Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Materials for

Oxidation-induced C-H amination leads new avenue to build C-N bonds

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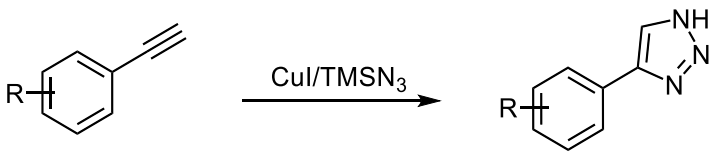
1. General Information

All manipulations were carried out by standard Schlenk techniques. Unless otherwise noted, analytical grade solvents and commercially available reagents were used to conduct the reactions. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is between 60-90°C). Gradient flash chromatography was conducted eluting with a continuous gradient using petroleum ether and ethyl acetate. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with tetramethylsilane as an internal standard. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ^{1}H), $CDCl_3$ (77.3 ppm for ^{13}C). High resolution mass spectra (HRMS) were measured with LTQ-Orbitrap Elite (Thermo-Fisher Scientific, Waltham, MA, USA) instrument and accurate masses were reported for the molecular ion + Hydrogen (M+H).

2. General Procedures for the synthesis of 4-substituted 1,2,3 –triazoles (*1*)

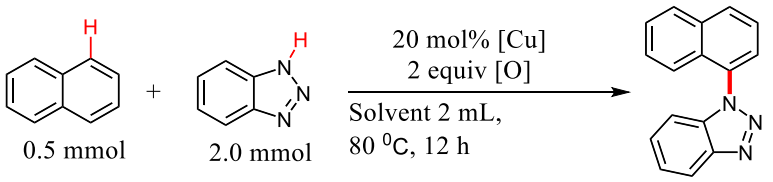


A mixture of phenylacetylene (10 mmol) , $TMSN_3$ (12 mmol) and 5 mol% CuI were stirred in 10 mL solvent (DMF/MeOH = 4/1) at 100℃ for 6 hours under N_2 atmosphere. After completion of the reaction, the mixture was extracted three times using ethyl acetate and brine, the organic layer was dried using Na_2SO_4, the target product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate.

3. Condition Screening

In a 25 mL schlenk tube, naphthalene (0.5 mmol), benzene azimide (2.0 mmol), 20 mol% Cu catalyst (0.1 mmol) and 2 equivalent oxidant were stirred in 2 mL solvent for 12 hours under N_2 atmosphere.

After completion of the reaction, the mixture was diluted by ethyl acetate. The yield was determined by GC.

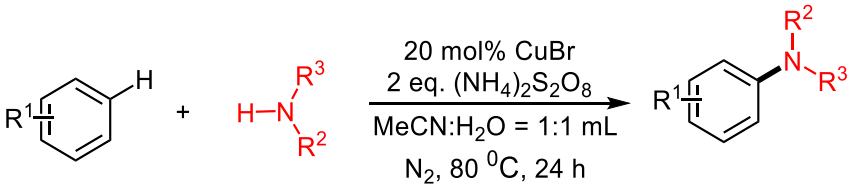


Entry	[Cu]	[O]	Solvent	Yield%[a]
1	$CuCl_2$	$Na_2S_2O_8$	MeCN/H_2O	63
2	$CuBr_2$	$Na_2S_2O_8$	MeCN/H_2O	65
3	$Cu(OTf)_2$	$Na_2S_2O_8$	MeCN/H_2O	76
4	$Cu(acac)_2$	$Na_2S_2O_8$	MeCN/H_2O	46
5	$Cu(OAc)_2$	$Na_2S_2O_8$	MeCN/H_2O	70
6	CuBr	$Na_2S_2O_8$	MeCN/H_2O	83[b]
7	CuBr	$K_2S_2O_8$	MeCN/H_2O	85
8	CuBr	$(NH_4)_2S_2O_8$	MeCN/H_2O	86(92[b])
9	CuBr	TBHP	MeCN/H_2O	1
10	CuBr	$PhI(OAc)_2$	MeCN/H_2O	4
11	CuBr	$(NH_4)_2S_2O_8$	MeCN	42
12	CuBr	$(NH_4)_2S_2O_8$	H_2O	36
13	CuBr	$(NH_4)_2S_2O_8$	DMF	4
14	CuBr	$(NH_4)_2S_2O_8$	DMSO	32
15	CuBr	$(NH_4)_2S_2O_8$	DCE	27
16	-	$Na_2S_2O_8$	MeCN/H_2O	43[b]
17	CuBr	-	MeCN/H_2O	n.d.
18[c]	CuBr	$Na_2S_2O_8$	MeCN/H_2O	n.d.

[a] GC yield, [b] isolated yield, [c] temperature is 25 °C. n.d. not decteted.

Table. S1. Conditions Screening

4. General Procedures for C-H/N-H cross-coupling reactions



In a 25 mL schlenk tube, aromatcs (0.5 mmol), azoles (2.0 mmol), 20 mol% CuBr and 2 equivalent $(NH_4)_2S_2O_8$ were stirred in 2 mL solvent (MeCN/H_2O = 1/1) for 12 hours under N_2 atmosphere. After completion of the reaction, as indicated by TLC and GC-MS, the mixture was diluted by ethyl acetate.

The pure product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate.

5. Calculation Details

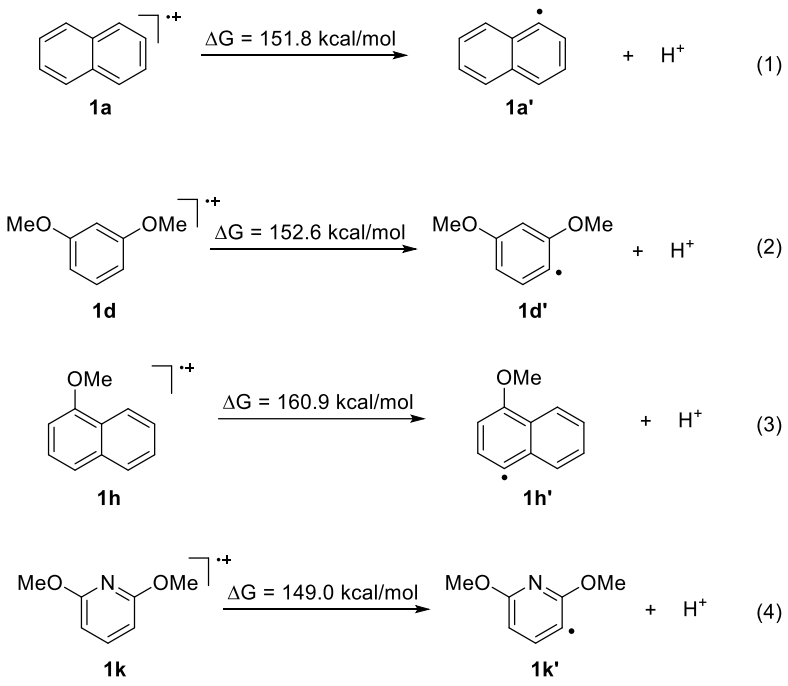
5.1 Complete reference for Gaussian 09

Gaussian 09, Revision A.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.

5.2 B3LYP absolute calculation energies, enthalpies, and free energies.

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs. B3LYP functional (*2*) with 6-31+G(d,p) basis set was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition structures and to derive the thermo chemical corrections for the enthalpies and free energies. The solvent effects were considered by single point calculations on the gas-phase stationary points with a SMD continuum solvation model (*3,4*). B3LYP with basis set 6-31+G(d,p) is used in the solvation single point calculations. The energies given below are the B3LYP calculated Gibbs free energies in water.

The reaction energies for the deprotonation of radical cation **1a**, **1d**, **1j** and**1m** are shown in Eq. 1~4, respectively. Obviously, these free energies are too high that the deprotonation of radical cation could not occur in this work.



Energy of lose one proton of radical cation.

Geometry	$E_{(elec)}$	$E_{(water)}$	$\Delta H_{(gas\ phase)}$	$\Delta G_{(gas\ phase)}$	IF*
1a	-500.171985	-500.247016	0.190787	0.144717	-
1d	-461.033656	-461.113699	0.175594	0.129081	-
1h	-477.070765	-477.163246	0.163904	0.117638	-
1k	-385.624459	-385.704740	0.155000	0.114917	-
H^+	0.000000	-0.215180	0.002360	-0.010000	-
1a'	-499.749093	-499.752607	0.177466	0.131865	-
1d'	-460.628458	-460.632966	0.162773	0.116728	-
1h'	-476.675724	-476.688737	0.151269	0.105819	-
1k'	-385.222918	-385.225250	0.142145	0.102539	-

* IF: The imaginary frequencies for the transition states.

5.3 B3LYP geometries for all the optimized compounds and transition states.

1a **1h**

C	3.04888800	-0.61351500	-0.00001800	C	1.13843800	-0.24029700	-0.00014800

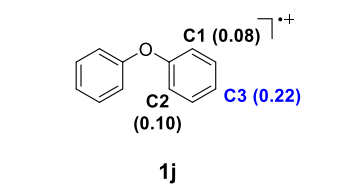
C	2.49572700	0.66620800	-0.00002300	C	1.19923900	1.21434400	-0.00060700
C	1.08953600	0.84613300	-0.00000400	C	-0.00003100	1.91786900	0.00001700
C	0.24267600	-0.30826500	0.00002000	C	-1.19926100	1.21428300	0.00062400
C	0.81839000	-1.58801800	0.00001700	C	-1.13839700	-0.24036400	0.00014100
C	2.21275400	-1.73605300	0.00000200	N	0.00002200	-0.91901200	-0.00003100
H	1.15616800	3.01163000	-0.00003700	H	-0.00004700	3.00287400	0.00001900
H	4.12681800	-0.73784600	-0.00002900	H	2.14975700	1.73393400	-0.00139000
H	3.14030100	1.54039800	-0.00003700	H	-2.14980400	1.73381100	0.00143400
C	0.51167200	2.13747600	-0.00001000	O	-2.21486800	-0.98900800	-0.00023300
C	-1.18931700	-0.10859300	0.00004200	O	2.21485500	-0.98893800	0.00039600
H	0.18016700	-2.46458000	0.00003100	C	-3.56129900	-0.44539100	-0.00015900
H	2.64256500	-2.73262300	0.00000200	H	-4.20707700	-1.32074800	-0.00046000
C	-1.73324600	1.20453300	0.00002700	H	-3.72938800	0.14415000	0.90420200
C	-0.88738400	2.30194800	0.00000500	H	-3.72931500	0.14467800	-0.90417500
H	-2.80644600	1.35033200	0.00003800	C	3.56131000	-0.44542700	0.00002600
H	-1.30885800	3.30195600	-0.00000100	H	4.20699900	-1.32085600	0.00122500
O	-1.92436500	-1.20254900	0.00004600	H	3.72953200	0.14327600	-0.90484800
C	-3.37396200	-1.15768400	-0.00006900	H	3.72929400	0.14543500	0.90353600
H	-3.73291000	-0.65679800	-0.90229700				
H	-3.68428300	-2.20039300	-0.00003800	**1k**			
H	-3.73302500	-0.65671100	0.90206600	C	2.45476800	-0.69666800	0.00000000
1d				C	1.23755100	-1.40353800	-0.00000100
C	1.20636500	1.20151700	0.00020200	C	0.00000500	-0.71655500	0.00000000
C	1.20296500	-0.25141500	-0.00010100	C	0.00000200	0.71655300	0.00000000
C	0.00001000	-0.95625100	-0.00017000	C	1.23754500	1.40354000	-0.00000100
C	-1.20290900	-0.25123500	-0.00034400	C	2.45476500	0.69667100	0.00000000
C	-1.20633700	1.20181000	-0.00041800	H	-1.24429700	-2.49008000	0.00000100
C	-0.00001000	1.89507100	-0.00000500	H	3.39262500	-1.24264100	0.00000100
H	2.14464300	1.74358700	0.00071400	H	1.24430100	-2.49007200	0.00000000
H	0.00001000	-2.03990700	-0.00021400	C	-1.23754100	-1.40354400	0.00000100
H	-2.14472200	1.74367800	-0.00073300	C	-1.23754700	1.40354300	0.00000000

H	0.00025300	2.97970400	0.00020100	H	1.24429800	2.49007400	-0.00000100
O	-2.31300900	-0.96772000	-0.00000800	H	3.39261900	1.24265000	0.00000100
O	2.31312900	-0.96799500	-0.00017500	C	-2.45477400	0.69667200	0.00000000
C	3.63378700	-0.37083400	0.00023000	C	-2.45477100	-0.69667500	0.00000000
H	3.77946200	0.22556200	0.90436200	H	-1.24429800	2.49008000	0.00000000
H	4.31775200	-1.21696800	-0.00130300	H	-3.39263600	1.24264800	0.00000000
H	3.77918000	0.22843700	-0.90200400	H	-3.39262900	-1.24265600	0.00000100
C	-3.63398600	-0.37100800	0.00041600	**H^+**			
H	-4.31749400	-1.21752100	0.00166300	H	0.00000000	0.00000000	0.00000000
H	-3.77906200	0.22744500	0.90323400	H	-3.70927200	0.26725000	-0.89568700
H	-3.78030500	0.22577700	-0.90331500	**1h'**			
1a'				C	-1.19087000	-0.21907000	0.00011900
C	-3.06749000	-0.50894900	-0.00001000	C	-1.19181600	1.17355000	0.00002800
C	-2.50804400	0.75170800	-0.00000700	C	-0.02840200	1.90245000	-0.00001500
C	-1.09611400	0.91529200	-0.00000400	C	1.18972400	1.20308400	0.00000200
C	-0.25520400	-0.25310400	-0.00000300	C	1.11422500	-0.20234000	-0.00000200
C	-0.86535000	-1.53440300	-0.00000600	N	-0.03499500	-0.87905000	0.00006400
C	-2.24055500	-1.65875200	-0.00000900	H	-0.03624000	2.98959900	-0.00003700
H	-4.14780600	-0.62270100	-0.00001300	H	2.13221100	1.73550200	-0.00001100
H	-3.13339100	1.63923900	-0.00000800	O	2.20093700	-1.01590000	-0.00000500
C	-0.43740500	2.15673200	-0.00000100	O	-2.29801000	-0.98933800	-0.00000500
C	1.17143600	-0.07876800	0.00000000	C	3.49643300	-0.42590900	-0.00005500
H	-0.23019000	-2.41319100	-0.00000500	H	4.19888900	-1.25999500	-0.00005500
H	-2.69342800	-2.64607600	-0.00001100	H	3.65789000	0.18529100	-0.89678600
C	1.73967100	1.18256900	0.00000300	H	3.65794400	0.18533700	0.89663400
C	0.90592900	2.34353900	0.00000300	C	-3.55026400	-0.30035500	-0.00006000
H	2.81528500	1.31460800	0.00000500	H	-4.31455700	-1.07808800	-0.00022500
H	1.35906700	3.33092200	0.00000500	H	-3.65447000	0.32447100	0.89451000
O	1.88695600	-1.24381100	0.00000000	H	-3.65429800	0.32467800	-0.89450400
C	3.30637000	-1.17106000	0.00002500	**1k'**			
H	3.67897800	-0.65858300	0.89607500	C	2.45429400	-0.82232800	0.00000000

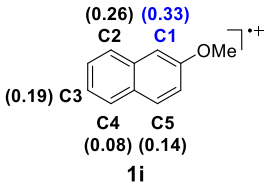
H	3.65735800	-2.20396200	0.00003300	C	1.22949400	-1.41243700	0.00000000
H	3.67901100	-0.65858700	-0.89601400	C	-0.01462400	-0.76391400	0.00000000

1d'

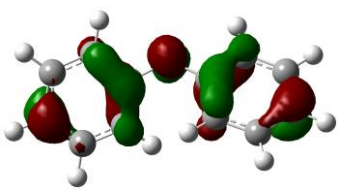
C	1.19535800	1.15467800	0.00000200	C	0.03547200	0.67890200	0.00000000
C	1.25407100	-0.23386400	-0.00003100	C	1.30421300	1.32633600	0.00000000
C	0.03296900	-0.92121700	-0.00005100	C	2.48031400	0.60598100	0.00000000
C	-1.17614400	-0.21204700	-0.00005400	H	-1.29983800	-2.50611100	0.00000100
C	-1.19262900	1.19293500	-0.00001600	H	3.37884700	-1.39270300	0.00000000
C	0.03225500	1.88573000	0.00001800	C	-1.27626400	-1.42060500	0.00000000
H	0.02357000	-2.00653500	-0.00006300	C	-1.19322300	1.39526200	0.00000000
H	-2.12076200	1.75141100	-0.00001800	H	1.33254100	2.41288200	-0.00000100
H	0.04262700	2.97239400	0.00005000	H	3.43804100	1.11988000	0.00000000
O	-2.30201000	-0.99044000	-0.00011700	C	-2.40150600	0.73083000	0.00000000
O	2.40055800	-0.96625300	-0.00003100	C	-2.44351400	-0.68723500	0.00000000
C	3.62153000	-0.22749800	0.00000500	H	-1.16390100	2.48224400	-0.00000100
H	3.69805100	0.40260900	0.89444900	H	-3.33014200	1.29438500	0.00000000
H	4.42128600	-0.96931900	-0.00020000	H	-3.40349100	-1.19533200	0.00000000
H	3.69790500	0.40294500	-0.89421200				
C	-3.57143000	-0.35178200	0.00019000				
H	-4.30874500	-1.15588800	0.00025000				
H	-3.70891900	0.26707300	0.89624400				



1j



1i



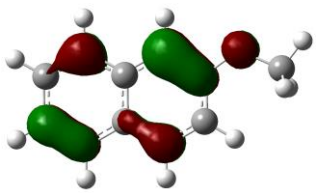


Figure S1. The Mulliken atomic spin densities (in parenthesis) and lowest unoccupied molecular orbitals (*β*-LUMOs) of radical cation species **1j** and **1i**.

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$G_{(corr\text{-}B3LYP)}$[2]	$H_{(corr\text{-}B3LYP)}$[3]	IF[4]
1j	-538.367496	0.147120	0.195125	-
1i	-500.273805	0.143492	0.189719	-

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [3]The thermal correction to enthalpy calculated by B3LYP in gas phase. [4] The B3LYP calculated imaginary frequencies.

3. B3LYP geometries for the optimized compounds.

1j

C	-3.77109500	0.60480200	0.08356600
C	-3.55127400	-0.67462500	-0.45126700
H	-2.89639600	2.31464400	1.06890100
C	-2.70628500	1.34947600	0.61602700
C	-2.27781200	-1.20756300	-0.46422100
C	-1.21001500	-0.43160600	0.03223700
C	-1.41977900	0.84395600	0.59663500
H	-2.06942400	-2.19191500	-0.86422100
H	-0.60353900	1.38463500	1.05671500
O	-0.00000500	-1.04503200	0.00003200
H	-4.38061000	-1.24656700	-0.84804800
H	-4.77460500	1.01226700	0.10829000

C	1.21001800	-0.43152600	-0.03212600
C	1.41972500	0.84399100	-0.59652100
C	2.27781700	-1.20751700	0.46422500
C	2.70628300	1.34946000	-0.61604600
H	0.60350200	1.38478100	-1.05649800
C	3.55131500	-0.67462400	0.45117000
H	2.06944500	-2.19189600	0.86416800
C	3.77111300	0.60478600	-0.08367300
H	2.89635000	2.31462100	-1.06895500
H	4.38063200	-1.24661500	0.84789000
H	4.77461300	1.01223500	-0.10853700

1i

C	-3.35857400	0.39850600	0.00001400
C	-2.26707900	1.28053700	0.00001400
C	-0.95991100	0.79196400	-0.00000600
C	-0.74621500	-0.62719700	-0.00001800
C	-1.87295800	-1.50053700	-0.00004100
C	-3.15975800	-0.98630200	-0.00001900
H	0.01171600	2.73111900	-0.00001200
H	-4.36553800	0.79842700	0.00003500
H	-2.44168700	2.35061600	0.00001800
C	0.17855000	1.65945600	-0.00000700
C	0.56006400	-1.11507800	0.00001200
H	-1.71010700	-2.57235400	-0.00007400
H	-4.01145500	-1.65499900	-0.00003300
C	1.67167300	-0.22184600	0.00005400
C	1.46417400	1.17806600	0.00000400
H	0.76669900	-2.17921000	-0.00005100
H	2.30113600	1.86180900	0.00001700
O	2.84813500	-0.81505100	0.00015200

C	4.07758400	-0.04959100	-0.00010700
H	4.13491000	0.56451900	0.90004800
H	4.86963800	-0.79230000	-0.00053600
H	4.13431600	0.56491300	-0.90003100

6. Mechanism Studies

6.1 Radical Inhibition Experiment

In a 25 mL schlenk tube, naphthalene (0.5 mmol), benzotriazole (2.0 mmol), 20 mol% CuBr, 2 equivalent TEMPO (1.0 mmol) and 2 equivalent $(NH_4)_2S_2O_8$ were stirred in 2 mL solvent ($MeCN/H_2O$ = 1/1) for 12 hours under N_2 atmosphere. Then the reaction mixture was monitored using GC-MS, no predicted product was detected.

6.2 KIE Experiment

In a 25 mL schlenk tube, naphthalene (0.25 mmol), naphthalene-d_8 (0.25 mmol), benzotriazole (2.0 mmol), 20 mol% CuBr and 2 equivalent $(NH_4)_2S_2O_8$ were stirred in 2 mL solvent ($MeCN/H_2O$ = 1/1) for 10 min under N_2 atmosphere, then the reaction mixture was quenched by 2 mL ethyl acetate, the target product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate. The ratio of common product and deuterated producted was obtained from GC-MS.

6.3 EPR Data Collection and Analysis

6.3.1 General Information

EPR spectra were recorded on a Bruker X-band A200 spectrometer. The sample was taken out into a thin small tube and then recorded by EPR spectrometer at indicated temperature and parameters.

6.3.2 Experimental Details

A dried Schlenk tube equipped with a stir bar was loaded with $CuBr_2$ (0.5 mmol, 111.5 mg), naphthalene (1.0 mmol, 128 mg) under the atmosphere of nitrogen at room temperature. After 30 mins, the solution sample was taken out into a small tube and then analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.387 GHz. Typical spectrometer parameters are shown as follows, scan range: 800 G; center field set: 3112 G; time

constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00 × 104; microwave power: 5.87 mW.

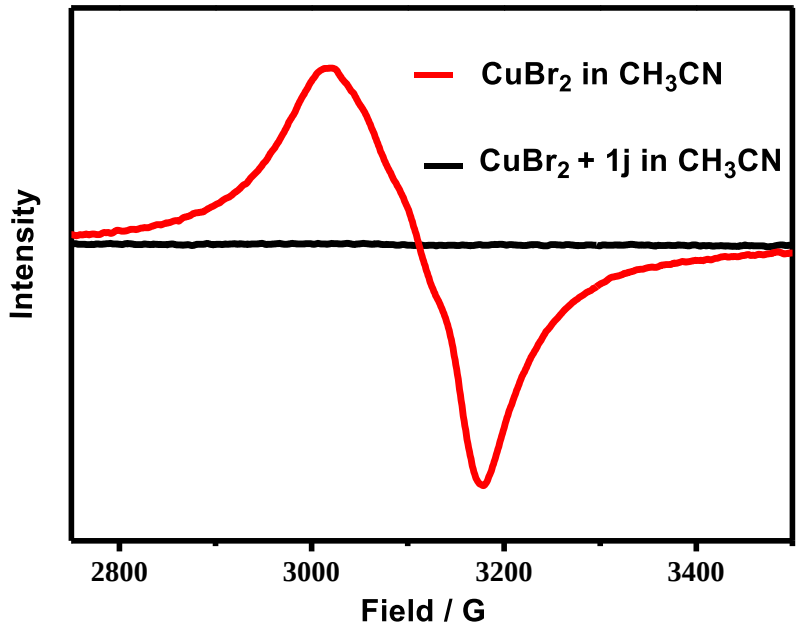


Figure S2 EPR evidence for single electron transfer between naphthalene and $CuBr_2$.

6.4 XANES and EXAFS Data Collection and Analysis

6.4.1 General Information

X-ray absorption measurements were acquired in transmission mode at beamline 17C11 at National Synchrotron Radiation Research Center (NSSRC) in Taiwan. A pure Cu foil spectrum (edge energy 8979 eV) was acquired simultaneously with each measurement for energy calibration. Multiple scans were taken to reduce the noise.

All solution samples were placed in a sample holder (the XAS solution cell) made of PEEK (polyether ether ketone) equipped with a screw top and O-ring fitting to prevent exposure to air and water (*5*). For solution samples, the Cu concentration was adjusted to be 0.05 - 0.1 M with a path

length of 3.5 mm. The sample holder was placed in a quartz tube (1–in. OD, 10–in. length) sealed with Kapton windows by two Ultra-Torr fittings and then used for transmission mode measurement.

The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point of the edge. The data procedures were carried out using the Athena software package using standard methods (*6*). Standard procedures based on Artemis software (Demeter 0.9.20) were used to extract the extended X-ray absorption fine structure (EXAFS) data.

7. Characterization of Products

7.1 Single Crystal Data

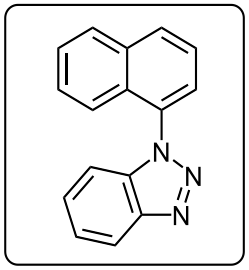
CCDC Number: 1486071

Bond length and Angles

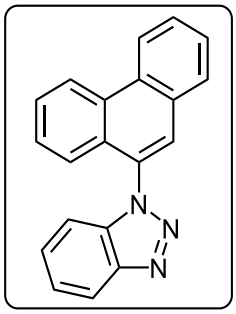
Number	Atom 1	Atom 2	Length	Number	Atom 1	Atom 2	Atom 3	Angle
1	C1	N1	1.438(2)	1	N1	C1	C2	119.9(1)
2	C1	C2	1.418(2)	2	N1	C1	C10	118.2(1)
3	C1	C10	1.362(2)	3	C2	C1	C10	121.9(1)
4	N1	N2	1.365(2)	4	C1	N1	N2	121.0(1)
5	N1	C11	1.362(2)	5	C1	N1	C11	128.7(1)
6	C2	C3	1.417(2)	6	N2	N1	C11	109.9(1)
7	C2	C7	1.421(2)	7	C1	C2	C3	123.8(1)
8	N2	N3	1.298(2)	8	C1	C2	C7	117.1(1)
9	C3	H3	0.99(1)	9	C3	C2	C7	119.1(1)
10	C3	C4	1.366(2)	10	N1	N2	N3	108.8(1)
11	N3	C16	1.378(2)	11	C2	C3	H3	118.1(8)
12	C4	H4	1.00(2)	12	C2	C3	C4	120.1(1)
13	C4	C5	1.403(2)	13	H3	C3	C4	121.8(8)
14	C5	H5	1.00(2)	14	N2	N3	C16	108.5(1)
15	C5	C6	1.355(2)	15	C3	C4	H4	119.8(9)
16	C6	H6	0.99(2)	16	C3	C4	C5	120.8(1)
17	C6	C7	1.419(2)	17	H4	C4	C5	119.4(9)
18	C7	C8	1.412(2)	18	C4	C5	H5	120.2(9)
19	C8	H8	0.94(2)	19	C4	C5	C6	120.6(1)
20	C8	C9	1.362(2)	20	H5	C5	C6	119.3(9)
21	C9	H9	0.94(2)	21	C5	C6	H6	121(1)
22	C9	C10	1.401(2)	22	C5	C6	C7	120.7(1)
23	C10	H10	0.96(2)	23	H6	C6	C7	118(1)

24	C11	C12	1.390(2)	24	C2	C7	C6	118.7(1)
25	C11	C16	1.391(2)	25	C2	C7	C8	119.8(1)
26	C12	H12	1.00(2)	26	C6	C7	C8	121.5(1)
27	C12	C13	1.370(2)	27	C7	C8	H8	117(1)
28	C13	H13	0.97(2)	28	C7	C8	C9	120.9(1)
29	C13	C14	1.402(3)	29	H8	C8	C9	122(1)
30	C14	H14	0.93(2)	30	C8	C9	H9	121(1)
31	C14	C15	1.359(3)	31	C8	C9	C10	120.0(2)
32	C15	H15	0.96(2)	32	H9	C9	C10	119(1)
33	C15	C16	1.402(2)	33	C1	C10	C9	120.3(1)
				34	C1	C10	H10	118.2(9)
				35	C9	C10	H10	121.5(9)
				36	N1	C11	C12	133.1(1)
				37	N1	C11	C16	104.3(1)
				38	C12	C11	C16	122.6(1)
				39	C11	C12	H12	120(1)
				40	C11	C12	C13	115.9(1)
				41	H12	C12	C13	124(1)
				42	C12	C13	H13	121(1)
				43	C12	C13	C14	122.1(2)
				44	H13	C13	C14	117(1)
				45	C13	C14	H14	116(1)
				46	C13	C14	C15	122.0(2)
				47	H14	C14	C15	122(1)
				48	C14	C15	H15	124(1)
				49	C14	C15	C16	116.9(2)
				50	H15	C15	C16	119(1)
				51	N3	C16	C11	108.5(1)
				52	N3	C16	C15	131.0(1)
				53	C11	C16	C15	120.5(1)

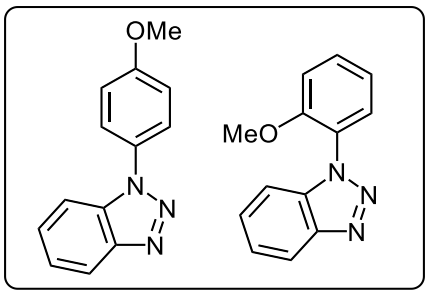
7.2 NMR Data and HRMS Data



1-(Naphthalen-1-yl)-1H-benzo[d][1,2,3]triazole (**3a**): 112.7 mg (yield: 92%, 0.5 mmol scale), light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 8.5 Hz, 1H), 8.07-8.05 (m, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.57-7.55 (m, 1H), 7.42-7.47 (m, 4H), 7.33 – 7.26 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.8, 134.8, 134.5, 132.7, 130.6, 129.2, 128.5, 128.3, 127.8, 127.2, 125.4, 124.7, 124.5, 122.8, 120.2, 110.5. HRMS: Calculated for $(M+H)^+$: 246.1026; found: 246.1022.

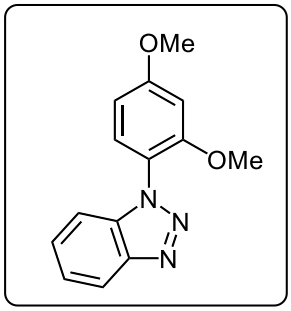


1-(Phenanthren-9-yl)-1H-benzo[d][1,2,3]triazole (**3b**): 62.3 mg (yield: 42%, 0.5 mmol scale), white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.00 (d, *J* = 8.4 Hz, 1H), 8.95 (d, *J* = 8.3 Hz, 1H), 8.31 – 8.19 (m, 2H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.85 – 7.68 (m, 3H), 7.61 – 7.41 (m, 4H), 7.16 (d, *J* = 8.2 Hz, 1H).^{13}C NMR (101 MHz, DMSO-d_6) δ = 145.0, 134.5, 130.9, 130.5, 130.4, 130.3, 129.5, 128.8, 128.1, 128.0, 127.8, 127.5, 126.3, 124.7, 123.8, 123.3, 122.8, 119.7, 110.6. HRMS: Calculated for $(M+H)^+$: 296.1182, found: 296.1179.

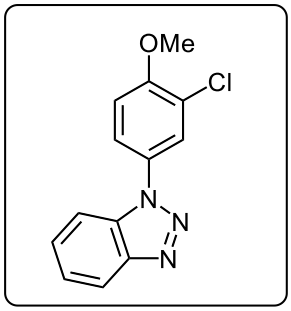


1-(4-Methoxyphenyl)-1H-benzo[d][1,2,3]triazole (**3c**)**:** 63.5 mg (yield: 56%, 0.5 mmol scale), light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 8.3 Hz, 1.4H), 7.65 – 7.62 (m, 3H), 7.54 –

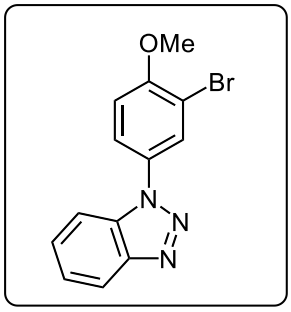
7.46 (m, 2H), 7.44 (d, *J* = 4.7 Hz, 0.5H), 7.41 – 7.31 (m, 2H), 7.14-7.11 (m, 1H), 7.09 – 7.07 (m, 1.8H), 3.86 (s, 3H), 3.76 (s, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.8, 153.7, 146.3, 145.7, 134.1, 132.6, 131.1, 130.0, 128.2, 128.1, 127.6, 125.3, 124.6, 124.3, 123.9, 121.1, 120.2, 119.9, 115.0, 112.4, 111.3, 110.3, 55.8, 55.7. HRMS: Calculated for $(M+H)^+$: 226.0975, found: 226.0973.



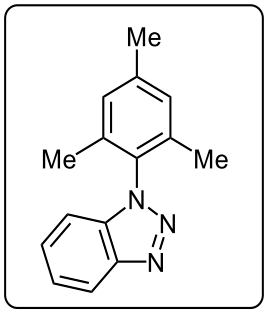
1-(2,4-Dimethoxyphenyl)-1H-benzo[d][1,2,3]triazole (**3d**): 92.4 mg (yield: 72%, 0.5 mmol scale), light white liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.8 Hz, 1H), 7.37 (m, 4H), 6.74 – 6.50 (m, 2H), 3.87 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.9, 155.0, 145.5, 134.3, 128.9, 127.5, 123.8, 119.7, 118.3, 111.0, 104.8, 99.6, 55.8, 55.8. HRMS: Calculated for $(M+H)^+$: 256.1081, found: 256.1074.



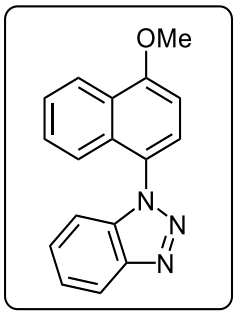
1-(3-Chloro-4-methoxyphenyl)-1H-benzo[d][1,2,3]triazole (**3e**): 46.5 mg (yield: 36%, 0.5 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 2.6 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.43 – 7.39 (m, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.3, 146.3, 132.4, 130.2, 128.5, 125.1, 124.5, 123.6, 122.5, 120.4, 112.5, 110.1,56.6. HRMS: Calculated for $(M+H)^+$: 260.0585, found: 260.0583.



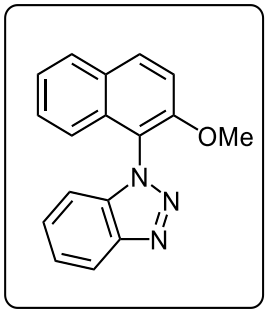
1-(3-Bromo-4-methoxyphenyl)-1H-benzo[d][1,2,3]triazole (**3f**): 61.2 mg (yield: 40%, 0.5 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 2.6 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.55 (m, 1H), 7.43 (m, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.3, 146.4, 132.4, 130.5, 128.5, 128.2, 124.6, 123.4, 120.4, 112.5, 112.3, 110.1, 56.8. HRMS: Calculated for $(M+H)^+$: 304.0080, found: 304.0077.



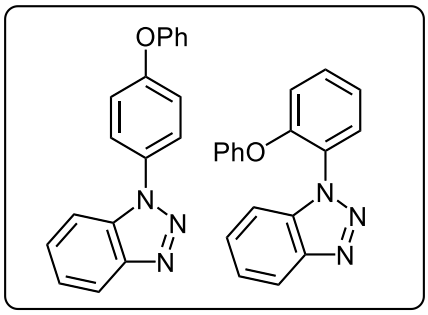
1-Mesityl-1H-benzo[d][1,2,3]triazole (**3g**): 92.1 mg (yield: 78%, 0,5 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.40 – 7.34 (m, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.03 (s, 2H), 2.36 (s, 3H), 1.83 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.4, 140.2, 136.1, 133.8, 131.6, 129.3, 128.0, 124.0, 120.0, 109.8, 21.2, 17.4. HRMS: Calculated for $(M+H)^+$: 238.1339, found: 238.1337.



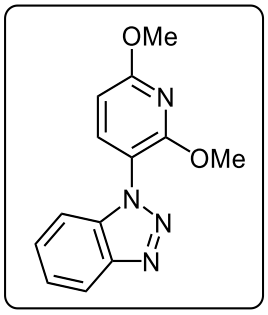
1-(4-Methoxynaphthalen-1-yl)-1H-benzo[d][1,2,3]triazole (**3h**): 100.7 mg (yield: 73%, 0.5 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 8.5 Hz, 1H), 8.27 – 8.05 (m, 1H), 7.60 – 7.50 (m, 2H), 7.42 (m, 3H), 7.31 – 7.17 (m, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.9, 145.6, 134.9, 130.1, 128.0, 128.0, 126.2, 126.0, 125.4, 125.1, 124.2, 122.6, 122.2, 119.9, 110.4, 102.9, 55.9. HRMS: Calculated for $(M+H)^+$: 276.1131, found: 276.1135.



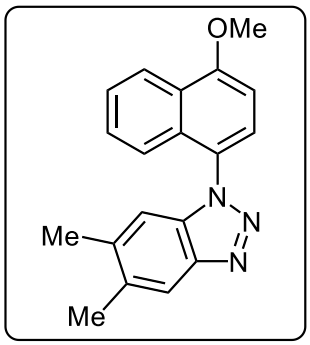
1-(3-Methoxynaphthalen-1-yl)-1H-benzo[d][1,2,3]triazole (**3i**): 111.1 mg (yield: 81%, 0.5 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 – 8.16 (m, 1H), 8.09 (d, *J* = 9.1 Hz, 1H), 7.90 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.54 – 7.34 (m, 5H), 7.22 – 7.13 (m, 1H), 7.09 – 6.95 (m, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.2, 145.6, 135.1, 132.3, 131.6, 128.9, 128.4, 128.1, 127.9, 124.7, 124.1, 121.5, 120.1, 117.6, 113.3, 110.5, 56.7. HRMS: Calculated for $(M+H)^+$: 276.1131, found: 276.1130.



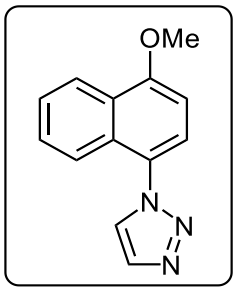
1-(4-Phenoxyphenyl)-1H-benzo[d][1,2,3]triazole/1-(2-phenoxyphenyl)-1H benzo[d][1,2,3]triazole (**3j**): 59.3mg (yield: 41%, 0.5 mmol scale),white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.19 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 0.23H), 7.91 – 7.83 (m, 2.93H), 7.79 (dd, *J* = 7.9, 1.6 Hz, 0.23H), 7.72 – 7.62 (m, 1.57H), 7.61 – 7.55 (m, 0.26H), 7.54 – 7.41 (m, 3.39H), 7.34 – 7.19 (m, 3.32H), 7.21 – 7.13 (m, 1.81H), 7.09 (d, *J* = 7.4 Hz, 0.22H), 6.96 – 6.91 (m, 0.38H); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 157.3, 155.2, 145.7, 133.1, 132.0, 131.8, 131.5, 130.4, 130.1, 128.8, 128.7, 128.4, 126.8, 125.0, 124.8, 124.6, 124.4, 124.2, 119.7, 119.5, 119.4, 118.5, 111.2, 111.0. HRMS: Calculated for $(M+H)^+$: 288.1131,found: 288.1132.



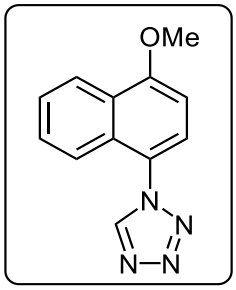
1-(2,6-Dimethoxypyridin-3-yl)-1H-benzo[d][1,2,3]triazole (**3k**): 84.2 mg (yield: 66%, 0.5 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.42 (m, 1H), 7.42 – 7.33 (m, 2H), 6.49 (d, *J* = 8.3 Hz, 1H), 4.01 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.6, 156.8, 145.7, 139.2, 134.0, 127.8, 124.0, 120.0, 112.2, 110.9, 102.0, 54.2, 54.0. HRMS: Calculated for $(M+H)^+$: 257.1033, found: 257.1031.



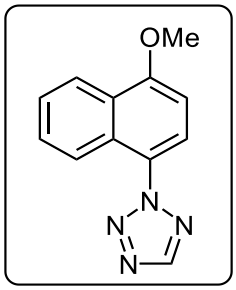
1-(4-Methoxynaphthalen-1-yl)-5,6-dimethyl-1H-benzo[d][1,2,3]triazole (**4a**): 107.6 mg (yield: 71%, 0.5 mmol scale), brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.32 (d, *J* = 8.3 Hz, 1H), 7.96 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.54 – 7.50 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.12 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 4.09 (s, 3H), 2.39 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.3, 144.0, 138.7, 134.0, 133.8, 129.9, 128.3, 126.5, 126.0, 125.2, 124.7, 122.2, 121.8, 118.5, 109.5, 104.0, 56.2, 20.2, 19.9.



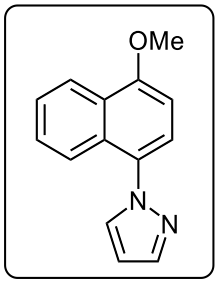
1-(4-Methoxynaphthalen-1-yl)-1H-1,2,3-triazole (**4b**): 76.9 mg (yield: 68%, 0.5 mmol scale), yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 – 8.27 (m, 1H), 7.89 (d, *J* = 16.9 Hz, 2H), 7.53 – 7.46 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.34 (m, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.8, 133.6, 129.6, 128.2, 126.6, 126.4, 126.3, 125.7, 124.2, 122.5, 121.8, 102.5, 55.9. HRMS: Calculated for $(M+H)^+$: 226.0975, found: 226.0974.



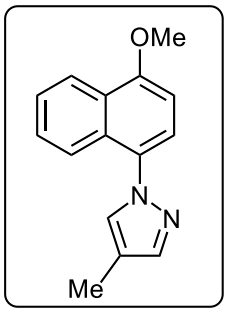
1-(4-Methoxynaphthalen-1-yl)-1H-tetrazole (**4c-1**): 45.1 mg (yield: 40%, 0.5 mmol scale), yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.91 (s, 1H), 8.37 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.27 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 4.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.7, 144.4, 129.3, 128.8, 126.8, 125.8, 124.8, 122.9, 122.5, 121.1, 102.6, 56.1. HRMS: Calculated for $(M+H)^+$: 227.0927, found: 227.0929.



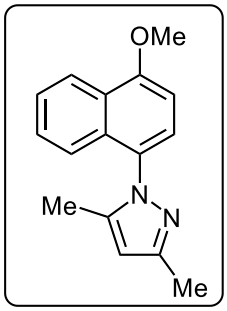
2-(4-Methoxynaphthalen-1-yl)-2H-tetrazole (**4c-2**): 18.9 mg (yield: 17%, 0.5 mmol scale), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77 (s, 1H), 8.40 – 8.38 (m, 1H), 7.79 – 7.69 (m, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.55 (m, 2H), 6.88 (d, *J* = 0.3 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.6, 153.0, 128.7, 128.4, 126.6, 125.9, 124.4, 122.7, 122.2, 102.6,, 56.1. HRMS: Calculated for $(M+H)^+$: 227.0927, found: 227.0928.



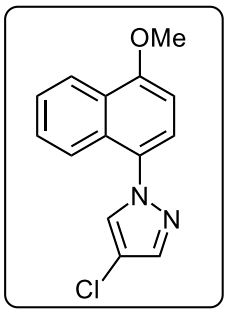
1-(4-Methoxynaphthalen-1-yl)-1H-pyrazole (**4d**): 65.4 mg (yield: 58%, 0.5 mmol scale), reddish brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 – 8.24 (m, 1H), 7.81 (s, 1H), 7.70 (s, 1H), 7.61 – 7.59 (m, 1H), 7.52 – 7.47 (m, 2H), 7.45 – 7.39 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.58 – 6.46 (m, 1H), 4.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.8, 140.5, 131.9, 130.6, 130.5, 127.7, 126.0, 125.8, 123.8, 122.8, 122.3, 106.2, 102.6 , 55.8. HRMS: Calculated for $(M+H)^+$: 225.1022, found: 225.1018.



1-(4-Methoxynaphthalen-1-yl)-4-methyl-1H-pyrazole (**4e**): 83.2 mg (yield: 70%, 0.5 mmol scale), brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 – 8.25 (m, 1H), 7.74 – 7.65 (m, 1H), 7.63 (s, 1H), 7.58 – 7.47 (m, 3H), 7.42 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 4.02 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.6, 141.1, 130.8, 130.6, 130.4, 127.6, 125.9, 125.8, 123.6, 122.9, 122.2, 116.6, 102.6, 55.8, 9.0. HRMS: Calculated for $(M+H)^+$: 239.1179, found: 239.1177.

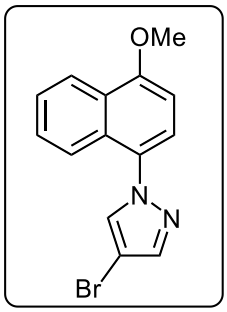


1-(4-Methoxynaphthalen-1-yl)-3,5-dimethyl-1H-pyrazole (**4f**): 90 mg (yield: 71%, 0.5 mmol scale), yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.30 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.04 (s, 1H), 3.99 (s, 3H), 2.35 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.9, 148.6, 141.6, 131.8, 129.0, 127.7, 125.8, 125.8, 125.6, 122.8, 122.2, 105.0, 102.6, 55.7, 13.7, 11.4. HRMS: Calculated for $(M+H)^+$: 253.1335, found: 253.1330.

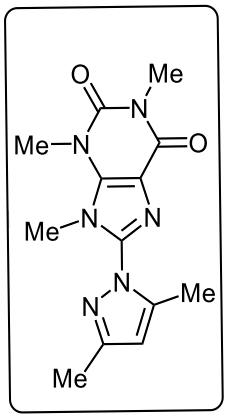


4-Chloro-1-(4-methoxynaphthalen-1-yl)-1H-pyrazole (**4g**): 56.8 mg (yield: 44%, 0.5 mmol scale), brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 – 8.28 (m, 1H), 7.73 (d, *J* = 12.9 Hz, 2H), 7.66 – 7.57 (m, 1H), 7.56 – 7.48 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 4.03 (s, 3H); ^{13}C

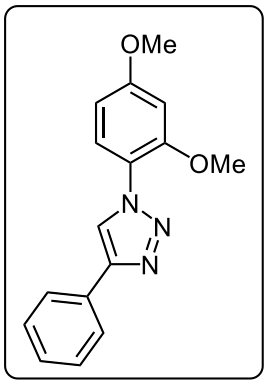
NMR (101 MHz, $CDCl_3$) δ = 156.2, 139.0, 130.1, 130.0, 129.8, 128.0, 126.2, 125.8, 124.0, 122.4, 122.4, 110.9, 102.6, 55.8. HRMS: Calculated for $(M+H)^+$: 259.0633, found: 259.0634.



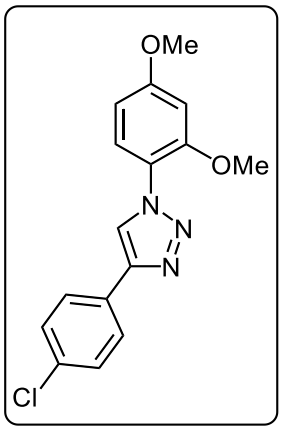
4-Bromo-1-(4-methoxynaphthalen-1-yl)-1H-pyrazole (**4h**): 56.1 mg (yield: 37%, 0.5 mmol scale), brown solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.33 (dd, *J* = 6.6, 3.0 Hz, 1H), 7.76 (d, *J* = 13.8 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.57 – 7.50 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.2, 141.1, 132.0, 130.13, 129.9, 128.0, 126.2, 125.9, 124.0, 122.5, 122.4, 102.6, 94.1, 55.9. HRMS: Calculated for $(M+H)^+$: 303.0128, found: 303.0128.



8-(3,5-Dimethyl-1H-pyrazol-1-yl)-1,3,9-trimethyl-3,4,5,9-tetrahydro-1H-purine-2,6-dione (**4i**): 61.0 mg (yield: 85%, 0.25 mmol scale), white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 6.01 (s, 1H), 3.99 (s, 3H), 3.54 (s, 3H), 3.39 (s, 3H), 2.39 (s, 3H), 2.25 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ = 155.3, 152.0, 151.6, 146.4, 143.4, 143.3, 108.3, 106.7, 77.5, 77.2, 76.8, 33.5, 29.9, 28.1, 13.7, 12.2. HRMS: Calculated for $(M+H)^+$: 289.1408, found: 289.1403.



1-(2,4-Dimethoxyphenyl)-4-phenyl-1H-1,2,3-triazole (**6a**): 60.1 mg (yield: 43%, 0.5 mmol scale), white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.78 (d, J = 4.8 Hz, 1H), 7.93 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 8.7 Hz, 1H), 7.47-7.44 (m, 2H), 7.36-7.32 (m, 1H), 6.96 – 6.80 (m, 1H), 6.75 – 6.65 (m, 1H), 3.86 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 161.4, 153.4, 146.1, 130.6, 129.0, 128.1, 127.1, 125.4, 123.6, 119.2, 105.4, 99.6, 56.3, 55.8. HRMS: Calculated for $(M+H)^+$: 282.1237, found: 282.1231.



4-(4-Chlorophenyl)-1-(2,4-dimethoxyphenyl)-1H-1,2,3-triazole (**6b**): 67.3 mg (yield%: 43%, 0.5 mmol scale), light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.86 (s, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.55-7.52 (m, 3H), 6.84 (s, 1H), 6.76 – 6.50 (m, 1H), 3.86 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 161.3, 153.2, 145.0, 132.4, 129.5, 129.0, 127.0, 123.8, 119.1, 105.3, 99.5, 62.2, 59.7. HRMS: Calculated for $(M+H)^+$: 316.0847, found: 316.0844.

8. Reference

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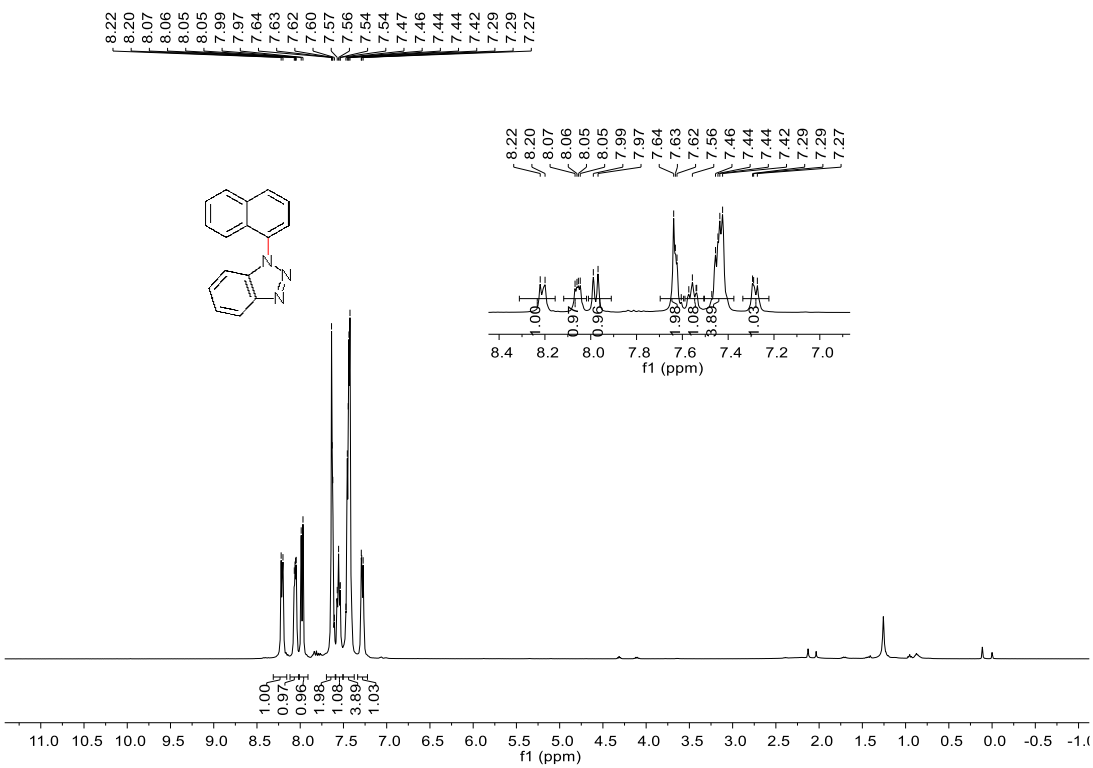
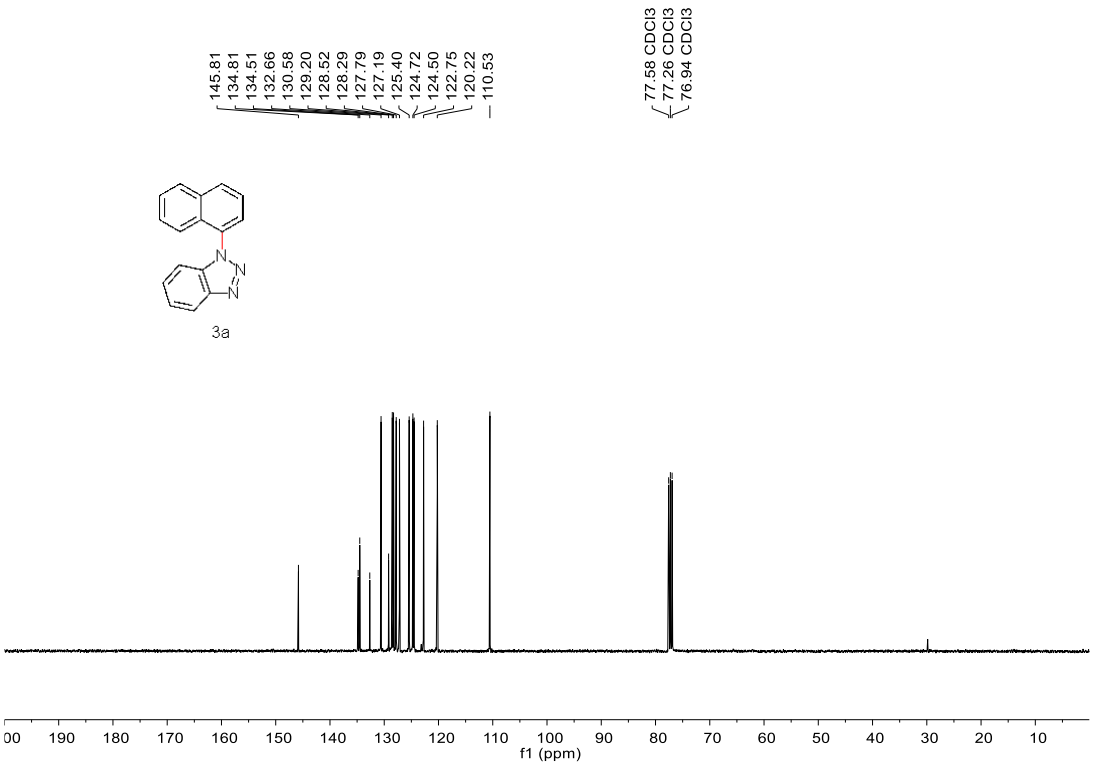
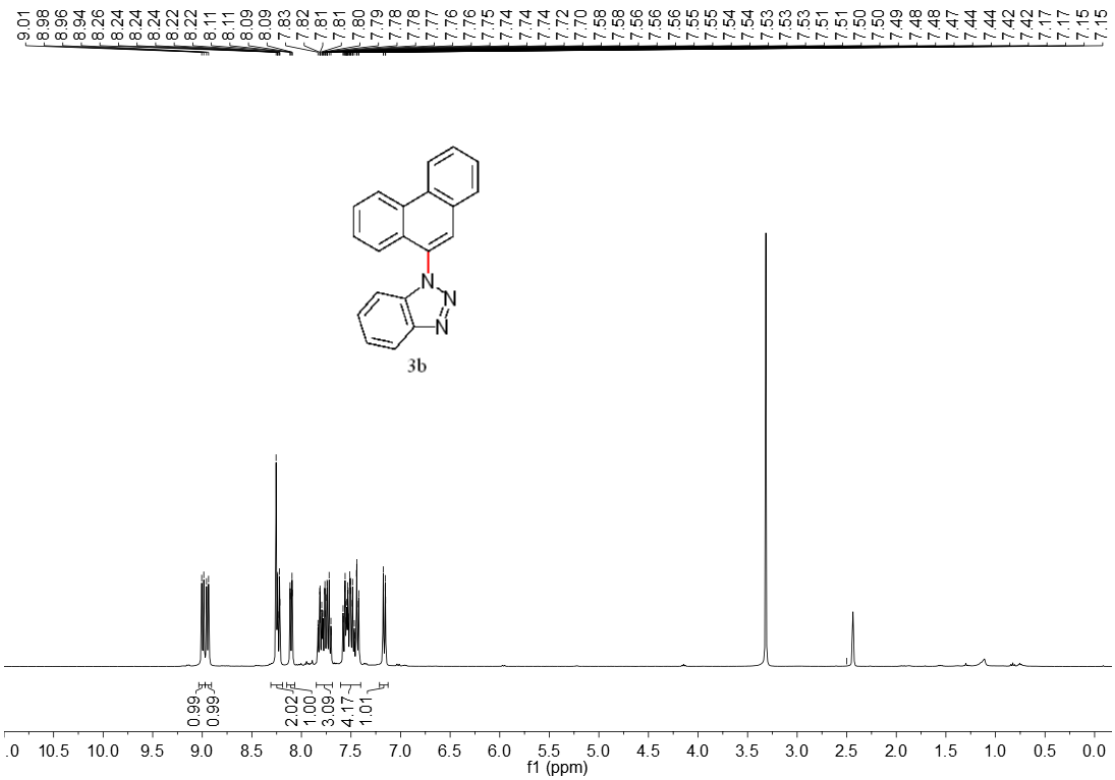
9. NMR spectra of the products



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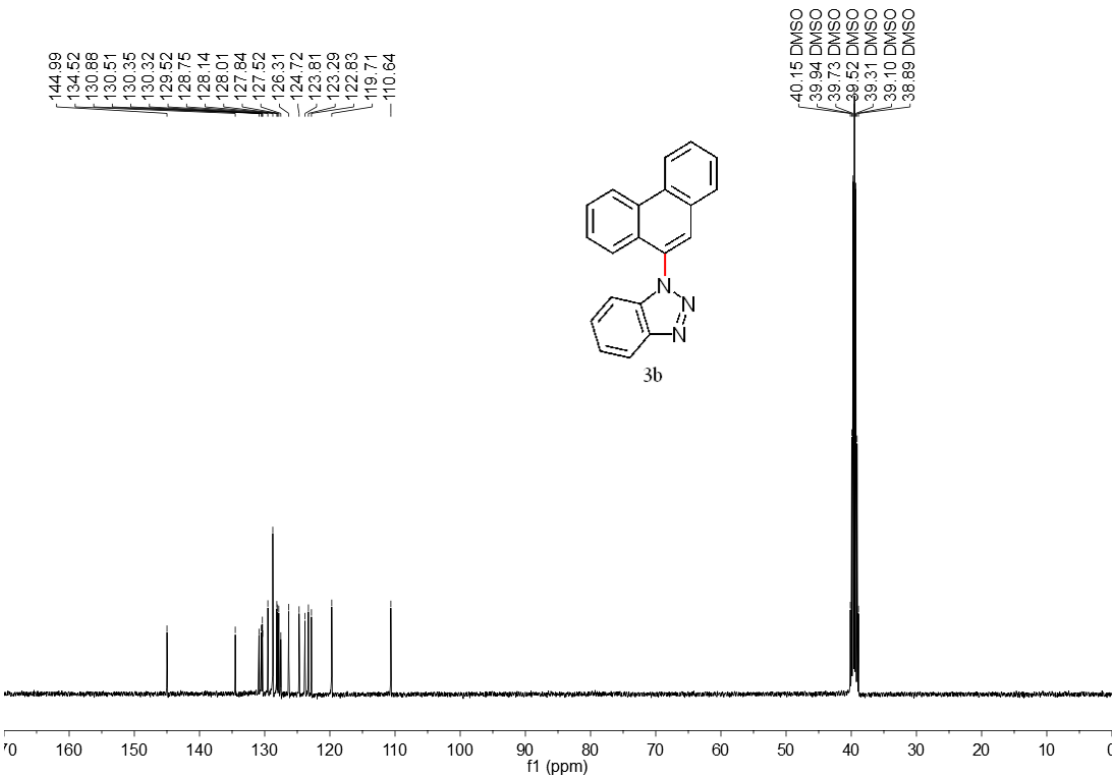
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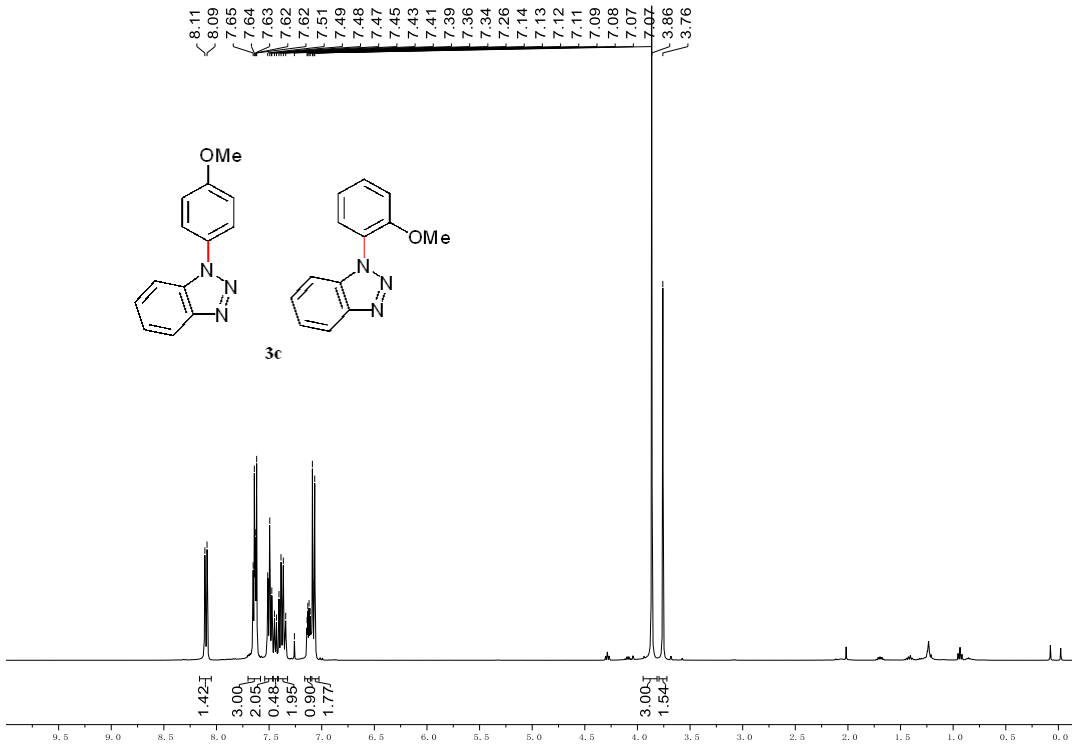
f1 (ppm)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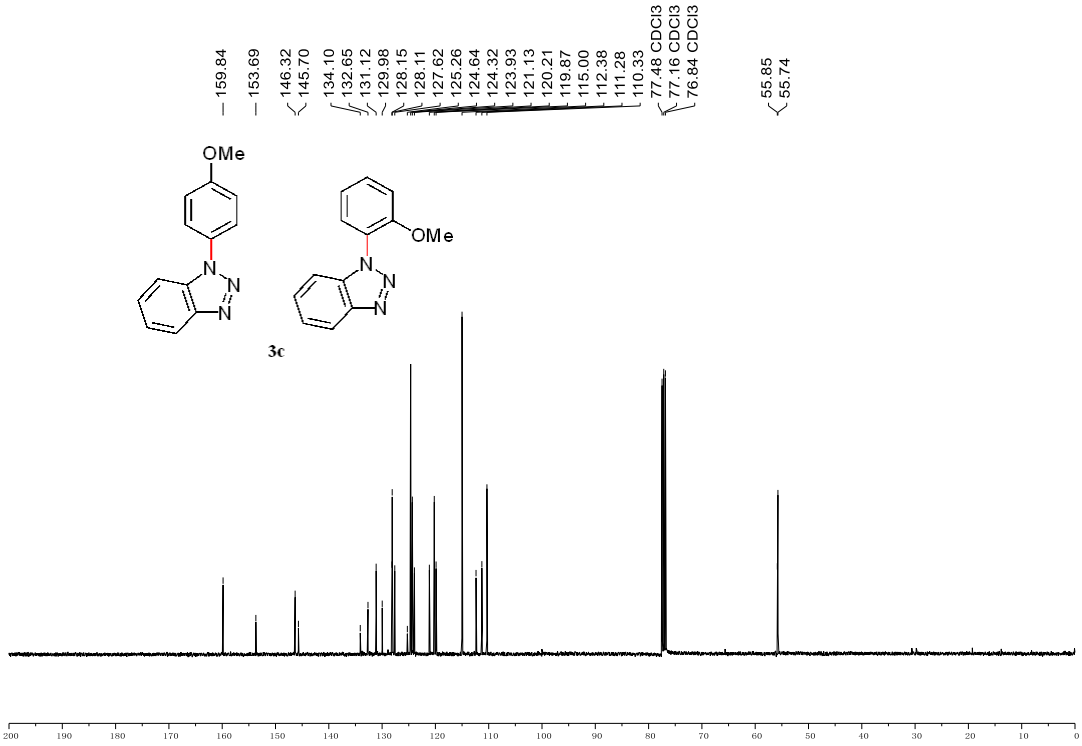
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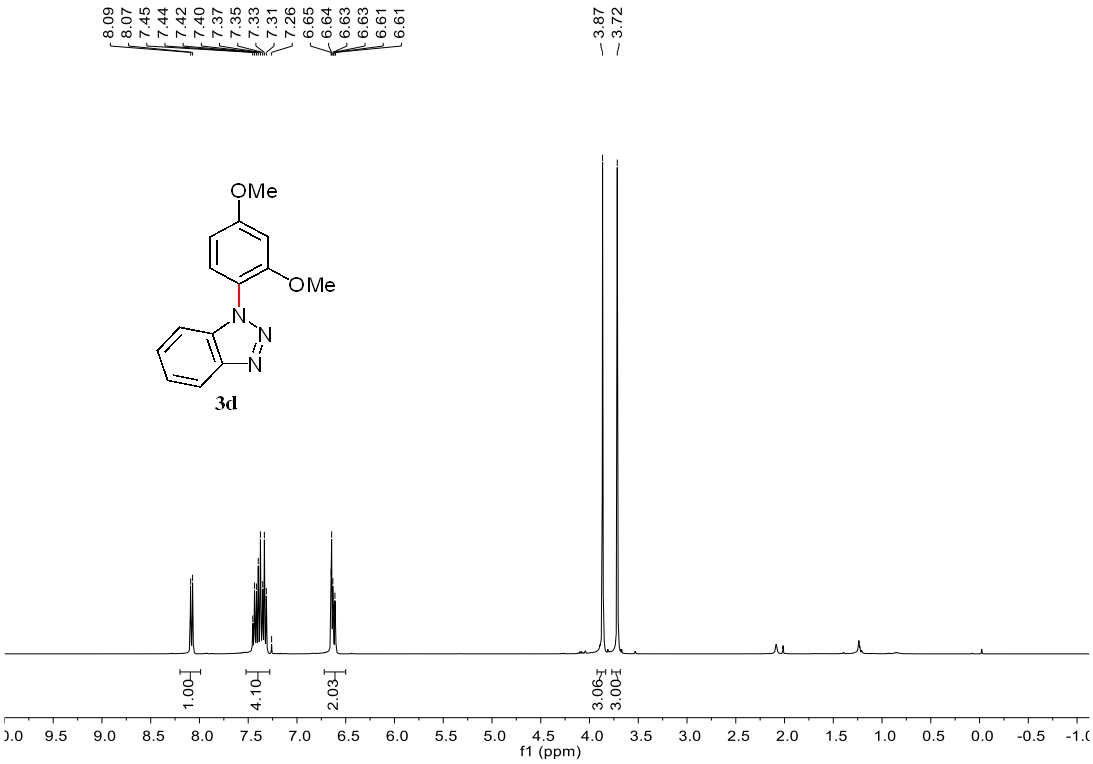
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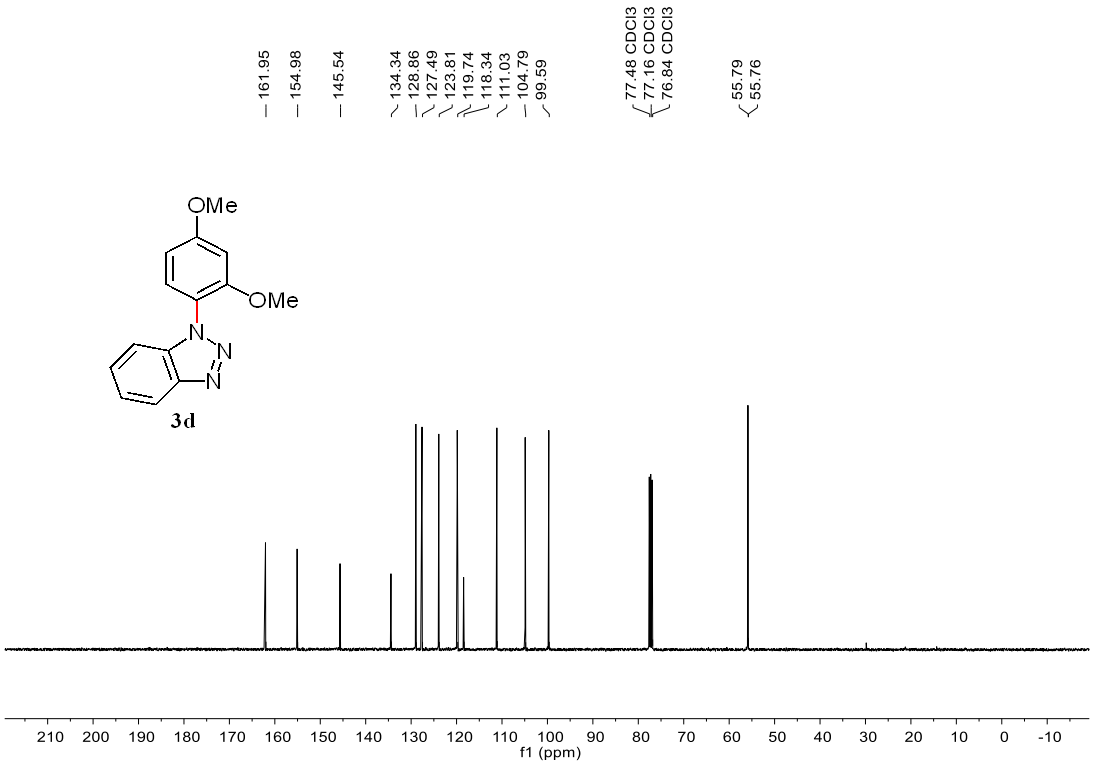
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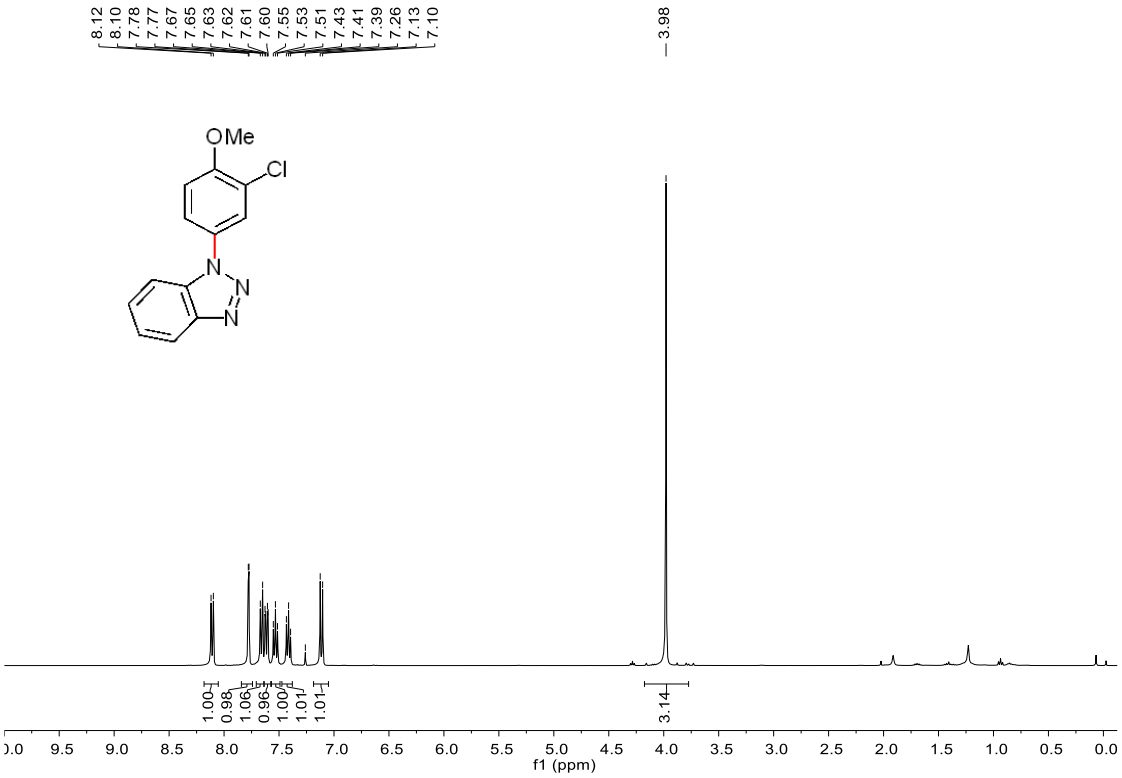
f1 (ppm)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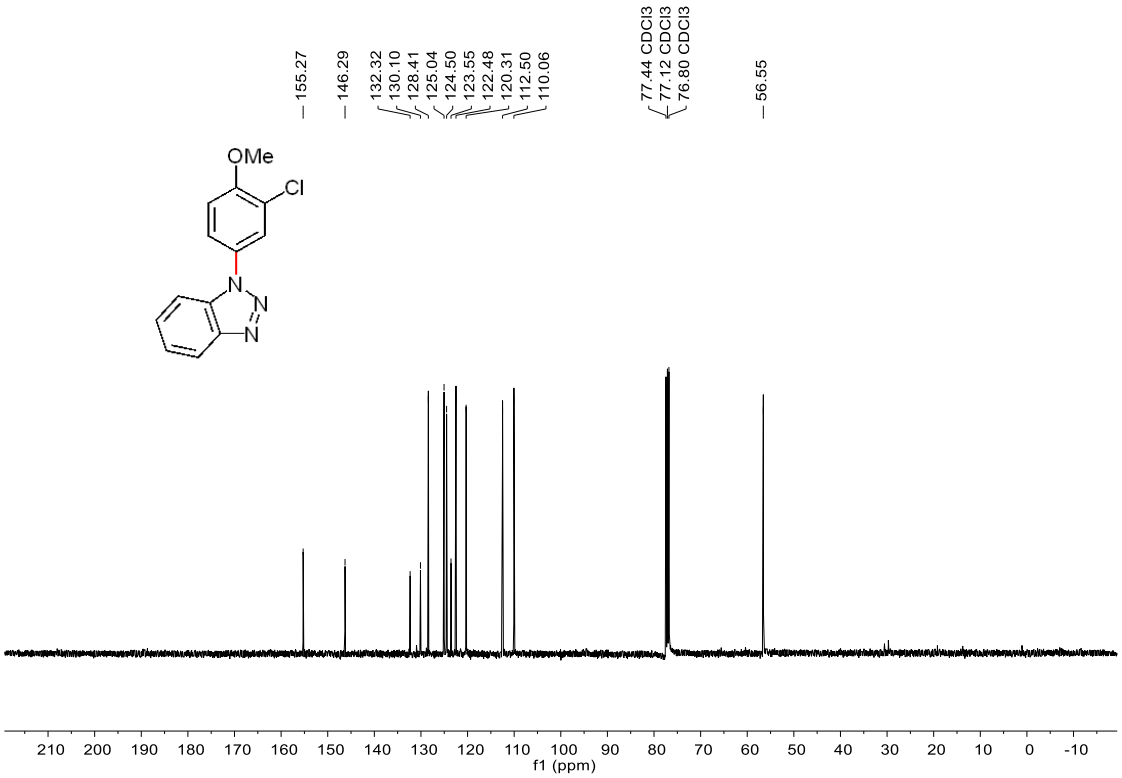
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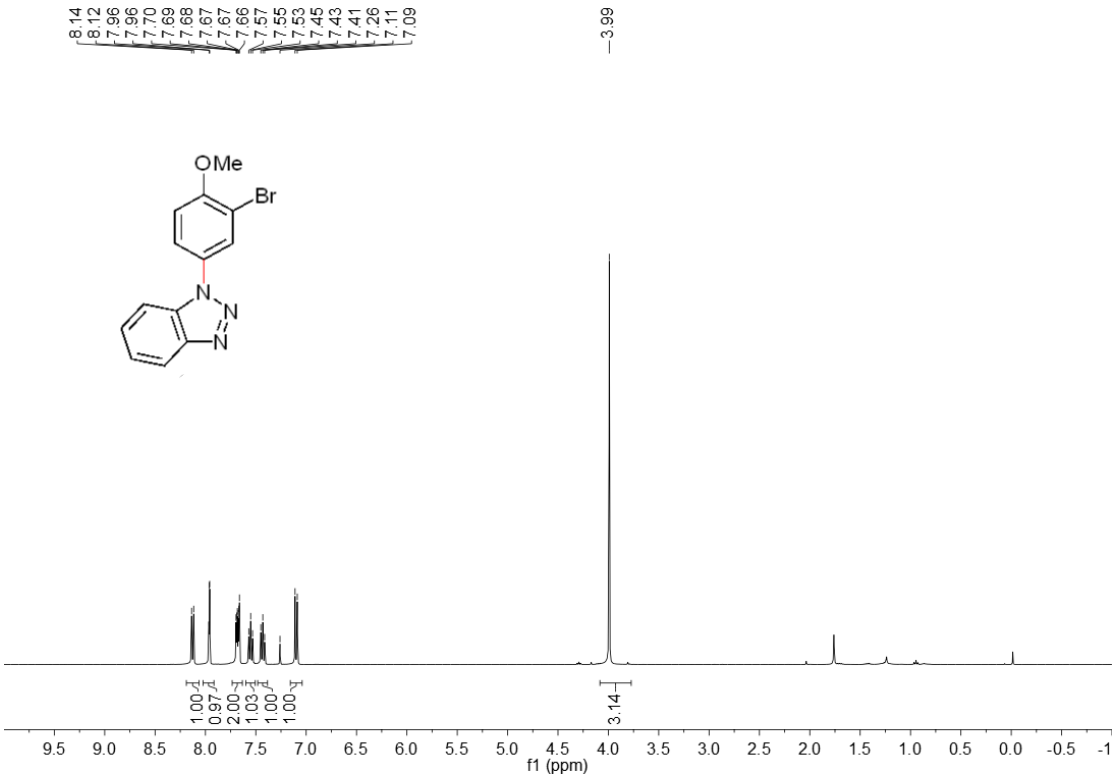
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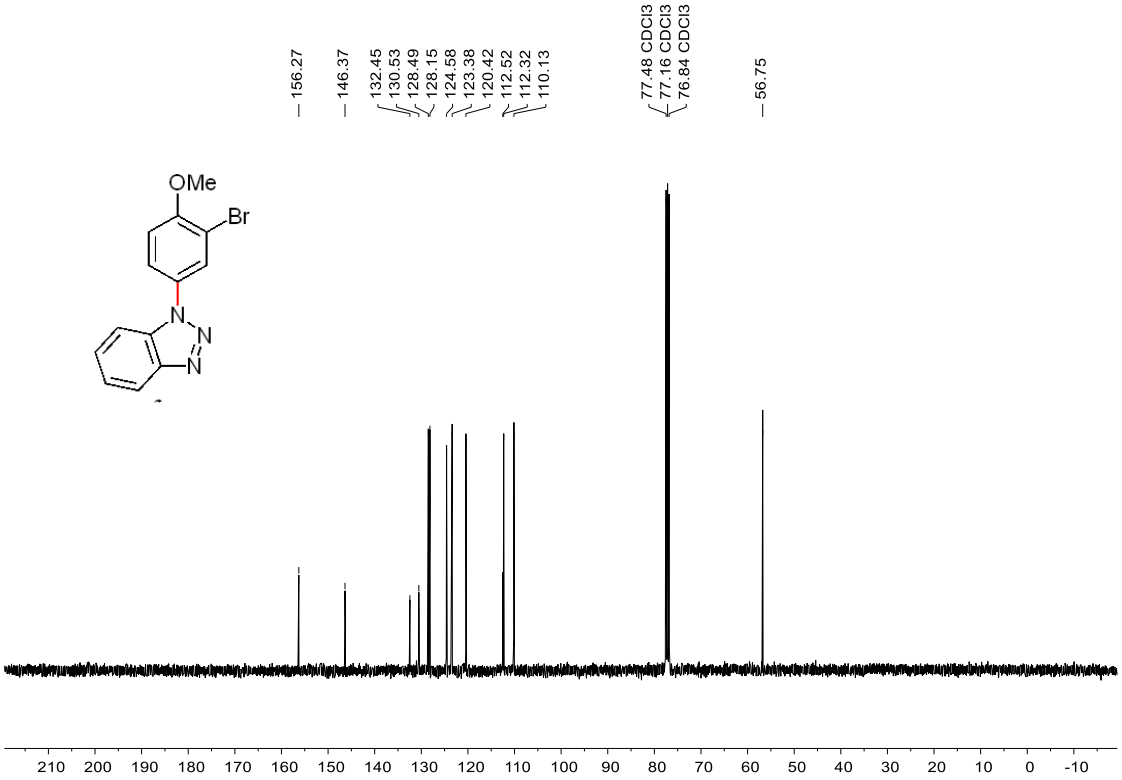
1.00
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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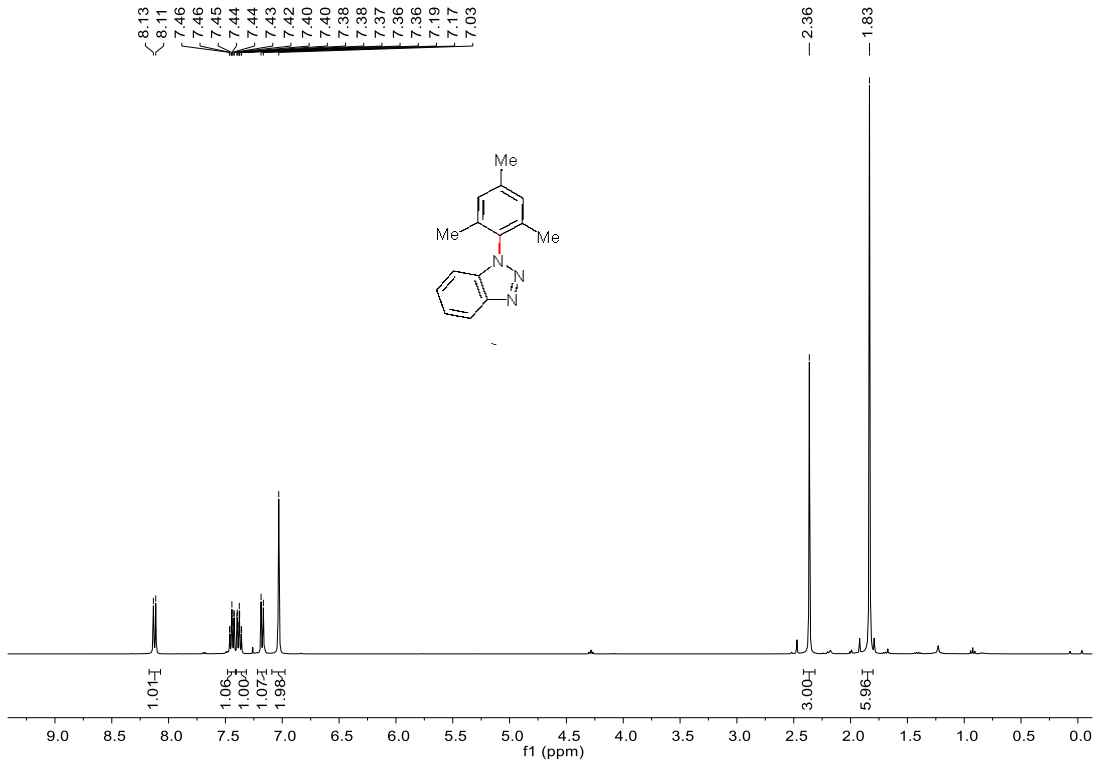
146.37
132.45
130.53
128.49
128.15
124.58
123.38
120.42
112.52
112.32
110.13
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.75
OMe
Br
N
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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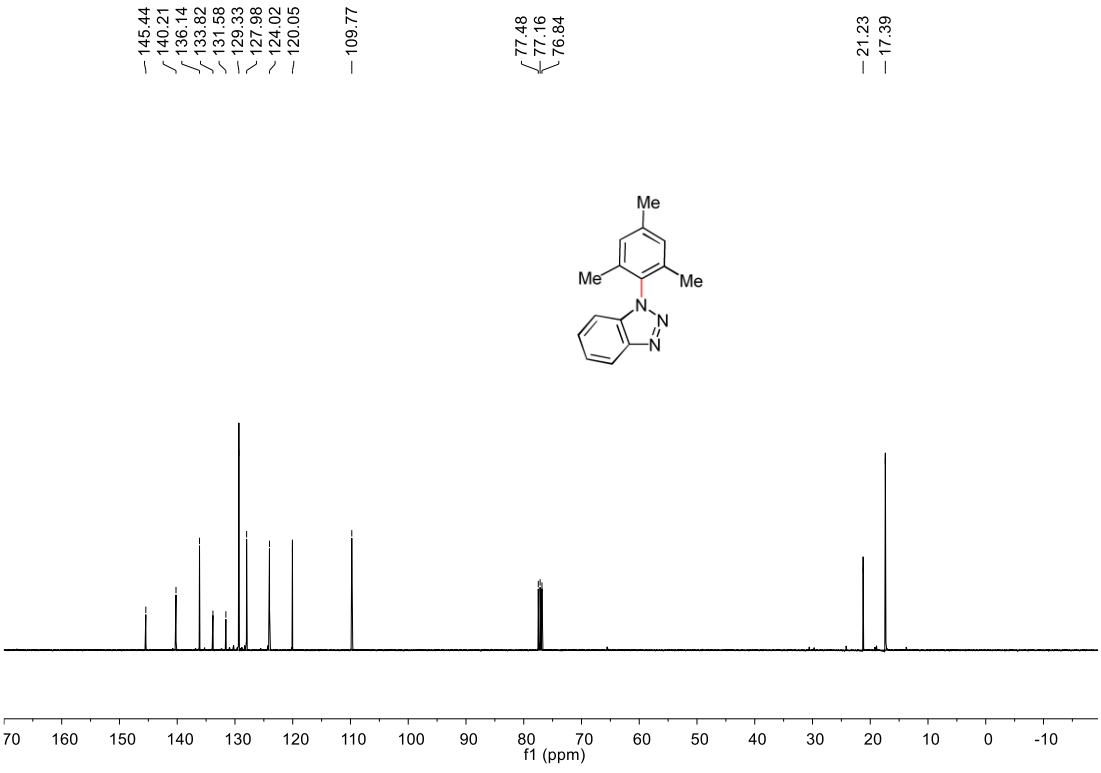
7.44
7.43
7.42
7.40
7.40
7.38
7.38
7.37
7.36
7.36
7.19
7.17
7.03
2.36
1.83
Me
Me
Me
N
N
N
1.01
1.06
1.00
1.07
1.98
3.00
5.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.44
140.21
136.14
133.82
131.58
129.33
127.98
124.02
120.05
109.77
77.48
77.16
76.84
21.23
17.39
Me
Me
Me
N
N
N
70
160
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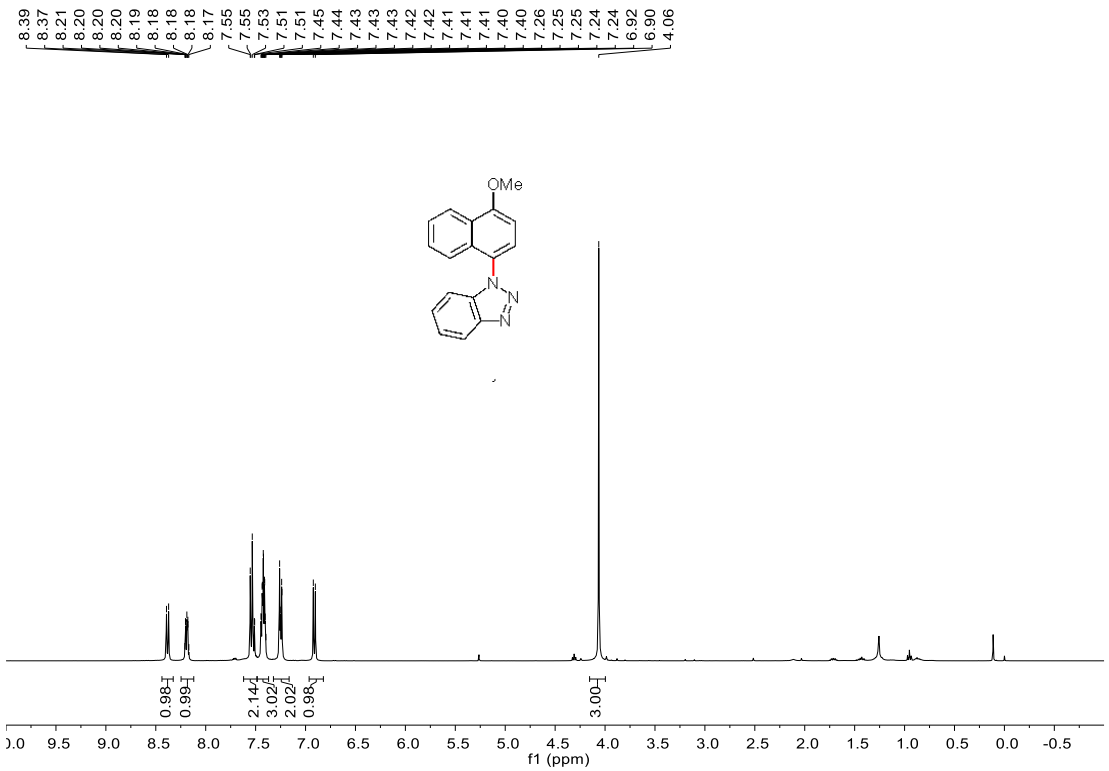
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.37
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8.20
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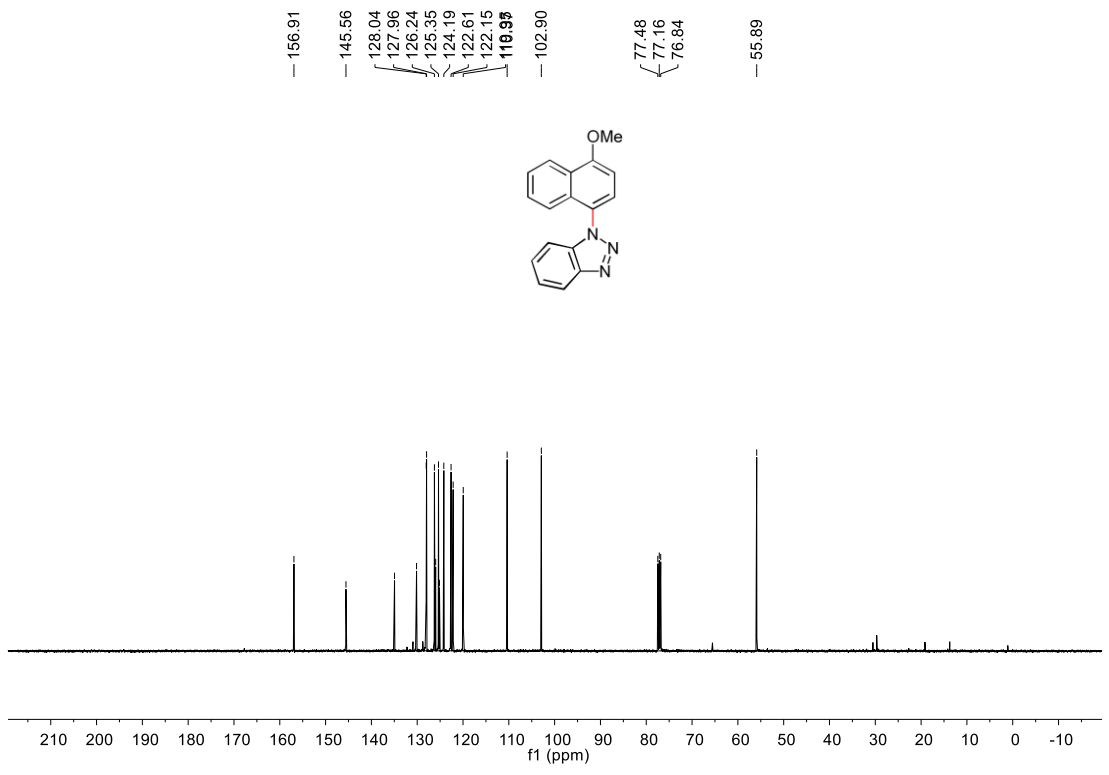
8.20
8.19
8.18
8.18
8.18
8.17
7.55
7.55
7.53
7.51
7.51
7.45
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.26
7.25
7.25
7.24
7.24
6.92
6.90
4.06
OMe
N
N
N
0.98
0.99
2.14
3.02
2.02
0.98
3.00
f1 (ppm)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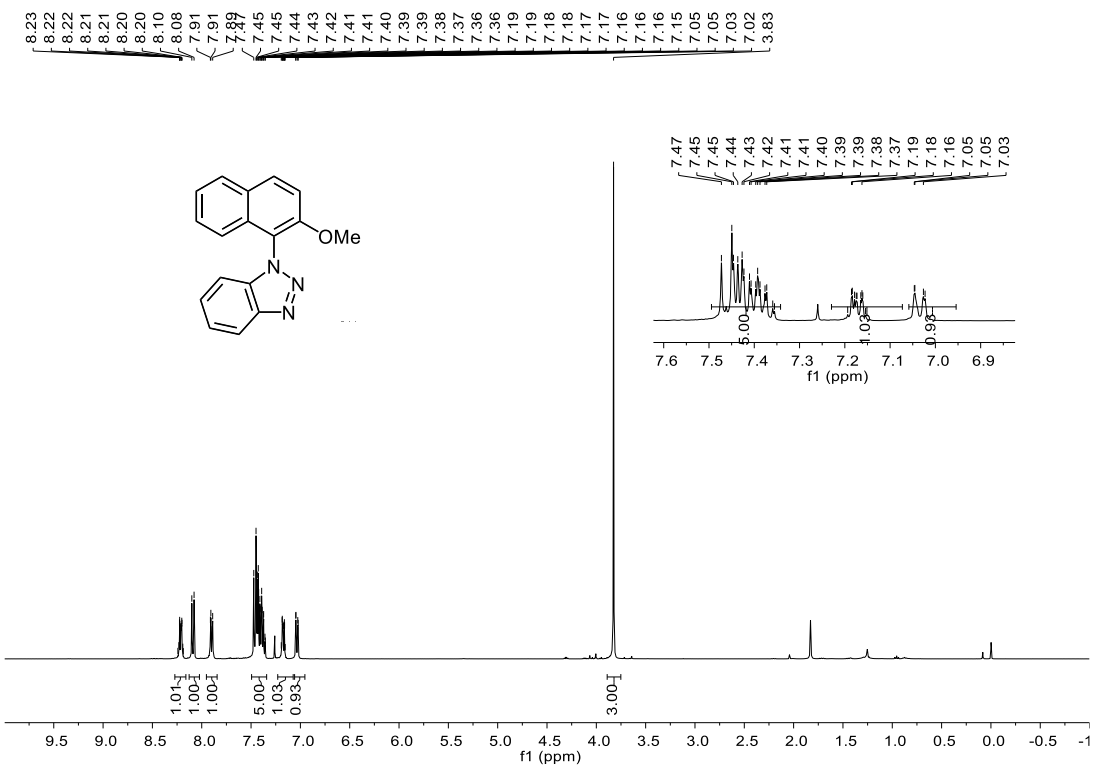
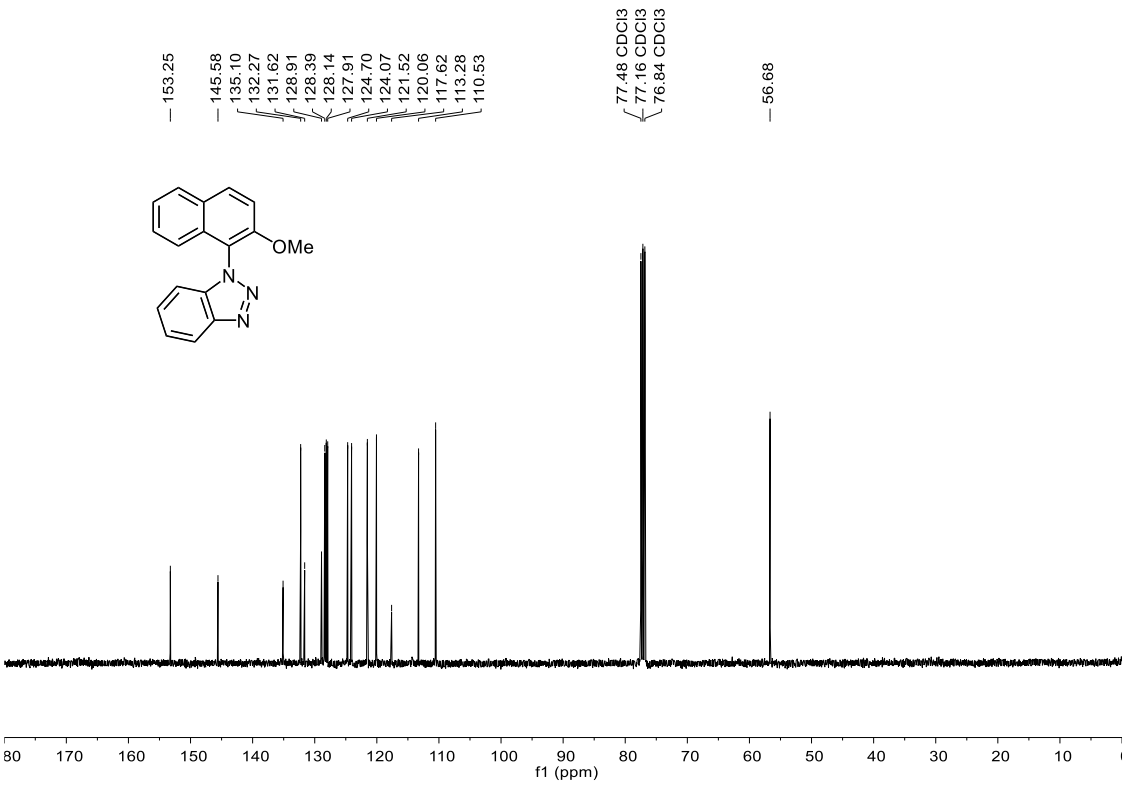
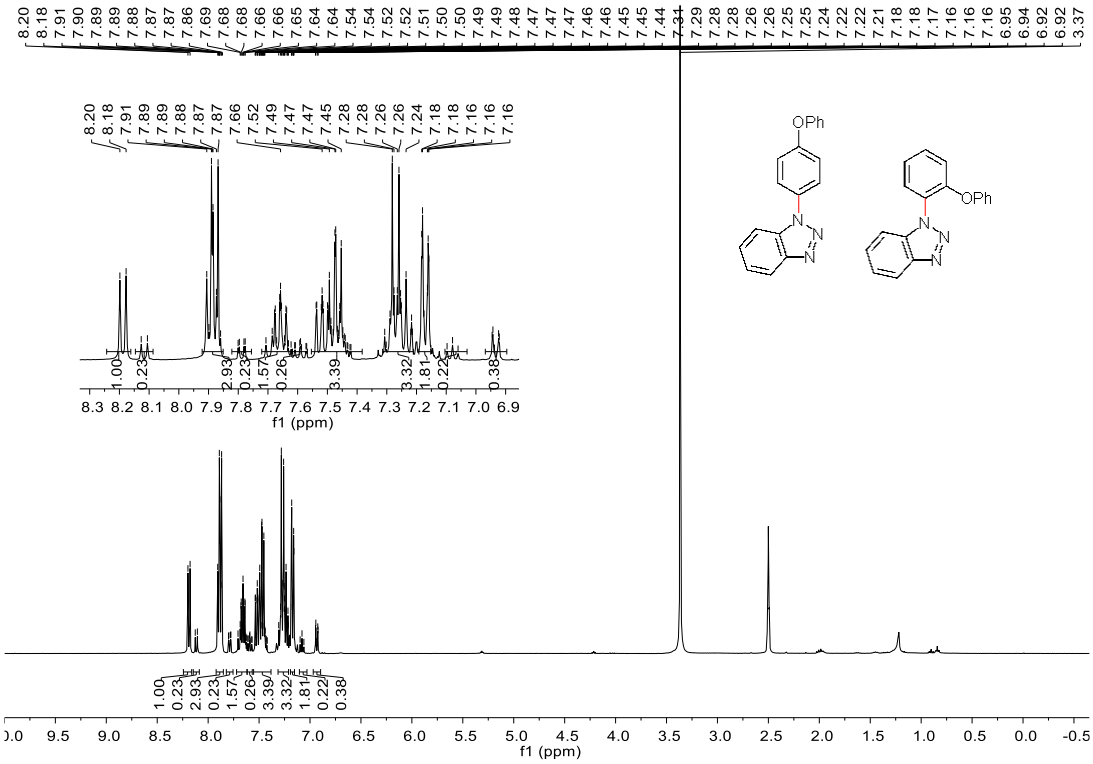
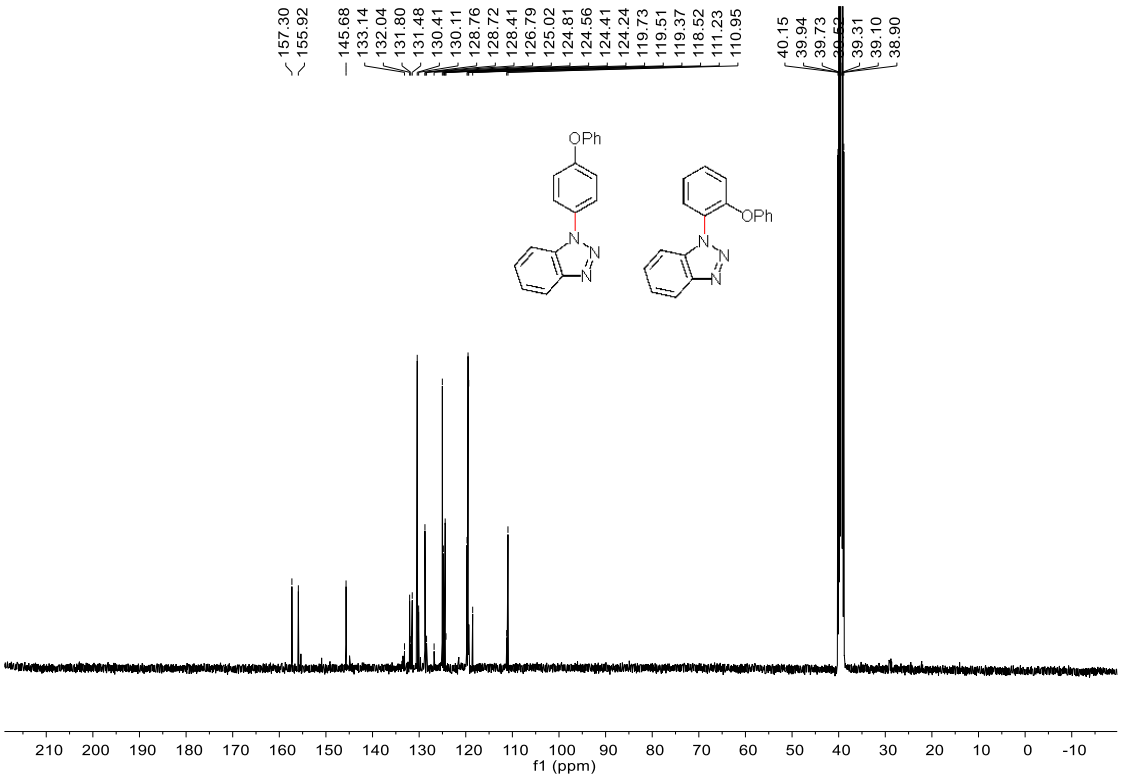
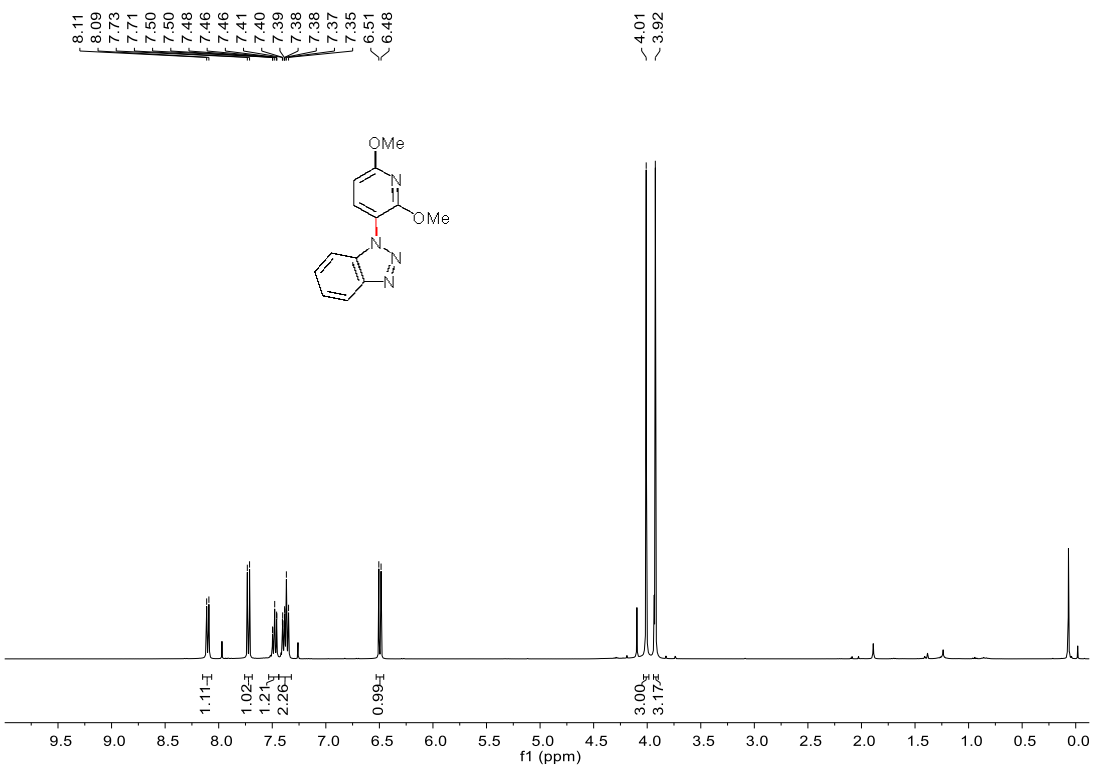
145.56
128.04
127.96
126.24
125.35
124.19
122.61
122.15
110.95
102.90
77.48
77.16
76.84
55.89
OMe
N
N
N
f1 (ppm)

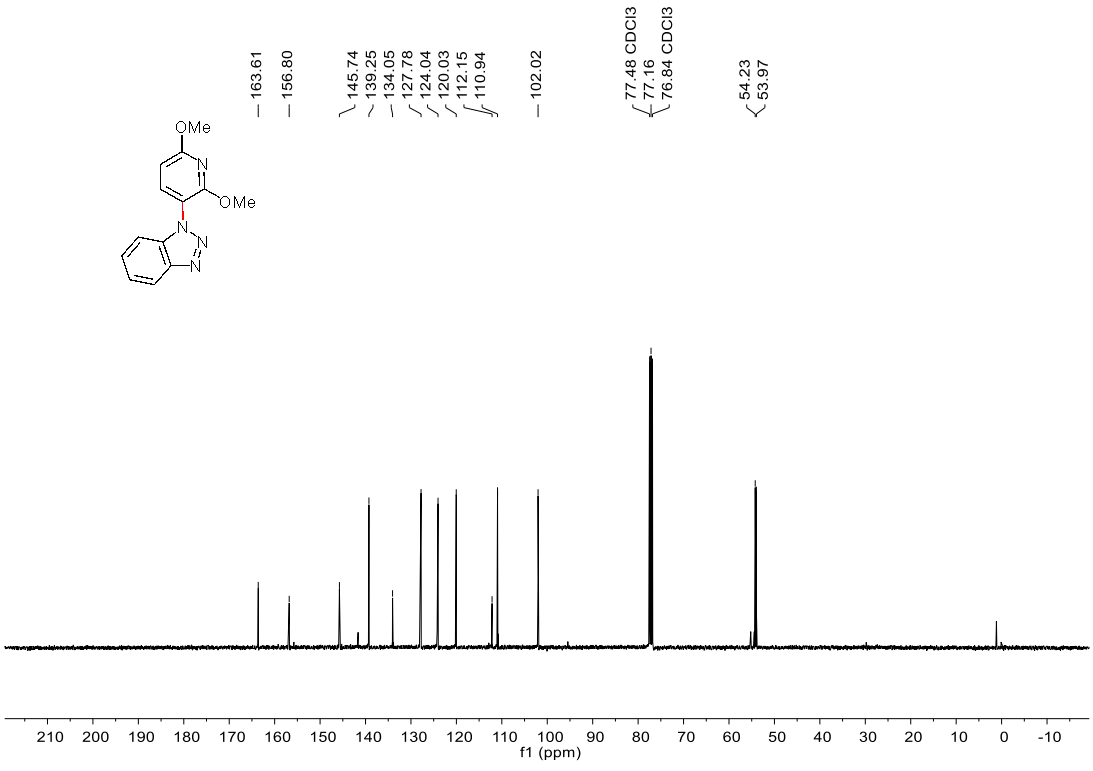

8.23 8.22 8.22 8.21 8.21 8.20 8.20 8.10 8.08 7.91 7.91 7.89 7.87 7.45 7.45 7.44 7.43 7.42 7.41 7.41 7.40 7.39 7.39 7.38 7.37 7.36 7.36 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.16 7.15 7.05 7.05 7.03 7.02 3.83
OMe
N
N
N
7.47 7.45 7.45 7.44 7.43 7.42 7.41 7.41 7.40 7.39 7.39 7.38 7.37 7.19 7.18 7.16 7.05 7.05 7.03
5.00
1.03
0.98
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.01
1.00
1.00
5.00
1.03
0.93
3.00
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)

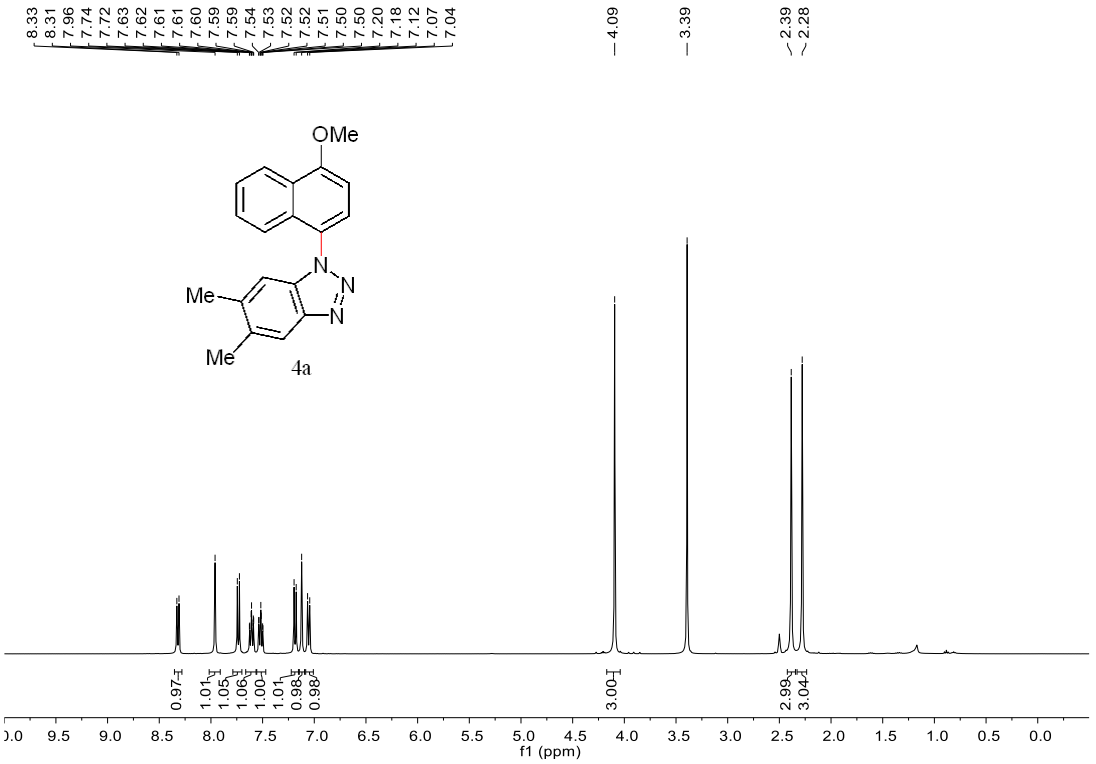

153.25
145.58
135.10
132.27
131.62
128.91
128.39
128.14
127.91
124.70
124.07
121.52
120.06
117.62
113.28
110.53
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.68
OMe
N
N
N
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

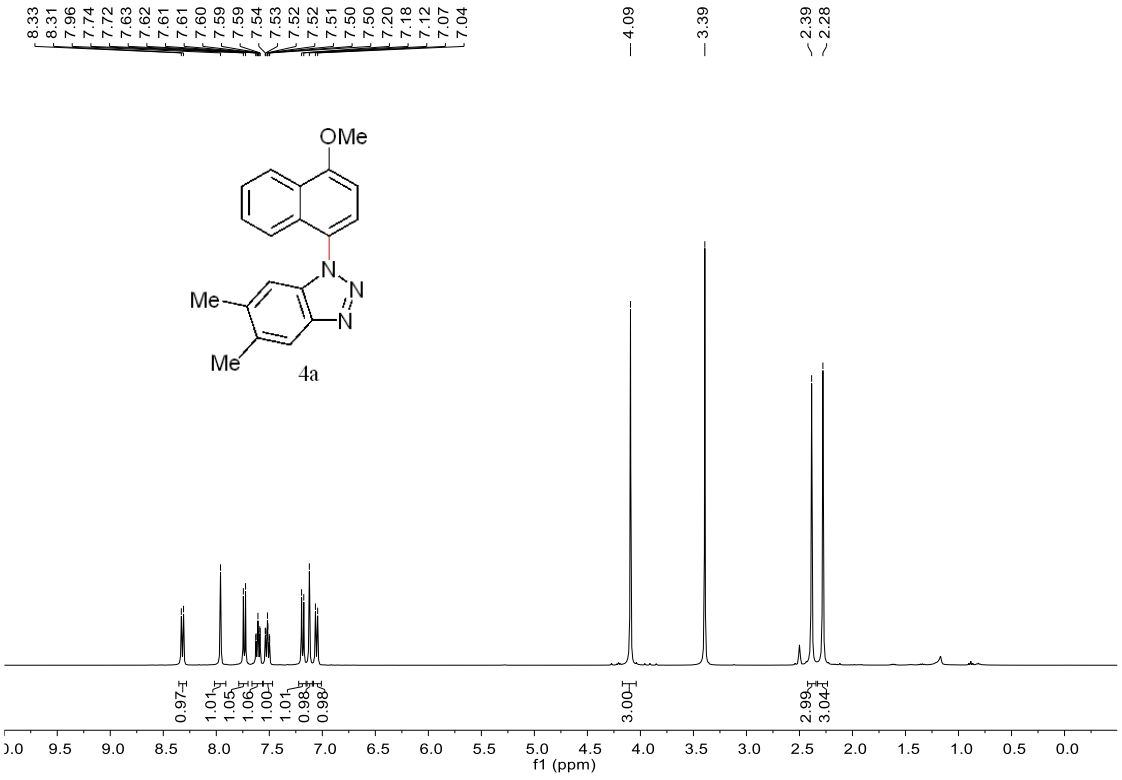

8.20 8.18 7.91 7.90 7.89 7.89 7.88 7.87 7.87 7.86 7.69 7.68 7.68 7.66 7.66 7.65 7.64 7.64 7.54 7.54 7.52 7.52 7.51 7.50 7.50 7.49 7.49 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.34 7.29 7.28 7.28 7.26 7.26 7.25 7.25 7.24 7.22 7.22 7.21 7.18 7.18 7.17 7.16 7.16 7.16 6.95 6.94 6.92 6.92 3.37
OPh
OPh
1.00 0.23 2.93 0.23 1.57 0.26 3.39 3.32 1.81 0.22 0.38
f1 (ppm)

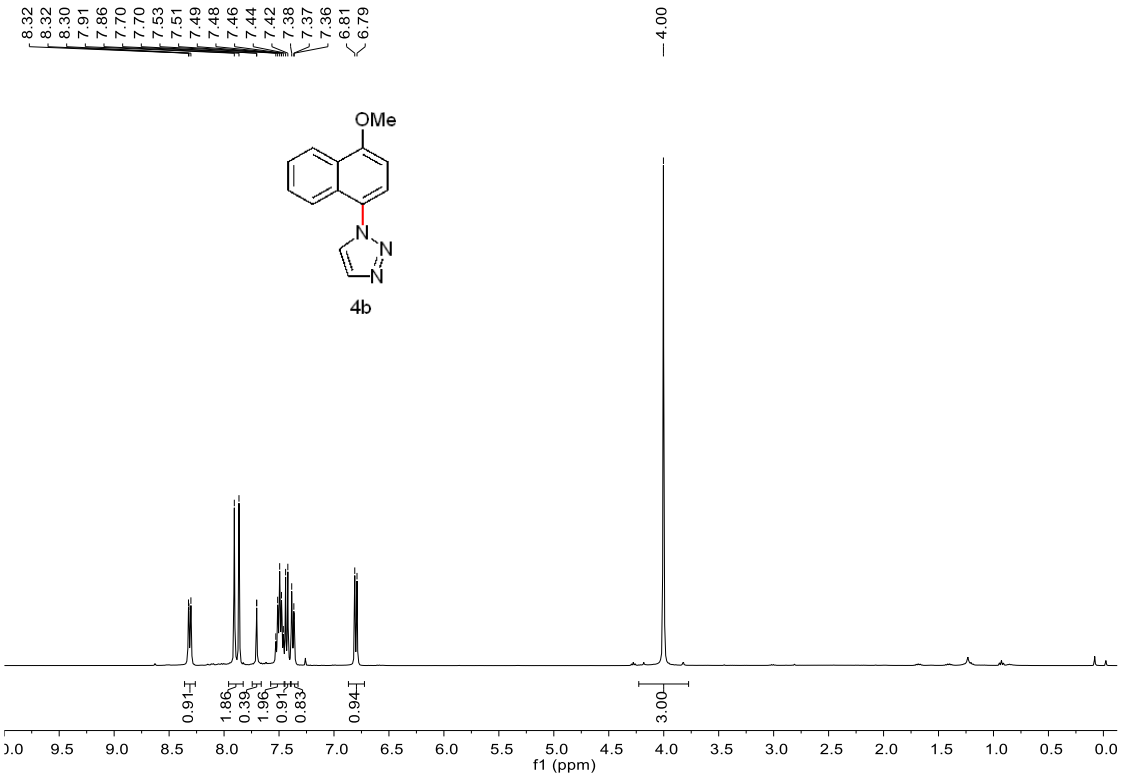

157.30 155.92 145.68 133.14 132.04 131.80 131.48 130.41 130.11 128.76 128.72 128.41 126.79 125.02 124.81 124.56 124.41 124.24 119.73 119.51 119.37 118.52 111.23 110.95 40.15 39.94 39.73 39.52 39.31 39.10 38.90
OPh
OPh
f1 (ppm)

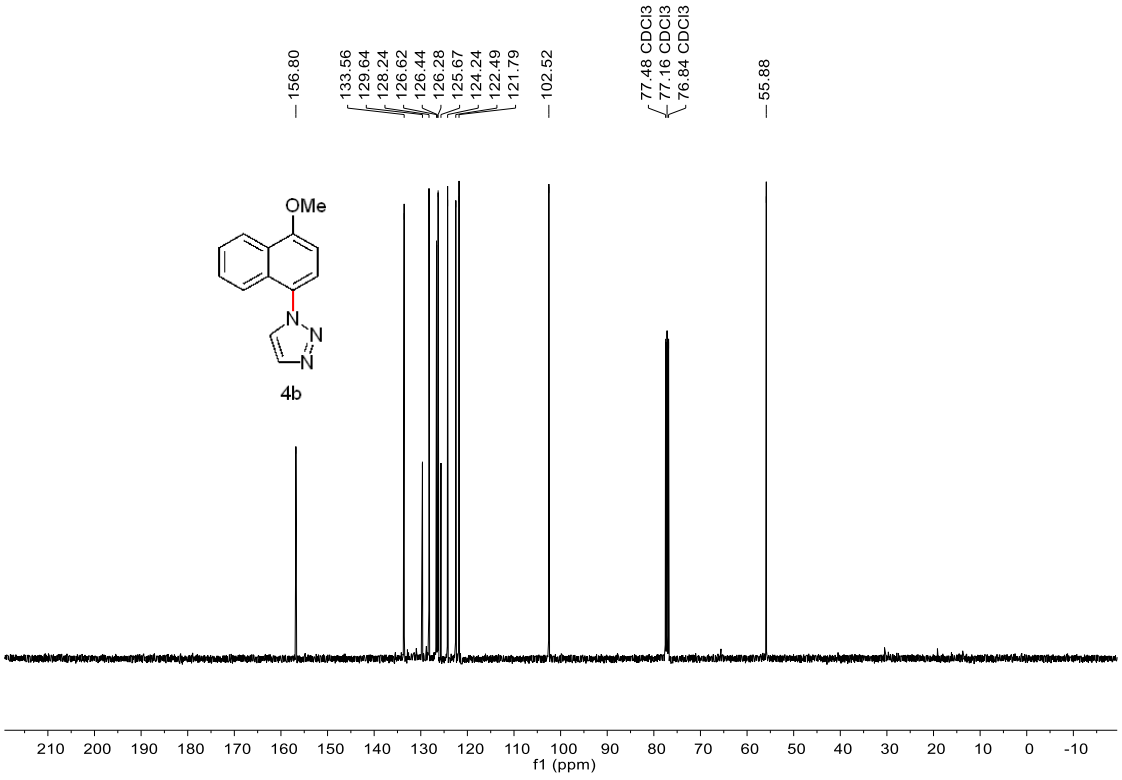

8.11
8.09
7.73
7.71
7.50
7.50
7.48
7.46
7.46
7.41
7.40
7.39
7.38
7.38
7.37
7.35
6.51
6.48
4.01
3.92
OMe
OMe
1.11
1.02
1.21
2.26
0.99
3.00
3.17
f1 (ppm)


163.61
156.80
145.74
139.25
134.05
127.78
124.04
120.03
112.15
110.94
102.02
77.48 CDCl3
77.16
76.84 CDCl3
54.23
53.97
OMe
OMe
f1 (ppm)


8.33
8.31
7.96
7.74
7.72
7.63
7.62
7.61
7.61
7.60
7.59
7.59
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.20
7.18
7.12
7.07
7.04
4.09
3.39
2.39
2.28
OMe
N
N
N
Me
Me
4a
0.97
1.01
1.05
1.06
1.00
1.01
0.98
0.98
3.00
2.99
3.04
f1 (ppm)


8.33
8.31
7.96
7.74
7.72
7.63
7.62
7.61
7.61
7.60
7.59
7.59
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.20
7.18
7.12
7.07
7.04
4.09
3.39
2.39
2.28
OMe
N
N
N
Me
Me
4a
0.97
1.01
1.05
1.06
1.00
1.01
0.98
0.98
3.00
2.99
3.04
f1 (ppm)


8.32
8.32
8.30
7.91
7.86
7.70
7.70
7.53
7.51
7.49
7.48
7.46
7.44
7.42
7.38
7.37
7.36
6.81
6.79
4.00
OMe
N
N
N
4b
0.91
1.86
0.39
1.96
0.91
0.83
0.94
3.00
f1 (ppm)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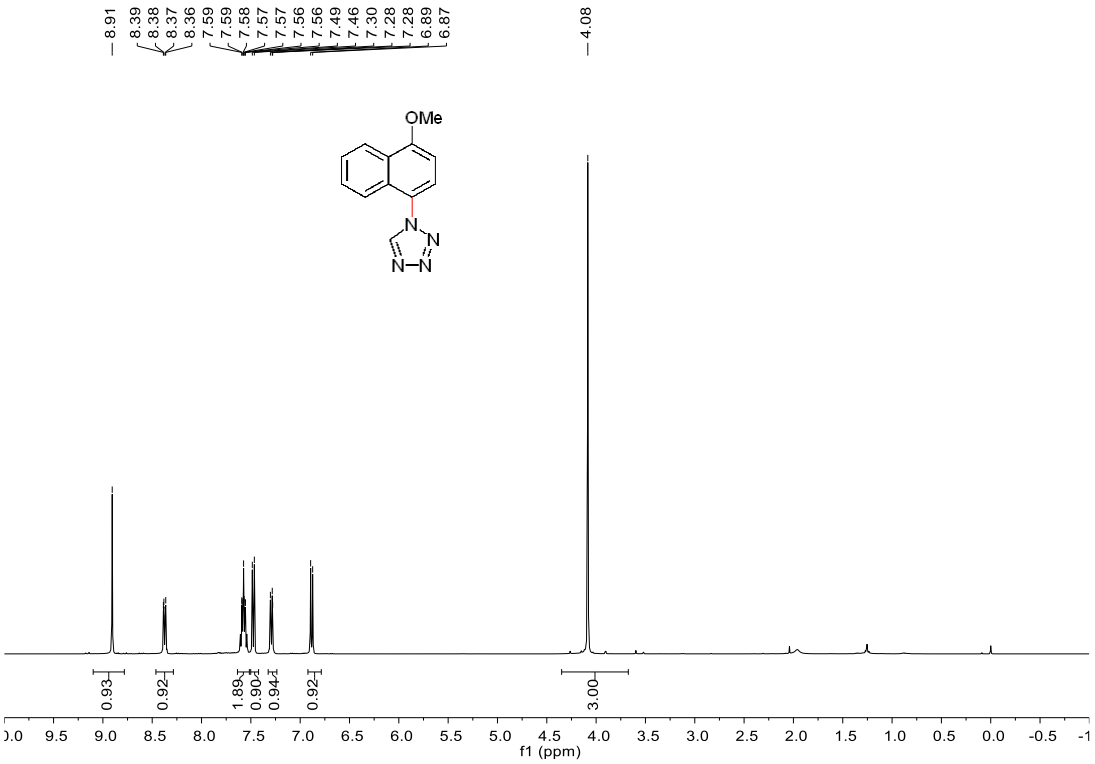
133.56
129.64
128.24
126.62
126.44
126.28
125.67
124.24
122.49
121.79
102.52
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.88
OMe
N
N
N
4b
f1 (ppm)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8.39
8.38
8.37
8.36
7.59
7.59
7.58
7.57
7.57
7.56
7.56
7.49
7.46
7.30
7.28
7.28
6.89
6.87
4.08
OMe
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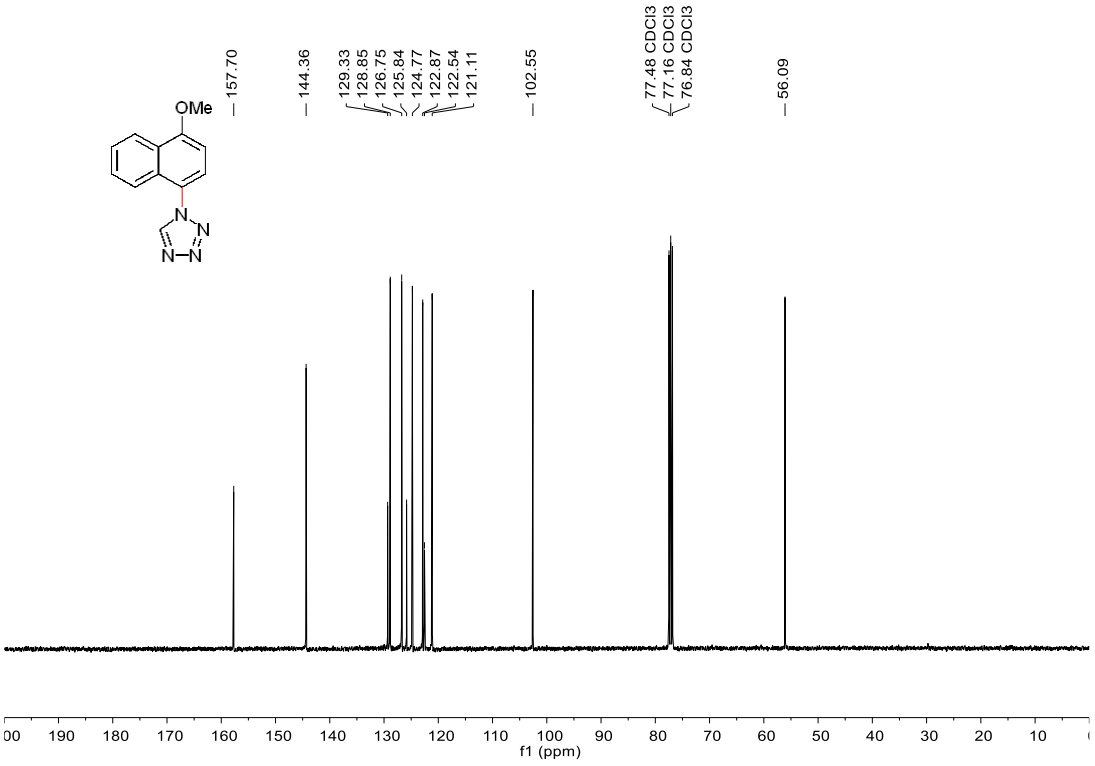
N
N
0.93
0.92
1.89
0.90
0.94
0.92
3.00
f1 (ppm)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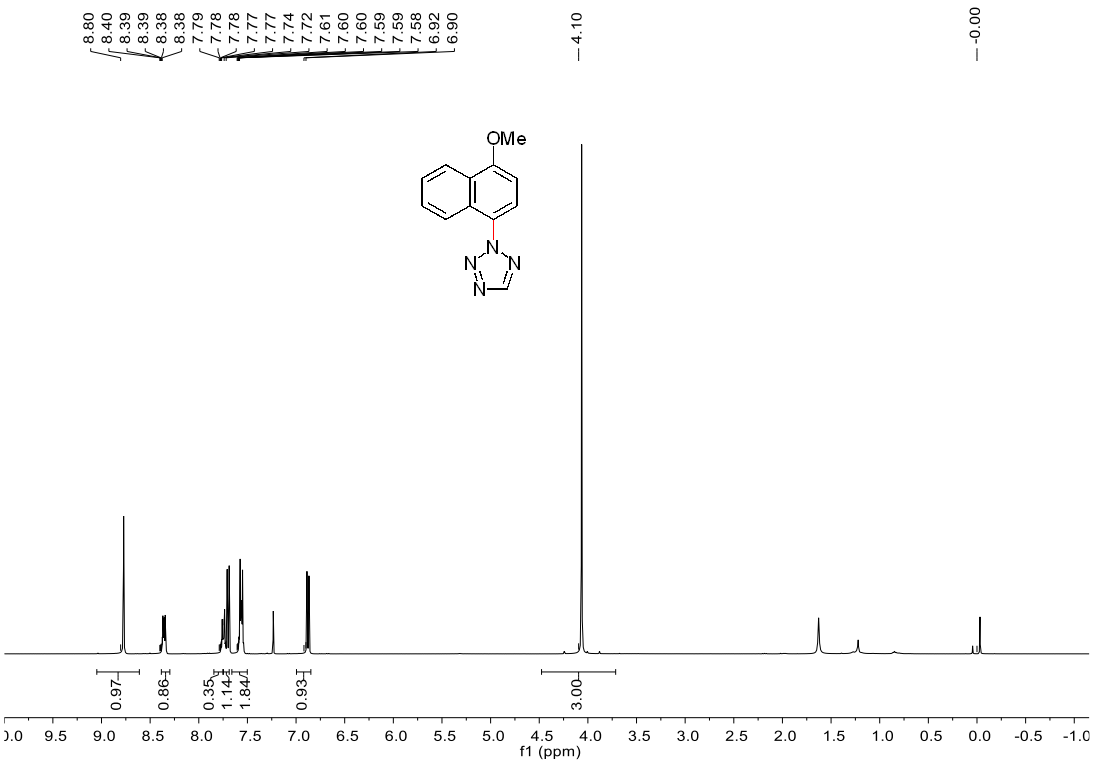
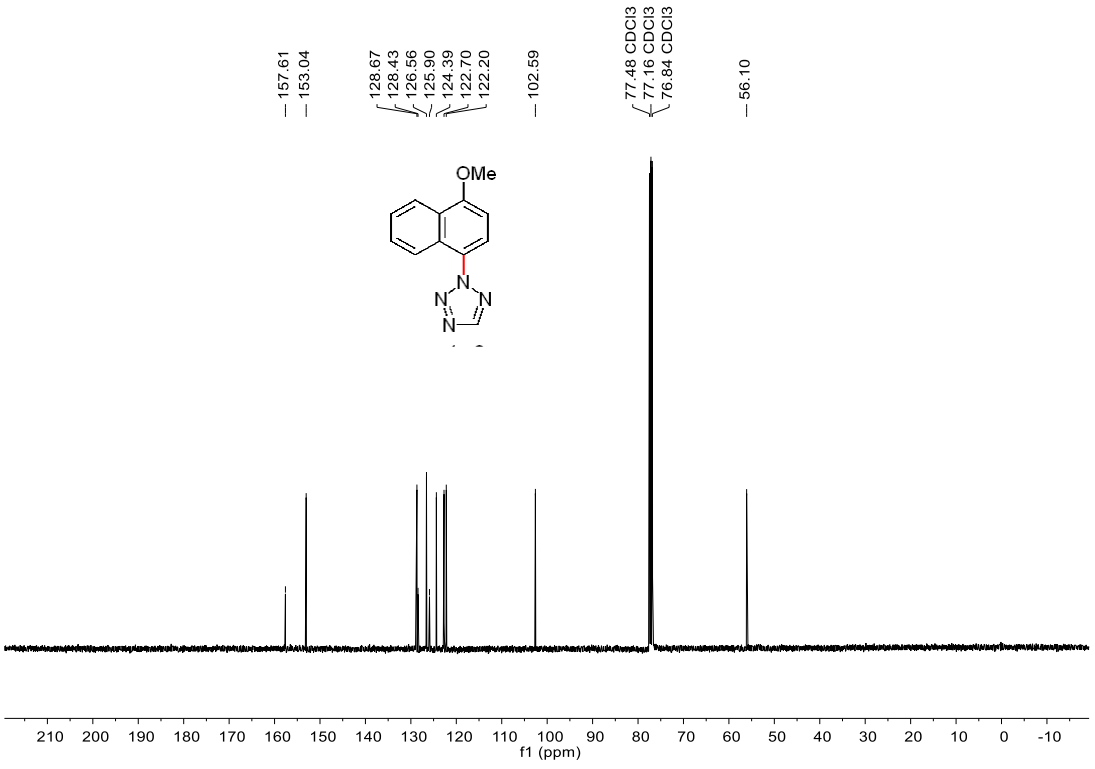
129.33
128.85
126.75
125.84
124.77
122.87
122.54
121.11
102.55
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.09
OMe
N
N
N
N
f1 (ppm)


8.80
8.40
8.39
8.39
8.38
8.38
7.79
7.78
7.78
7.77
7.77
7.74
7.72
7.61
7.60
7.60
7.59
7.59
7.58
6.92
6.90
4.10
-0.00
OMe
N
N
N
N
0.97
0.86
0.35
1.14
1.84
0.93
3.00
f1 (ppm)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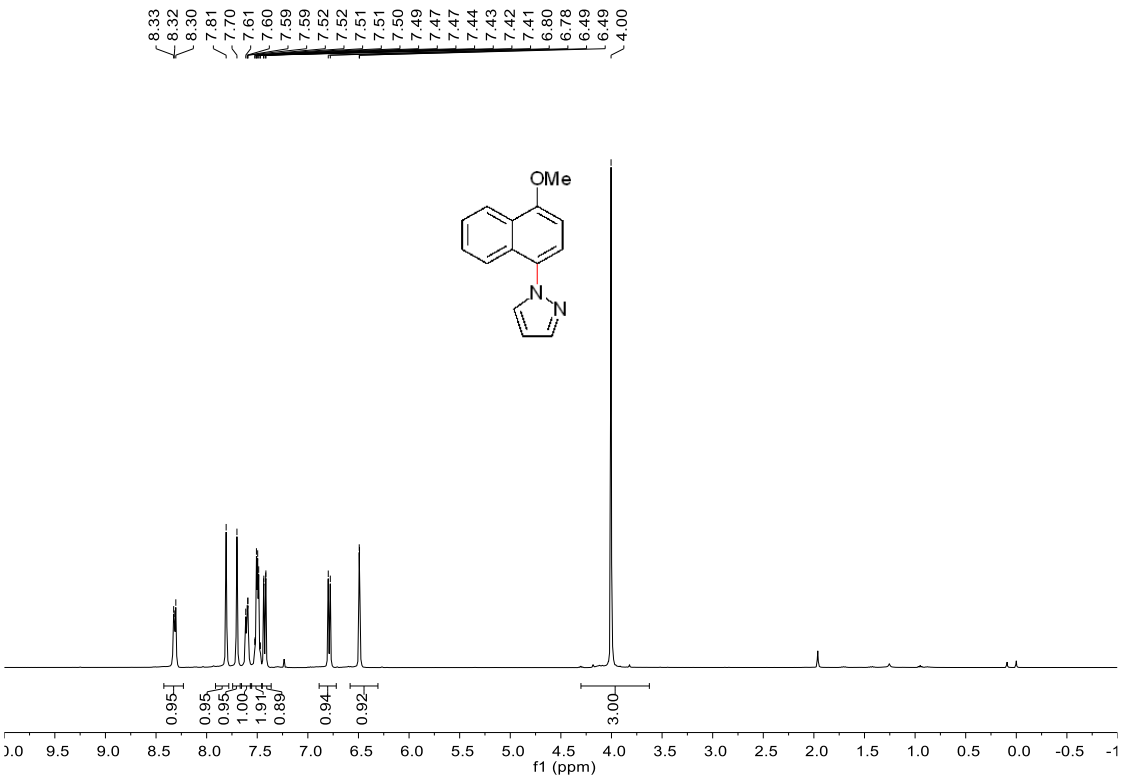
128.43
126.56
125.90
124.39
122.70
122.20
102.59
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.10
OMe
N
N
N
N
f1 (ppm)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8.32
8.30
7.81
7.70
7.61
7.60
7.59
7.59
7.52
7.52
7.51
7.51
7.50
7.49
7.47
7.47
7.44
7.43
7.42
7.41
6.80
6.78
6.49
6.49
4.00
OMe
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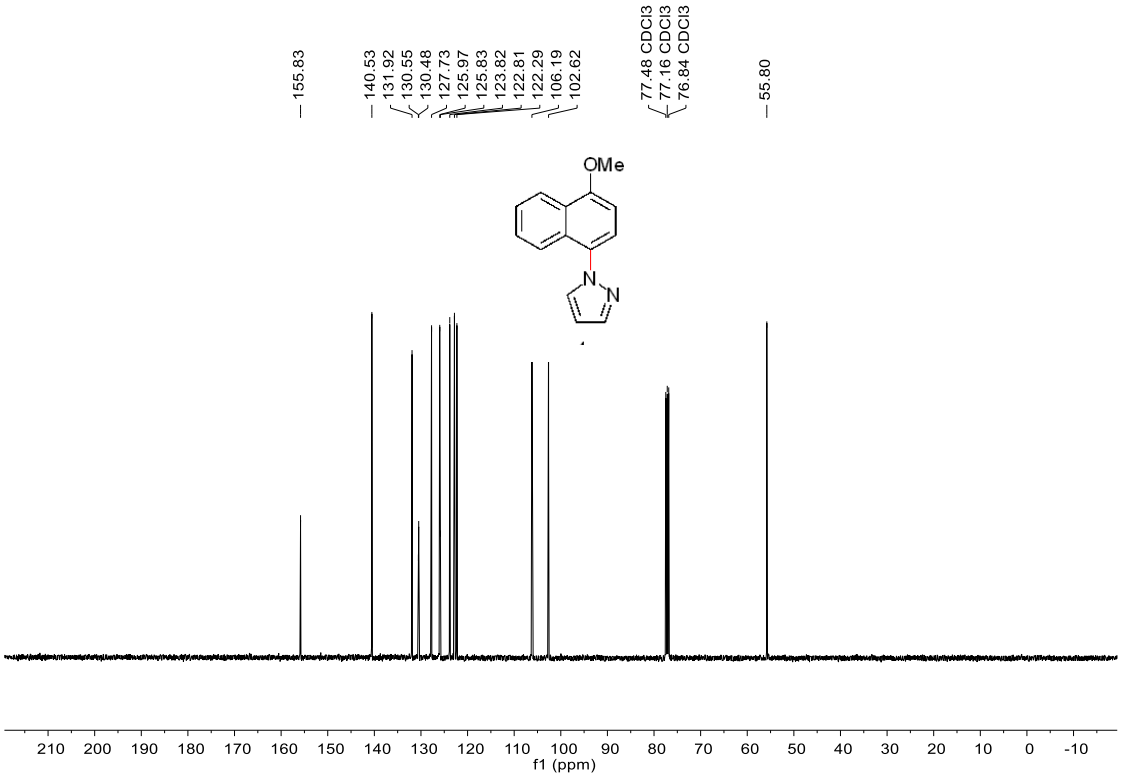
N
0.95
0.95
0.95
1.00
1.91
0.89
0.94
0.92
3.00
f1 (ppm)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140.53
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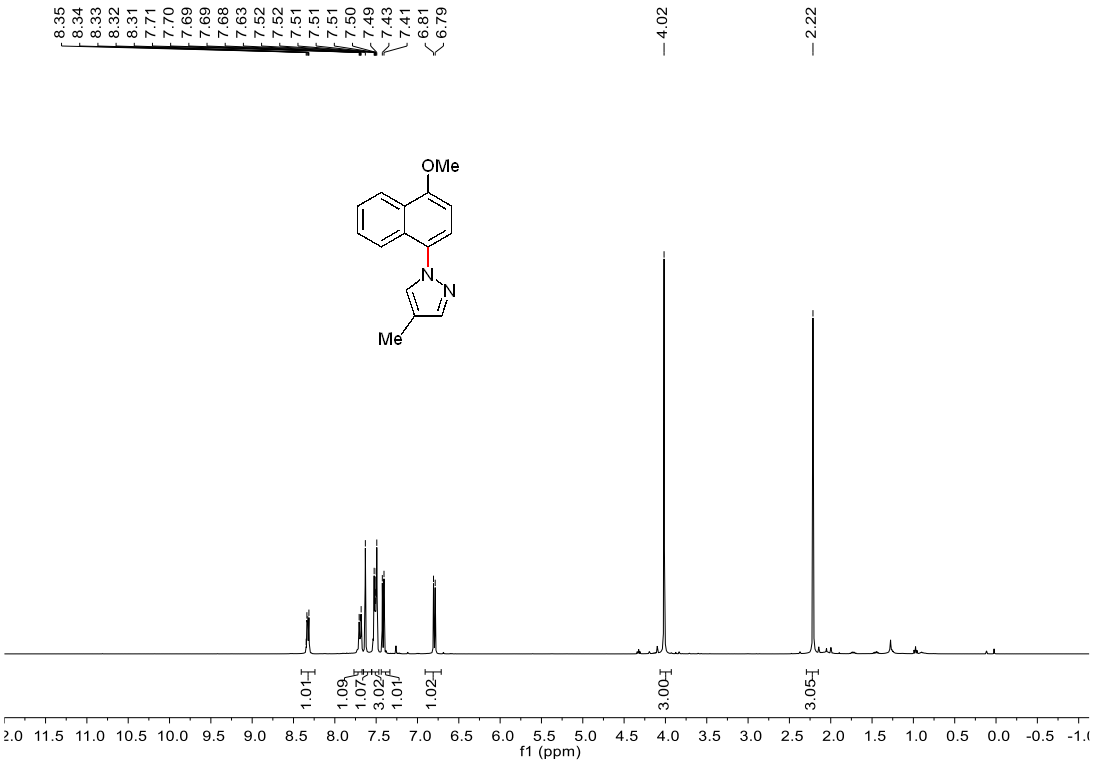
130.48
127.73
125.97
125.83
123.82
122.81
122.29
106.19
102.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.80
OMe
N
N
f1 (ppm)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7.69
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7.68
7.63
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7.51
7.51
7.51
7.50
7.49
7.43
7.41
6.81
6.79
4.02
2.22
OMe
N
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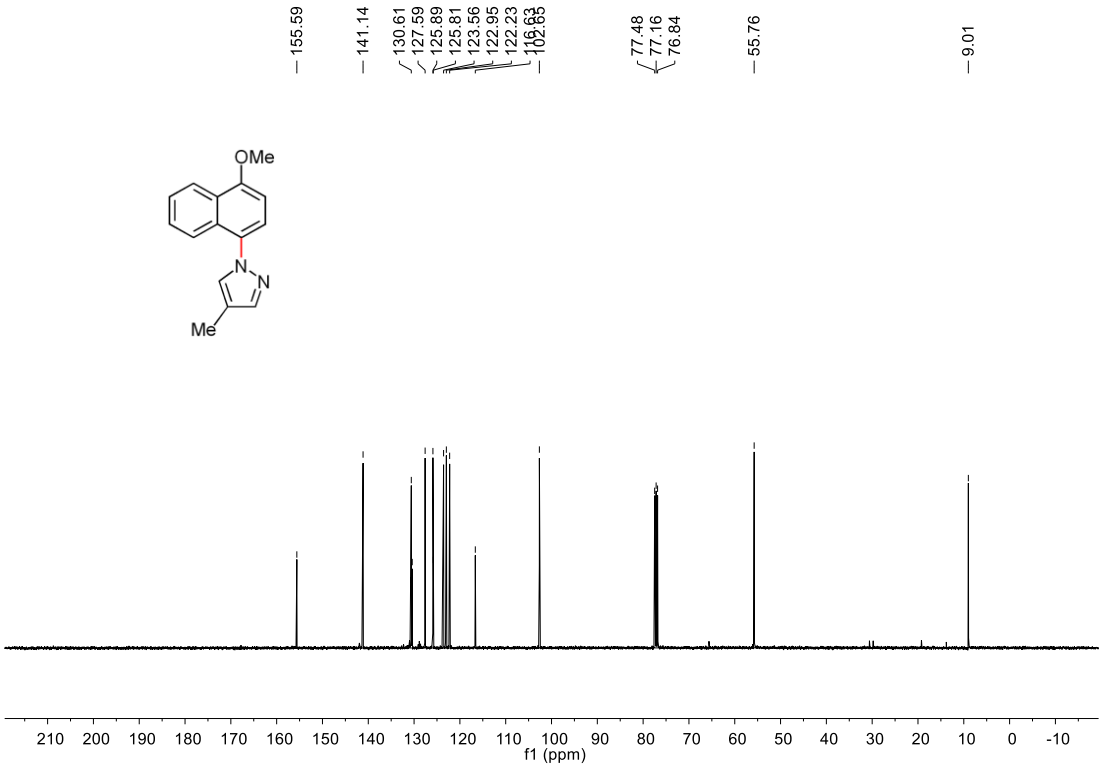
Me
1.01
1.09
1.07
3.02
1.01
1.02
3.00
3.05
f1 (ppm)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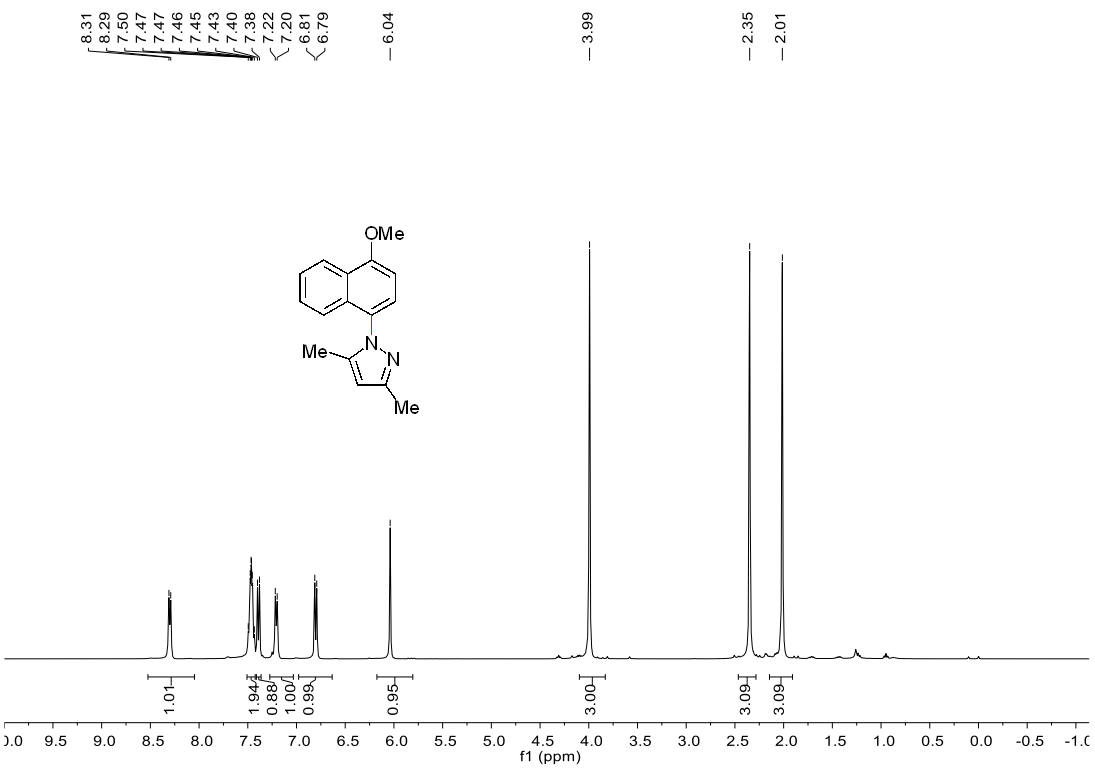
130.61
127.59
125.89
125.81
123.56
122.95
122.23
116.63
102.65
77.48
77.16
76.84
55.76
9.01
OMe
N
N
Me
f1 (ppm)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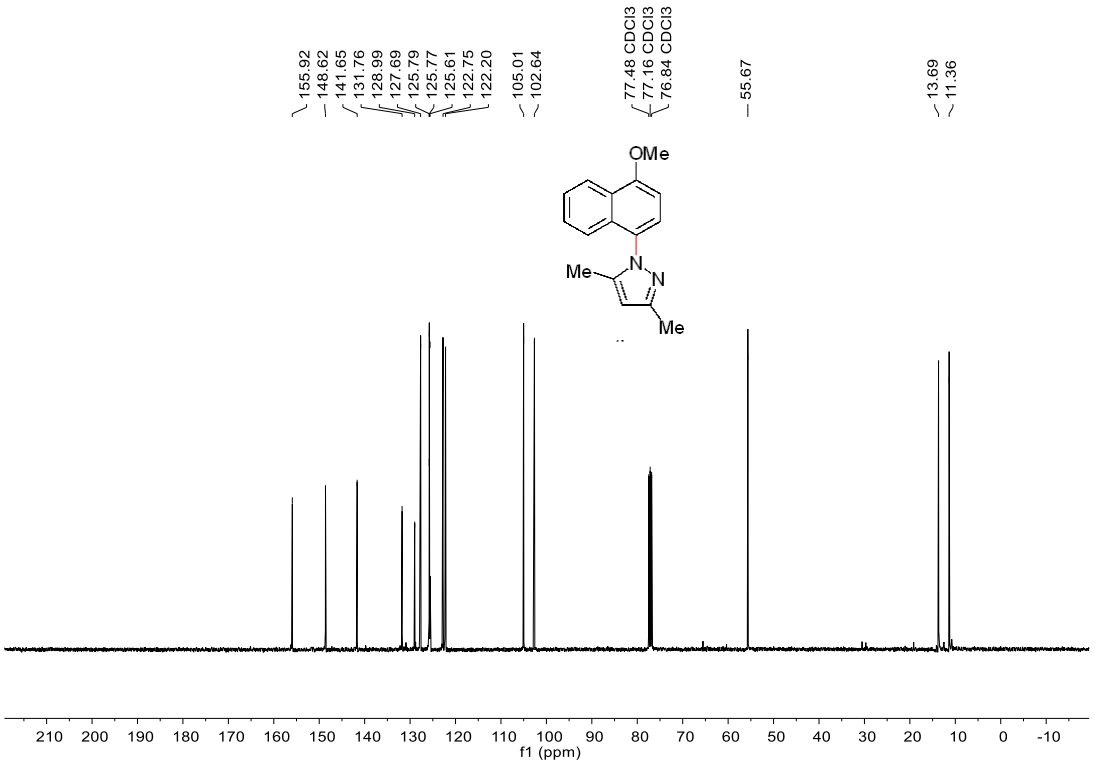
7.47
7.46
7.45
7.43
7.40
7.38
7.22
7.20
6.81
6.79
6.04
3.99
2.35
2.01
OMe
Me
N
N
Me
1.01
1.94
0.88
1.00
0.99
0.95
3.00
3.09
3.09
f1 (ppm)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148.62
141.65
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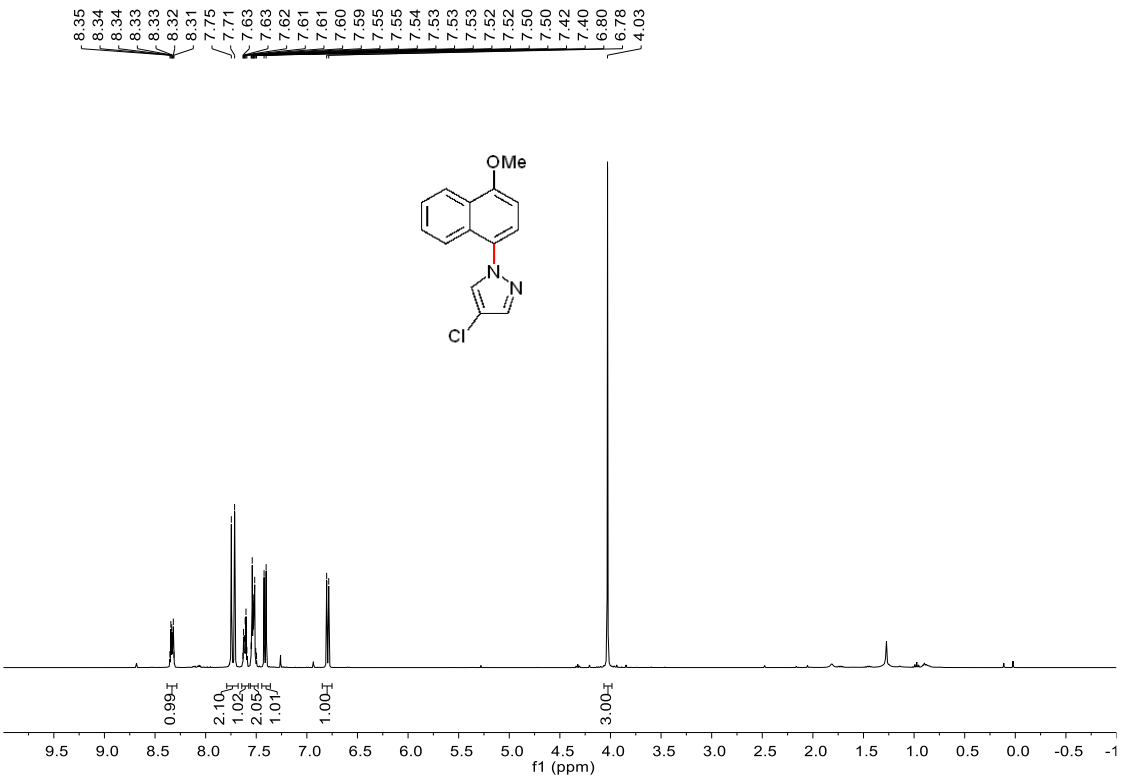
128.99
127.69
125.79
125.77
125.61
122.75
122.20
105.01
102.64
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.67
13.69
11.36
OMe
Me
N
N
Me
f1 (ppm)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8.34
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8.33
8.32
8.31
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7.71
7.63
7.63
7.62
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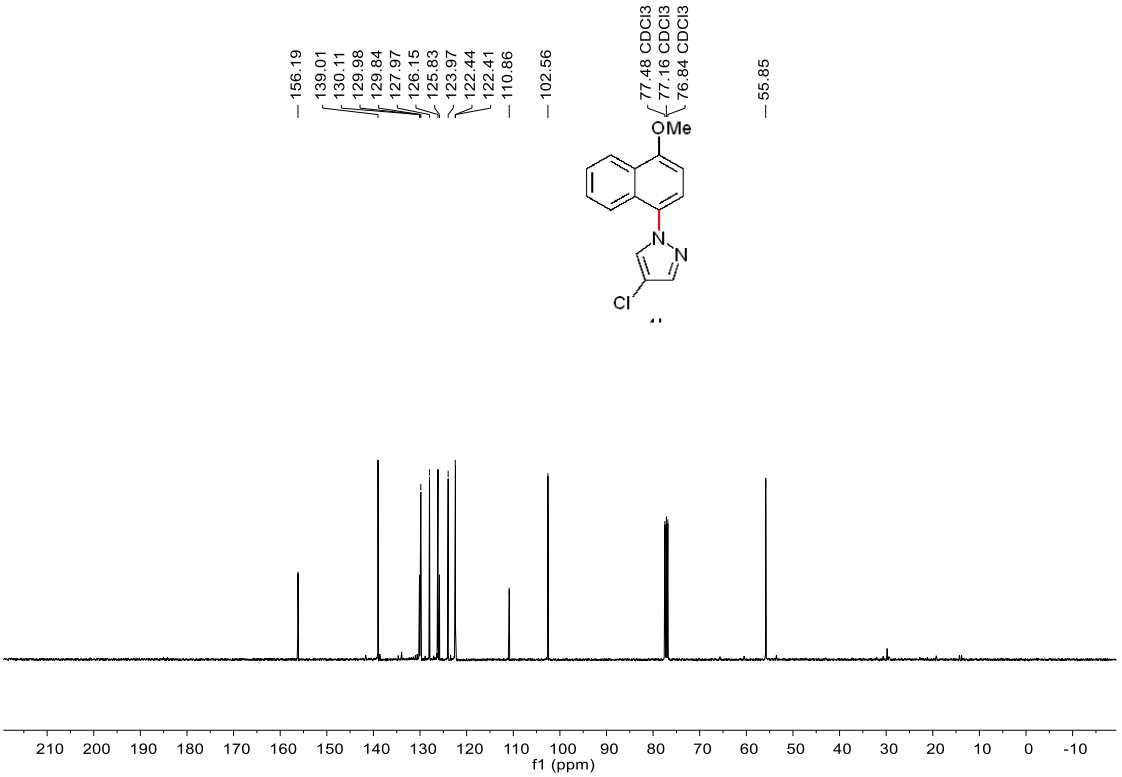
7.61
7.60
7.59
7.55
7.55
7.54
7.53
7.53
7.53
7.52
7.52
7.50
7.50
7.42
7.40
6.80
6.78
4.03
OMe
N
N
Cl
0.99
2.10
1.02
2.05
1.01
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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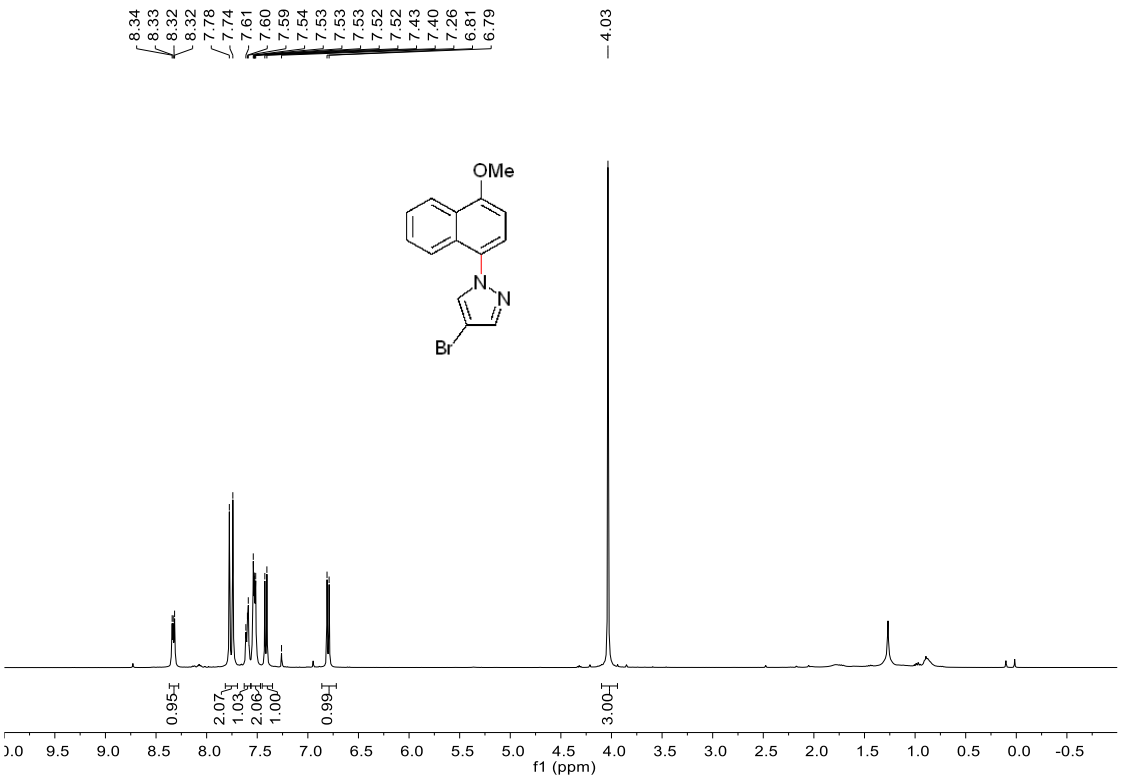
129.98
129.84
127.97
126.15
125.83
123.97
122.44
122.41
110.86
102.56
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.85
OMe
N
N
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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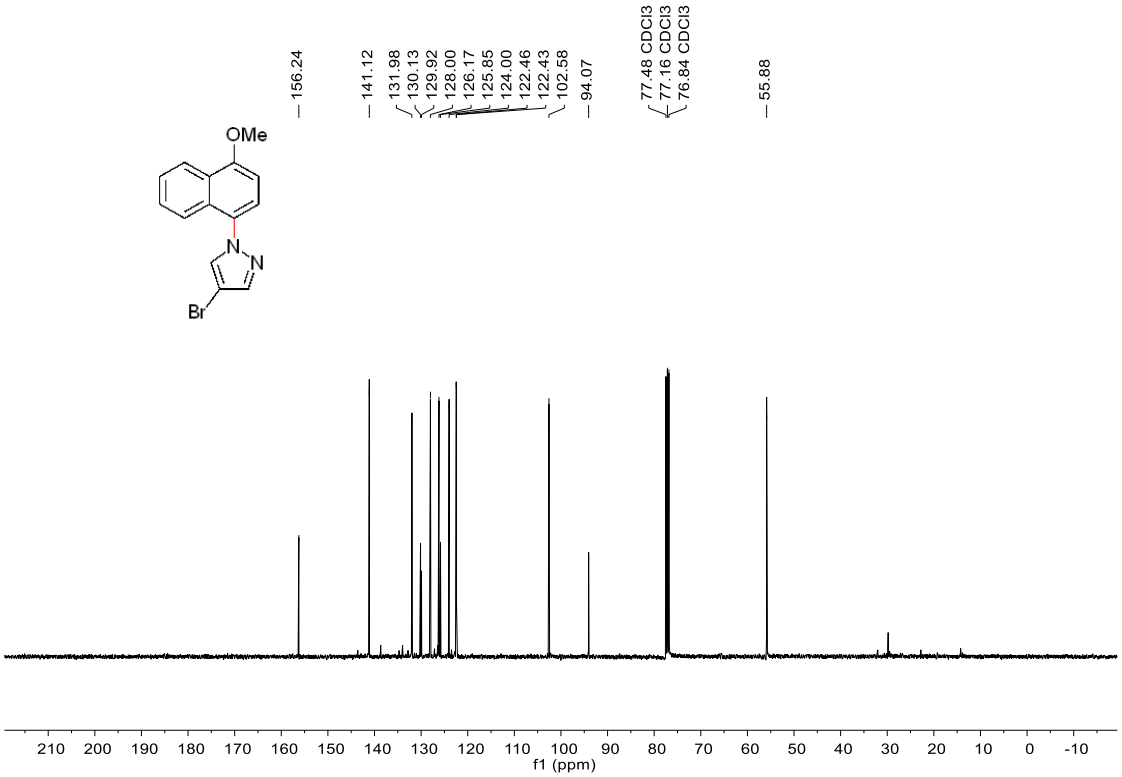
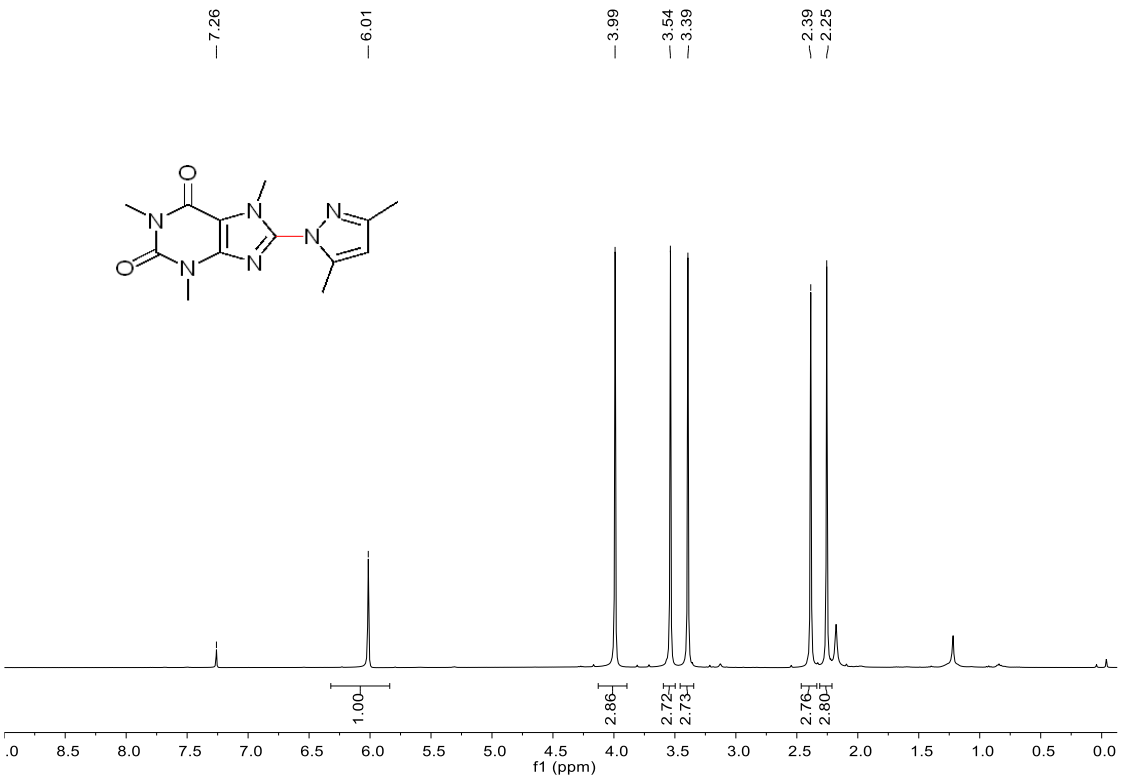
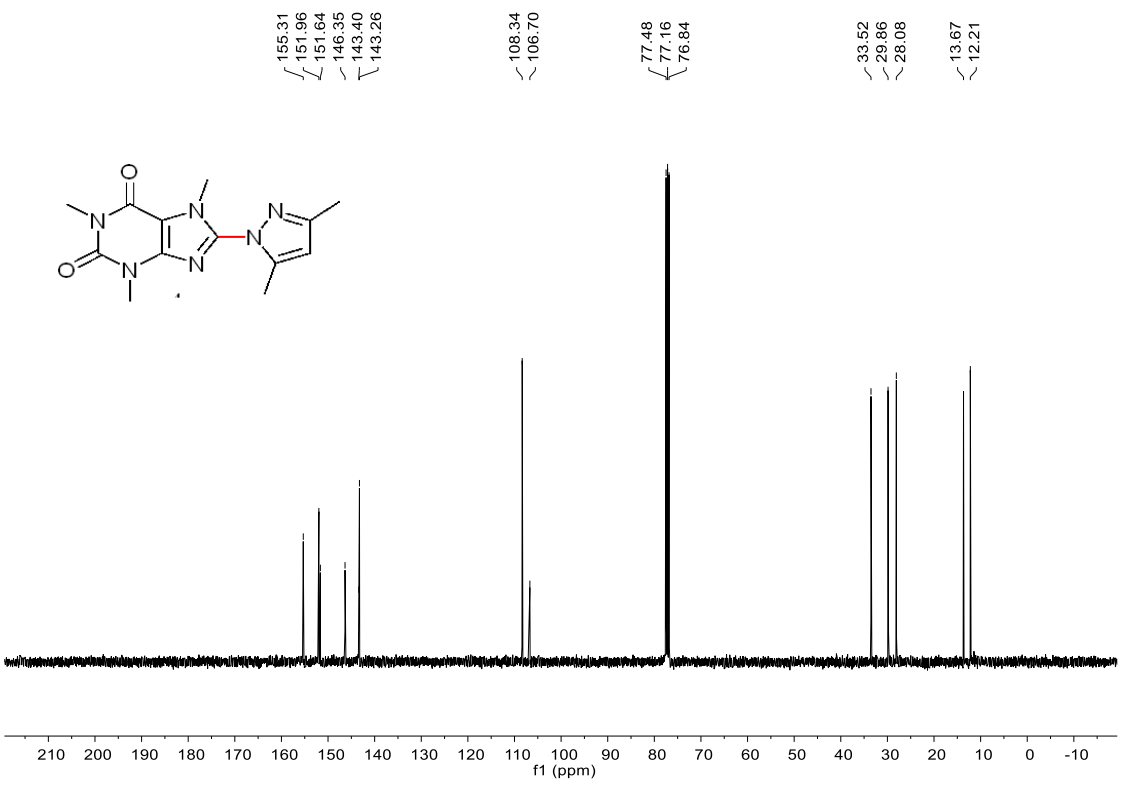
8.33
8.32
8.32
7.78
7.74
7.61
7.60
7.59
7.54
7.53
7.53
7.53
7.52
7.52
7.43
7.40
7.26
6.81
6.79
4.03
OMe
N
N
Br
0.95
2.07
1.03
2.06
1.00
0.99
3.00
f1 (ppm)


156.24
141.12
131.98
130.13
129.92
128.00
126.17
125.85
124.00
122.46
122.43
102.58
94.07
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.88
OMe
N
N
Br
f1 (ppm)


7.26
6.01
3.99
3.54
3.39
2.39
2.25
1.00
2.86
2.72
2.73
2.76
2.80
f1 (ppm)


155.31
151.96
151.64
146.35
143.40
143.26
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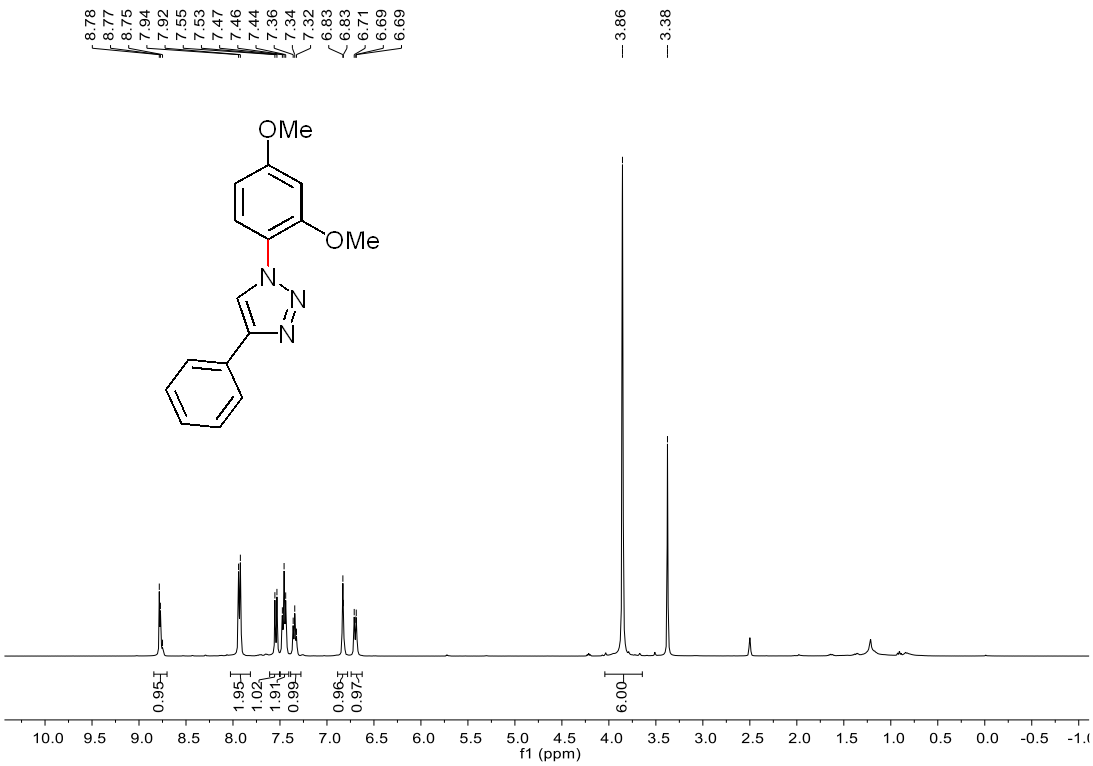
77.48
77.16
76.84
33.52
29.86
28.08
13.67
12.21
f1 (ppm)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8.77
8.75
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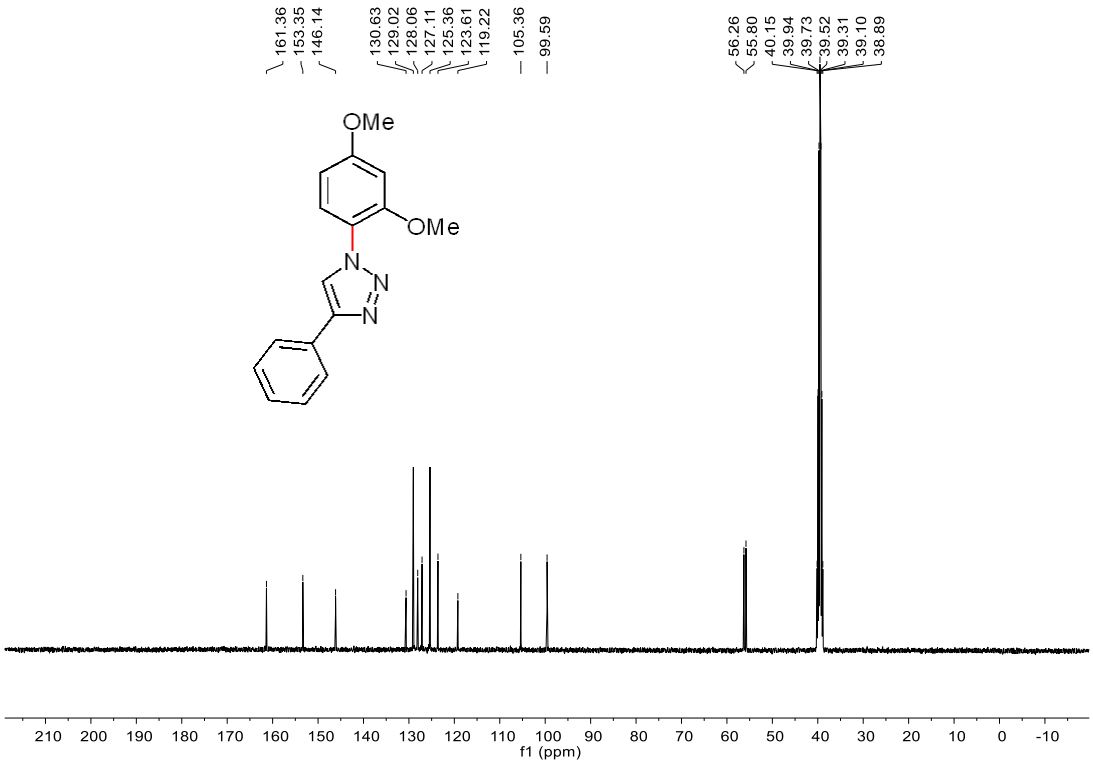
7.92
7.55
7.53
7.47
7.46
7.44
7.36
7.34
7.32
6.83
6.83
6.71
6.69
6.69
3.86
3.38
OMe
OMe
N
N
N
0.95
1.95
1.02
1.91
0.99
0.96
0.97
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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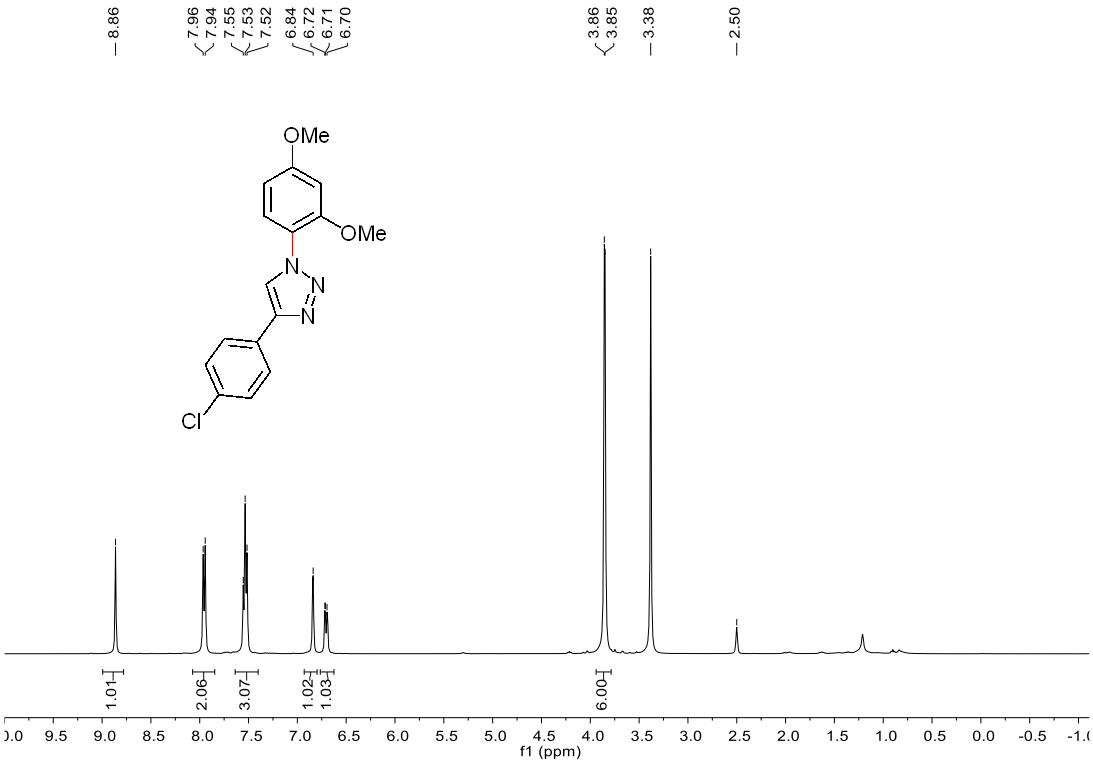
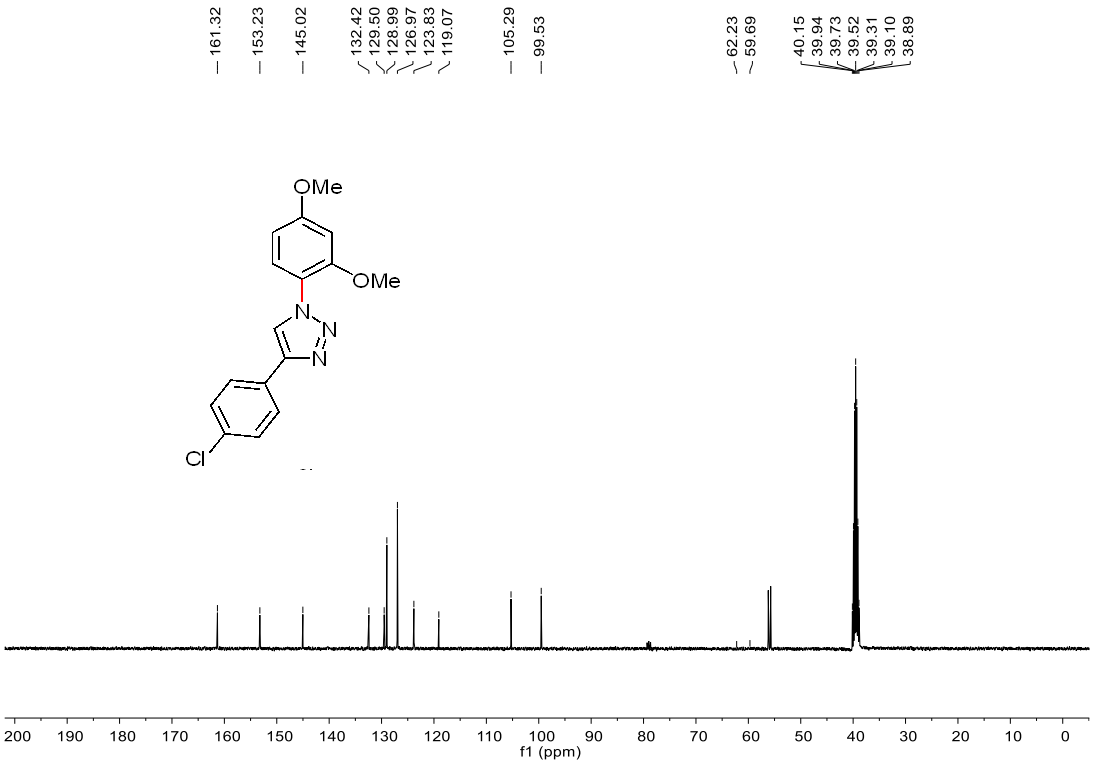
153.35
146.14
130.63
129.02
128.06
127.11
125.36
123.61
119.22
105.36
99.59
56.26
55.80
40.15
39.94
39.73
39.52
39.31
39.10
38.89
OMe
OMe
N
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.86
7.96
7.94
7.55
7.53
7.52
6.84
6.72
6.71
6.70
3.86
3.85
3.38
2.50
OMe
OMe
N
N
N
Cl
1.01
2.06
3.07
1.02
1.03
6.00
f1 (ppm)


161.32
153.23
145.02
132.42
129.50
128.99
126.97
123.83
119.07
105.29
99.53
62.23
59.69
40.15
39.94
39.73
39.52
39.31
39.10
38.89
OMe
OMe
N
N
N
Cl
f1 (ppm)