High Yielding Palladium-Catalyzed Intramolecular Alkane Arylation: Reaction Development and Mechanistic Studies

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Supporting Information

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Computational Details

All DFT calculations were performed using the Gaussian 03 package.[1] Stationary points on the potential energy surface were obtained using the B3LYP exchange-correlation functional[2,3] with the DZVP basis[4] for the Pd atom and the TZVP basis[5] for the other atoms. Geometry optimizations were performed with the GDIIS optimizer.[6,7] Preliminary calculations were performed by using the DZVP basis for all atoms. Such a combination is necessary to reduce the effects of basis set superposition errors (BSSE)[8] in geometry and thermochemistry, and to provide a balanced description of ionic and covalent contributions to chemical bonding.[9] Tight SCF convergence criteria (10^{-8} a.u.) were used for all calculations. The converged wave functions were tested to confirm that they correspond to the ground-state surface. Harmonic frequency calculations were used to determine the nature of the stationary points and the intrinsic reaction

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Lyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.01*, Gaussian, Inc.: 2003.
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[7] Farkas, O.; Schlegel, H. B., *J. Chem. Phys.* **1999,** 111, 10806-10814.
[8] Boys, S. F.; Bernardi, F., *Mol. Phys.* **1970,** 19, 553.
[9] Gorelsky, S. I.; Basumallick, L.; Vura-Weis, J.; Sarangi, R.; Hedman, B.; Hodgson, K. O.; Fujisawa, K.; Solomon, E. I., *Inorg. Chem.* **2005,** 44, 4947-4960.

coordinate[10] scans were performed to confirm that the transition state (TS) found is connected to the reactants and the products. Gibbs free energies of the species were calculated using the unscaled frequencies and at 298 K and 1 atmosphere unless specified otherwise. The relevant optimized structures are shown in Figure 1, S1 and S2.

The phosphine ligand in the Pd species was modeled as $P(CH_3)_3$ and the base for proton abstraction was modeled as a coordinated acetate ion. The deuterium kinetic isotope effect (KIE) k_H/k_D for the reaction of the $Pd(P(CH_3)_3)(C_6H_4\text{-}O\text{-}C(CH_3)(CD_3)_2)(O_2CCH_3)$ species was calculated by treating classically the motion along the reaction coordinate and using $\Delta\Delta G^{\ddagger}$ at 413K (the temperature of the KIE experiment), 1.04 kcal/mol (Table S1). Thus, the calculation did not include any rate enhancements due to quantum mechanical tunneling.[11]

Atomic charges were calculated by natural population analysis (NPA)[12, 13] as implemented in Gaussian 03. Two- and three-center Mayer bond orders (B_{AB} and B_{ABC})[14,15,16] were obtained using the AOMix-L program.[9, 17] To analyze molecular orbital contributions to agostic interactions[18] in the species, the proton abstraction reaction in the $Pd(C_6H_5)(P(CH_3)_3)(CH_4)(O_2CCH_3)$ species was used (Figure S3). The analysis of molecular orbitals (MOs) in terms of fragment orbital

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[10] Gonzalez, C.; Schlegel, H. B., *J. Chem. Phys.* **1989,** 90, 2154.
[11] Garrett, B. C.; Truhlar, D. G., *J. Chem. Phys.* **1980,** 72, 3460.
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[13] Reed, A. E.; Curtiss, L. A.; Weinhold, F., *Chem. Rev.* **1988,** 88, 899-926.
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[15] Sannigrahi, A. B.; Kar, T., *Chem. Phys. Lett.* **1990,** 173, 569-572.
[16] Giambiagi, M.; Giambiagi, M. S.; Mundim, K. C., *Struct. Chem.* **1990,** 1, 123.
[17] Gorelsky, S. I. *AOMix: Program for Molecular Orbital Analysis*, version 6.35; University of Ottawa: Ottawa, Canada, 2007.
[18] Brookhart, M.; Green, M. L. H.; Parkin, G., *Proc. Nat. Acad. Sci. USA* **2007,** 104, 6908-6914.

(FO) contributions and the construction of the FO interaction diagram (Figure S4) were carried out using the AOMix-CDA program.[17, 19]

Solvent effects were evaluated at the single-point calculations of the solvation energies using the gas-phase geometries. Solvation energies in benzene were calculated using the PCM model[20] with the united atom topological model (UAHF). Gibbs free energies in the solution were estimated by addition of the solvation energy ΔG_{solv} to gas-phase Gibbs free energies (Table S1).

[19] Gorelsky, S. I.; Ghosh, S.; Solomon, E. I., *J. Am. Chem. Soc.* **2006,** 128, 278-290.
[20] Barone, V.; Cossi, M.; Tomasi, J., *J. Comput. Chem.* **1998,** 19, 404-417.

Table S1. Activation barriers (electronic energy difference ($\Delta E^{\ddagger}$) and Gibbs free energy at 298K ($\Delta G_{298K}^{\ddagger}$)), 3-center Pd-C-H bond order indices (B_{PdCH}) for the transition states and the reaction free energy change ($\Delta G_{r,298K}$) for the Pd^{II} palladation-deprotonation reaction step in the $Pd(P(CH_3)_3)(C_6H_4\text{-}O\text{-}R)(O_2CCH_3)$ complexes

$Pd(P(CH_3)_3)(C_6H_4\text{-}O\text{-}RH)(O_2CCH_3) = Pd(P(CH_3)_3)(C_6H_4\text{-}O\text{-}R) + HO_2CCH_3$.

The free energies in the C_6H_6 solvent are shown in parenthesis.

R**H** [a, b]	$\Delta E^{\ddagger}$ kcal/mol	$\Delta G_{298K}^{\ddagger}$ kcal/mol	B_{PdCH}	$\Delta G_{r,298K}$ Kcal/mol
$CH_2C\mathbf{H}_3$	31.5	32.6 (33.8)	0.116	20.6 (19.1)
$C(C\mathbf{H}_3)_3$	30.5	29.4[c] (27.7)	0.102	16.3 (13.1)
$C(C\mathbf{H}_3)_2(CH_2CH_3)$	30.3	28.8 (27.0)	0.100	15.6 (11.3)
$C(C\mathbf{H}_3)_2(CH_2CH_3)$ [d]	30.4	29.4 (27.5)	0.102	16.5 (12.0)
$C(CH_3)_2(C\mathbf{H}_2CH_3)$	35.0	34.2 (32.5)	0.102	15.5 (10.8)
$C(CH_3)_2(C\mathbf{H}_2CH_3)$ [d]	37.4	35.7 (34.5)	0.106	16.4 (11.9)
$C(CH_3)_2(CH_2C\mathbf{H}_3)$	36.0	34.9 (33.1)	0.112	21.9 (17.8)

a) **H** indicates the abstracted H atom, see Figure S2 for the corresponding structures.

b) see Figures 1 and S2 for the structures.

c) $\Delta G_{413K}^{\ddagger}$ is 30.44 kcal/mol and 31.48 kcal/mol for $Pd(P(CH_3)_3)(C_6H_4\text{-}O\text{-}C(C\mathbf{H}_3)(CD_3)_2)(O_2CCH_3)$ and $Pd(P(CH_3)_3)(C_6H_4\text{-}O\text{-}C(CH_3)(C\mathbf{D}_3)_2)(O_2CCH_3)$, respectively.

d) the second isomer, see Figure S2.

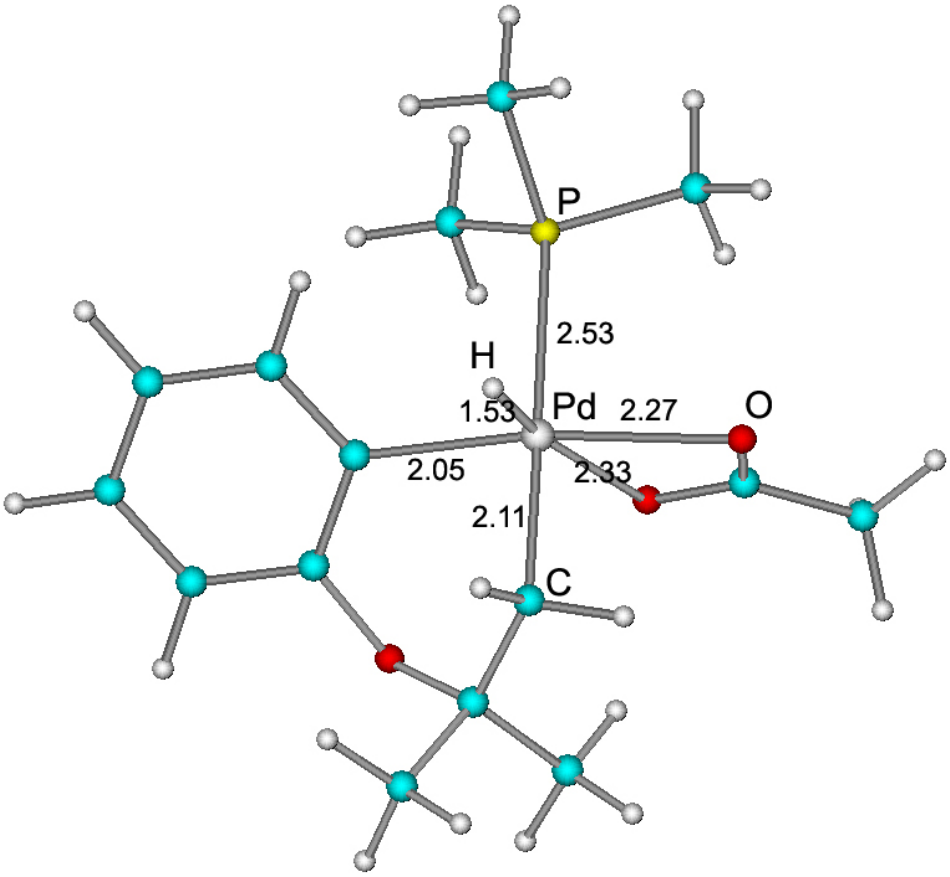


Figure S1. The structure of the Pd^{IV} intermediate (a local energy minimum) for the palladation-deprotonation reaction of the $Pd(C_6H_4\text{-}O\text{-}C(CH_3)_3)(P(CH_3)_3)(O_2CCH_3)$ complex (at the B3LYP/DZVP level). Relevant bond distances (Å) are shown.

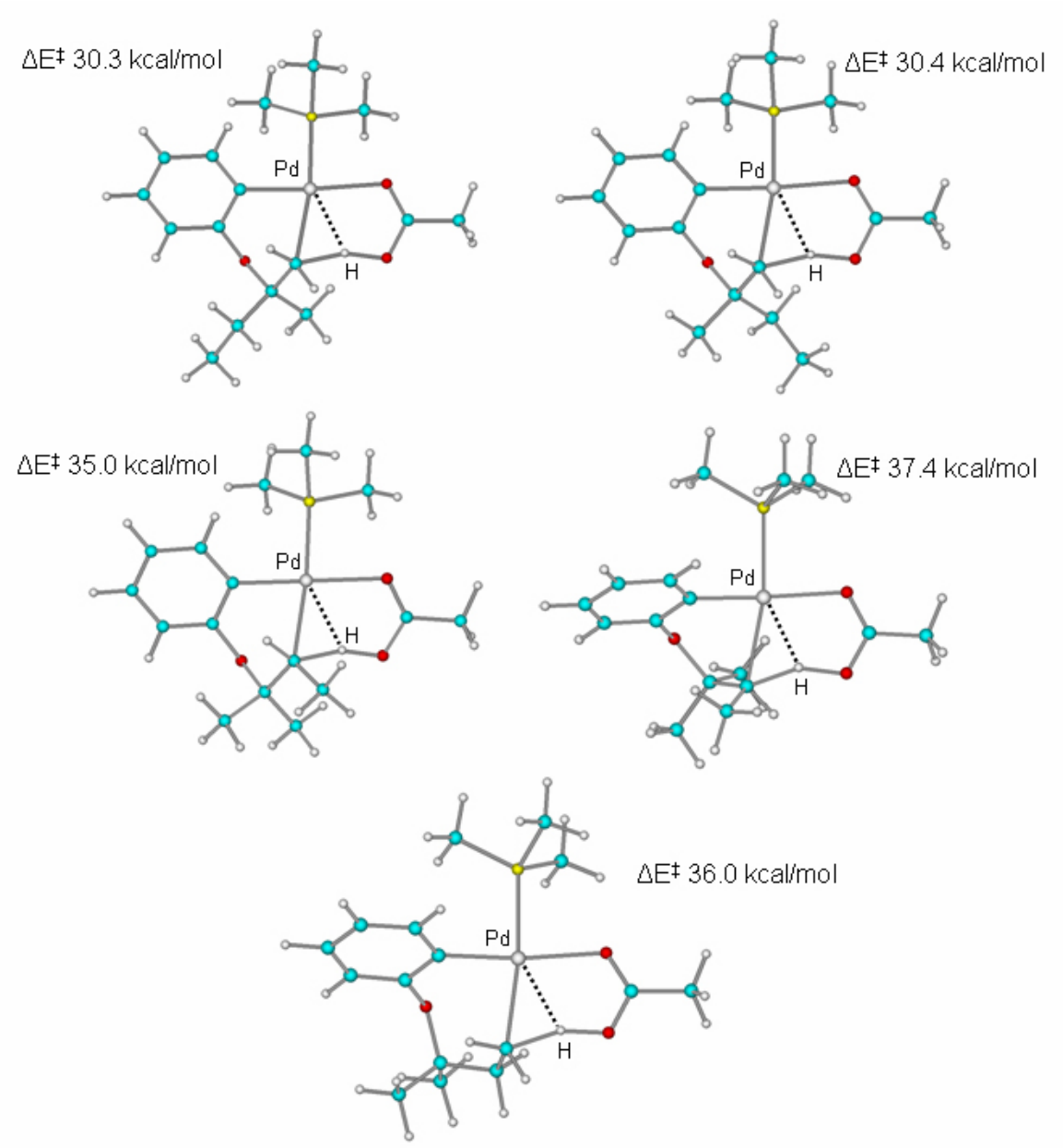
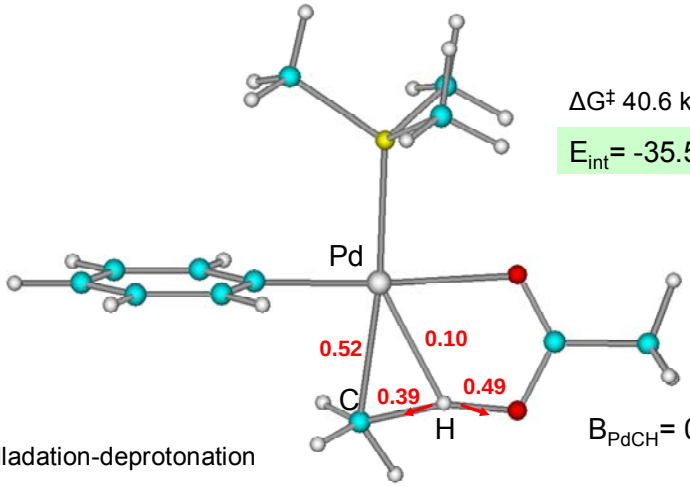


Figure S2. The transition state structures of the Pd^{II} palladation-deprotonation reactions of the $Pd(C_6H_4\text{-}O\text{-}C(CH_3)_2(CH_2CH_3))(P(CH_3)_3)(O_2CCH_3)$ complex.



	Reactant	TS	Product
$q_{NPA}(H)$	+0.21	+0.40	+0.51
$q_{NPA}(C)$	-0.83	-1.07	-0.95
$q_{NPA}(Pd)$	+0.59	+0.55	+0.45
B_{C-H}	0.98	0.39	0.00
B_{Pd-C}	0.00	0.52	0.76

Changes in the electron populations
The metal fragment:
HOFO ($2p_O$ of O_2CCH_3) 13.6%
LUFO (45% 5s,$4d_{Pd}$) 21.6%
The CH_4 fragment:
HOFO (σ_{C-H}) 20.9%
LUFO (σ^*_{C-H}) 15.0%

Figure S3. The transition state (TS) structure of the Pd^{II} palladation-deprotonation reaction of methane using $Pd(C_6H_5)(P(CH_3)_3)(O_2CCH_3)$. The Mayer 2-center bond orders for the TS structure are shown in red. The NPA-derived atomic charges and Mayer 2-center bond orders for the reactant and the product species are shown in the Table.

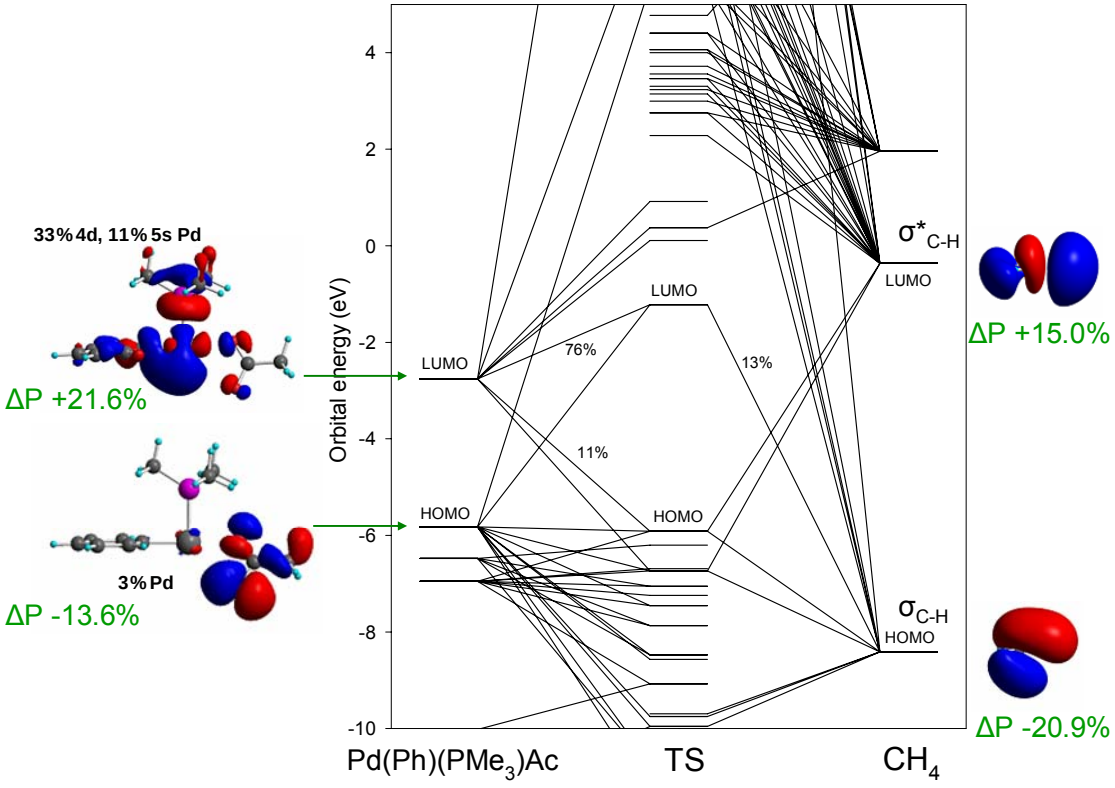


Figure S4. The molecular orbital diagram for the transition state of the Pd^{II} palladation-deprotonation reaction of methane using $Pd(C_6H_5)(P(CH_3)_3)(O_2CCH_3)$. The MOs of the metal and CH_4 fragments are shown on the left and on the right sides, respectively. Changes in the fragment orbital populations (ΔP) are shown in green.

The optimized XYZ coordinates (Å) of the $Pd(P(CH_3)_3)(C_6H_4\text{-}O\text{-}C(CH_3)_3)(O_2CCH_3)$ complex (the reactant)

Pd	0.989598	0.015511	-0.322831
C	-3.332584	-1.403881	-1.938149
C	-2.181985	-1.714986	-2.652925
C	-0.935574	-1.345539	-2.147559
C	-0.824990	-0.643338	-0.948259
C	-1.989478	-0.315504	-0.243912
C	-3.235678	-0.714711	-0.733668
O	-1.878159	0.313140	0.981080
H	-4.305330	-1.703957	-2.308877
H	-2.247709	-2.249725	-3.593097
H	-0.042949	-1.599167	-2.708524
H	-4.125644	-0.494196	-0.159115
C	-2.250234	1.728220	1.148978
C	-1.403849	2.175506	2.339382
H	-0.342674	2.096058	2.100511
H	-1.626053	3.212237	2.599354
H	-1.611867	1.550531	3.210083
C	-1.918606	2.552663	-0.093620
H	-0.862313	2.485079	-0.354814
H	-2.504304	2.230201	-0.955464
H	-2.157925	3.600768	0.098911
C	-3.740336	1.826168	1.491177
H	-3.984869	1.163809	2.323537
H	-3.992402	2.849159	1.780022
H	-4.365643	1.561494	0.638118
P	1.118816	-1.881165	0.954745
C	2.388534	-1.612546	2.266019
C	1.732335	-3.359795	0.038042
C	-0.347403	-2.512971	1.869500
H	2.595392	-2.537347	2.808587
H	3.301978	-1.236403	1.806319
H	2.026900	-0.856106	2.962314
H	1.872992	-4.205077	0.714894
H	1.010103	-3.630315	-0.731964
H	2.680186	-3.119385	-0.442980
H	-0.054910	-3.328253	2.534191
H	-0.791825	-1.701303	2.443132
H	-1.091454	-2.868940	1.158520
O	2.899162	1.105684	0.021886
C	2.535958	2.014323	-0.789124
O	1.405845	1.957217	-1.360417
C	3.469343	3.157200	-1.098661
H	4.021100	2.922218	-2.012335
H	2.903409	4.070976	-1.275952
H	4.184576	3.298411	-0.290035

The optimized XYZ coordinates (Å) of the Pd($P(CH_3)_3$)(C_6H_4-O-C($C\mathbf{H}_3)_3$)(O_2CCH_3) complex (the transition state)

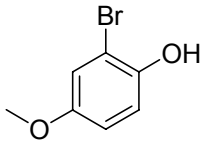
Pd	-0.497475	0.076629	-0.329222
C	4.238428	1.049475	-0.320532
C	3.408256	1.811486	-1.134734
C	2.035775	1.553621	-1.160276
C	1.480962	0.535088	-0.387930
C	2.334775	-0.261779	0.379861
C	3.703005	0.007064	0.429300
O	1.837453	-1.295682	1.134024
H	5.301859	1.252622	-0.280479
H	3.819426	2.607666	-1.744410
H	1.403394	2.161611	-1.798150
H	4.330972	-0.614172	1.056592
C	1.286497	-2.454639	0.410311
C	0.496531	-3.199782	1.482459
H	-0.320769	-2.581340	1.853503
H	0.074931	-4.122178	1.079326
H	1.147722	-3.450662	2.321618
C	0.398116	-2.048800	-0.773194
H	0.990509	-1.607414	-1.574440
H	0.041280	-2.981268	-1.229751
C	2.475352	-3.301003	-0.066980
H	3.107964	-3.584875	0.777028
H	2.123540	-4.211386	-0.556872
H	3.082675	-2.745912	-0.784107
P	-0.991051	2.257790	0.441075
C	0.266536	3.124858	1.474569
C	-2.487154	2.263613	1.522363
C	-1.417384	3.499483	-0.860005
H	-0.119394	4.082371	1.830038
H	0.517033	2.493574	2.327090
H	1.174494	3.283838	0.895589
H	-2.754484	3.281411	1.813813
H	-3.310328	1.795371	0.986141
H	-2.284101	1.674500	2.416891
H	-1.695863	4.455788	-0.412422
H	-0.563109	3.650601	-1.519140
H	-2.249678	3.121434	-1.453501
H	-1.052390	-2.044774	-0.547810
O	-2.695993	-0.304189	-0.315221
C	-3.039777	-1.506062	-0.384392
O	-2.205150	-2.468459	-0.463646
C	-4.502474	-1.874693	-0.380563
H	-4.746388	-2.388976	-1.311693
H	-4.700302	-2.571195	0.435434
H	-5.124533	-0.989346	-0.274987

General Methods:

All experiments were carried out under an atmosphere of argon. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ solutions using a Bruker AVANCE 400 spectrometer. High-resolution mass spectra were obtained on a Kratos Concept IIH. Infra-Red analysis was performed with a Bruker EQUINOX 55. HPLC Grade Et_2O and hexane were employed. Mesitylene was degassed with Argon prior to every use. Palladium sources were stored in a dessicator and were weighed out to air unless otherwise specified. All other reagents and solvents were used as is from commercial sources. Unless noted below, all other compounds have been reported in the literature or are commercially available.

Synthesis of Cyclization Precursor

3-bromo-4-hydroxyanisole



The 2-bromophenol was prepared following literature preparation[21] and exhibited the same spectral data as previously reported (99%).

[21] Zaja, M.; Connon, S.J.; Dunne, A.M.; Rivard, M.; Buschmann, N.; Jiricek, J.; Blechert, S. *Org. Lett.*, **2004**, *6*, 457.

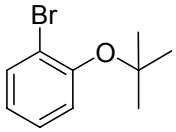
General Procedure A:

To a solution of phenol (5.8mmol) in dichloromethane (6.5mL) at -78^{o}C was added liquefied isobutylene (5mL). To this vigorously stirred solution was added slowly trifluoromethanesulfonic acid (0.46mmol) and the resulting mixture was stirred for an additional 4h at -78^{o}C. Triethylamine was then added (0.46mmol) and the solution was allowed to warm to room temperature. The solvents were then evaporated and the products were purified by column chromatography on silica gel using ether/hexanes mixtures.

General Procedure B:

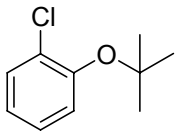
To a flask containing a suspension of potassium hydride (2.5mmol) in THF (3mL) at 0^{o}C was added slowly the corresponding tertiary alcohol (2.5mmol) and the solution was stirred for 10mins. The newly generated tertiary alkoxy was then added slowly to a solution of 2-bromo-1-fluoro-4-nitrobenzene (2.3mmol) in tetrahydrofuran (11mL) at 0^{o}C. The solution was then allowed to warm to room temperature and was stirred for 2h. Saturated aqueous ammonium chloride was then added and the solution was extracted with DCM and dried over magnesium sulfate. The products were then purified by column chromatography on silica gel using ether/hexanes mixtures.

2-*tert*-butoxybromobenzene



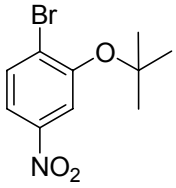
The compound was prepared following the general procedure A (99%): R_f = 0.51 (SiO_2, 6% ether/hexane); IR (ν_{max} /cm^{-1}): 2979, 1470, 1165; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.43 (9H, s), 6.91 (1H, td, *J*=7.9, 1.6Hz), 7.11 (1H, dd, *J*= 8.2, 1.6Hz), 7.19 (1H, td, *J*=8.2, 1.6Hz), 7.55 (1H, dd, *J*=7.9, 1.6Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 29.0, 81.3, 119.2, 123.9, 124.2, 127.8, 133.4, 153.3; HRMS calcd for $C_{10}H_{13}OBr$ (M+) 228.0150; found: 228.0132.

2-*tert*-butoxychlorobenzene



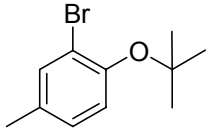
The compound was prepared following the general procedure A (98%): R_f = 0.43 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2982, 1473, 1165; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.41 (9H, s), 6.98 (1H, ddd, *J*=7.9, 7.1, 1.9Hz), 7.09-7.17 (1H, m), 7.36 (1H, dd, *J*=8.0, 1.6Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 28.9, 81.2, 124.0, 124.7, 127.0, 129.2, 130.3, 152.1; HRMS calcd for $C_{10}H_{13}OCl$ (M+) 184.0655; found: 184.0656.

1-tert-butoxy-2-bromo-5-nitrobenzene



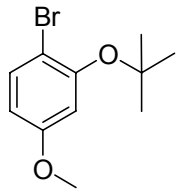
The compound was prepared following the general procedure B but employing potassium *tert*-butoxide (84%): R_f = 0.35 (SiO_2, 10% ether/hexane); IR (ν_{max} /cm^{-1}): 2982, 1580, 1518, 1474, 1344, 1283, 1155; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.54 (9H, s), 7.20 (1H, d, *J*=9.1Hz), 8.12 (1H, dd, *J*=9.1, 2.8Hz), 8.44 (1H, d, *J*=2.8Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 28.9, 83.4, 117.5, 119.9, 123.7, 129.0, 142.2, 159.3; HRMS calcd for $C_{10}H_{12}O_3NBr$ (M+) 273.0001; found: 273.0017.

1-tert-butoxy-2-bromo-4-methylbenzene



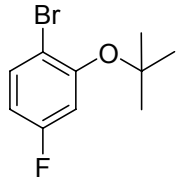
The compound was prepared following the general procedure A (99%): R_f = 0.25 (SiO_2, 2% ether/hexane); IR (ν_{max} /cm^{-1}): 2978, 1485, 1161; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.41 (9H, s), 2.27 (3H, s), 6.98-6.99 (2H, m), 7.36 (1H, s); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 20.4, 29.0, 80.9, 118.9, 123.8, 128.4, 133.6, 134.1, 150.8; HRMS calcd for $C_{11}H_{15}OBr$ (M+) 242.0306; found: 242.0290.

3-tert-butoxy-4-bromoanisole



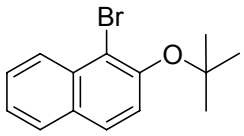
The compound was prepared following the general procedure A (99%): R_f = 0.25 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2977, 1599, 1487, 1366, 1264, 1217, 1163, 1038; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.39 (9H, s), 3.76 (3H, d, *J*=1.2Hz), 6.75 (1H, dd, *J*=8.9, 3.1Hz), 7.02 (1H, d, *J*=8.9Hz), 7.09 (1H, d, *J*=3.1Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 28.9, 55.6, 80.9, 113.6, 118.0, 119.5, 124.6, 146.8, 155.6; HRMS calcd for $C_{11}H_{15}O_2Br$ (M+) 258.0255; found: 258.0221.

1-tert-butoxy-2-bromo-5-fluorobenzene



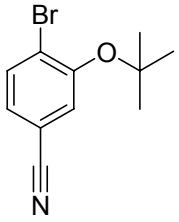
The compound was prepared following the general procedure A (93%): mp = 52-53°C(ether); R_f = 0.29 (SiO_2, 2% ether/hexane); IR (ν_{max} /cm^{-1}): 2974, 1600, 1475, 1151; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.45 (9H, s), 6.68 (1H, ddd, *J*=8.8, 7.8, 2.9Hz), 6.86 (1H, dd, *J*=10.2, 2.9Hz), 7.48 (1H, dd, *J*=8.8, 6.4Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 28.9, 82.1, 110.9 (d, *J*=17.6Hz), 111.2 (d, *J*=16.6Hz), 113.3 (d, *J*=3.9Hz), 133.4 (d, *J*=9.6Hz), 154.3 (d, *J*=10.5Hz), 161.9 (d, *J*=246.7Hz); ^{19}F NMR (377MHz, $CDCl_3$, 293K, TMS): -118.16; HRMS calcd for $C_{10}H_{12}OBrF$ (M+) 246.0056; found: 246.0060.

2-tert-butoxy-1-bromonaphthalene



The compound was prepared following the general procedure A using 30 mL of DCM instead (98%): R_f = 0.27 (SiO_2, 2% ether/hexane); IR (ν_{max} /cm^{-1}): 2980, 1474, 1165; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.49 (9H, s), 7.32 (1H, d, *J*=8.9Hz), 7.41 (1H, ddd, *J*= 8.1, 6.9, 1.1Hz), 7.54 (1H, ddd, *J*=8.3, 6.9, 1.1Hz), 7.69 (1H, d, *J*=8.9Hz), 7.77 (1H, d, *J*=8.1Hz), 8.26 (1H, d, *J*=8.3Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 29.4, 81.8, 117.1, 123.6, 125.0, 127.1, 127.3, 127.9, 127.9, 131.1, 133.2, 151.5; HRMS calcd for $C_{14}H_{15}OBr$ (M+-C_2H_6) 247.9837; found: 247.9810.

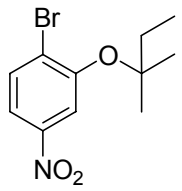
3-tert-butoxy-4-bromobenzonitrile



To a solution of 3-bromo-4-fluorobenzonitrile (0.5g, 2.5mmol, 1.0 eq.) in DMF (8mL) was added potassium *tert*-butoxide (0.42g, 3.8mmol, 1.5eq.) and the solution was heated to 135^oC overnight. The reaction was then quenched with water and the solution was extracted with Et_2O and dried over magnesium

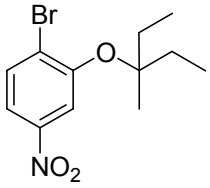
sulfate. The product was then purified by column chromatography on silica gel using 3% ether/hexane as the eluent. (81%): R_f = 0.21 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2981, 2228, 1594, 1484, 1370, 1271, 1160; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.50 (9H, s), 7.18 (1H, d, *J*=8.6Hz), 7.53 (1H, dd, *J*=8.5, 2.1Hz), 7.83 (1H, d, *J*=2.1Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 28.7, 82.8, 106.4, 117.4, 118.1, 121.5, 131.8, 136.6, 157.4; HRMS calcd for $C_{11}H_{12}NOBr$ (M+) 253.0102; found: 252.9895.

2-(tert-pentyloxy)-1-bromo-4-nitrobenzene



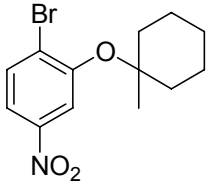
The compound was prepared following the general procedure B (73%): R_f = 0.41 (SiO_2, 10% ether/hexane); IR (ν_{max} /cm^{-1}): 2978, 1580, 1517, 1474, 1343, 1279, 1154; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.04 (3H, t, *J*=7.5Hz), 1.49 (6H, s), 1.86 (2H, q, *J*=7.5Hz), 7.17 (1H, d, *J*=9.1Hz), 8.12 (1H, dd, *J*=9.1, 2.8Hz), 8.44 (1H, d, *J*=2.8Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 8.4, 26.0, 35.0, 85.6, 116.9, 118.9, 123.6, 129.0, 141.7, 159.1; HRMS calcd for $C_{11}H_{14}O_3NBr$ (M+) 287.0157; found: 287.0147.

2-(3-methylpentan-3-yloxy)-1-bromo-4-nitrobenzene



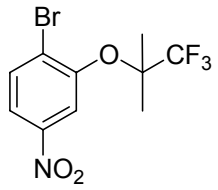
The compound was prepared following the general procedure B (76%): R_f = 0.26 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2975, 1582, 1516, 1472, 1341, 1275; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 0.98 (6H, t, *J*=7.5Hz), 1.44 (3H, s), 1.87 (4H, m), 7.13 (1H, d, *J*=9.2Hz), 8.11 (1H, dd, *J*=9.2, 2.8Hz), 8.45 (1H, d, *J*=2.8Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 8.1, 23.5, 31.5, 88.2, 116.4, 118.0, 123.7, 129.1, 141.5, 159.1; HRMS calcd for $C_{12}H_{16}O_3NBr$ (M+) 301.0314; found: 301.0292.

2-(1-methylcyclohexyloxy)-1-bromo-4-nitrobenzene



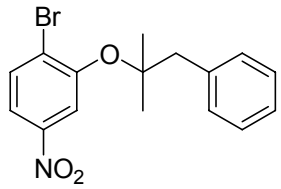
The compound was prepared following the general procedure B (69%): R_f = 0.28 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2936, 1582, 1516, 1473, 1341, 1246; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.30-1.39 (1H, m), 1.49 (3H, s), 1.51-1.77 (7H, m), 2.15-2.19 (2H, m), 7.16 (1H, d, *J*=9.2Hz), 8.12 (1H, dd, *J*=9.2, 2.8Hz), 8.45 (1H, d, *J*=2.8Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 22.0, 25.1, 25.9, 37.6, 84.3, 116.3, 117.9, 123.7, 139.1, 141.4, 158.9; HRMS calcd for $C_{13}H_{16}O_3NBr$ (M+) 313.0314; found: 313.0295.

2-(1,1,1-trifluoro-2-methylpropan-2-yloxy)-1-bromo-4-nitrobenzene



The compound was prepared following the general procedure B (79%): R_f = 0.25 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 3001, 1525, 1474, 1347, 1167, 1127; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.61 (6H, q, *J*=1.0Hz), 7.31 (1H, d, *J*=9.0Hz), 8.16 (1H, dd, *J*=9.0, 2.8Hz), 8.47 (1H, d, *J*=2.8Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 20.9 (q, *J*=1.2Hz), 82.4 (q, *J*=29.5Hz), 111.4, 119.0, 123.6, 125.1 (q, *J*=284.2Hz), 129.1, 144.1, 157.0; ^{19}F NMR (377MHz, $CDCl_3$, 293K, TMS): -86.4; HRMS calcd for $C_{10}H_9O_3NF_3Br$ (M+) 326.9718; found: 326.9698.

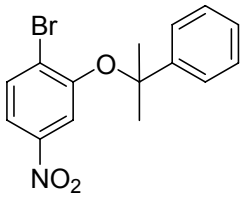
1-(2-(2-bromo-5-nitrophenoxy)-2-methylpropyl)benzene



The compound was prepared following the general procedure B (82%): R_f = 0.31 (SiO_2, 5% ether/hexane); IR (ν_{max} /cm^{-1}): 2979, 1516, 1343, 1279, 1118; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.46 (6H, s), 3.13 (2H, s), 7.12 (1H, d, *J*=9.1Hz), 7.24-7.31 (5H, m), 8.09 (1H, dd, *J*=9.1, 2.8Hz), 8.45 (1H, d, *J*=2.8Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K,

TMS): 26.3, 48.8, 85.4, 117.5, 120.2, 123.5, 126.6, 128.0, 129.0, 130.8, 136.6, 142.2, 159.0; HRMS calcd for $C_{16}H_{16}O_3NBr$ (M+) 349.0314; found: 349.0324.

1-(2-(2-bromo-5-nitrophenoxy)propan-2-yl)benzene



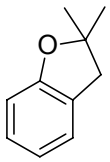
The compound was prepared following the general procedure B (83%): R_f = 0.30 (SiO_2, 5% ether/hexane); IR (ν_{max} /cm^{-1}): 2984, 1516, 1473, 1341, 1275, 1138; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.85 (6H, s), 6.36 (1H, d, *J*=9.2Hz), 7.28-7.41 (5H, m), 7.80 (1H, dd, *J*=9.2, 2.8Hz), 8.42 (1H, d, *J*=2.8Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 29.3, 83.9, 114.5, 116.8, 123.4, 124.9, 127.8, 128.9, 128.9, 141.0, 144.1, 158.4; HRMS calcd for $C_{15}H_{14}O_3NBr$ (M+) 335.0157; found: 335.0105.

General Cyclization Procedure:

Cs_2CO_3 (0.77 mmol), $Pd(OAc)_2$ (5mol %), PCy_3-HBF_4 (10mol %) and pivalic acid (30mol %) were weighed to air and placed in a screw capped vial (4mL) with a magnetic stir bar. The reaction vessel was evacuated and backfilled with argon (x3). The cyclization precursor (0.70mmol) was then added to the reaction vessel as a solution in mesitylene (3mL). The reaction was heated to 140ºC for 12 hours. Upon completion, the reaction was cooled to room temperature. The

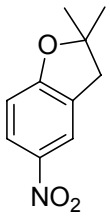
products were loaded directly onto a silica gel packed column chromatography and eluted using ether/hexane mixtures.

2,3-dihydro-2,2-dimethylbenzofuran



The compound was prepared following the general cyclization procedure at 135°C and exhibited the same spectral data as previously reported[22] (97%).

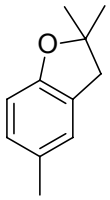
2,3-dihydro-2,2-dimethyl-5-nitrobenzofuran



The compound was prepared following the general cyclization procedure at 140°C (91%): mp = 67-68°C(ether); R_f = 0.22 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2974, 1596, 1507, 1337, 1281; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.53 (6H, s), 3.09 (2H,s), 6.75 (1H, d, *J*=8.8Hz), 8.04-8.05 (1H, m), 8.08 (1H, dd, *J*=8.8, 2.3Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 28.1, 41.9, 90.1, 109.3, 121.6, 125.8, 128.5, 141.5, 164.4; HRMS calcd for $C_{10}H_{11}O_3N$ (M+) 193.0739; found: 193.0440.

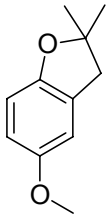
[22] Kataoka, N.; Shelby, Q.; Stambuli, J.P.; Hartwig, J.F. *J. Org. Chem.*, **2002**, *67*, 5553.

2,3-dihydro-2,2,5-trimethylbenzofuran



The compound was prepared following the general cyclization procedure at 135°C (92% contaminated with an additional 5% reduced product): R_f = 0.40 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2973, 1490, 1257; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.44 (6H, s), 2.26 (3H, s), 2.95 (2H,s), 6.61 (1H, d, *J*=8.1Hz), 6.88 (1H, d, *J*=8.1Hz), 6.93 (1H, s); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 20.7, 28.1, 42.9, 86.3, 109.0, 125.7, 127.0, 128.2, 19.0, 156.7; HRMS calcd for $C_{11}H_{14}O$ (M+) 162.1045; found: 162.1023

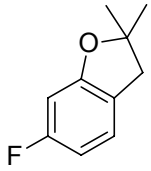
2,3-dihydro-5-methoxy-2,2-dimethylbenzofuran



The compound was prepared following the general cyclization procedure at 140°C (91%): R_f = 0.24 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2972, 1487, 1256, 1209, 1146, 1033; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.45 (6H, s), 2.98 (2H, s), 3.74 (3H,s), 6.61-6.66 (2H, m), 6.73 (1H, dd, *J*=2.2, 1.0Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS):

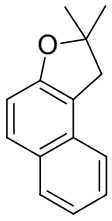
28.1, 43.3, 56.0, 86.5, 109.2, 111.5, 112.7, 128.0, 153.0, 153.7; HRMS calcd for $C_{11}H_{14}O_2$ (M+) 178.0994; found: 178.1003.

6-fluoro-2,3-dihydro-2,2-dimethylbenzofuran



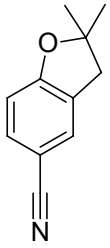
The compound was prepared following the general cyclization procedure at 135°C (68%): R_f = 0.31 (SiO_2, 2% ether/hexane); IR (ν_{max} /cm^{-1}): 2975, 1614, 1492, 1283, 1129, 1084; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.47 (6H, s), 2.94 (2H, s), 6.45 (1H, dd, *J*=9.6, 2.4Hz), 6.50 (1H, ddd, *J*=9.6, 8.1, 2.4Hz), 7.01 (1H, td, *J*=7.0, 1.1Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 28.1, 42.1, 88.4, 97.9 (d, *J*=26.2Hz), 106.3 (d, *J*=22.6Hz), 122.6 (d, *J*=2.6Hz), 125.2 (d, *J*=10.5Hz), 159.9 (d, *J*=13.0Hz), 163.2 (d, *J*=242.3Hz); ^{19}F NMR (377MHz, $CDCl_3$, 293K, TMS): -119.6; HRMS calcd for $C_{10}H_{11}FO$ (M+) 166.0794; found: 166.0803.

1,2-dihydro-2,2-dimethylnaphtho[2,1-b]furan



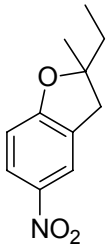
The compound was prepared following the general cyclization procedure at 155°C (79% contaminated with an additional 6% reduced product): R_f = 0.25 (SiO_2, 2% ether/hexane); IR (ν_{max} /cm^{-1}): 2972, 1631, 1465, 1261; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.53 (6H, s), 3.23 (2H,s), 7.06 (1H, d, *J*=8.8Hz), 7.26 (1H, ddd, *J*=8.1, 6.8, 1.3Hz), 7.42 (1H, ddd, *J*=8.1, 6.8, 1.2Hz), 7.51 (1H, td, *J*=8.3, 0.5Hz), 7.64 (1H, d, *J*=8.8Hz), 7.76 (1H, d, *J*=8.2Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 28.5, 4.7, 87.5, 112.4, 118.2, 122.5, 122.6, 126.5, 128.7, 128.9, 129.0, 131.1, 156.2; HRMS calcd for $C_{14}H_{14}O$ (M+) 198.1045; found: 198.1040.

2,3-dihydro-2,2-dimethylbenzofuran-5-carbonitrile



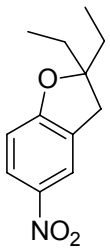
The compound was prepared following the general cyclization procedure at 140°C (78%): R_f = 0.14 (SiO_2, 5% ether/hexane); IR (ν_{max} /cm^{-1}): 2975, 2222, 1611, 1486, 1273, 1091; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.50 (6H, s), 3.04 (2H, s), 6.76 (1H, d, *J*=8.2), 7.41 (1H, s), 7.42 (1H, d, *J*=8.1Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 27.9, 41.8, 88.7, 102.8, 110.2, 119.6, 128.6, 129.0, 133.3, 162.3; HRMS calcd for $C_{11}H_{11}ON$ (M+) 173.0841; found: 173.0821.

2-ethyl-2,3-dihydro-2-methyl-5-nitrobenzofuran



The compound was prepared following the general cyclization procedure at 140°C (85%): mp = 45-46°C($CHCl_3$); R_f = 0.17 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2973, 1596, 1487,1336, 1255; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 0.98 (3H, t, *J*=6.7Hz), 1.47 (3H, s), 1.81 (2H, q, *J*=6.9Hz), 2.99 (1H, d, *J*=15.9Hz), 3.15 (1H, d, *J*=15.9Hz), 6.74 (1H, d, *J*=8.5Hz), 8.04 (1H, s), 8.07 (1H, d, *J*=8.5Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 8.1, 25.7, 33.6, 39.6, 92.6, 108.9, 121.4, 125.6, 128.4, 141.3, 164.5; HRMS calcd for $C_{11}H_{13}O_3N$ (M+) 207.0895; found: 207.0878.

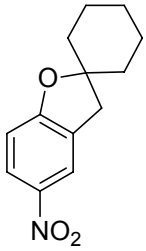
2,2-diethyl-2,3-dihydro-5-nitrobenzofuran



The compound was prepared following the general cyclization procedure at 140°C (96%): R_f = 0.21 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2972, 1514, 1334, 1267; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 0.94 (6H, t, *J*=7.5Hz), 1.77 (4H, q, *J*=7.5Hz), 3.06 (1H, s), 6.74 (1H, d, *J*=8.8Hz), 8.03 (1H, d, *J*=2.4Hz), 8.07 (1H, d, *J*=8.8, 2.4Hz); ^{13}C

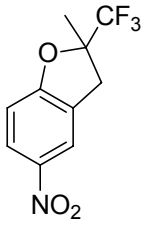
NMR (100MHz, $CDCl_3$, 293K, TMS): 7.6, 31.3, 37.1, 95.0, 108.6, 121.2, 125.6, 128.5, 141.2, 165.0; HRMS calcd for $C_{12}H_{15}O_3N$ (M+) 221.1052; found: 221.1028.+

5-nitrospiro-(benzofuran-2(3H),1'-cyclohexane)



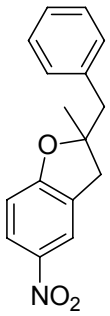
The compound was prepared following the general cyclization procedure at 140°C (90%): mp = 104-106°C; R_f = 0.14 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2931, 1593, 1504, 1339; ^1H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.44-1.54 (4H, m), 1.66-1.72 (2H, m), 1.75-1.80 (2H, m), 1.83-1.87 (2H, m), 3.03 (2H, s), 6.75 (1H, d, *J*=8.8Hz), 8.02 (1H, d, *J*=2.4Hz), 8.07 (1H, dd, *J*=8.8, 2.4Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 22.7, 24.8, 36.9, 40.1, 91.9, 109.1, 121.5, 125.6, 128.2, 141.2, 164.3; HRMS calcd for $C_{13}H_{15}O_3N$ (M+) 233.1052; found: 233.1049.

2-(trifluoromethyl)-2,3-dihydro-2-methyl-5-nitrobenzofuran



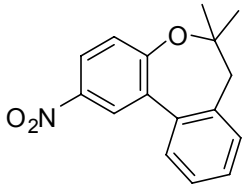
The compound was prepared following the general cyclization procedure at 140°C (88%): mp = 109-112°C(ether); R_f = 0.23 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 3097, 1514, 1348, 1177, 1146; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.71 (3H, d, *J*=0.8Hz), 3.21 (1H, d, *J*=16.8Hz), 3.62 (1H, d, *J*=16.8Hz), 6.91 (1H, d, *J*=8.8Hz), 8.10 (1H, d, *J*=1.1Hz), 8.15 (1H, dd, *J*=8.9, 2.4Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 20.9 (d, *J*=0.9Hz), 36.5 (d, *J*=1.1Hz), 87.9 (q, *J*=31.1Hz), 109.7, 121.2, 124.7 (q, *J*=282.8Hz), 126.0, 126.3, 142.7, 163.3; ^{19}F NMR (377MHz, $CDCl_3$, 293K, TMS): -88.3; HRMS calcd for $C_{10}H_8O_3NF_3$ (M+) 247.0456; found: 247.0449.

2-benzyl-2,3-dihydro-2-methyl-5-nitrobenzofuran



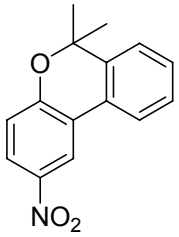
The compound was prepared following the general procedure B (57%): R_f = 0.28 (SiO_2, 5% ether/hexane); IR (ν_{max} /cm^{-1}): 2928, 1514, 1335, 1273; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.52 (3H, s), 2.99 (1H, d, *J*=16.0 Hz), 3.07 (2H, s), 3.27 (1H, d, *J*=16.0 Hz), 6.80 (1H, d, *J*=8.8Hz), 7.22-7.34 (5H, m), 8.09 (1H, d, *J*=2.5Hz), 8.10 (1H, dd, *J*=8.8, 2.5Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 26.4, 39.7, 46.6, 91.8, 109.1, 121.4, 125.8, 126.9, 128.2, 128.3, 130.4, 135.9, 141.5, 164.3; HRMS calcd for $C_{16}H_{15}O_3N$ (M+) 269.1052; found: 269.1059.

6,6-dimethyl-2-nitro-6,7-dihydrodibenzo[b,d]oxepine



The compound was obtained as the minor product in the 1-(2-(2-bromo-5-nitrophenoxy)-2-methylpropyl)benzene reaction in 34% yield: R_f = 0.24 (SiO_2, 5% ether/hexane); IR (ν_{max} /cm^{-1}): 2976, 1518, 1345, 1255, 1100; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.44 (6H, s), 2.66 (2H, s), 7.15 (1H, d, *J*=8.7Hz), 7.26 (1H, dd, *J*=7.4, 1.0Hz), 7.38 (1H, dt, *J*=7.4, 1.5Hz), 7.44 (1H, dt, *J*=7.5, 1.5Hz), 7.51 (1H, dd, *J*=7.6, 1.4Hz), 8.20 (1H, dd, *J*=8.8, 2.8Hz), 8.36 (1H, d, *J*=2.8Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 26.8, 44.3, 91.7, 124.0, 124.6, 124.7, 127.7, 128.2, 128.5, 129.6, 136.2, 136.3, 136.4, 144.4, 158.9; HRMS calcd for $C_{16}H_{15}O_3N$ (M+) 269.1052; found: 269.1048.

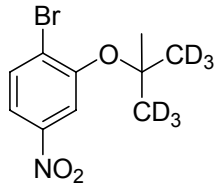
6,6-dimethyl-2-nitro-6H-benzo[c]chromene



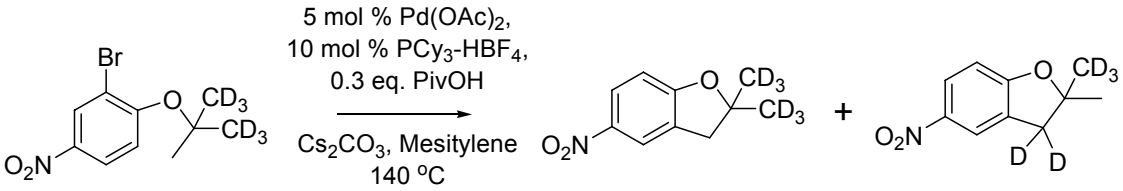
The compound was prepared following the general cyclization procedure at 140^{o}C (89%): mp = 92-95^{o}C(ether); R_f = 0.23 (SiO_2, 3% ether/hexane); IR (ν_{max} /cm^{-1}): 2982, 1518, 1339, 1266, 1106; ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.67 (6H, s), 7.00 (1H, d, *J*=8.9Hz), 7.25-7.27 (1H, m), 7.36-7.43 (2H, m), 7.76-7.79 (1H, s), 8.10 (1H, dd, *J*=8.9, 2.7Hz), 8.64 (1H, d, *J*=2.7Hz); ^{13}C NMR (100MHz, $CDCl_3$, 293K, TMS): 27.9, 79.5, 118.4, 118.9, 122.4, 122.5, 123.4, 124.9, 126.3, 128.2, 129.4, 138.7, 142.2, 158.2; HRMS calcd for $C_{15}H_{13}O_3N$ (M+) 255.0895; found: 255.0873.

Kinetic Isotope Effect Experiments

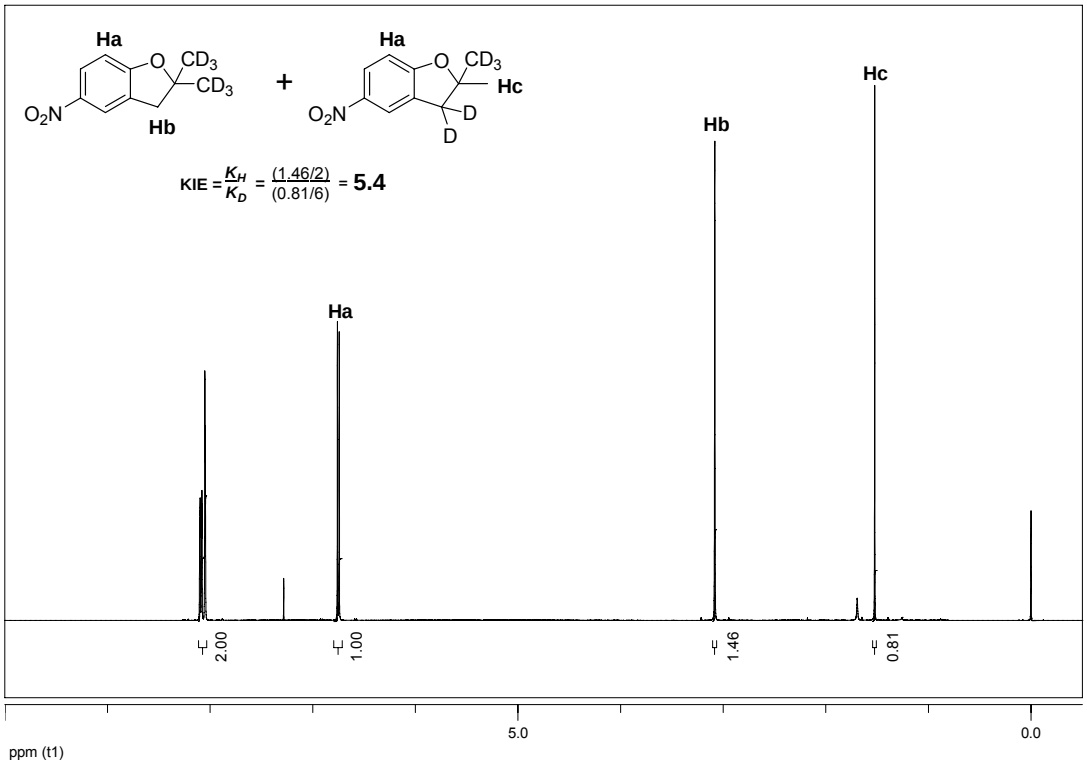
1-(1,1,1,3,3,3-hexadeuterated-2-methylpropoxy)-2-bromo-5-nitrobenzene



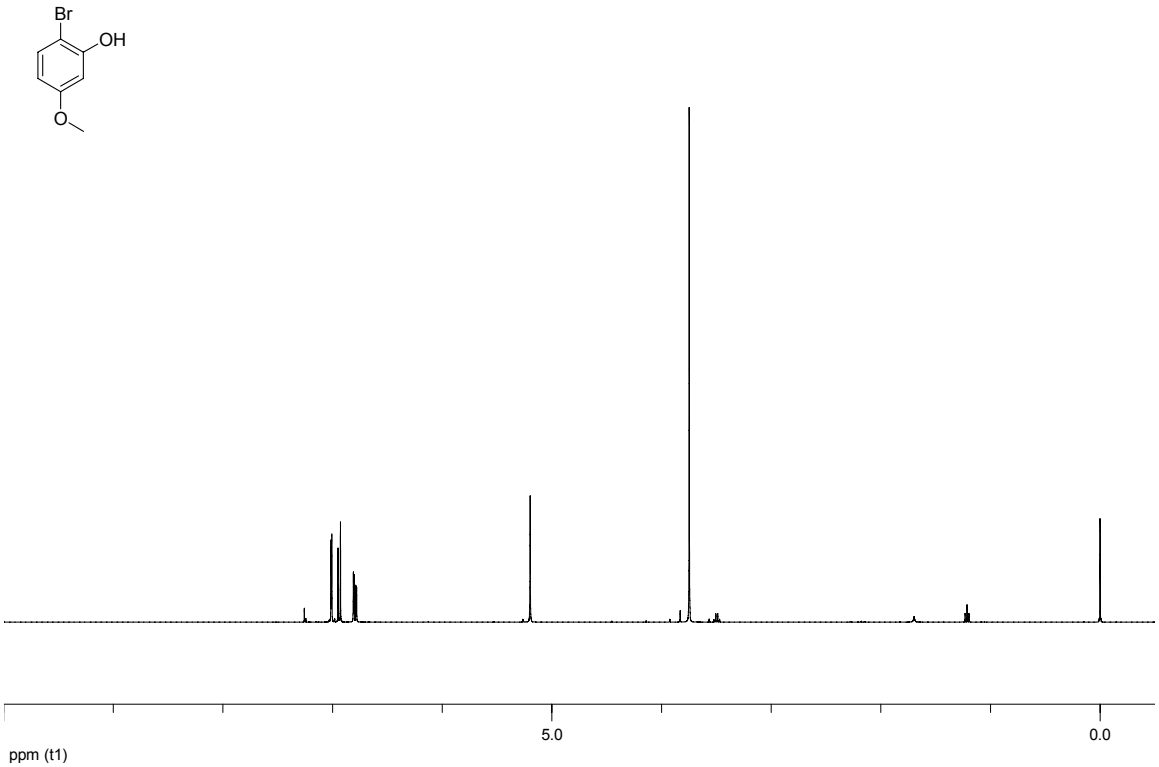
The compound was prepared following the general procedure B at 140°C (86%): ^{1}H NMR (400MHz, $CDCl_3$, 293K, TMS): 1.54 (3H, s), 7.20 (1H, d, *J*=9.1Hz), 8.12 (1H, dd, *J*=9.1, 2.8Hz), 8.44 (1H, d, *J*=2.8Hz);

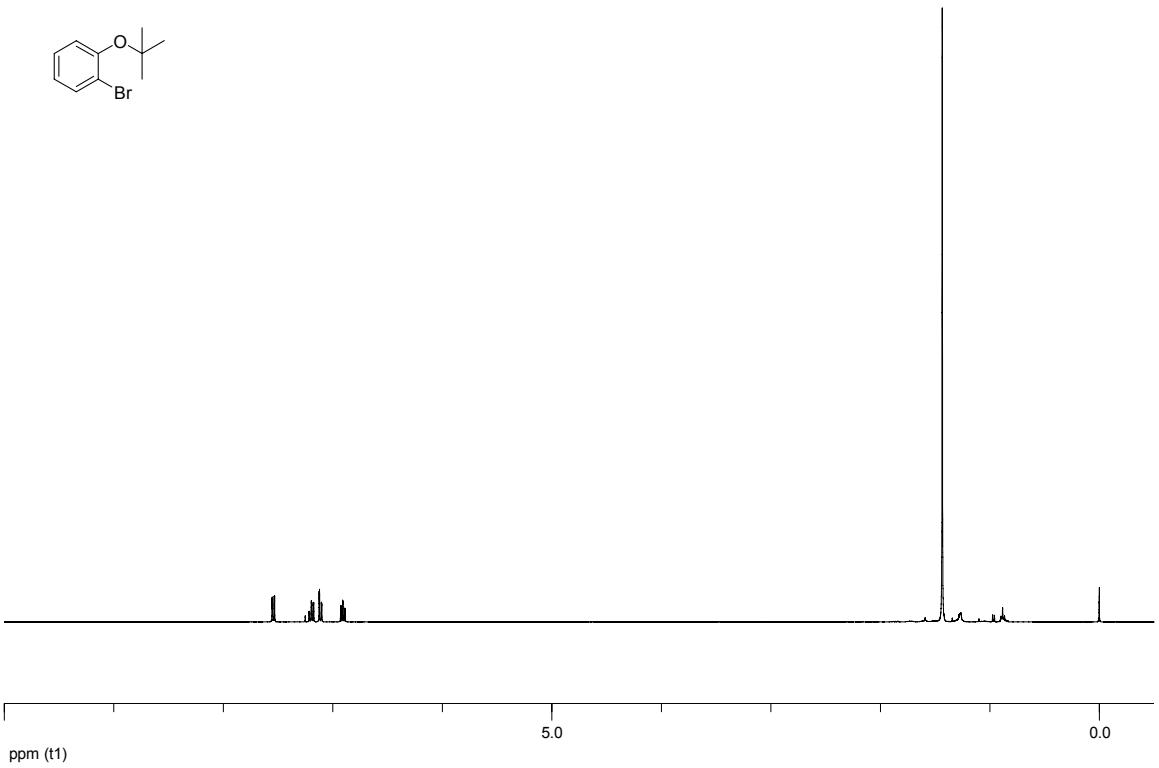


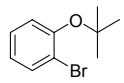
k_H/k_D = 5.4

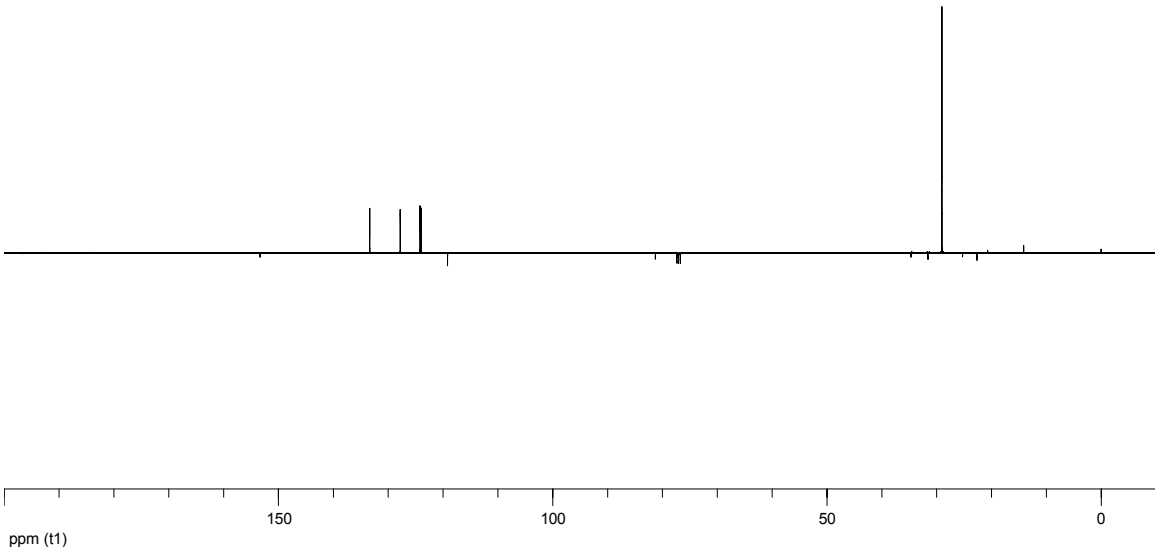


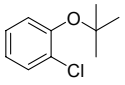
NMR Spectra



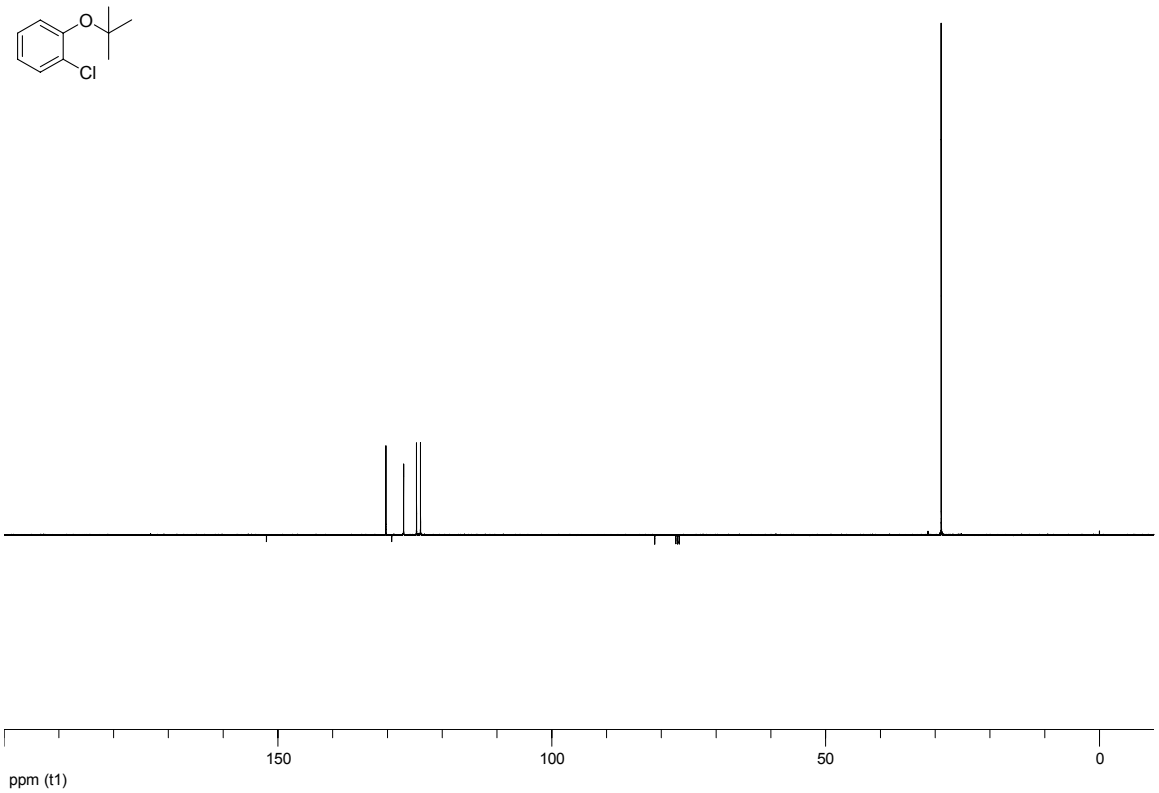


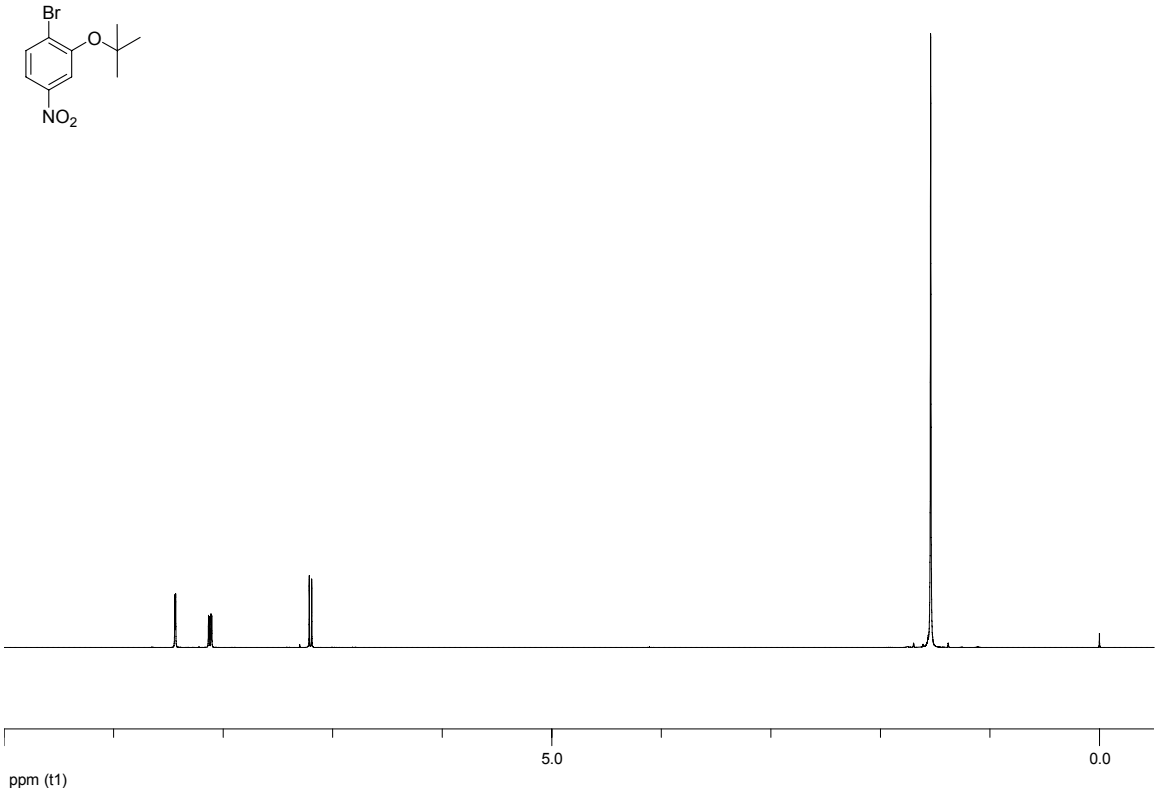

O
Br

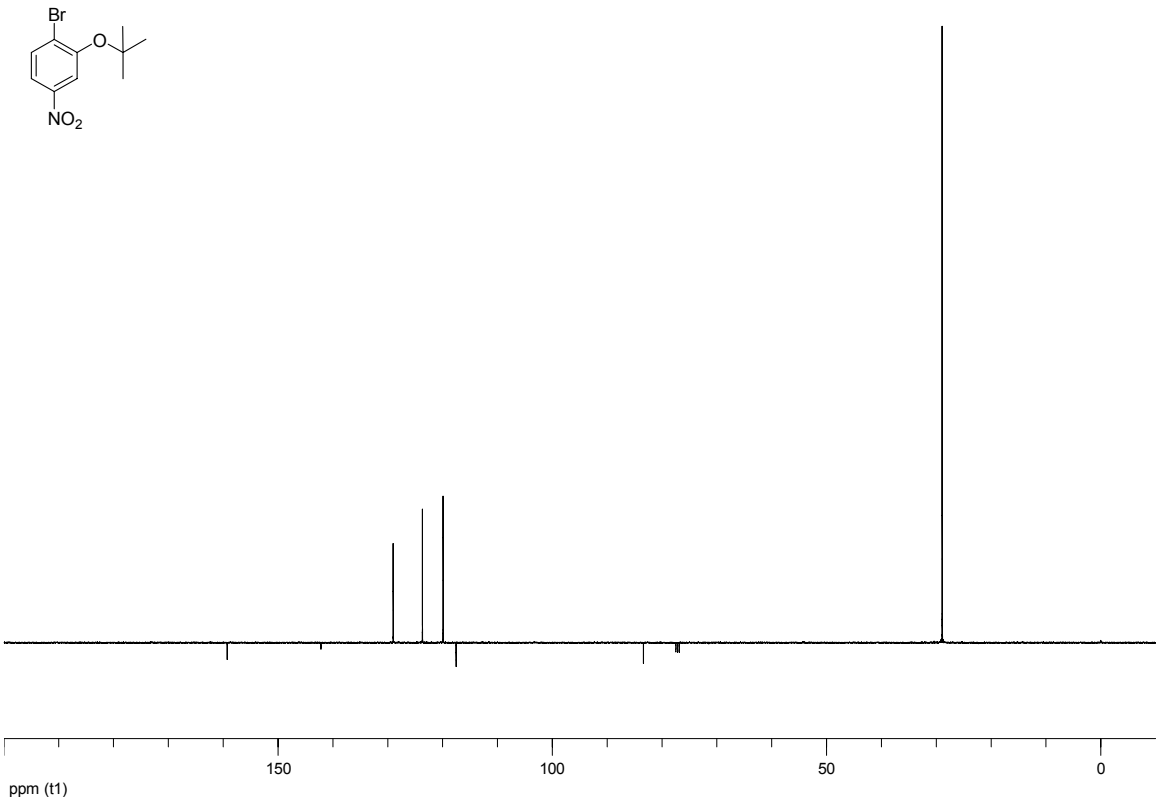

150
100
50
0
ppm (t1)

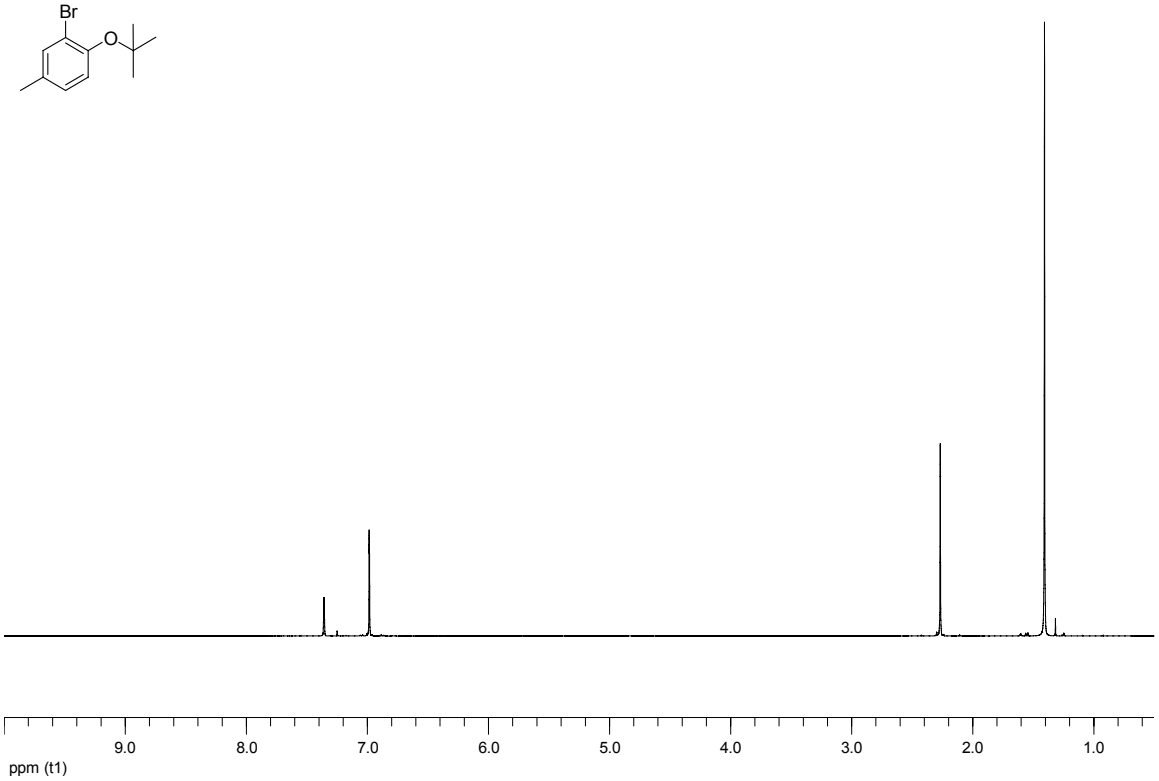

O
Cl

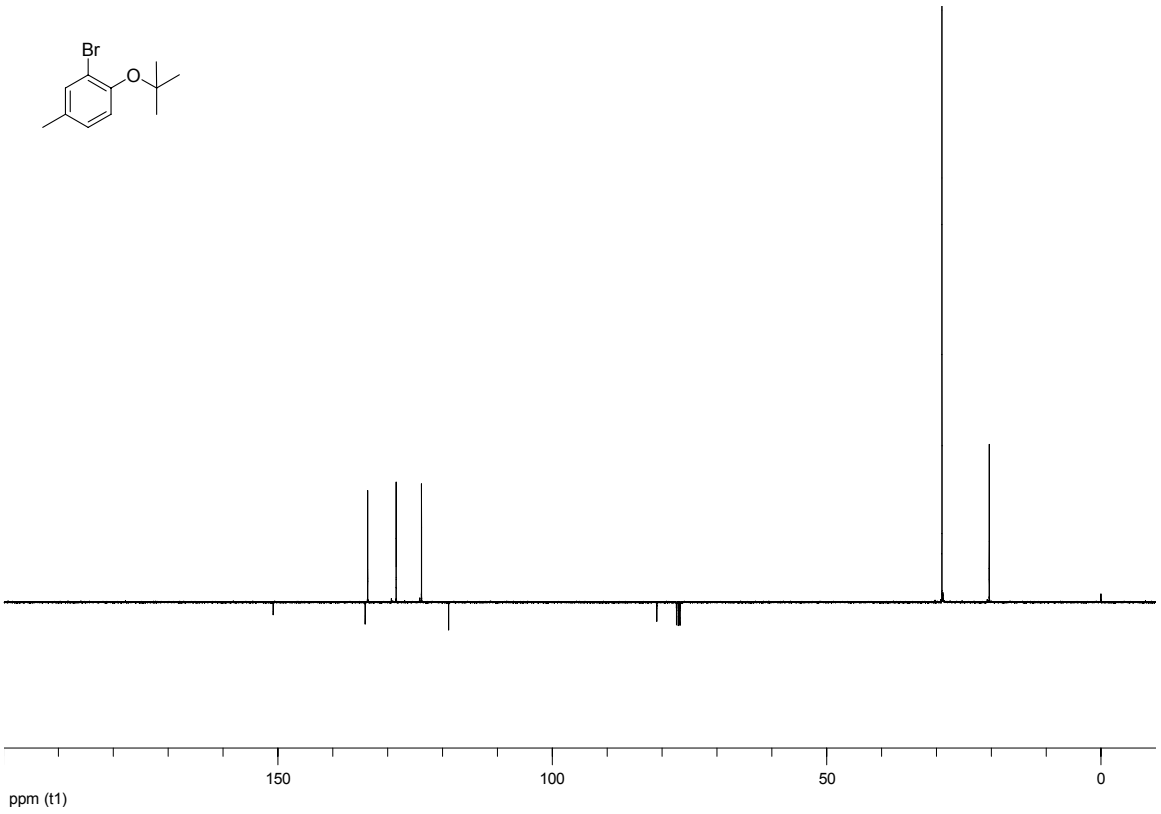
5.0
0.0
ppm (t1)


O
Cl
150
100
50
0
ppm (t1)


Br
O
NO2
5.0
0.0
ppm (t1)


Br
O
NO2
150
100
50
0
ppm (t1)


Br
O
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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O
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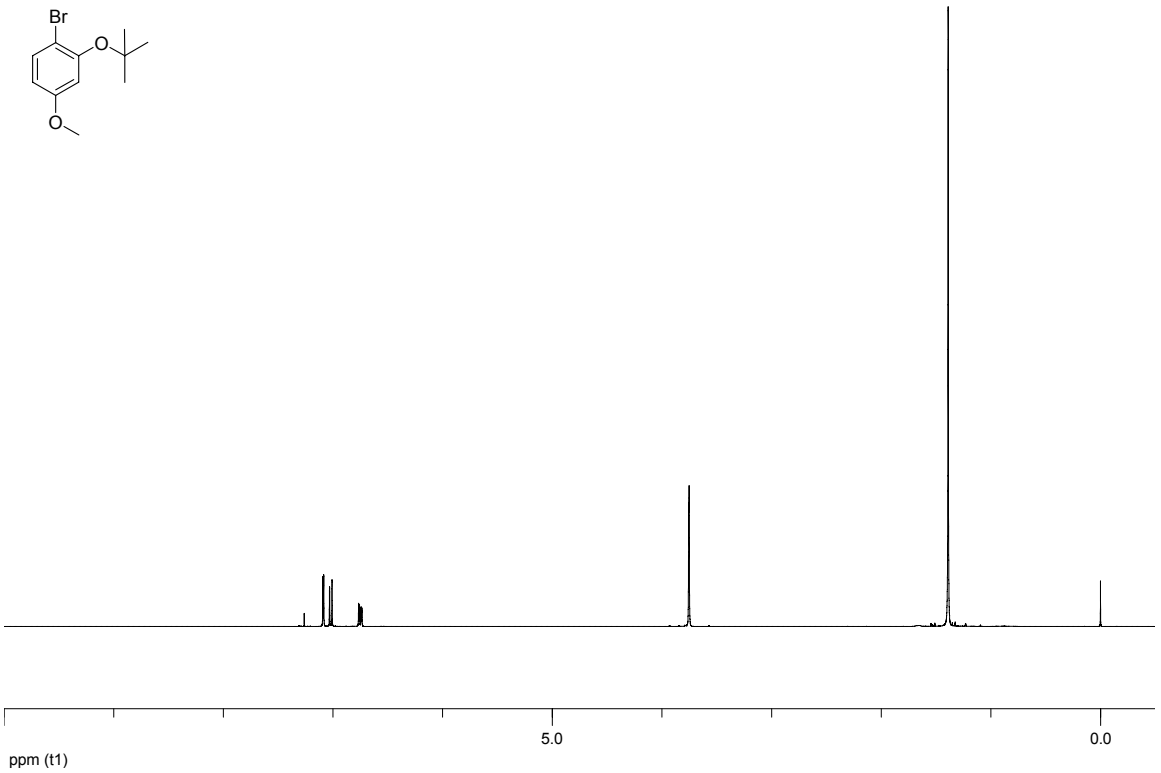
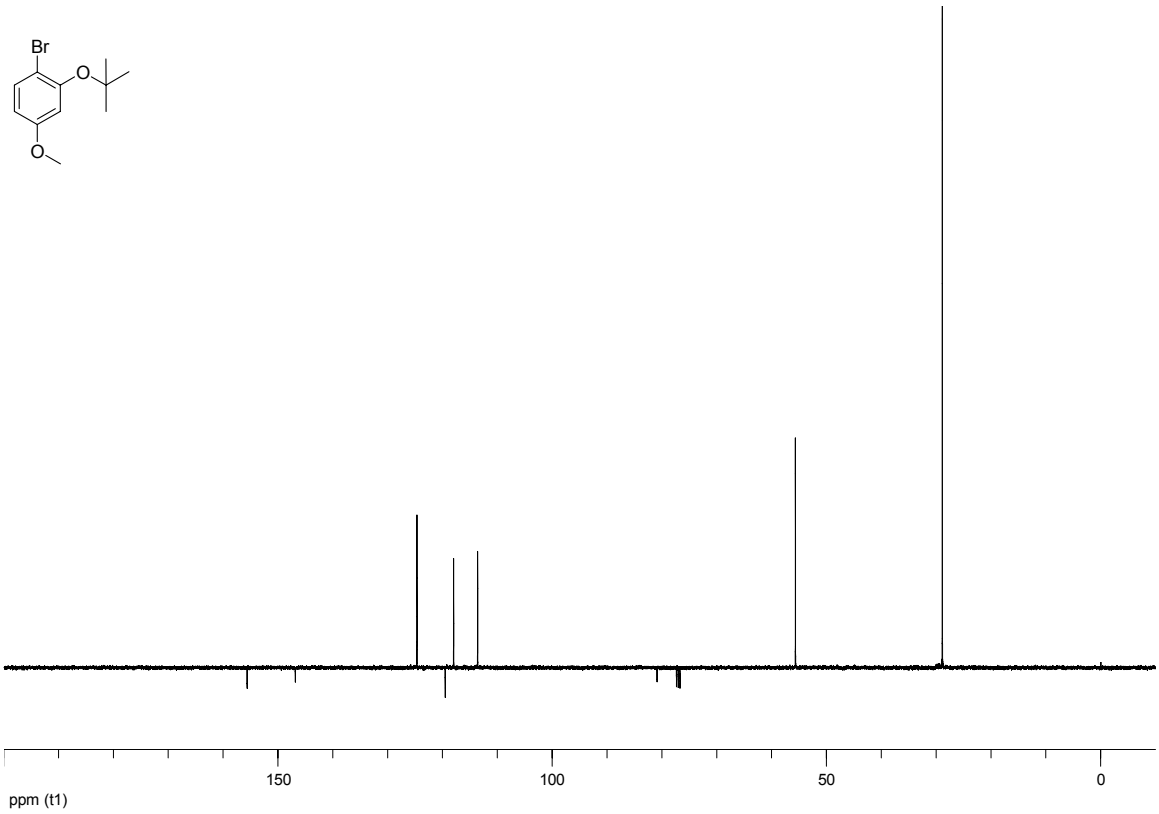
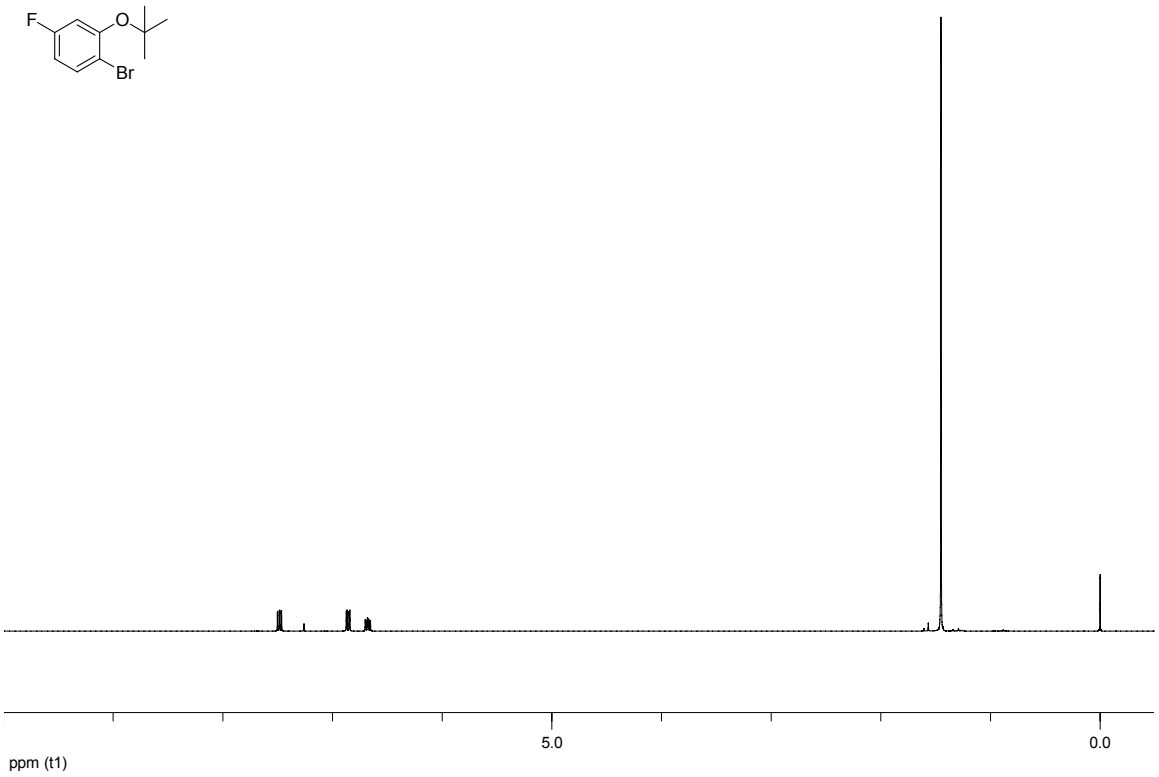
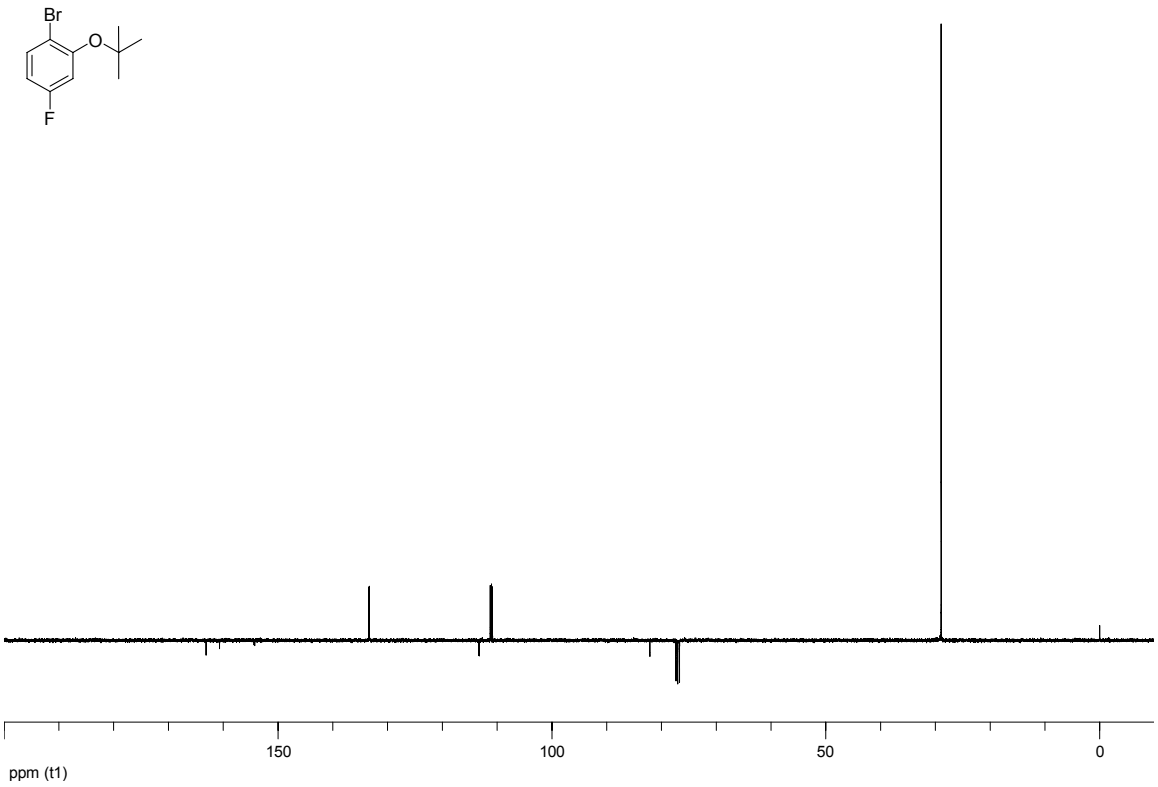
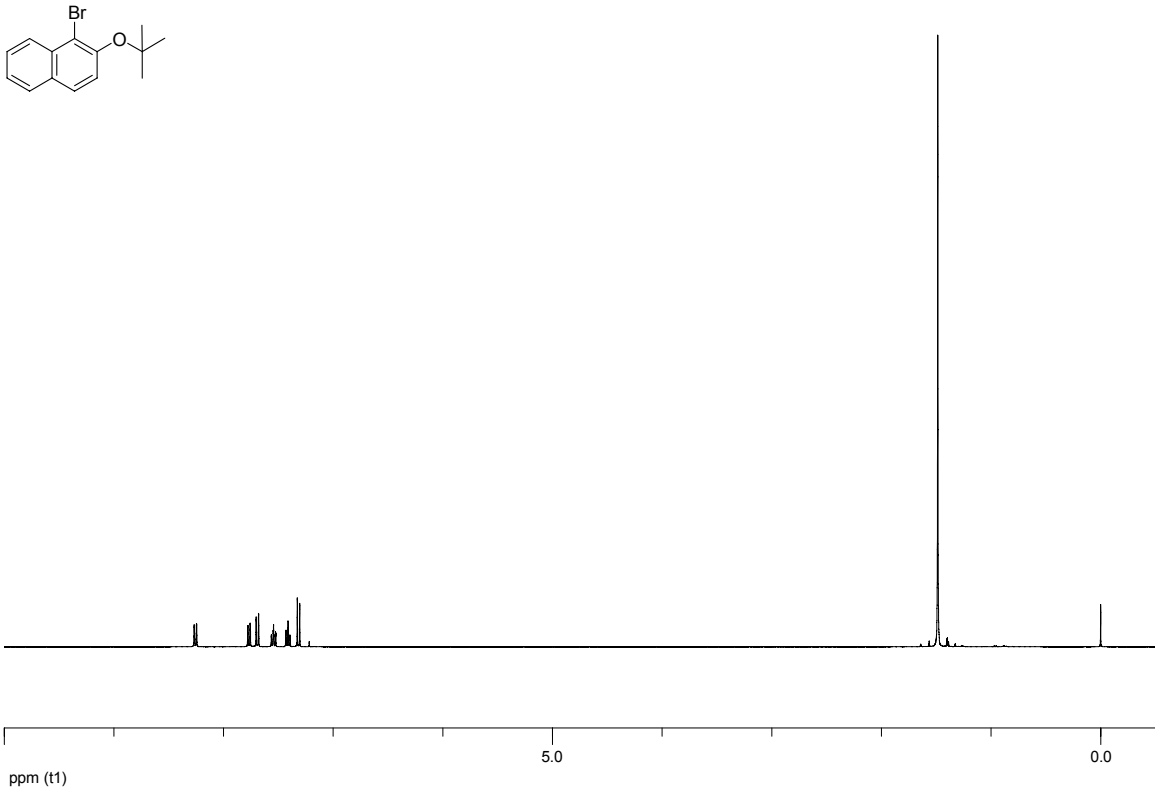
100
50
0
ppm (t1)


Br
O
O
5.0
0.0
ppm (t1)


Br
O
O
150
100
50
0
ppm (t1)


F
O
Br
5.0
0.0
ppm (t1)


Br
O
F
150
100
50
0
ppm (t1)


Br
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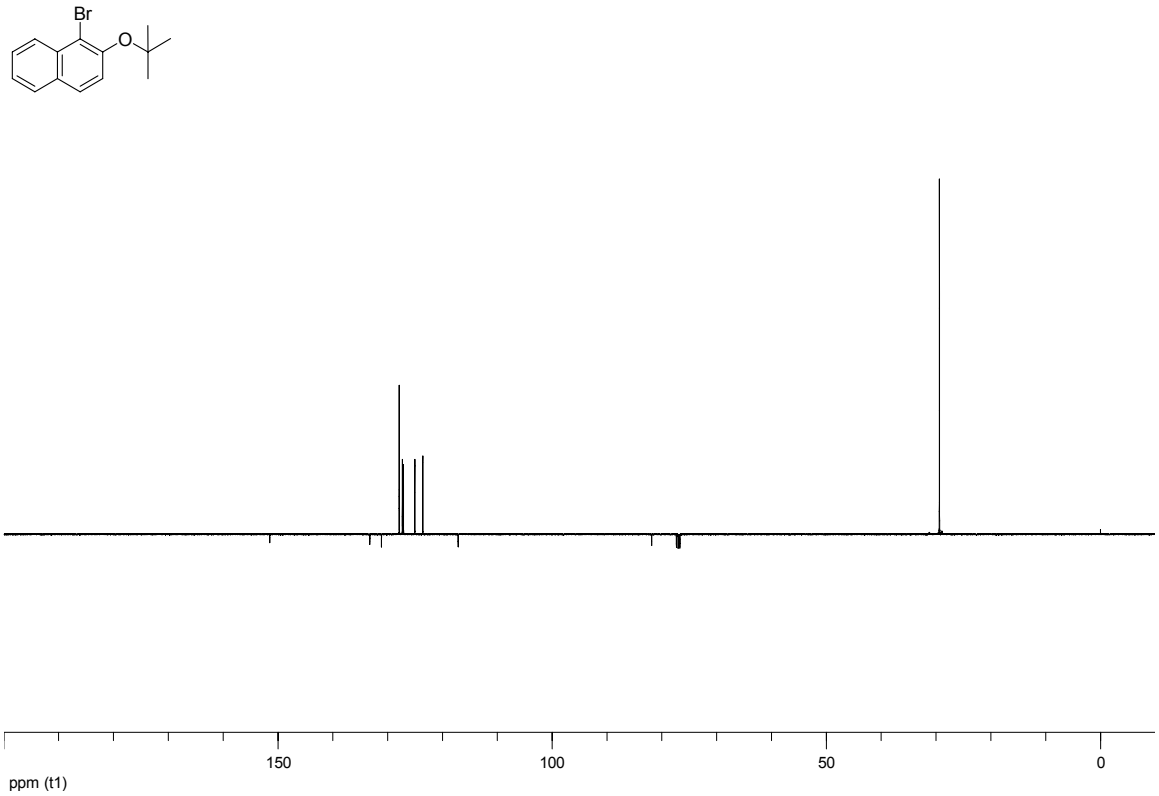
ppm (t1)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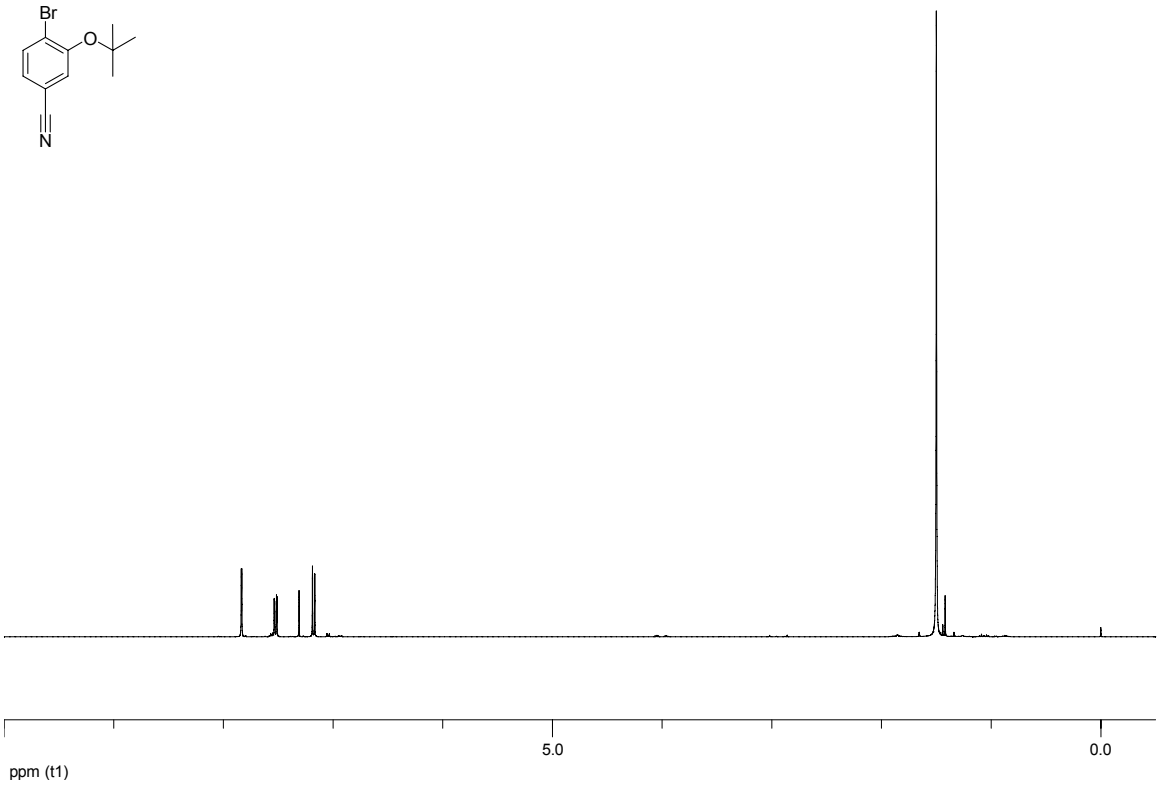
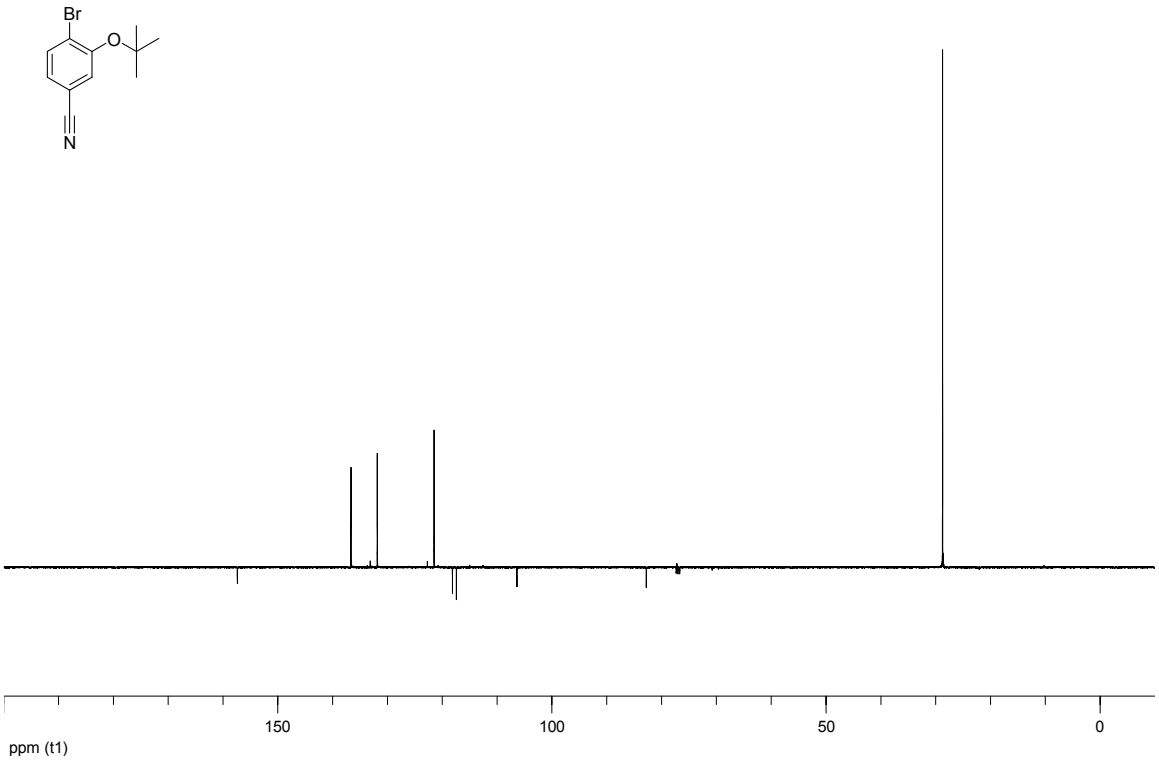
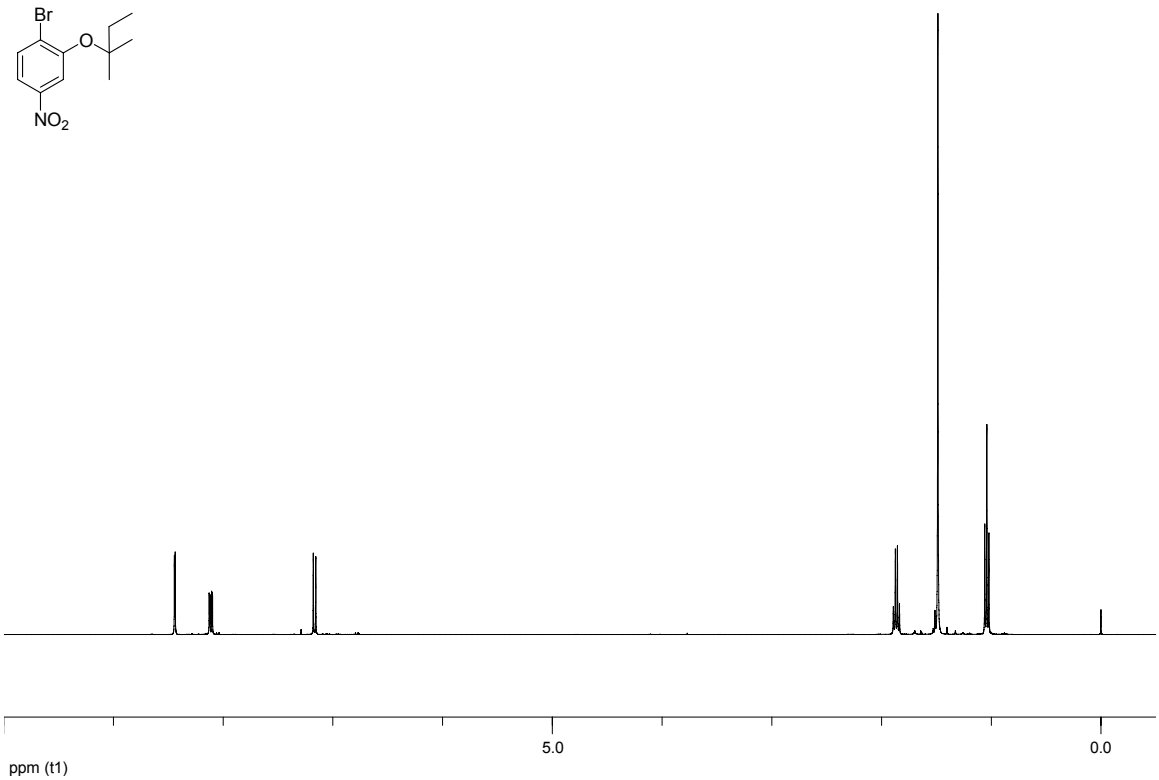
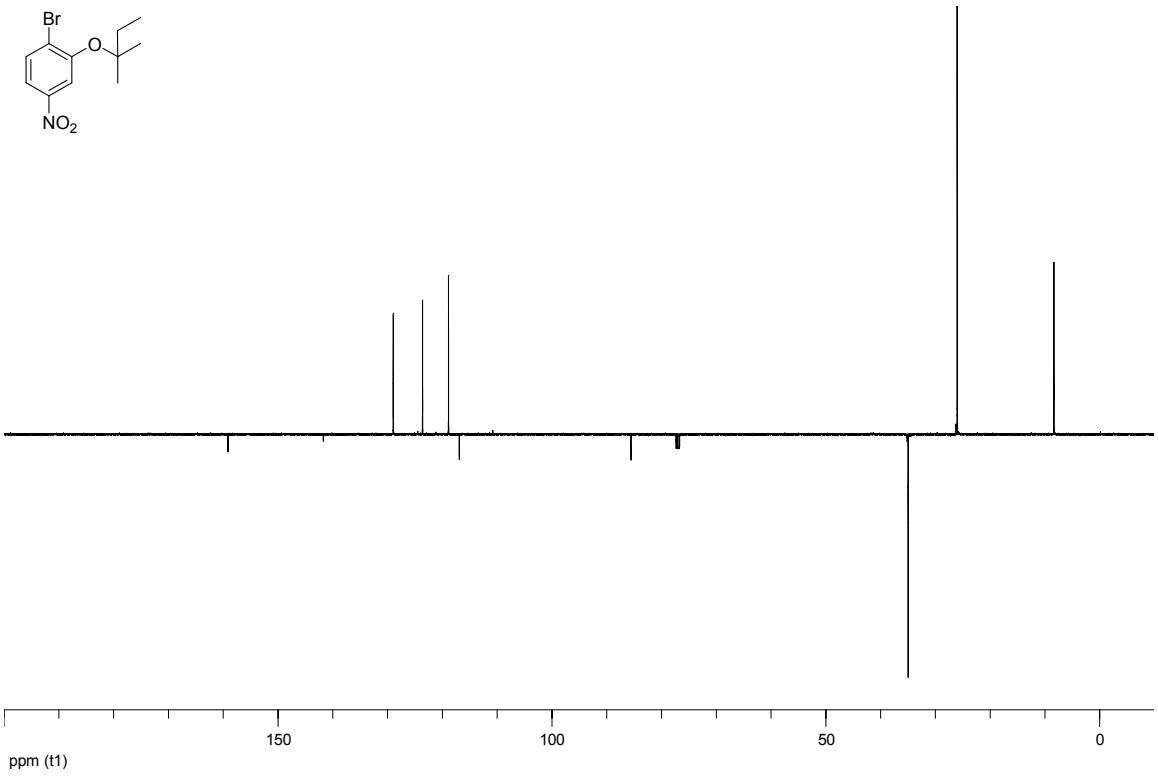
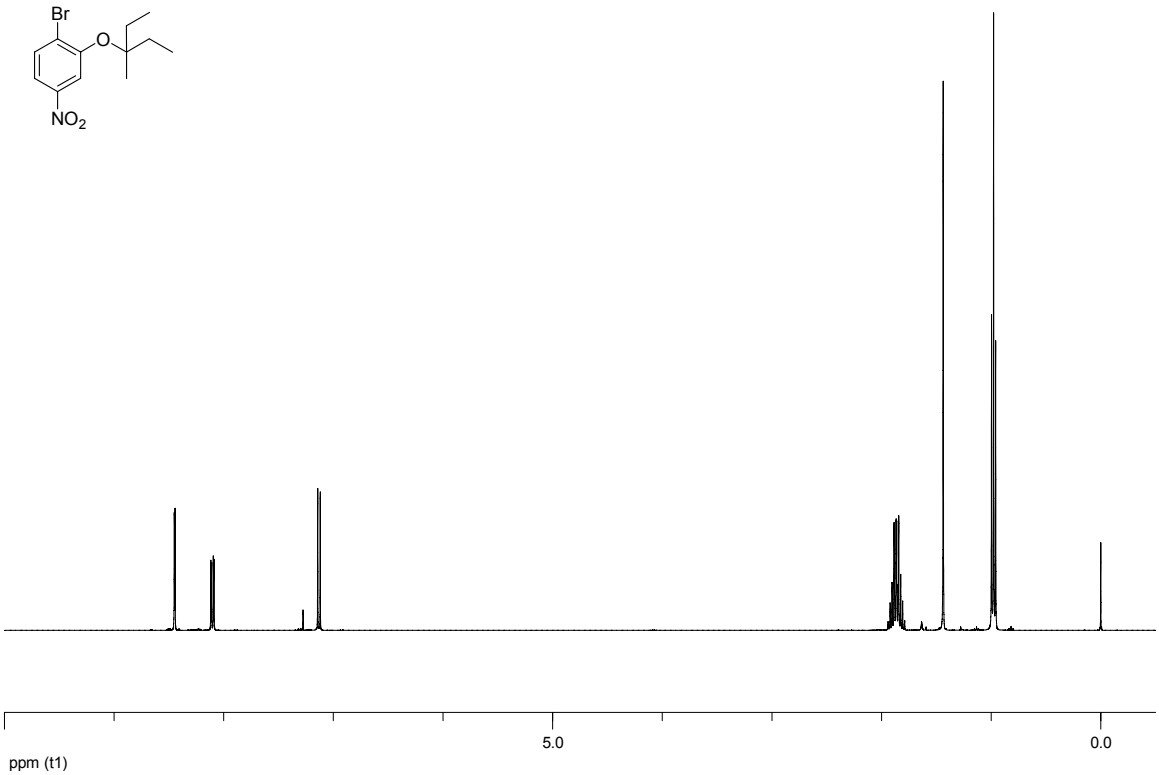
150
100
50
0
ppm (t1)

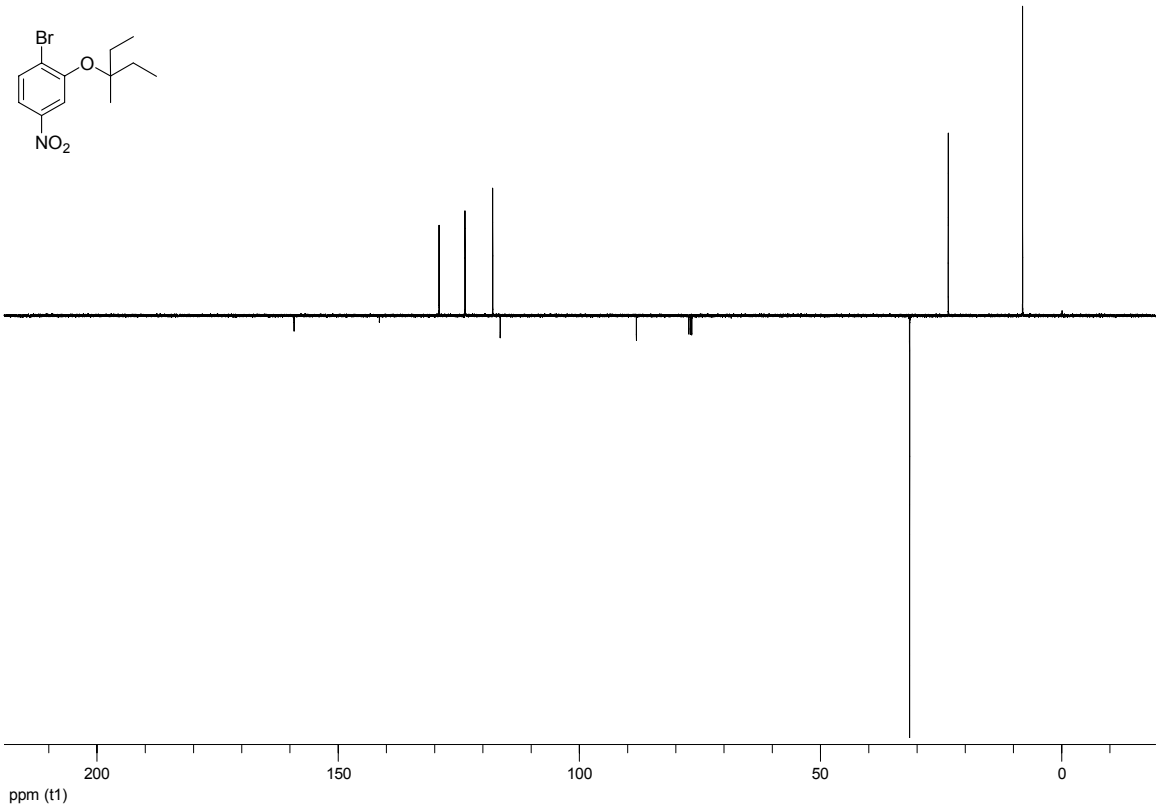

Br
O
N
5.0
0.0
ppm (t1)

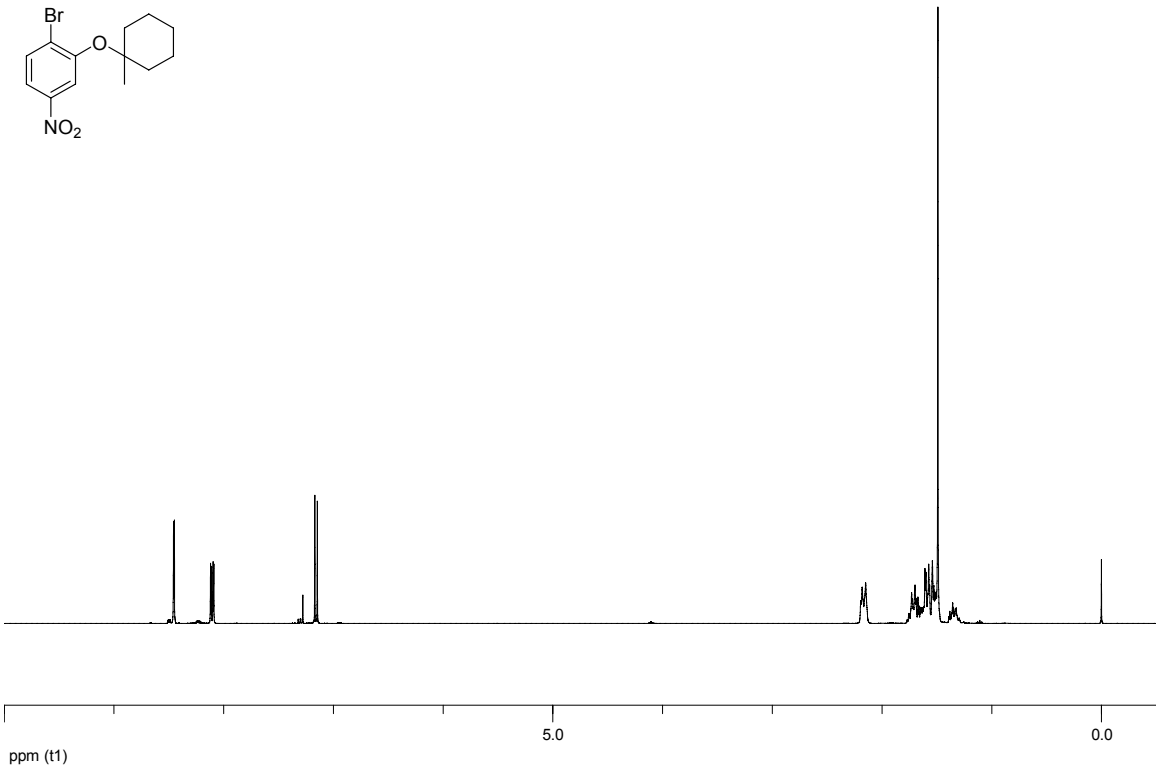

Br
O
N
150
100
50
0
ppm (t1)


Br
O
NO2
5.0
0.0
ppm (t1)


Br
O
NO2
150
100
50
0
ppm (t1)


Br
O
NO2
5.0
0.0
ppm (t1)


Br
O
NO2
200
150
100
50
0
ppm (t1)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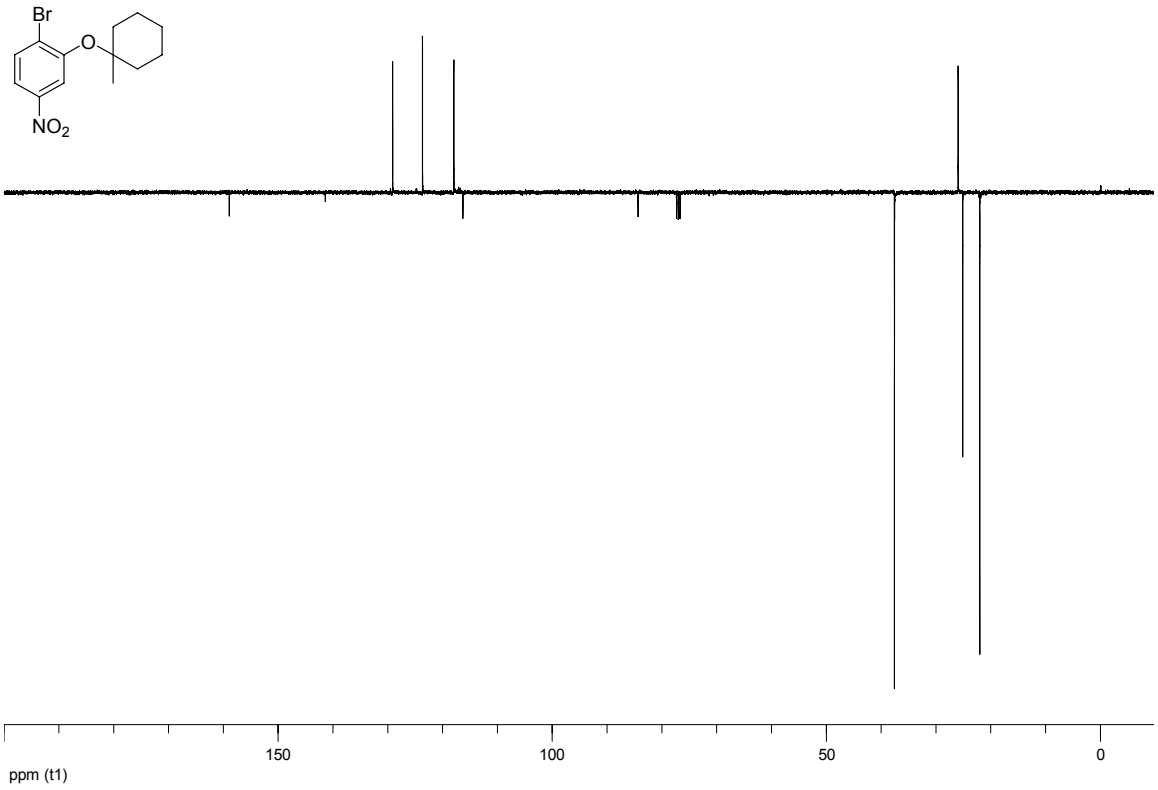
O
NO2
5.0
0.0
ppm (t1)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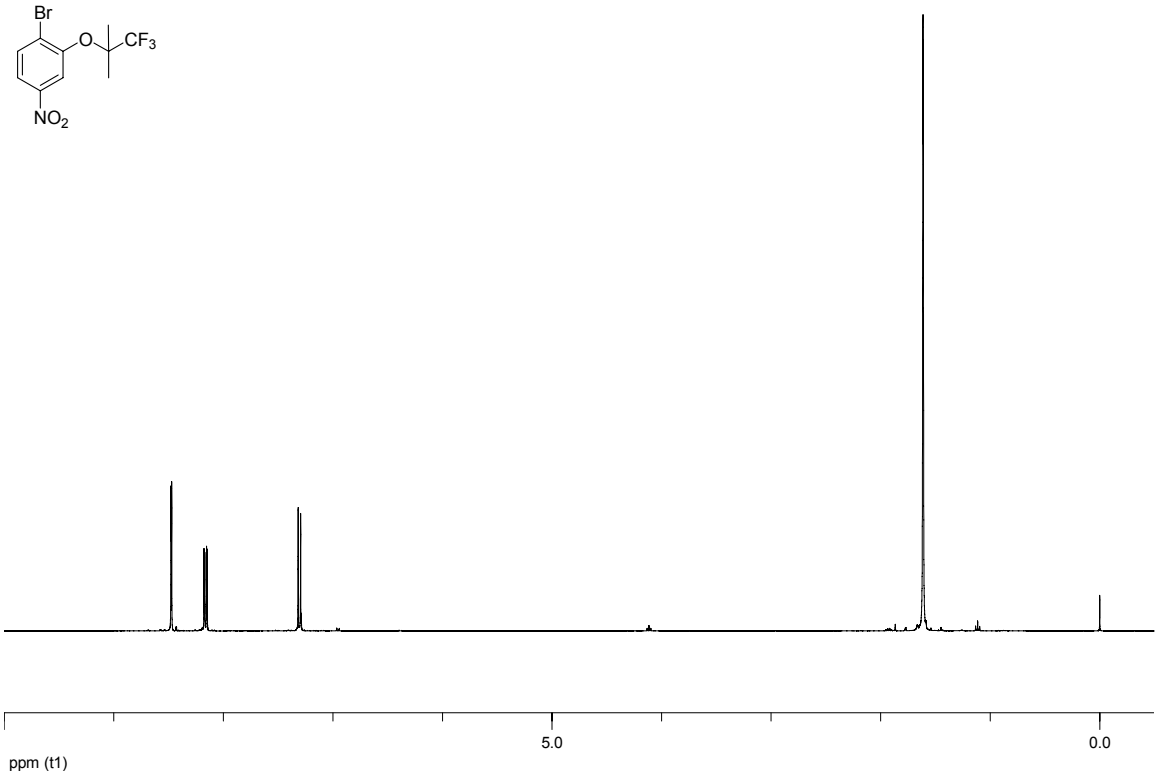
O
NO2
150
100
50
0
ppm (t1)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O
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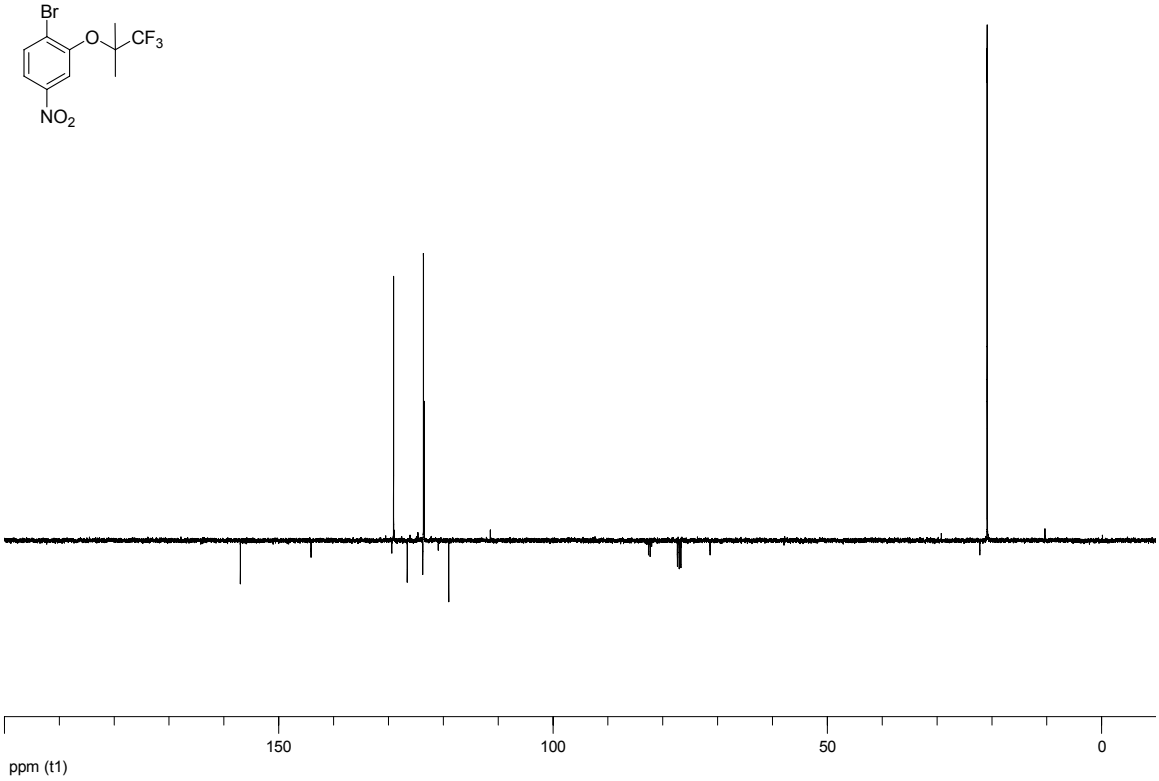
NO2
5.0
0.0
ppm (t1)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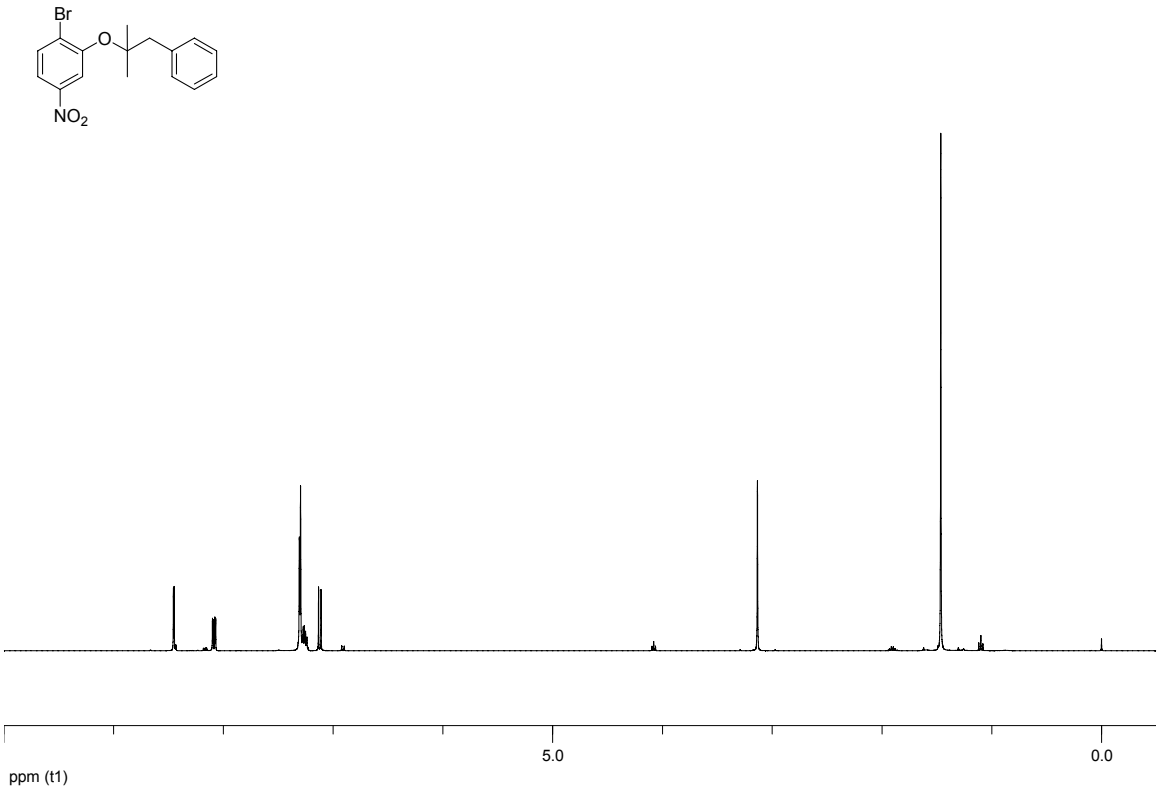
O
CF3
NO2
150
100
50
0
ppm (t1)


Br
O
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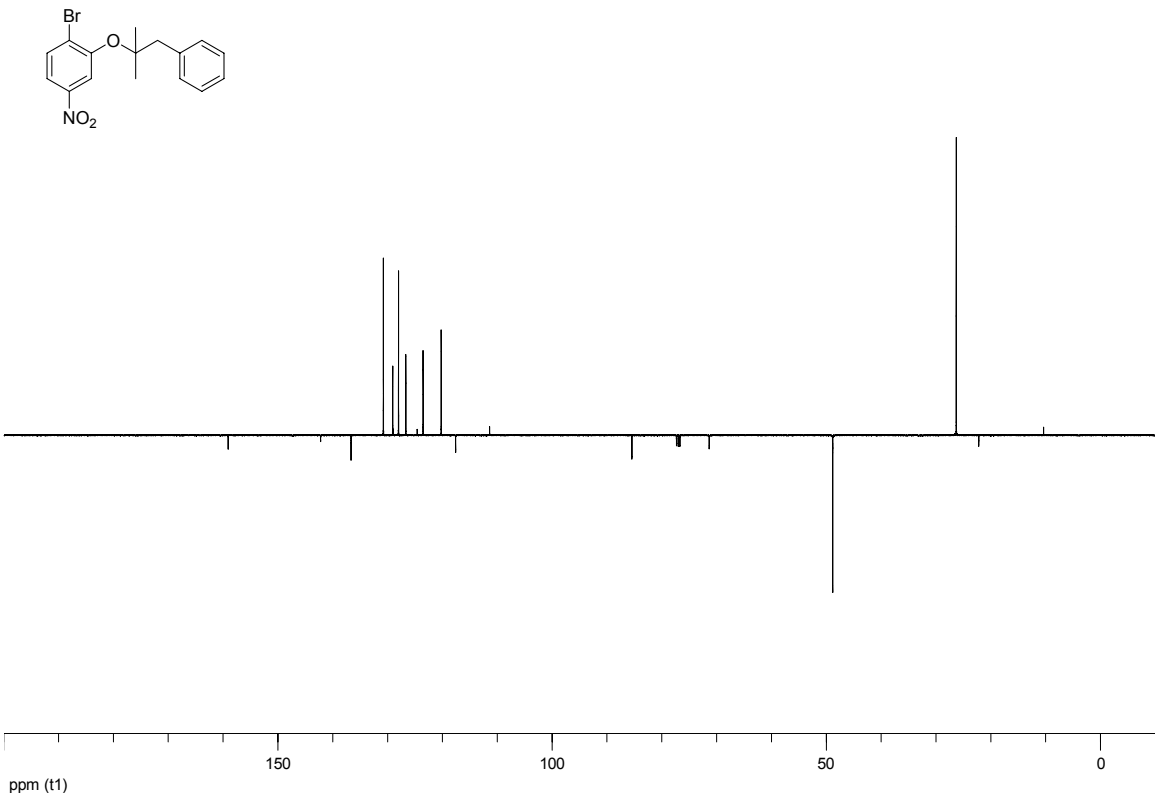
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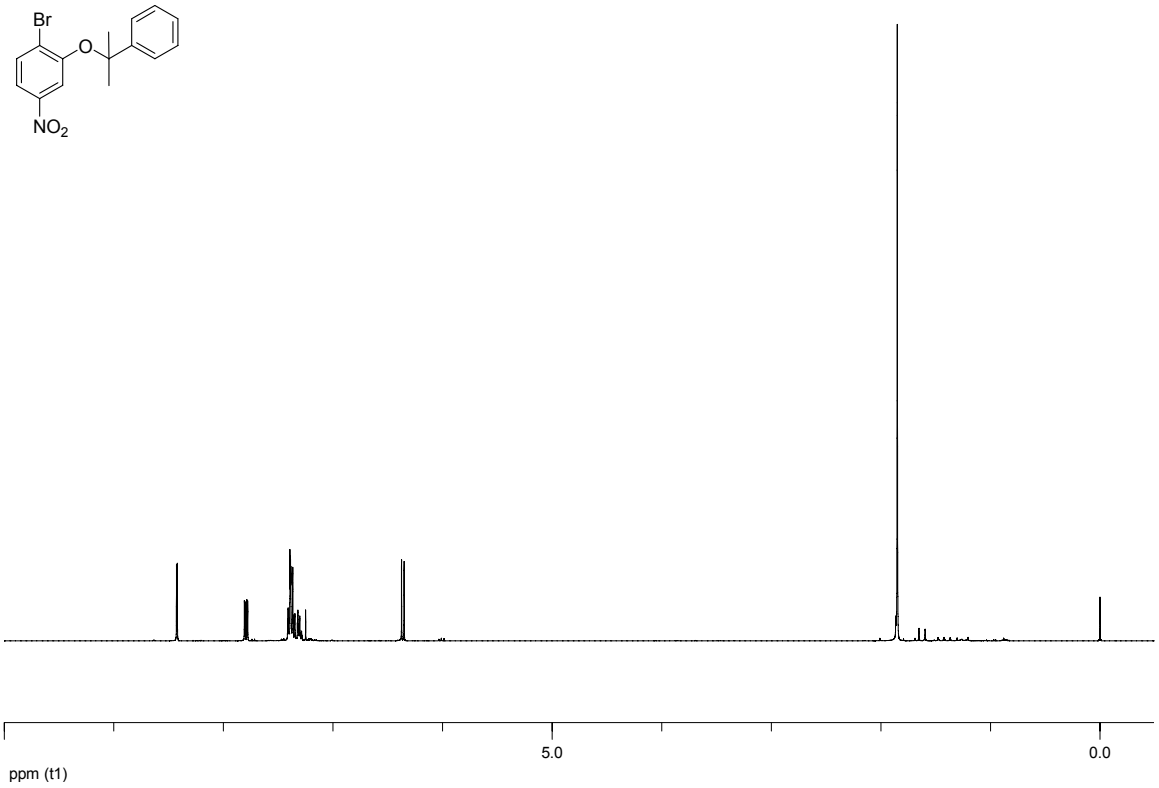
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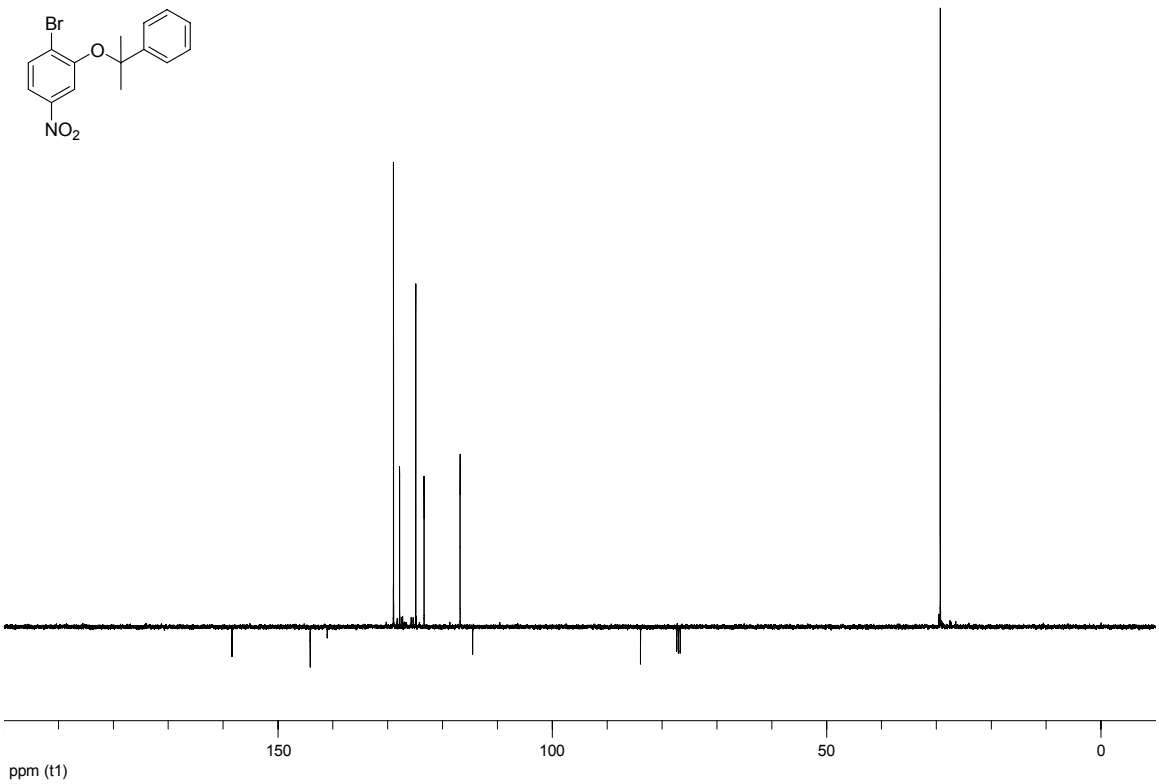
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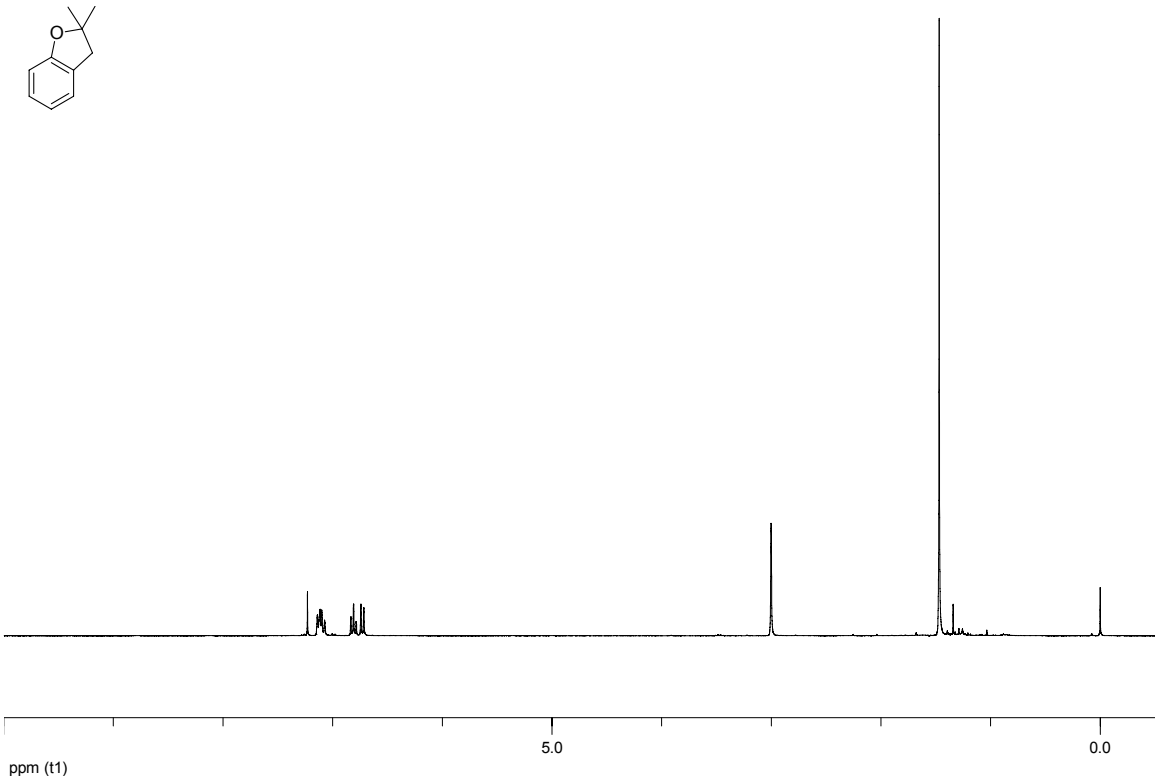
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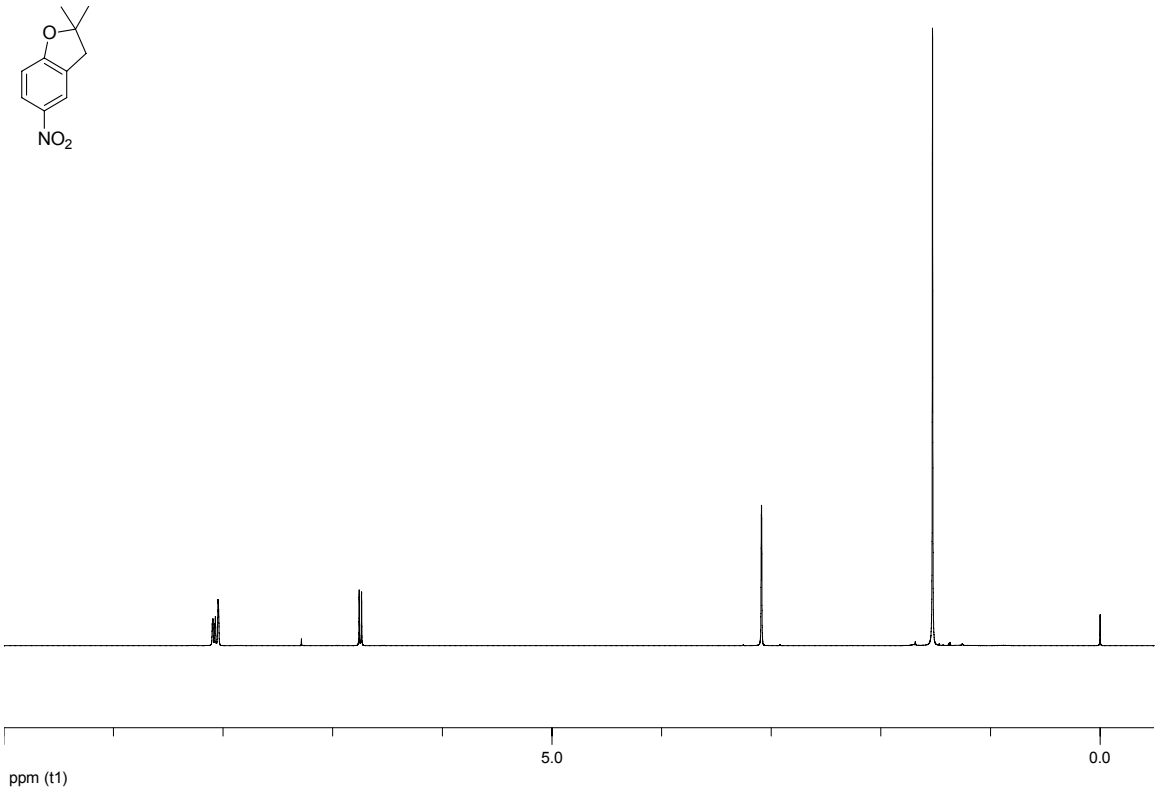
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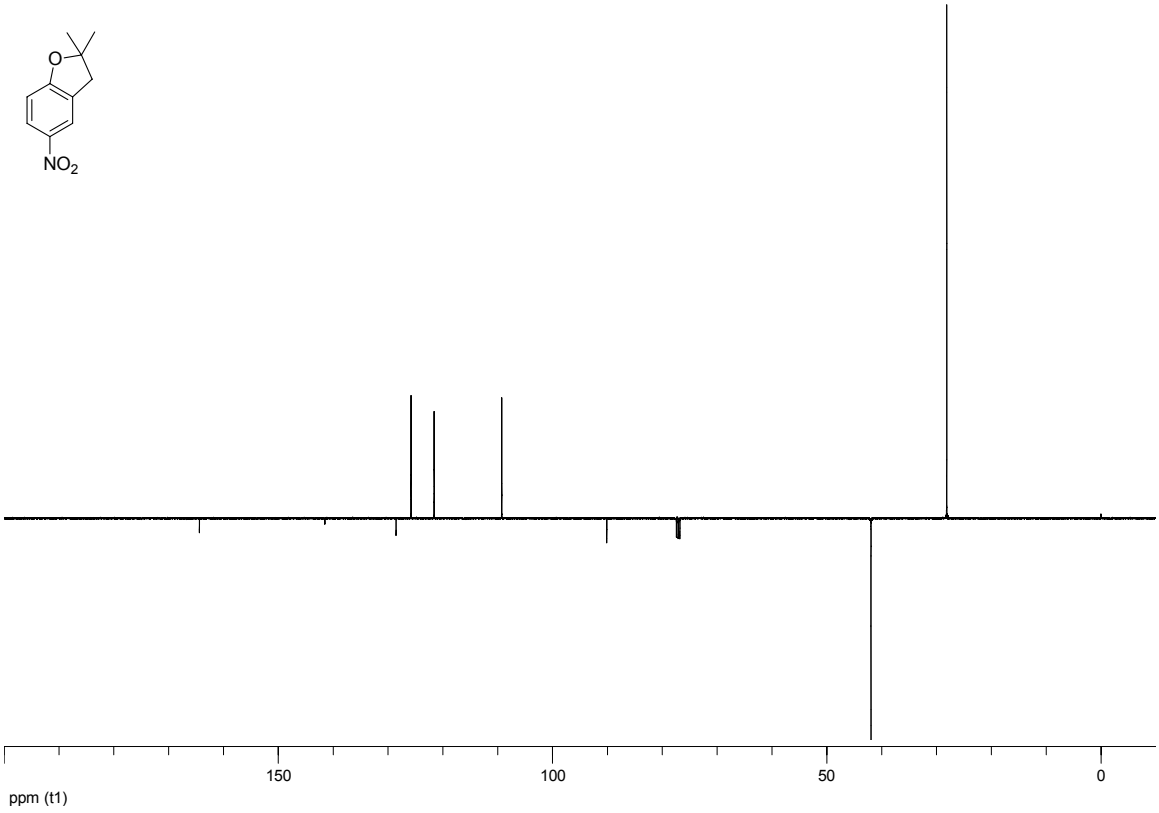
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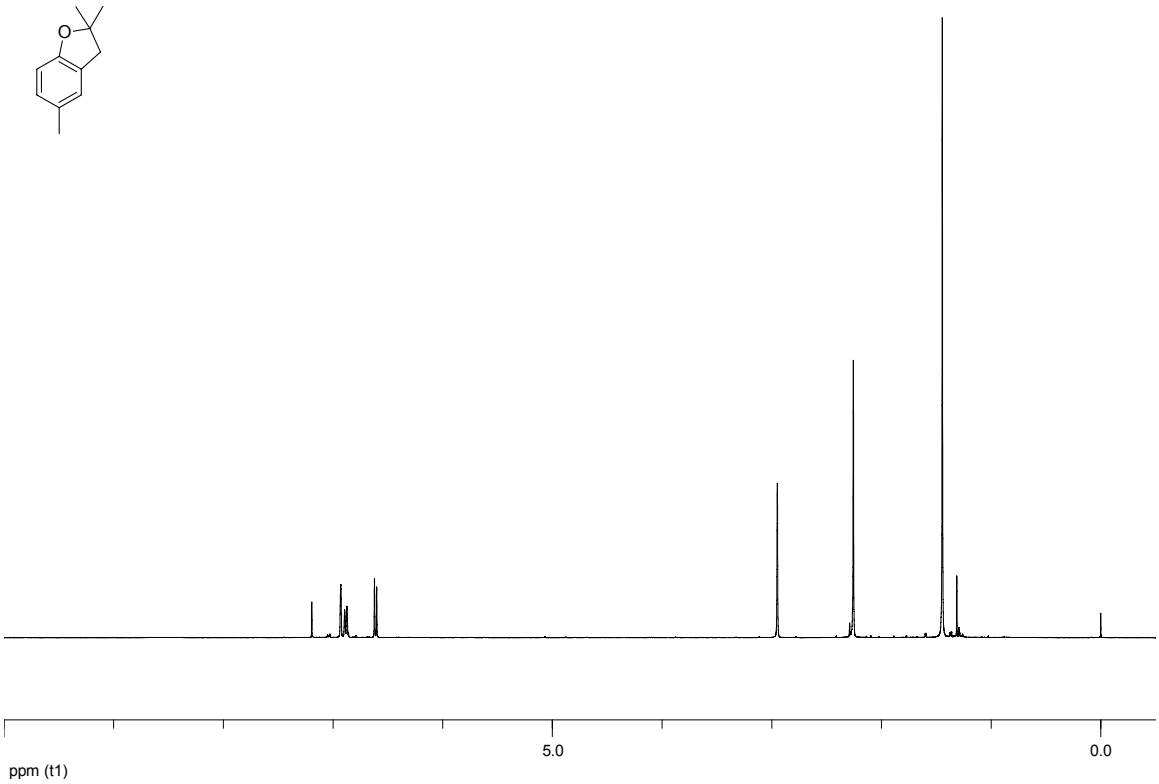
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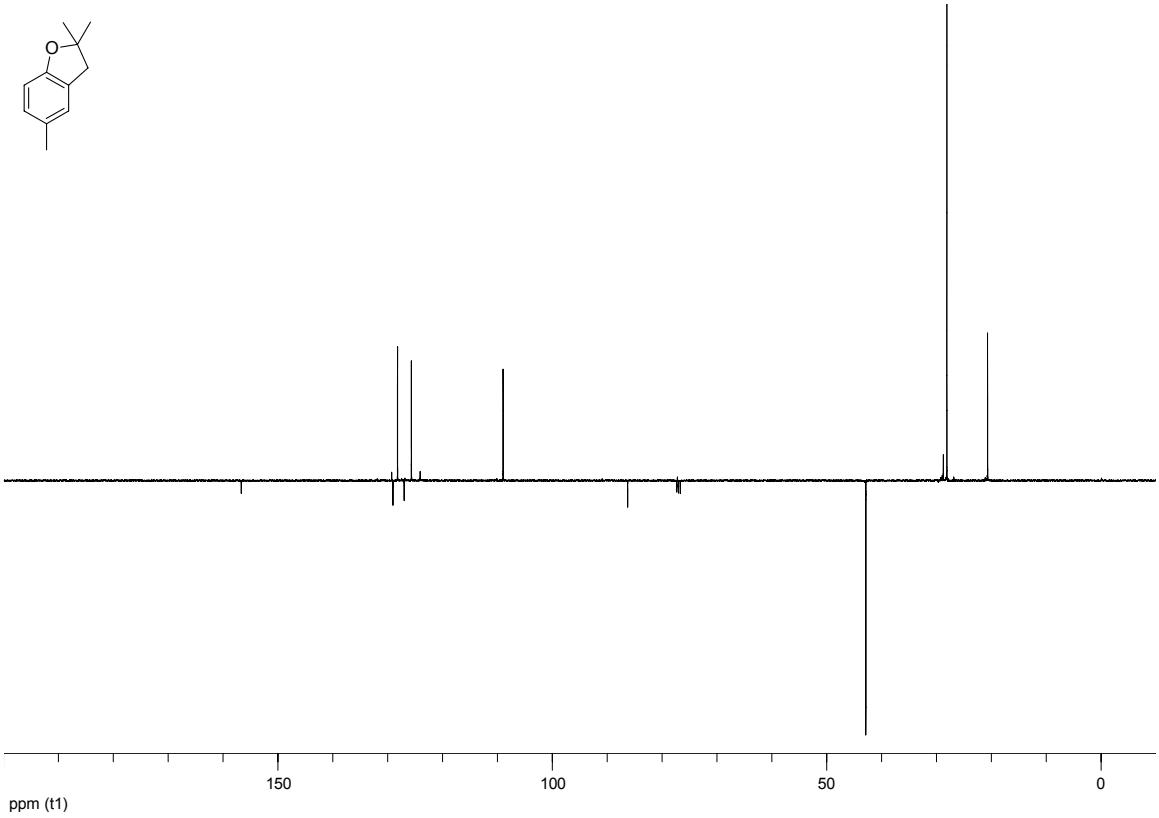
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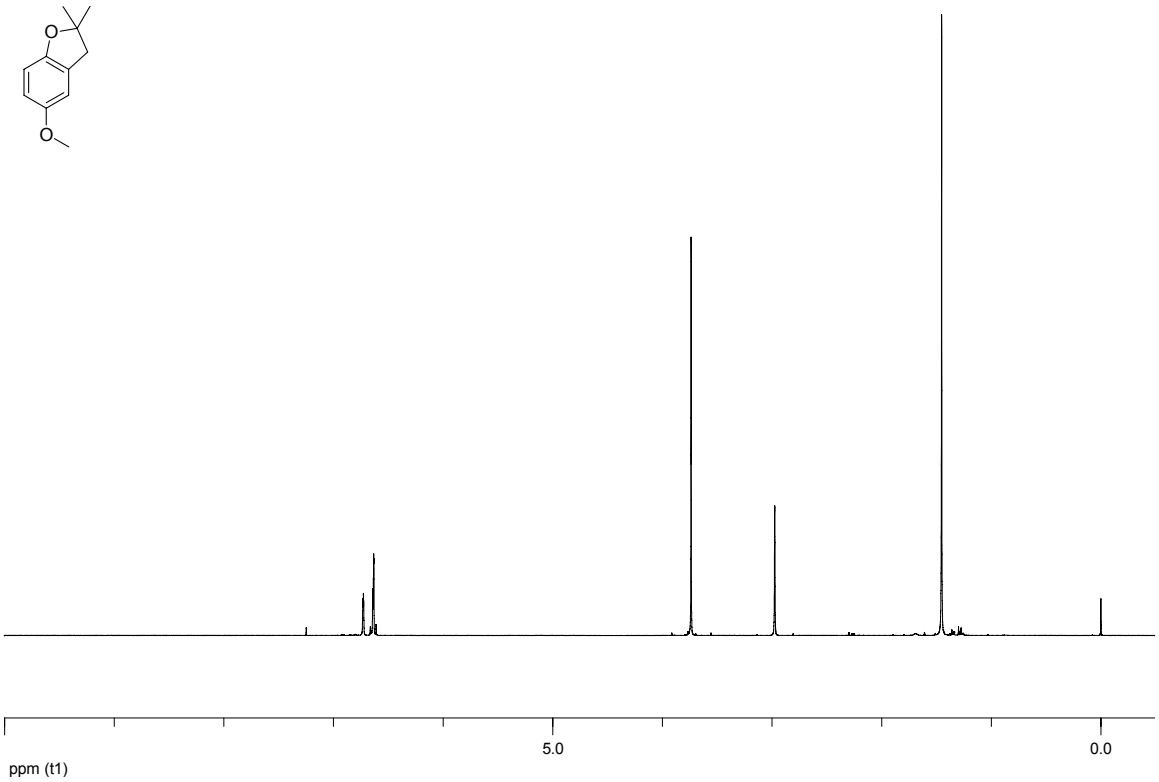
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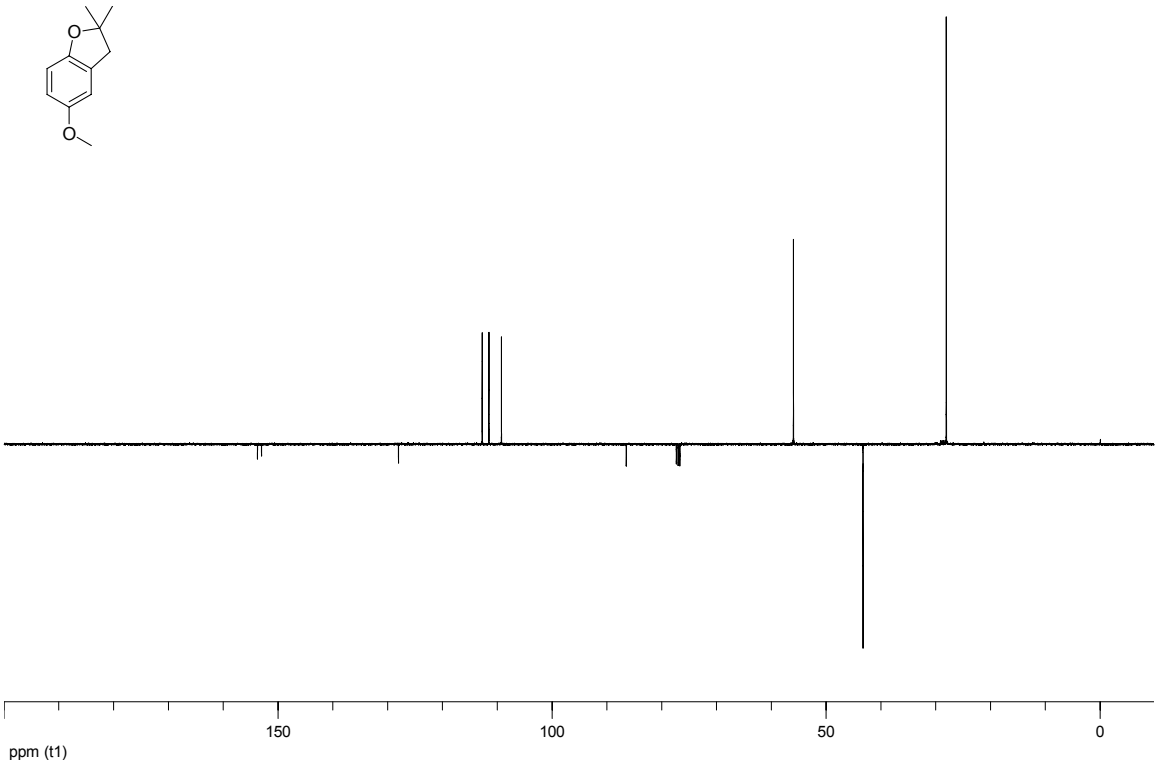
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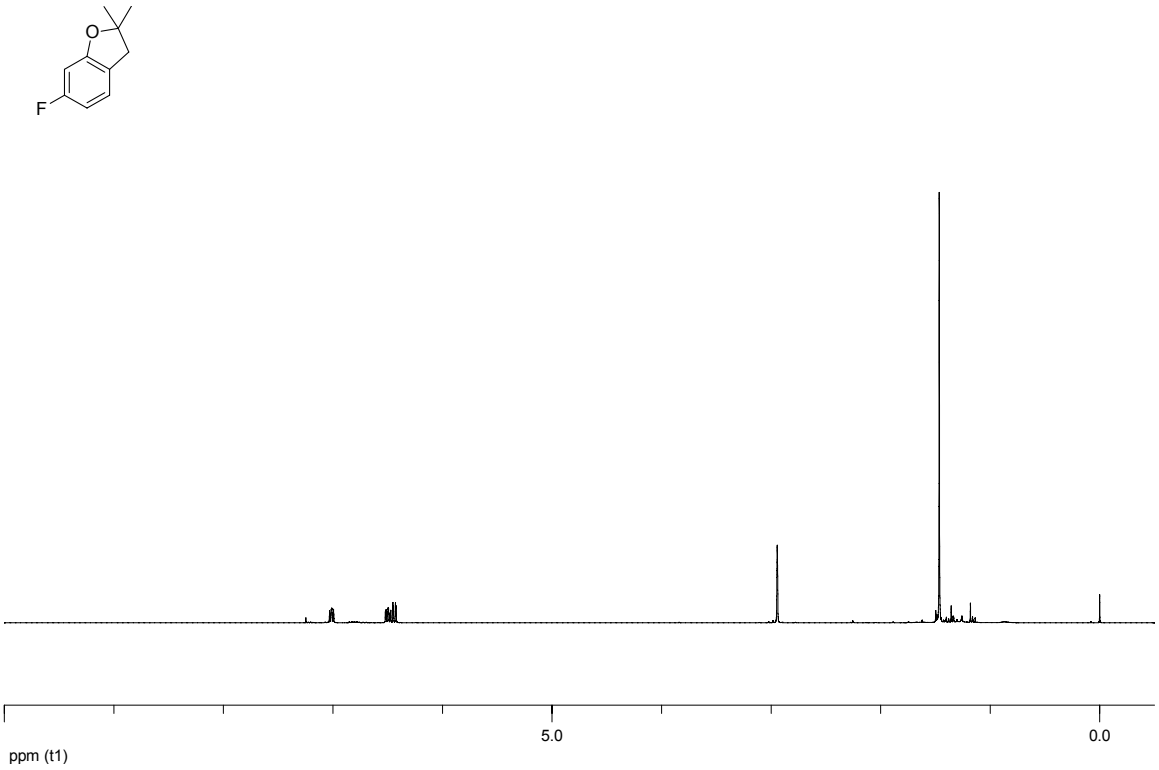
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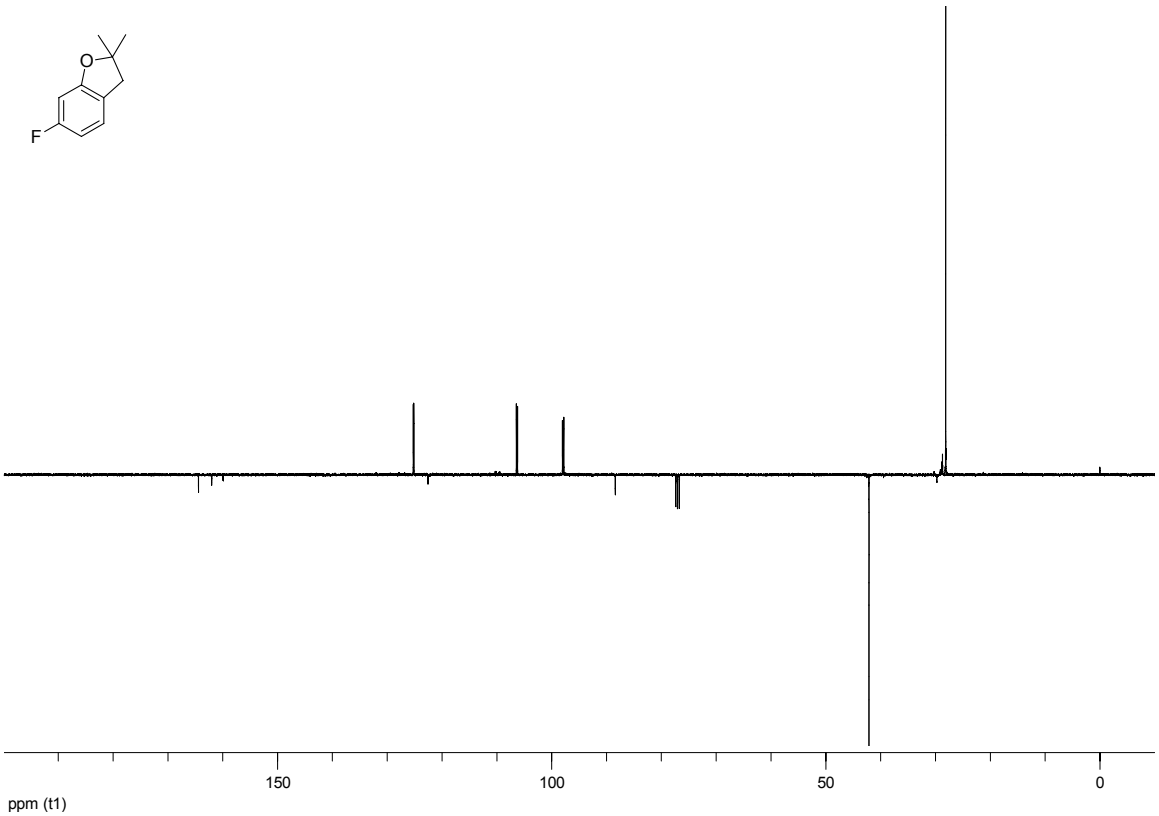
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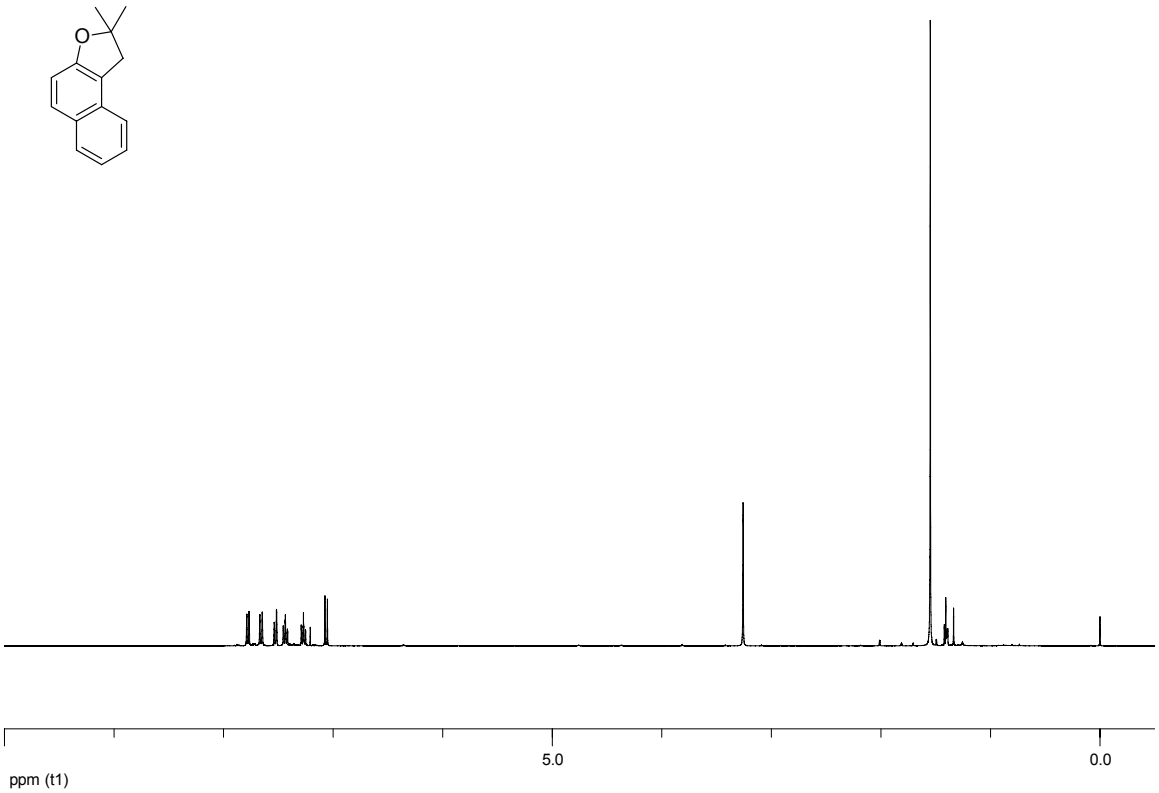
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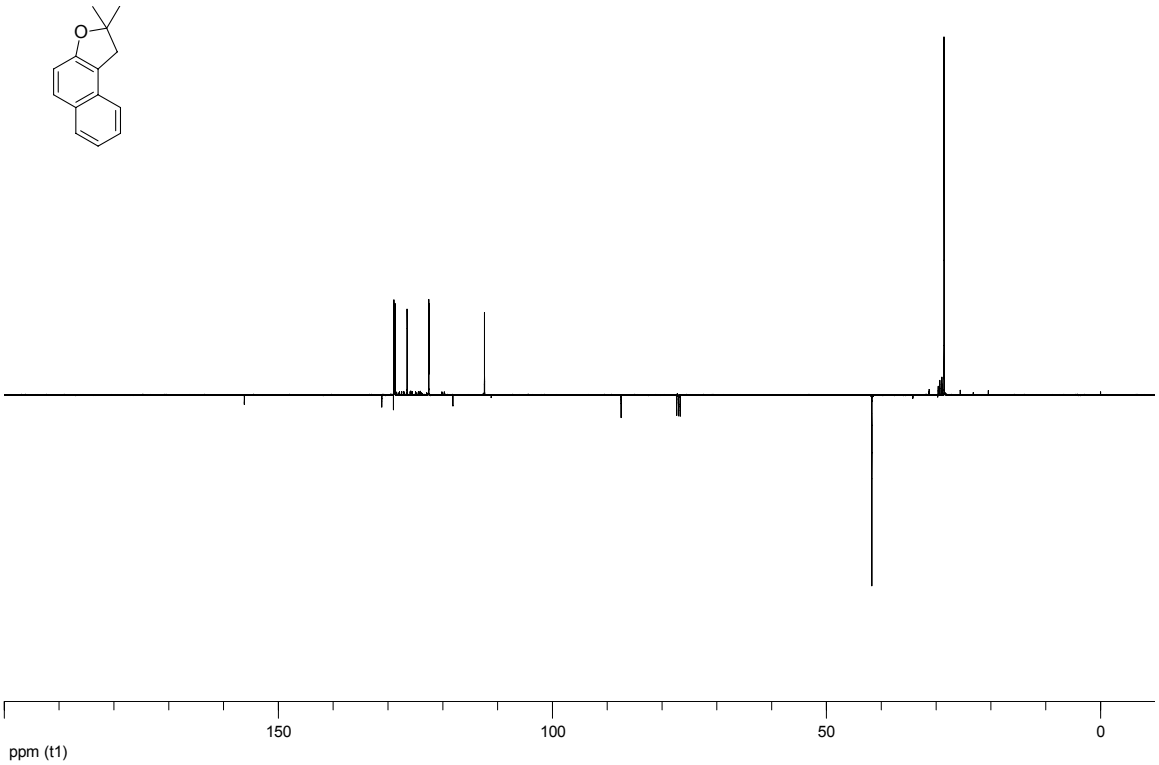
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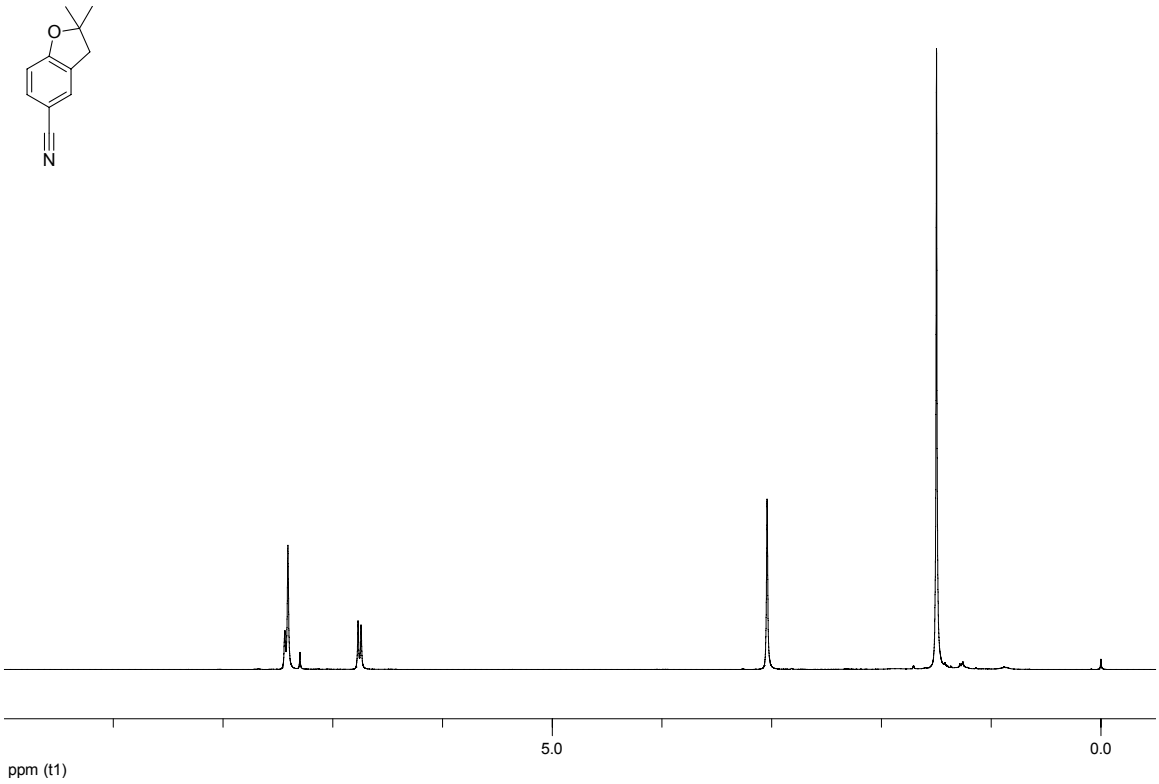
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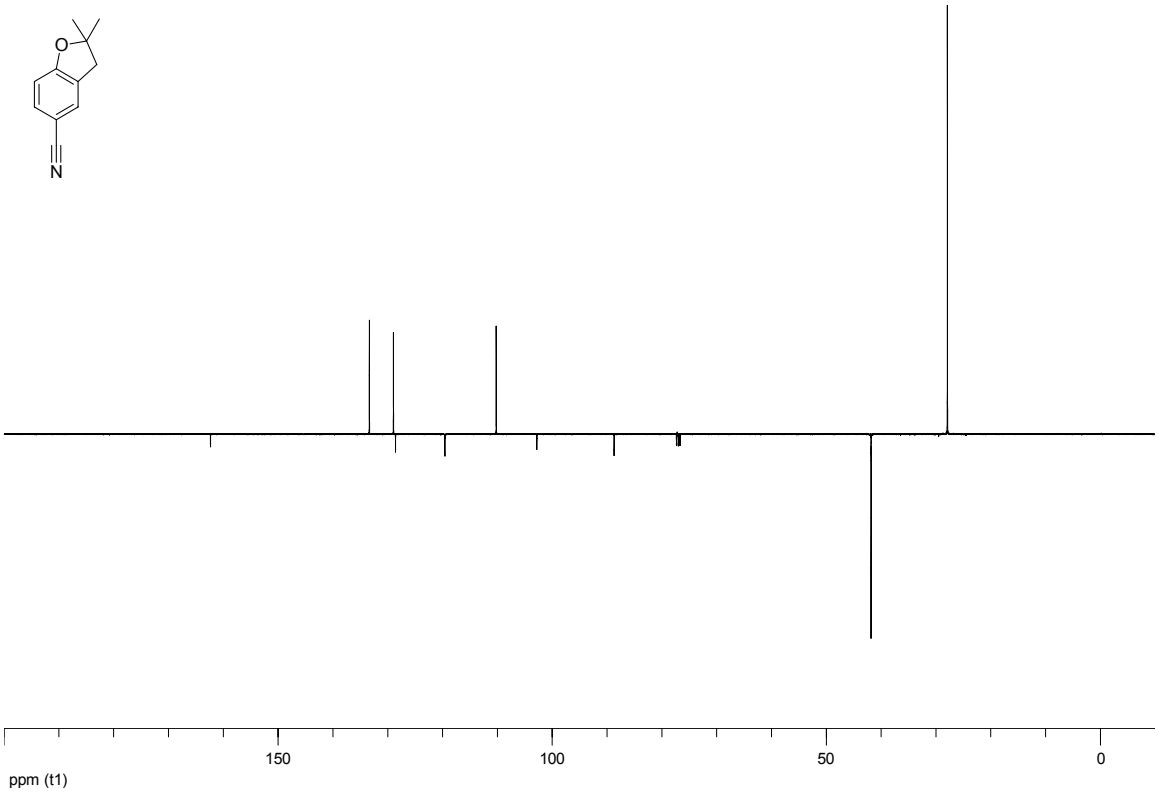
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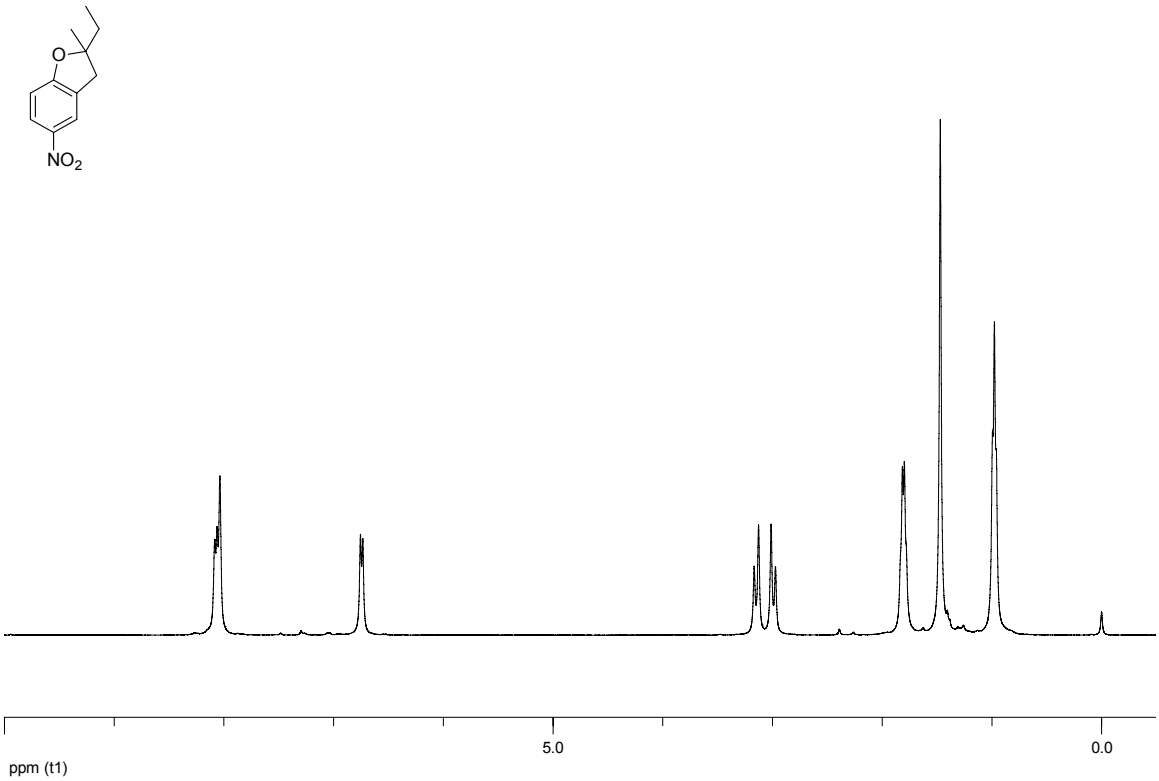
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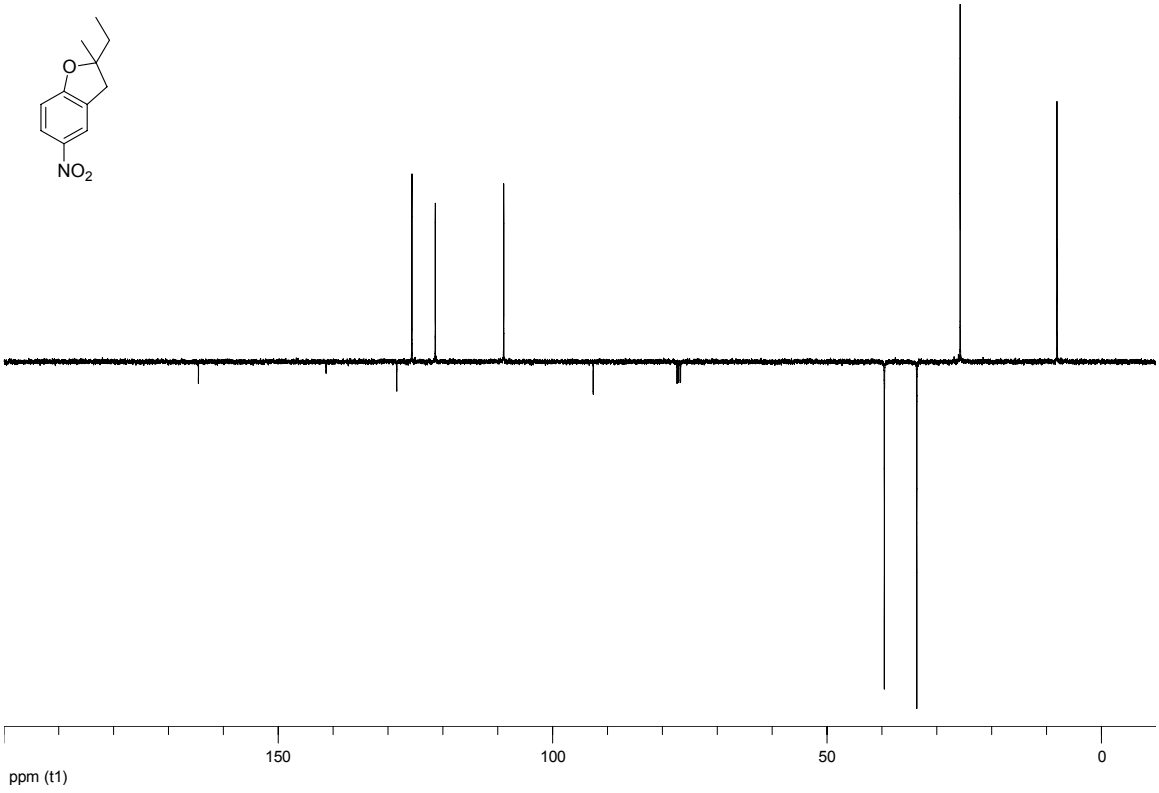
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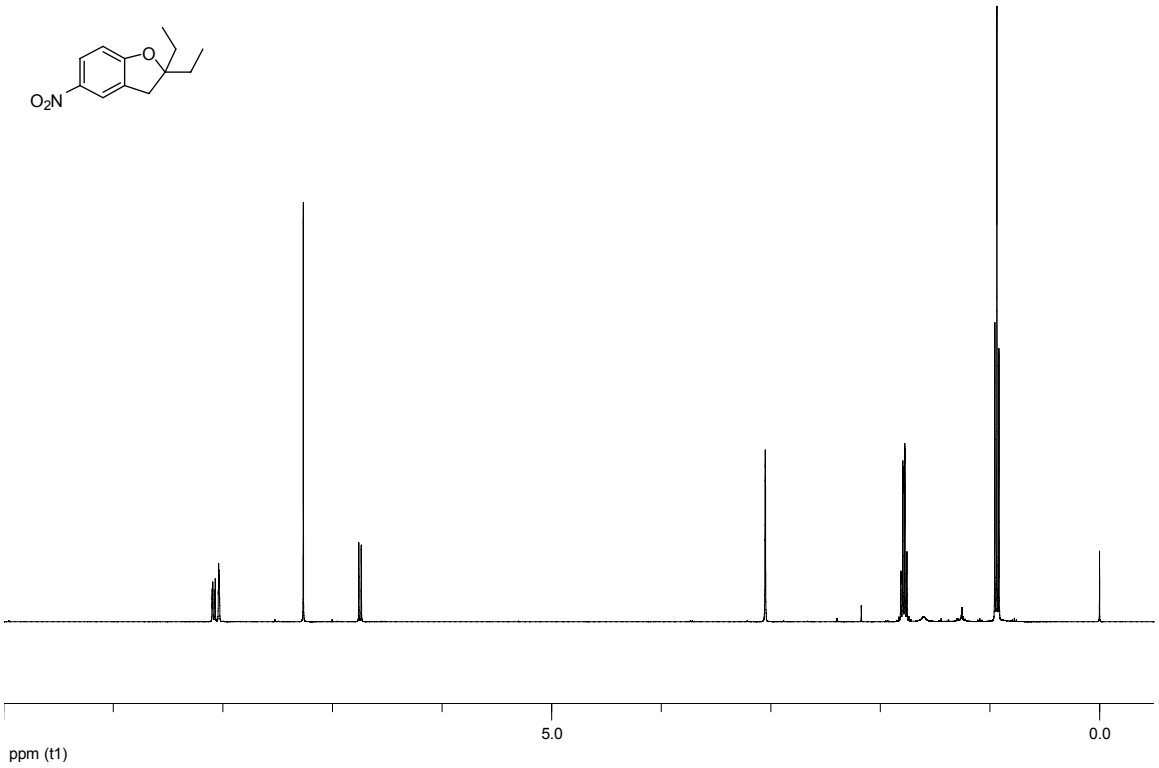
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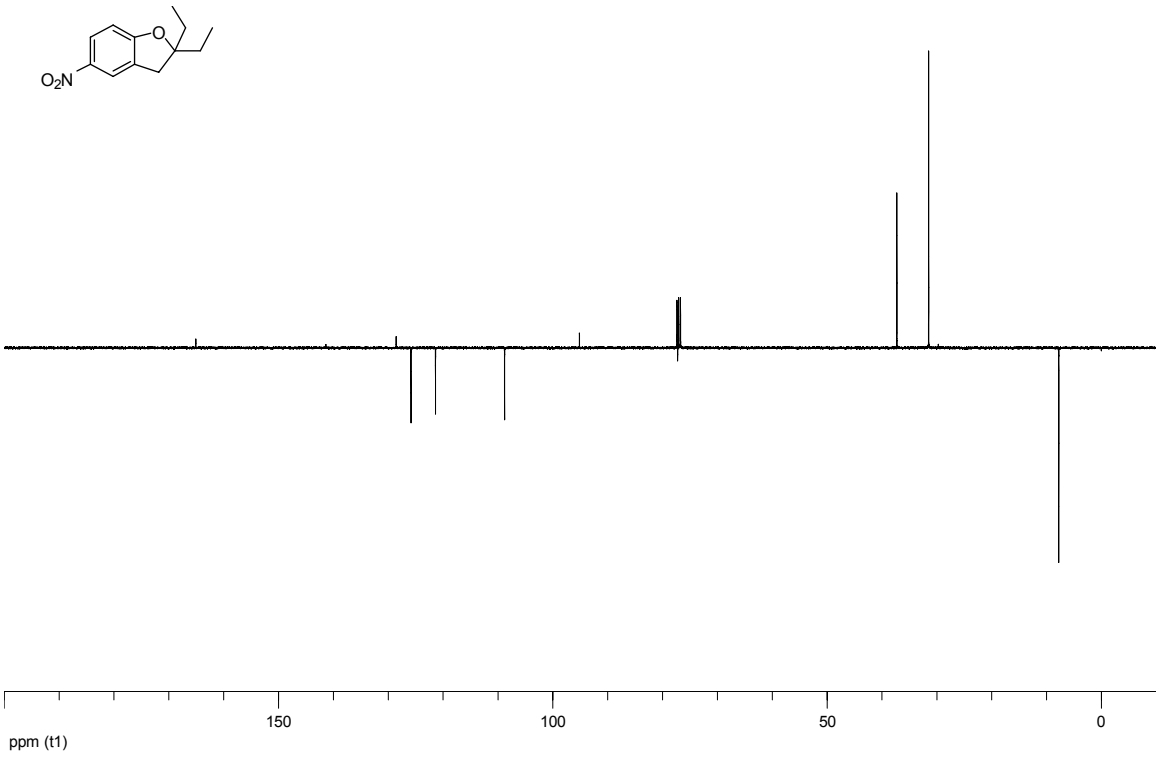
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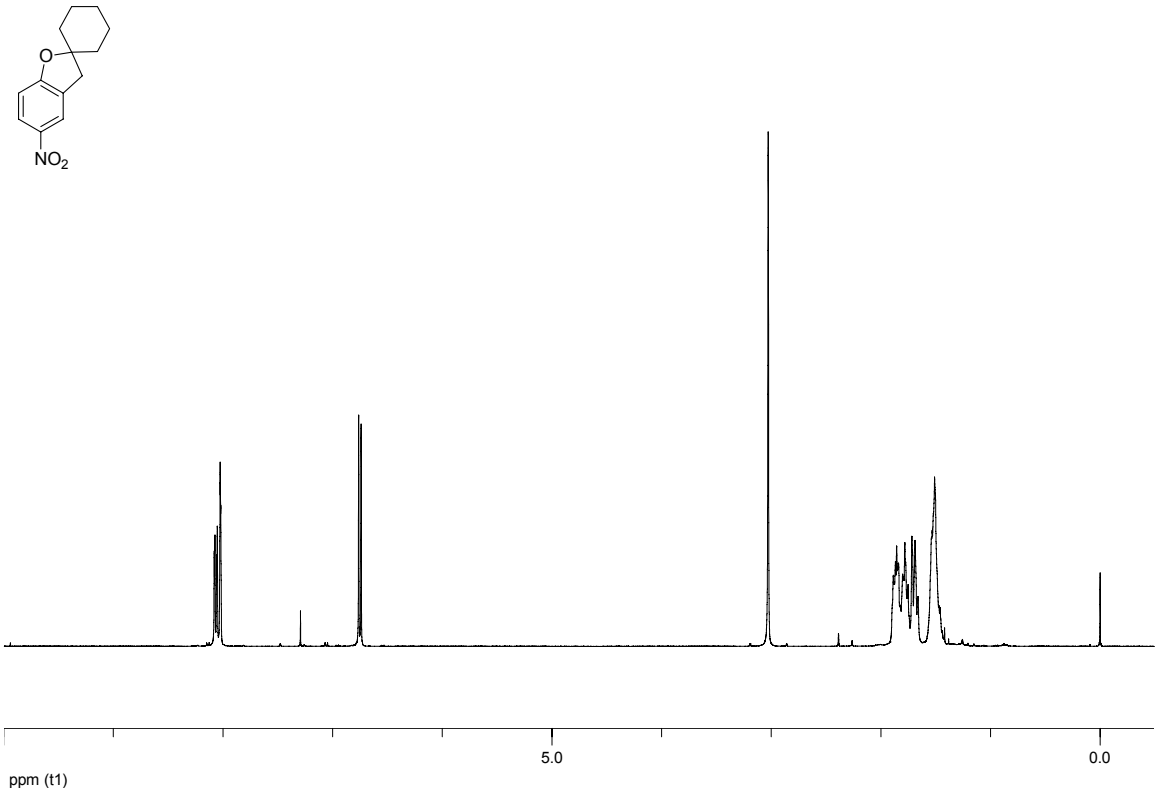
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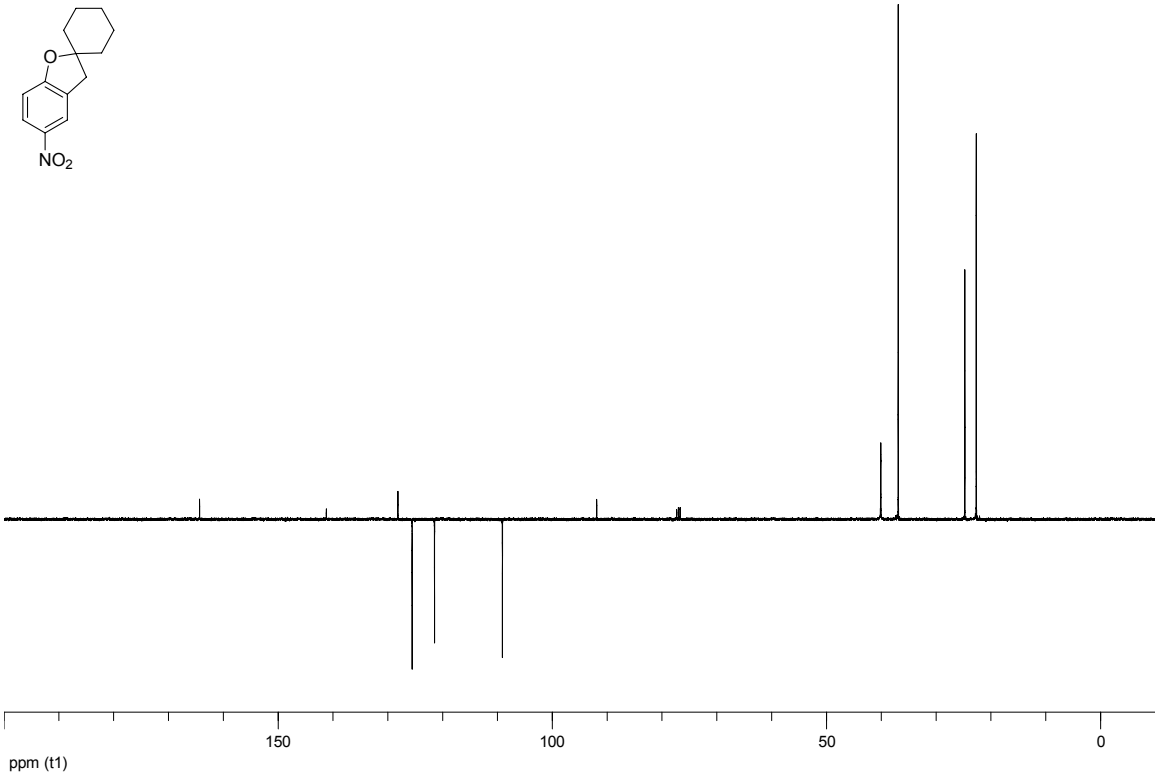
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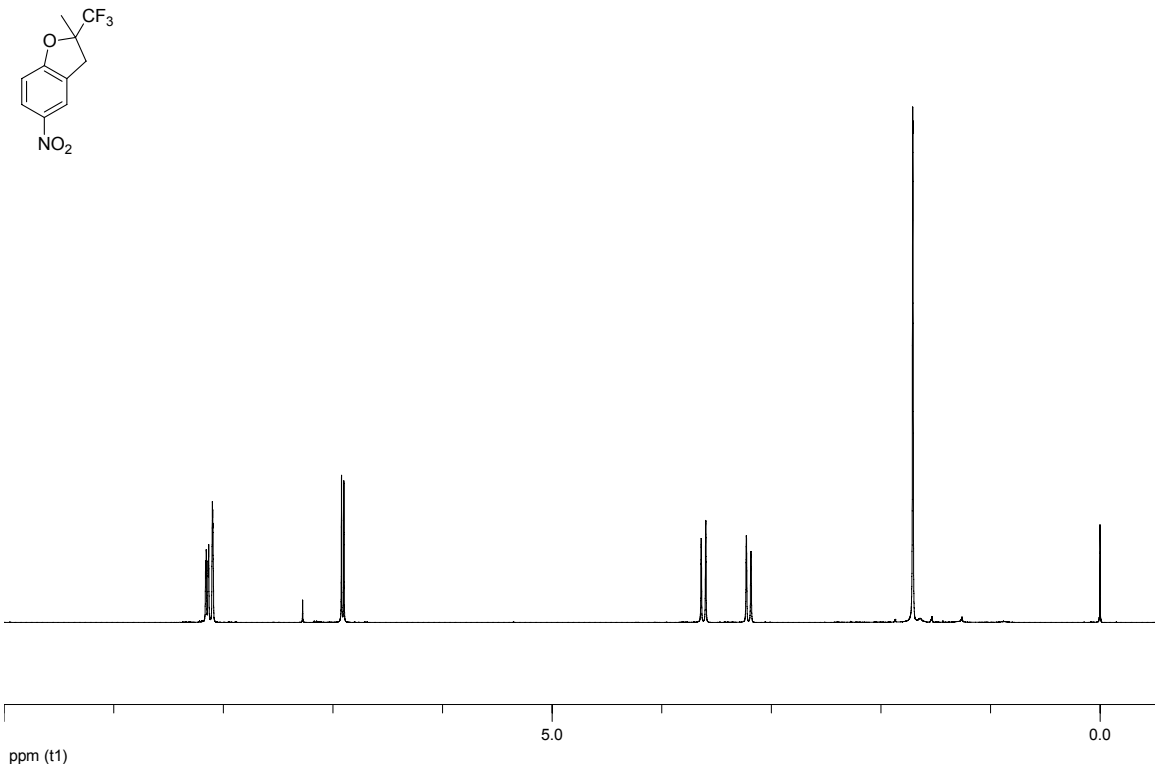
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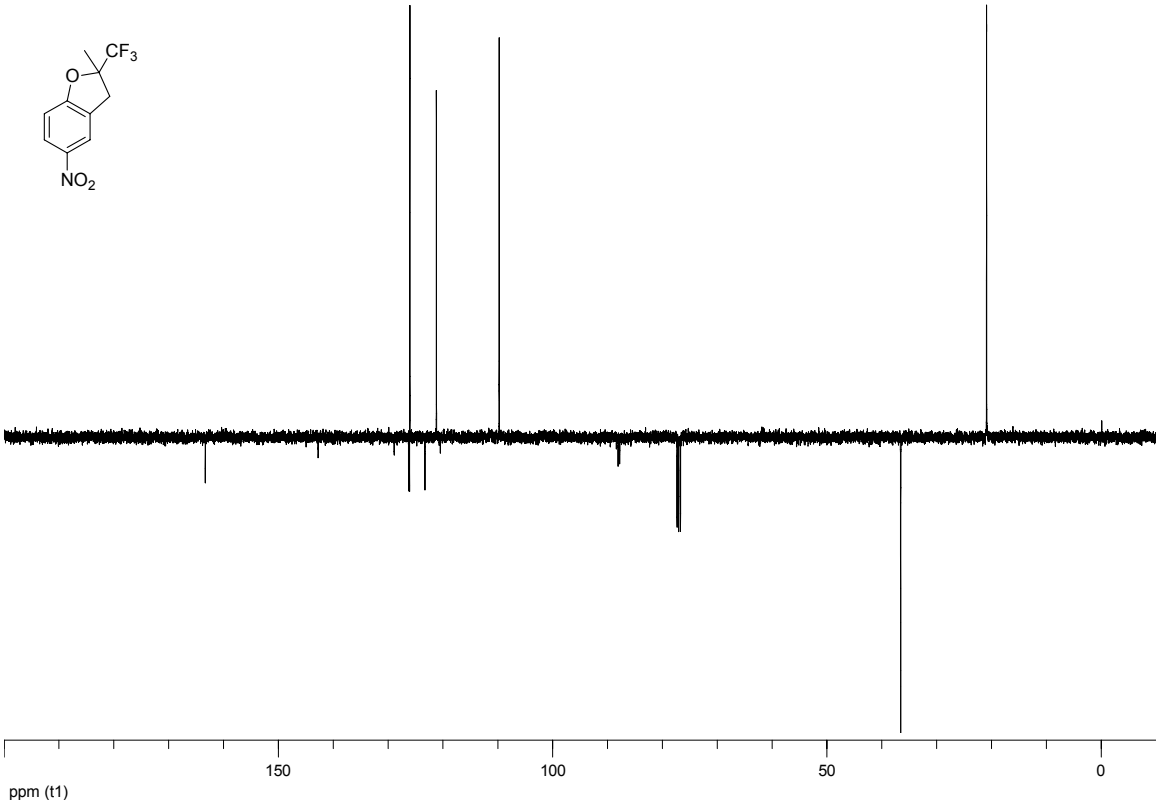
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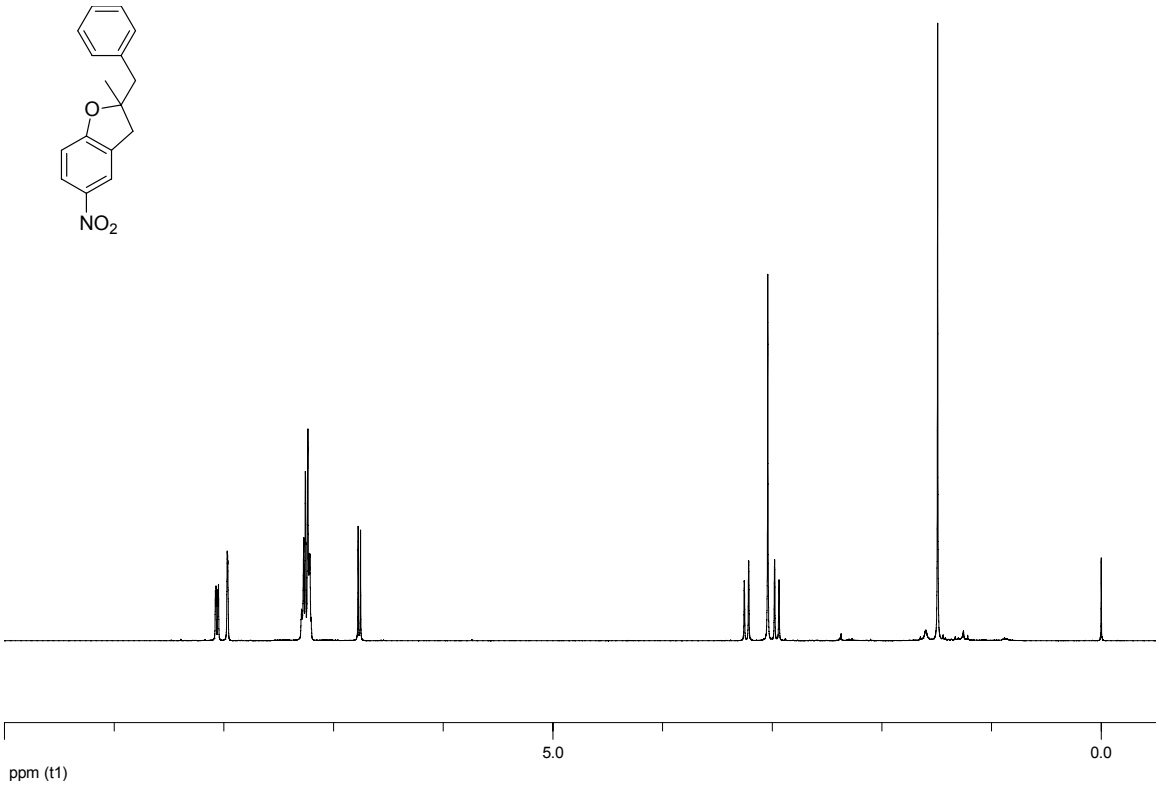
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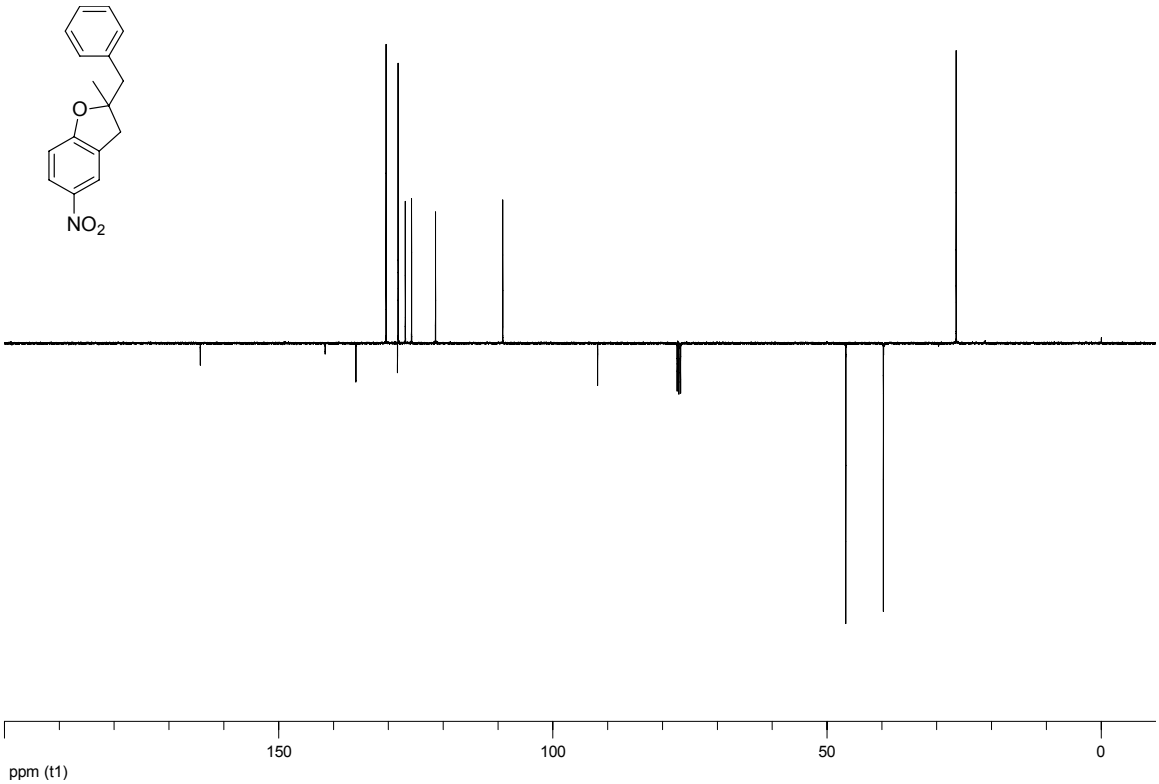
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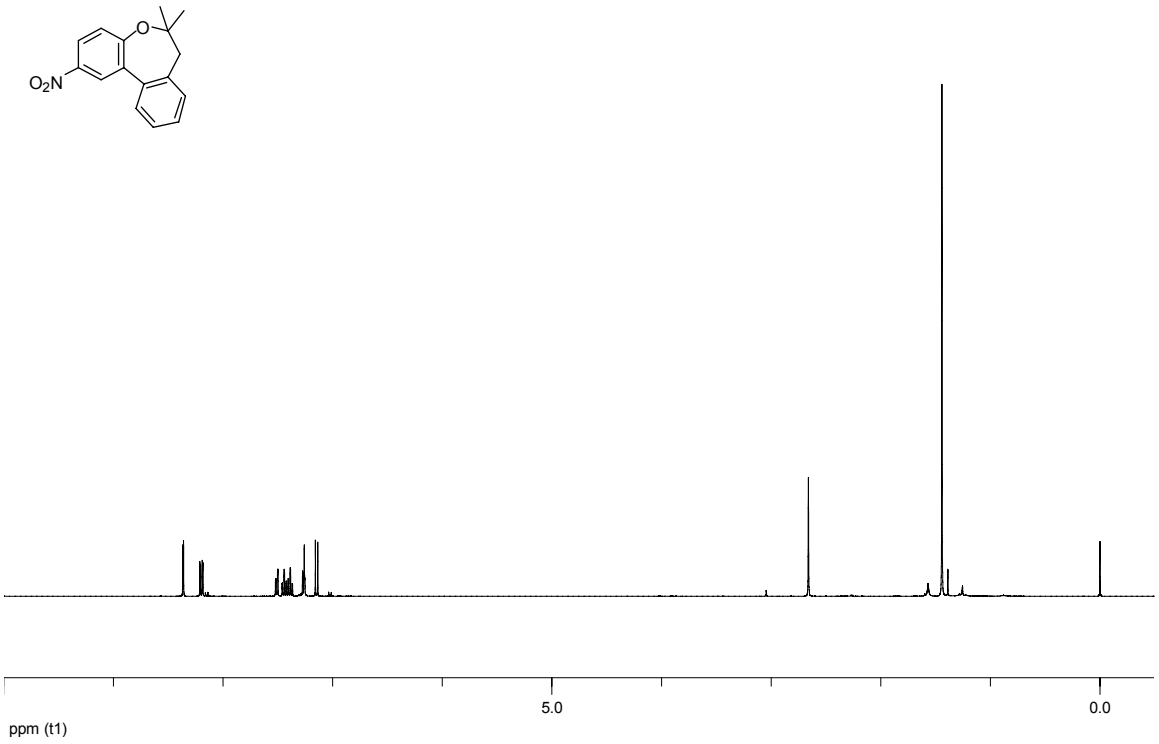
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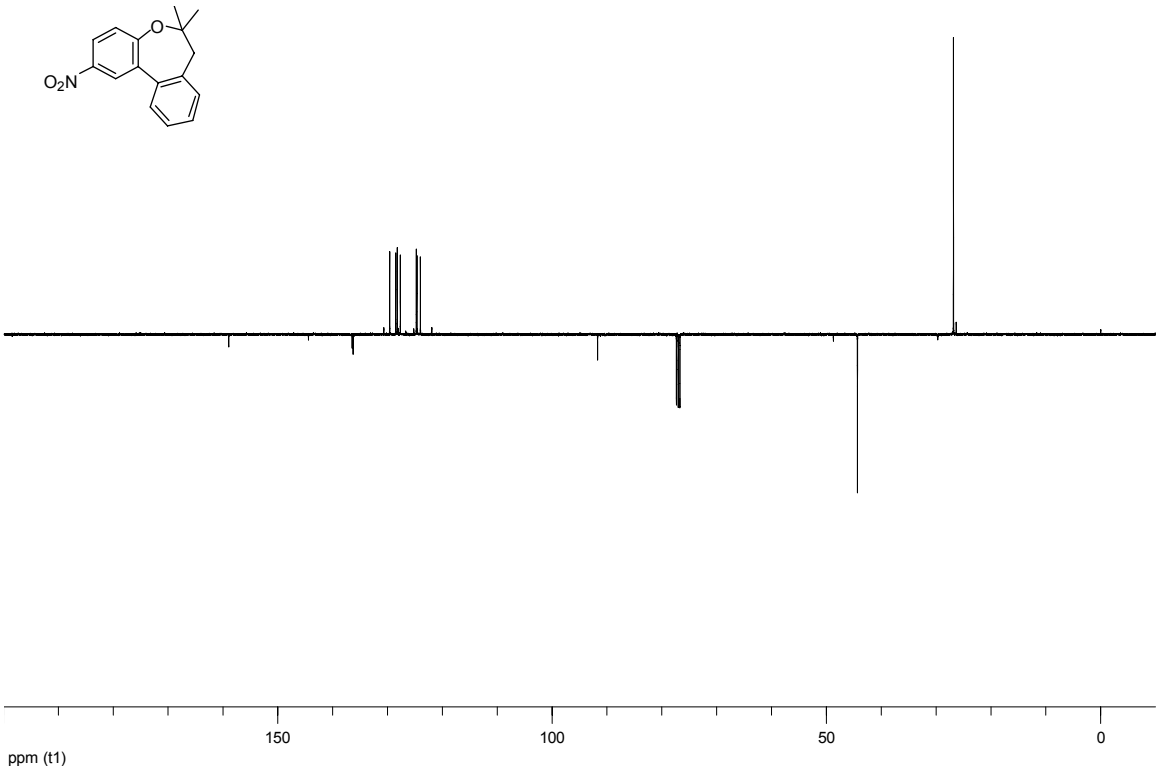
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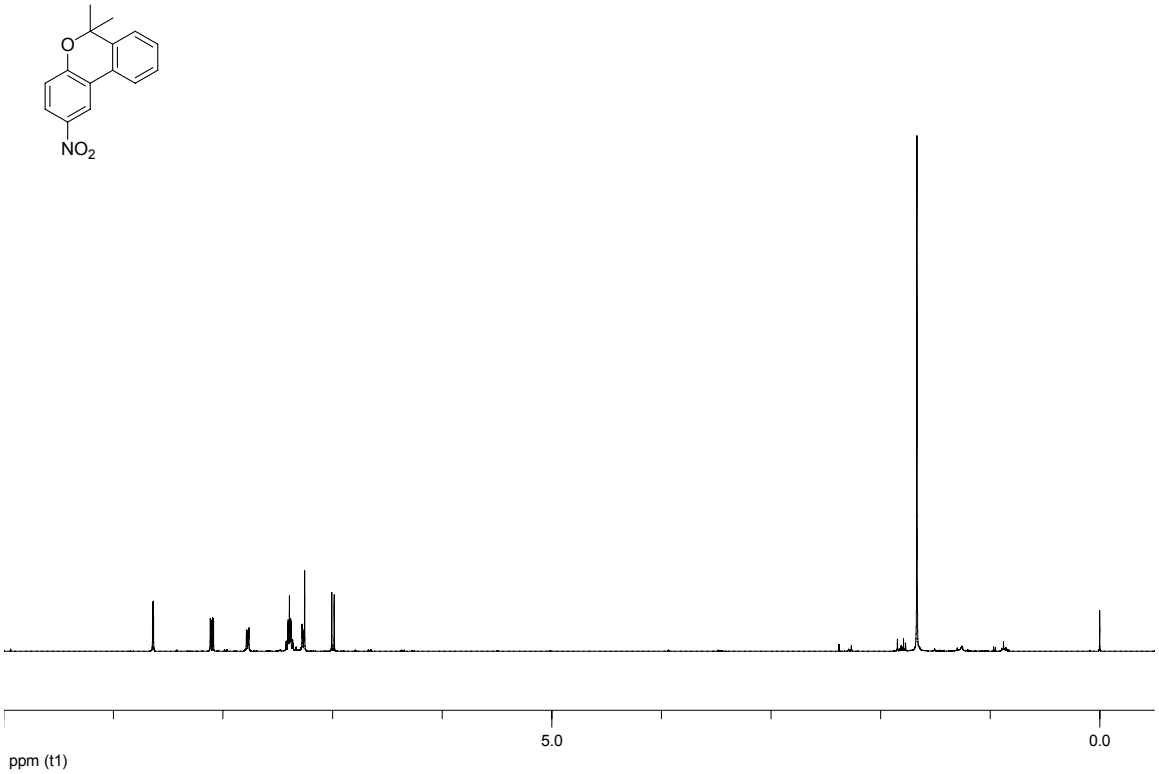
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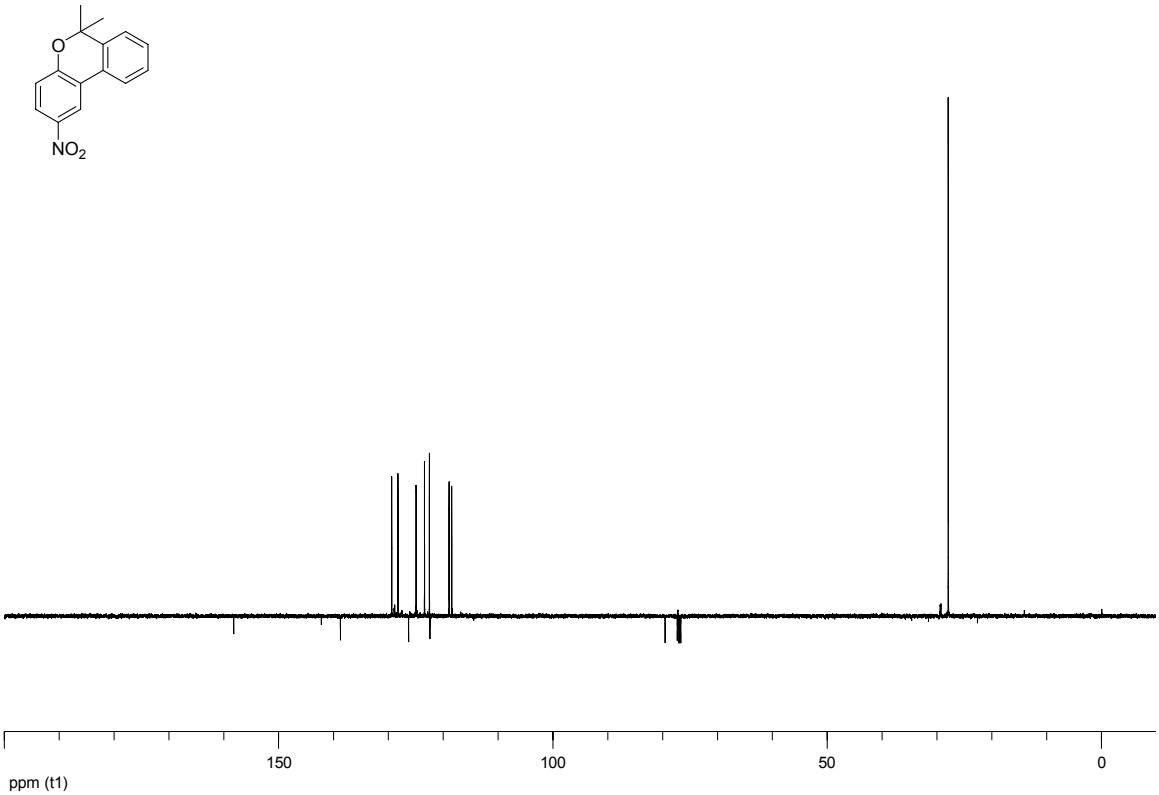
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