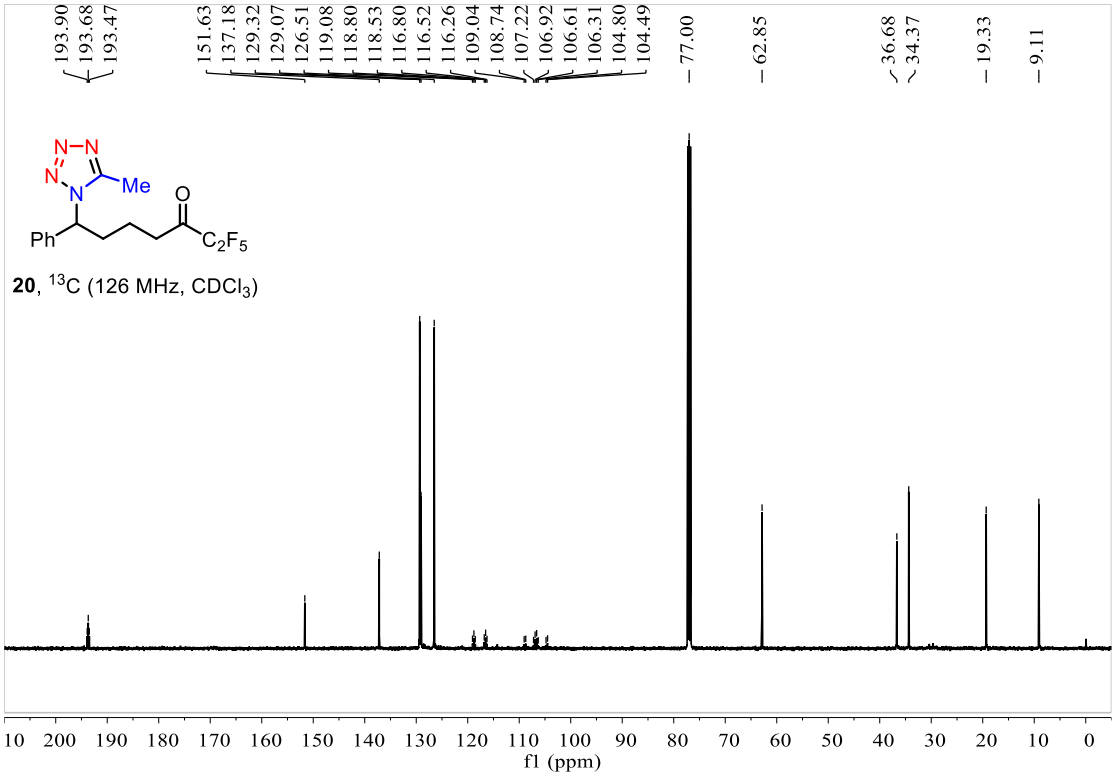
19, ^{1}H (500 MHz, CD_3OD)



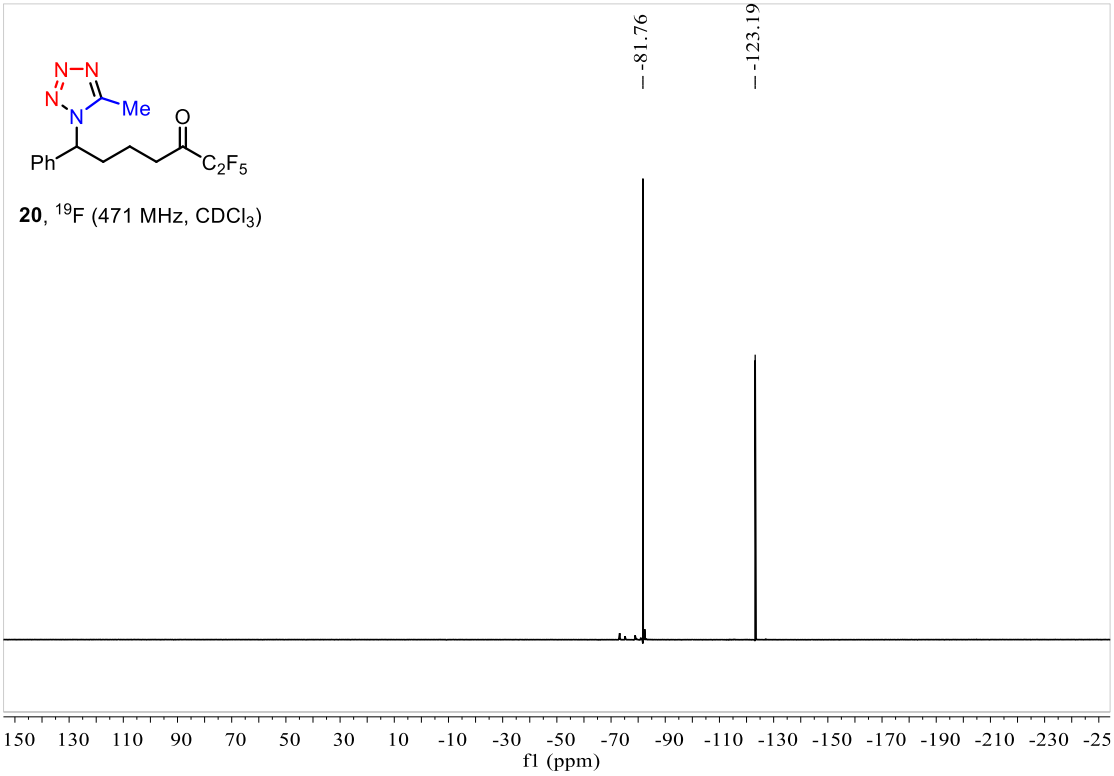
19, ^{13}C (126 MHz, CD_3OD)



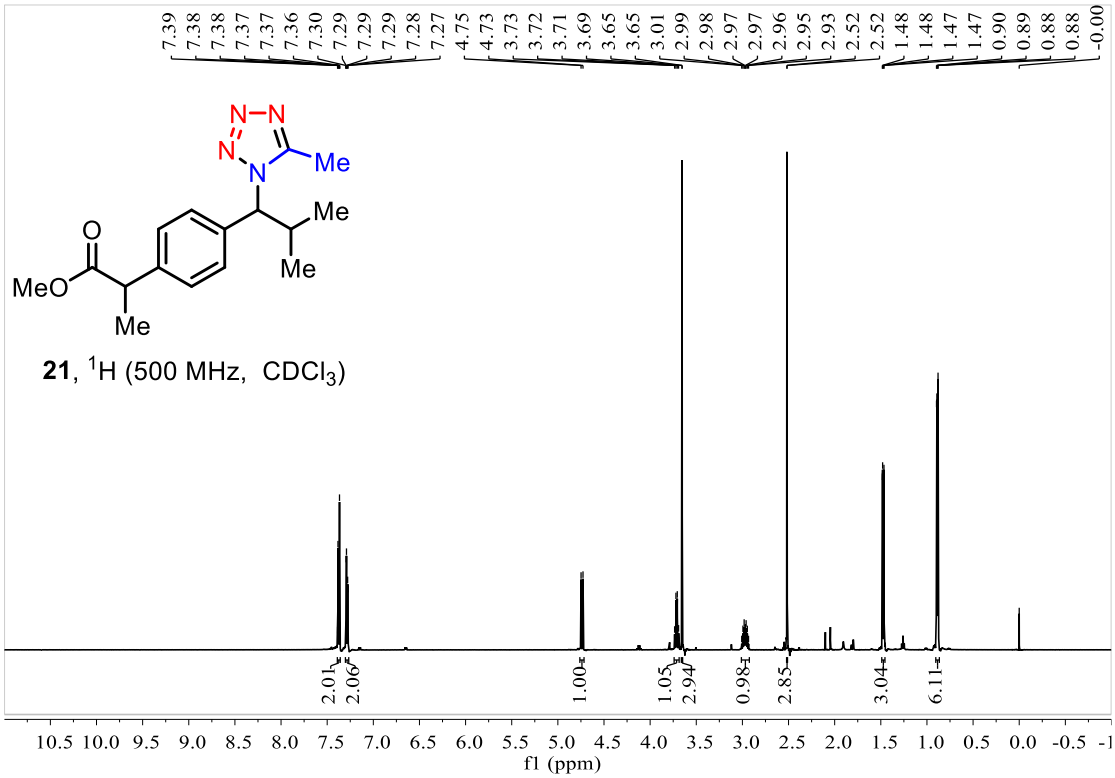
20, ^{1}H (500 MHz, $CDCl_3$)



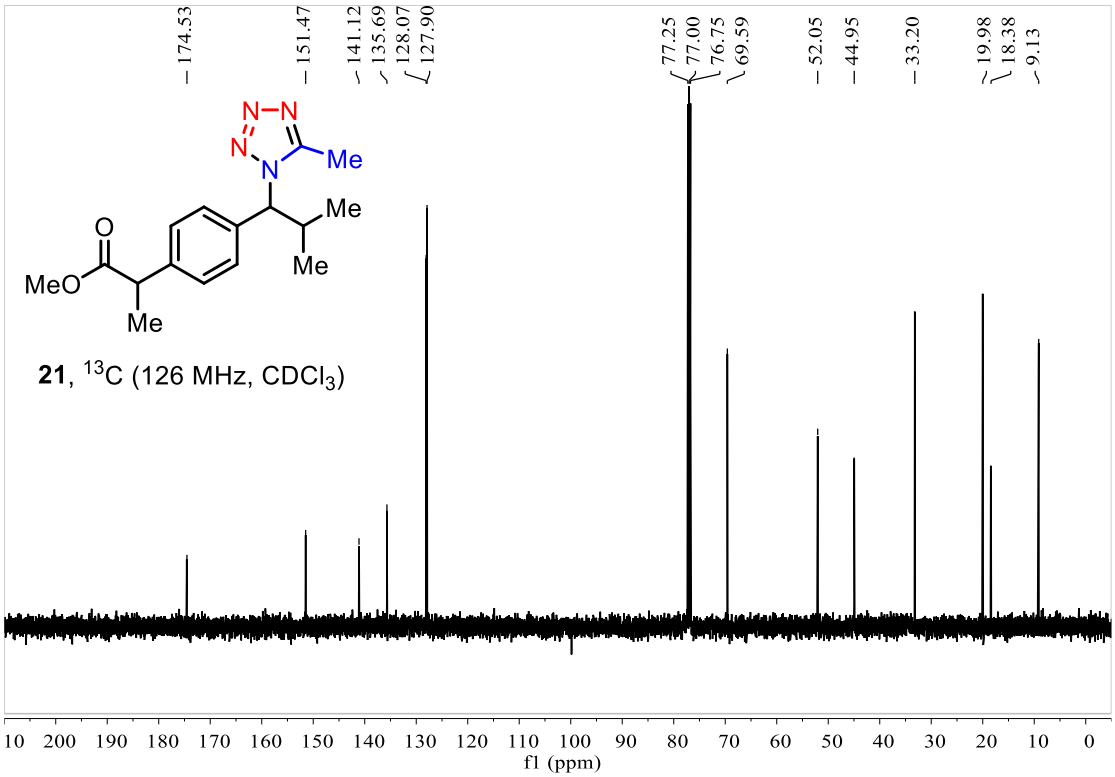
20, ^{13}C (126 MHz, $CDCl_3$)



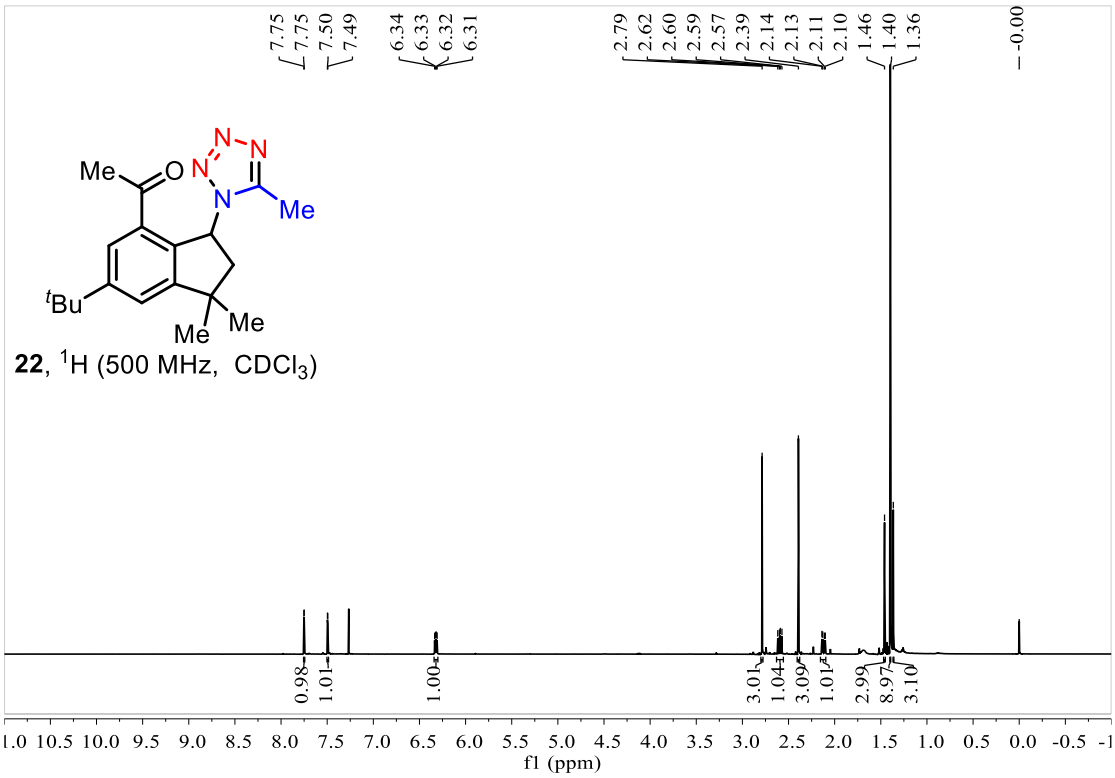
20, ^{19}F (471 MHz, $CDCl_3$)



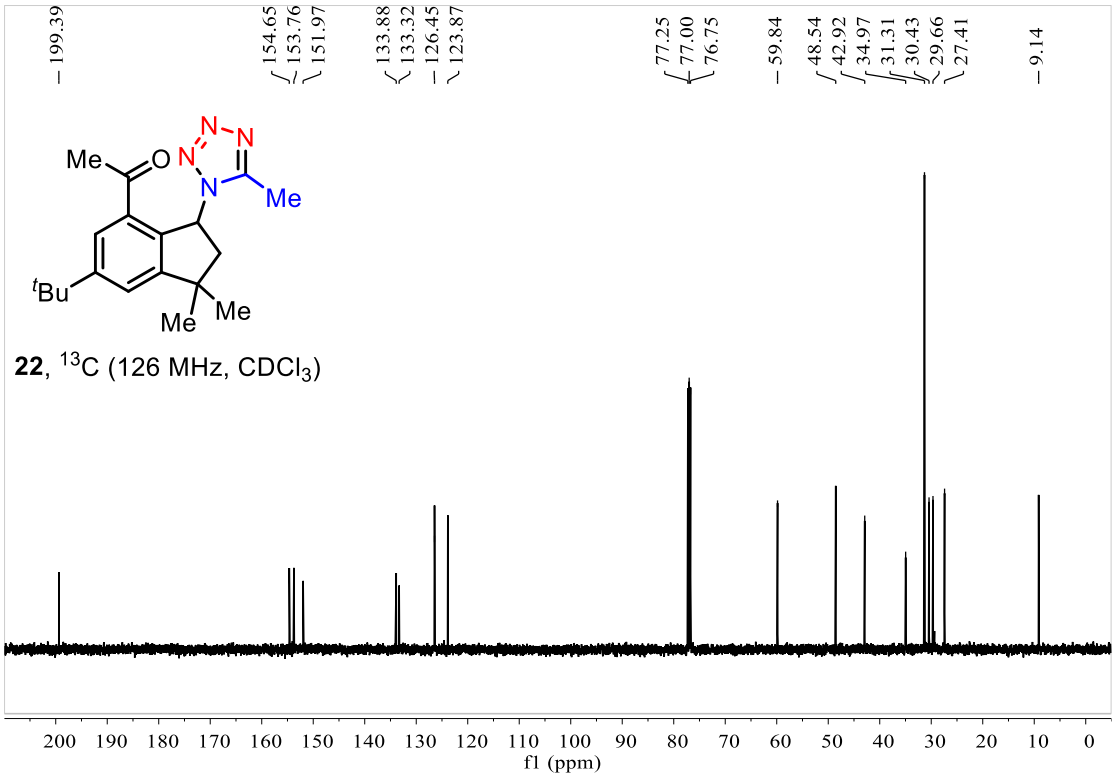
21, ^{1}H (500 MHz, $CDCl_3$)



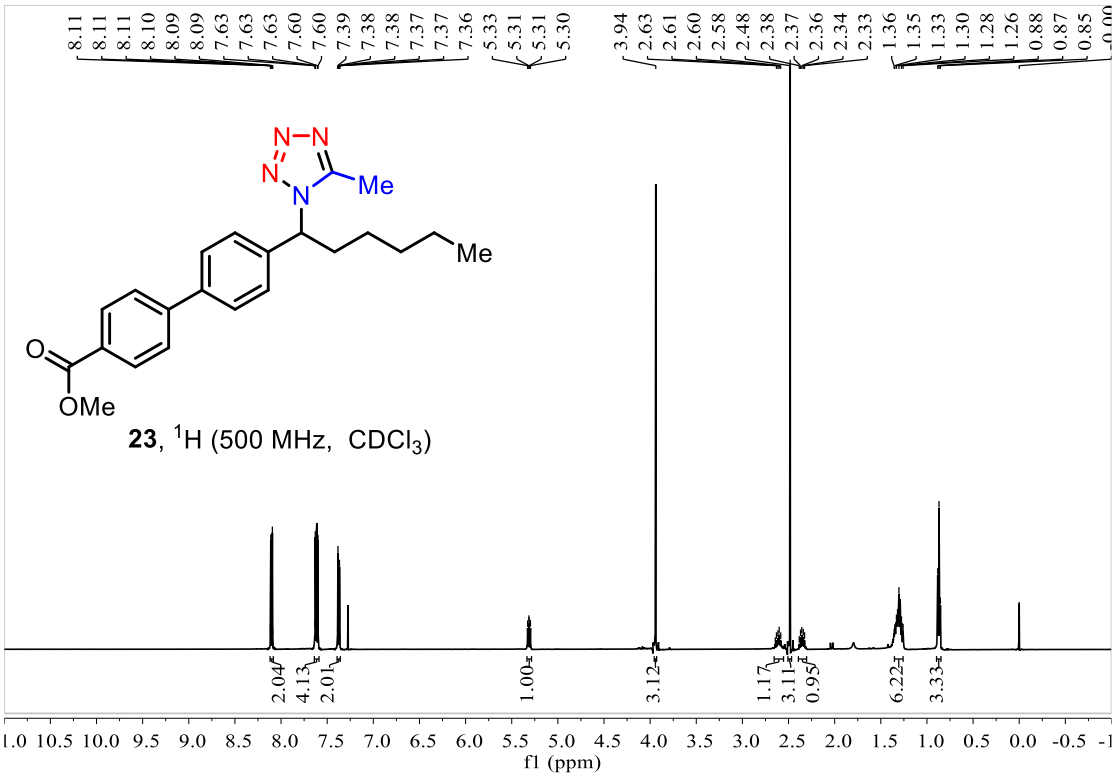
21, ^{13}C (126 MHz, $CDCl_3$)

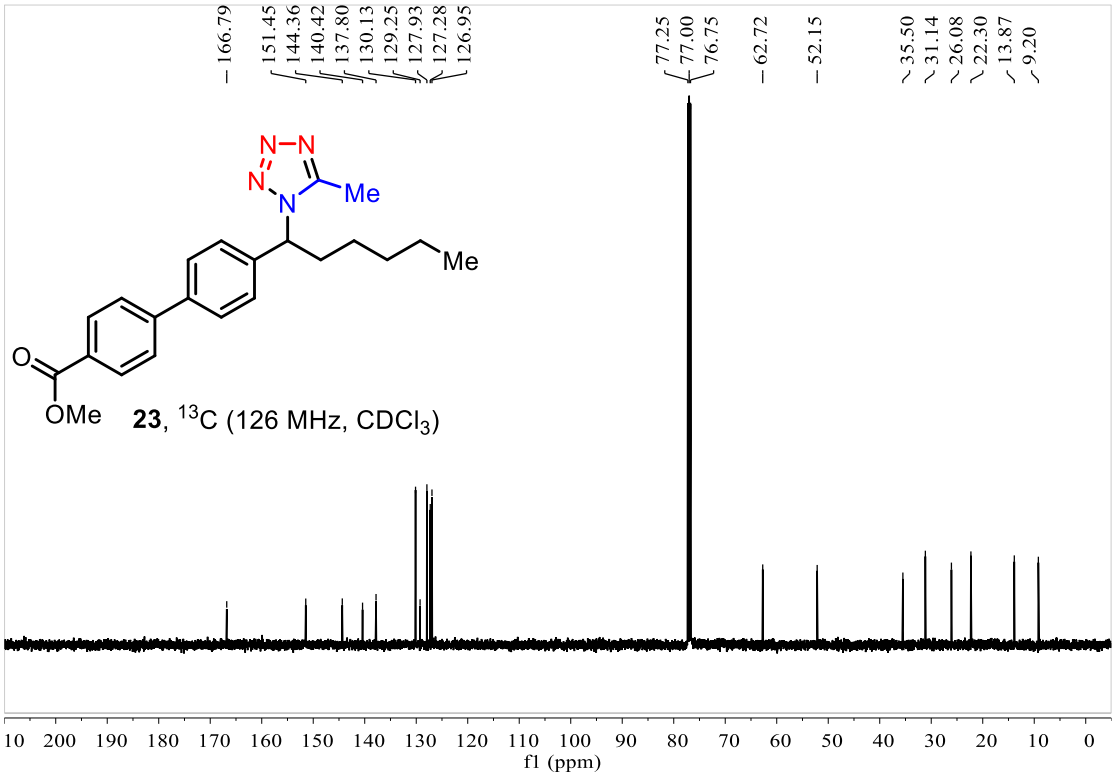


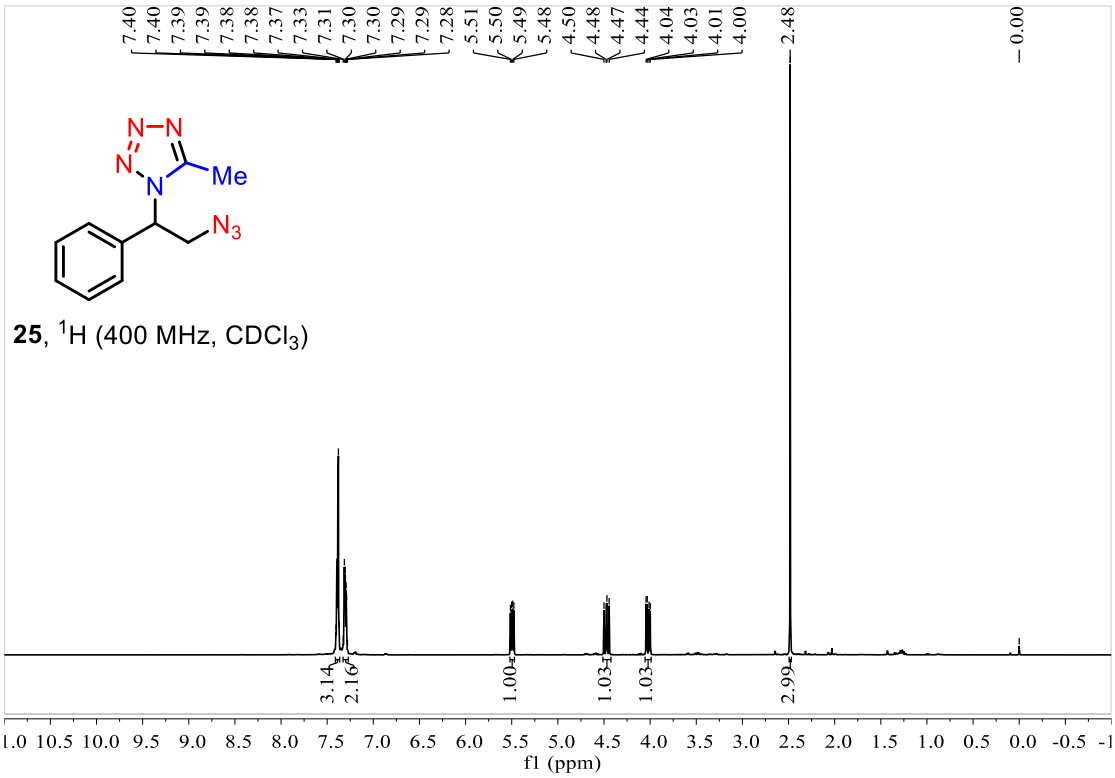
22, ^{1}H (500 MHz, $CDCl_3$)



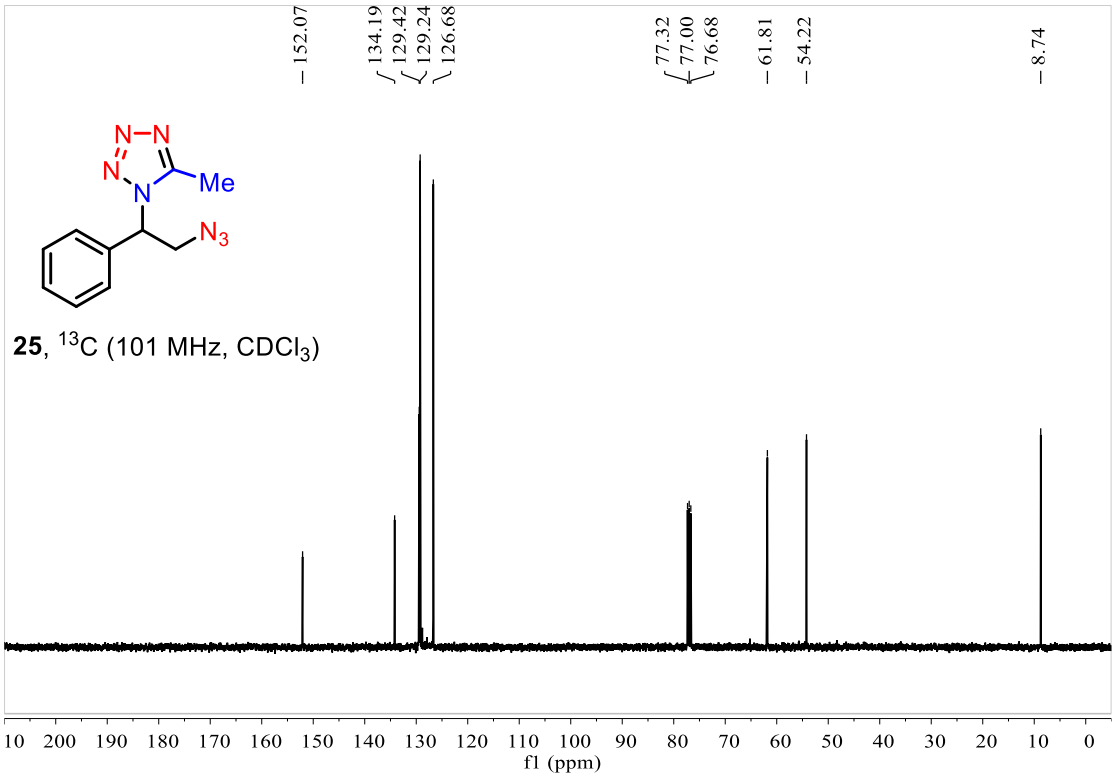
22, ^{13}C (126 MHz, $CDCl_3$)


8.11 8.11 8.11 8.10 8.09 8.09 7.63 7.63 7.60 7.60 7.39 7.38 7.38 7.37 7.37 7.36 5.33 5.31 5.31 5.30 3.94 2.63 2.61 2.60 2.58 2.48 2.38 2.37 2.36 2.34 2.33 1.36 1.35 1.33 1.30 1.28 1.26 0.88 0.87 0.85 0.00
N–N
N
N
Me
Me
O
OMe
23, 1H (500 MHz, CDCl3)
2.04 4.13 2.01 1.00 3.12 1.17 3.11 0.95 6.22 3.33
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

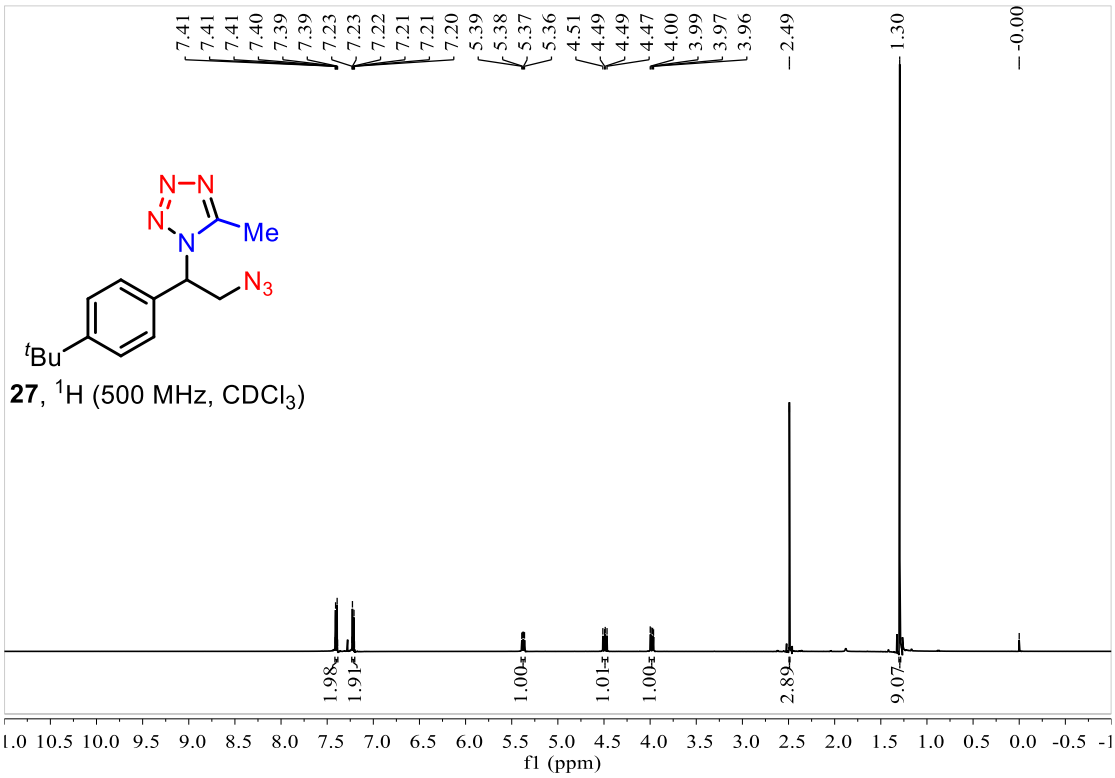

166.79 151.45 144.36 140.42 137.80 130.13 129.25 127.93 127.28 126.95
77.25 77.00 76.75 62.72 52.15 35.50 31.14 26.08 22.30 13.87 9.20
N–N
N
N
Me
Me
O
OMe
23, 13C (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



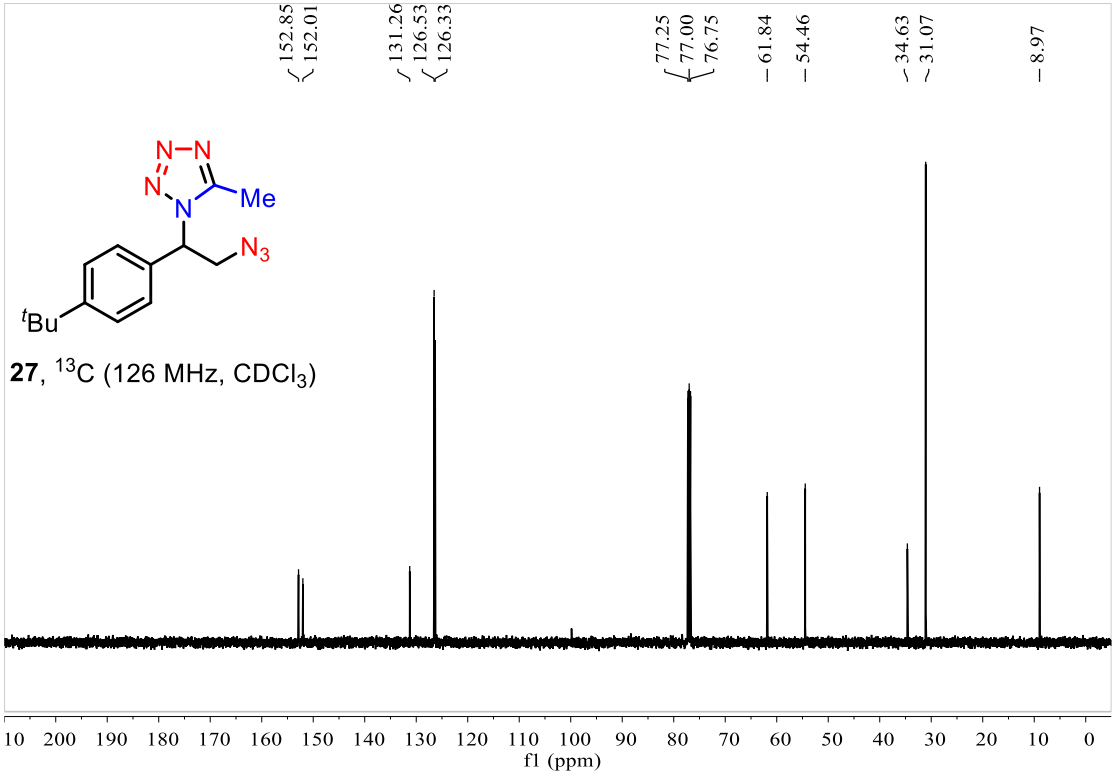
25, ^{1}H (400 MHz, $CDCl_3$)



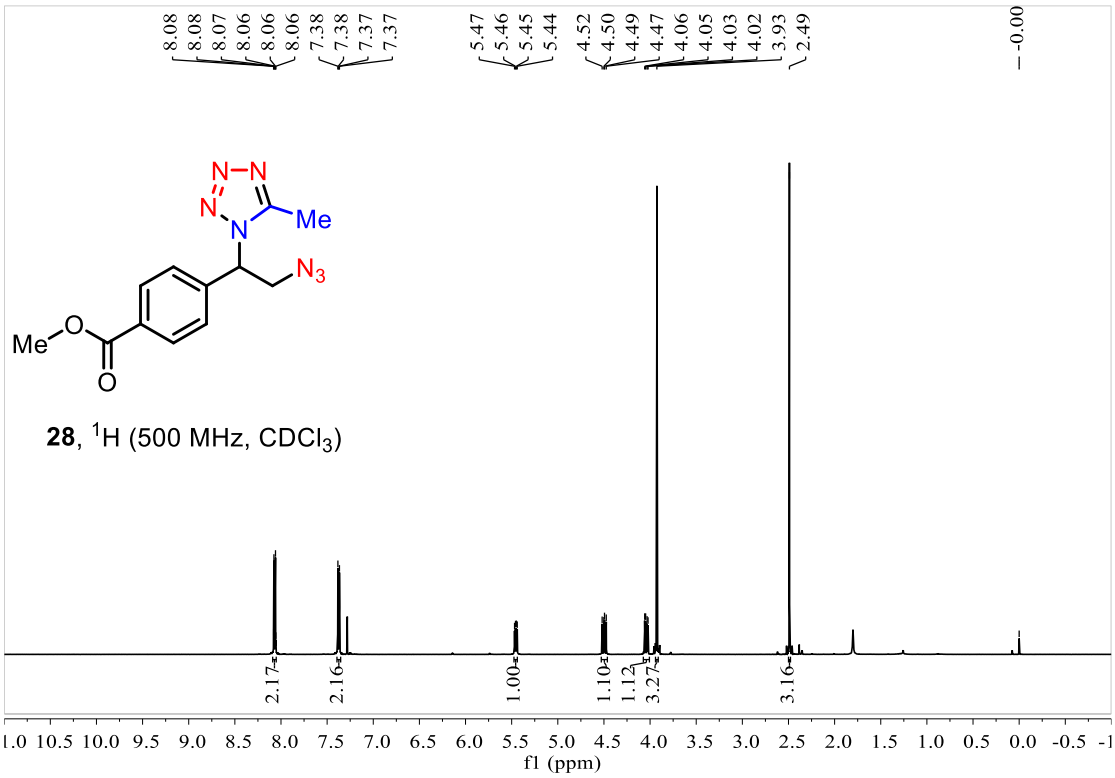
25, ^{13}C (101 MHz, $CDCl_3$)

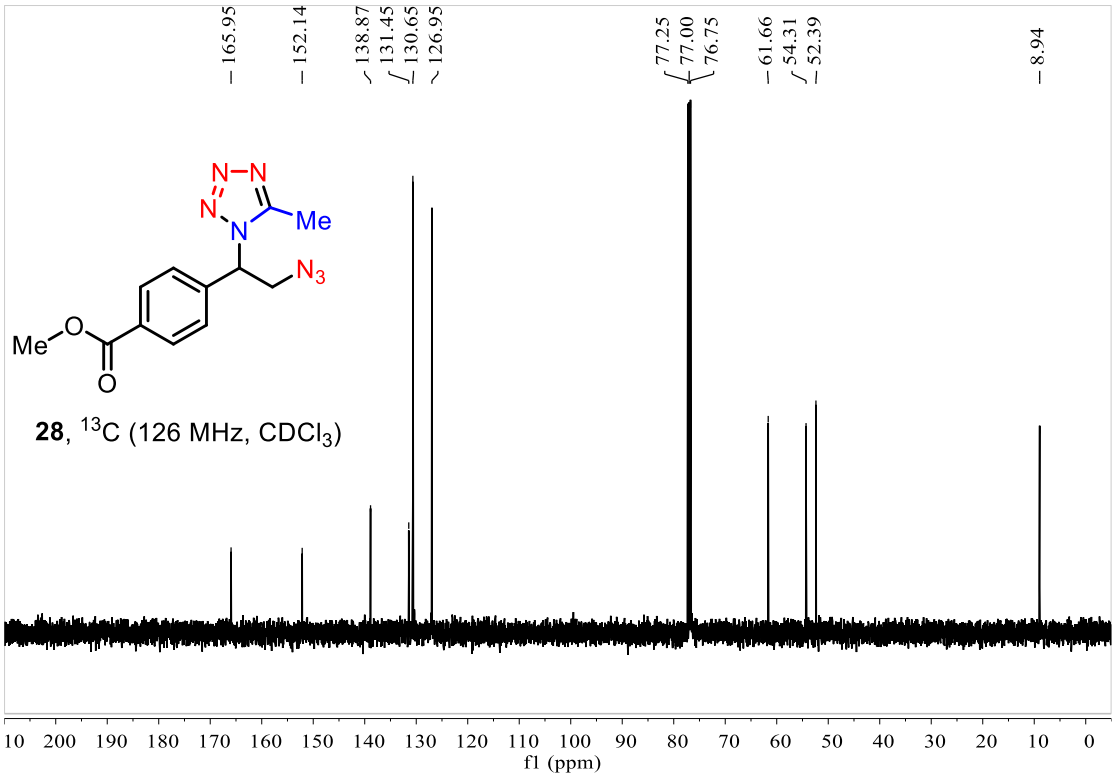


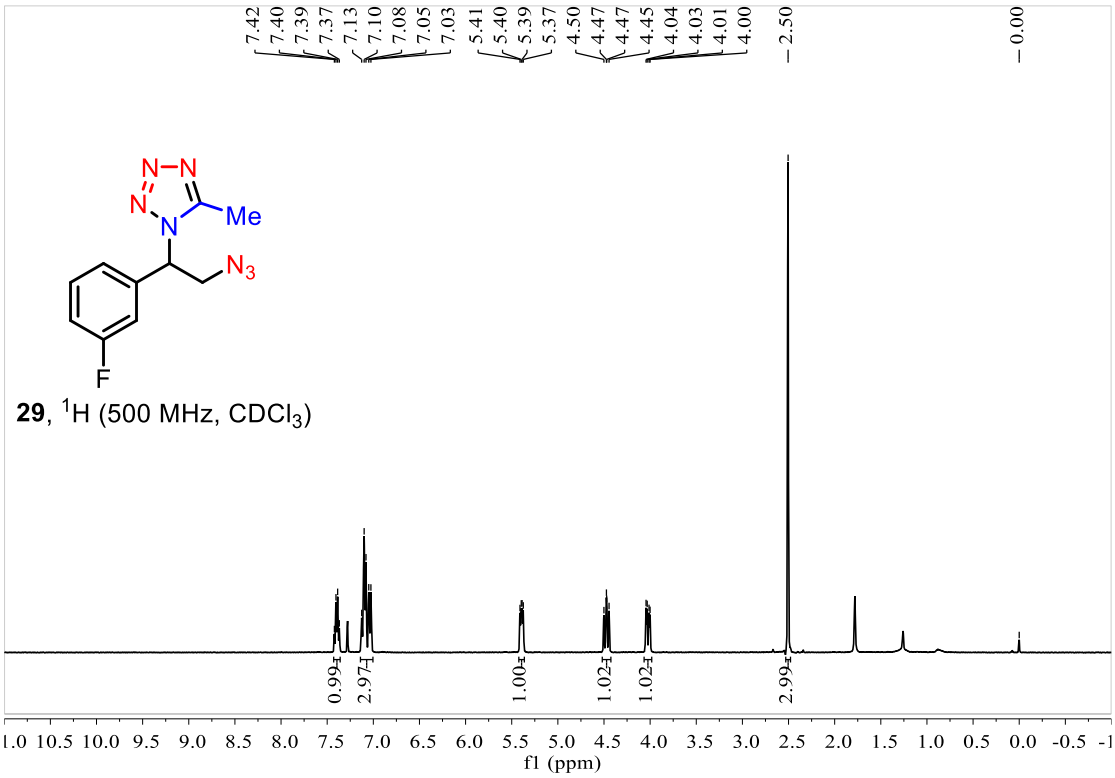
27, ^{1}H (500 MHz, $CDCl_3$)



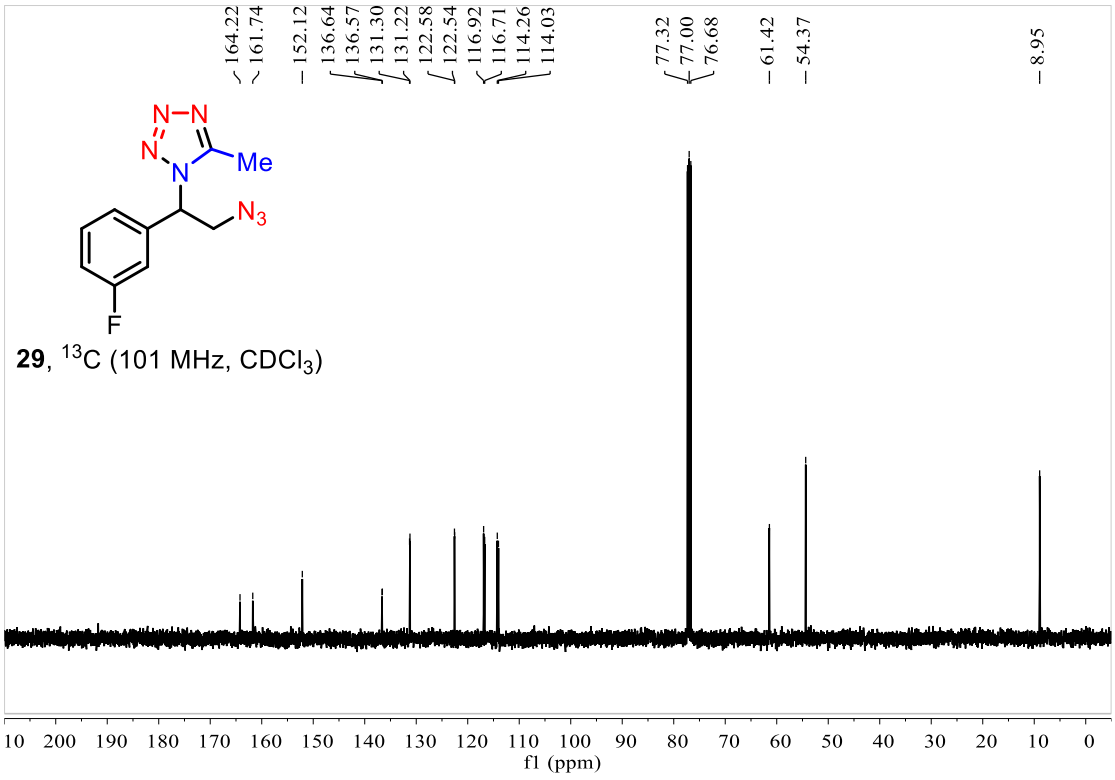
27, ^{13}C (126 MHz, $CDCl_3$)


8.08
8.08
8.07
8.06
8.06
8.06
7.38
7.38
7.37
7.37
5.47
5.46
5.45
5.44
4.52
4.50
4.49
4.47
4.06
4.05
4.03
4.02
3.93
2.49
-0.00
N–N
N
N
Me
N3
Me
O
O
28, 1H (500 MHz, CDCl3)
2.17
2.16
1.00
1.10
1.12
3.27
3.16
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

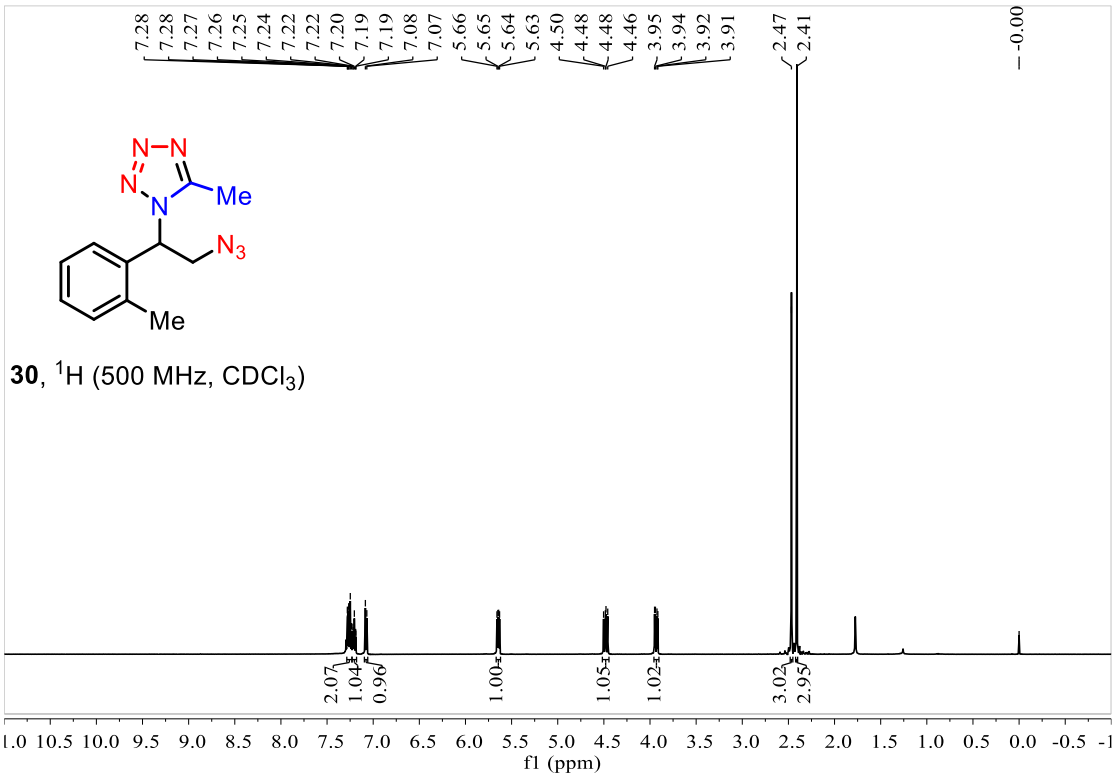

165.95
152.14
138.87
131.45
130.65
126.95
77.25
77.00
76.75
61.66
54.31
52.39
8.94
N–N
N
N
Me
N3
Me
O
O
28, 13C (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



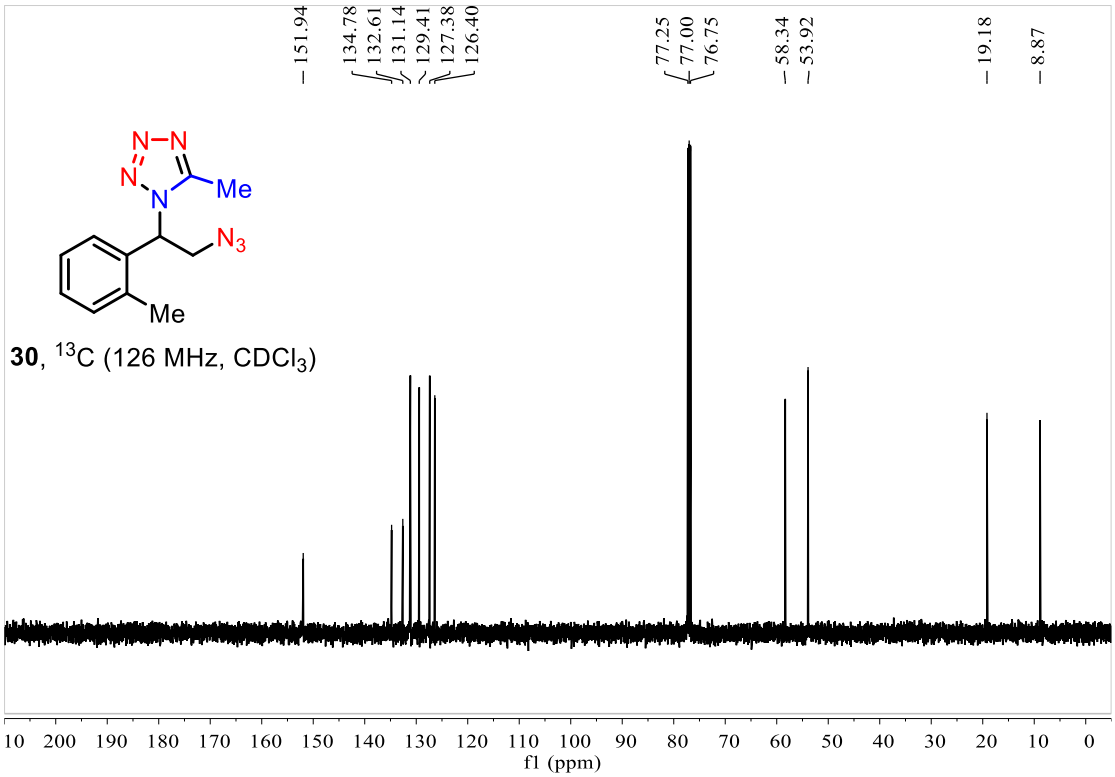
29, ^{1}H (500 MHz, $CDCl_3$)



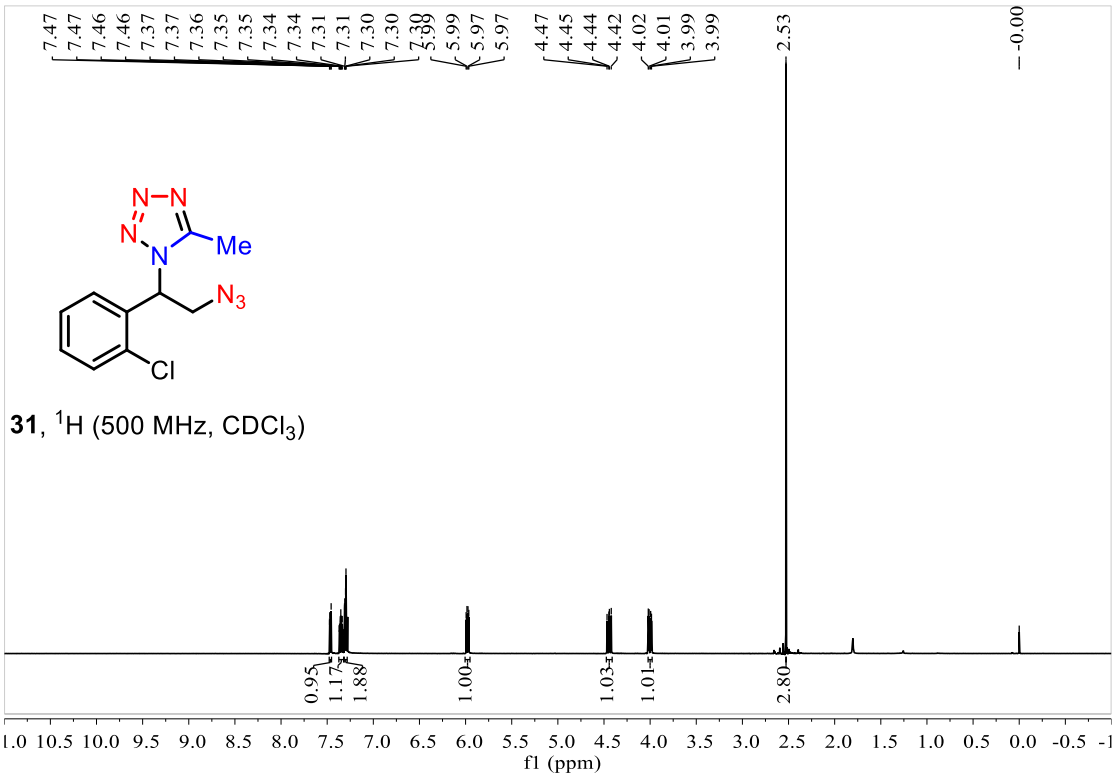
29, ^{13}C (101 MHz, $CDCl_3$)



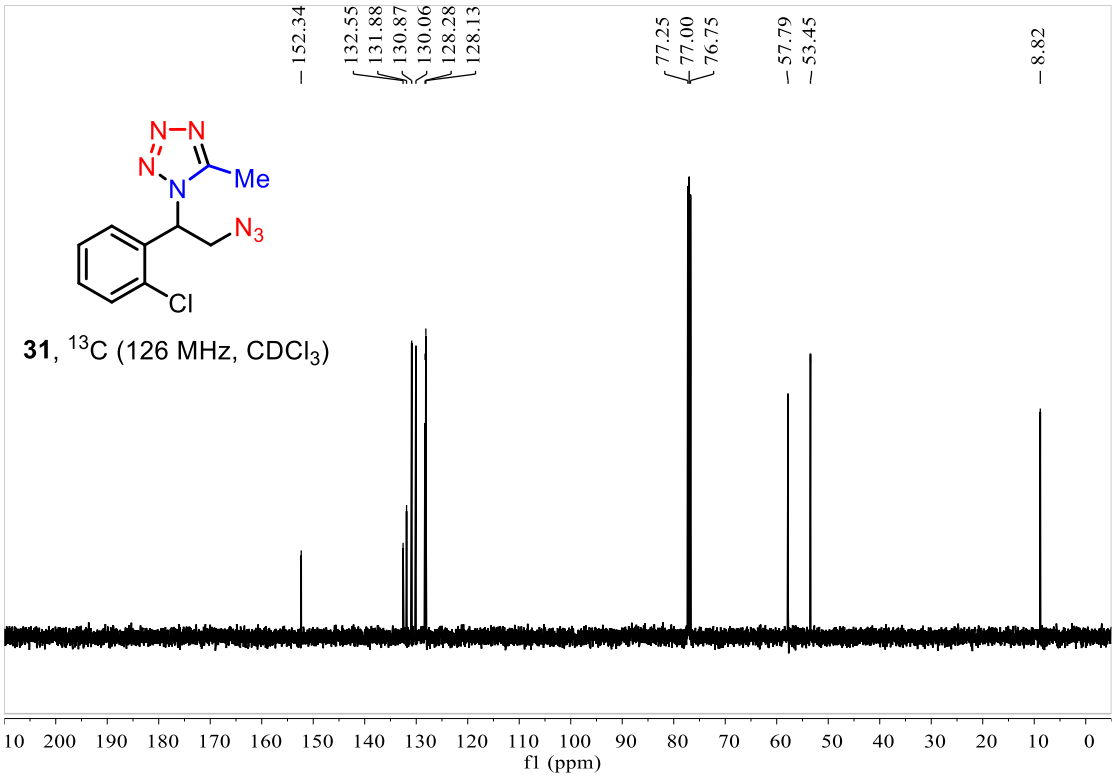
30, ^{1}H (500 MHz, $CDCl_3$)



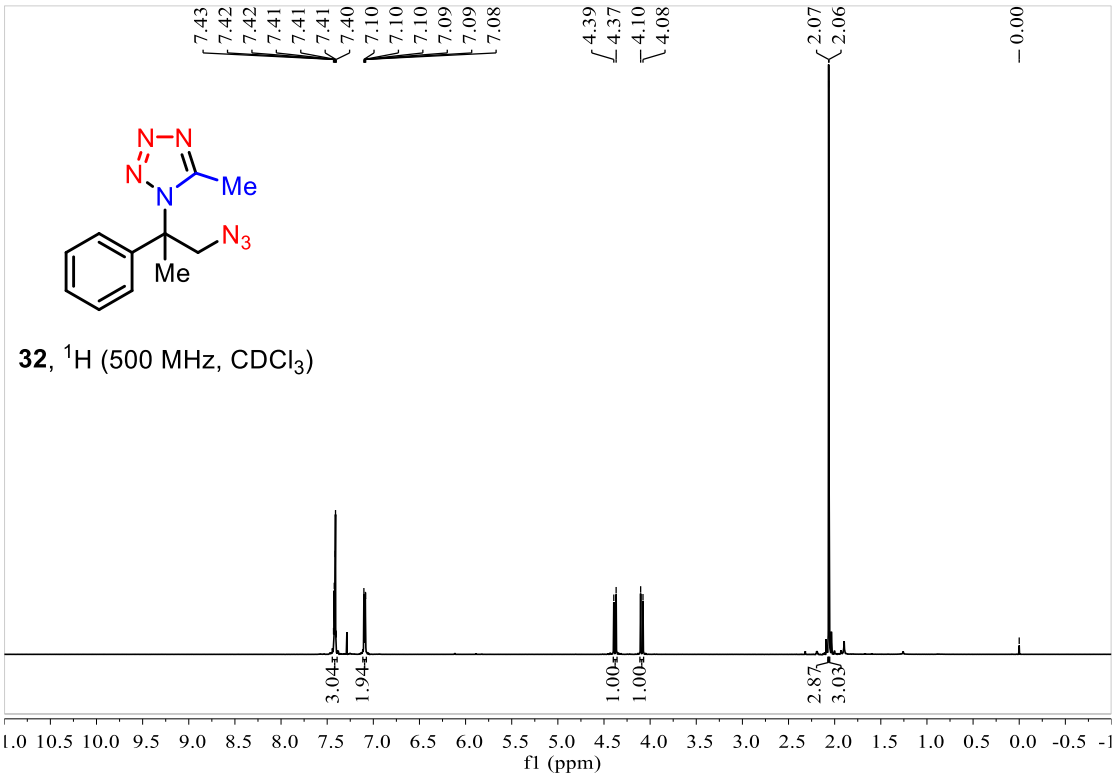
30, ^{13}C (126 MHz, $CDCl_3$)



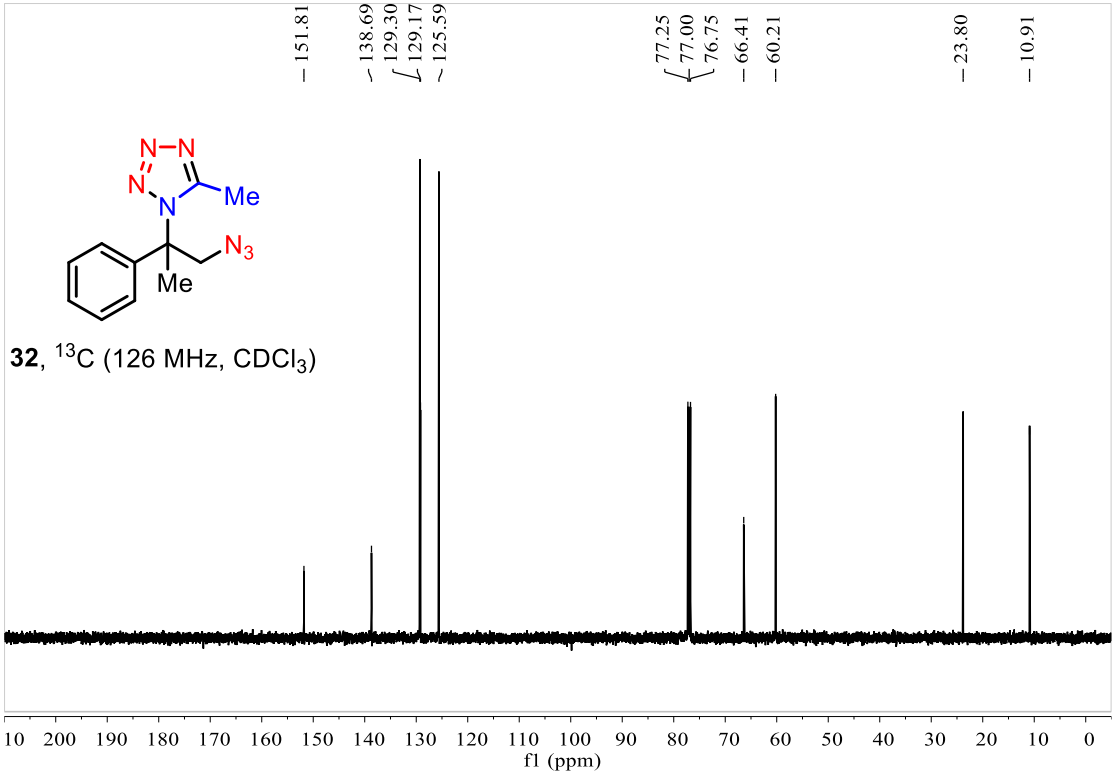
31, ^{1}H (500 MHz, $CDCl_3$)



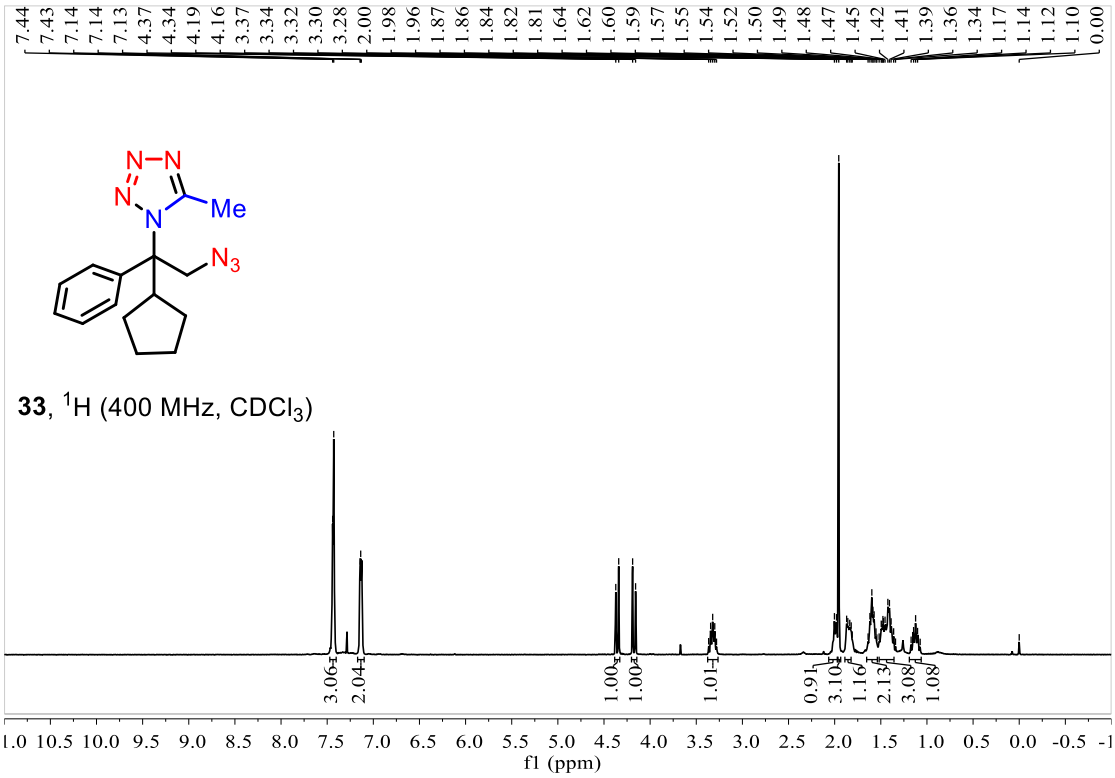
31, ^{13}C (126 MHz, $CDCl_3$)

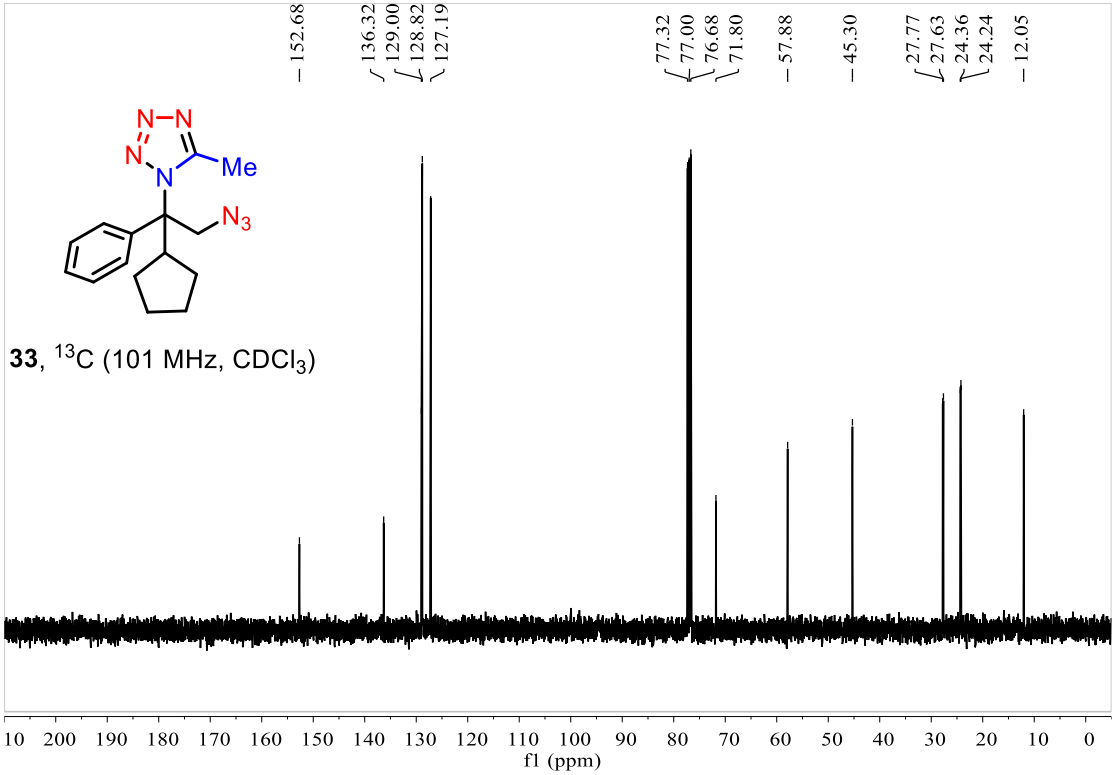


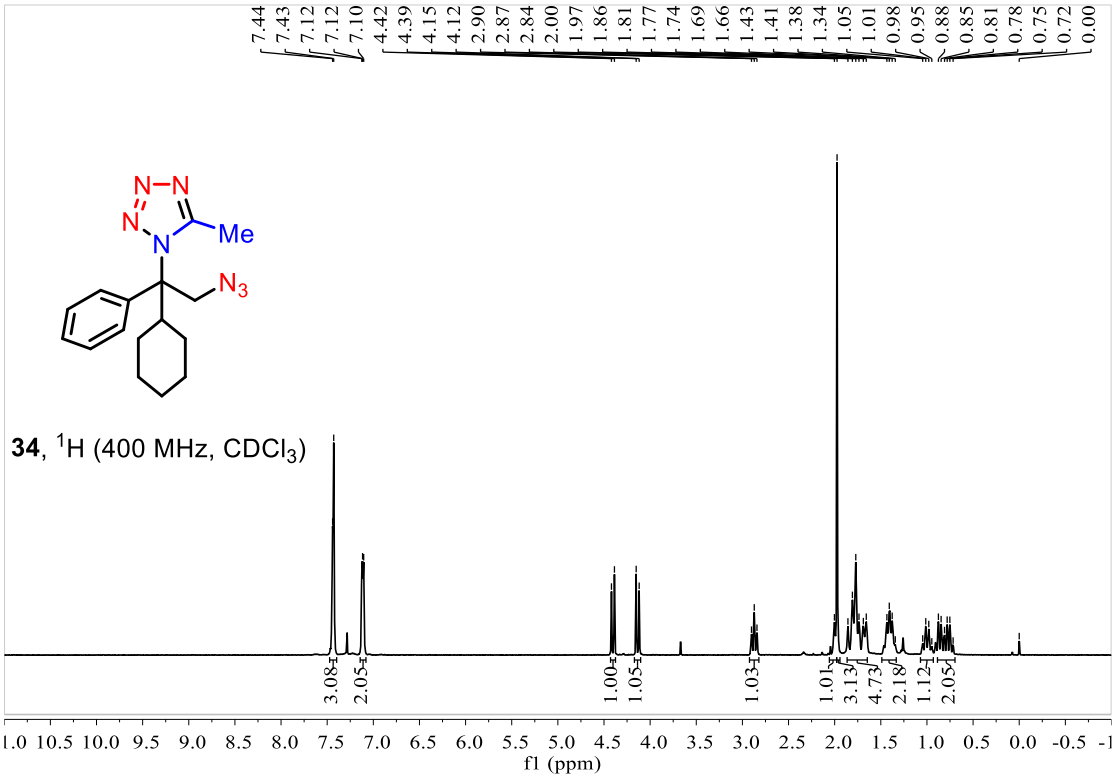
32, ^{1}H (500 MHz, $CDCl_3$)

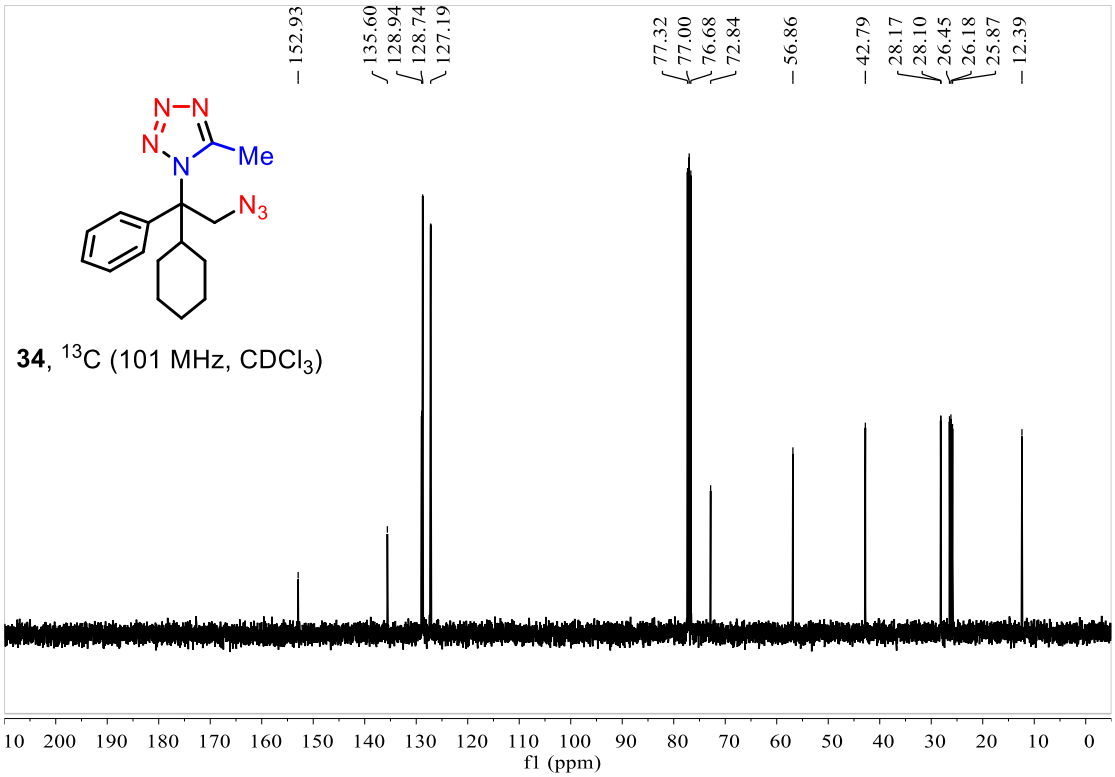


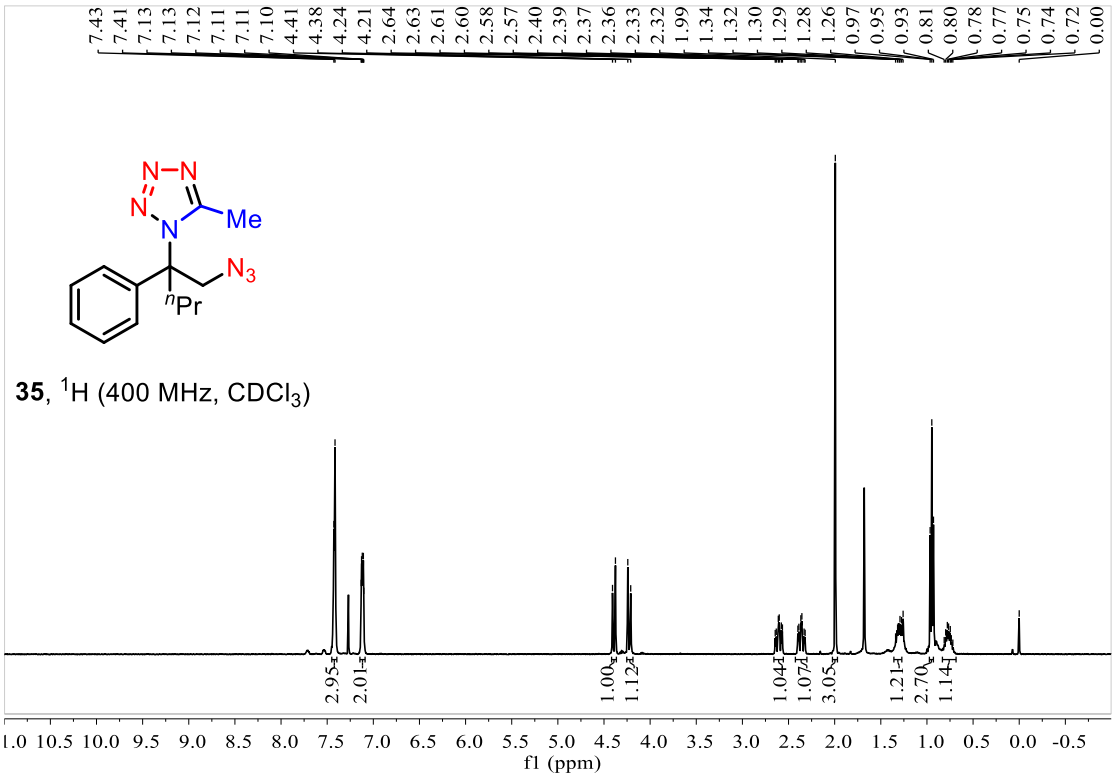
32, ^{13}C (126 MHz, $CDCl_3$)

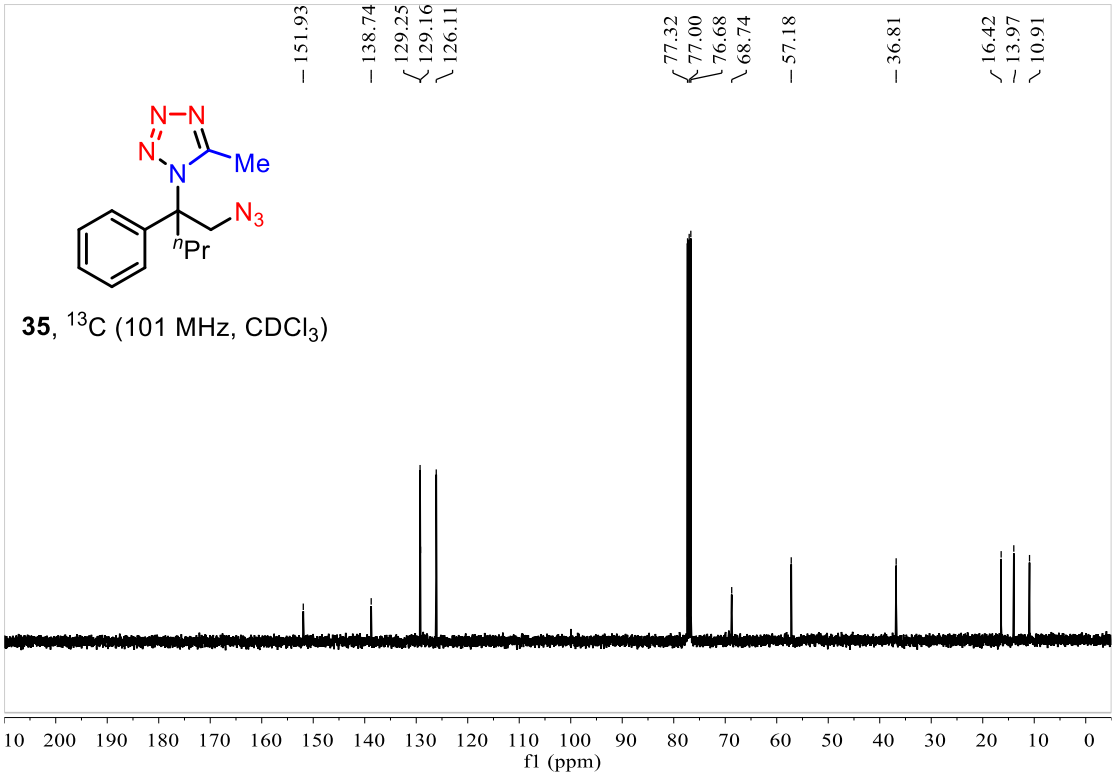

7.44 7.43 7.14 7.14 7.13 4.37 4.34 4.19 4.16 3.37 3.34 3.32 3.30 3.28 2.00 1.98 1.96 1.87 1.86 1.84 1.82 1.81 1.64 1.62 1.60 1.59 1.57 1.55 1.54 1.52 1.50 1.49 1.48 1.47 1.45 1.42 1.41 1.39 1.36 1.34 1.17 1.14 1.12 1.10 0.00
N–N
N
N
Me
N3
33, 1H (400 MHz, CDCl3)
3.06 2.04 1.00 1.00 1.01 0.91 3.10 1.16 2.13 3.08 1.08
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

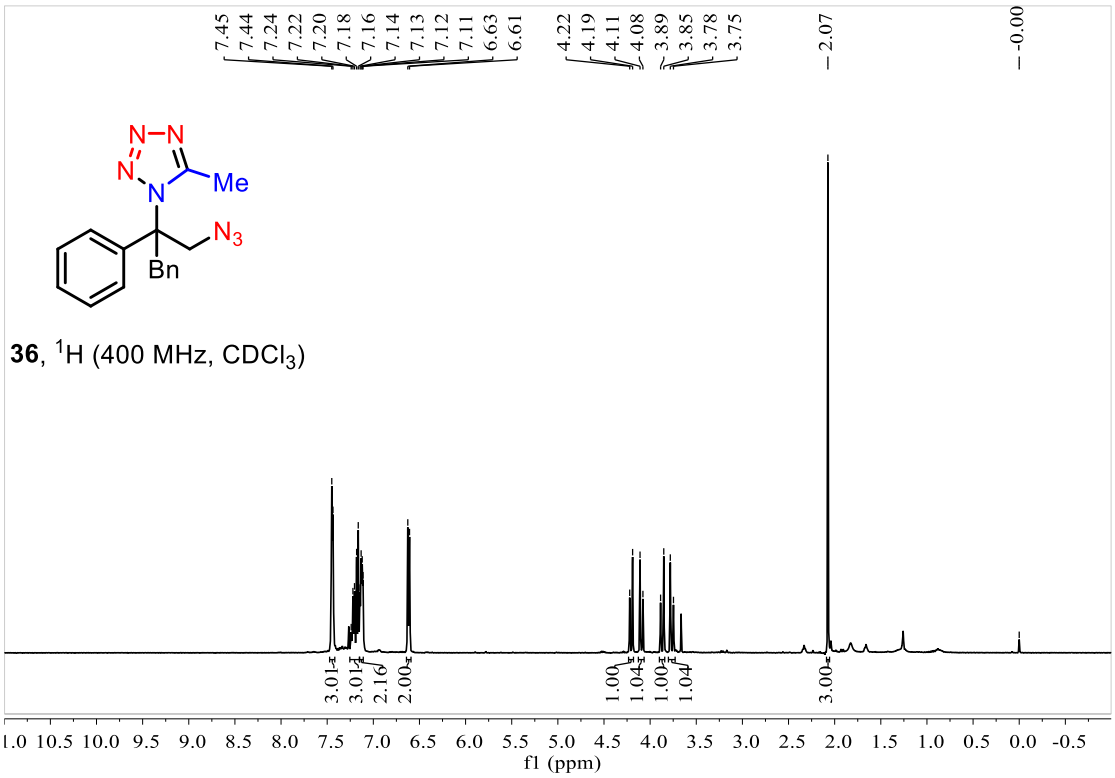

152.68
136.32
129.00
128.82
127.19
77.32
77.00
76.68
71.80
57.88
45.30
27.77
27.63
24.36
24.24
12.05
N–N
N
N
Me
N3
33, 13C (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.44
7.43
7.12
7.12
7.10
4.42
4.39
4.15
4.12
2.90
2.87
2.84
2.00
1.97
1.86
1.81
1.77
1.74
1.69
1.66
1.43
1.41
1.38
1.34
1.05
1.01
0.98
0.95
0.88
0.85
0.81
0.78
0.75
0.72
0.00
N–N
N
N
Me
N3
34, 1H (400 MHz, CDCl3)
3.08
2.05
1.00
1.05
1.03
1.01
3.13
4.73
2.18
1.12
2.05
f1 (ppm)

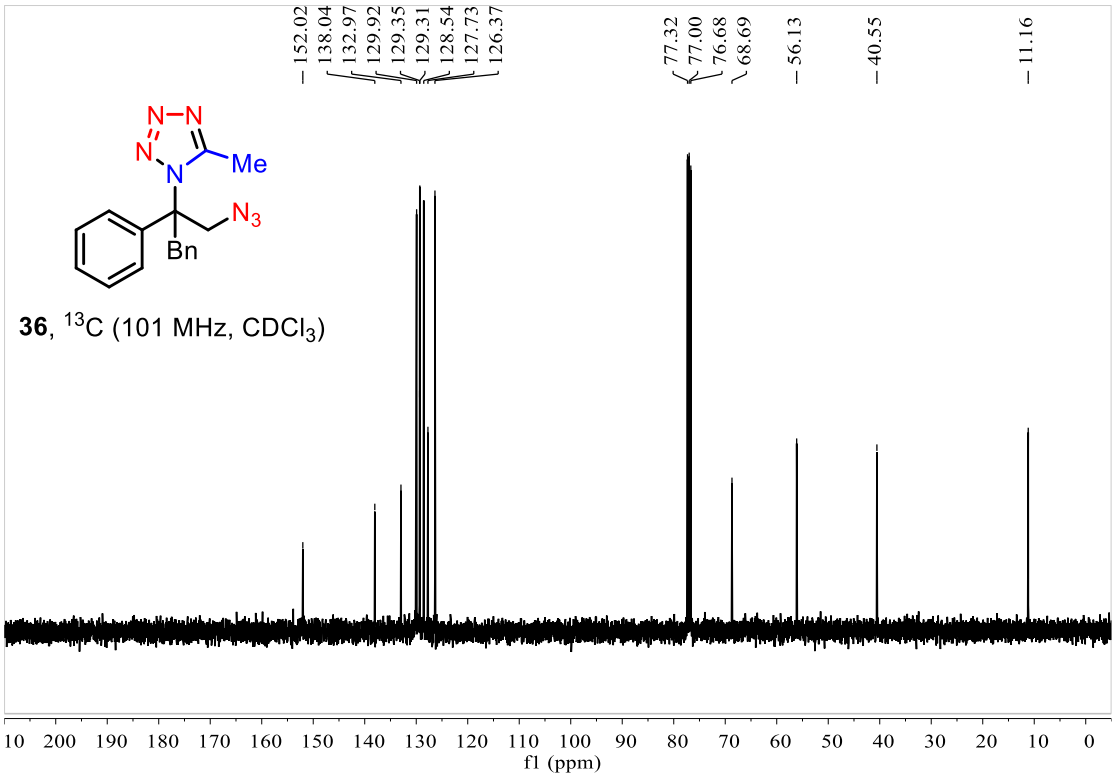

152.93
135.60
128.94
128.74
127.19
77.32
77.00
76.68
72.84
56.86
42.79
28.17
28.10
26.45
26.18
25.87
12.39
N–N
N
N
Me
N3
34, 13C (101 MHz, CDCl3)
f1 (ppm)


7.43 7.41 7.13 7.13 7.12 7.11 7.11 7.10 4.41 4.38 4.24 4.21 2.64 2.63 2.61 2.60 2.58 2.57 2.40 2.39 2.37 2.36 2.33 2.32 1.99 1.34 1.32 1.30 1.29 1.28 1.26 0.97 0.95 0.93 0.81 0.80 0.78 0.77 0.75 0.74 0.72 0.00
N–N
N
N
Me
N3
nPr
35, 1H (400 MHz, CDCl3)
2.95 2.01 1.00 1.12 1.04 1.07 3.05 1.21 2.70 1.14
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

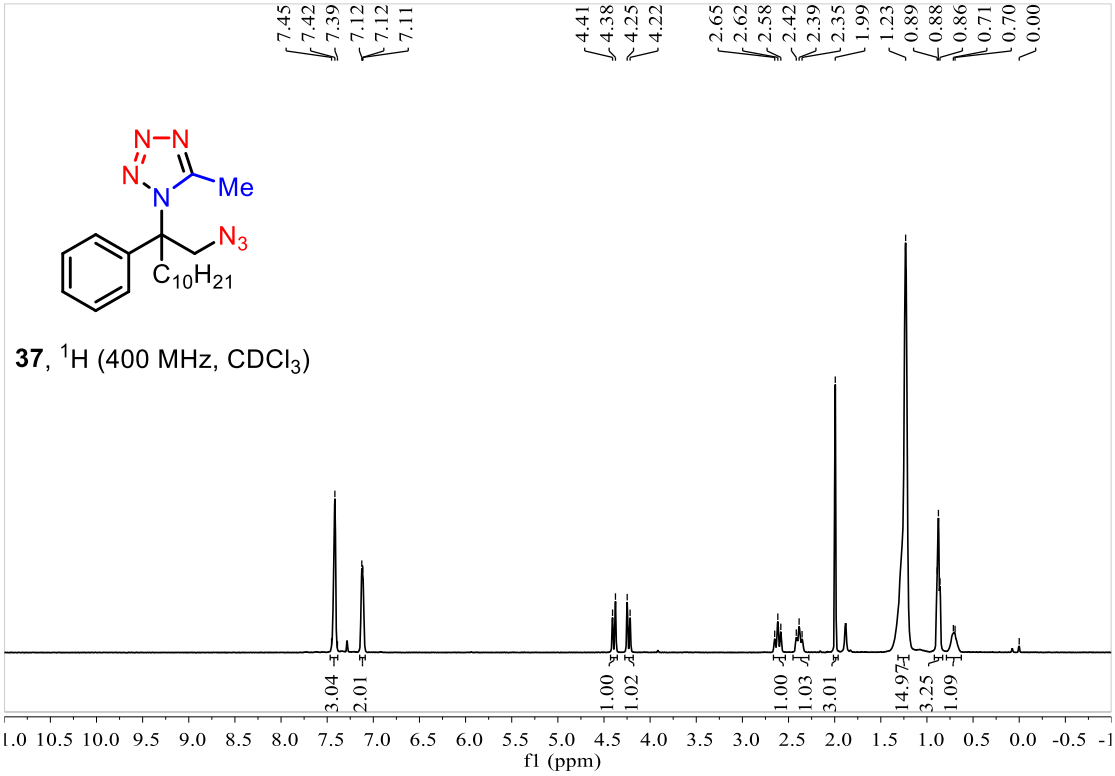

151.93 138.74 129.25 129.16 126.11 77.32 77.00 76.68 68.74 57.18 36.81 16.42 13.97 10.91
N–N
N
N
Me
N3
nPr
35, 13C (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

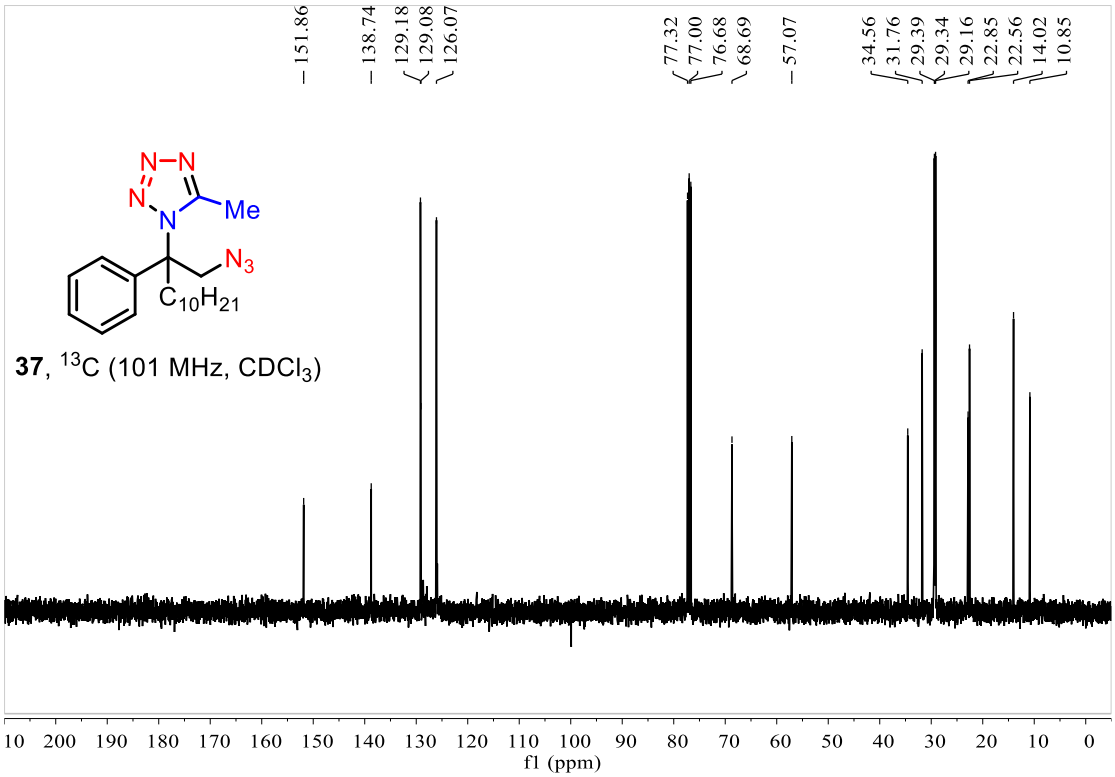


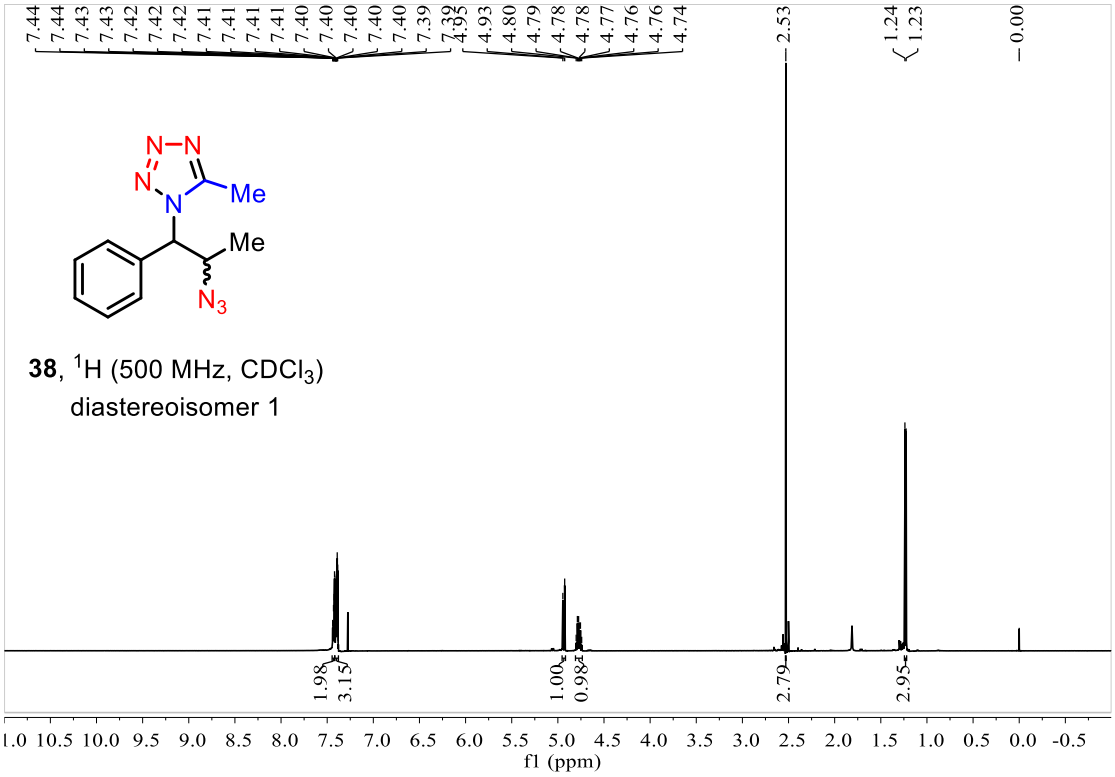
36, ^{1}H (400 MHz, $CDCl_3$)

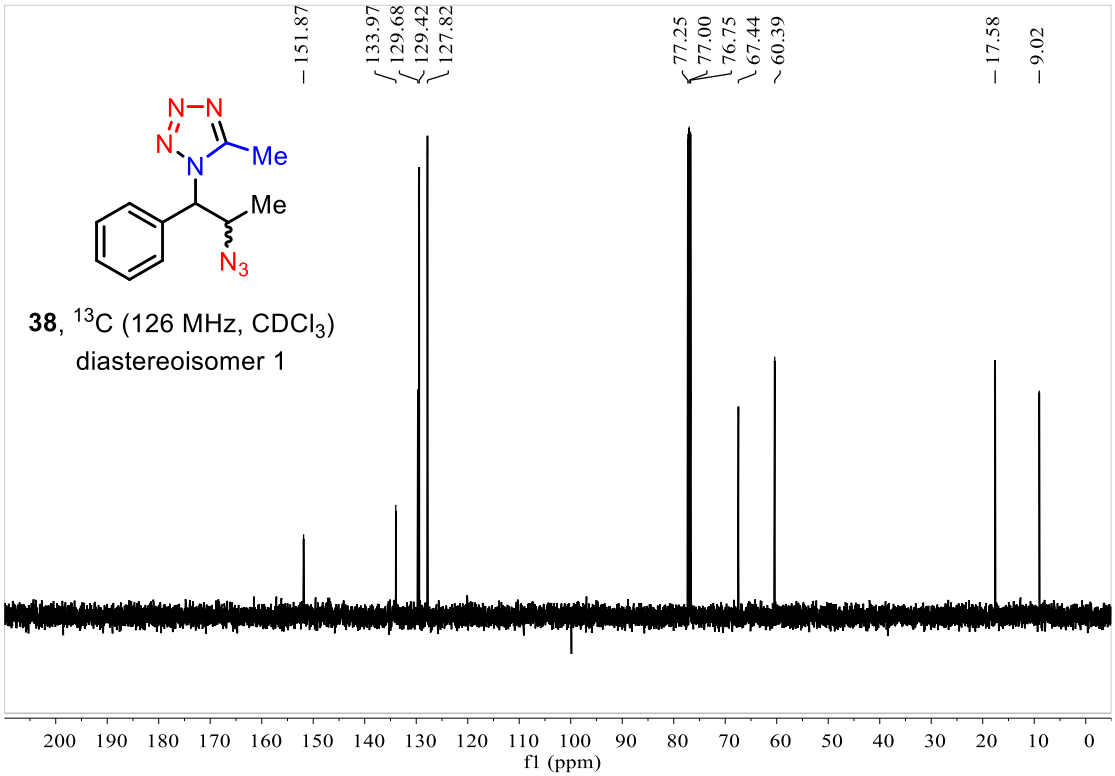


36, ^{13}C (101 MHz, $CDCl_3$)

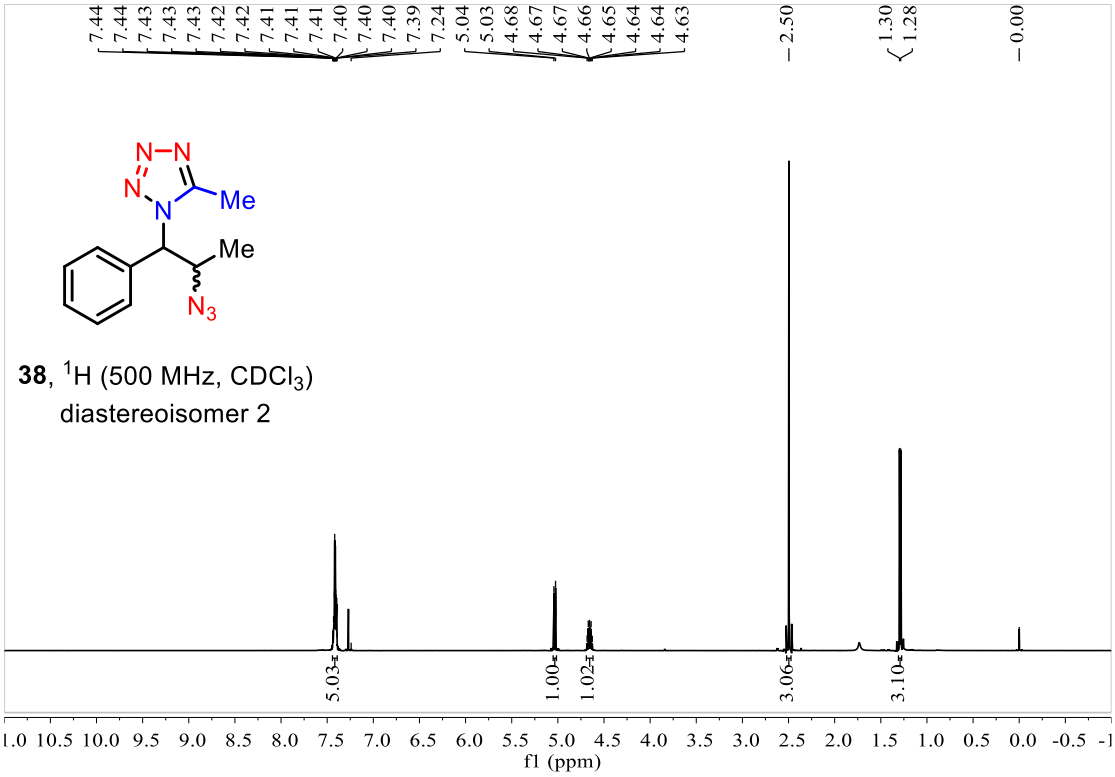

7.45
7.42
7.39
7.12
7.12
7.11
4.41
4.38
4.25
4.22
2.65
2.62
2.58
2.42
2.39
2.35
1.99
1.23
0.89
0.88
0.86
0.71
0.70
0.00
N–N
N
N
Me
N3
C10H21
37, 1H (400 MHz, CDCl3)
3.04
2.01
1.00
1.02
1.00
1.03
3.01
14.97
3.25
1.09
f1 (ppm)

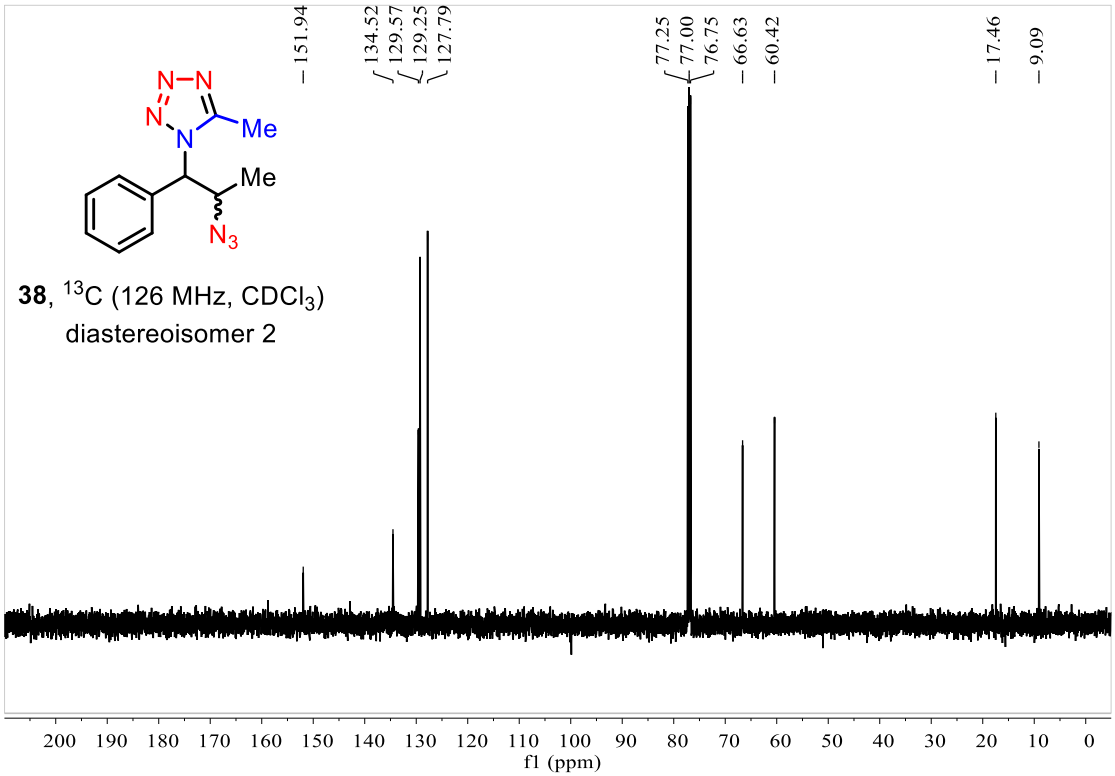

151.86
138.74
129.18
129.08
126.07
77.32
77.00
76.68
68.69
57.07
34.56
31.76
29.39
29.34
29.16
22.85
22.56
14.02
10.85
N–N
N
N
Me
N3
C10H21
37, 13C (101 MHz, CDCl3)
f1 (ppm)

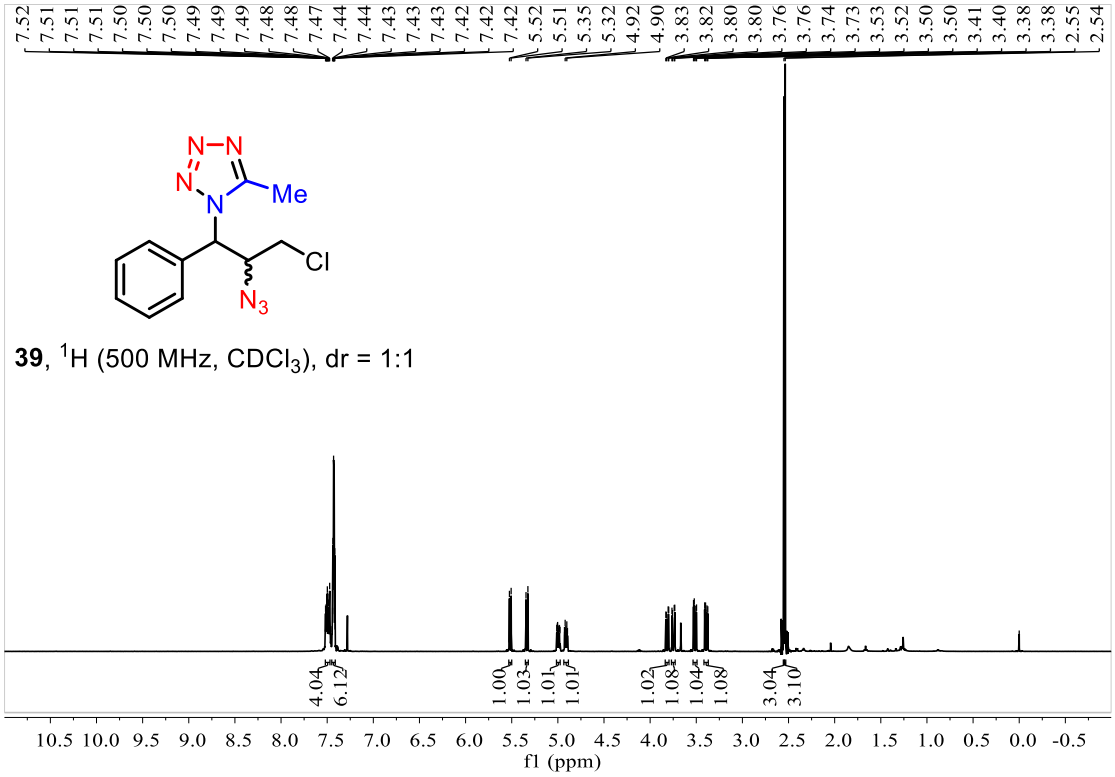

7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.41
7.40
7.40
7.40
7.40
7.40
7.39
7.39
4.95
4.93
4.80
4.79
4.78
4.78
4.77
4.76
4.76
4.74
2.53
1.24
1.23
0.00
N–N
N
N
Me
Me
N3
38, 1H (500 MHz, CDCl3)
diastereoisomer 1
1.98
3.15
1.00
0.98
2.79
2.95
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


151.87
133.97
129.68
129.42
127.82
77.25
77.00
76.75
67.44
60.39
17.58
9.02
N–N
N
N
Me
Me
N3
38, 13C (126 MHz, CDCl3)
diastereoisomer 1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

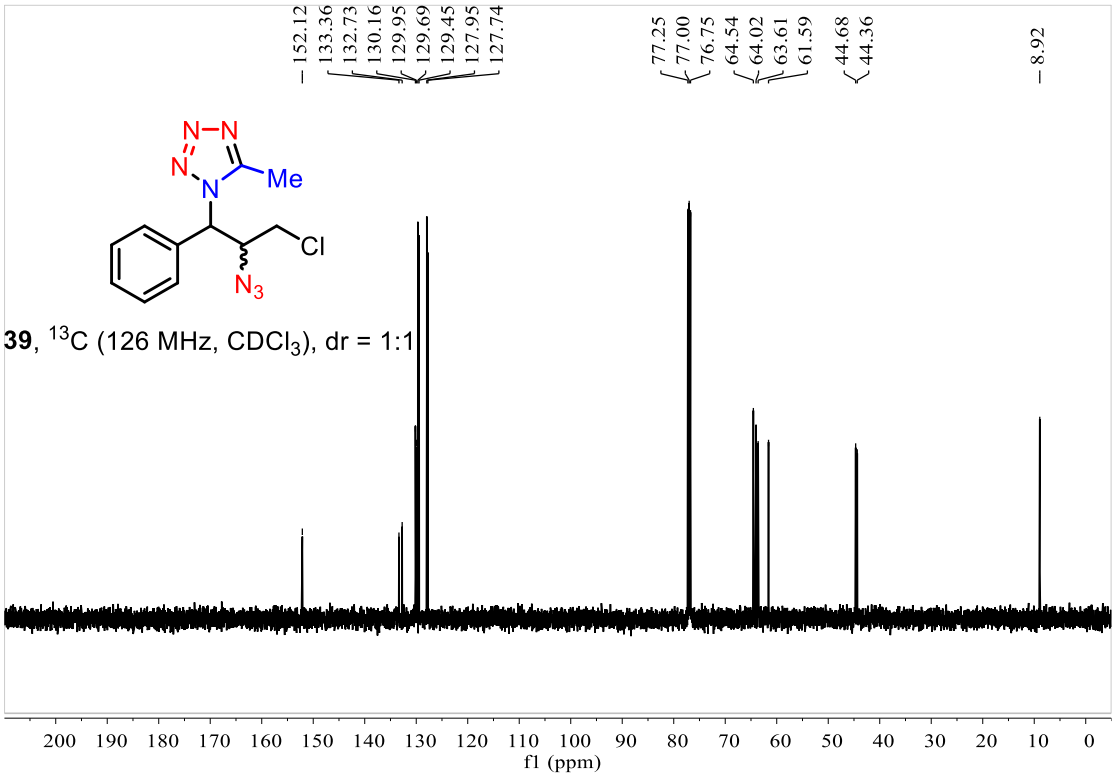
diastereoisomer 2



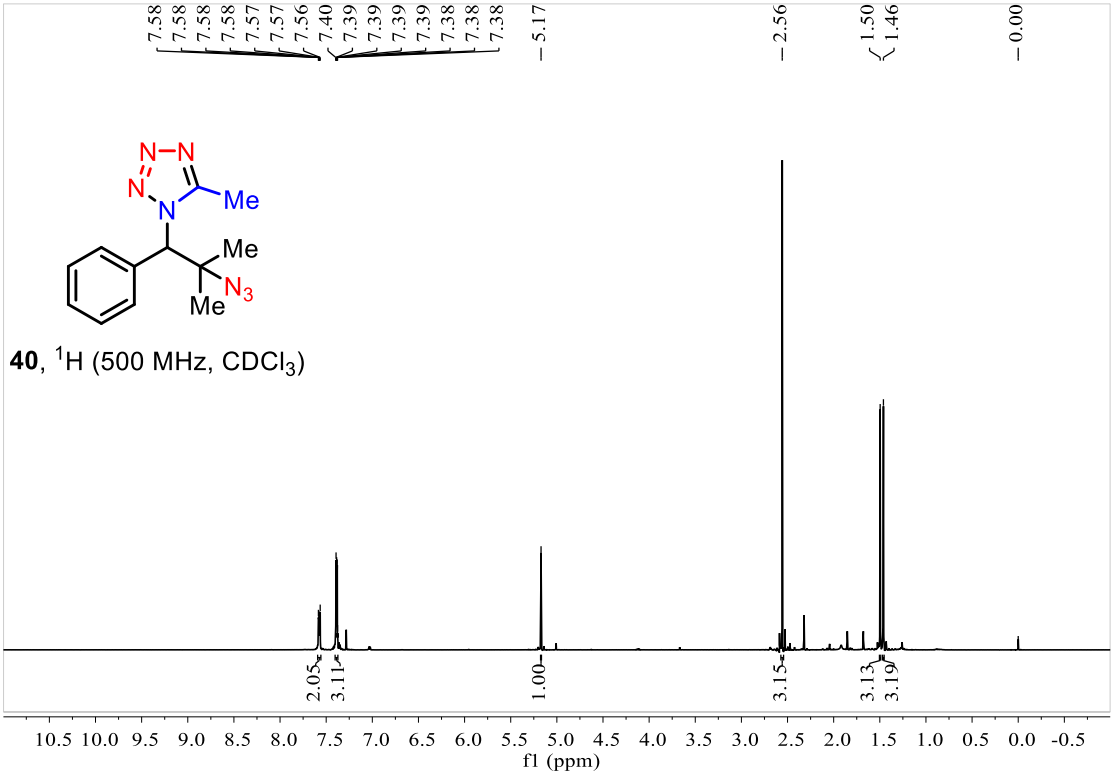




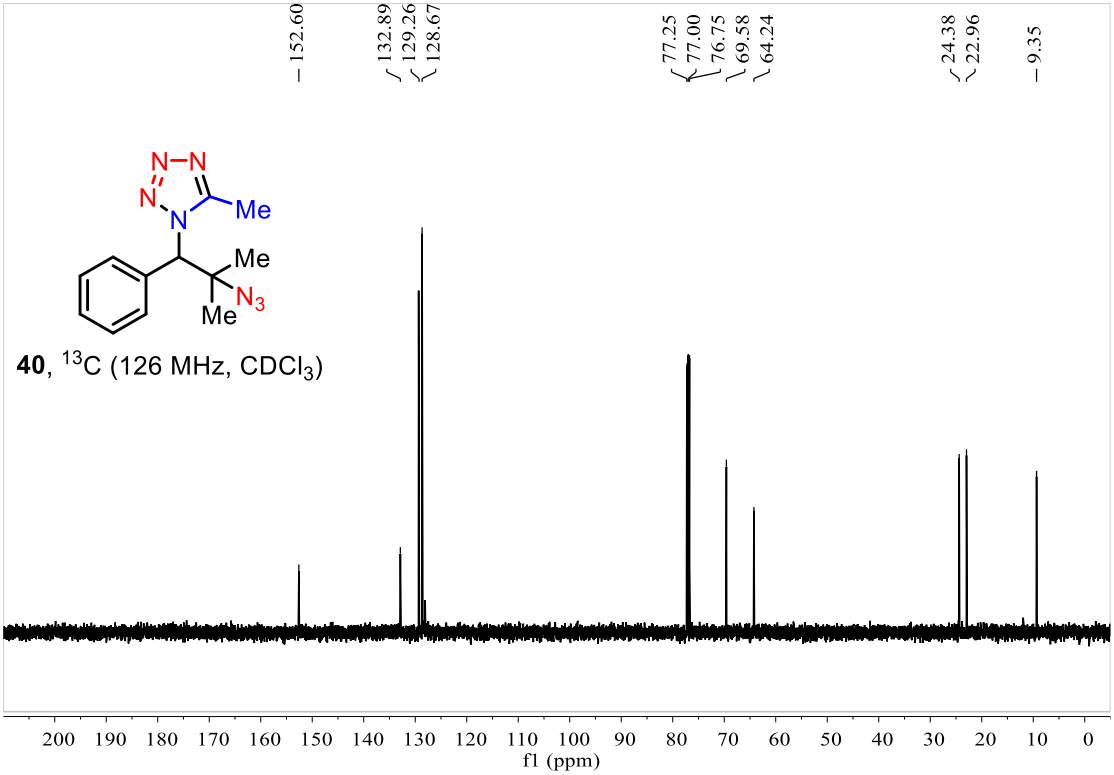
39, ^{1}H (500 MHz, $CDCl_3$), dr = 1:1



39, ^{13}C (126 MHz, $CDCl_3$), dr = 1:1

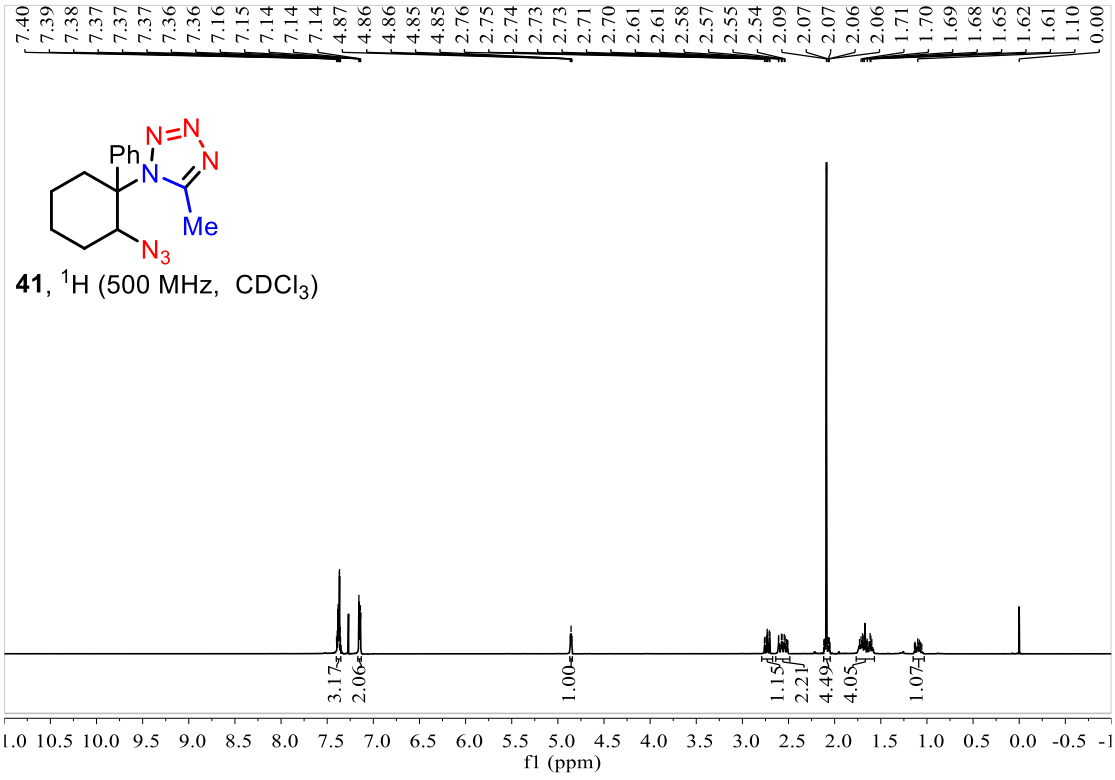


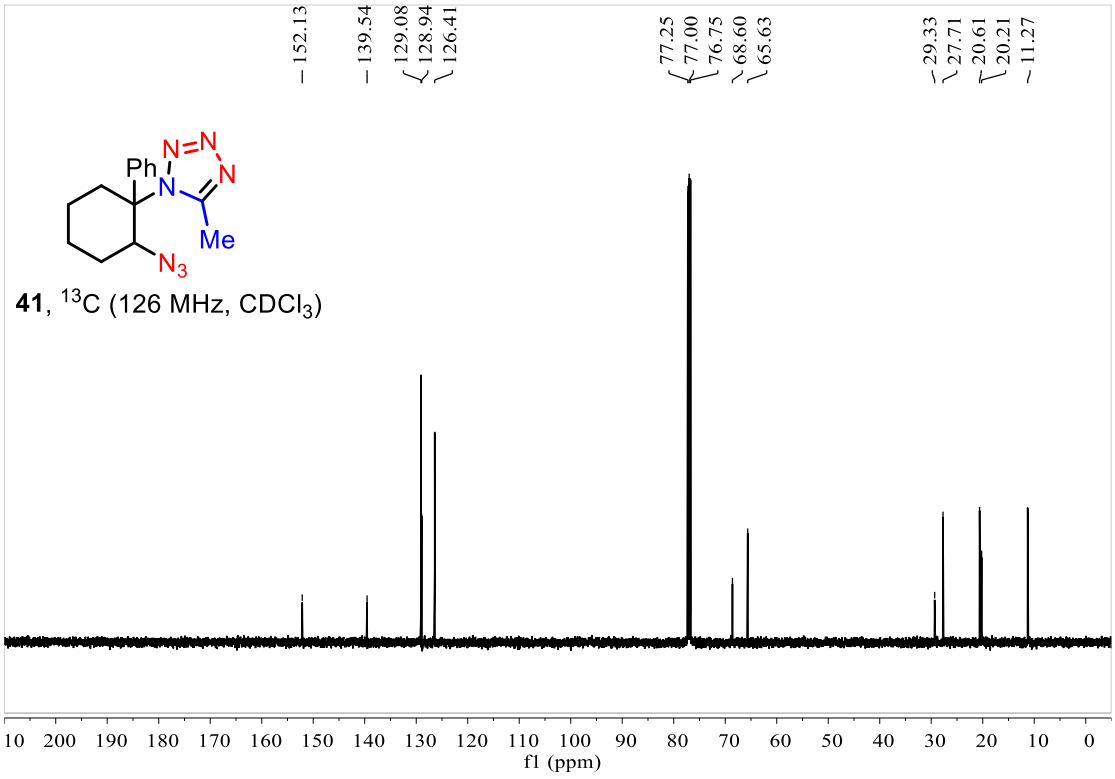
40, ^{1}H (500 MHz, $CDCl_3$)



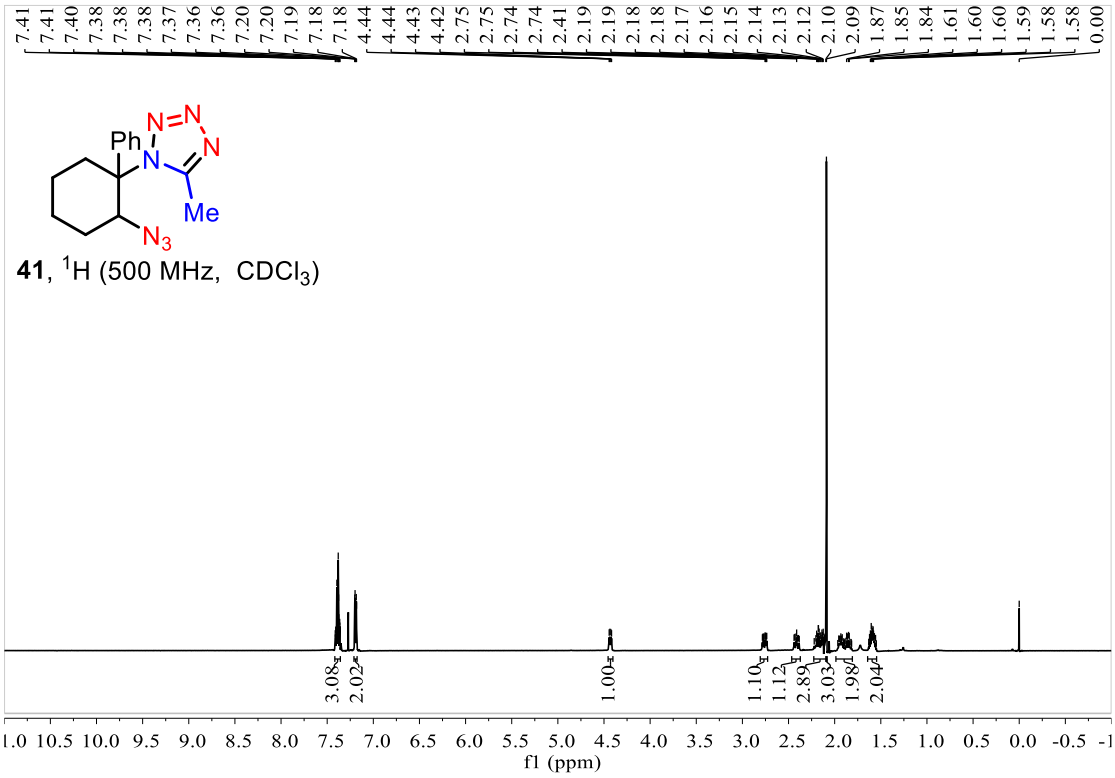
40, ^{13}C (126 MHz, $CDCl_3$)

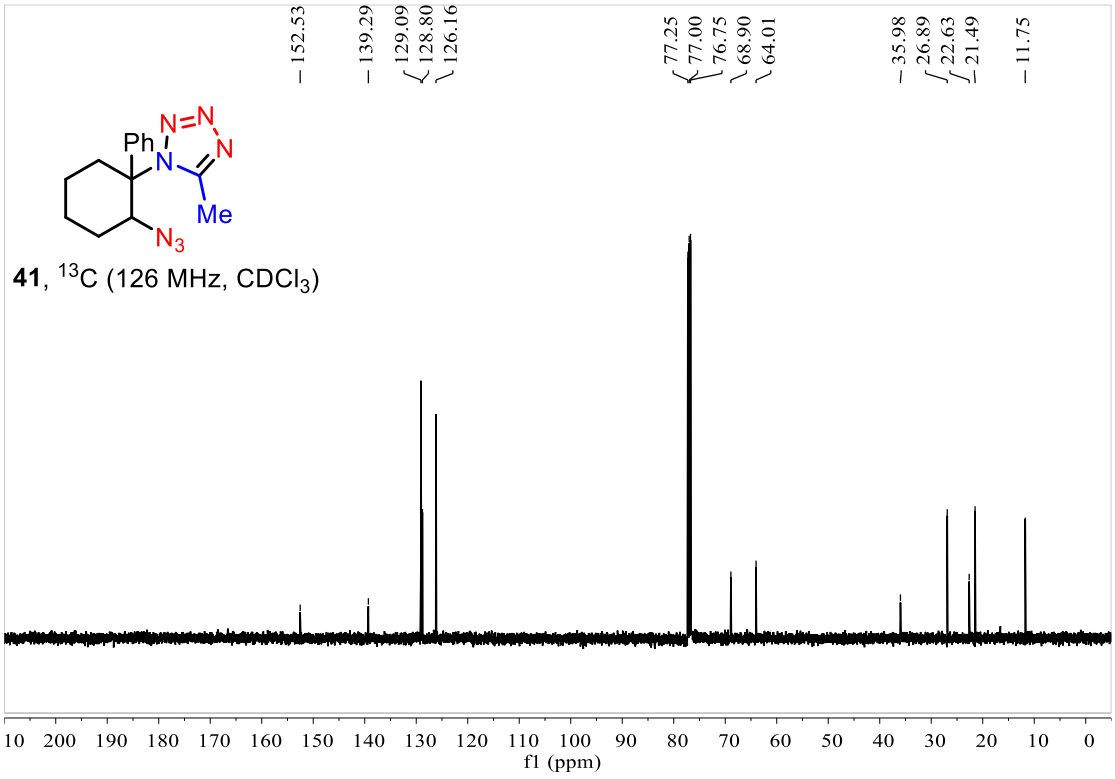
diastereoisomer 1:

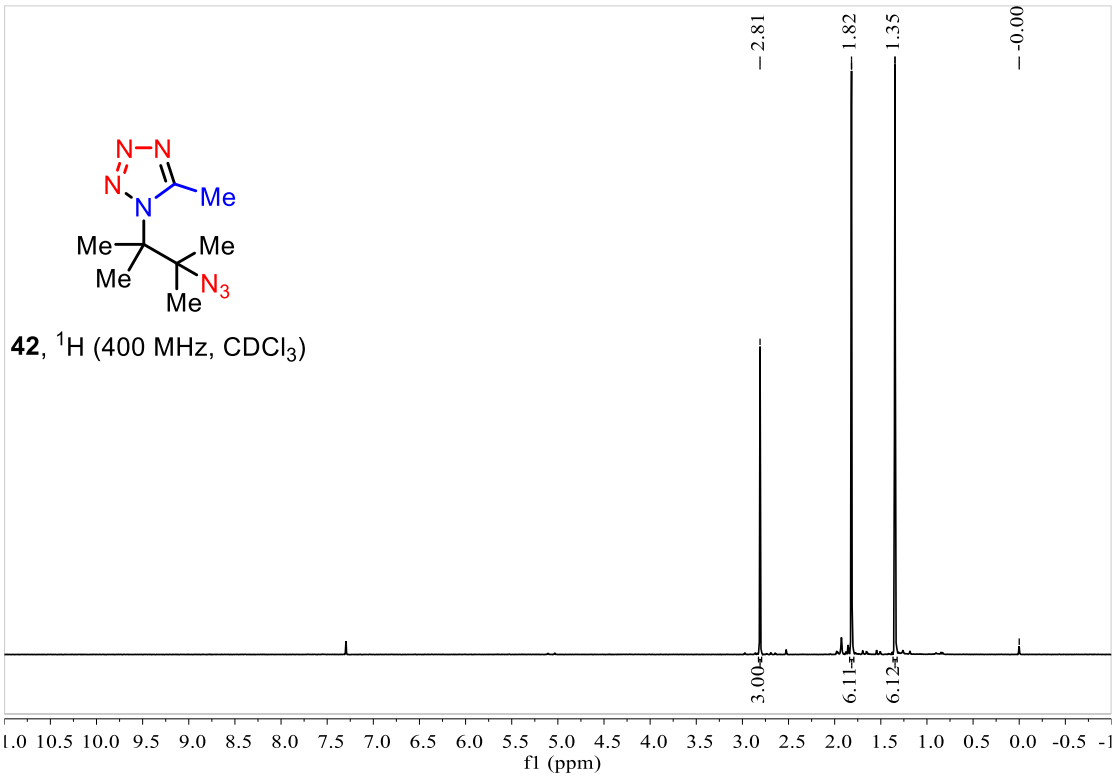




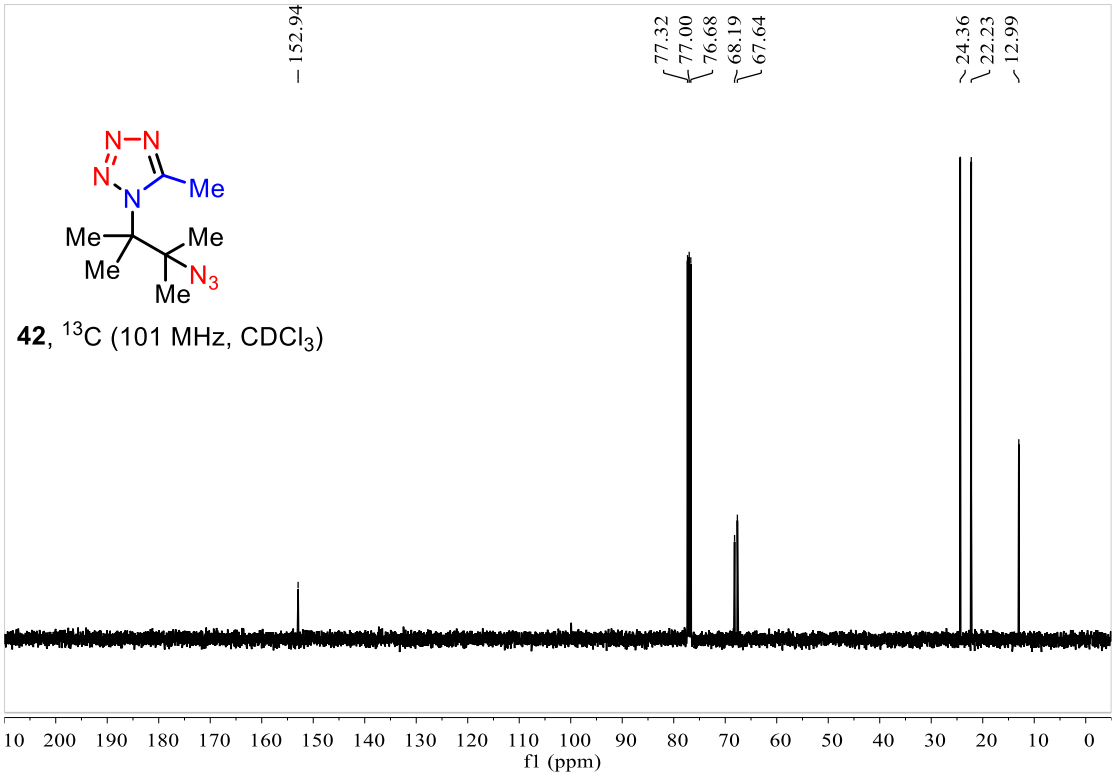
diastereoisomer 2:



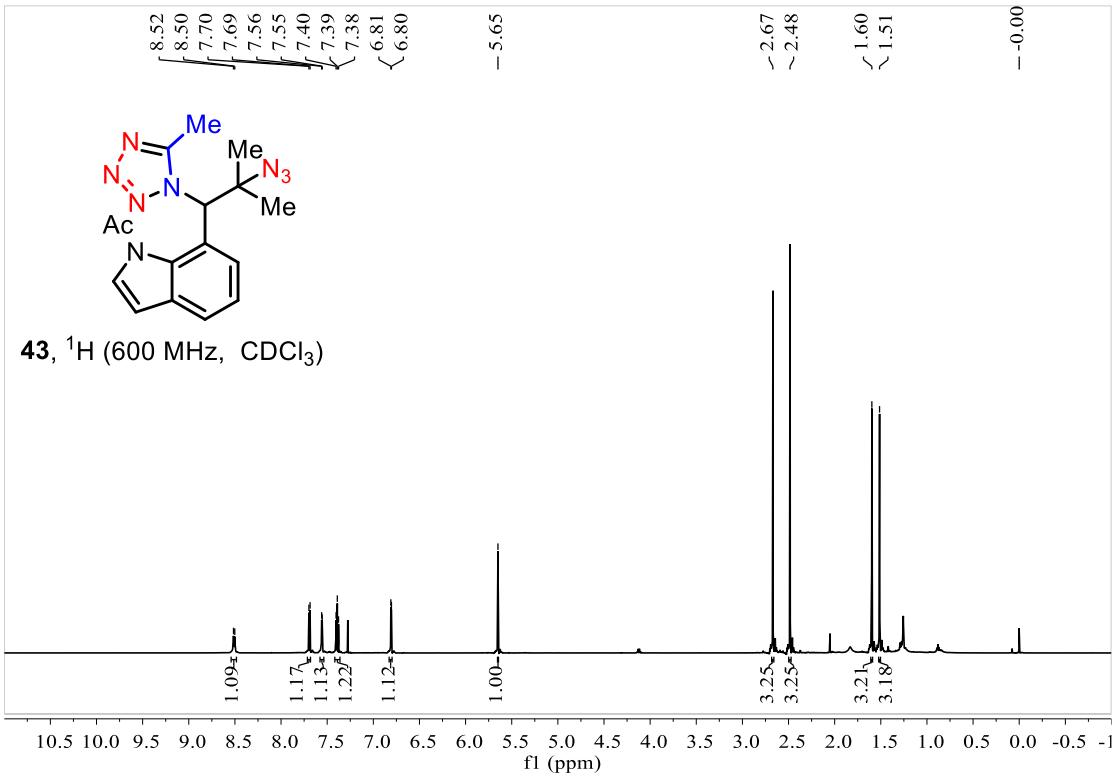




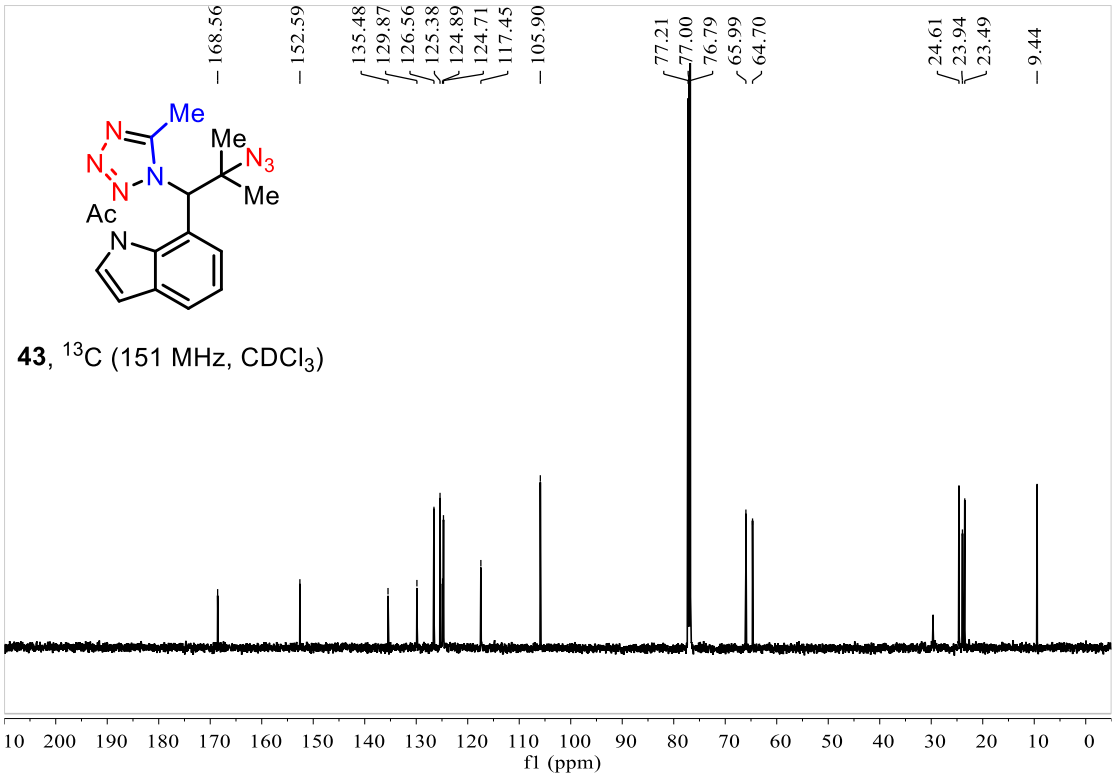
42, ^{1}H (400 MHz, $CDCl_3$)



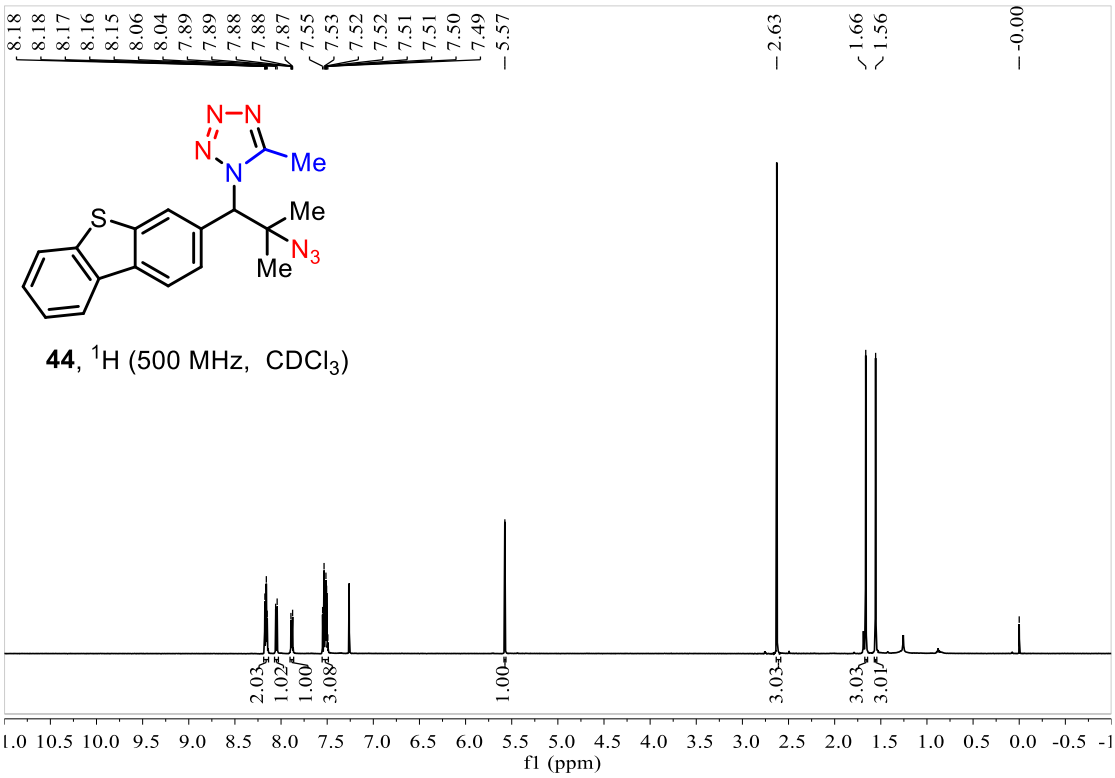
42, ^{13}C (101 MHz, $CDCl_3$)



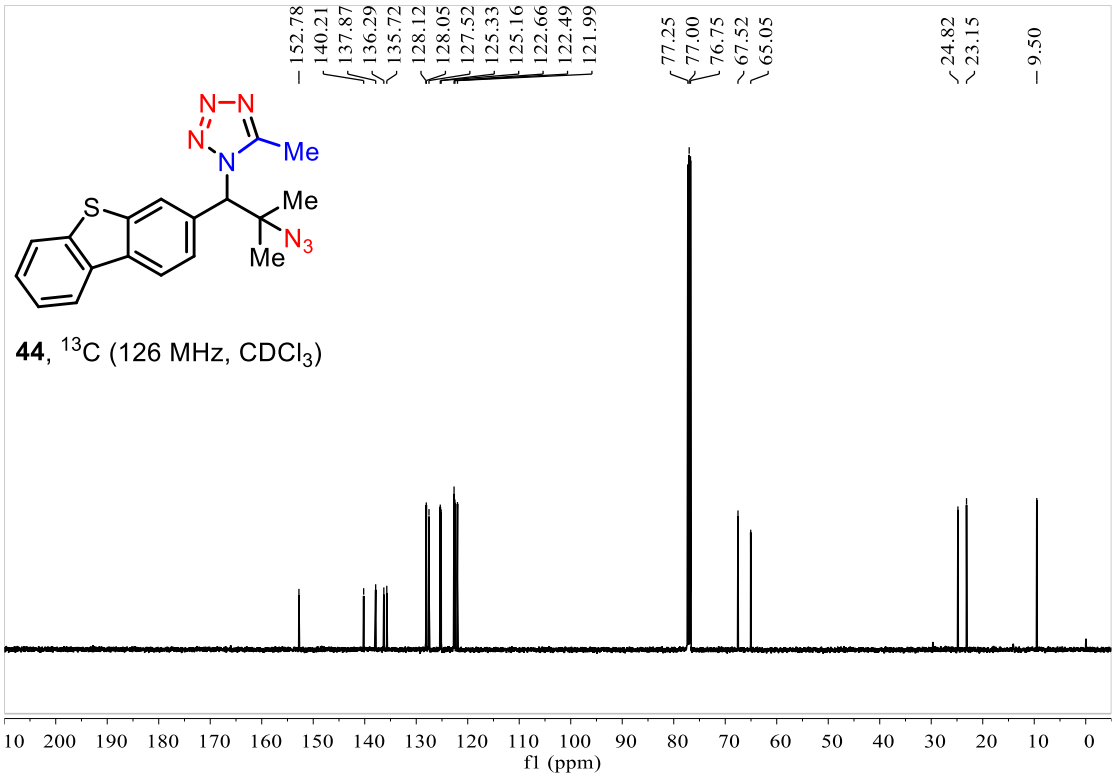
43, ^{1}H (600 MHz, $CDCl_3$)



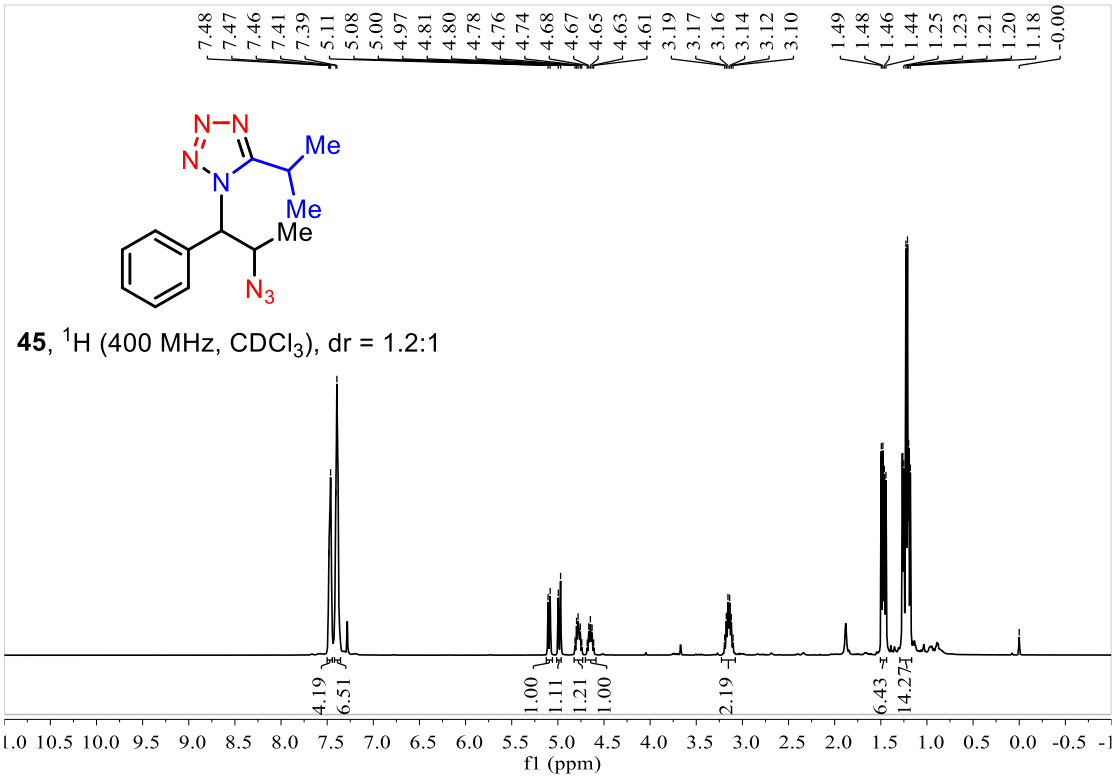
43, ^{13}C (151 MHz, $CDCl_3$)

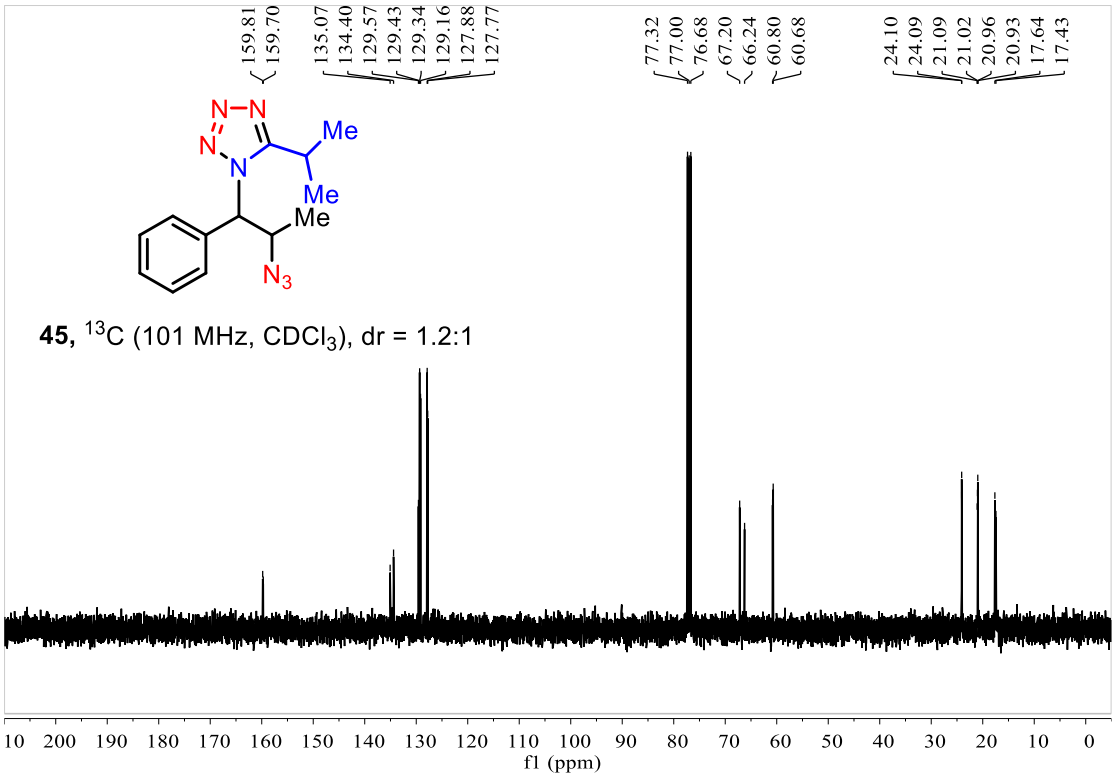


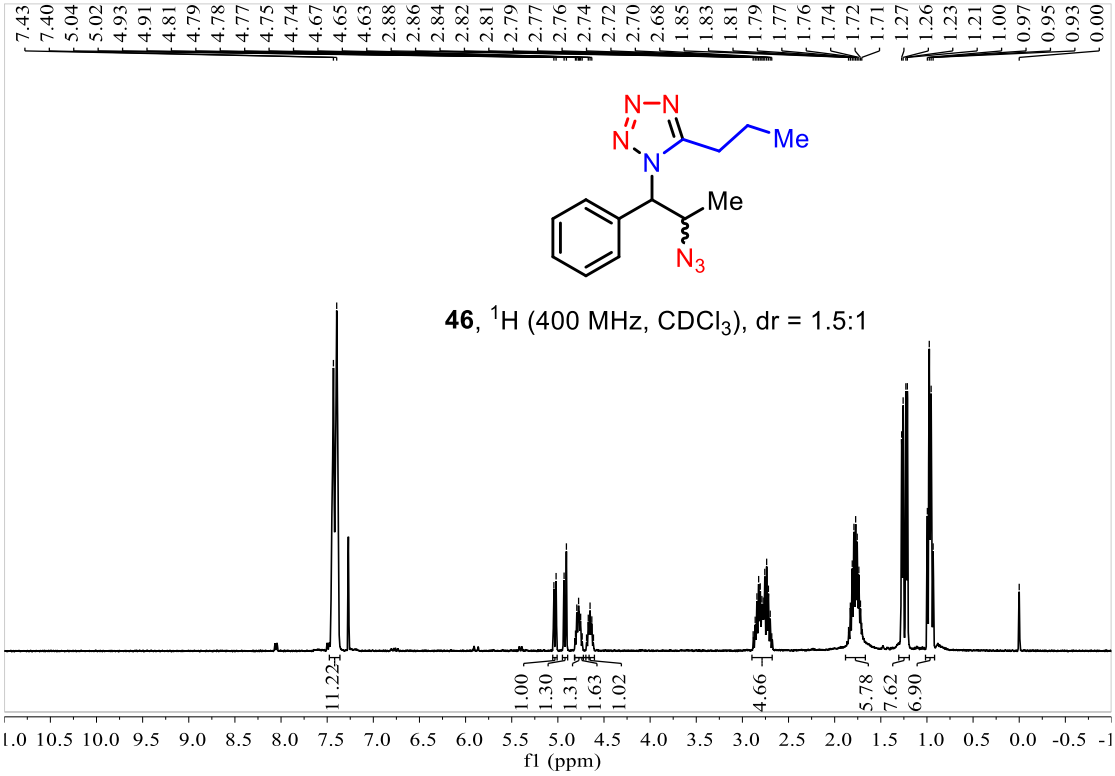
44, ^{1}H (500 MHz, $CDCl_3$)

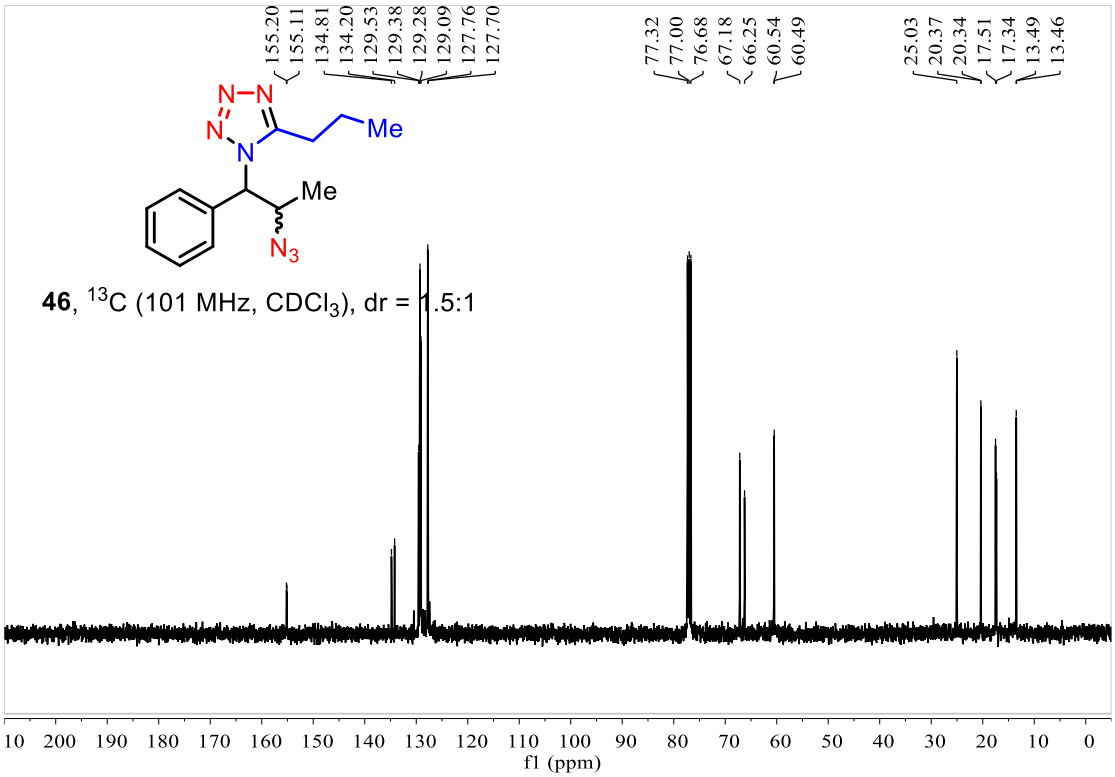


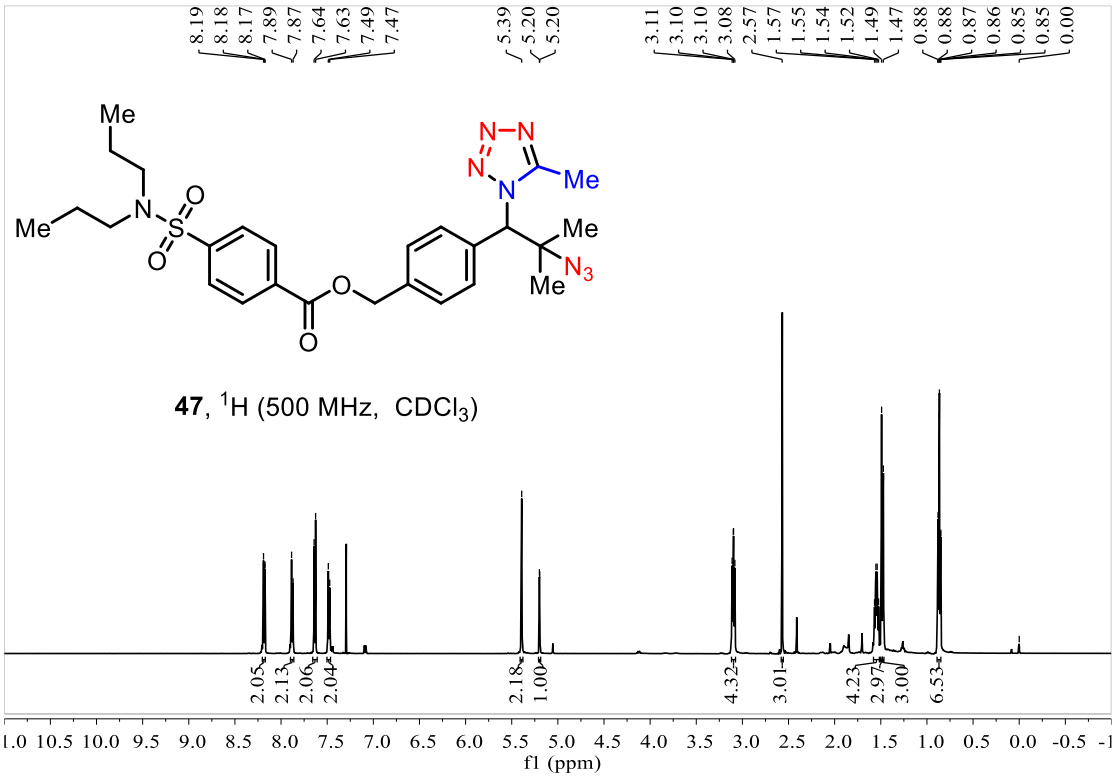
44, ^{13}C (126 MHz, $CDCl_3$)


7.48 7.47 7.46 7.41 7.39 5.11 5.08 5.00 4.97 4.81 4.80 4.78 4.76 4.74 4.68 4.67 4.65 4.63 4.61 3.19 3.17 3.16 3.14 3.12 3.10 1.49 1.48 1.46 1.44 1.25 1.23 1.21 1.20 1.18 -0.00
N–N
N
N
Me
Me
Me
N3
45, 1H (400 MHz, CDCl3), dr = 1.2:1
4.19 6.51 1.00 1.11 1.21 1.00 2.19 6.43 14.27
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

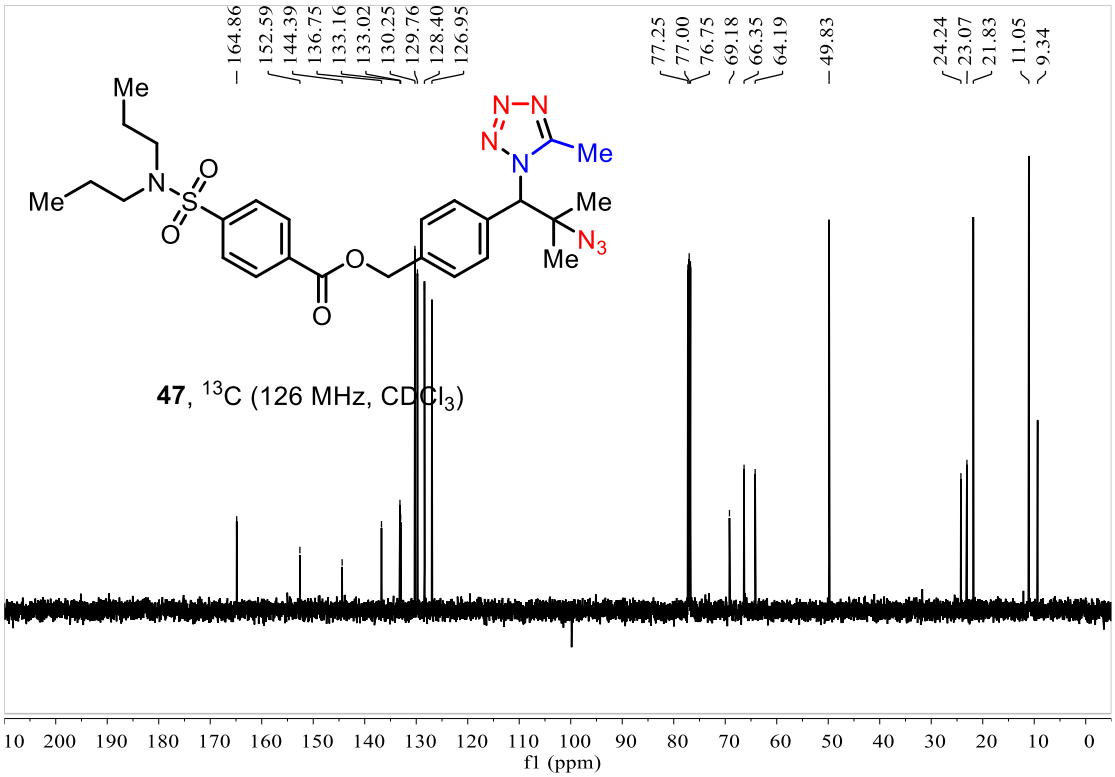

159.81 159.70 135.07 134.40 129.57 129.43 129.34 129.16 127.88 127.77 77.32 77.00 76.68 67.20 66.24 60.80 60.68 24.10 24.09 21.09 21.02 20.96 20.93 17.64 17.43
N–N
N
N
Me
Me
Me
N3
45, 13C (101 MHz, CDCl3), dr = 1.2:1
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.43 7.40 5.04 5.02 4.93 4.91 4.81 4.79 4.78 4.77 4.75 4.74 4.67 4.65 4.63 2.88 2.86 2.84 2.82 2.81 2.79 2.77 2.76 2.74 2.72 2.70 2.68 1.85 1.83 1.81 1.79 1.77 1.76 1.74 1.72 1.71 1.27 1.26 1.23 1.21 1.00 0.97 0.95 0.93 0.00
N–N
N
N
Me
Me
N3
46, 1H (400 MHz, CDCl3), dr = 1.5:1
11.22 1.00 1.30 1.31 1.63 1.02 4.66 5.78 7.62 6.90
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

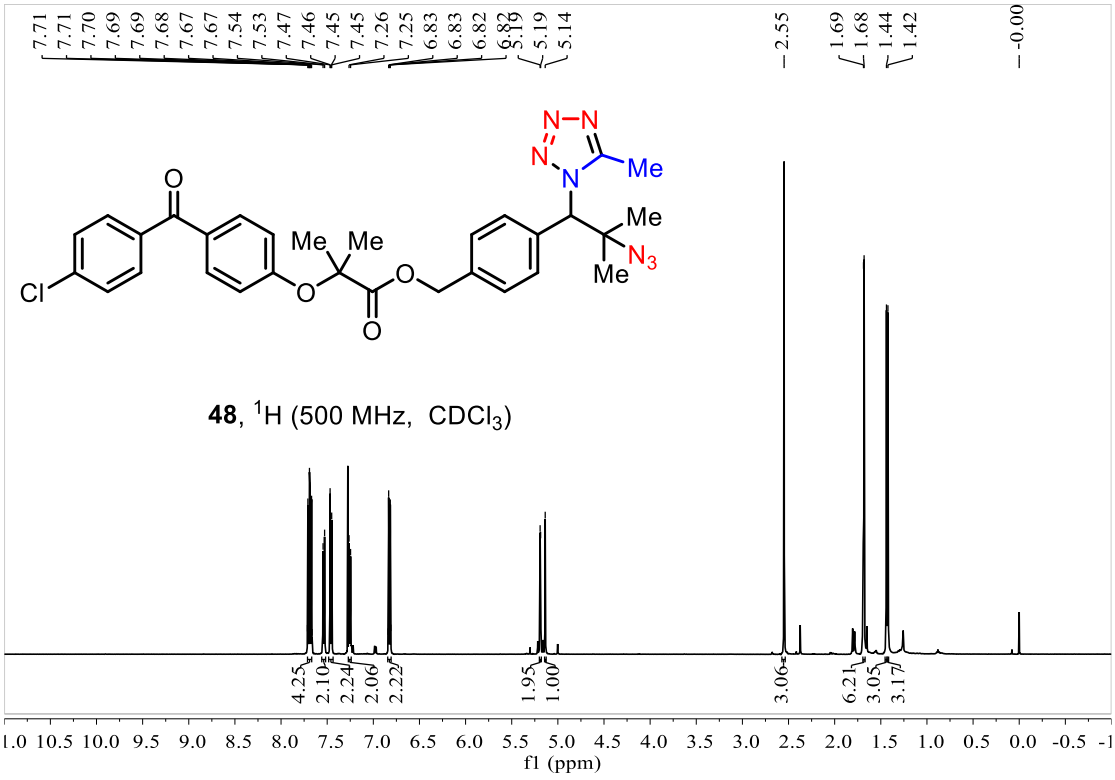

155.20 155.11 134.81 134.20 129.53 129.38 129.28 129.09 127.76 127.70
77.32 77.00 76.68 67.18 66.25 60.54 60.49
25.03 20.37 20.34 17.51 17.34 13.49 13.46
N–N
N
N
Me
Me
N3
46, 13C (101 MHz, CDCl3), dr = 1.5:1
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



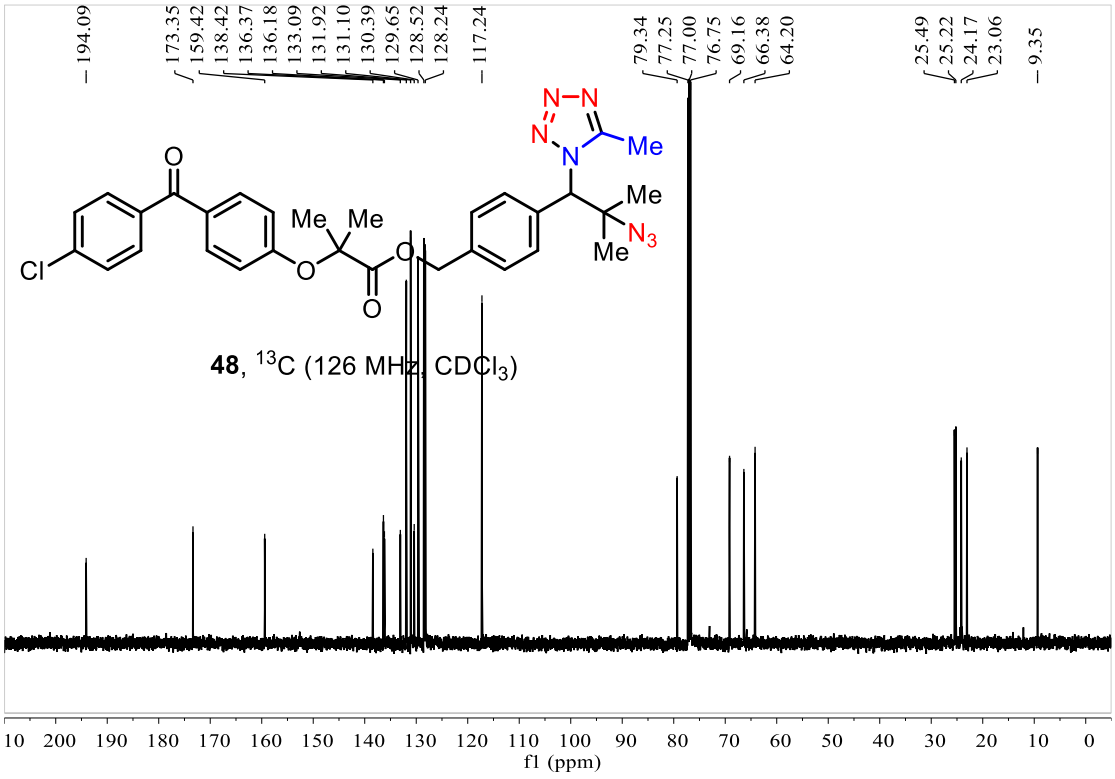
47, ^{1}H (500 MHz, $CDCl_3$)



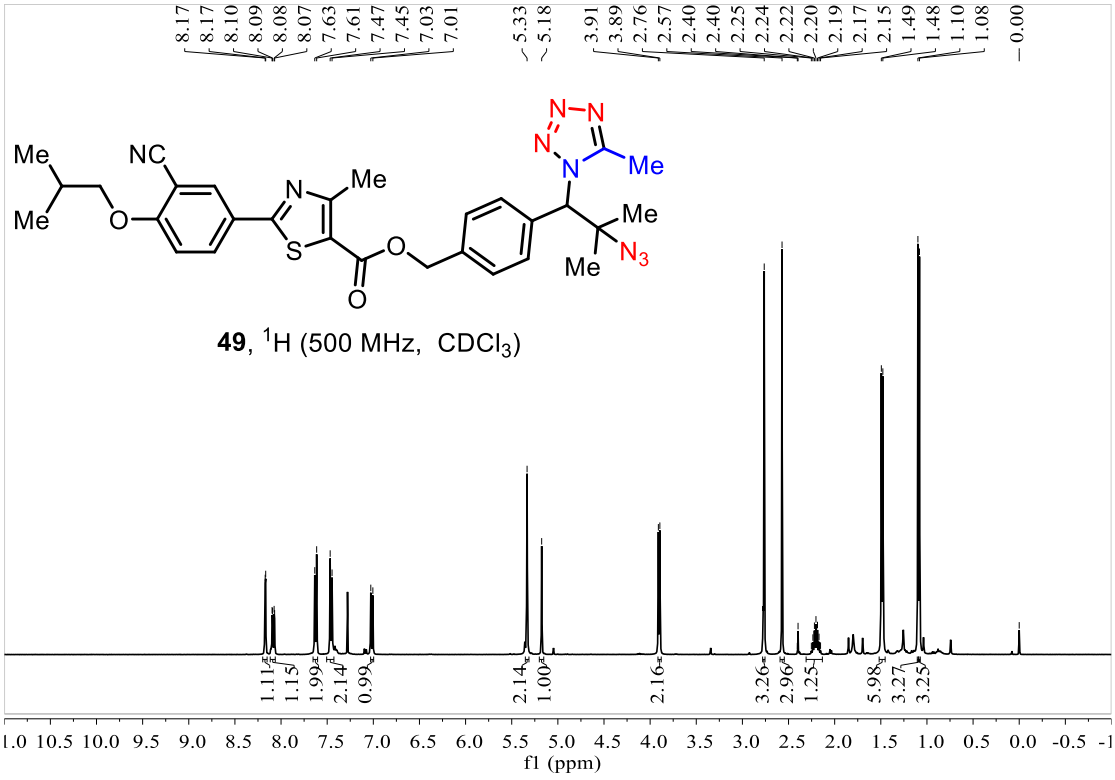
47, ^{13}C (126 MHz, $CDCl_3$)



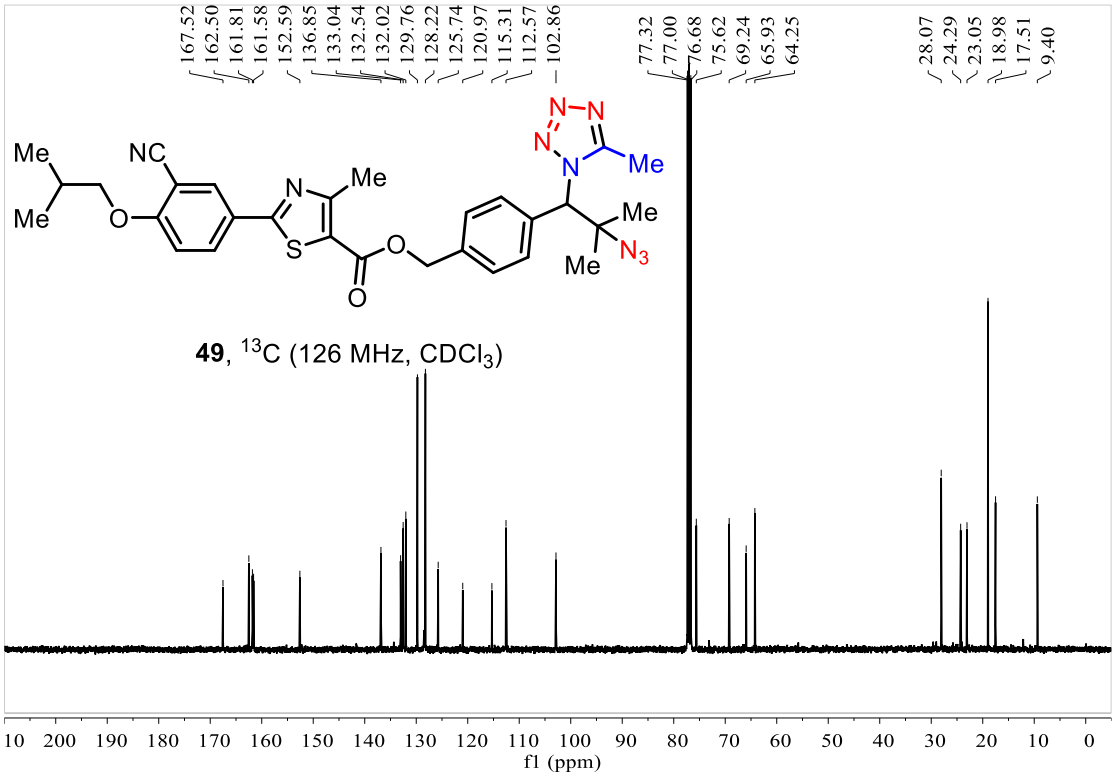
48, ^{1}H (500 MHz, $CDCl_3$)



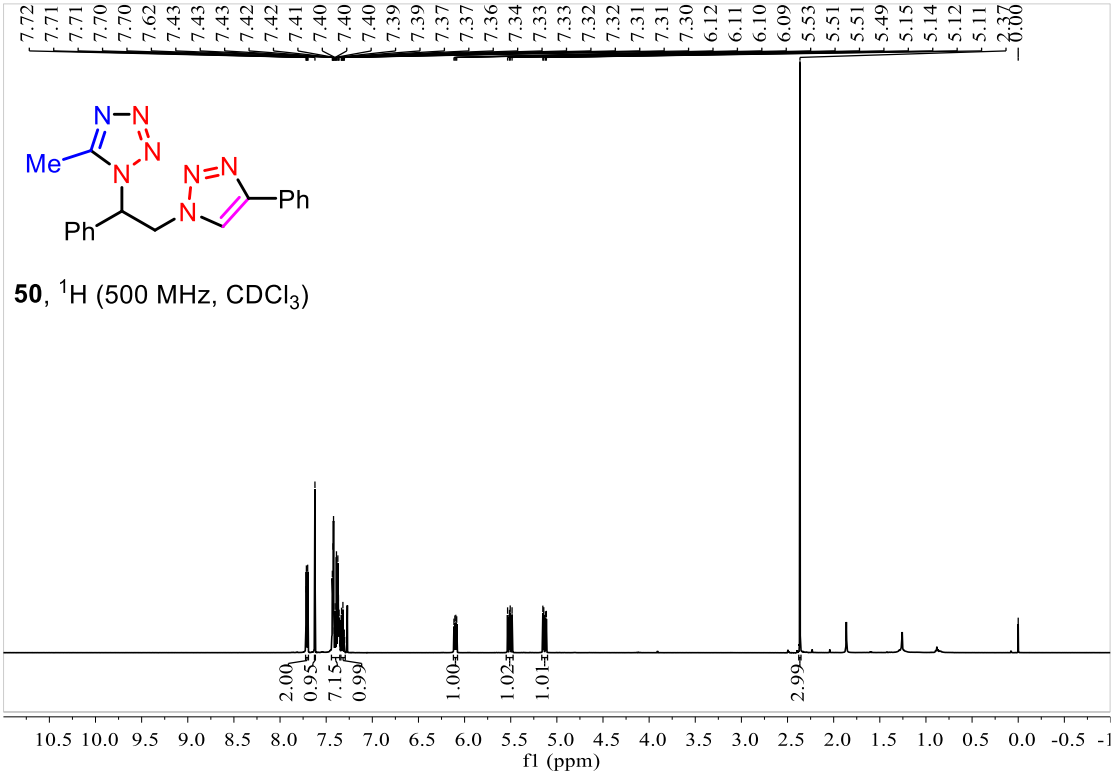
48, ^{13}C (126 MHz, $CDCl_3$)



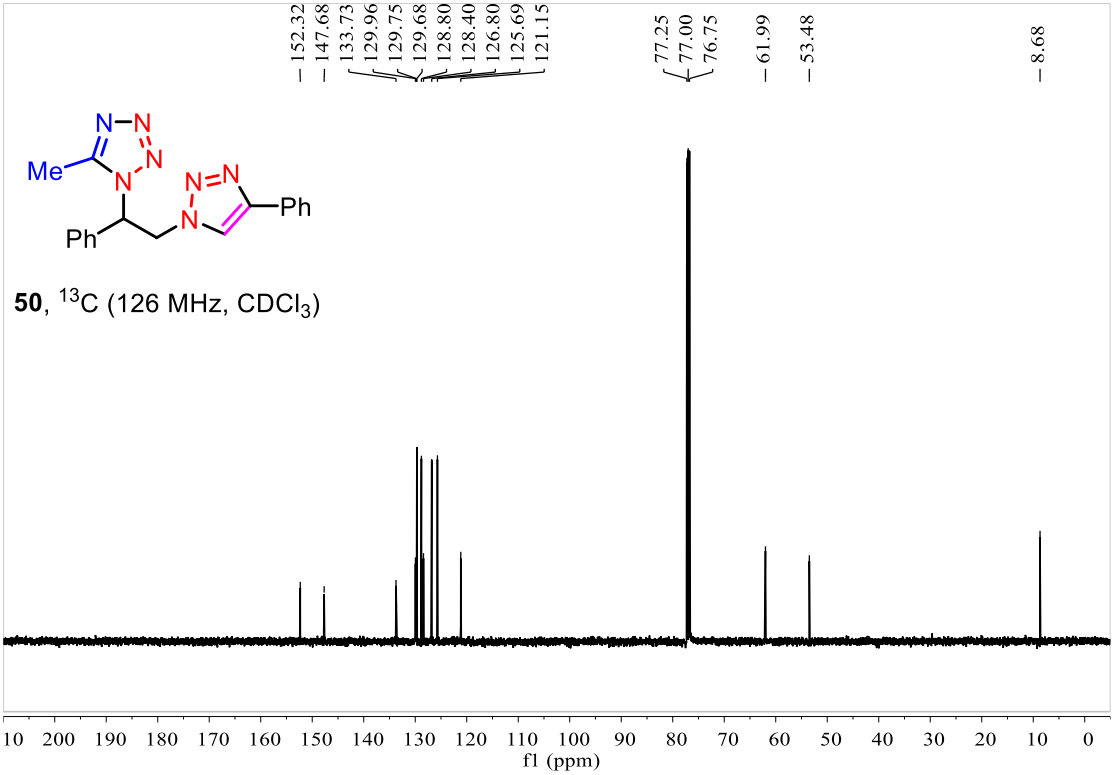
49, ^{1}H (500 MHz, $CDCl_3$)



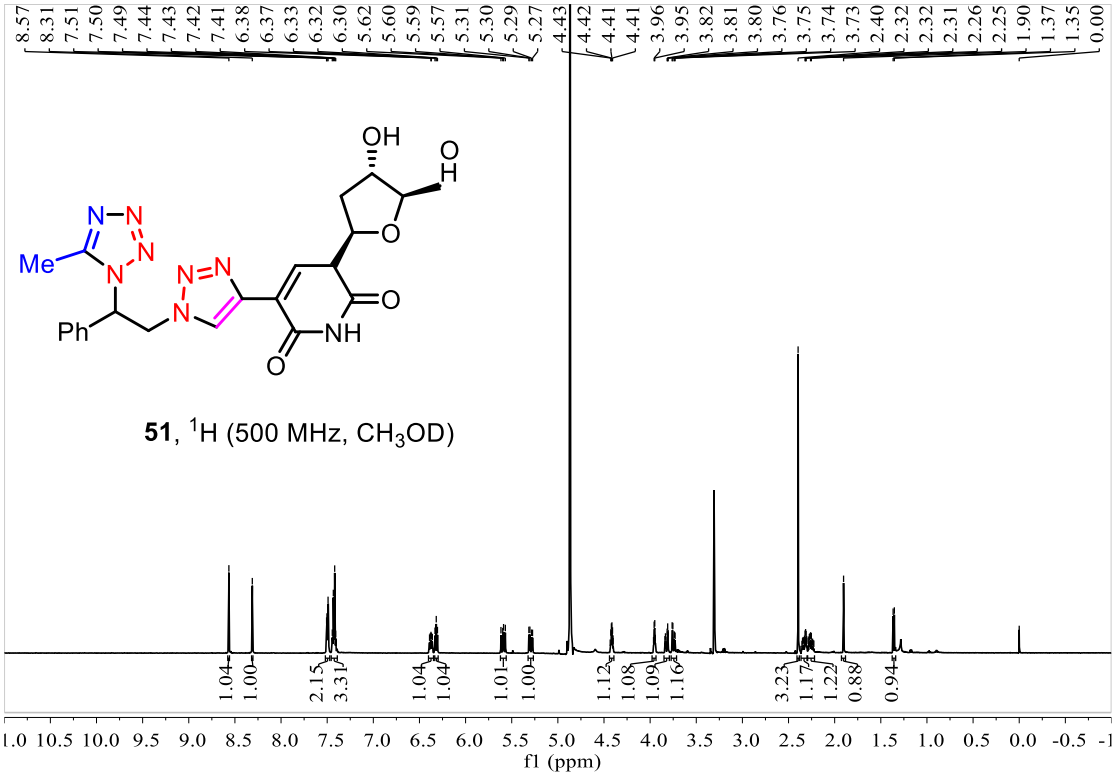
49, ^{13}C (126 MHz, $CDCl_3$)



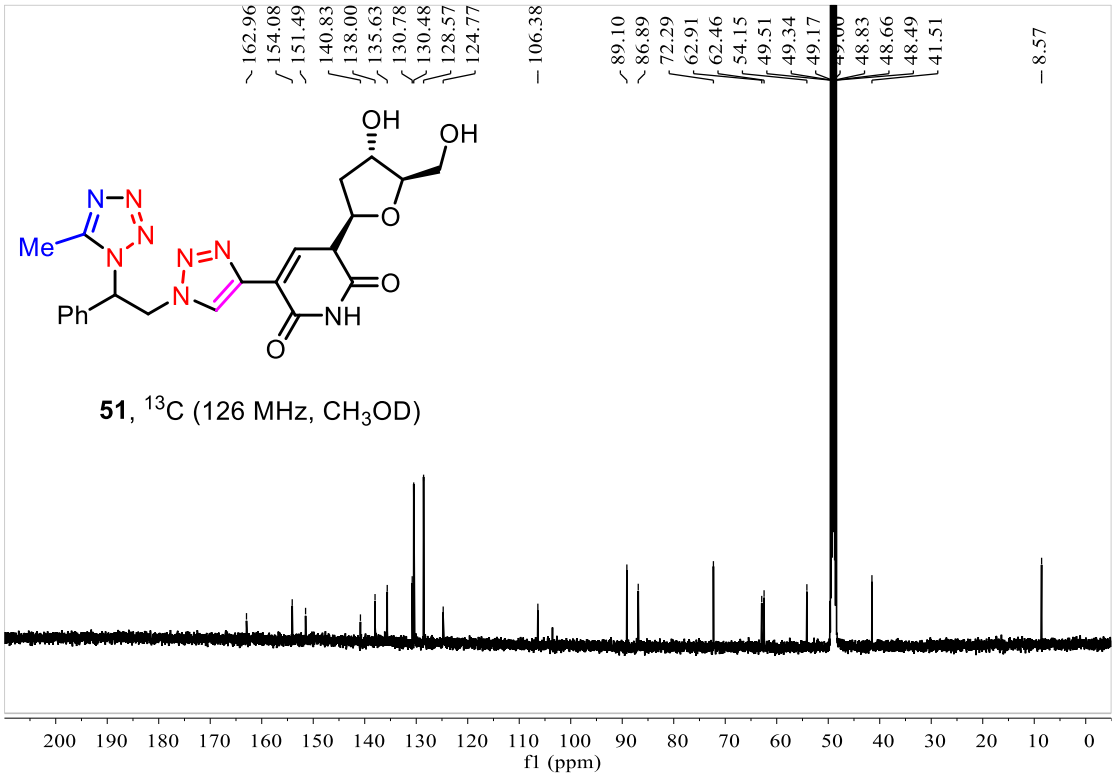
50, ^{1}H (500 MHz, $CDCl_3$)



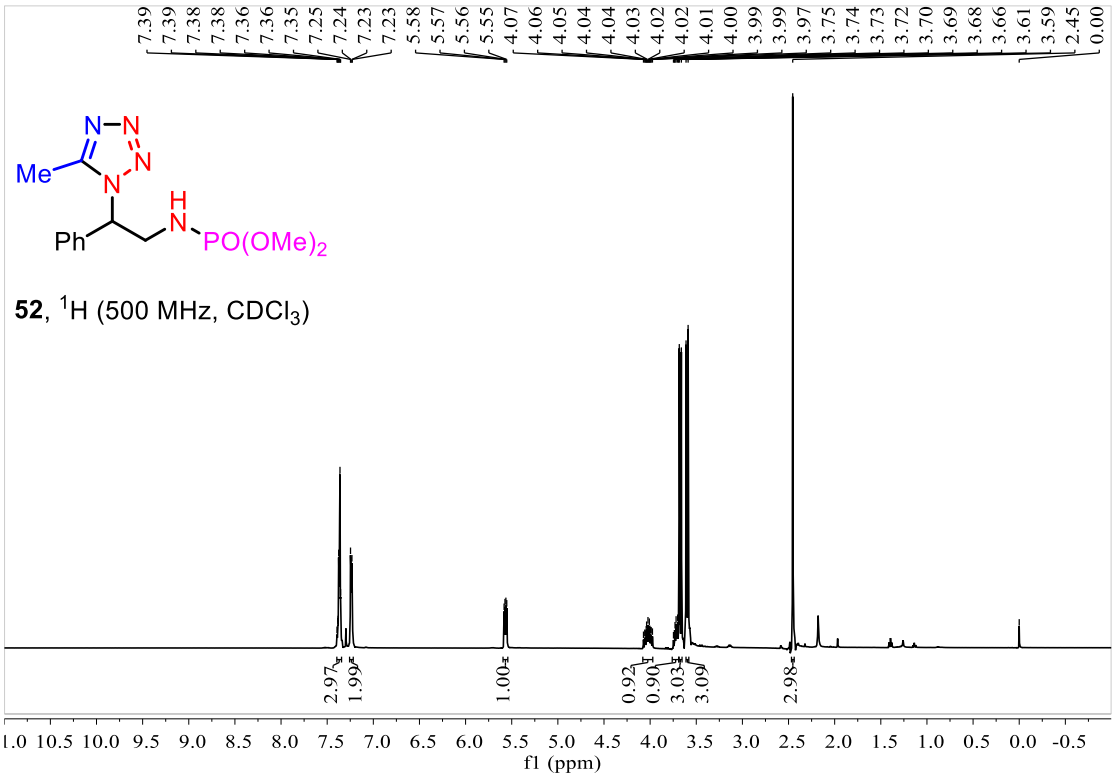
50, ^{13}C (126 MHz, $CDCl_3$)

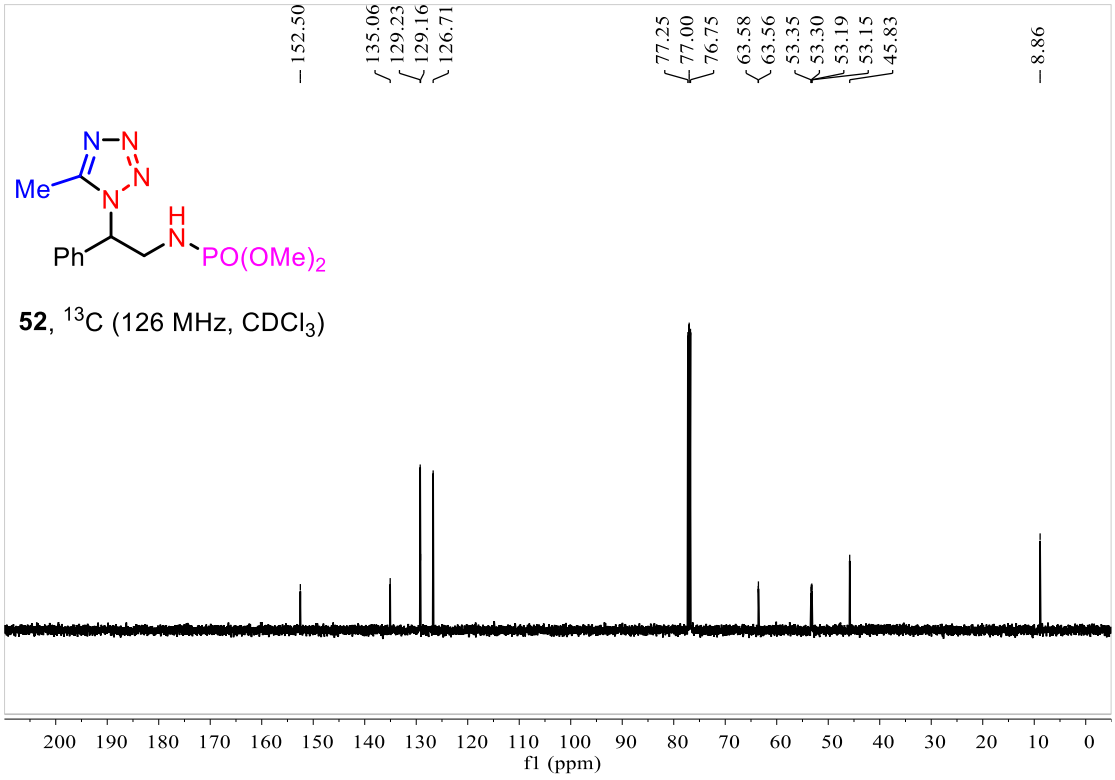


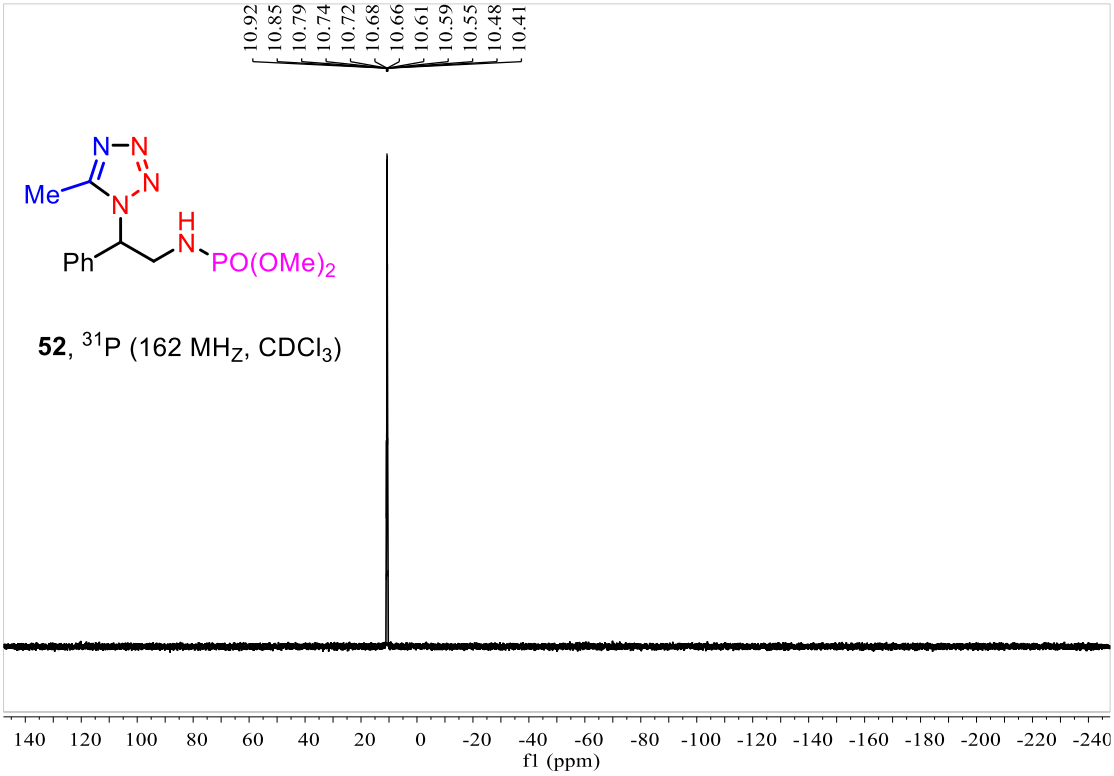
51, ^{1}H (500 MHz, CH_3OD)

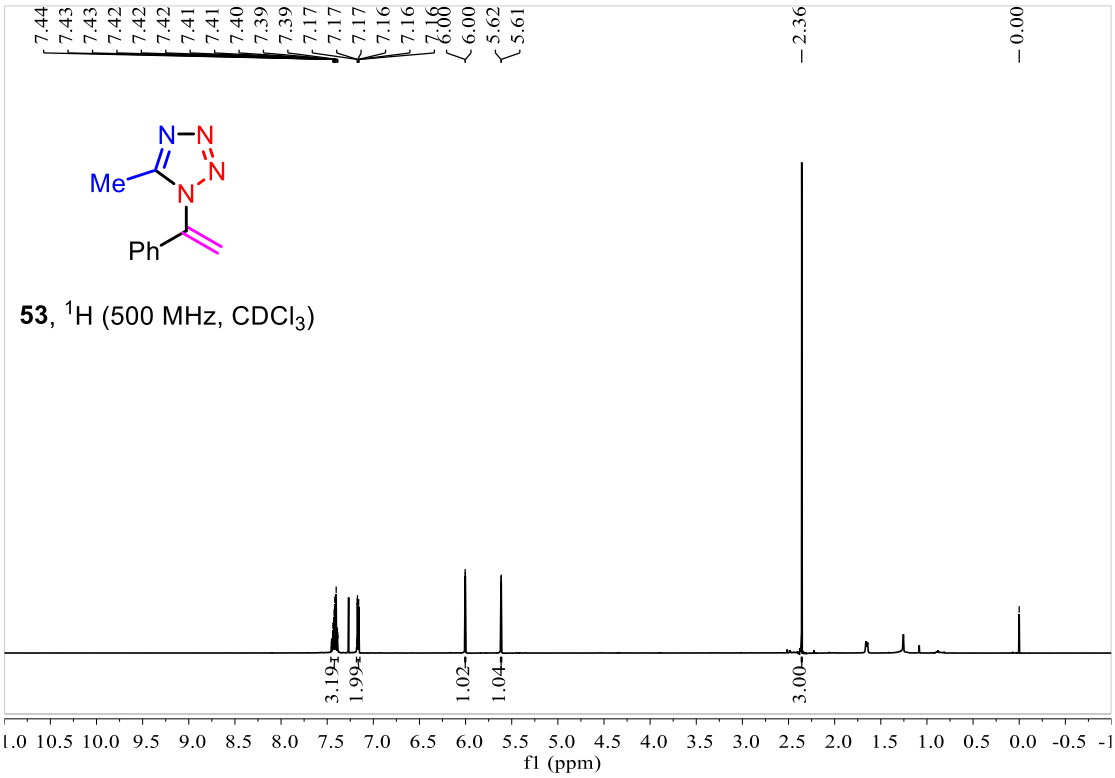


51, ^{13}C (126 MHz, CH_3OD)

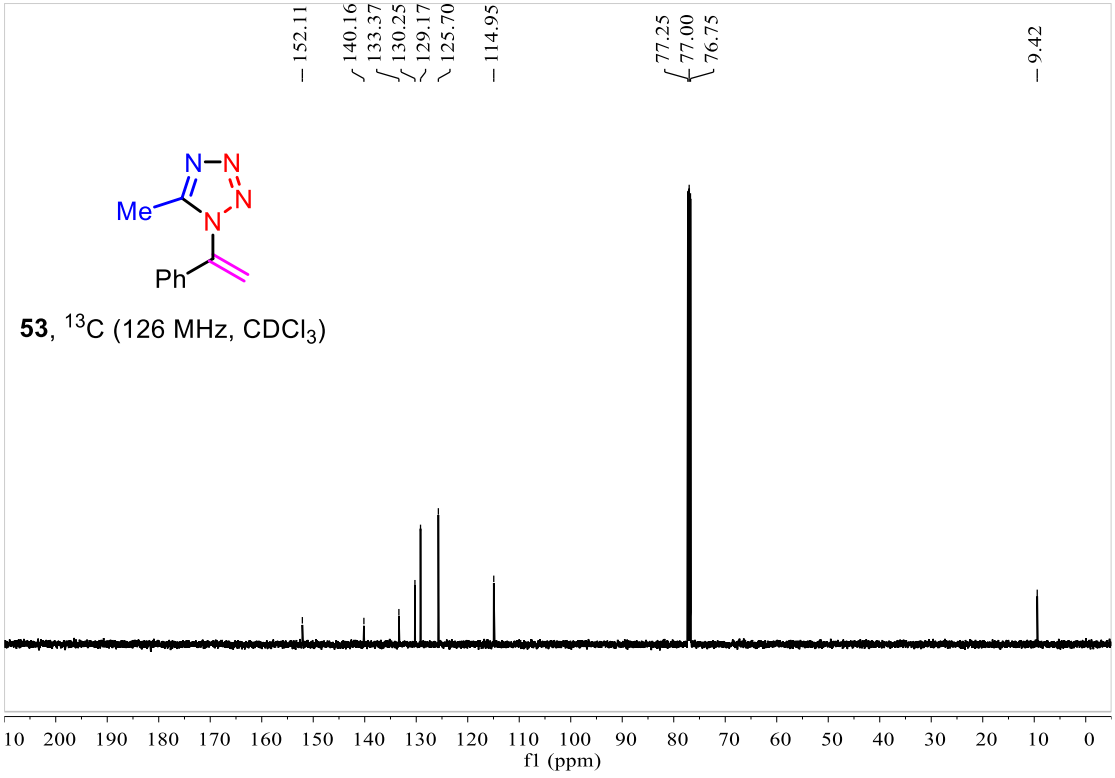

7.39 7.39 7.38 7.38 7.36 7.36 7.35 7.25 7.24 7.23 7.23 5.58 5.57 5.56 5.55 4.07 4.06 4.05 4.04 4.04 4.03 4.02 4.02 4.01 4.00 3.99 3.99 3.97 3.75 3.74 3.73 3.72 3.70 3.69 3.68 3.66 3.61 3.59 2.45 0.00
Me
Ph
PO(OMe)2
52, 1H (500 MHz, CDCl3)
2.97 1.99 1.00 0.92 0.90 3.03 3.09 2.98
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


152.50
135.06 129.23 129.16 126.71
77.25 77.00 76.75
63.58 63.56
53.35 53.30 53.19 53.15
45.83
8.86
Me
Ph
PO(OMe)2
52, 13C (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

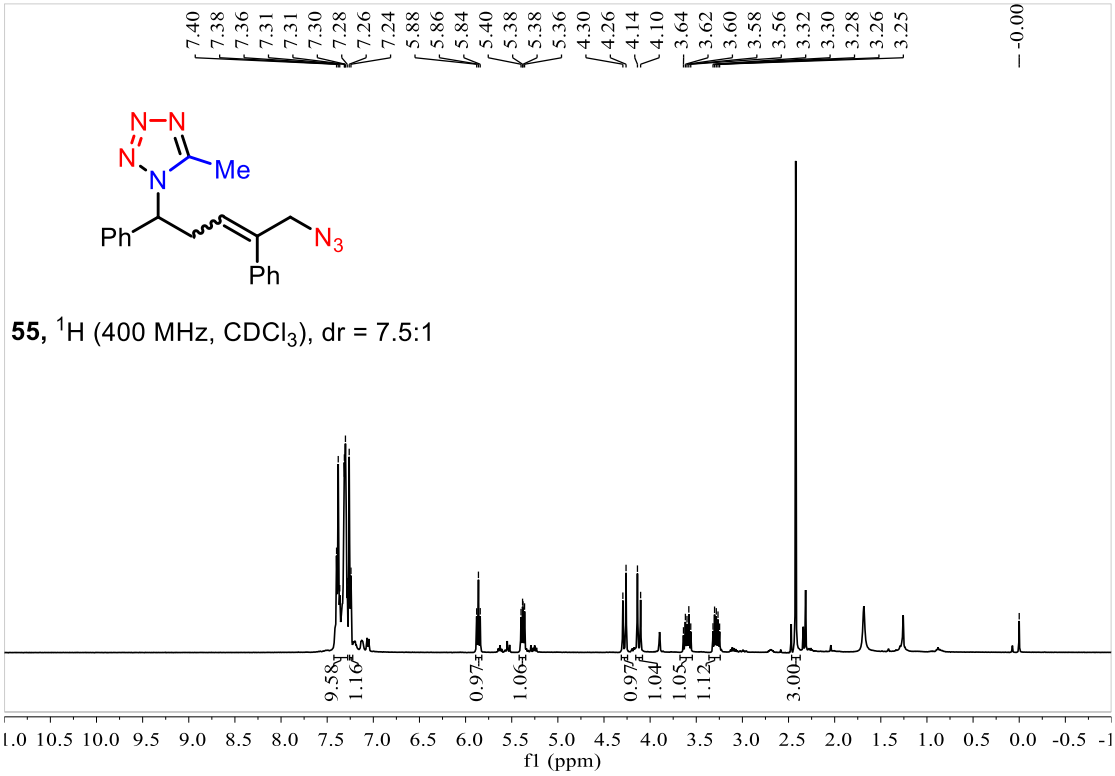

10.92
10.85
10.79
10.74
10.72
10.68
10.66
10.61
10.59
10.55
10.48
10.41
Me
Ph
PO(OMe)2
52, 31P (162 MHZ, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)



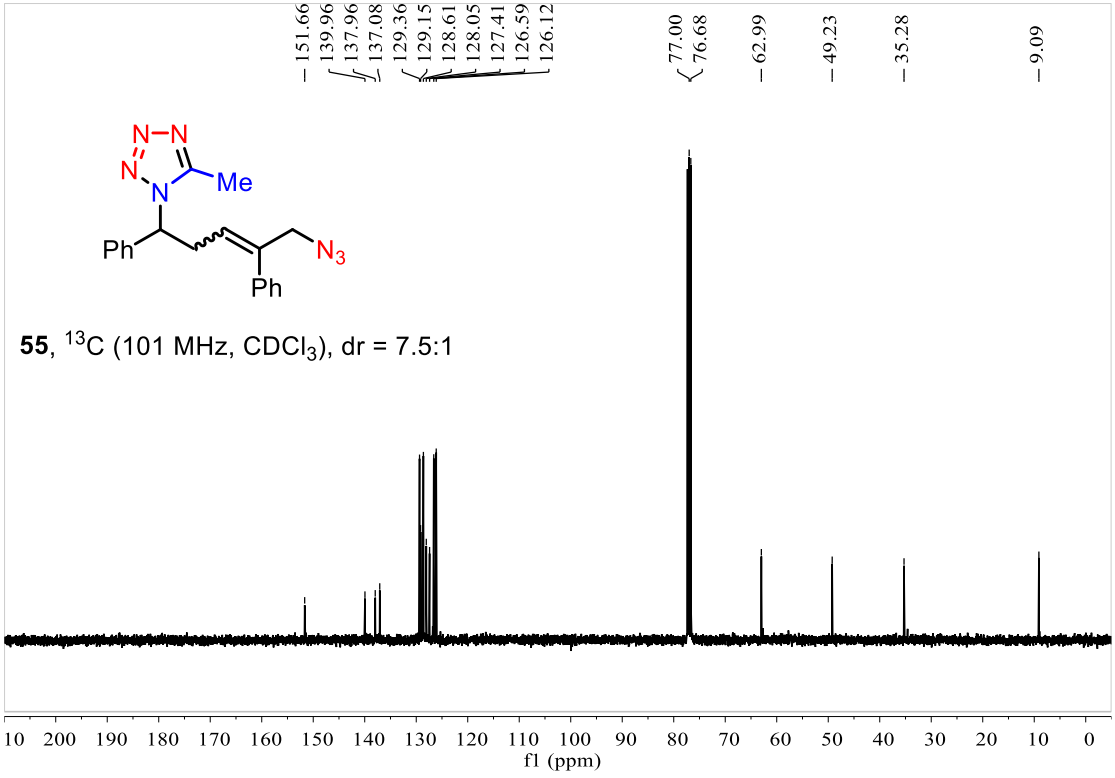
53, ^{1}H (500 MHz, $CDCl_3$)



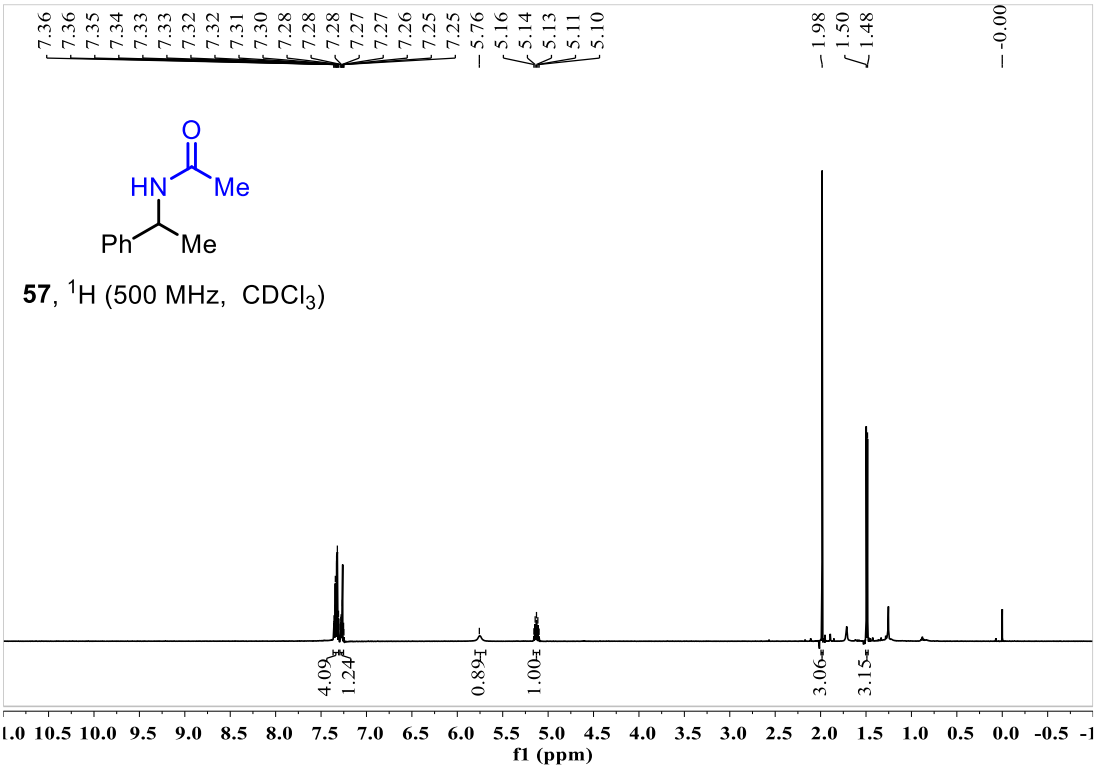
53, ^{13}C (126 MHz, $CDCl_3$)



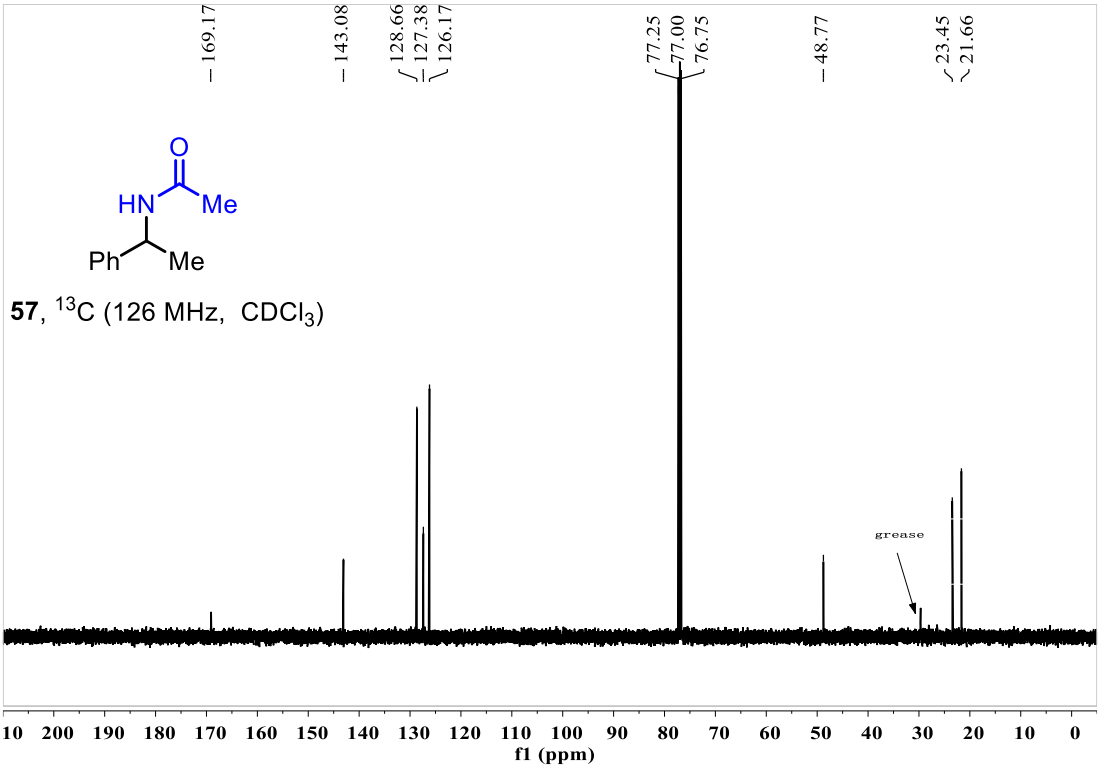
55, ^{1}H (400 MHz, $CDCl_3$), dr = 7.5:1



55, ^{13}C (101 MHz, $CDCl_3$), dr = 7.5:1



57, ^{1}H (500 MHz, $CDCl_3$)



57, ^{13}C (126 MHz, $CDCl_3$)