Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Metal-Free Carbonitration of Alkenes Using $K_2S_2O_8$

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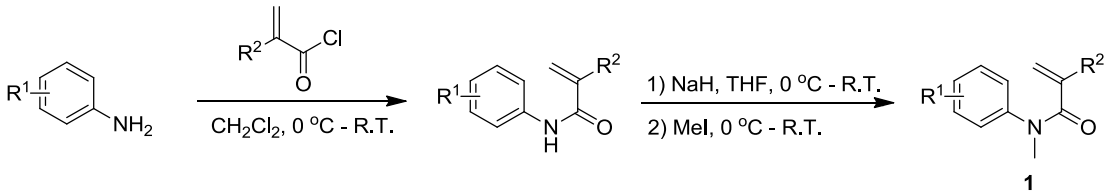
1. General information

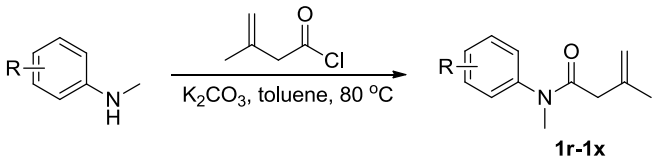
^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ 400 spectrometer in $CDCl_3$ with TMS as internal standard. ^{19}F NMR were recorded on the same instrument. IR spectra were recorded on a Nexus 670 FT-IR spectrometer and only major peaks are reported in cm^{-1}. HRMS data were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer. MS data were determined on a Bruker ESI-MS. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. Typical Procedures for the Synthesis of Substrates

The preparation of amide **1** were described in previous reports, and the NMR spectroscopy were consisted with the those data. [S1]



The synthesis of substrate **1r-1x**

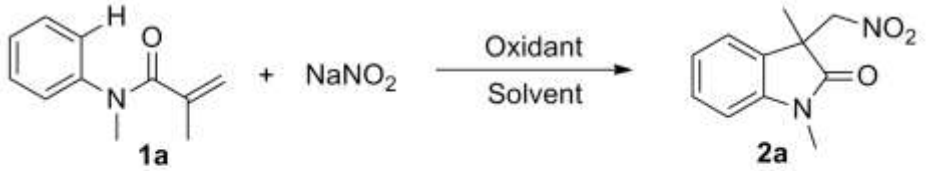


To a stirred solution of *N*-methylaniline (10 mmol) in toluene (20 mL) were added anhydrous K_2CO_3 (15 mmol) and acyl chloride (15 mmol). The mixture was heated to 80 ℃ for 12 h. After completion, the reaction was quenched with H_2O and extracted with EtOAc . The extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure and purification by silica gel flash chromatography to afford the amide **1r-1x**.

3. General procedure for arylnitration of alkenes

In a sealed tube, amide **1** (0.40 mmol), $NaNO_2$ (55 mg, 0.80 mmol), $K_2S_2O_8$ (216 mg, 0.80 mmol) and anhydrous CH_3CN (2 mL) were added. The mixture was allowed to stir at 120 ℃ for 16 hours. The reaction was cooled to room temperature and diluted with EtOAc, then filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by column chromatography to give the product **2**.

Table S1. Reaction Conditions Screening.[a]



1a 2a

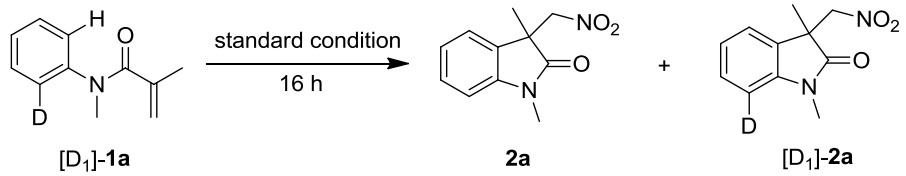
Entry	Oxidant (equiv)	MNO_2 (equiv)	Solvent	Yield (%)[b]
1	$Na_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	CH_3CN	Trace
2	$(NH_4)_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	CH_3CN	16
3	$K_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	CH_3CN	71
4	Oxone (2.0)	$NaNO_2$ (2.0)	CH_3CN	14
5	$K_2S_2O_8$ (2.0)	KNO_2 (2.0)	CH_3CN	70
6	$K_2S_2O_8$ (2.0)	$AgNO_2$ (2.0)	CH_3CN	66
7	$K_2S_2O_8$ (2.0)	$Na_3Co(NO_2)_6$ (2.0)	CH_3CN	0
8[c]	$K_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	CH_3CN	86(75)[d]
9[c]	$K_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	toluene	41
10[c]	$K_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	DMF	24
11[c]	$K_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	DMSO	40
12[c]	$K_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	1,4-dioxane	50
13[c]	$K_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	CH_3NO_2	62
14[c]	$K_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	PhCl	65
15[c]	$K_2S_2O_8$ (2.0)	$NaNO_2$ (2.0)	DCE	42
16[c]	$K_2S_2O_8$ (1.5)	$NaNO_2$ (2.0)	CH_3CN	78
17[c]	$K_2S_2O_8$ (1.0)	$NaNO_2$ (2.0)	CH_3CN	72
18[c]	$K_2S_2O_8$ (2.0)	$NaNO_2$ (3.0)	CH_3CN	65
19[c]	-	$NaNO_2$ (2.0)	CH_3CN	N.R.

[a] Reaction conditions: **1a** (0.4 mmol) in dry CH_3CN (4 mL) with stirring at 120 ℃ for 16 h.
[b] GC estimation using biphenyl as internal reference, N.R. = no reaction.
[c] 2 mL CH_3CN was used.
[d] Isolated yield.

4. Competing kinetic isotope effect (KIE) and radical trapping experiments

a) Intramolecular KIE experiment

[D_1]-**1a** were synthesized deuterium substrates according the literature procedure.[S2] In a sealed tube, [D_1]-**1a** (70 mg, 0.40 mmol), $NaNO_2$ (55 mg, 0.80 mmol), $K_2S_2O_8$ (216 mg, 0.80 mmol), and anhydrous CH_3CN (2 mL) were added. The mixture was allowed to stir at 120 ℃ for 16 hours. The reaction was cooled to room temperature and diluted with EtOAc, then filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by column chromatography to give the product **2a** and [D_1]-**2a**. The products were under ^{1}H-NMR analysis (Figure S1).



[D_1]-**1a** **2a** [D_1]-**2a**

58% yield, K_H/K_D = 0.9

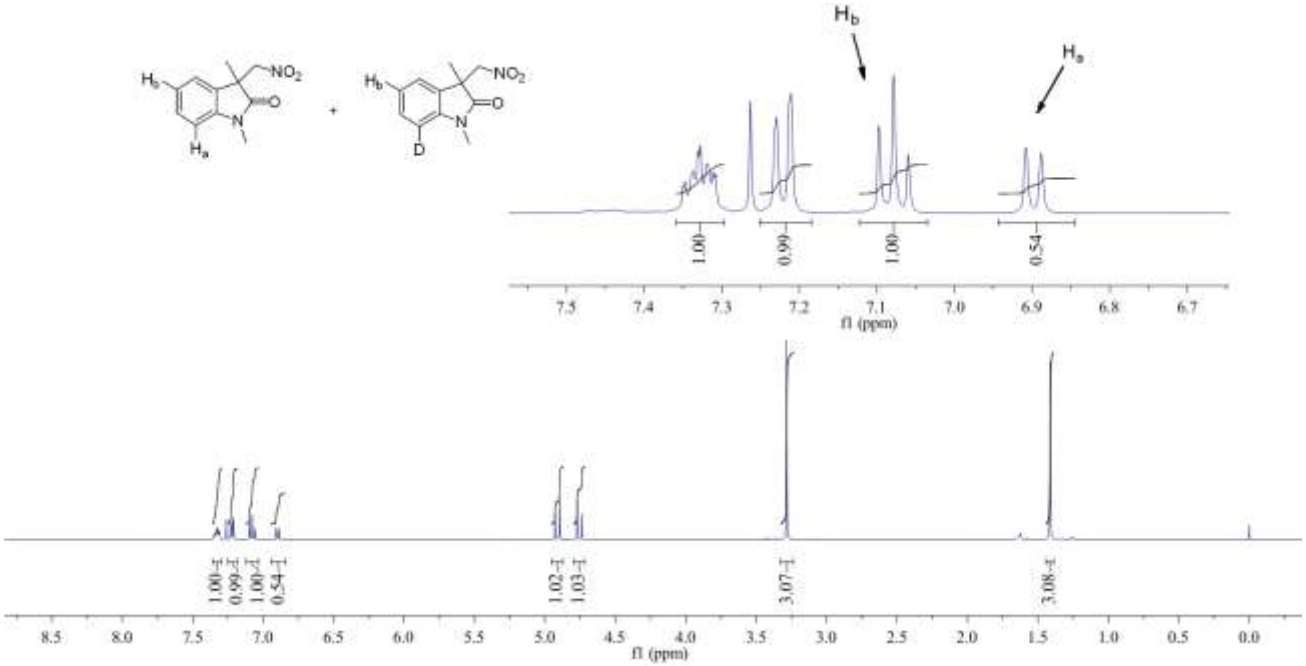
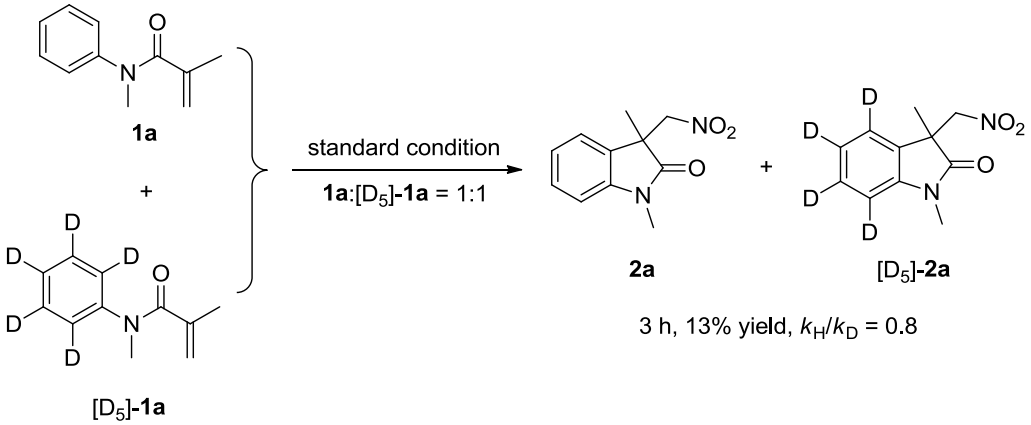


Figure S1. ^{1}H NMR spectra of the mixture of compound **2a** and [D_1]-**2a**.

b) Intermolecular KIE experiment

[D_5]-**1a** were synthesized deuterium substrates according the literature procedure.[S2] In a sealed tube, **1a** (35 mg, 0.20 mmol), [D_5]-**1a** (36 mg, 0.20 mmol), $NaNO_2$ (55 mg, 0.80 mmol), $K_2S_2O_8$ (216 mg, 0.80 mmol), and anhydrous CH_3CN (2 mL) were added. The mixture was allowed to stir at 120 ℃ for 3 hours. The reaction was cooled to room temperature and diluted with EtOAc, then filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by column chromatography to give the product **2a** and [D_5]-**2a**. The products were under ^{1}H-NMR analysis (Figure S2).



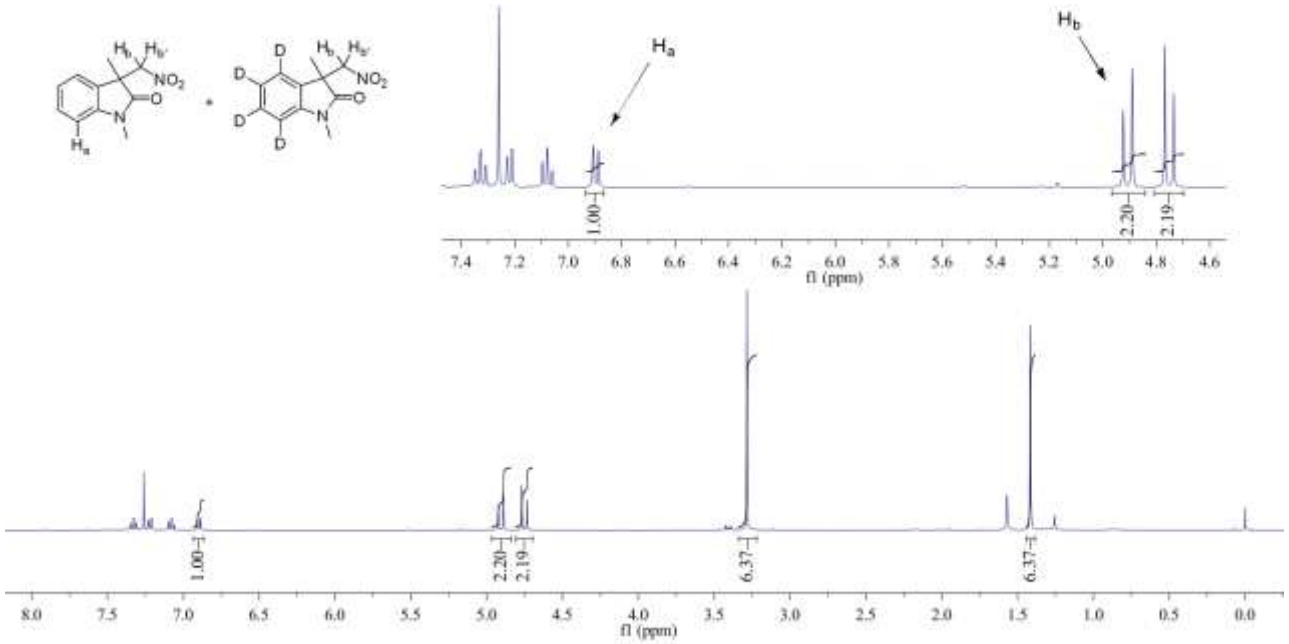
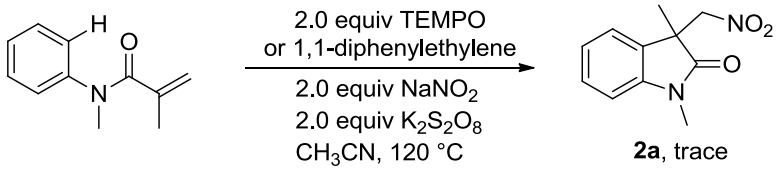


Figure S2. ^{1}H NMR spectra of the mixture of compound **2a** and [D_5]-**2a**.

c) Radical trapping experiment



5. Synthesis of 1,3-dimethylindolin-2-one (3a)

To a solution of compound **2a** (220 mg, 1.0 mmol) in 6 mL of MeOH, 16 mL of a 0.5 M of Na_2HPO_4 in a 1 N solution of NaOH were added. After 1 h, 2.0 mmol of Oxone in 3 mL of water were added to the stirred suspension. The resulting mixture was stirred at room temperature for 1 h, and was extracted with ethyl acetate. The organic layers was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure and purification by silica gel flash chromatography to afford 1,3-dimethylindolin-2-one (103 mg, 64% yield). The NMR spectroscopy were consisted with previous report.[S3a] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.21 (m, 2H), 7.06-7.02 (m, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.41 (q, *J* = 7.6 Hz, 1H), 3.19 (s, 3H), 1.47 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 143.8, 130.5, 127.7, 123.3, 122.2, 107.8, 40.3, 26.0, 15.2. ESI-MS: m/z = 162 (M+H).

6. Synthesis of 3-hydroxy-1,3-dimethylindolin-2-one (3b)

The compound **2a** (220 mg, 1.0 mmol) in *t*-BuOH (2 mL) at 25 ℃ was treated with aqueous buffered KOH (0.5 M in KOH and 1.25 M in K_2HPO_4, 2.5 mL). The mixture was stirred under nitrogen for 2 minutes and then aqueous $KMnO_4$ (0.5 M, 8 mL, 4 mmol) was added with slight cooling to maintain the temperature at 25 ℃. After stirring for a further 60 min., saturated Na_2SO_3 was added with cooling, and extracted with EtOAc. The extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure and purification by silica gel flash chromatography to afford 3-hydroxy-1,3-dimethylindolin-2-one (135 mg, 76% yield). The NMR spectroscopy were consisted with previous report. [S3b] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.33-7.29 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.87 (s, 1H), 3.18 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 142.7, 131.6, 129.4, 123.4, 123.2, 108.4, 73.6, 26.2, 24.7. ESI-MS: m/z = 178 (M+H).

7. Synthesis of 3-(aminomethyl)-1,3-dimethylindolin-2-one (3c)

To a solution of compound **2a** (220 mg, 1.0 mmol) in methanol (6 mL) at 5 ℃ were added ammonium formate (252 mg, 4.0 mmol) and 10% palladium on carbon (33 mg). The reaction was allowed to warm to 25 ℃, where it was stirred for 12 h. After this time, the reaction mixture was filtered through a bed of Celite. The filtrate was concentrated under reduced pressure to afford a crude residue and purified by column chromatography to give the product 3-(aminomethyl)-1,3-dimethylindolin-2-one (163 mg, 86% yield). The NMR spectroscopy were consisted with previous report.[S3c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 3.23 (s, 3H), 3.10 (d, *J* = 12.8 Hz, 1H), 2.96 (d, *J* = 13.2 Hz, 1H), 1.37 (s, 2H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 143.4, 132.1, 127.7, 122.2, 122.1, 107.1, 50.3, 49.0, 25.7, 19.8. ESI-MS: m/z = 191 (M+H).

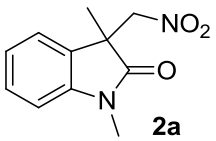
Reference:

[S1] a) A. Pinto, Y. Jia, L. Neuville, J. Zhu, *Chem. Eur. J.* **2007**, *13*, 961-967; b) H. Wei, T. Piou, J. Dufour, L. Neuville, J. Zhu, *Org. Lett.*, **2011**, *13*, 2244–2247; c) X. Mu, T. Wu, H. Wang, Y. Guo, G. Liu, *J. Am. Chem. Soc.* **2012**, *134*, 878–881; d) S. Biros, R. Yeh, K. Raymond, *Angew. Chem., Int. Ed.* **2008**, *47*, 6062–6064; e) N. Campbell, A. Finch, S. Rokita, *ChemPhysChem* **2010**, *11*, 1768–1773; f) D. Walba, W. Thurmes, R. Haltiwanger, *J. Org. Chem.* **1988**, *53*, 1046–1056; g) C. Shaffer, S. Harriman, Y. Koen, R. Hanzlik, *J. Am. Chem. Soc.* **2001**, *123*, 8502–8508.

[S2] a) A. Pinto, L. Neuville, P. Retailleau, J. Zhu, *Org. Lett.* **2006**, *8*, 4927–4930; b) I. J. S. Fairlamb, A. R. Kapdi, A. F. Lee, G. P. Mcglacken, F. Weissburger, A. H. M. de Vries, L. S. van de Vondervoort, *Chem. Eur. J.* **2006**, *12*, 8750–8761.

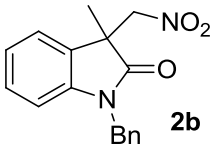
[S3] a) K. H. Shaughnessy, B. C. Hamann and J. F. Hartwig, *J. Org. Chem.* **1998**, *63*, 6546–6553; b) I. Gorokhovik, L. Neuville and J. Zhu *Org. Lett.* **2011**, *13*, 5536–5539; c) K. Matcha, R. Narayan, A. P. Antonchick, *Angew. Chem. Int. Ed.* **2013**, *52*, 7985–7989.

8. Characterization of new compounds.



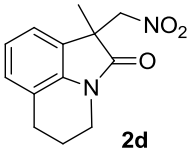
2a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dt, *J* = 0.8 Hz, 7.6 Hz, 1H), 7.23-7.21 (m, 1H), 7.08 (dt, *J* = 0.8 Hz, 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.91 (d, *J* = 13.2 Hz, 1H), 4.76 (d, *J* = 13.2 Hz, 1H), 3.28 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 143.5, 129.2 ,129.1, 122.9, 122.4, 108.8, 79.0, 47.0, 26.6, 21.7. IR (film) υ_{max}: 3441, 2080, 1639, 1556, 1371, 1249, 1126, 741, 701, 647 cm^{-1}. HRMS calc. for $C_{11}H_{12}N_2O_3$ $(M+H)^+$, 221.0921; found, 221.0918.



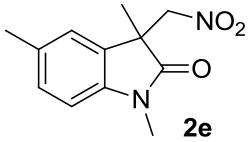
2b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 4H), 7.28-7.25 (m, 1H), 7.22-7.16 (m, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.06-4.91 (m, 3H), 4.81 (d, *J* = 13.6 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 142.6, 135.4, 129.1, 129.0, 128.8, 127.6, 127.2, 122.9, 122.3, 109.9, 78.6, 47.1, 44.1, 22.3. IR (film) υ_{max}: 2928, 2564, 1900, 1745, 1613, 1555, 1490, 1454, 1384, 1182, 754, 650 cm^{-1}. HRMS calc. for $C_{17}H_{16}N_2O_3$ $(M+H)^+$, 297.1234; found, 297.1237.



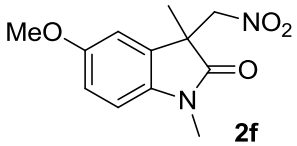
2d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (dd, *J* = 3.2 Hz, 7.6 Hz, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 4.88 (d, *J* = 13.2 Hz, 1H), 4.75 (d, *J* = 13.2 Hz, 1H), 3.83-3.72 (m, 2H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.06-2.01 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 139.2, 128.0, 127.6, 122.3, 120.8, 120.8, 120.3, 79.1, 48.2, 39.1, 24.4, 21.3, 21.0. IR (film) υ_{max}: 3450, 2929, 2873, 1711, 1629, 1554, 1483, 1388, 1357, 1244, 1169, 783, 639 cm^{-1}. HRMS calc. for $C_{13}H_{14}N_2O_3$ $(M+H)^+$, 247.1077; found, 247.1079.



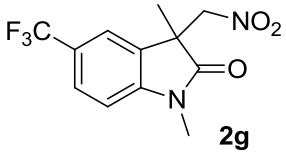
2e

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.0 Hz, 1H), 7.03 (s, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.90 (d, *J* = 13.6 Hz, 1H), 4.74 (d, *J* = 13.6 Hz, 1H), 3.26 (s, 3H), 2.33 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 141.1, 132.5, 129.4, 129.1, 123.2, 108.5, 79.0, 47.0, 26.6, 21.8, 21.0. IR (film) υ_{max}: 3449, 2928, 2079, 1742, 1622, 1555, 1502, 1383, 1250, 1124, 812, 643, 556 cm^{-1}. HRMS calc. for $C_{12}H_{14}N_2O_3$ $(M+H)^+$, 235.1077; found, 235.1080.



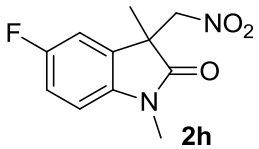
2f

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85-6.78 (m, 1H), 4.90 (d, *J* = 13.6 Hz, 1H), 4.74 (d, *J* = 13.6 Hz, 1H), 3.77 (s, 3H), 3.25 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 156.1, 136.9, 130.4, 113.1, 110.2, 109.1, 78.9, 55.7, 47.4, 26.6, 21.7. IR (film) υ_{max}: 3457, 2960, 2079, 1638, 1554, 1382, 1291, 1212, 1122, 1037, 806, 736 cm^{-1}. HRMS calc. for $C_{12}H_{14}N_2O_4$ $(M+H)^+$, 251.1026; found, 251.1030.



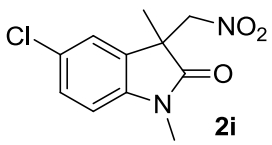
2g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.46 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.97 (d, *J* = 14.0 Hz, 1H), 4.81 (d, *J* = 14.0 Hz, 1H), 3.33 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 146.6, 129.9, 127.0 (q, $J_{C\text{-}F}$ = 4.0 Hz), 125.1 (q, $J_{C\text{-}F}$ = 32.0 Hz), 124.1 (q, $J_{C\text{-}F}$ = 270.0 Hz), 119.4 (q, $J_{C\text{-}F}$ = 4.0 Hz), 108.6, 78.5, 46.9, 26.8, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.48. IR (film) υ_{max}: 3447, 2952, 2079, 1726, 1627, 1558, 1457, 1376, 1276, 1163, 1118, 1064, 905, 825 cm^{-1}. HRMS calc. for $C_{12}H_{11}F_3N_2O_3$ $(M+H)^+$, 289.0795; found, 289.0802.



2h

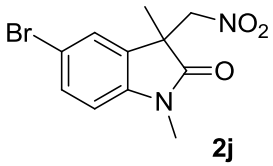
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-6.98 (m, 2H), 6.83 (dd, *J* = 4.0 Hz, 8.4 Hz, 1H), 4.93 (d, *J* = 13.6 Hz, 1H), 4.74 (d, *J* = 13.6 Hz, 1H), 3.28 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 159.3 (d, $J_{C\text{-}F}$ = 241 Hz), 139.5, 130.7 (d, $J_{C\text{-}F}$ = 8 Hz), 115.5 (d, $J_{C\text{-}F}$ = 23 Hz), 110.9 (d, $J_{C\text{-}F}$ = 25 Hz), 109.4 (d, $J_{C\text{-}F}$ = 8 Hz), 78.7, 47.4, 26.8, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -119.61. IR (film) υ_{max}: 3441, 2083, 1638, 1558, 1496, 1469, 1381, 1278, 1117, 695, 613 cm^{-1}. HRMS calc. for $C_{11}H_{11}FN_2O_3$ $(M+H)^+$, 239.0829; found, 239.0826.



2i

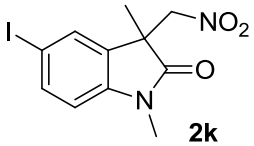
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.93 (d, *J* = 14.0 Hz, 1H), 4.70 (d, *J* = 14.0 Hz, 1H), 3.28 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 130.8,

129.2, 128.3, 123.0, 109.8, 78.6, 47.1, 26.8, 21.7. IR (film) υ_{max}: 3438, 2083, 1637, 1556, 1492, 1460, 1422, 1363, 1274, 1248, 1164, 1130, 811, 711, 640 cm^{-1}. HRMS calc. for $C_{11}H_{11}ClN_2O_3$ $(M+H)^+$, 255.0531; found, 255.0536.



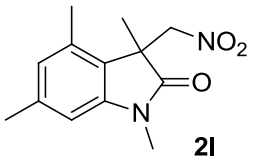
2j

^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.93 (d, *J* = 13.6 Hz, 1H), 4.74 (d, *J* = 14.0 Hz, 1H), 3.27 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 142.6, 132.1, 131.2, 125.7, 115.4, 110.3, 78.6, 47.0, 26.7, 21.7. IR (film) υ_{max}: 3447, 2085, 1711, 1638, 1555, 1491, 1420, 1347, 1128, 811, 710, 638 cm^{-1}. HRMS calc. for $C_{11}H_{11}BrN_2O_3$ $(M+H)^+$, 299.0026; found, 299.0030.



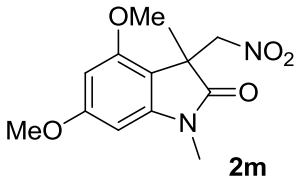
2k

^1H NMR (400 MHz, $CDCl_3$): δ 7. 65 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 13.6 Hz, 1H), 4.73 (d, *J* = 14.0 Hz, 1H), 3.26 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 143.3, 138.0, 131.6, 131.1, 110.8, 85.1, 78.5, 46.8, 26.7, 21.7. IR (film) υ_{max}: 3448, 2086, 1640, 1554, 1489, 1459, 1345, 1247, 1126, 809, 707, 637 cm^{-1}. ESI-MS: *m/z* = 347 $(M+H)^+$



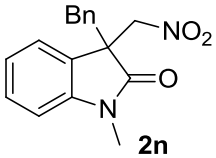
2l

^1H NMR (400 MHz, $CDCl_3$): δ 6.65 (s, 1H), 6.55 (s, 1H), 5.02-4.92 (m, 2H), 3.25 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 144.0, 139.2, 133.7, 125.9, 122.9, 107.5, 78.4, 47.8, 26.6, 21.5, 19.6, 17.9. IR (film) υ_{max}: 3445, 3032, 2936, 2086, 1710, 1622, 1551, 1453, 1386, 1339, 1152, 1066, 841, 665, 596 cm^{-1}. HRMS calc. for $C_{13}H_{16}N_2O_3$ $(M+H)^+$, 249.1234; found, 249.1237.



2m

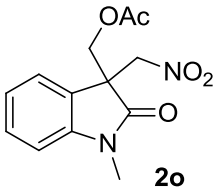
^1H NMR (400 MHz, $CDCl_3$): δ 6.15 (d, *J* = 2.0 Hz, 1H), 6.12 (d, *J* = 1.6 Hz, 1H), 5.04 (d, *J* = 13.2 Hz, 1H), 4.85 (d, *J* = 12.8 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.23 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 162.3, 156.6, 145.6, 106.6, 92.5, 89.0, 77.9, 55.6, 55.5, 47.0, 26.8, 19.7. IR (film) υ_{max}: 3446, 2935, 2084, 1719, 1623, 1555, 1457, 1335, 1257, 1213, 1154, 815, 737, 643 cm^{-1}. HRMS calc. for $C_{13}H_{16}N_2O_5$ $(M+H)^+$, 281.1132; found, 281.1139.



2n

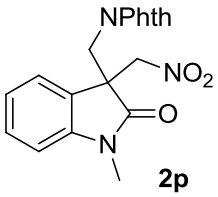
^1H NMR (400 MHz, $CDCl_3$): δ 7.27-7.23 (m, 1H), 7.16-7.03 (m, 5H), 6.81-6.79 (m, 2H), 6.64 (d, *J* = 7.6 Hz, 1H), 5.09 (d, *J* = 13.6 Hz, 1H), 4.87 (d, *J* = 13.6 Hz, 1H), 3.03-3.02 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 144.1, 133.1, 130.0, 129.3, 127.8, 127.3, 126.4, 123.3, 122.4, 108.5, 78.1, 52.6, 41.4, 26.2. IR (film) υ_{max}: 3456, 2922, 2092, 1713,

1614, 1555, 1495, 1471, 1379, 1256, 1096, 752, 701 cm^{-1}. HRMS calc. for $C_{17}H_{16}N_2O_3$ $(M+H)^+$, 297.1234; found, 137.1241.



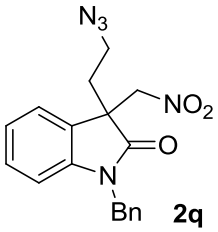
2o

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.06-4.97 (m, 2H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.14 (d, *J* = 11.2 Hz, 1H), 3.29 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 169.8, 144.1, 130.0, 125.0, 123.6, 123.0, 109.0, 76.0, 64.9, 50.8, 26.7, 20.5. IR (film) υ_{max}: 3456, 2924, 2736, 2254, 1713, 1613, 1555, 1469, 1377, 1224, 1155, 1049, 734 cm^{-1}. HRMS calc. for $C_{13}H_{14}N_2O_5$ $(M+H)^+$, 279.0975; found, 279.0977.



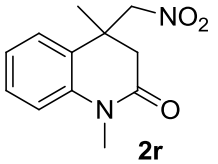
2p

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (m, 2H), 7.76-7.74 (m, 2H), 7.35 (dt, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.15 (d, *J* = 2.0 Hz, 2H), 4.01 (d, *J* = 14.4 Hz, 1H), 3.92 (d, *J* = 14.4 Hz, 1H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 168.0, 144.1, 134.4, 131.5, 130.0, 125.5, 123.8, 122.9, 122.8, 109.2, 76.9, 51.0, 41.3, 26.8. IR (film) υ_{max}: 3452, 2958, 2924, 2091, 1643, 1465, 1377, 1216, 1157, 759, 668 cm^{-1}. HRMS calc. for $C_{19}H_{15}N_3O_5$ $(M+H)^+$, 366.1084; found, 366.1086.



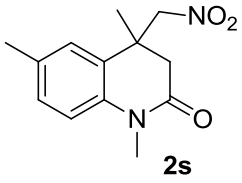
2q

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.20 (m, 7H), 7.07-7.03 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.03-4.83 (m, 4H), 3.15-3.01 (m, 2H), 2.23-2.16 (m, 1H), 2.07-2.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 143.3, 135.2, 129.7, 128.8, 127.8, 127.4, 125.9, 123.1, 122.9, 110.0, 78.6, 49.7, 46.2, 44.4, 34.2. IR (film) υ_{max}: 3436, 2924, 2102, 1715, 1613, 1556, 1490, 1468, 1379, 1179, 754, 699, 651, 554 cm^{-1}. HRMS calc. for $C_{18}H_{17}N_5O_3$ $(M+H)^+$, 352.1404; found, 352.1410.



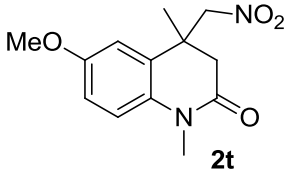
2r

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 1H), 7.29 (dd, *J* = 1.2 Hz, 7.2 Hz, 1H), 7.15-7.07 (m, 2H), 4.52-4.43 (m, 2H), 3.42 (s, 3H), 2.88 (d, *J* = 16.4 Hz, 1H), 2.62 (d, *J* = 16.4 Hz, 1H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 139.4, 129.4, 127.5, 123.7, 115.5, 81.7, 41.8, 37.2, 29.5, 23.1. IR (film) υ_{max}: 3458, 2974, 2100, 1675, 1601, 1550, 1456, 1420, 1373, 1154, 935, 858, 759, 499 cm^{-1}. HRMS calc. for $C_{12}H_{14}N_2O_3$ $(M+H)^+$, 235.1077; found, 235.1077.



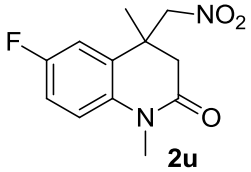
2s

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.4 Hz, 1H), 7.07 (s, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.49-4.41 (m, 2H), 3.39 (s, 3H), 2.86 (d, *J* = 16.4 Hz, 1H), 2.62 (d, *J* = 16.4 Hz, 1H), 2.34 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 137.1, 133.3, 129.6, 127.4, 125.8, 115.4, 81.8, 41.9, 37.2, 29.5, 23.2, 20.8. IR (film) υ_{max}: 3446, 2966, 2924, 2085, 1648, 1551, 1463, 1416, 1369, 1143, 814, 732 cm^{-1}. HRMS calc. for $C_{13}H_{16}N_2O_3$ $(M+H)^+$, 249.1234; found, 249.1235.



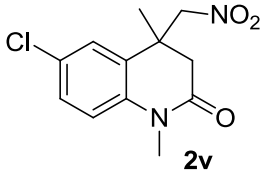
2t

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (d, *J* = 8.4 Hz, 1H), 6.89-6.84 (m, 2H), 4.50-4.42 (m, 2H), 3.81 (s, 3H), 3.38 (s, 3H), 2.84 (d, *J* = 16.4 Hz, 1H), 2.61 (d, *J* = 16.0 Hz, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 155.8, 133.0, 129.1, 116.4, 113.0, 112.0, 81.7, 55.6, 41.8, 37.3, 29.6, 23.1. IR (film) υ_{max}: 3445, 2962, 2074, 1642, 1553, 1509, 1462, 1374, 1245, 811, 753, 625, 604, 565 cm^{-1}. HRMS calc. for $C_{13}H_{16}N_2O_4$ $(M+H)^+$, 265.1183; found, 265.1185.



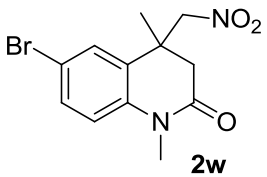
2u

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-6.99 (m, 3H), 4.49-4.42 (m, 2H), 3.39 (s, 3H), 2.84 (d, *J* = 16.4 Hz, 1H), 2.63 (d, *J* = 16.0 Hz, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 158.9 (d, J_{C-F} = 243.0 Hz), 135.8, 129.6 (d, J_{C-F} = 7.0 Hz), 116.8 (d, J_{C-F} = 8.0 Hz), 115.6 (d, J_{C-F} = 22.0 Hz), 112.8 (d, J_{C-F} = 25.0 Hz), 81.4, 41.7, 73.2, 29.7, 23.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -118.59. IR (film) υ_{max}: 3454, 2962, 2926, 2081, 1733, 1640, 1413, 1351, 1271, 1244, 1110, 1078, 890, 730, 665 cm^{-1}. HRMS calc. for $C_{12}H_{13}FN_2O_3$ $(M+H)^+$, 253.0983; found, 253.0987.



2v

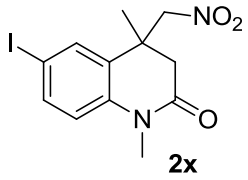
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 4.50-4.42 (m, 2H), 3.39 (s, 3H), 2.87 (d, *J* = 16.4 Hz, 1H), 2.64 (d, *J* = 16.4 Hz, 1H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 138.1, 129.3, 129.1, 125.6, 116.8, 81.4, 41.6, 37.2, 29.6, 23.1. IR (film) υ_{max}: 3451, 2959, 2922, 2073, 1676, 1550, 1494, 1470, 1414, 1358, 1274, 1140, 876, 719 cm^{-1}. HRMS calc. for $C_{12}H_{13}ClN_2O_3$ $(M+H)^+$, 269.0687; found, 269.0689.



2w

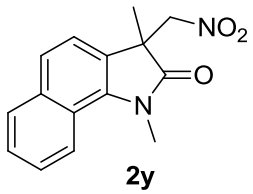
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 8.8 Hz, 0.8 Hz, 1H), 7.38 (d, *J* = 1.6 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H),

4.50-4.42 (m, 2H), 3.38 (s, 3H), 2.87 (d, *J* = 16.4 Hz, 1H), 2.63 (d, *J* = 16.4 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 138.7, 132.1, 129.7, 128.4, 117.1, 116.5, 81.5, 41.6, 37.2, 29.6, 23.1. IR (film) υ_{max}: 3441, 2080, 1641, 1467, 1409, 1353, 1241, 1140, 717, 647 cm^{-1}. HRMS calc. for $C_{12}H_{13}BrN_2O_3$ $(M+H)^+$, 313.0182; found, 313.0184.



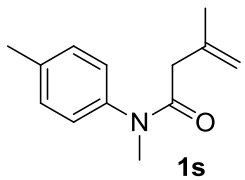
2x

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 4.49-4.41 (m, 2H), 3.37 (s, 3H), 2.86 (d, *J* = 16.4 Hz, 1H), 2.62 (d, *J* = 16.4 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 139.4, 138.1, 134.1, 129.9, 117.5, 86.8, 81.5, 41.6, 37.1, 29.5, 23.1. IR (film) υ_{max}: 3446, 2967, 2079, 1733, 1641, 1412, 1271, 1244, 1111, 1078, 890, 738 cm^{-1}. HRMS calc. for $C_{12}H_{13}IN_2O_3$ $(M+H)^+$, 361.0044; found, 361.0046.



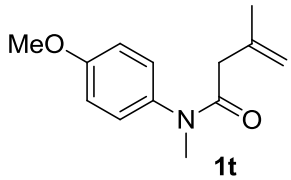
2y

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.54-7.48 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 5.69 (d, *J* = 16.0 Hz, 1H), 4.98 (d, *J* = 16.0 Hz, 1H), 3.61 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 136.2, 134.0, 133.7, 127.2, 126.8, 123.0, 121.2, 119.2, 109.3, 81.5, 46.7, 30.1, 29.1. IR (film) υ_{max}: 3444, 3030, 2924, 1651, 1589, 1548, 1453, 1424, 1380, 1322, 1281, 822, 771 cm^{-1}. HRMS calc. for $C_{15}H_{14}N_2O_3$ $(M+H)^+$, 271.1077; found, 271.1089.



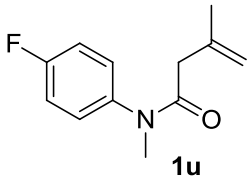
1s

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.82 (s, 1H), 4.63 (s, 1H), 3.26 (s, 3H), 2.84 (s, 2H), 2.38 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 141.6, 140.0, 137.6, 130.2, 127.0, 113.5, 42.8, 37.4, 22.6, 21.0. IR (film) υ_{max}: 3428, 2923, 1660, 1515, 1433, 1375, 1258, 1122, 891, 826, 723, 558 cm^{-1}. ESI-MS: *m/z* = 226 $(M+Na)^+$.



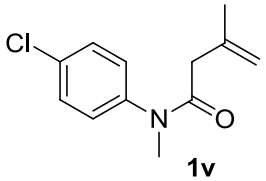
1t

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.81 (s, 1H), 4.63 (s, 1H), 3.83 (s, 3H), 3.25 (s, 3H), 2.84 (s, 2H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 158.8, 140.0, 136.9, 128.2, 114.6, 113.4, 55.3, 42.7, 37.4, 22.6. IR (film) υ_{max}: 3428, 2922, 1666, 1512, 1437, 1377, 1298, 1248, 1189, 1123, 1032, 893, 839, 733 cm^{-1}. ESI-MS: *m/z* = 220 $(M+H)^+$.



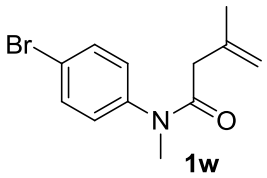
1u

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.19 (m, 2H), 7.12-7.88 (m, 2H), 4.82 (s, 1H), 4.62 (s, 1H), 3.26 (s, 3H), 2.84 (s, 2H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 161.6 (d, $J_{C\text{-}F}$ = 247.0 Hz), 140.0 (d, $J_{C\text{-}F}$ = 3.0 Hz), 139.6, 128.9 (d, $J_{C\text{-}F}$ = 9.0 Hz), 116.4 (d, $J_{C\text{-}F}$ = 23.0 Hz), 113.5, 42.8, 37.3, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.47. IR (film) υ_{max}: 3418, 3077, 1661, 1510, 1433, 1376, 1311, 1223, 1123, 1016, 895, 845, 590 cm^{-1}. ESI-MS: *m/z* = 208 $(M+H)^+$.



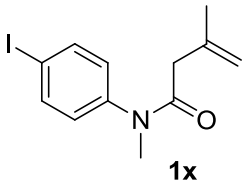
1v

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.83 (s, 1H), 4.63 (s, 1H), 3.26 (s, 3H), 2.84 (s, 2H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 142.6, 139.6, 133.5, 129.8, 128.6, 113.7, 42.9, 37.3, 22.6. IR (film) υ_{max}: 3455, 3079, 2922, 1901, 1661, 1491, 1434, 1372, 1307, 1257, 1122, 1092, 1015, 894, 778, 726, 555 cm^{-1}. ESI-MS: *m/z* = 224 $(M+H)^+$.



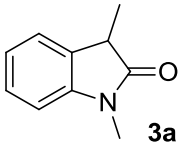
1w

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.83 (s, 1H), 4.63 (s, 1H), 3.26 (s, 3H), 2.85 (s, 2H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 143.0, 139.6, 132.7, 128.9, 121.4, 113.7, 42.8, 37.2, 22.5. IR (film) υ_{max}: 3457, 2926, 2088, 1656, 1486, 1435, 1372, 1308, 1258, 1121, 1072, 1012, 894, 836, 721, 553 cm^{-1}. ESI-MS: *m/z* = 268 $(M+H)^+$.



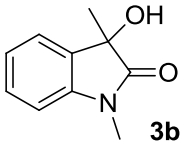
1x

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.83 (s, 1H), 4.63 (s, 1H), 3.26 (s, 3H), 2.85 (s, 2H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 143.8, 139.7, 138.8, 129.2, 113.8, 92.8, 42.9, 37.3, 22.6. IR (film) υ_{max}: 3433, 2922, 1658, 1483, 1373, 1256, 1121, 1008, 893, 832, 719, 553 cm^{-1}. ESI-MS: *m/z* = 316 $(M+H)^+$.



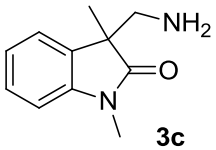
3a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.21 (m, 2H), 7.06-7.02 (m, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.41 (q, *J* = 7.6 Hz, 1H), 3.19 (s, 3H), 1.47 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 143.8, 130.5, 127.7, 123.3, 122.2, 107.8, 40.3, 26.0, 15.2. ESI-MS: *m/z* = 162 $(M+H)^+$.



3b

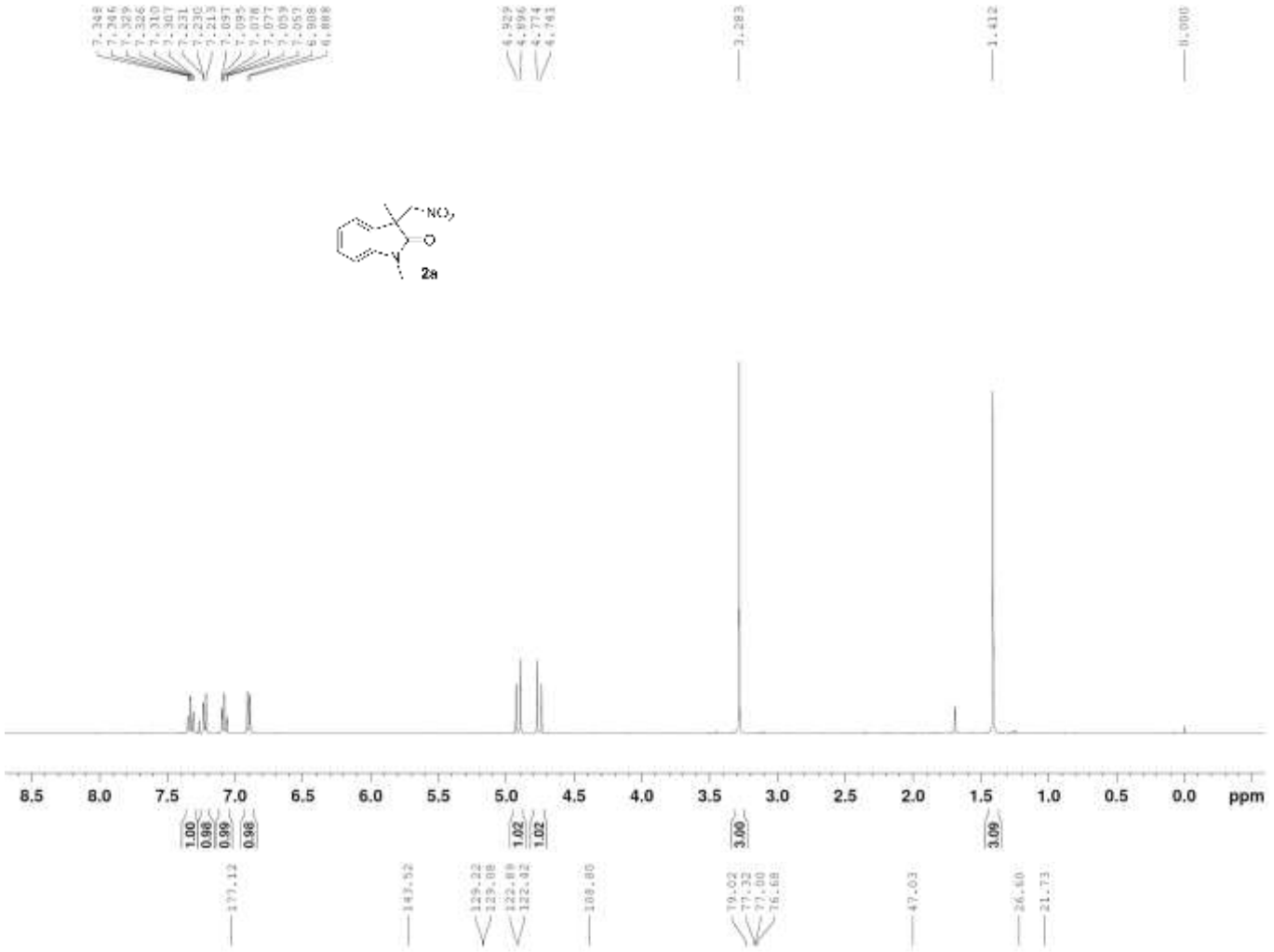
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.33-7.29 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.87 (s, 1H), 3.18 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 142.7, 131.6, 129.4, 123.4, 123.2, 108.4, 73.6, 26.2, 24.7. ESI-MS: *m/z* = 178 $(M+H)^+$.

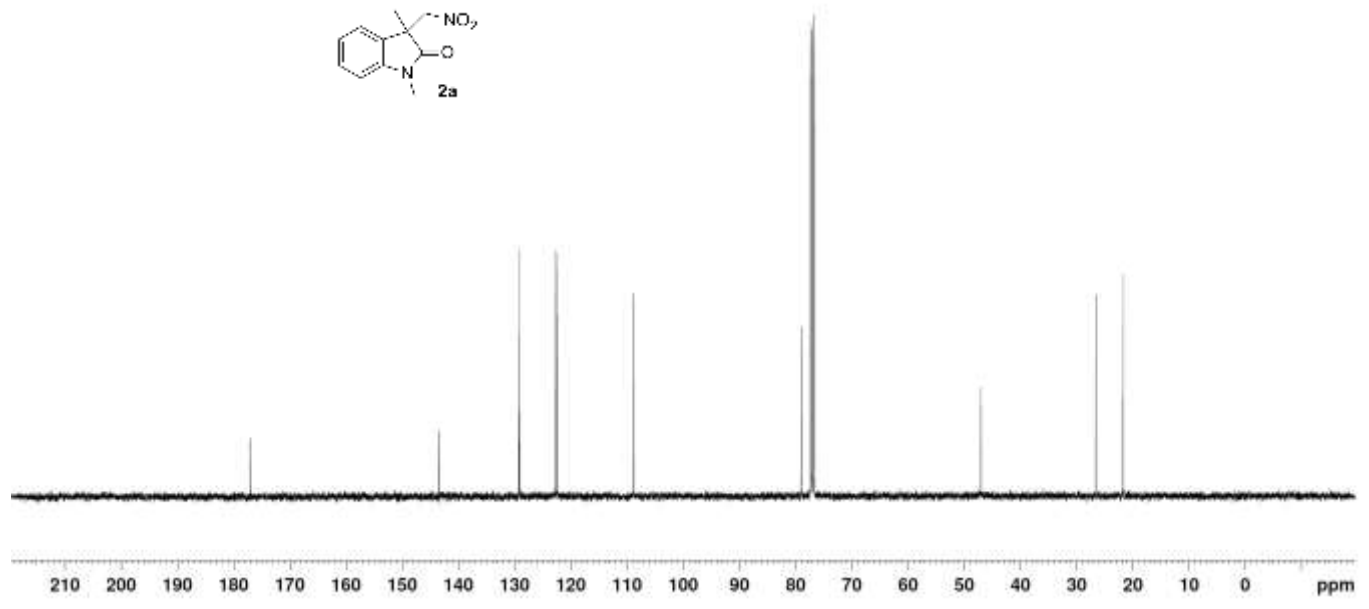


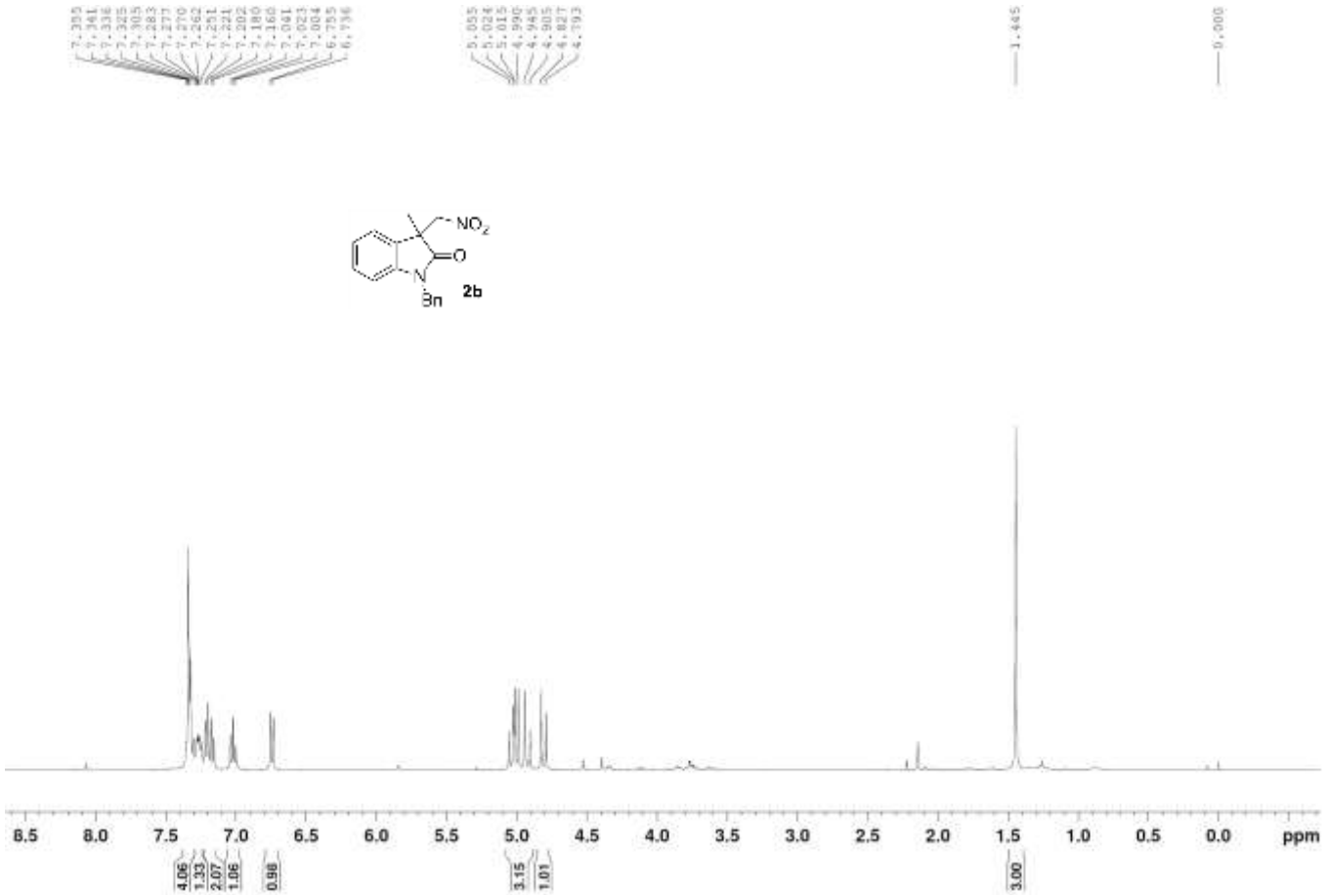
3c

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 3.23 (s, 3H), 3.10 (d, *J* = 12.8 Hz, 1H), 2.96 (d, *J* = 13.2 Hz, 1H), 1.37 (s, 2H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 143.4, 132.1, 127.7, 122.2, 122.1, 107.1, 50.3, 49.0, 25.7, 19.8. ESI-MS: *m/z* = 191 $(M+H)^+$.

9. Charts of new compounds



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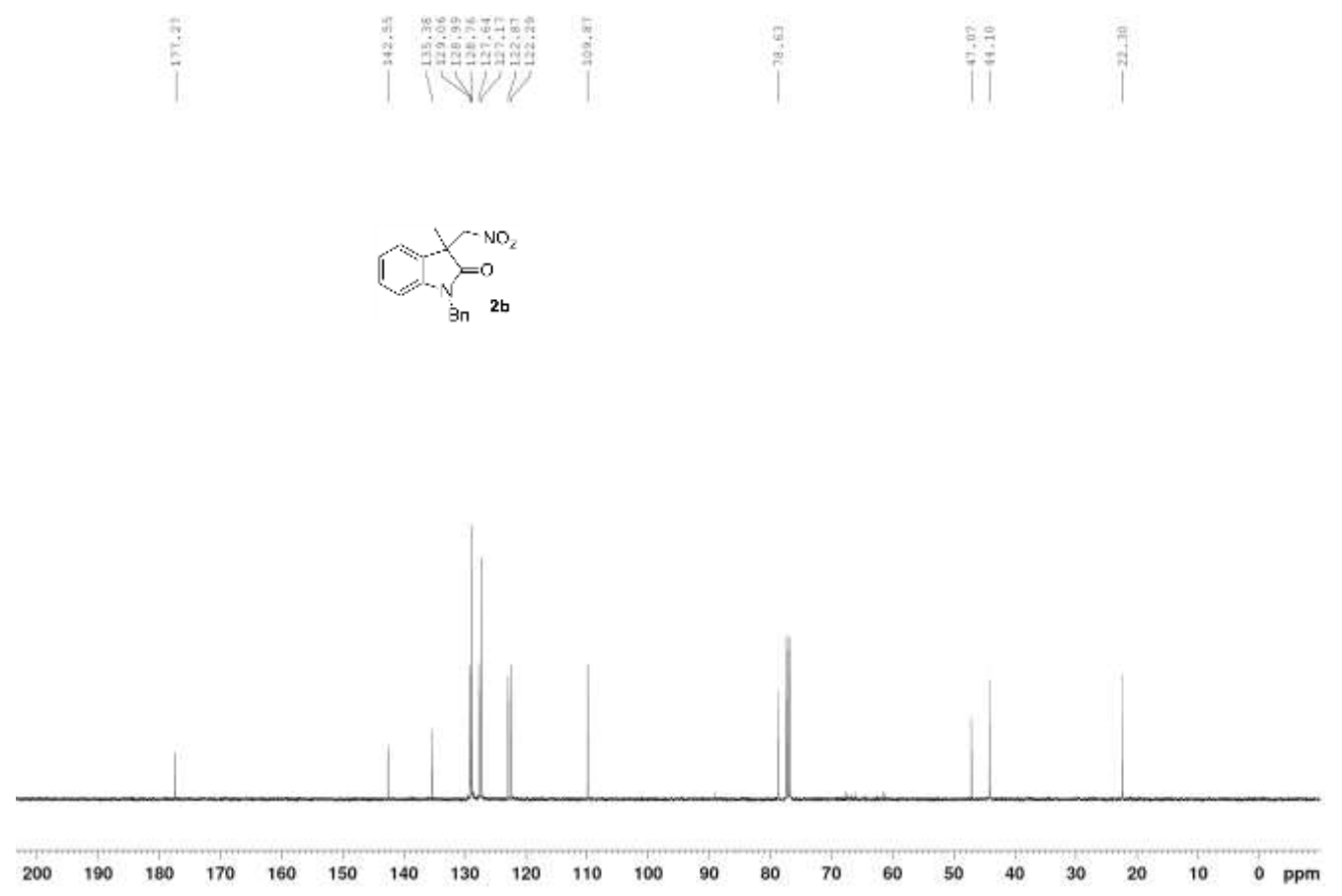
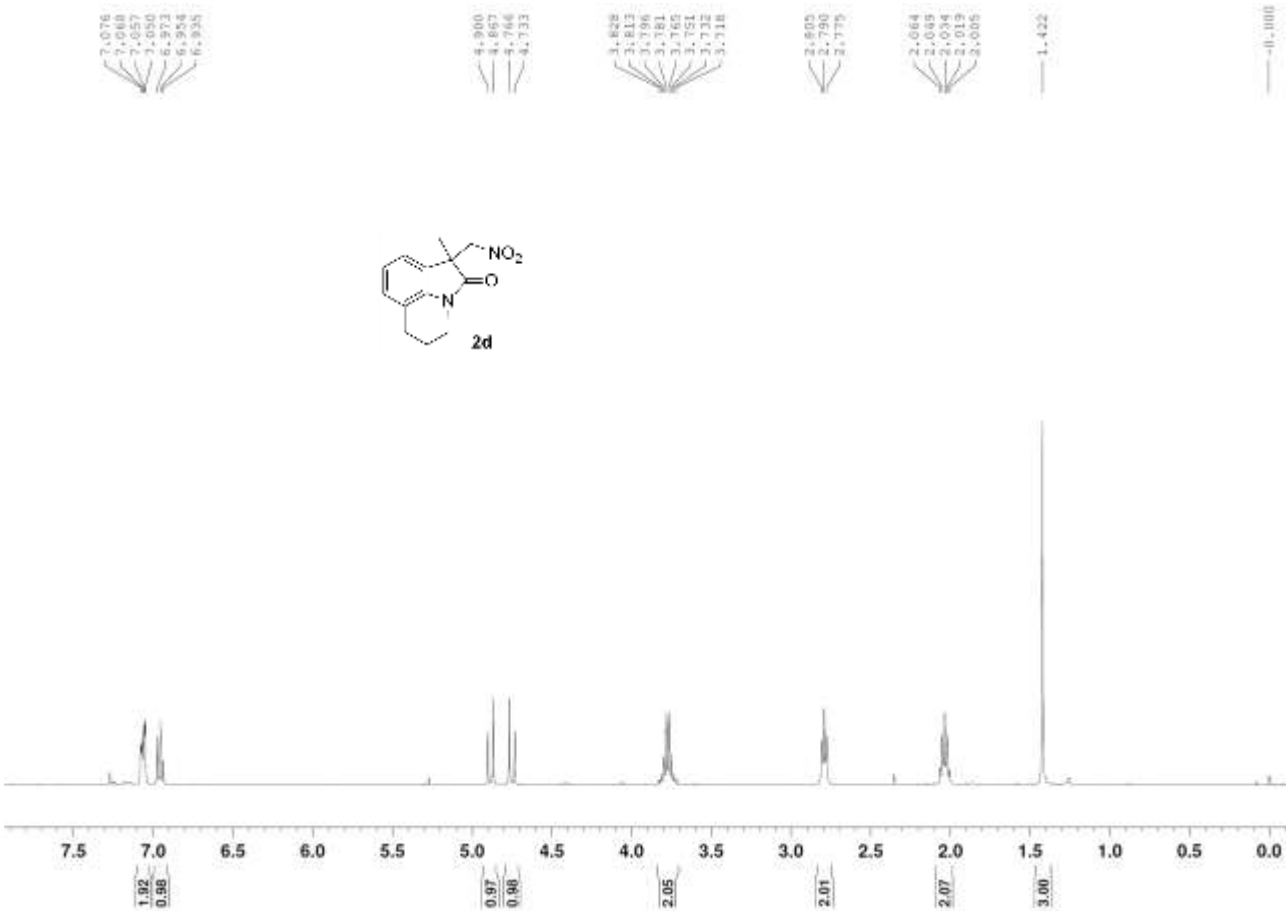
O
N
Bn
2b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


NO2
O
N
Bn
2b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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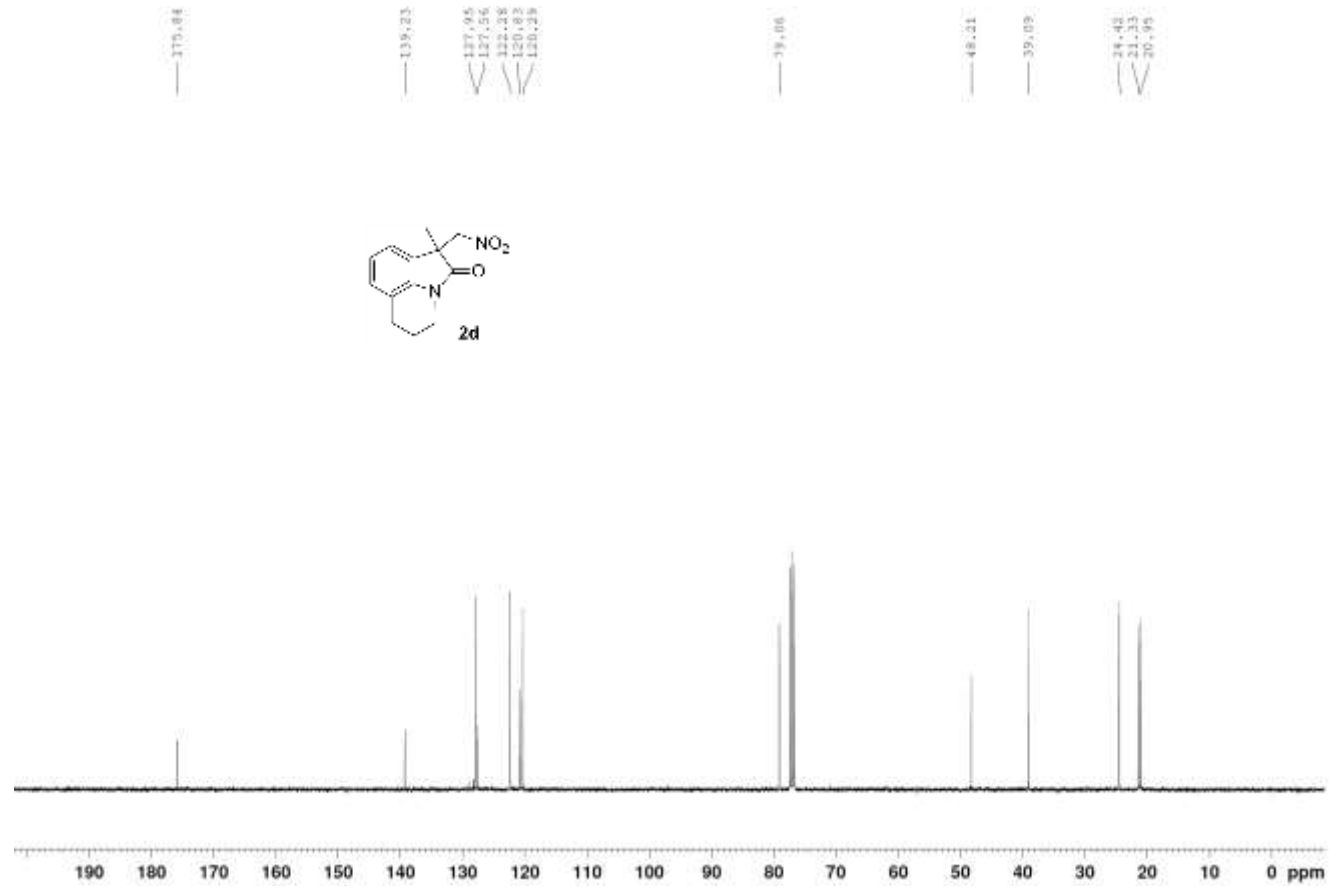
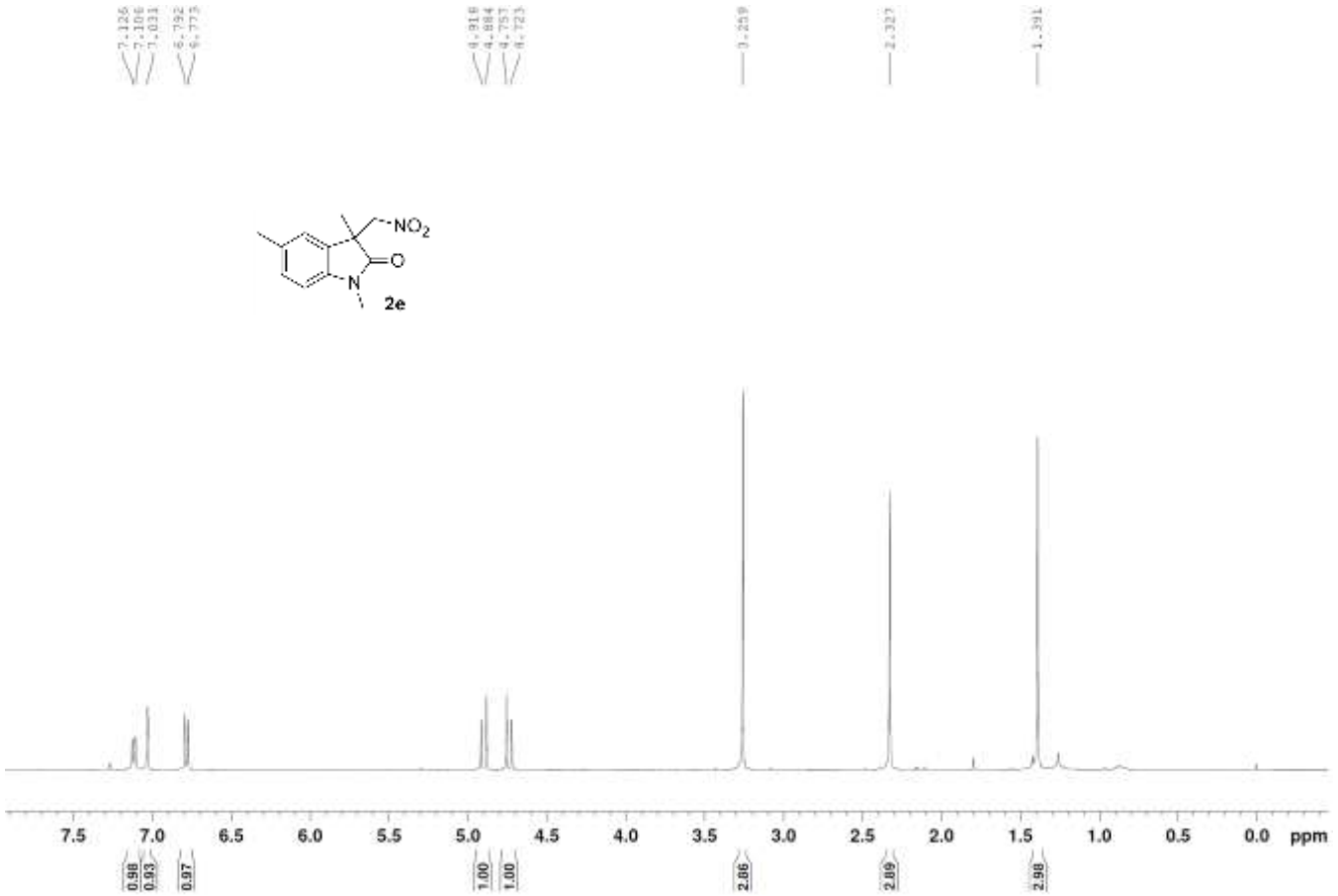
7.068
7.057
7.050
6.973
6.954
6.935
4.900
4.867
4.766
4.733
3.828
3.813
3.796
3.781
3.765
3.751
3.732
3.718
2.805
2.790
2.775
2.064
2.049
2.034
2.019
2.005
1.422
0.000
NO2
O
N
2d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
1.92
0.98
0.97
0.98
2.05
2.01
2.07
3.00


175.84
139.23
127.95
127.56
122.28
120.83
120.29
79.06
48.21
39.09
24.42
21.33
20.95
NO2
O
N
2d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.106
7.031
6.792
6.775
4.916
4.884
4.751
4.723
3.259
2.327
1.391
NO2
O
N
2e
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
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0.0
ppm
0.98
0.93
0.97
1.00
1.00
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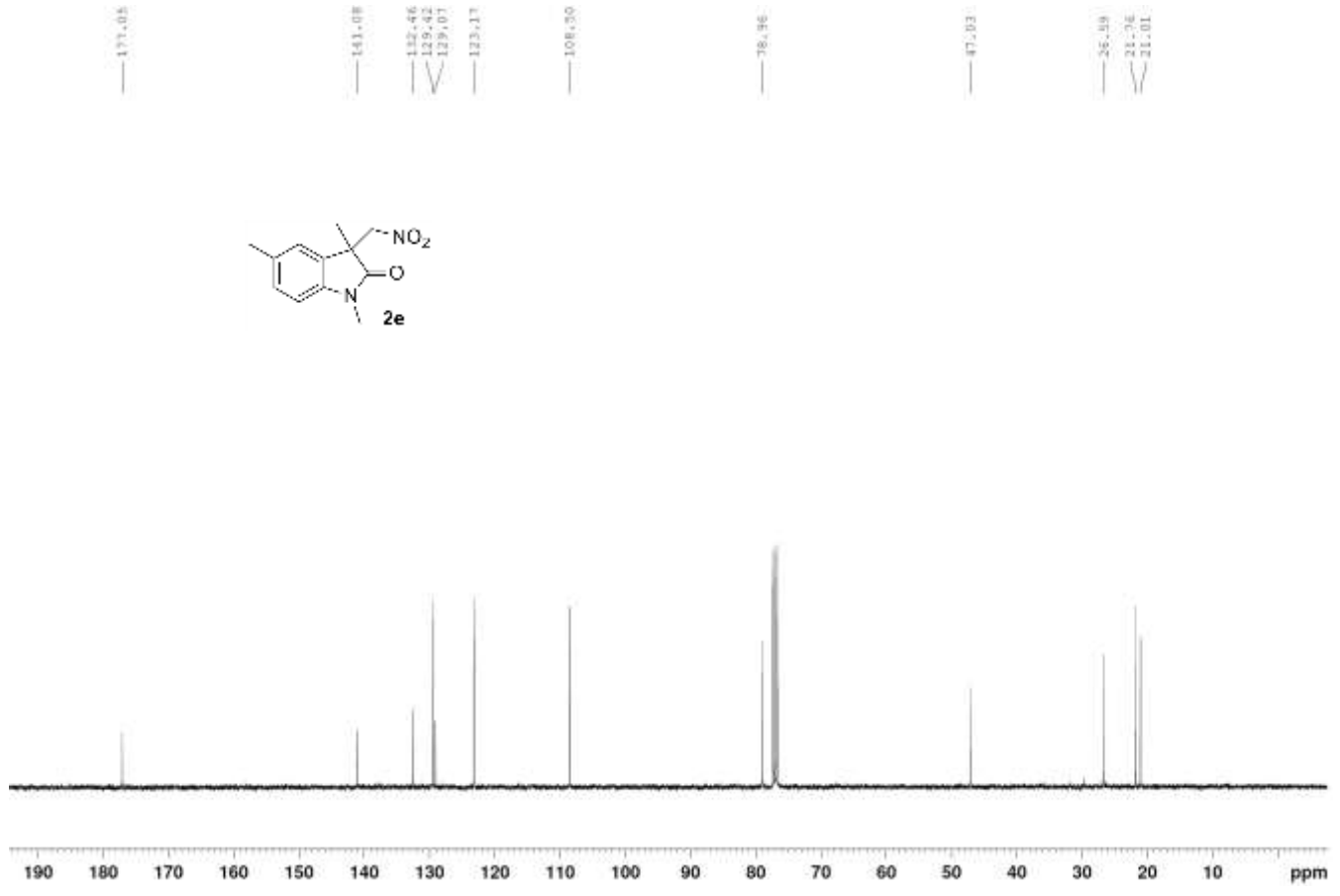
2.89
2.98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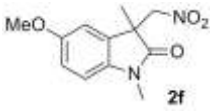
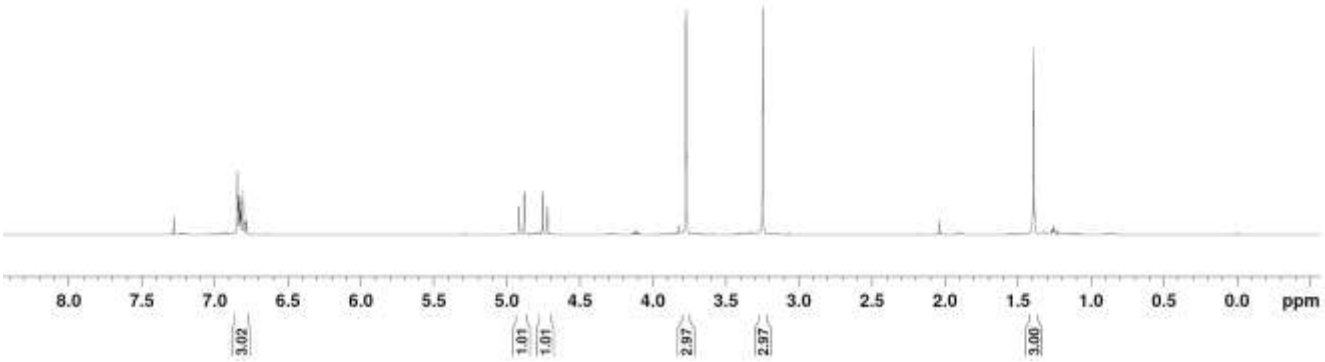
141.08
132.46
129.42
129.07
123.17
108.30
78.98
47.03
26.59
21.26
21.01
NO2
O
N
2e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


6.846
6.841
6.829
6.823
6.807
6.801
6.790
6.784
4.917
4.883
4.757
4.723
3.773
3.248
1.393
0.000


MeO
NO2
O
N

2f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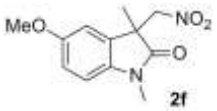
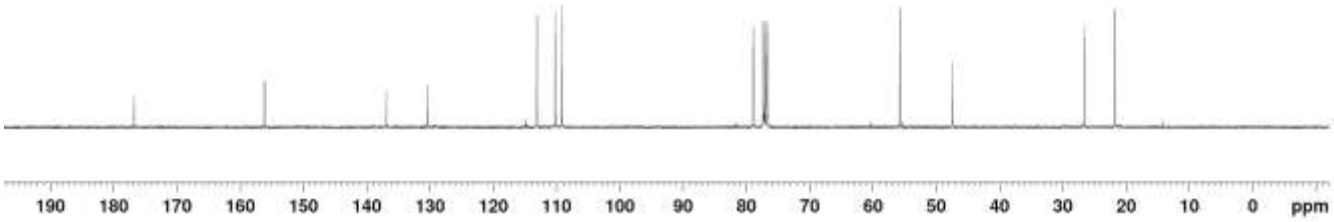
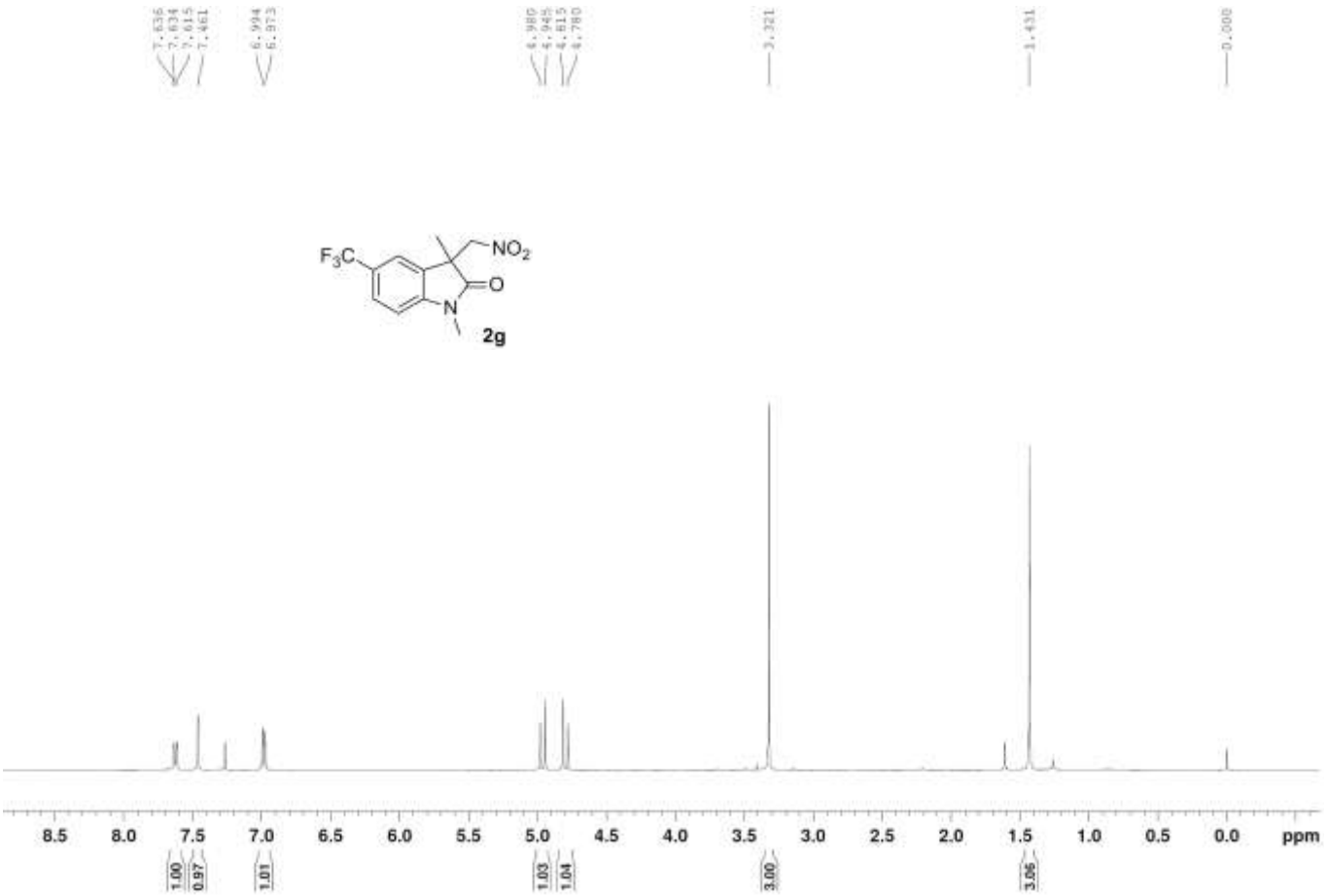
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.02
1.01
1.01
2.97
2.97
3.00


176.33
156.14
136.87
130.41
113.08
110.21
109.08
78.89
55.74
47.35
26.62
21.72


MeO
NO2
O
N

2f


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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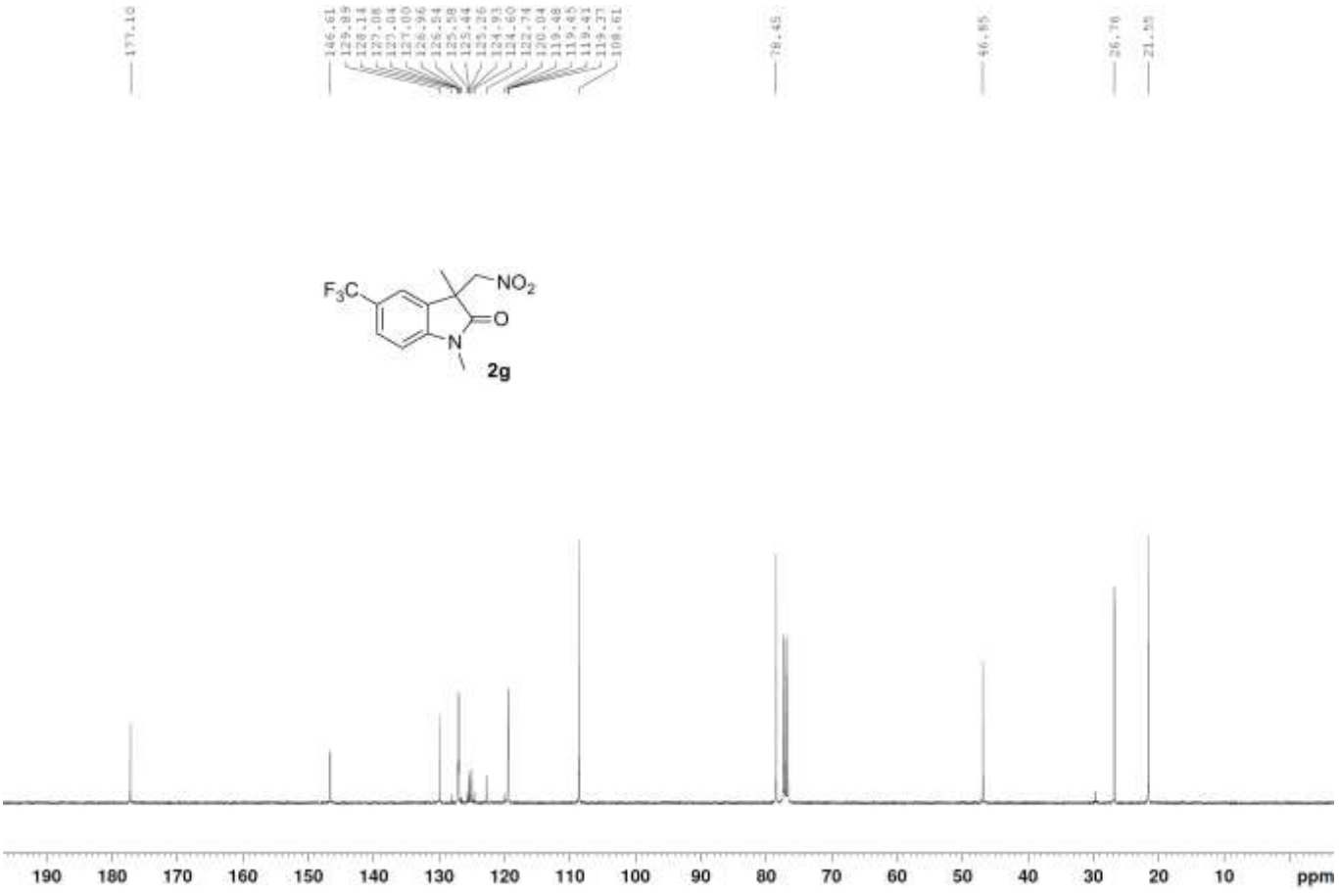
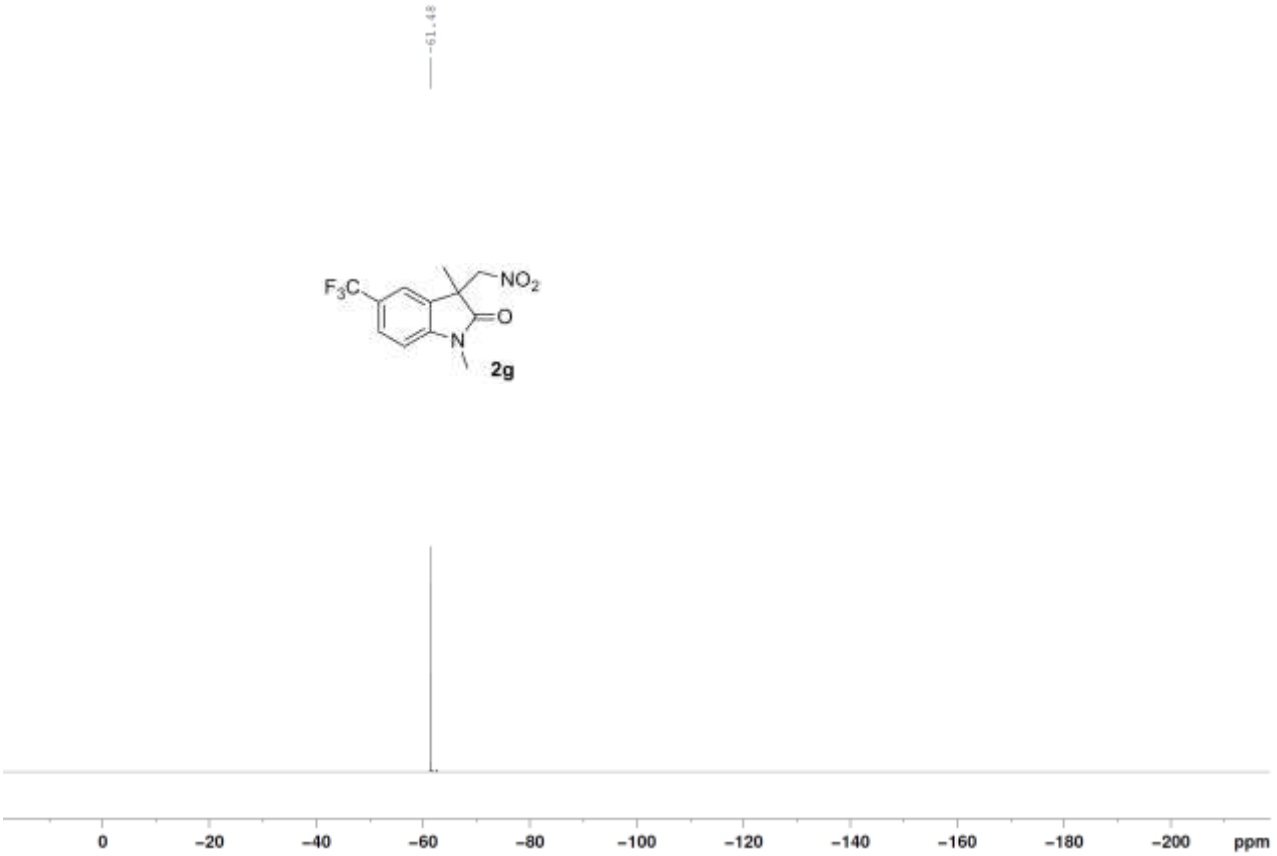
7.634
7.615
7.461
6.994
6.973
4.980
4.945
4.815
4.780
3.321
1.431
0.000
F3C
NO2
O
N
2g
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
0.97
1.01
1.03
1.04
3.00
3.06


177.10
146.61
129.89
128.14
127.08
127.04
127.00
126.96
126.54
125.58
125.44
125.26
124.93
124.60
122.74
120.04
119.48
119.45
119.41
119.37
108.61
78.45
46.85
26.76
21.55
F3C
NO2
O
N
2g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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F3C
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O
N
2g
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-60
-80
-100
-120
-140
-160
-180
-200
ppm


7.066
7.059
7.043
7.037
7.021
7.015
7.007
7.001
6.988
6.982
6.847
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6.826
6.816
4.963
4.909
4.757
4.723
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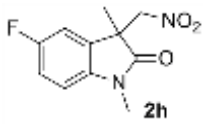
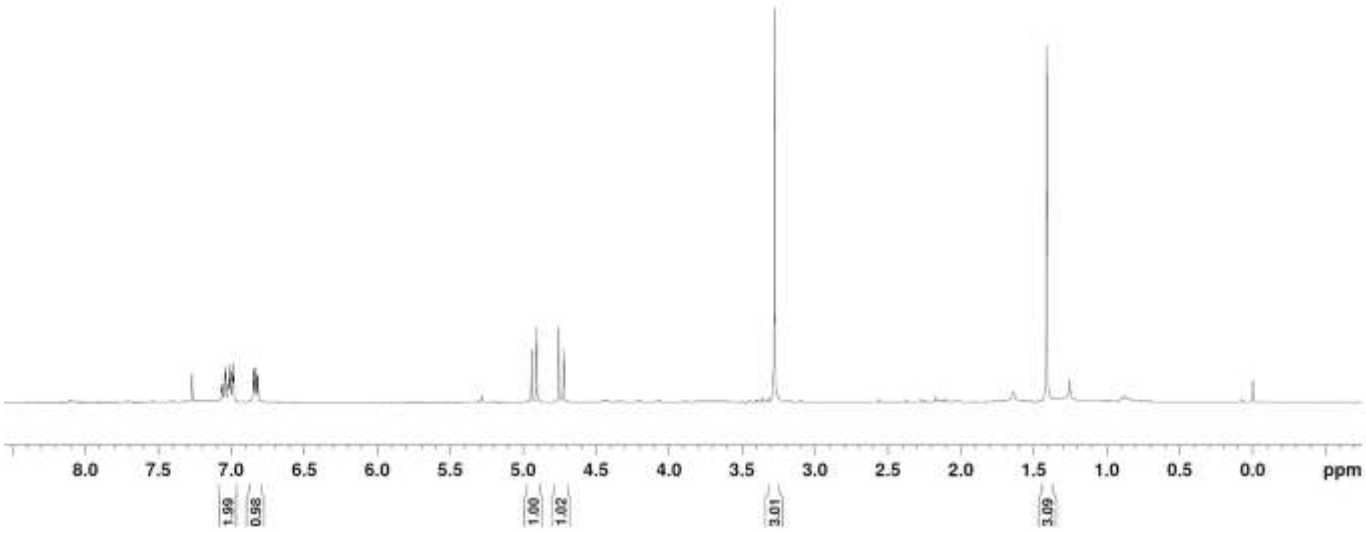
1.413
0.000


F
NO2
O
N
2h


8.0
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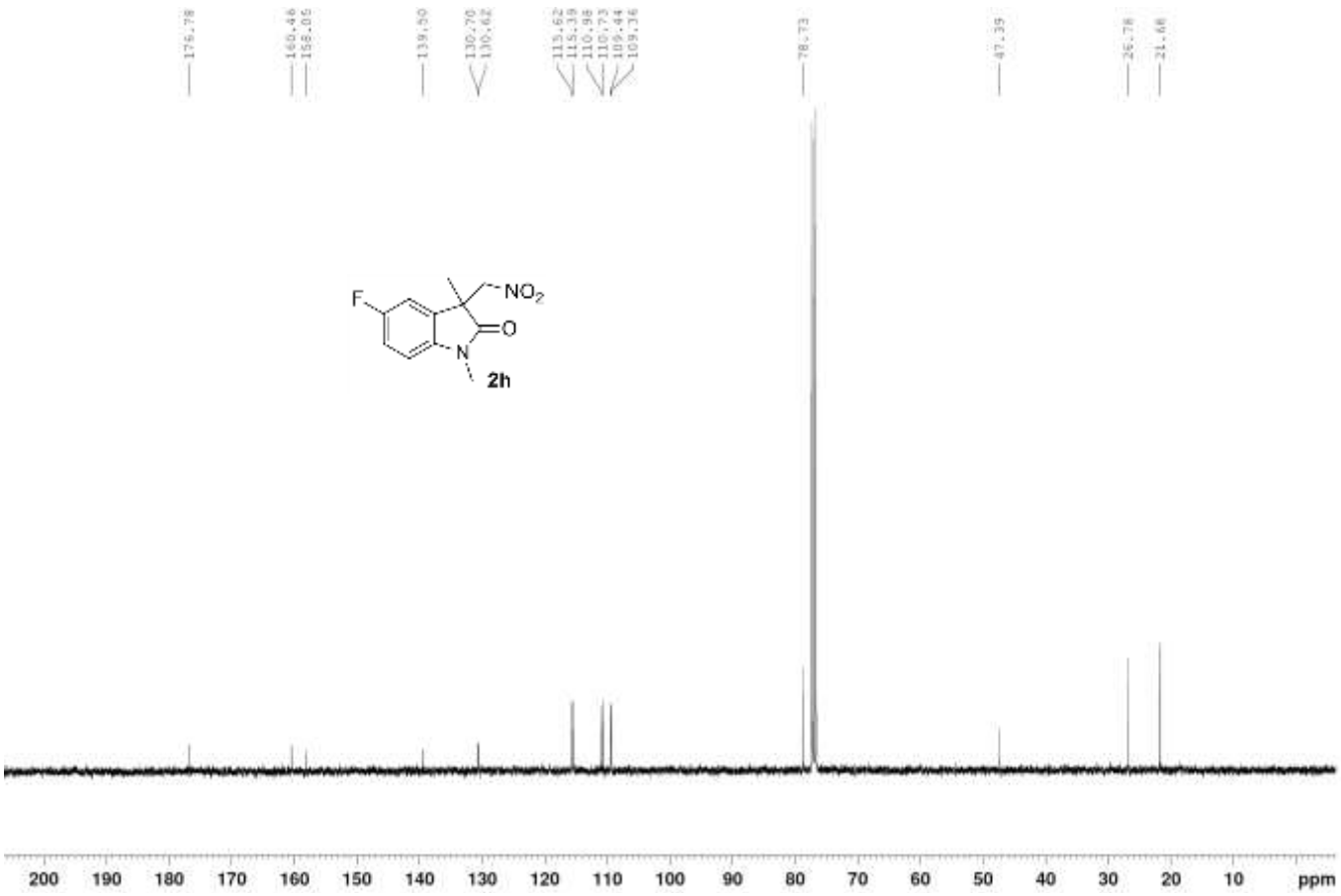
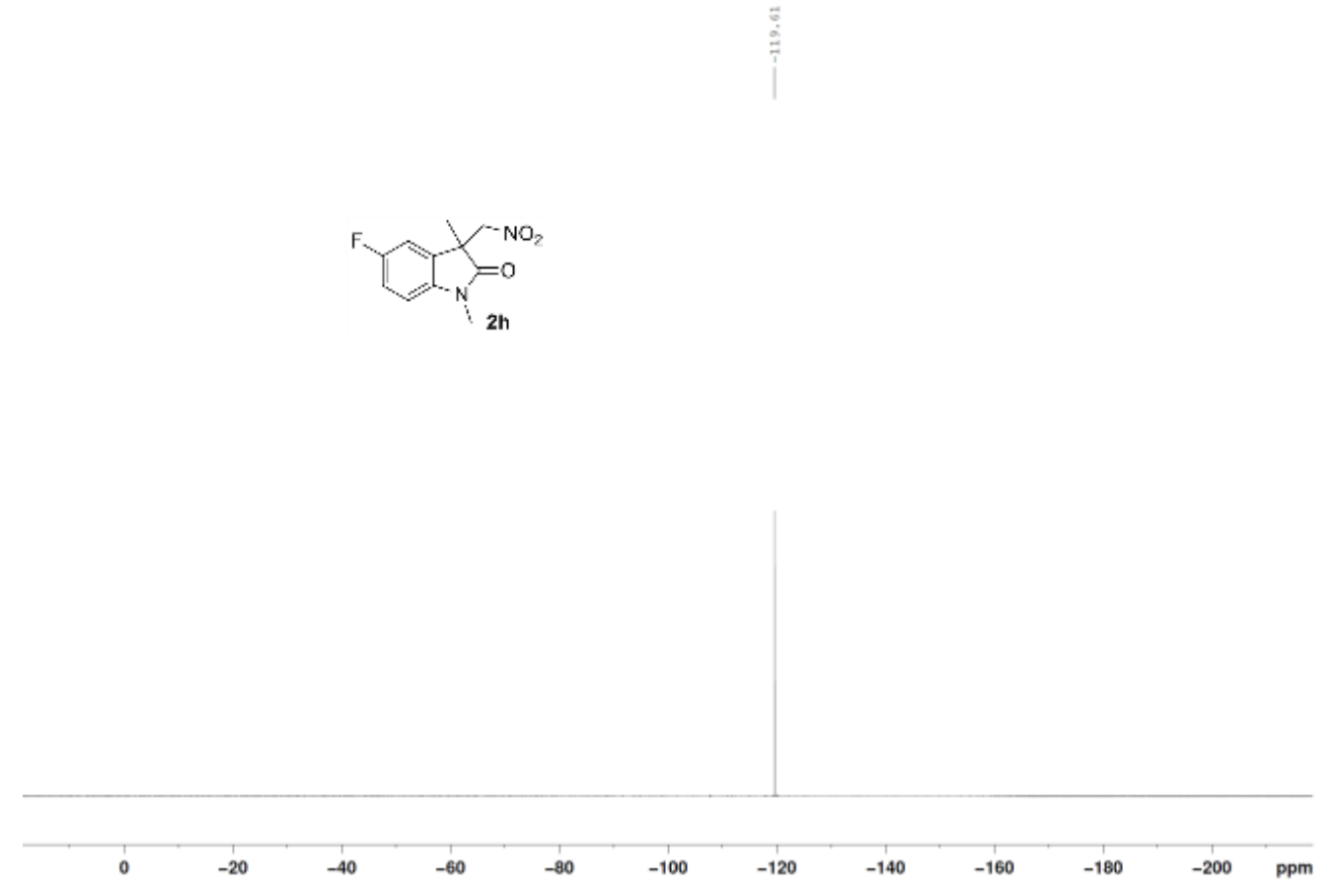
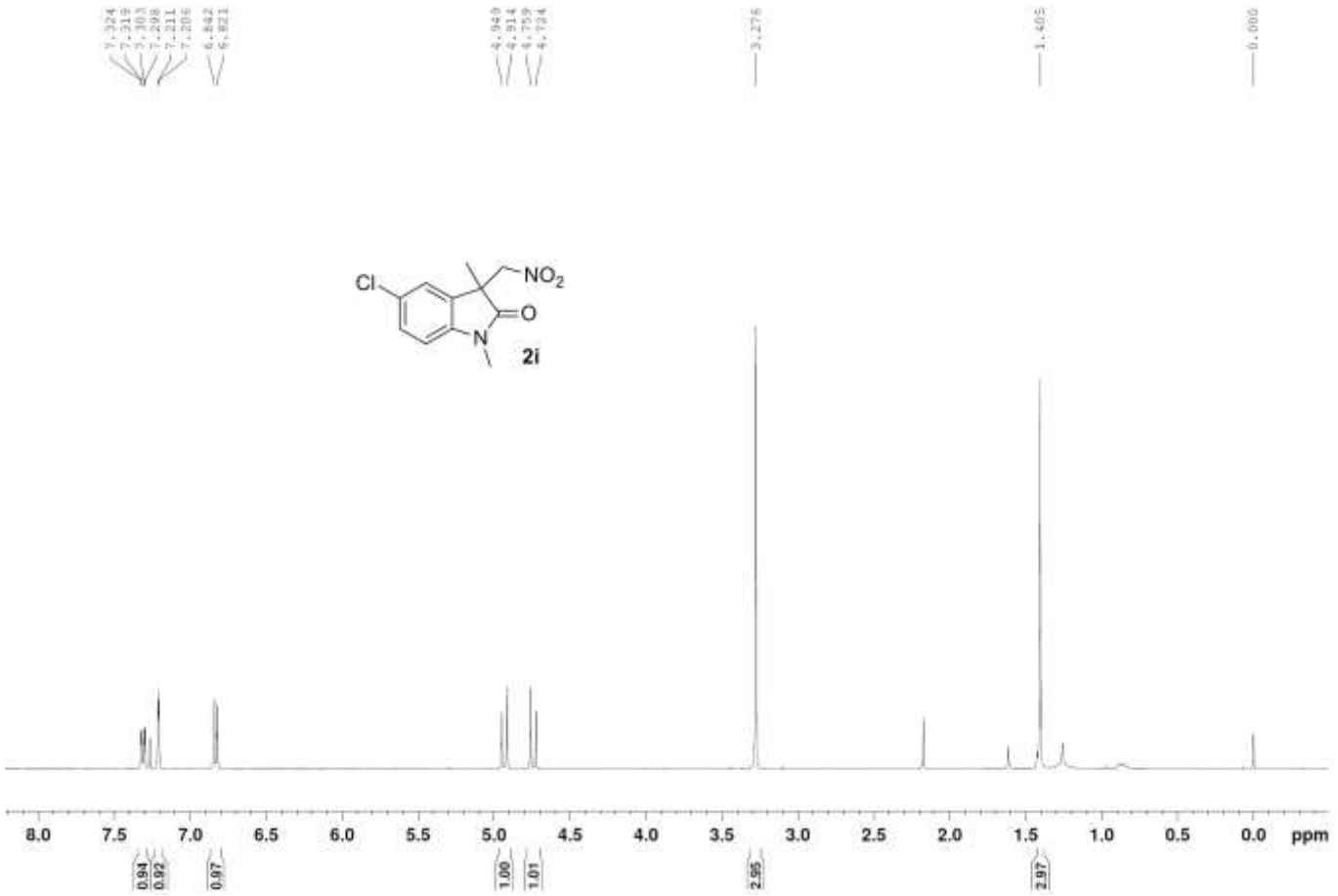
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.99
0.98
1.00
1.02
3.01
3.09


176.78
160.46
158.05
139.50
130.70
130.62
115.62
115.39
110.98
110.73
109.44
109.36
78.73
47.39
26.78
21.68
F
NO2
O
N
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-119.61
F
NO2
O
N
2h
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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7.298
7.211
7.206
6.842
6.821
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4.914
4.759
4.724
3.276
1.405
0.000
Cl
NO2
O
N
2i
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
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0.5
0.0
ppm
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0.92
0.97
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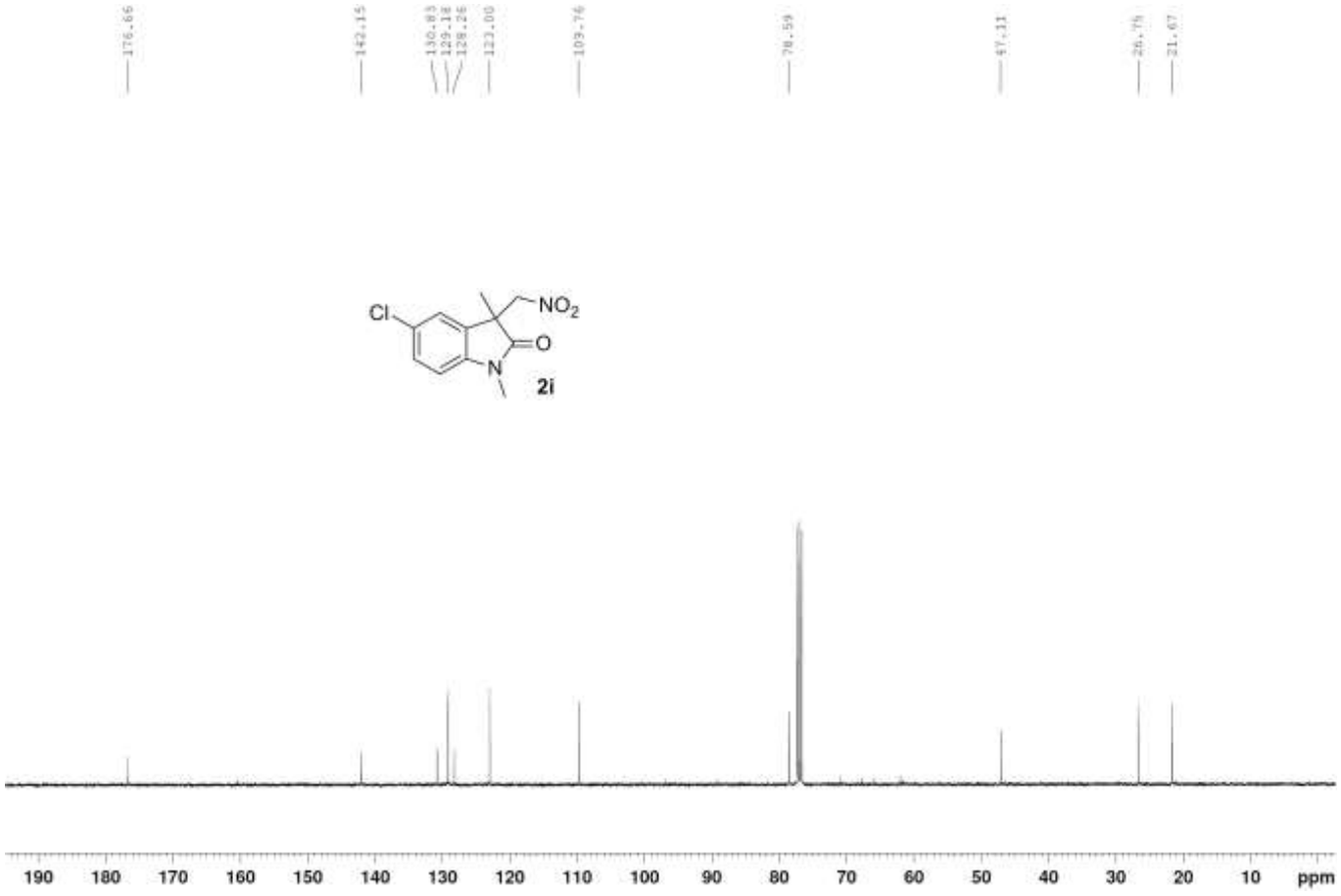
1.01
2.95
2.97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129.18
128.26
123.00
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78.59
47.11
26.75
21.67
Cl
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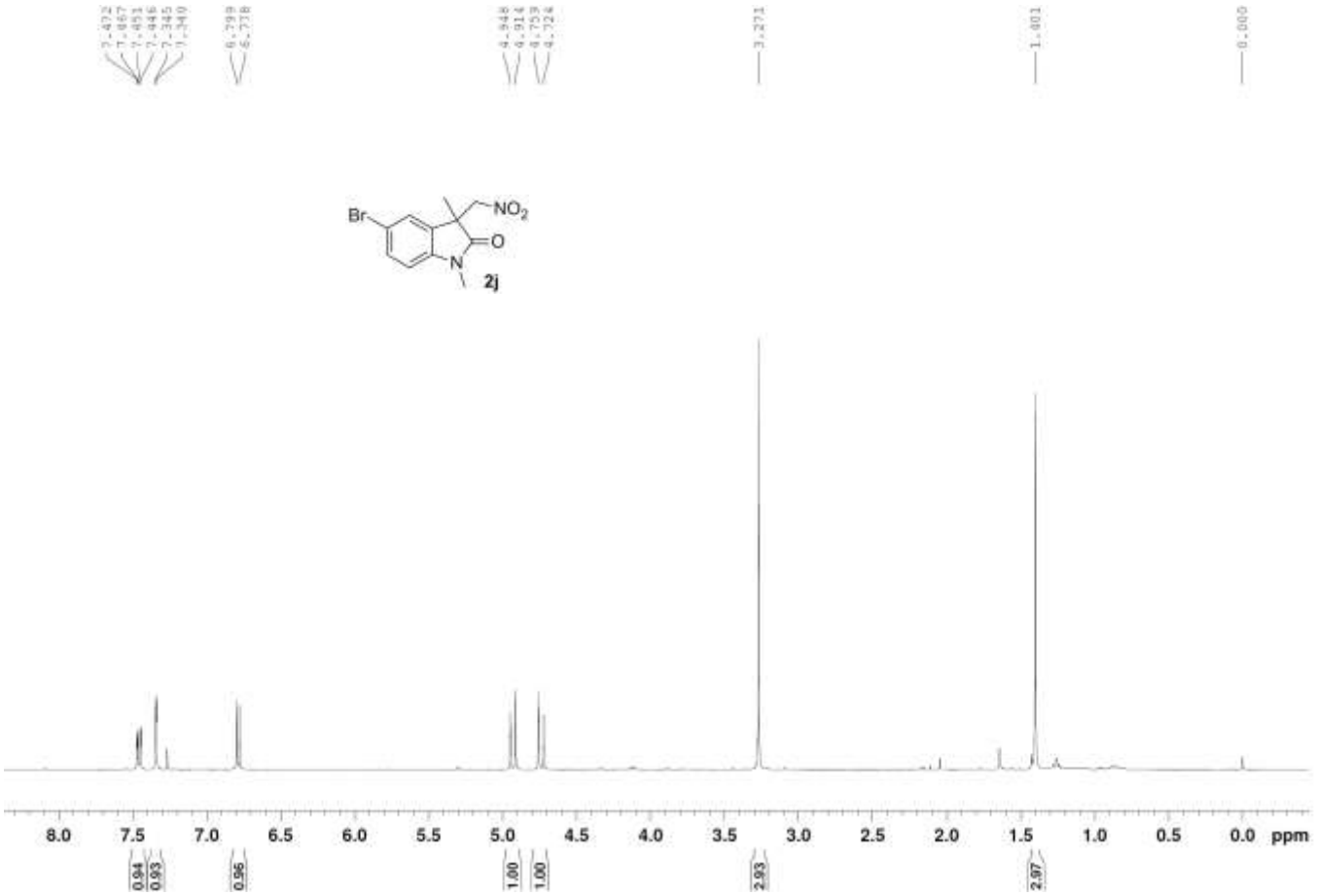
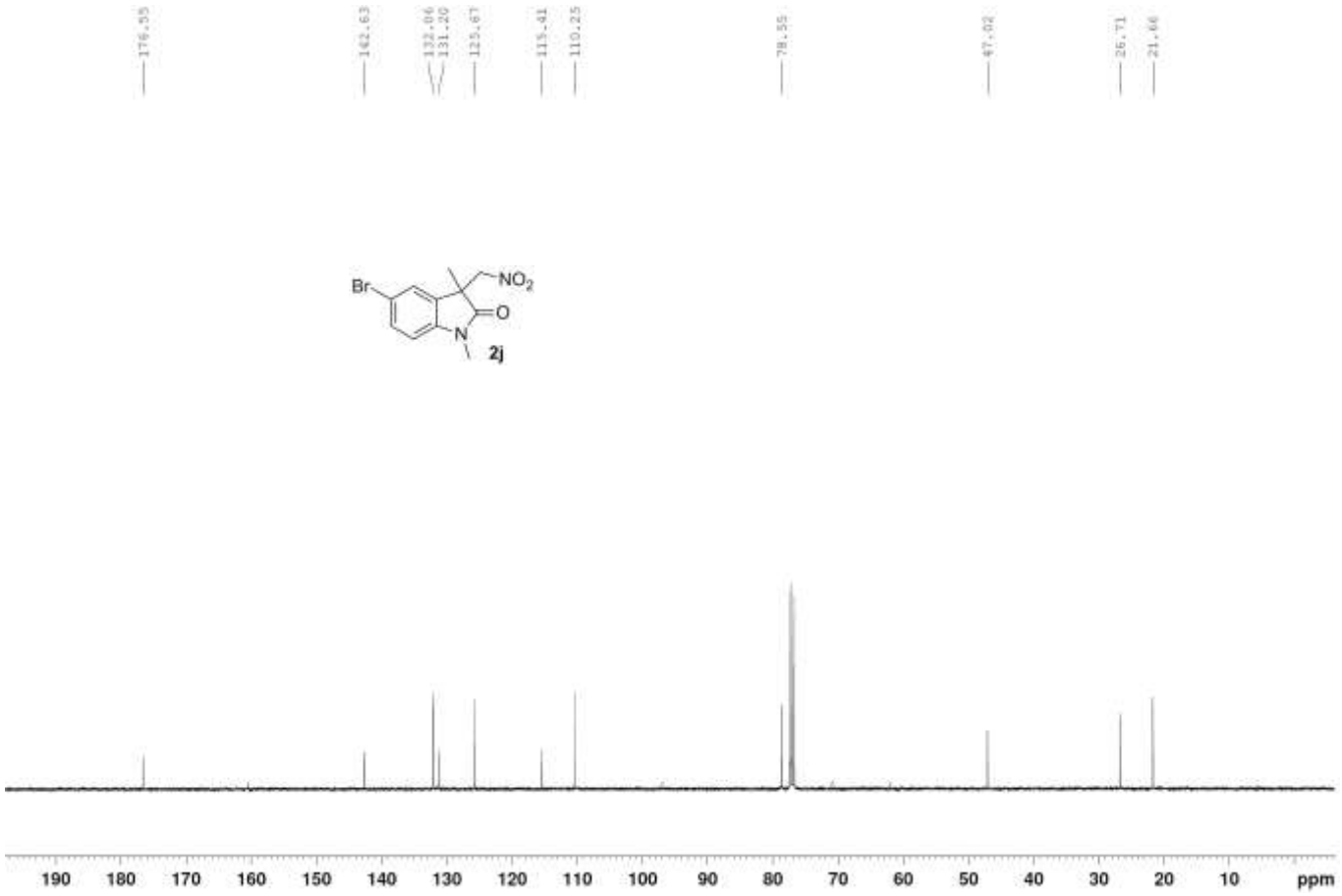
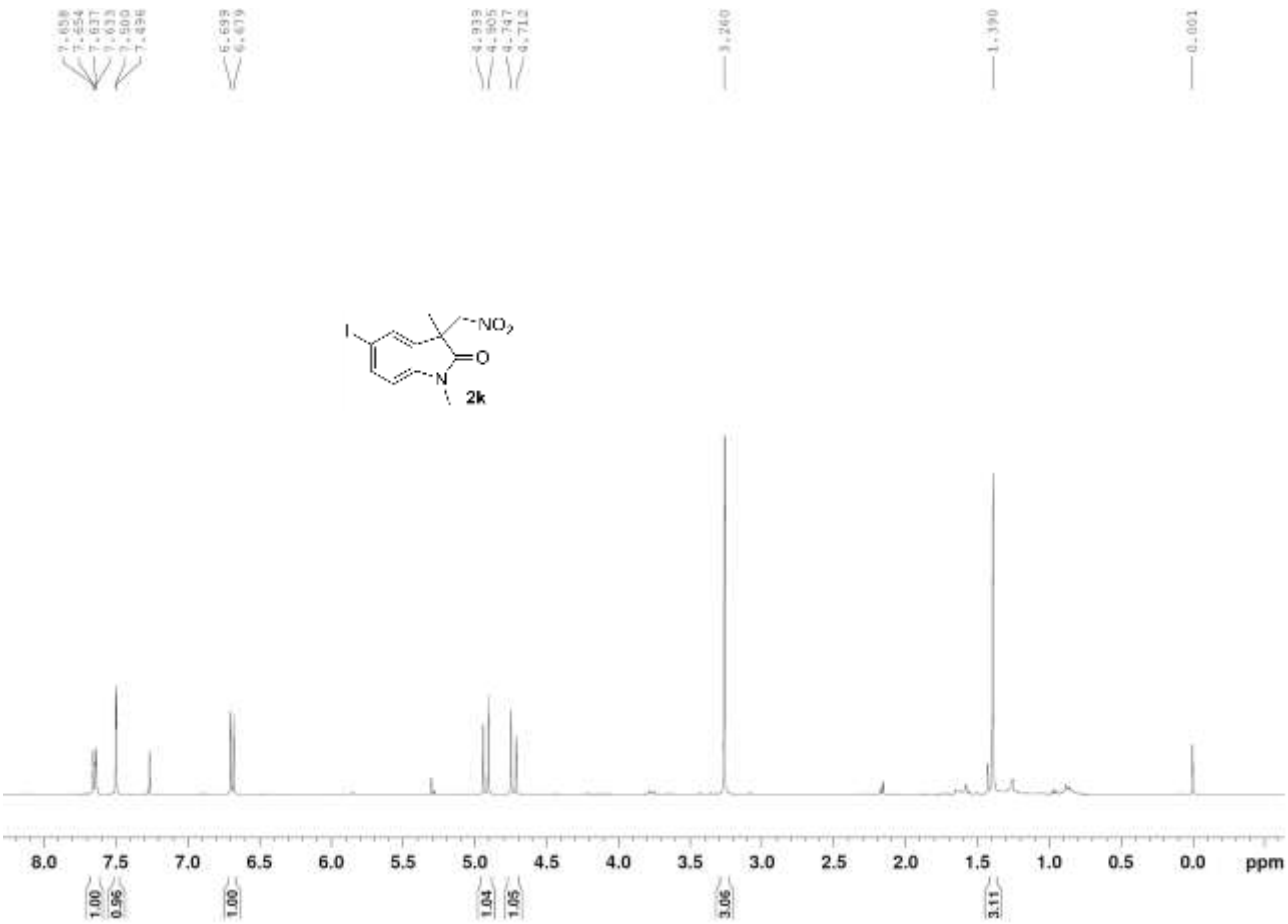
O
N
2i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



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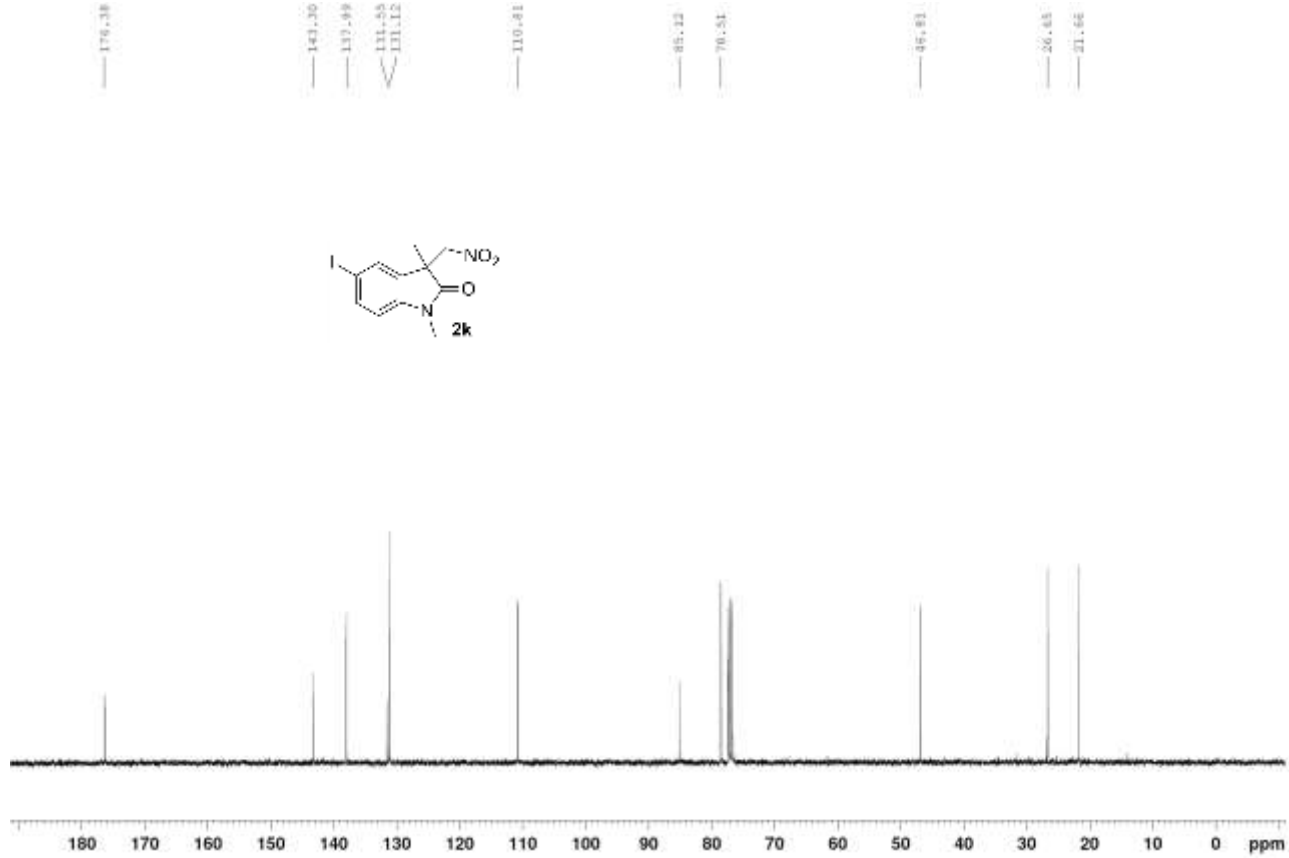
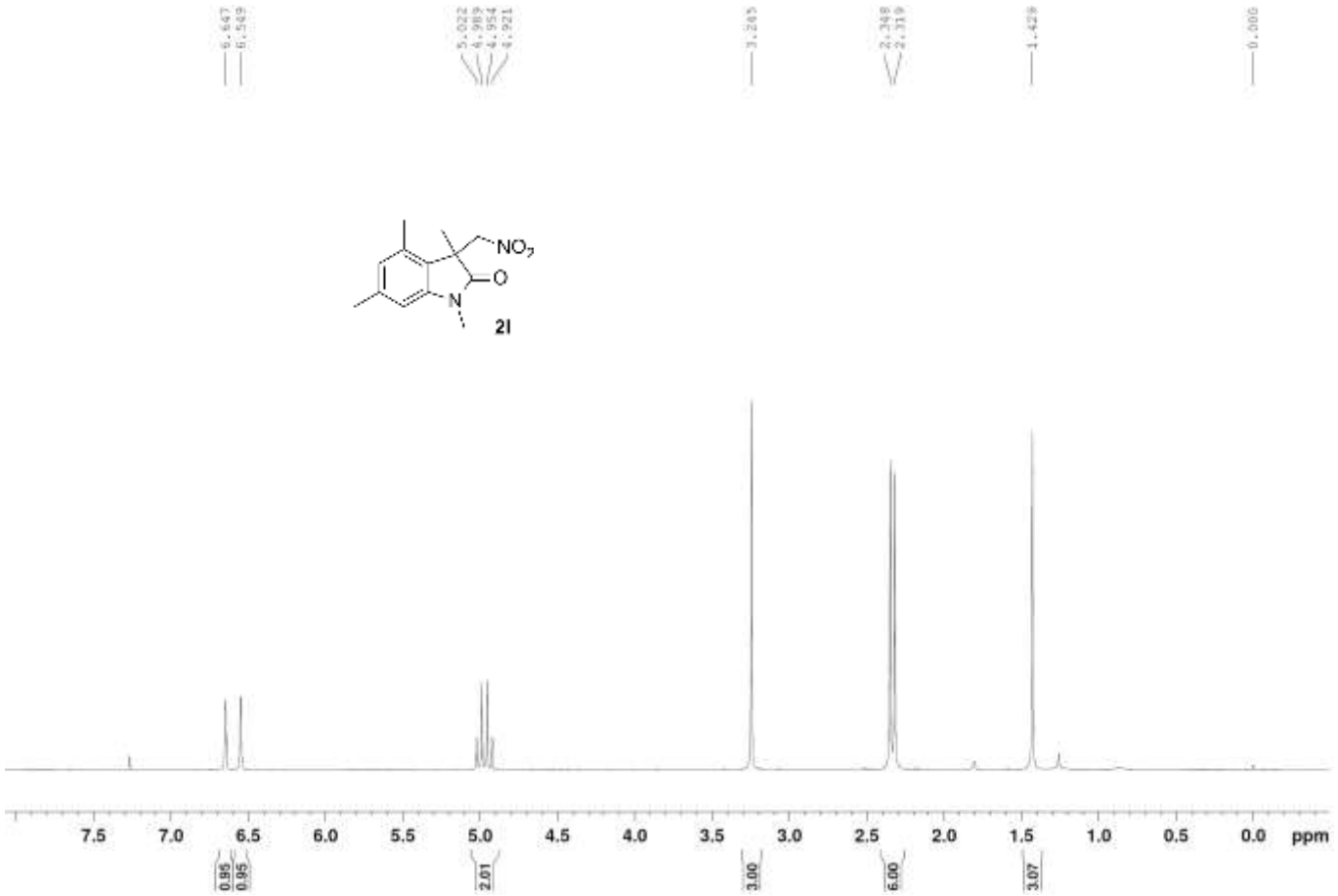
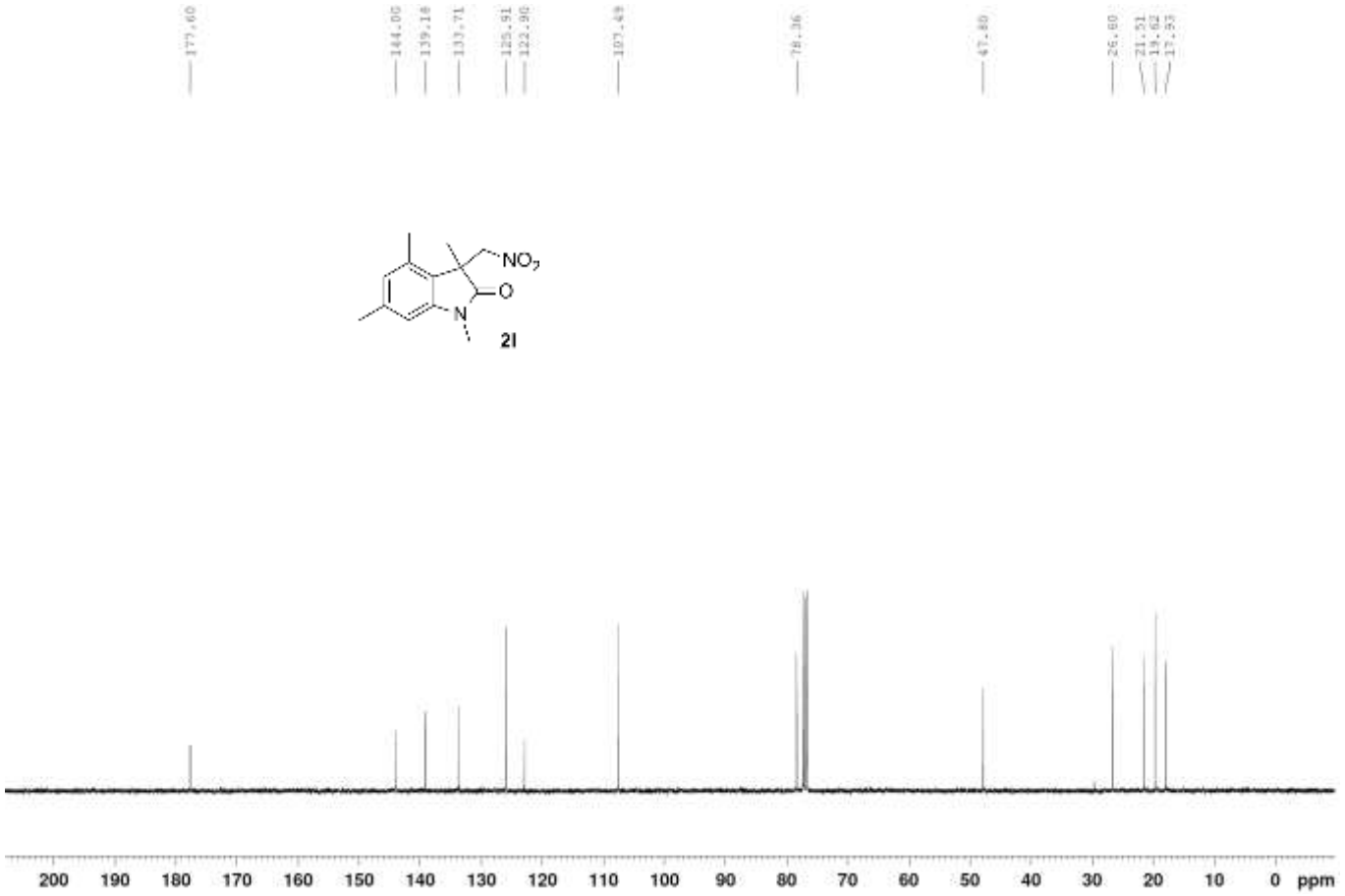
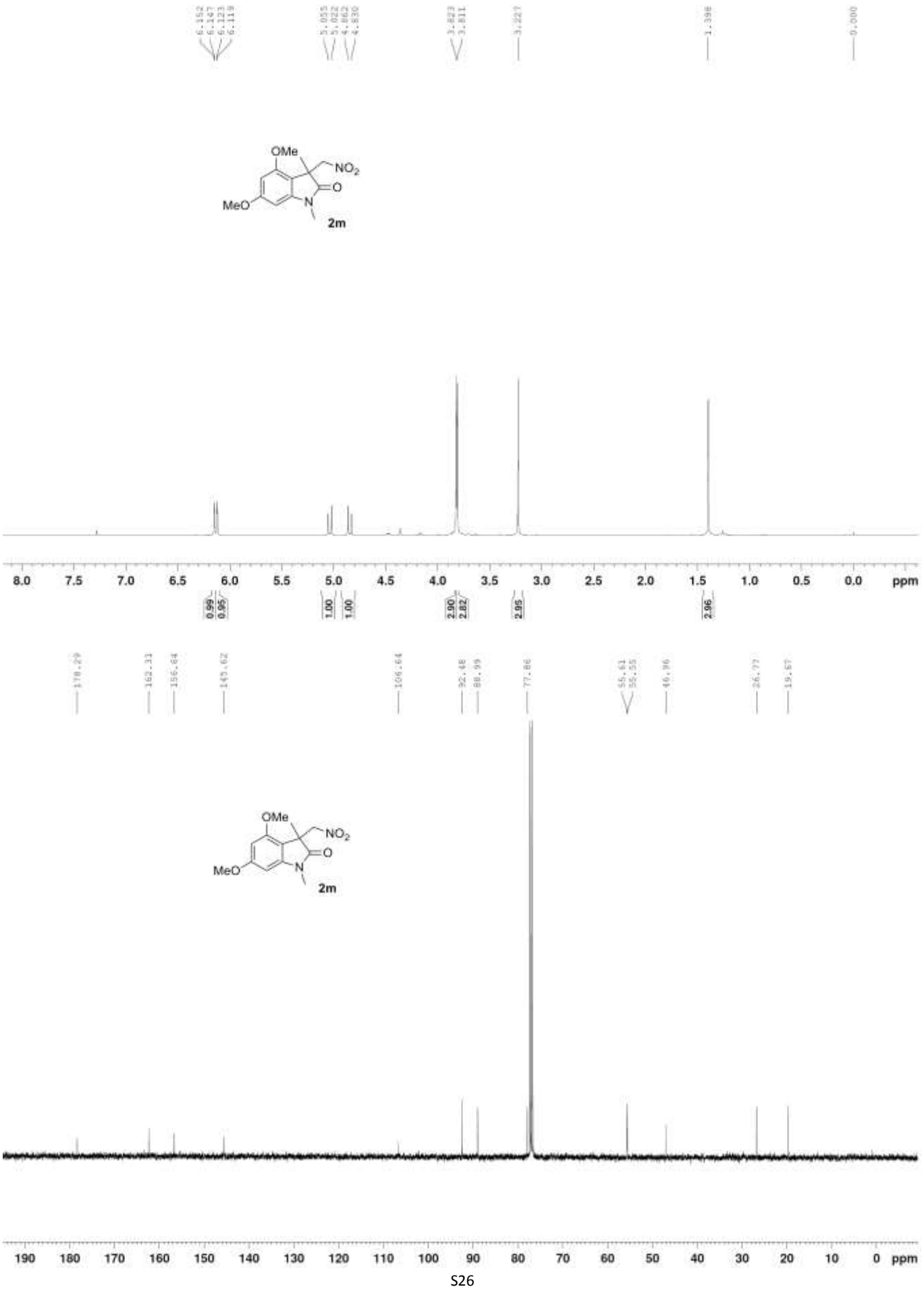
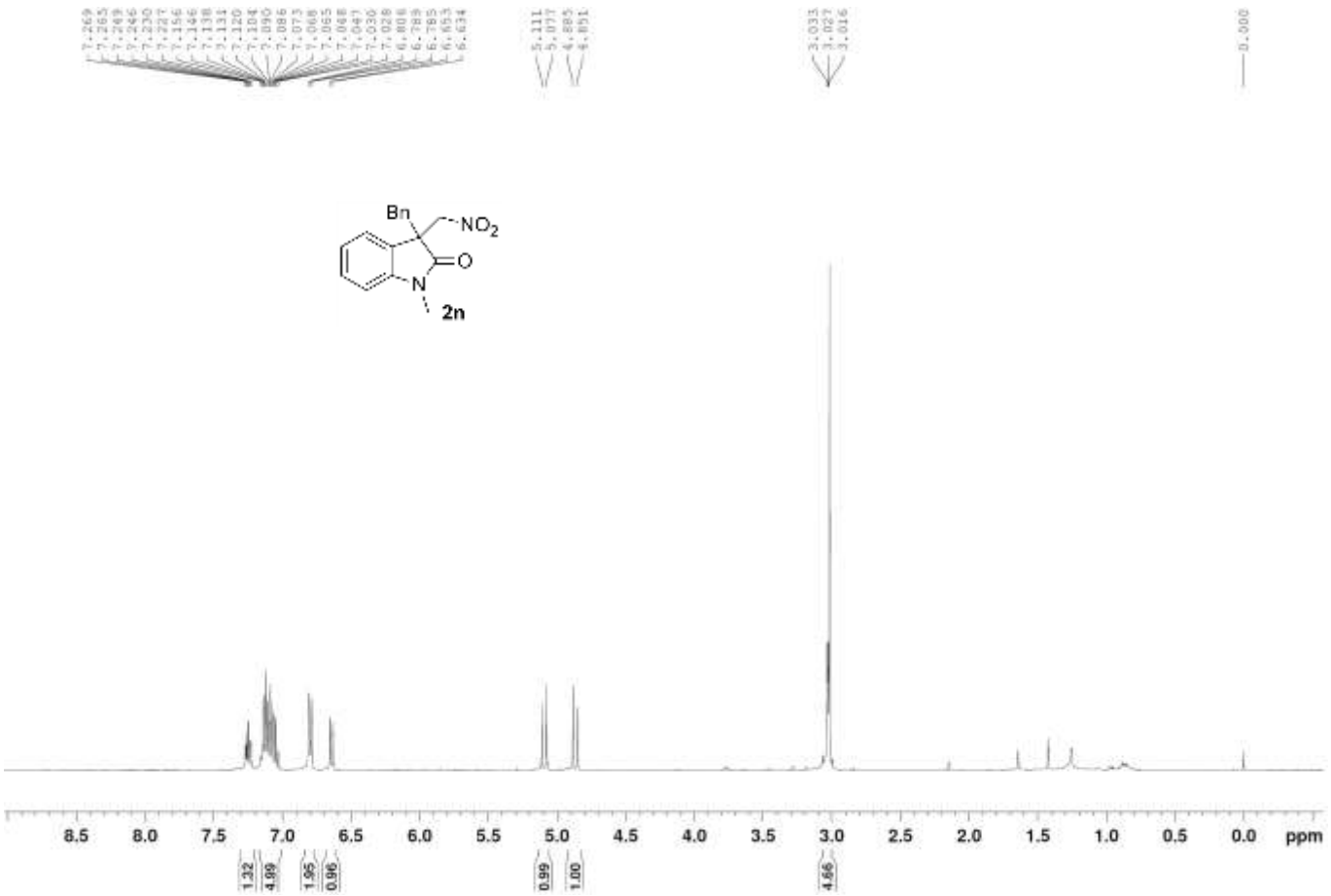
7.654
7.637
7.633
7.500
7.496
6.699
6.679
4.939
4.905
4.747
4.712
3.260
1.390
0.001
NO2
I
O
N
2k
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
0.96
1.00
1.04
1.05
3.06
3.11

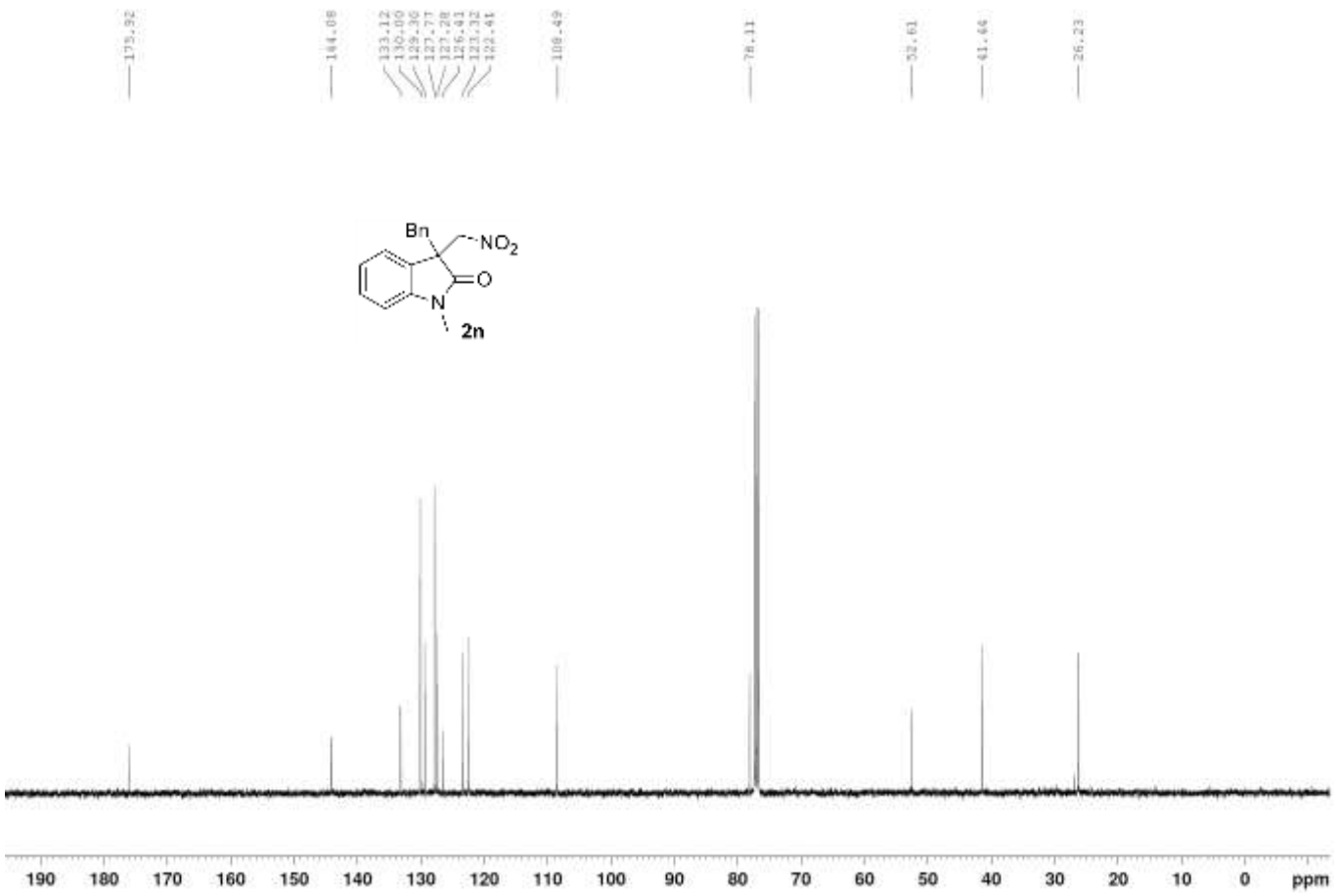

176.38
143.30
137.99
131.55
131.12
110.81
85.12
70.51
46.83
26.65
21.66
NO2
I
O
N
2k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

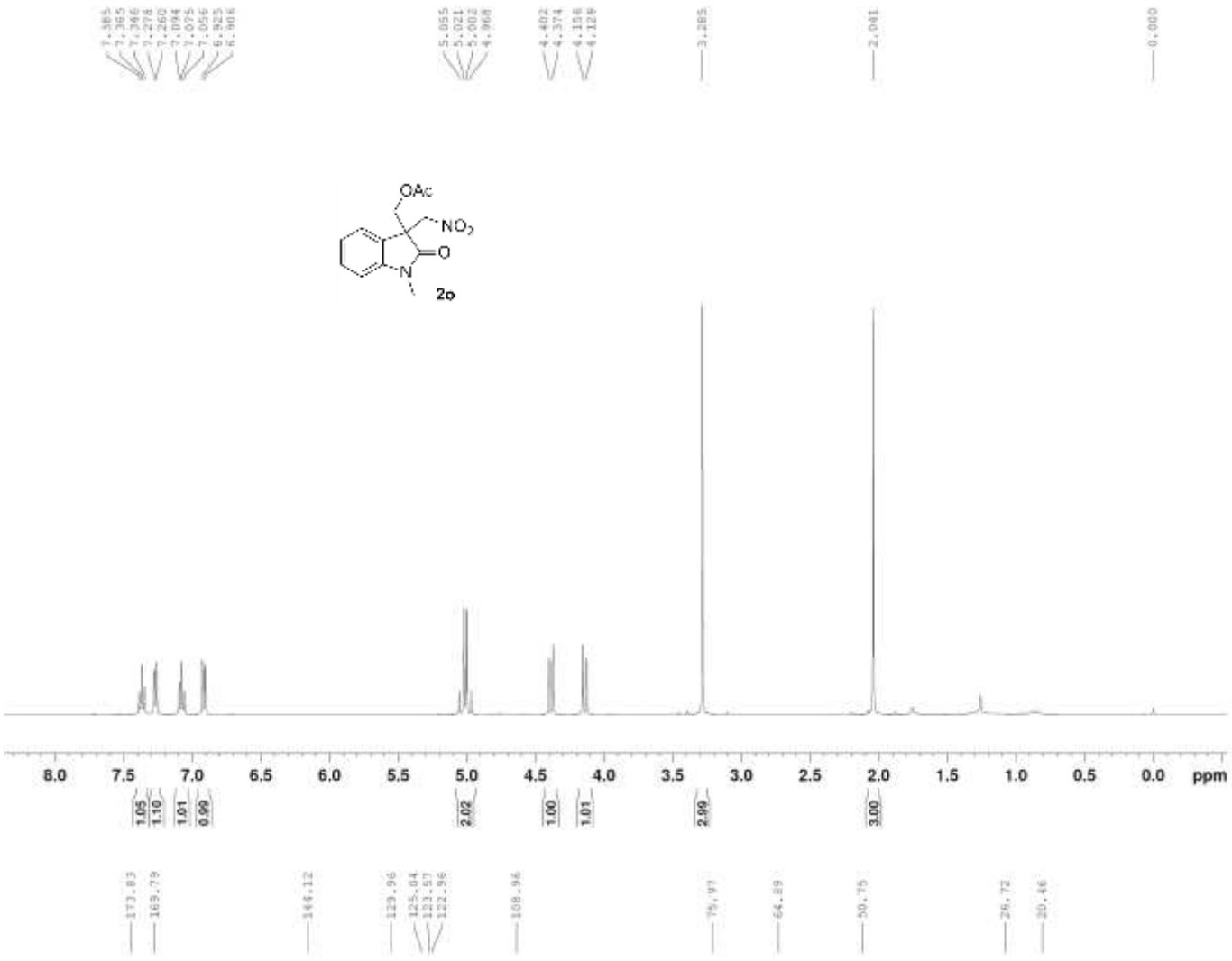

6.647
6.569
5.022
4.989
4.954
4.921
3.265
2.348
2.319
1.429
0.000
NO2
O
N
2l
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
0.95
2.01
3.00
6.00
3.07

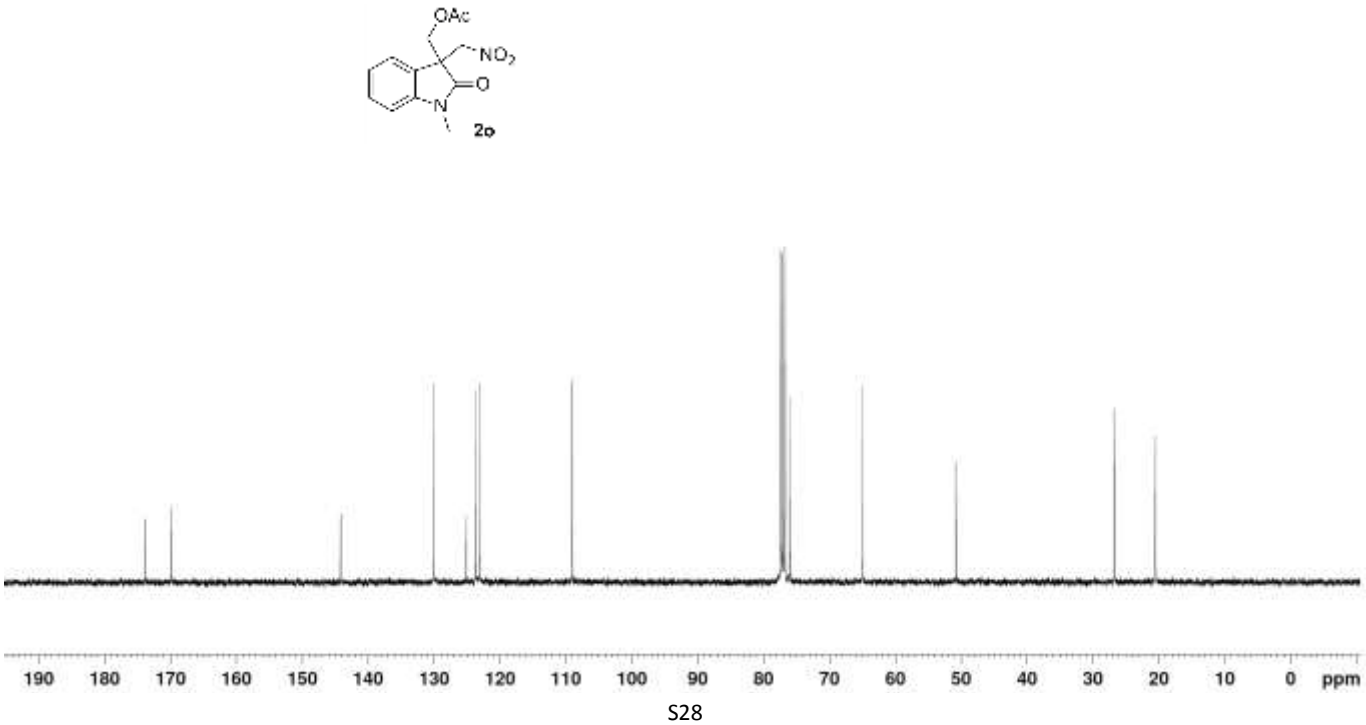

177.60
144.00
139.18
133.71
125.91
122.90
107.49
78.36
47.80
26.60
21.51
19.62
17.93
NO2
O
N
2l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

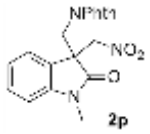

6.152
6.147
6.123
6.119
5.035
5.022
4.862
4.830
3.823
3.811
3.227
1.398
0.000
OMe
NO2
O
MeO
N
2m
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.99
0.95
1.00
1.00
2.90
2.82
2.95
2.96
170.29
162.31
156.64
145.62
106.64
92.48
88.99
77.86
55.61
55.55
46.96
26.77
19.67
OMe
NO2
O
MeO
N
2m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Bn
NO2
O
N
2n
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 ppm

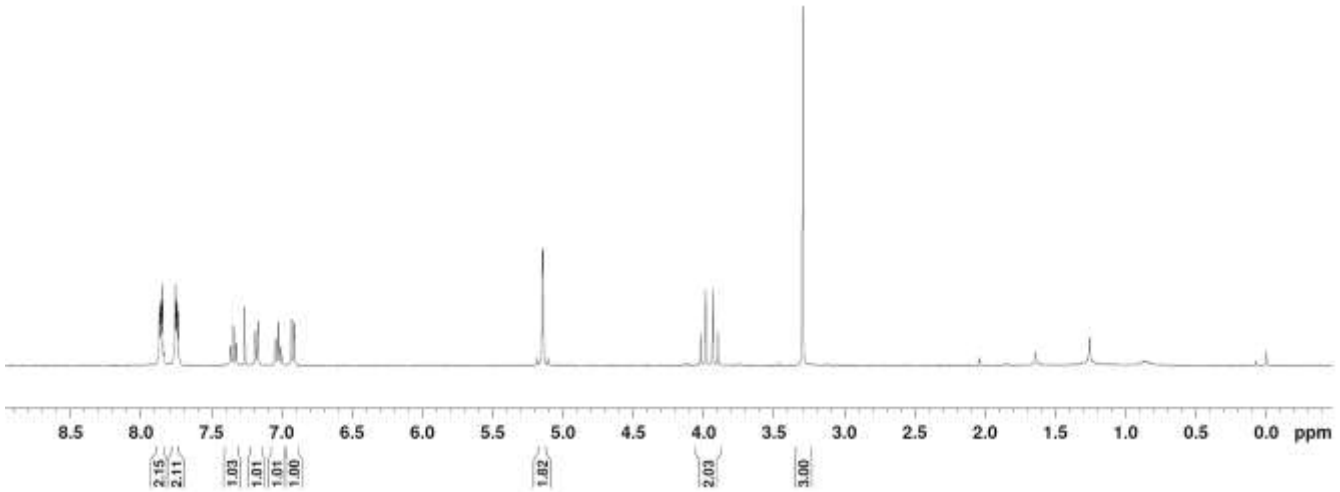

Bn
NO2
O
N
2n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

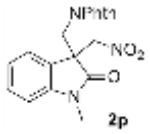

7.385
7.385
7.346
7.278
7.260
7.094
7.075
7.056
6.925
6.906
5.055
5.021
5.002
4.966
4.402
4.374
4.156
4.128
3.285
2.041
0.000
OAc
NO2
O
N
2o
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.05
1.10
1.01
0.99
2.02
1.00
1.01
2.99
3.00


173.83
169.79
144.12
129.96
125.04
123.57
122.96
108.96
75.97
64.89
50.75
26.72
20.46
OAc
NO2
O
N
2o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

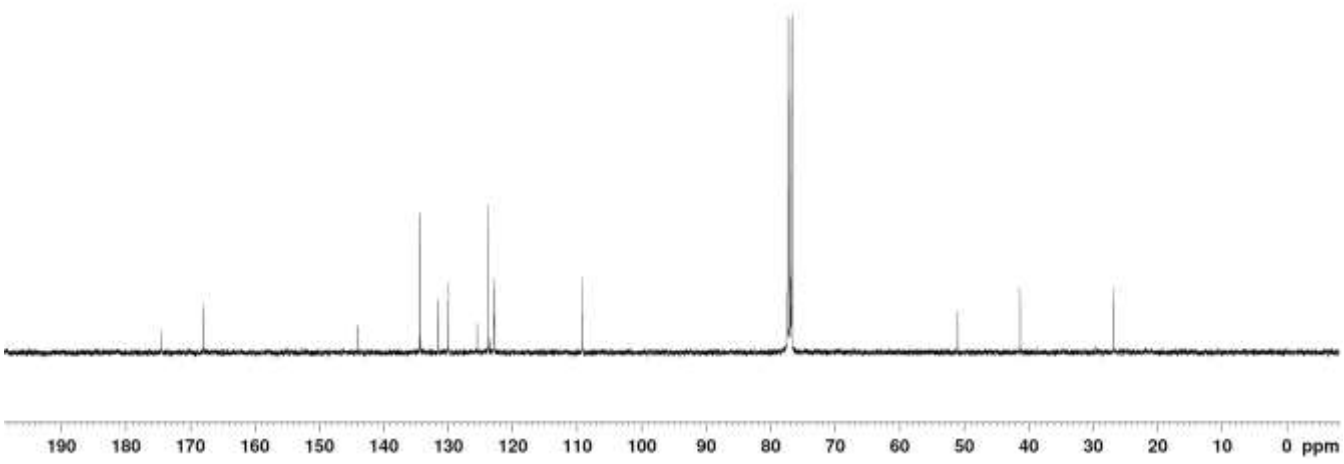

NPhth
NO2
O
N

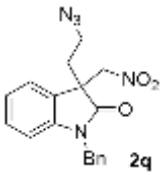
2p


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 ppm
2.15 2.11 1.03 1.01 1.01 1.00 1.82 2.03 3.00

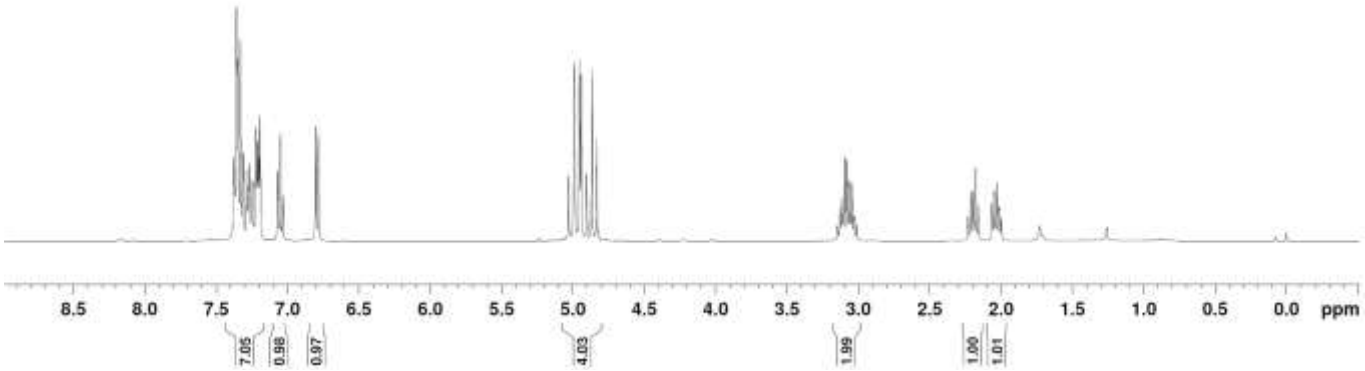

NPhth
NO2
O
N

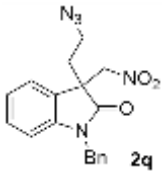
2p


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

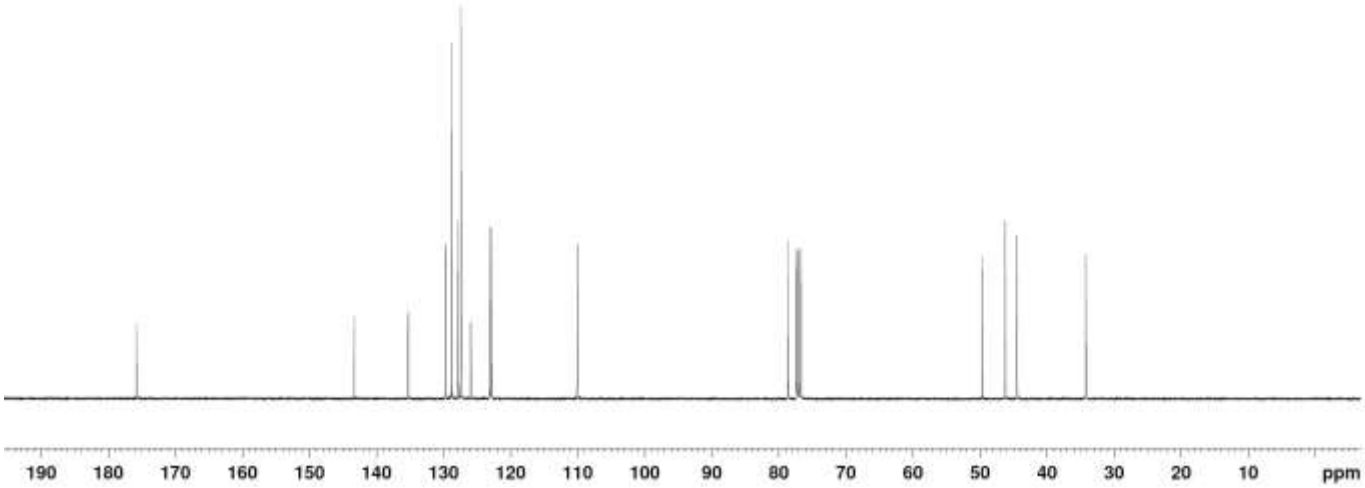

N3
NO2
O
N
Bn

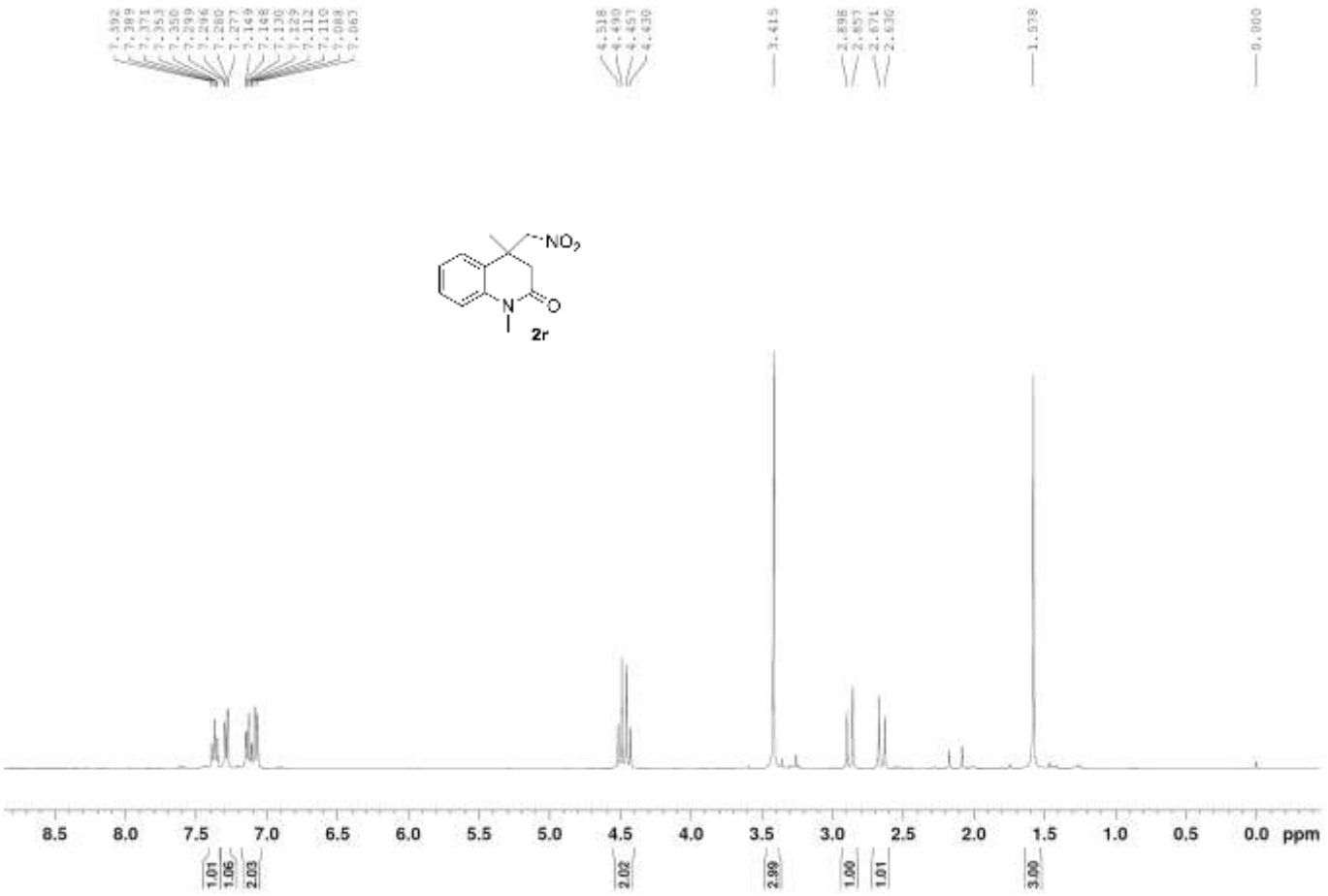
2q

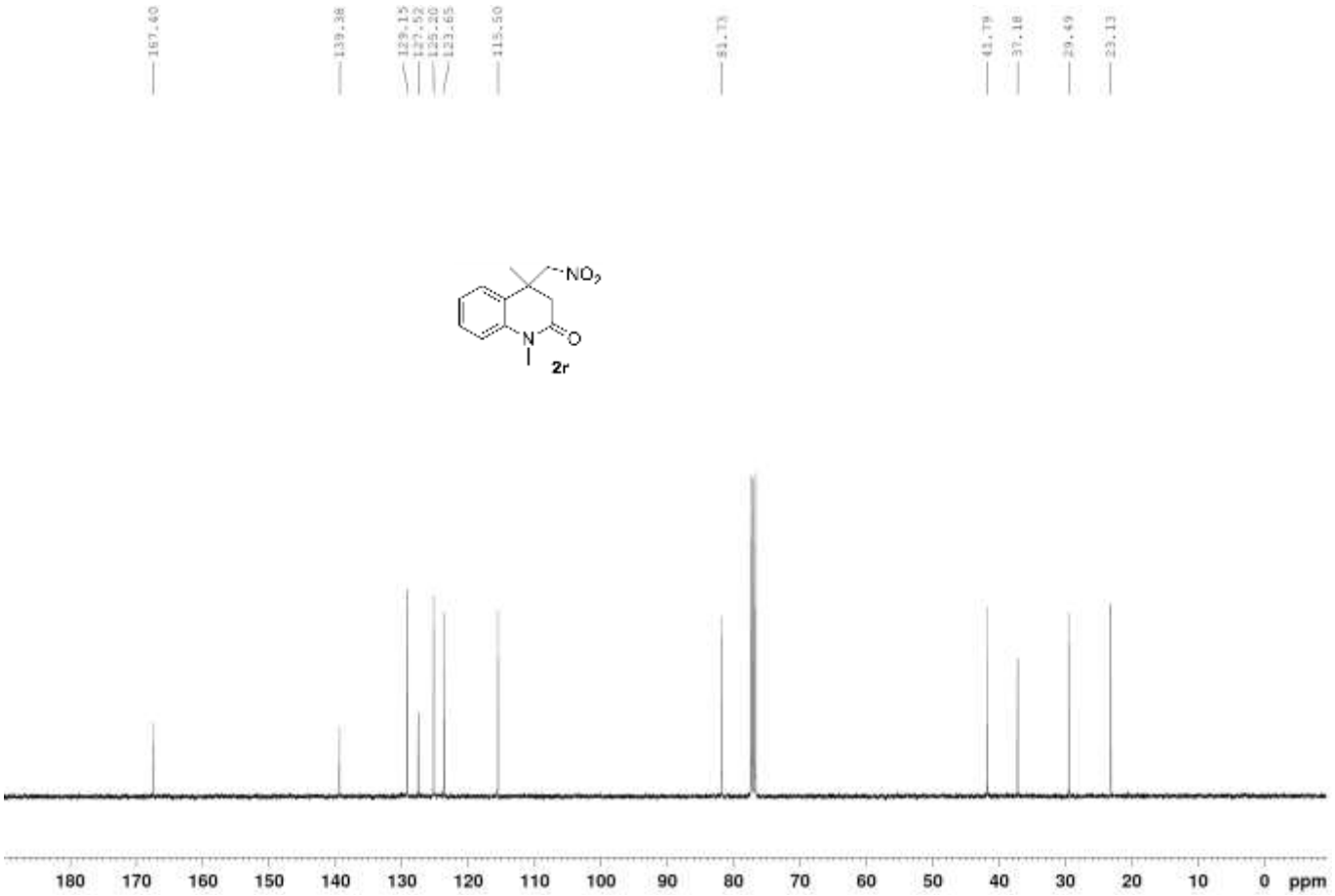

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
7.05
0.98
0.97
4.03
1.99
1.00
1.01

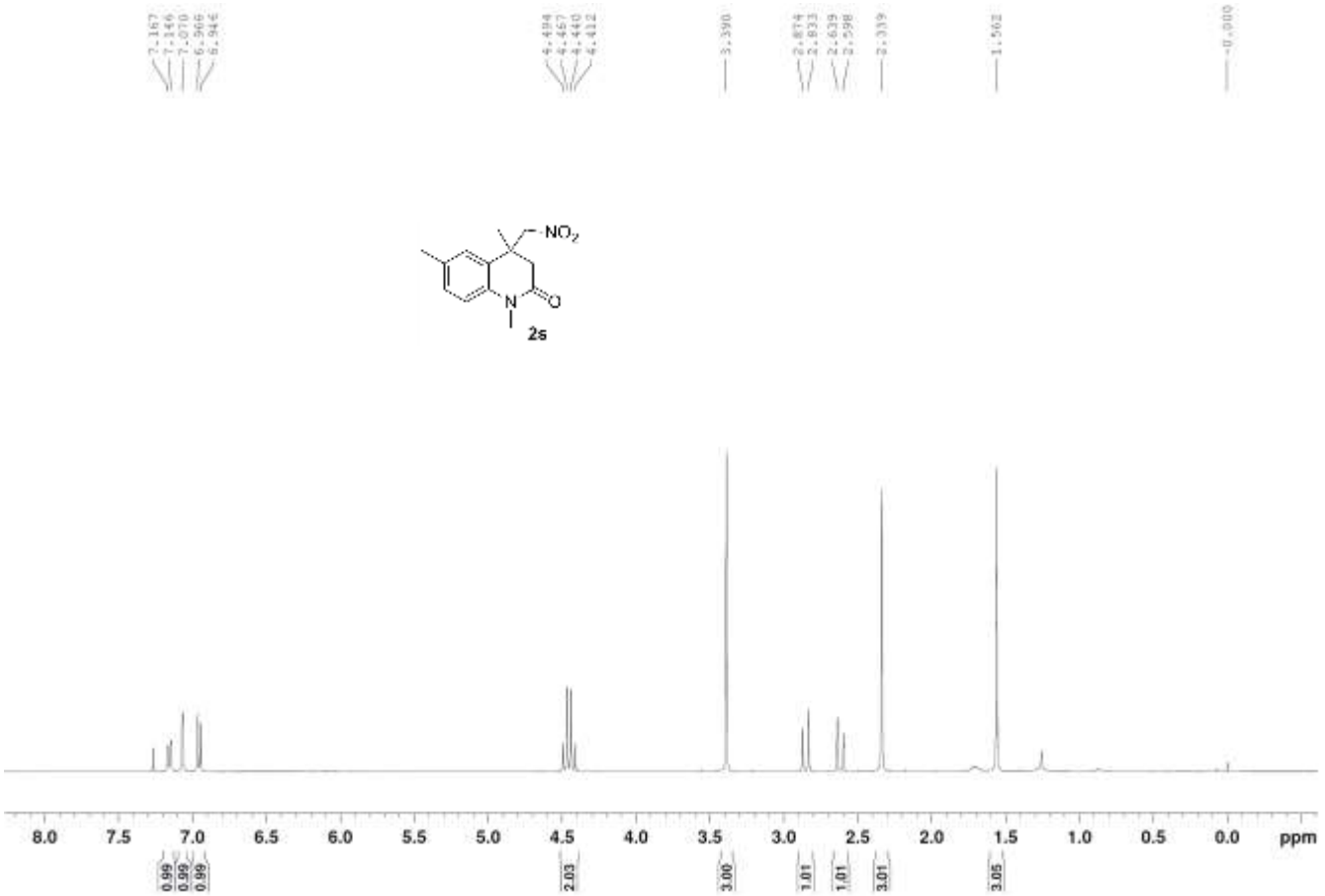

N3
NO2
O
N
Bn

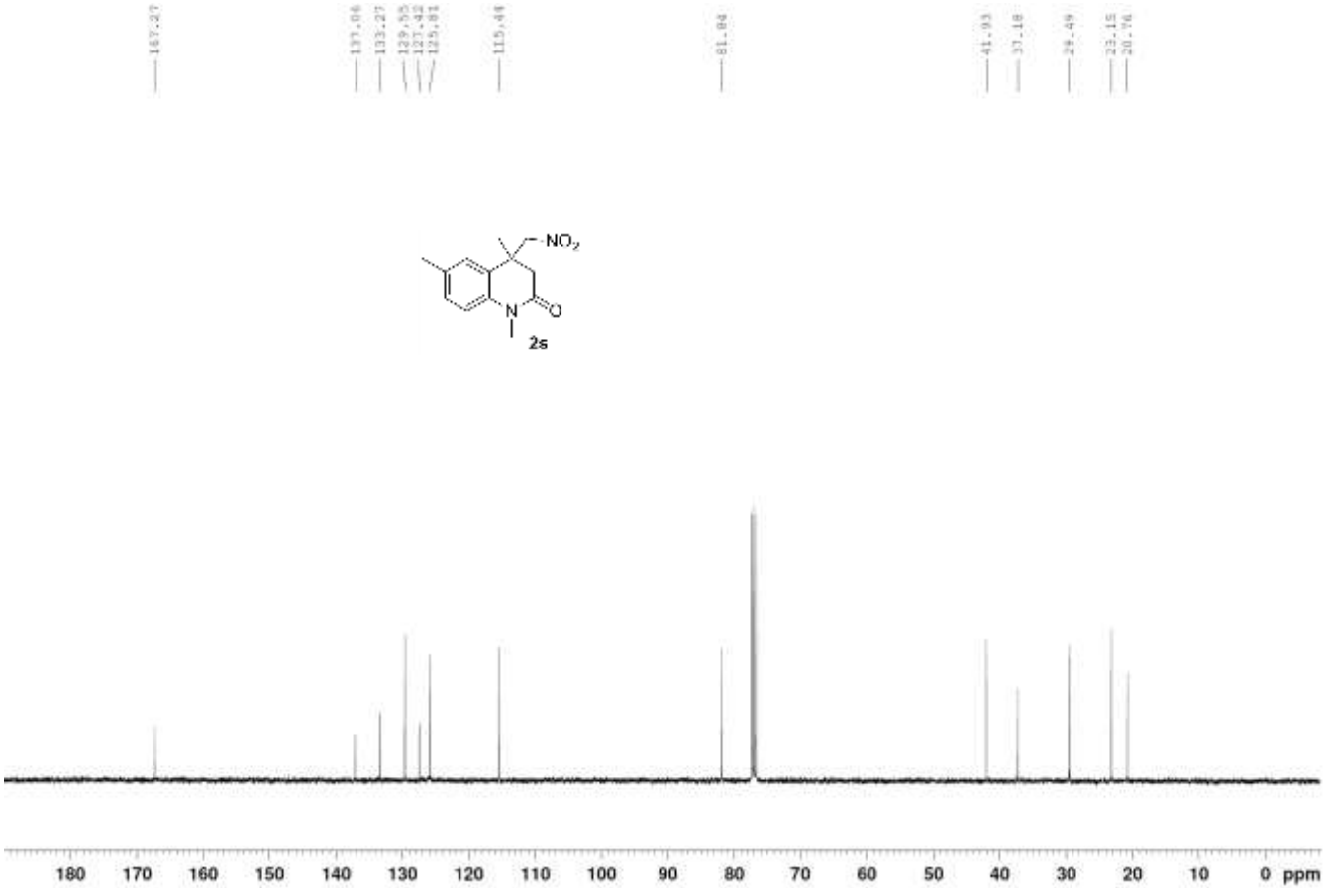
2q

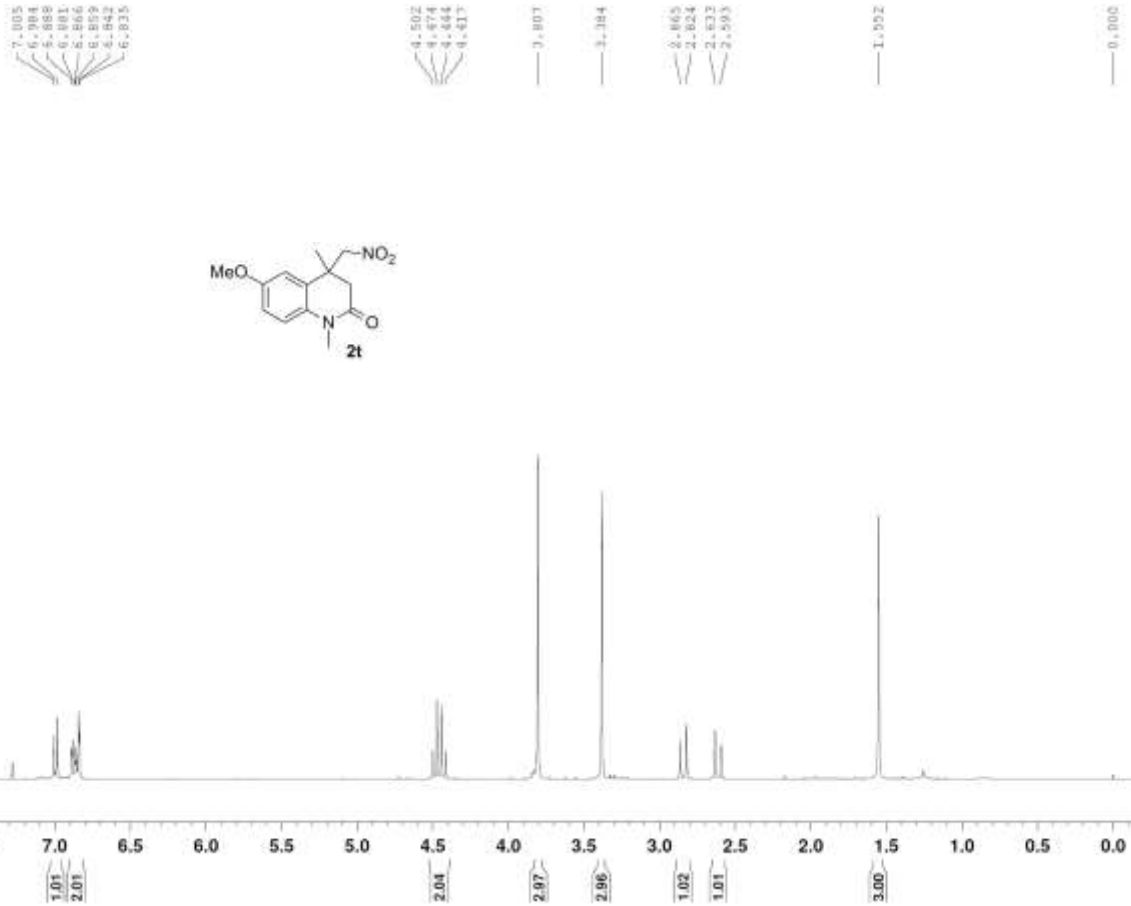

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

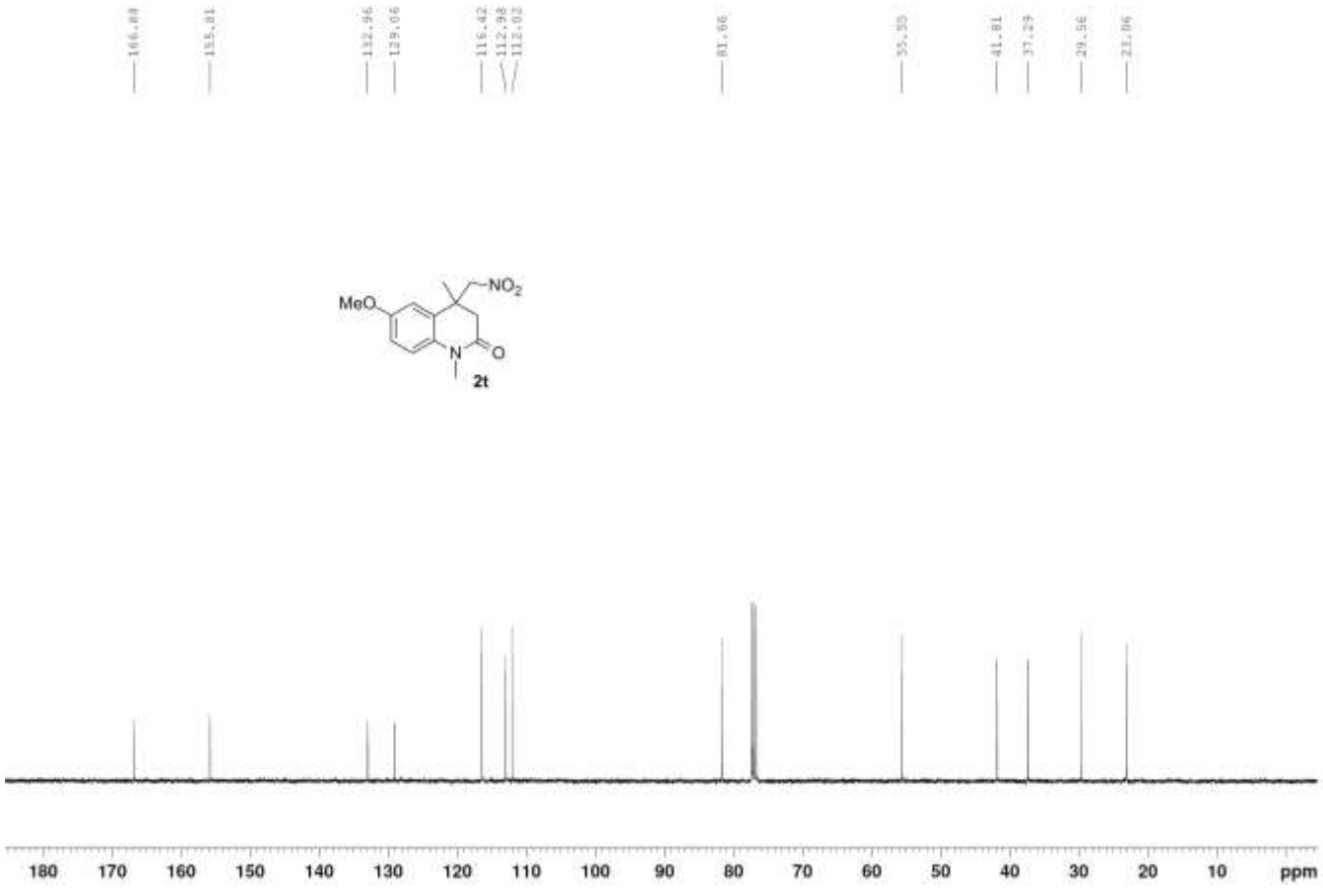

7.392
7.389
7.371
7.353
7.350
7.299
7.246
7.240
7.227
7.169
7.148
7.130
7.129
7.112
7.110
7.088
7.067
4.518
4.490
4.457
4.430
3.415
2.898
2.857
2.671
2.636
1.978
0.000
NO2
O
N
2r
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
1.06
2.03
2.02
2.99
1.00
1.01
3.00

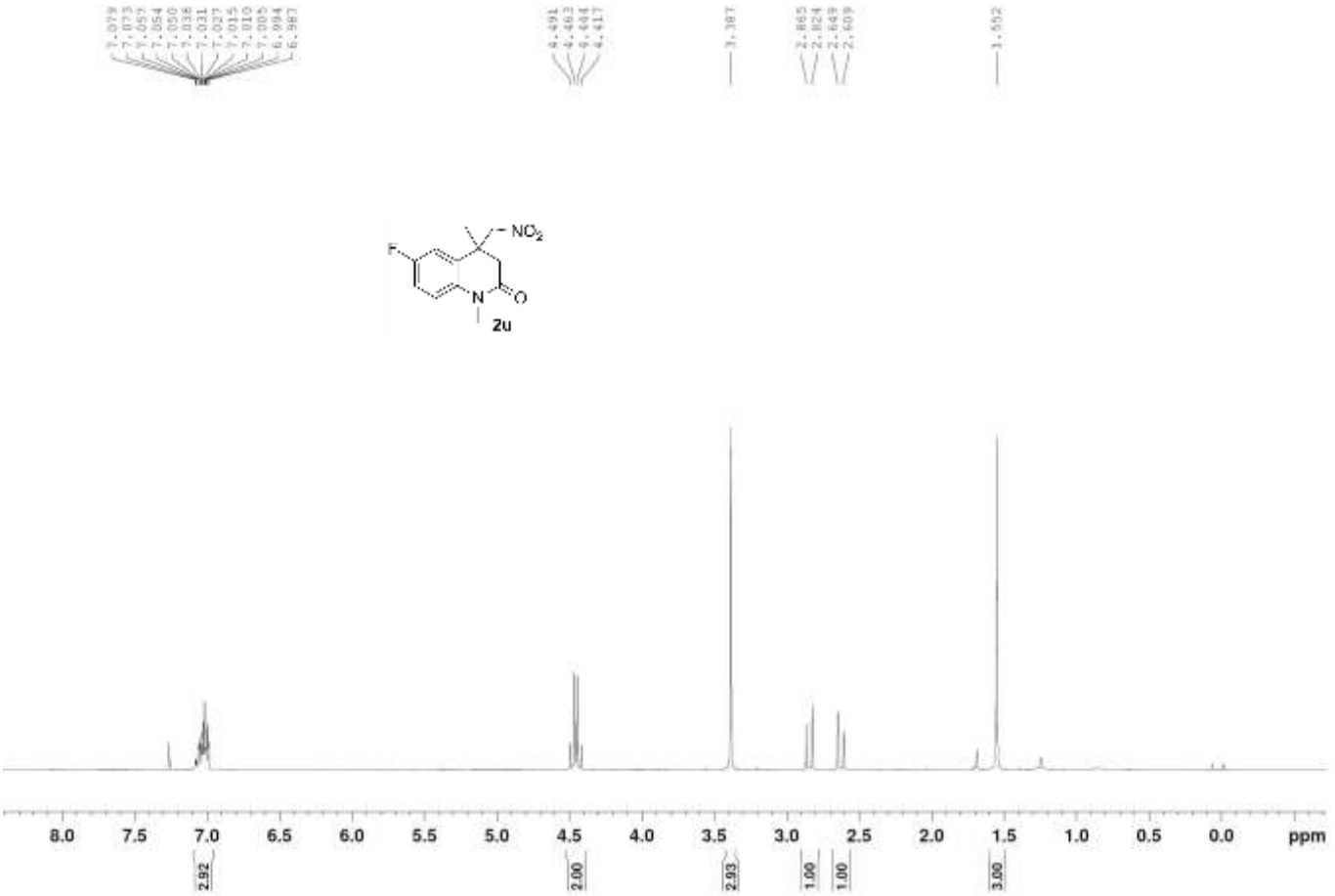

167.40
139.38
129.15
127.52
125.20
123.65
115.50
81.73
41.79
30.18
29.49
23.13
NO2
O
N
2r
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

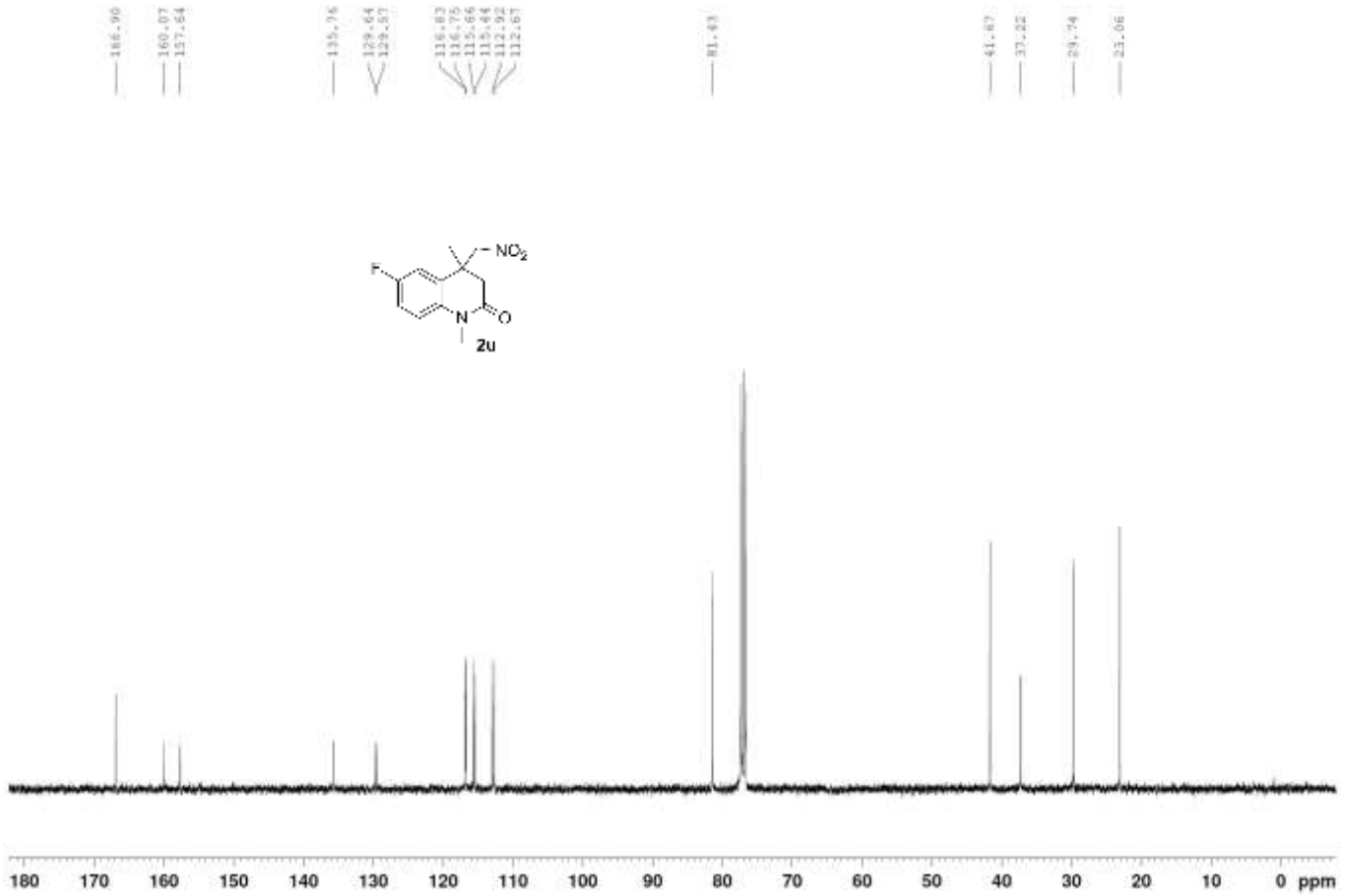

7.167
7.156
7.070
6.966
6.946
4.494
4.467
4.440
4.412
3.390
2.874
2.833
2.639
2.598
2.339
1.562
-0.000
NO2
N
O
2s
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.99
0.99
0.99
2.03
3.00
1.01
1.01
3.01
3.05

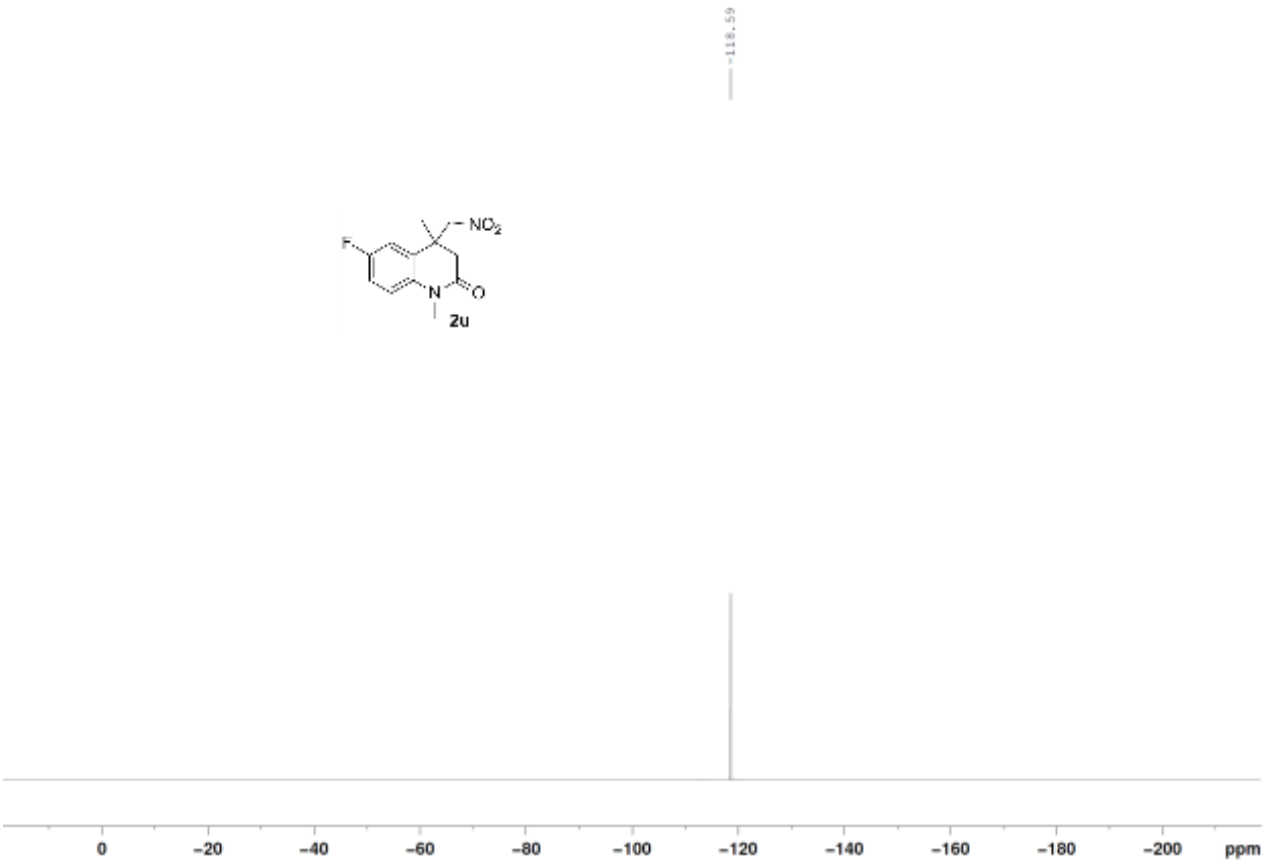

167.27
137.06
133.27
129.55
127.42
125.81
115.44
81.04
41.93
37.18
29.49
23.15
20.76
NO2
N
O
2s
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.005
6.904
6.888
6.881
6.866
6.859
6.842
6.835
4.502
4.474
4.444
4.417
3.807
3.384
2.865
2.624
2.633
2.593
1.552
0.000
MeO
NO2
N
O
2t
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
ppm
1.01
2.01
2.04
2.97
2.96
1.02
1.01
3.00

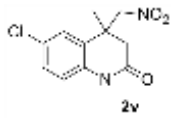

166.69
155.81
132.96
129.06
116.42
112.98
112.02
81.66
55.55
41.81
37.29
29.56
23.06
MeO
NO2
N
O
2t
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

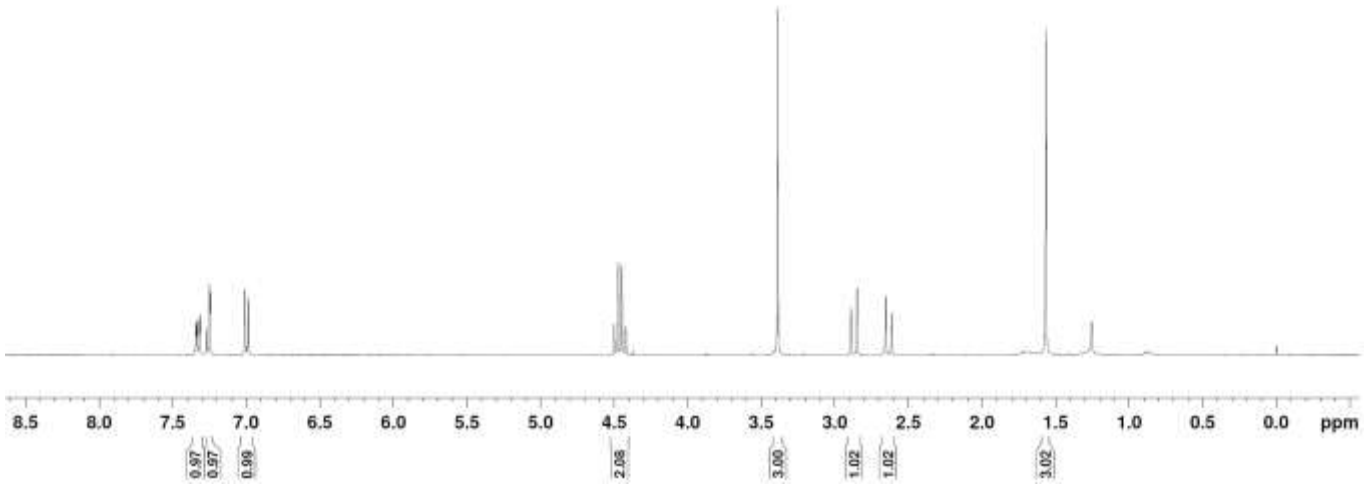

7.079
7.073
7.057
7.054
7.050
7.038
7.031
7.027
7.015
7.010
7.005
6.994
6.987
4.491
4.463
4.444
4.417
3.387
2.865
2.824
2.669
2.609
1.552
NO2
F
N
O
2u
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.92
2.00
2.93
1.00
1.00
3.00

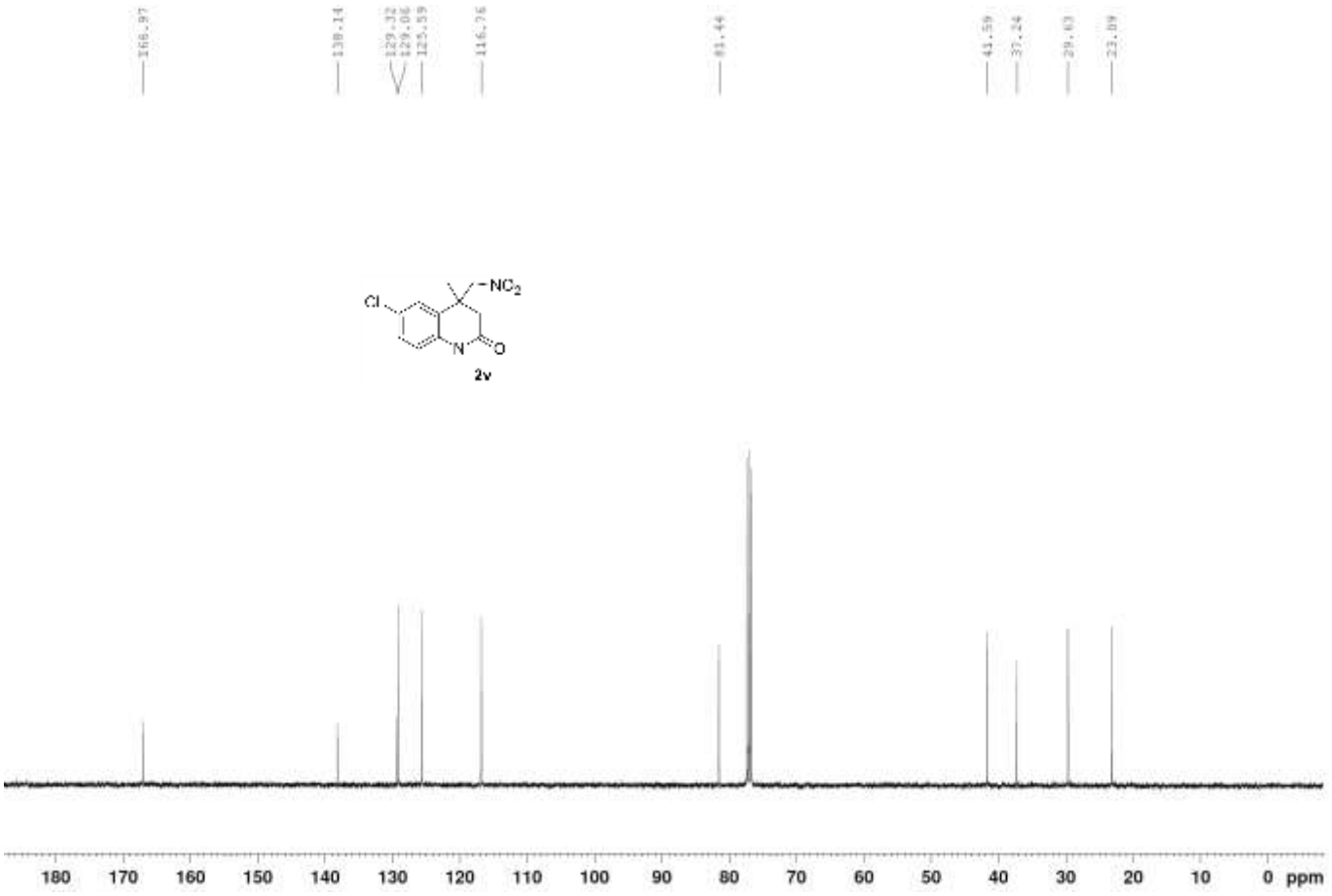

166.90
160.07
157.64
135.76
129.64
129.57
116.83
116.75
115.66
115.44
112.92
112.67
81.43
41.67
37.22
29.74
23.06
NO2
F
N
O
2u
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

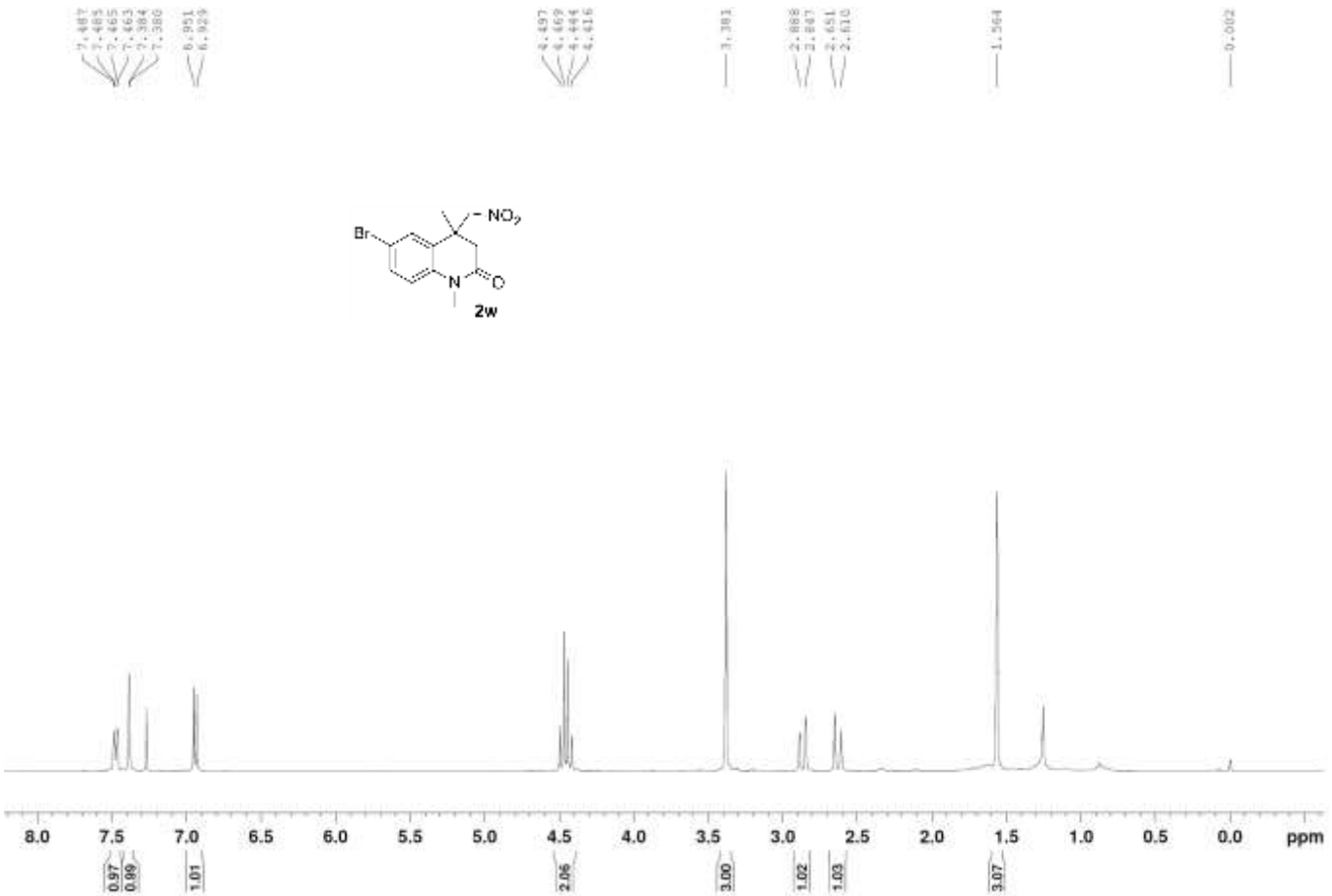

-118.59
F
NO2
O
N
2u
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

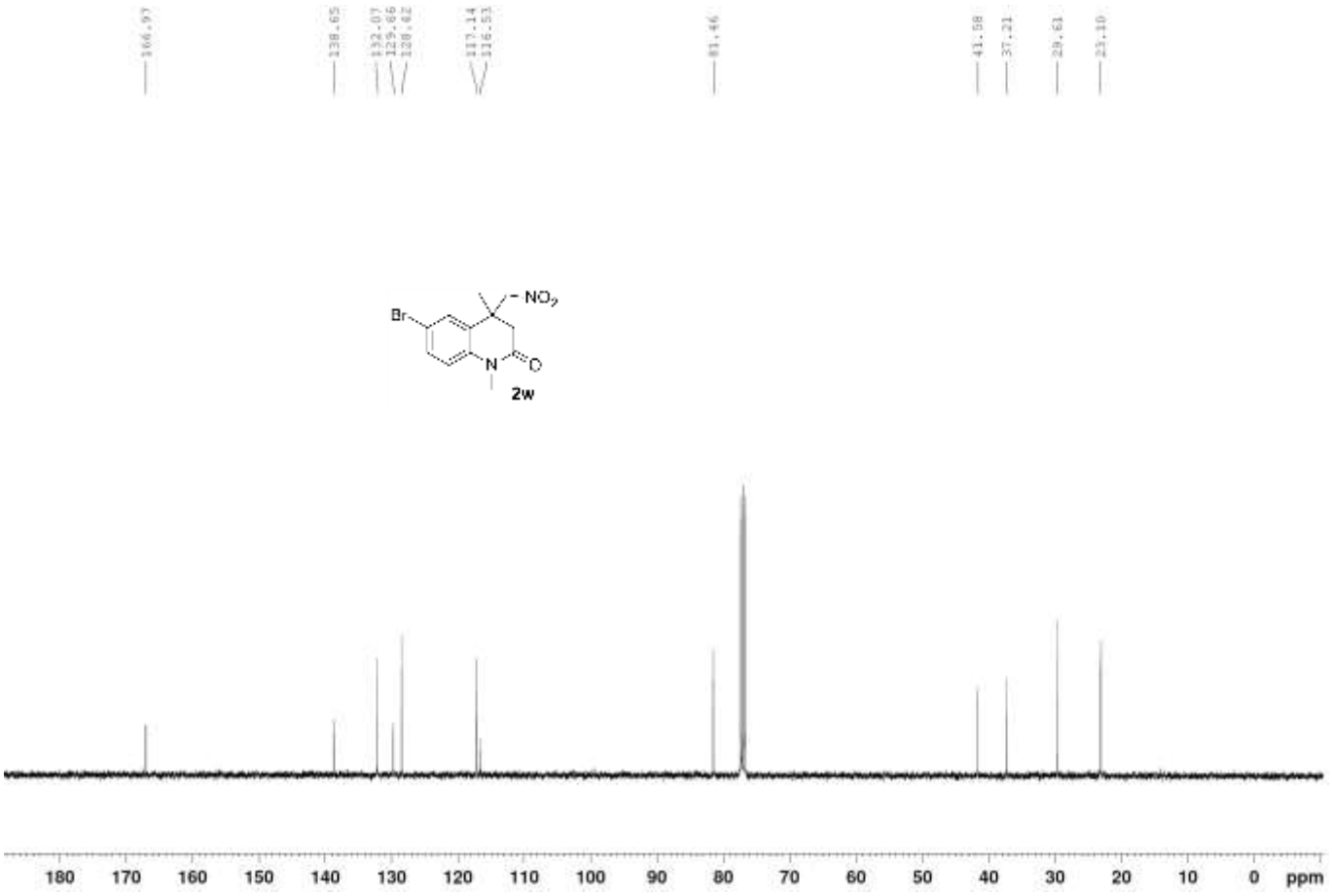

7.344
7.338
7.322
7.316
7.252
7.247
7.010
6.988
4.501
4.475
4.448
4.420
3.390
2.893
2.650
2.656
2.615
1.568
0.000

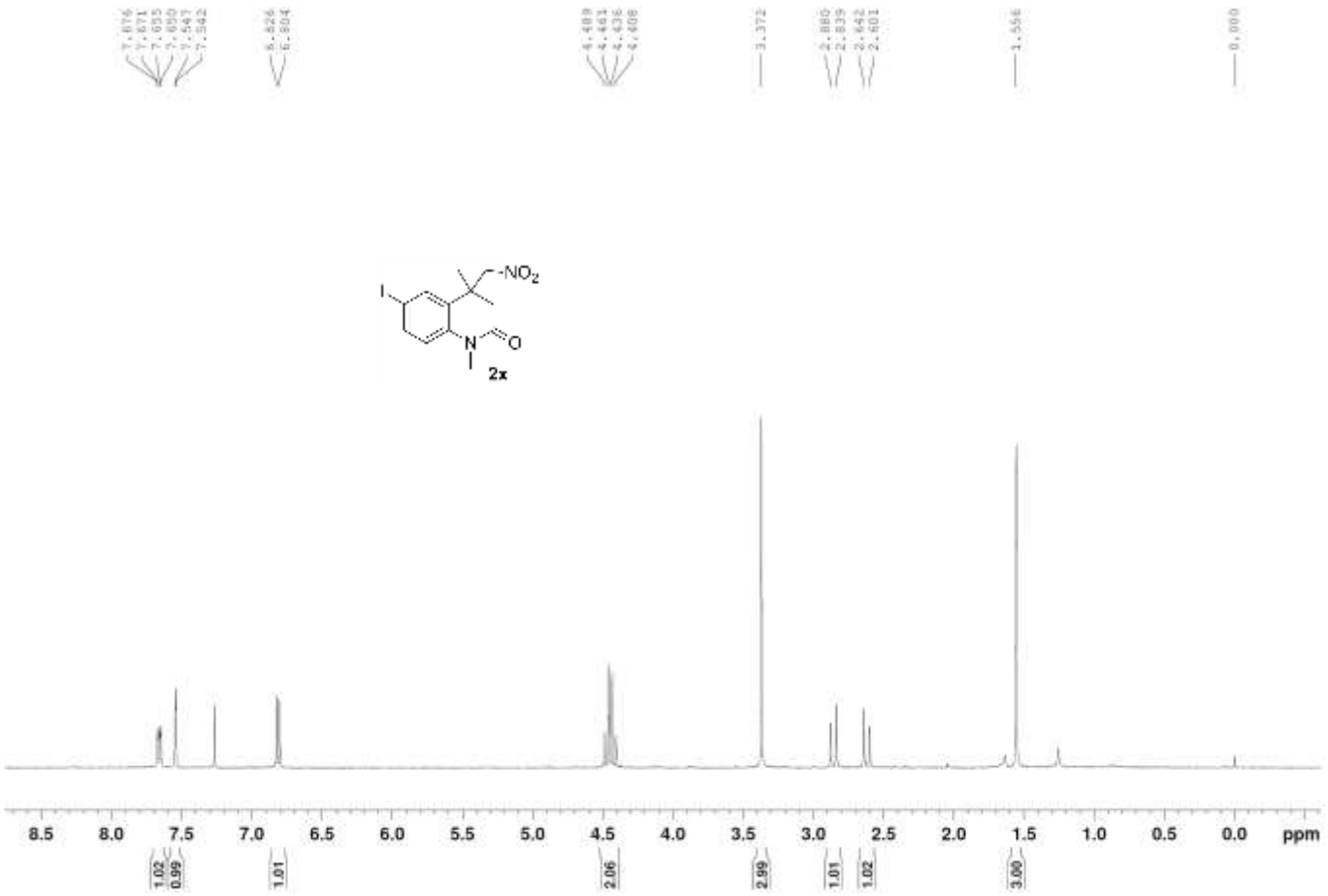

Cl
NO2
O
N
2v

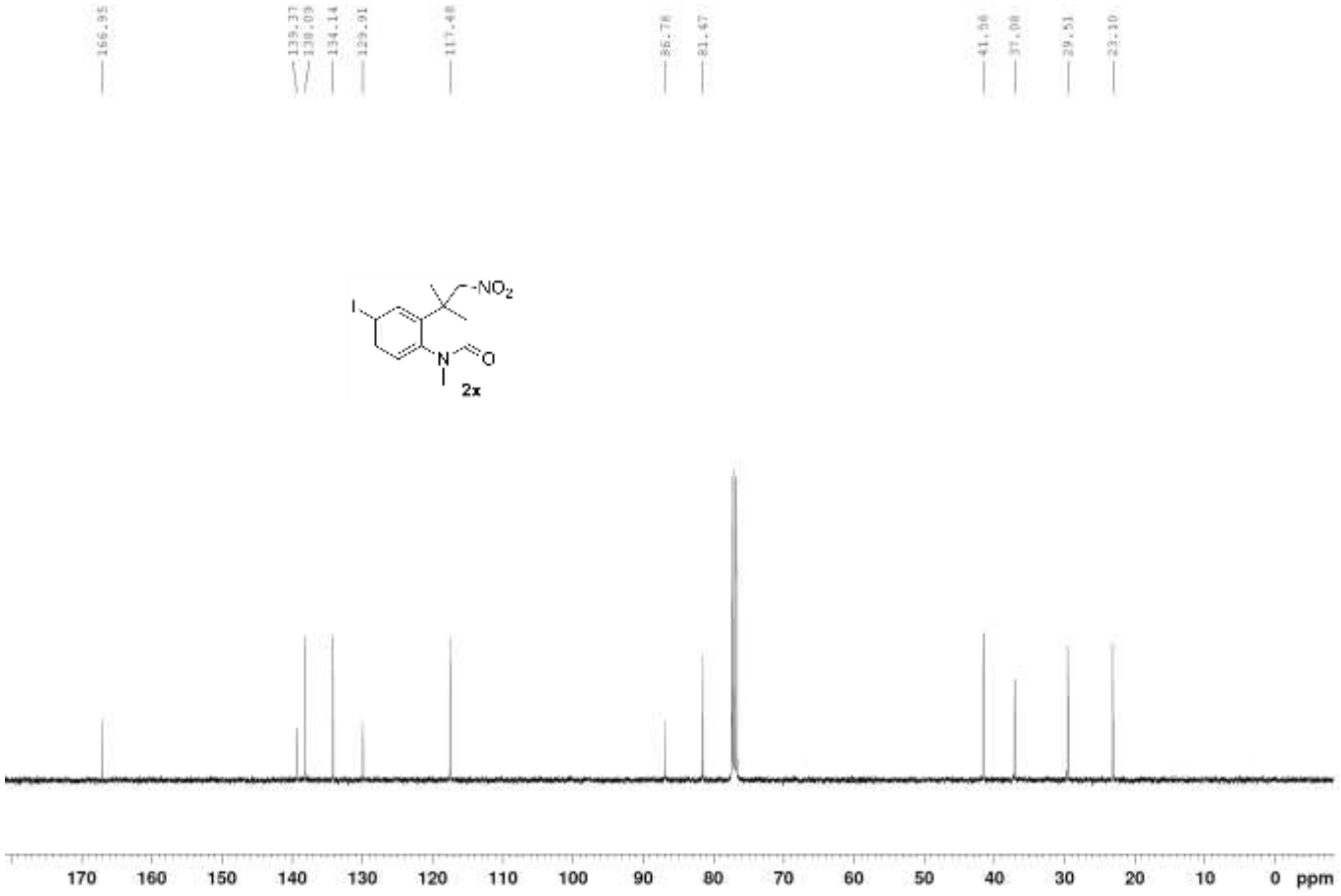

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.97
0.97
0.99
2.08
3.00
1.02
1.02
3.02

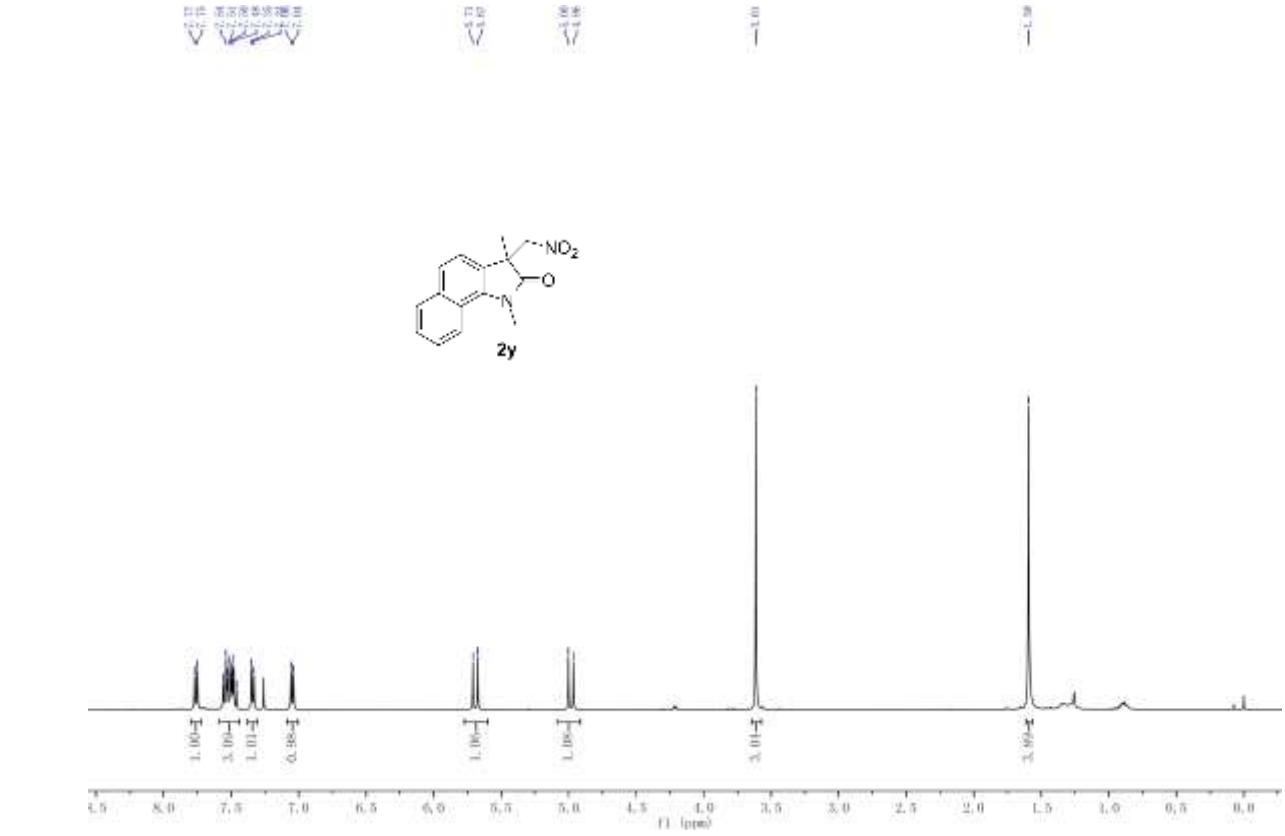

166.97
139.14
129.32
129.06
125.59
116.76
83.44
41.59
37.24
29.63
23.09
Cl
NO2
N
O
2v
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

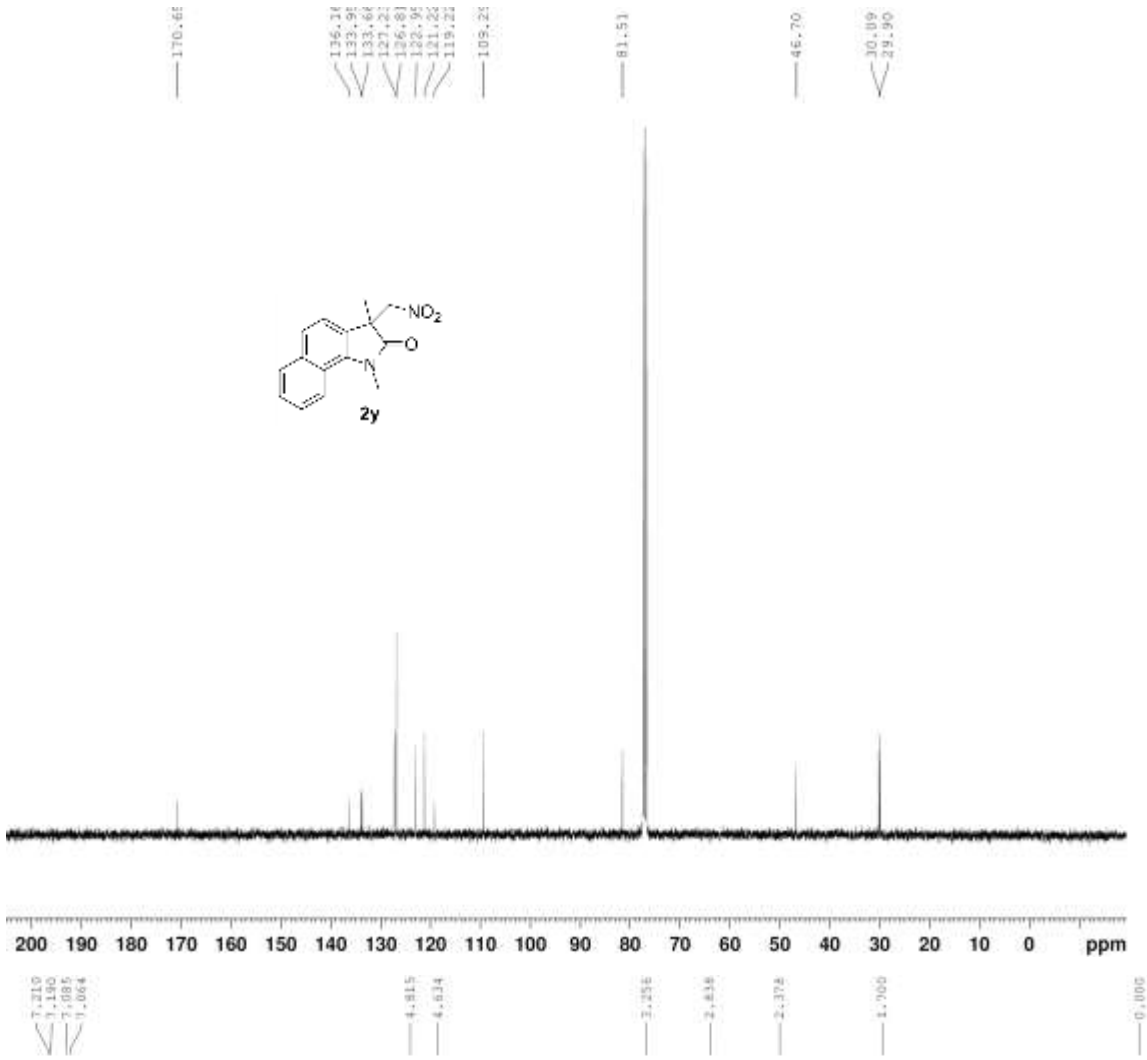

7.487
7.485
7.465
7.463
7.384
7.380
6.951
6.929
4.497
4.469
4.444
4.416
3.381
2.888
2.867
2.651
2.610
1.564
0.002
Br
NO2
N
O
2w
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.97
0.89
1.01
2.06
3.00
1.02
1.03
3.07

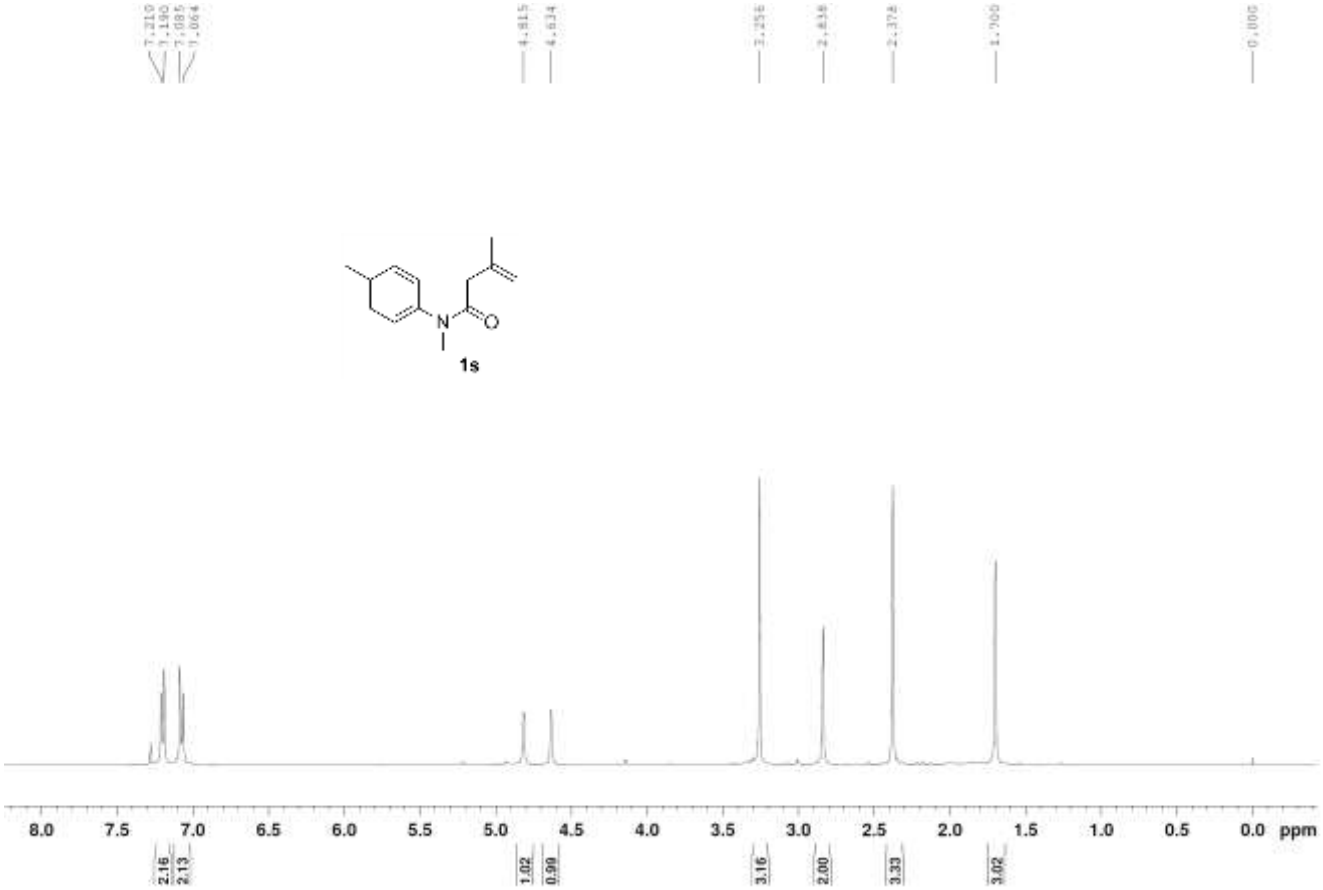

166.97
138.65
132.07
129.86
128.62
117.14
116.53
81.46
41.58
37.21
29.61
23.10
Br
NO2
N
O
2w
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

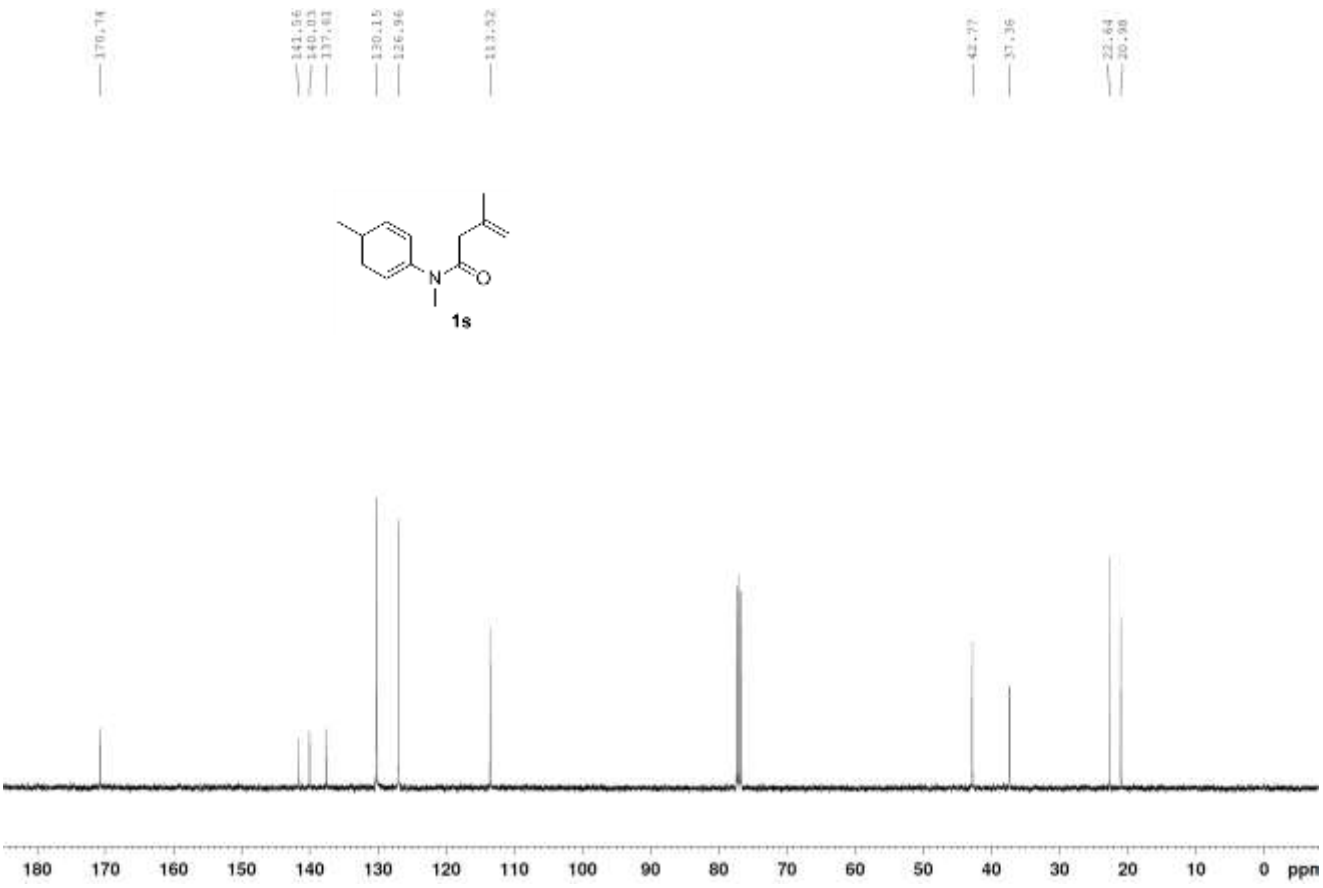

7.676
7.671
7.655
7.650
7.547
7.542
6.826
6.804
4.469
4.461
4.436
4.408
3.372
2.880
2.839
2.642
2.601
1.556
0.000
I
NO2
N
O
2x
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.02
0.99
1.01
2.06
2.99
1.01
1.02
3.00

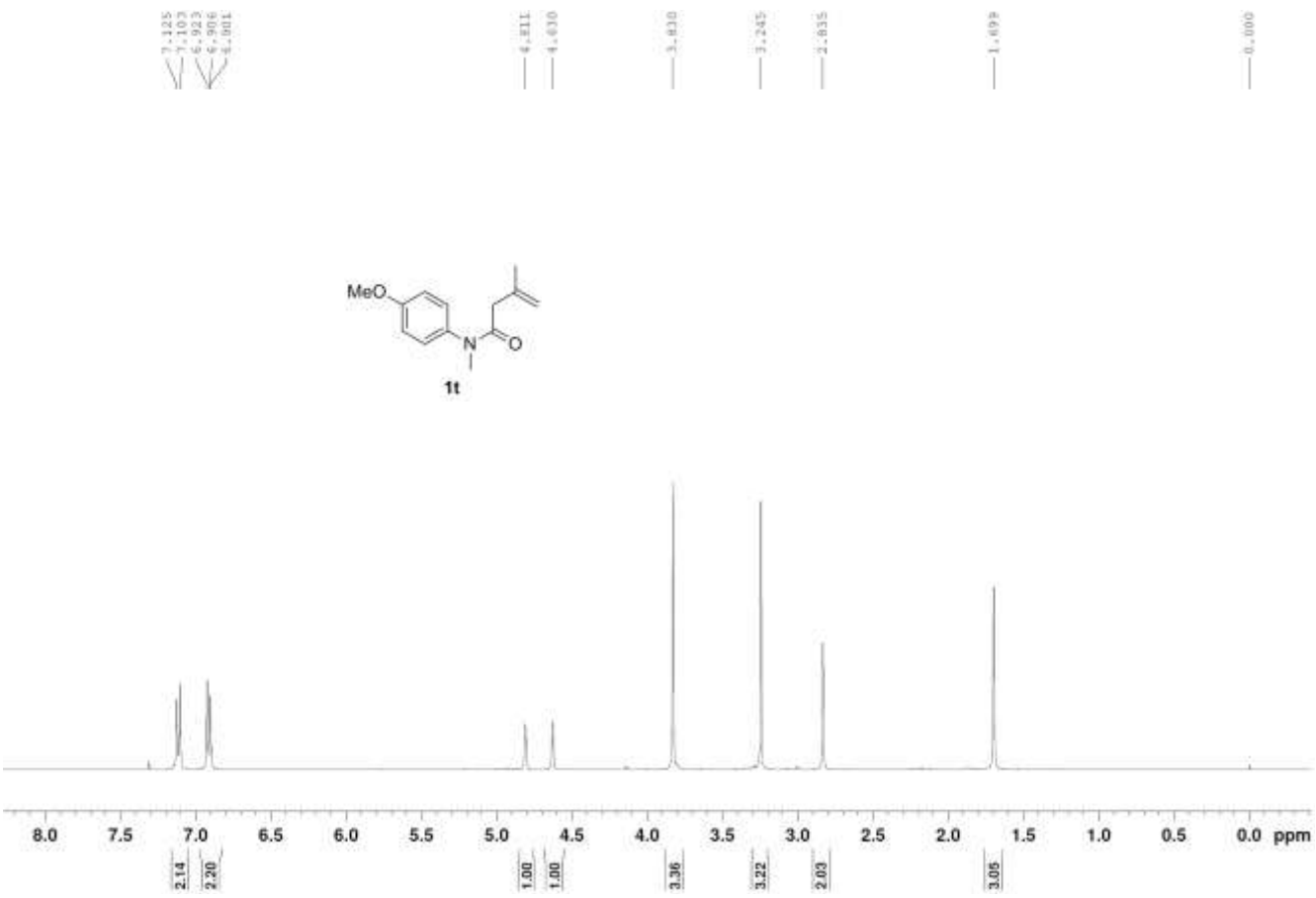

166.95
139.37
138.09
134.14
129.91
117.48
86.78
81.47
41.56
37.00
29.51
23.10
NO2
I
N
O
2x
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

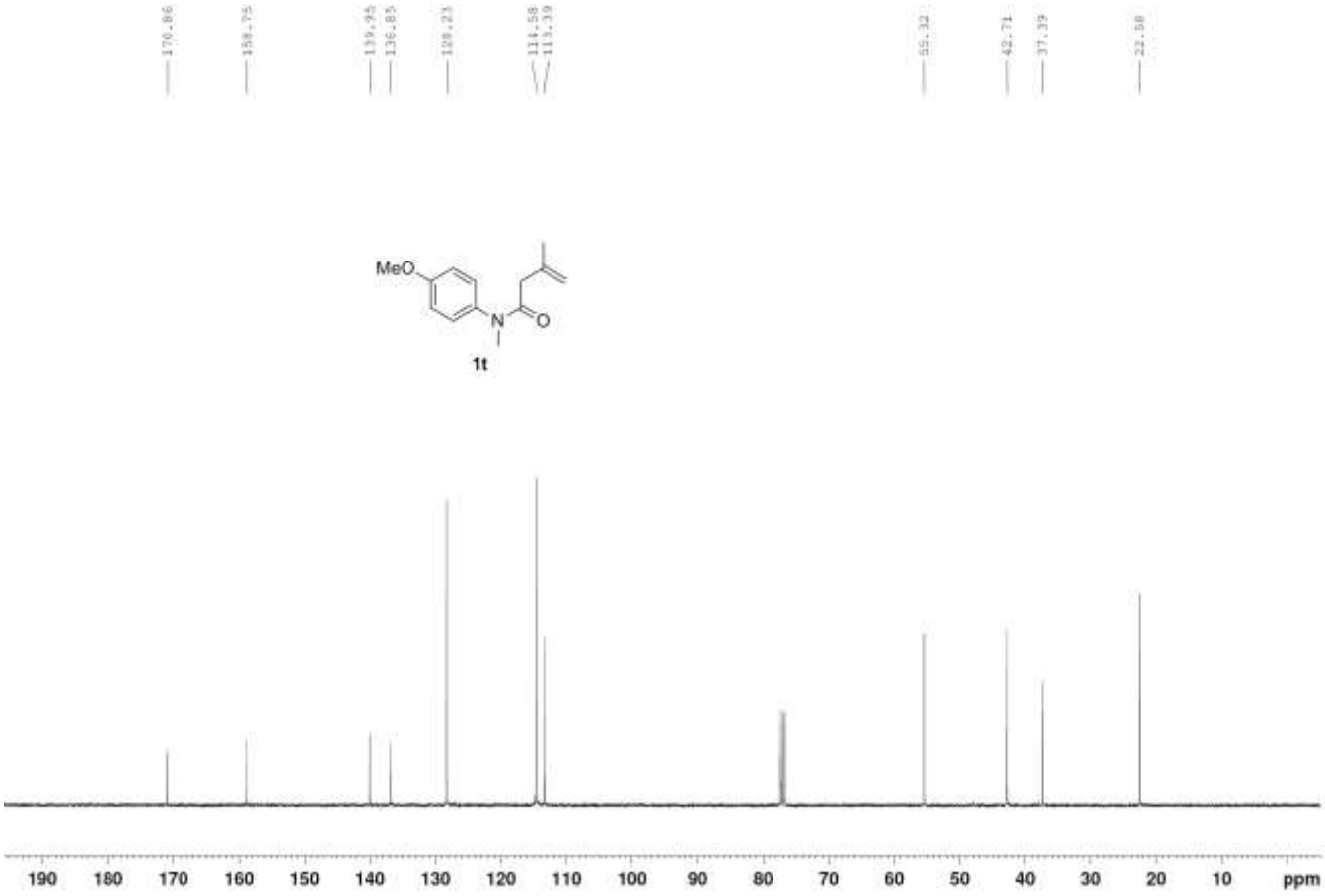

NO2
O
N
2y
1.00
3.09
1.01
0.98
1.06
1.06
3.01
3.89
f1 (ppm)

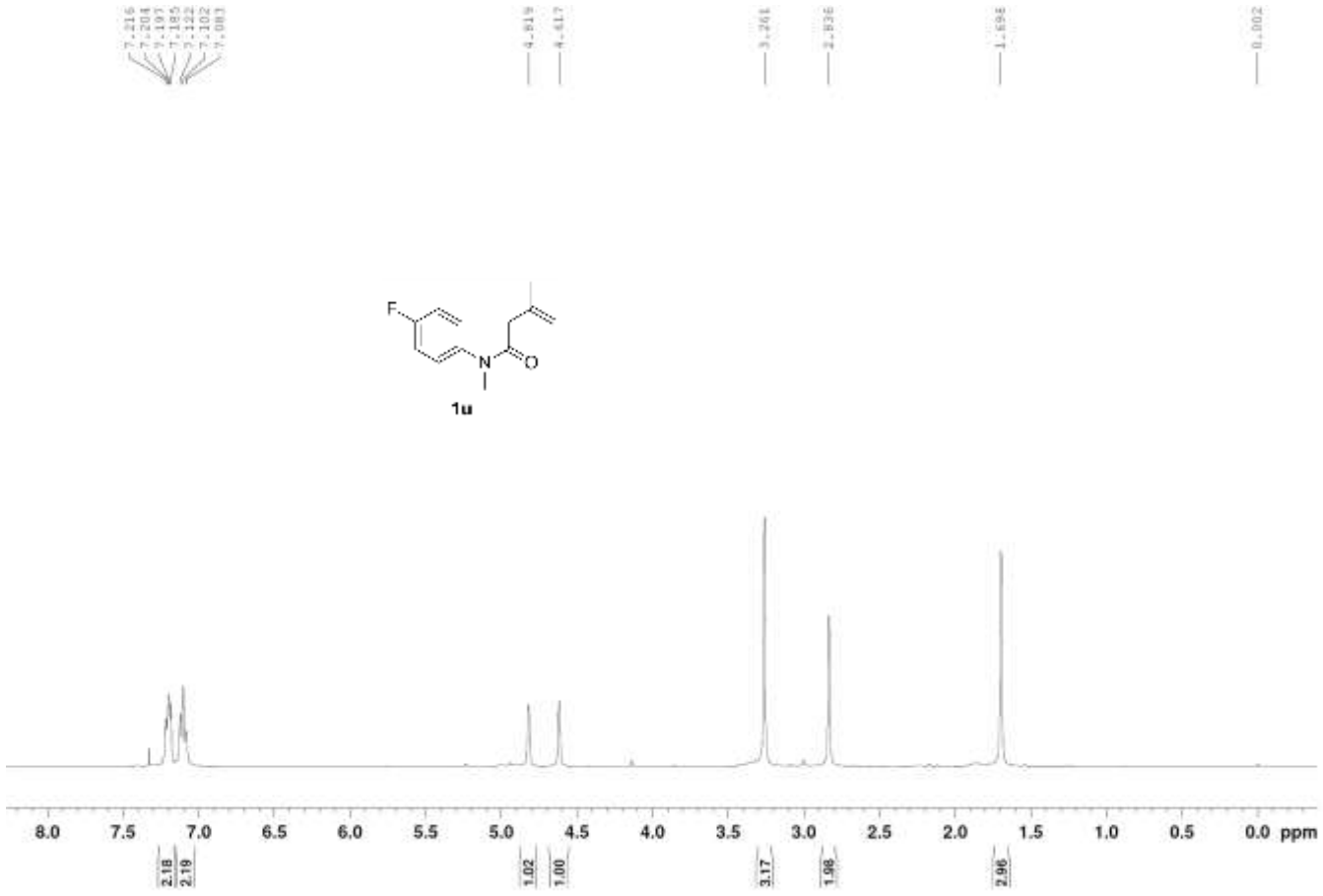

NO2
O
N
2y
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

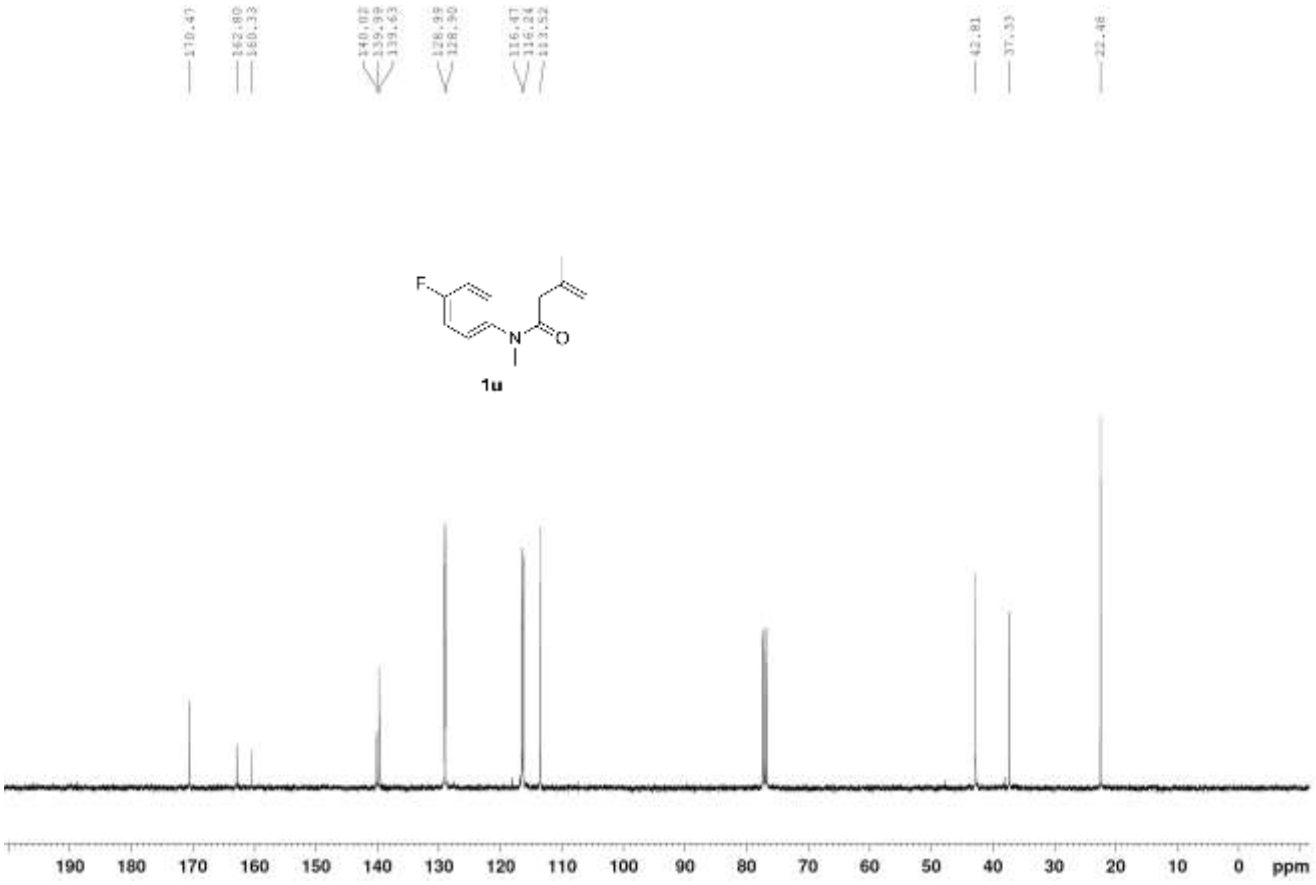

N
O
1s
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.16
2.13
1.02
0.99
3.16
2.00
3.33
3.02

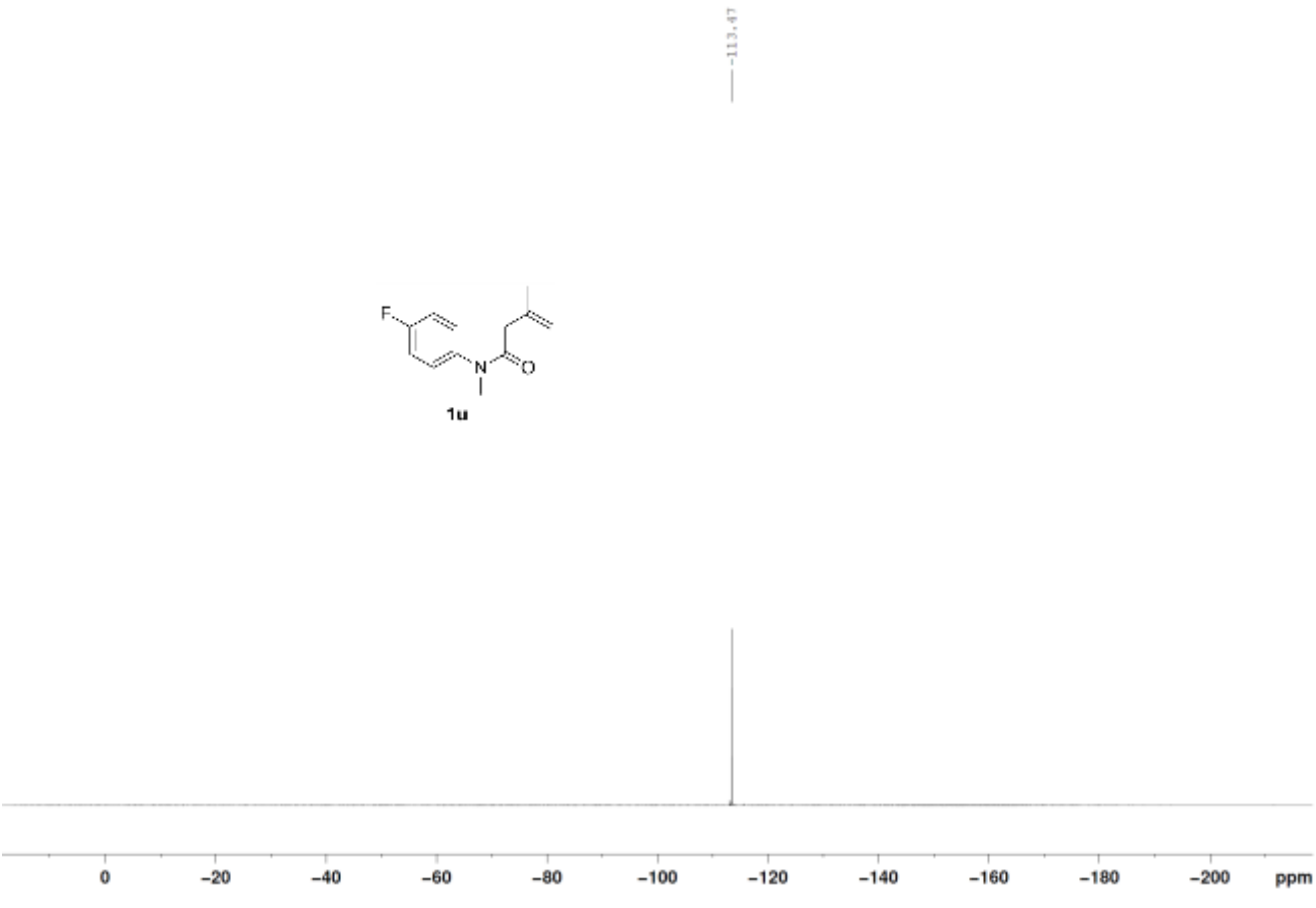

170.74
141.96
140.03
137.61
130.15
126.96
113.52
42.77
37.36
22.64
20.98
1s
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

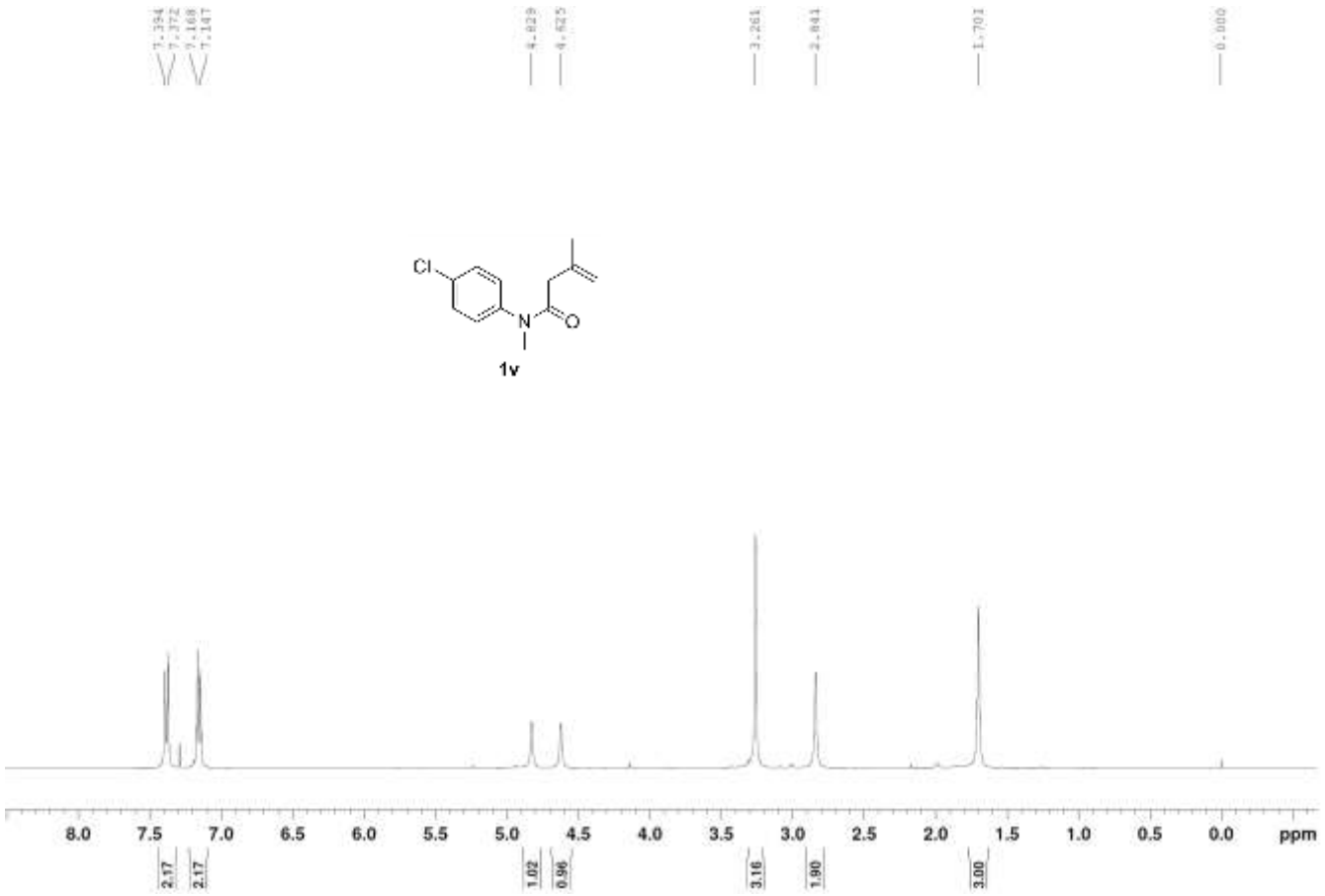

7.125
7.103
6.923
6.906
6.001
4.811
4.630
3.830
3.245
2.835
1.699
0.000
MeO
1t
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.14
2.20
1.00
1.00
3.36
3.22
2.03
3.05

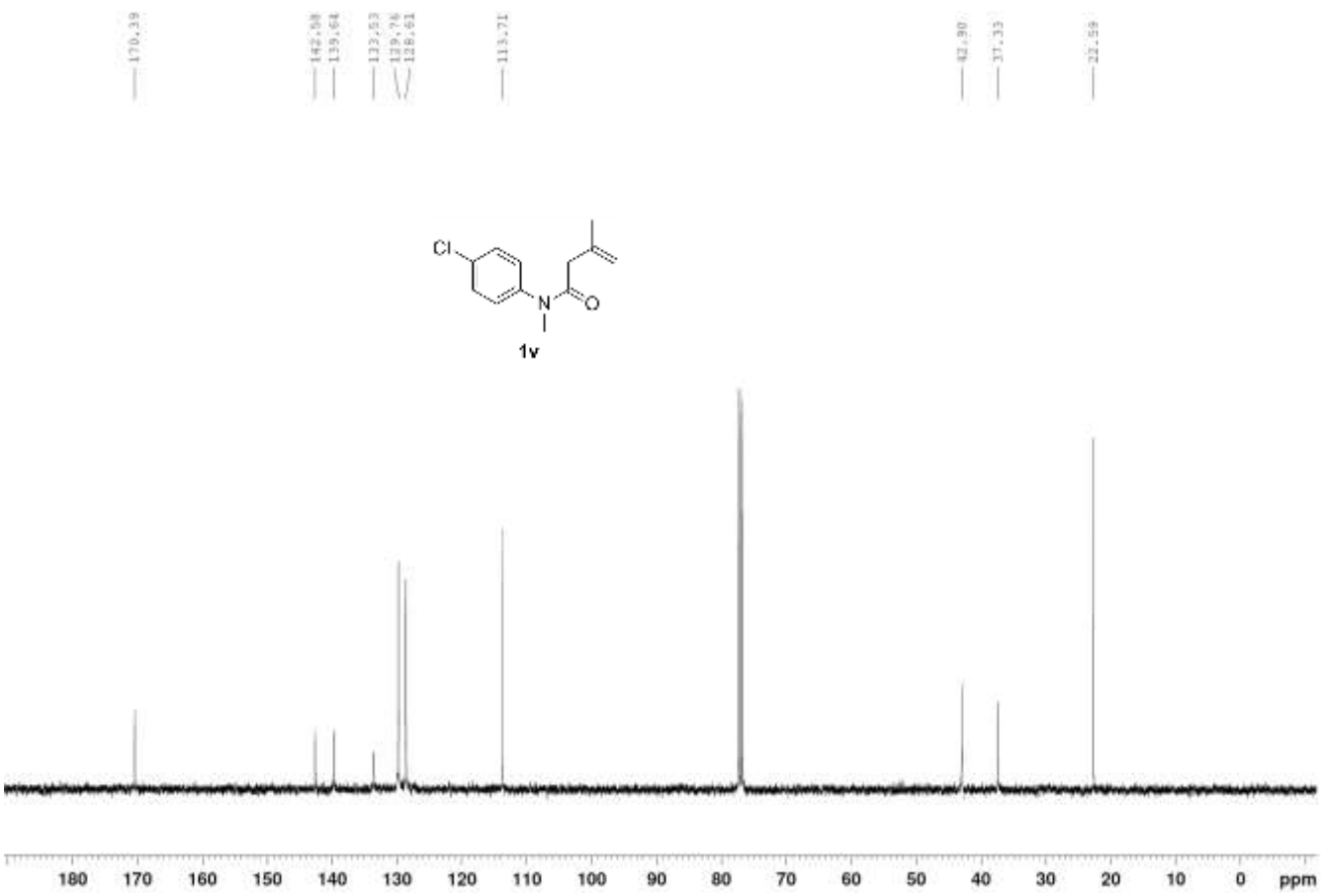

170.86
158.75
139.95
136.85
128.23
114.58
113.39
55.32
42.71
37.39
22.58
MeO
N
O
1t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

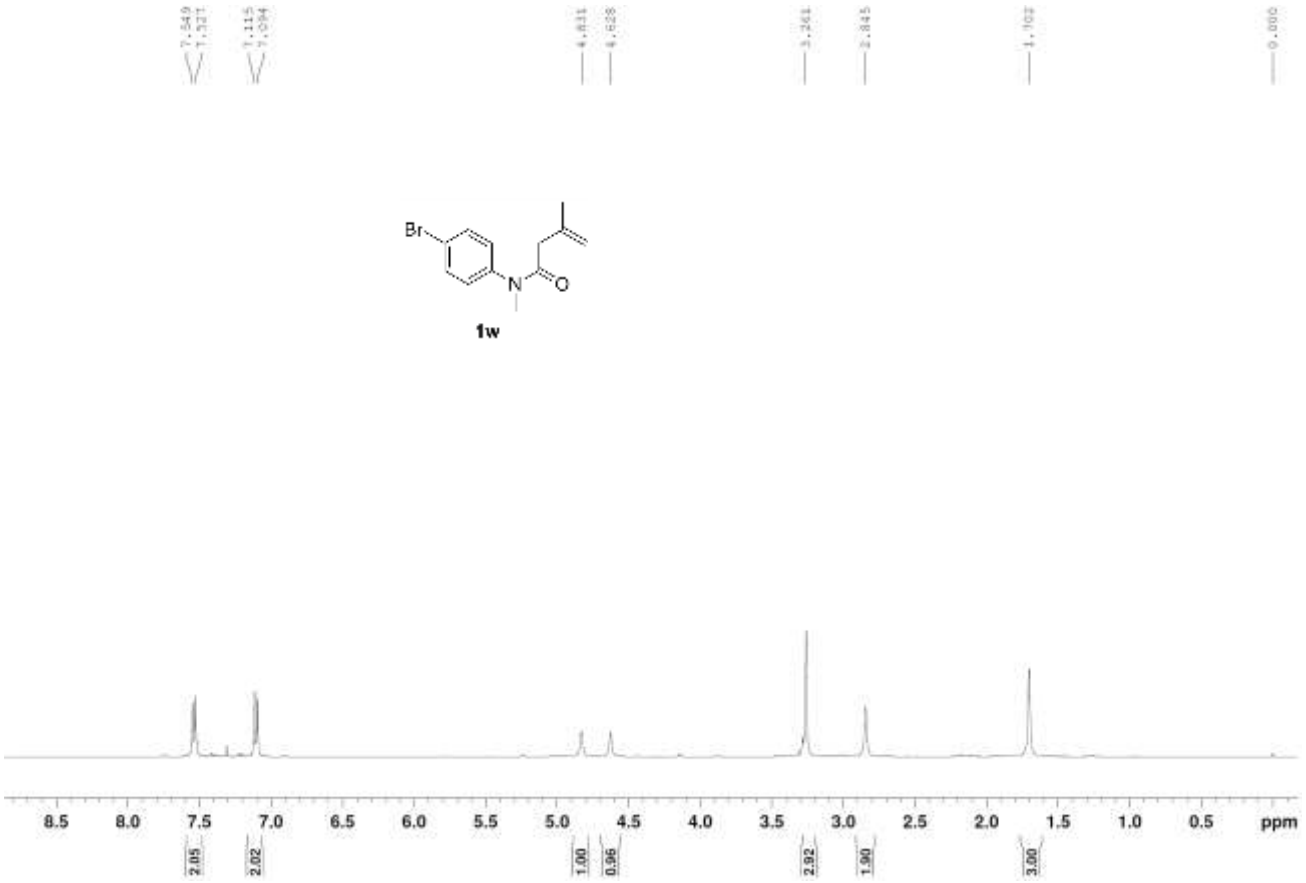

7.216
7.204
7.197
7.185
7.122
7.102
7.083
4.819
4.417
3.261
2.836
1.698
0.002
F
N
O
1u
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.18
2.19
1.02
1.00
3.17
1.98
2.96

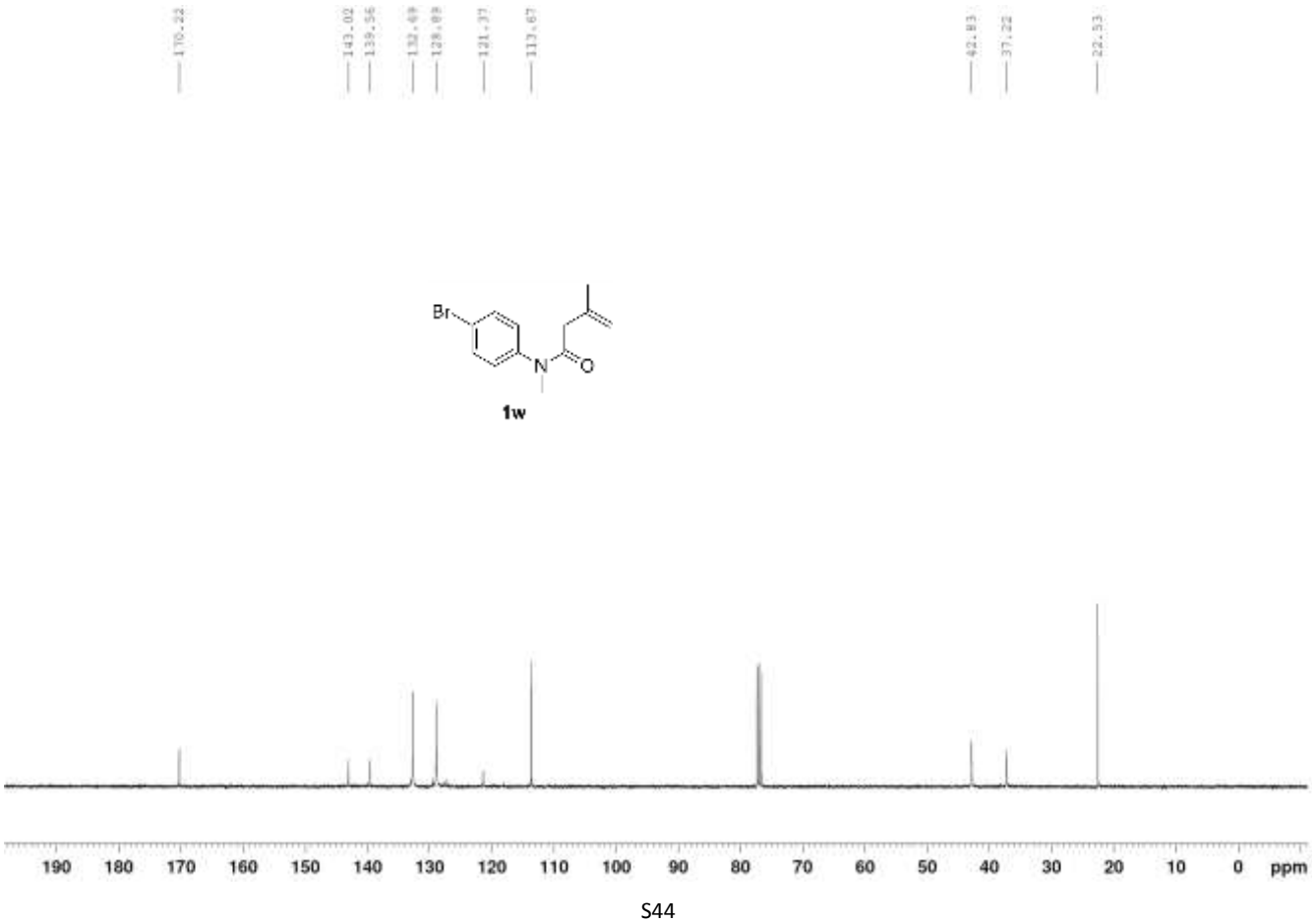

170.47
162.80
160.33
140.02
139.99
139.63
128.98
128.90
116.47
116.24
113.52
42.81
37.33
22.46
F
N
O
1u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

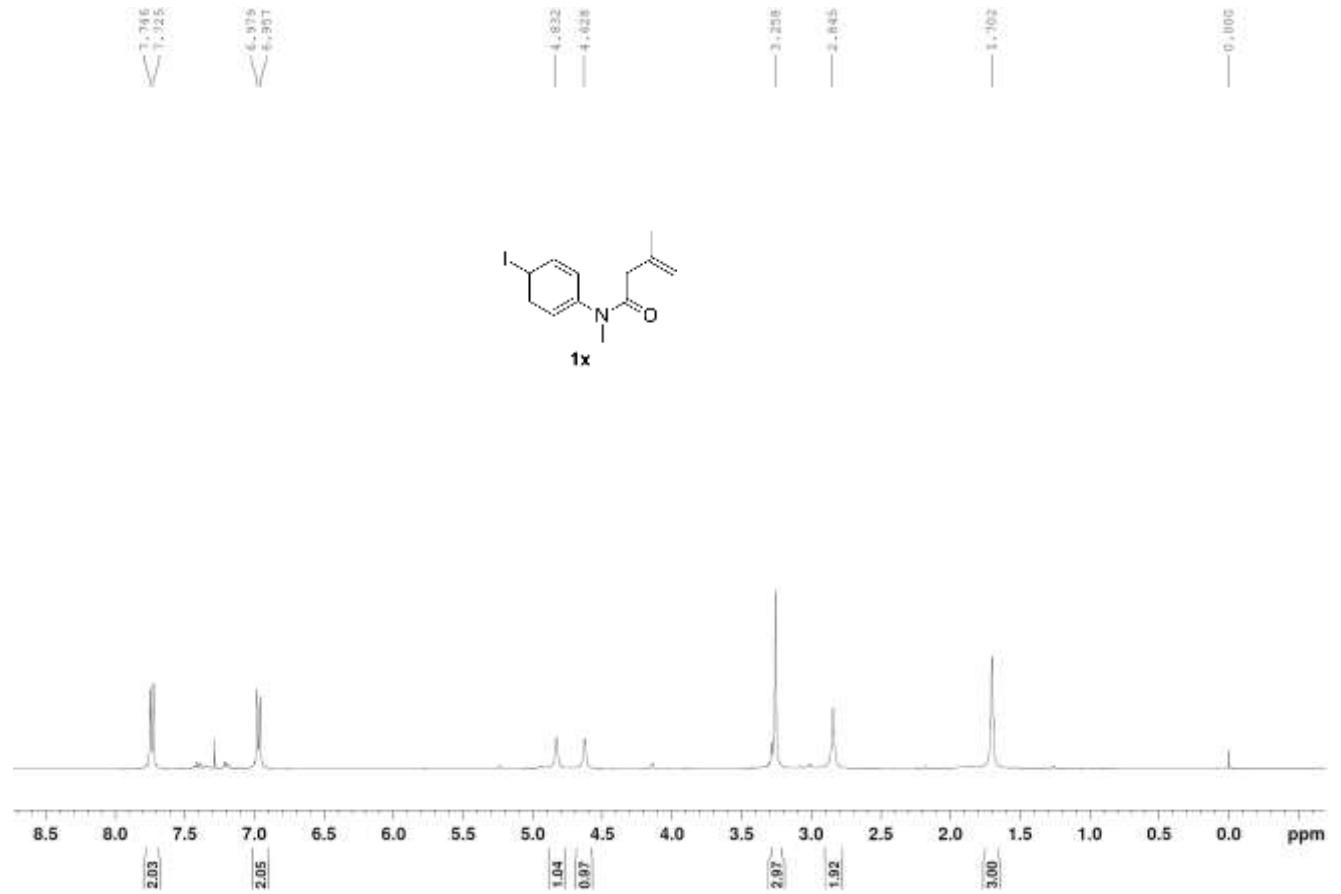

-113.47
F
N
O
1u
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

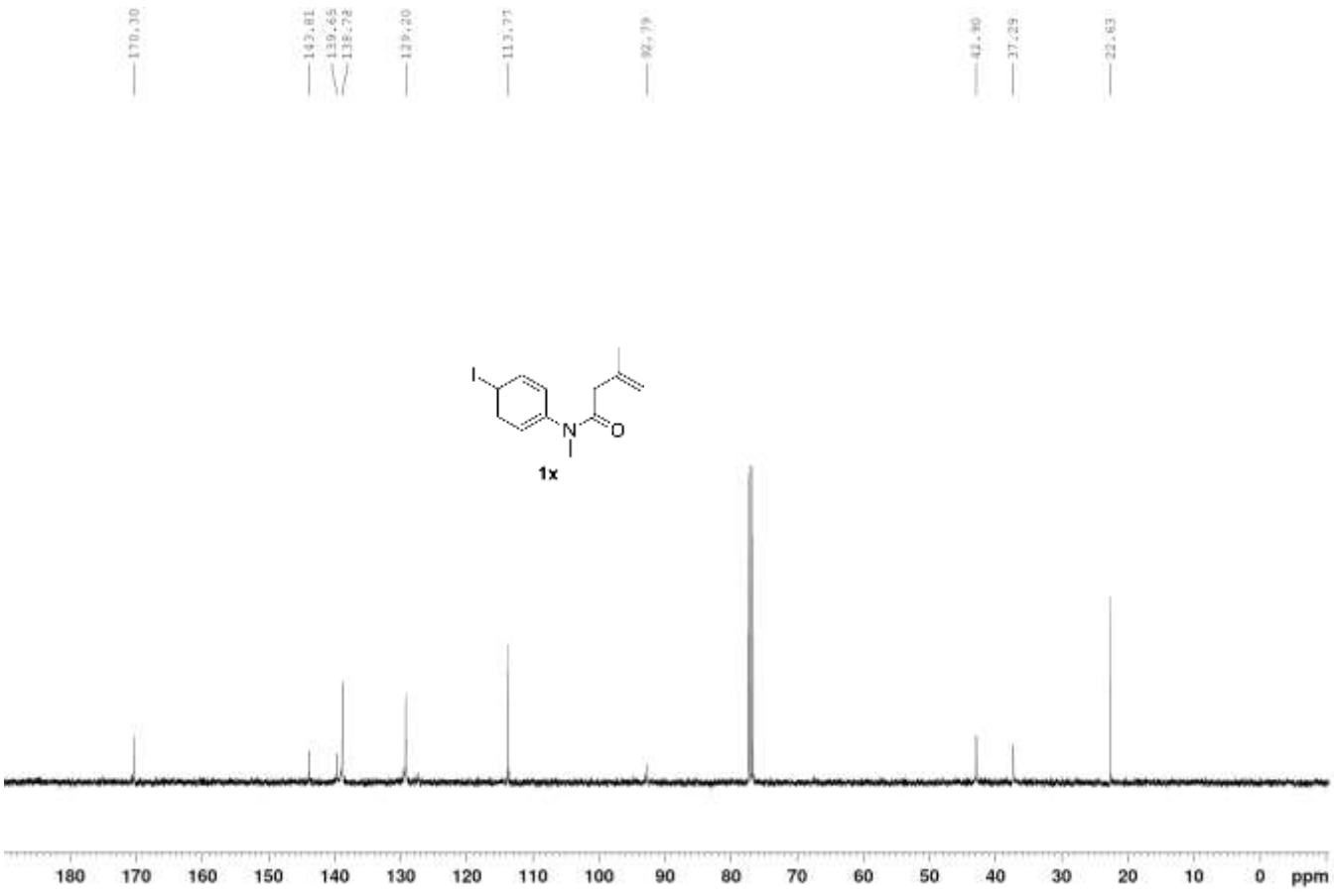

7.394
7.372
7.168
7.147
4.829
4.625
3.261
2.641
1.701
0.000
Cl
N
O
1v
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.17
2.17
1.02
0.96
3.16
1.90
3.00

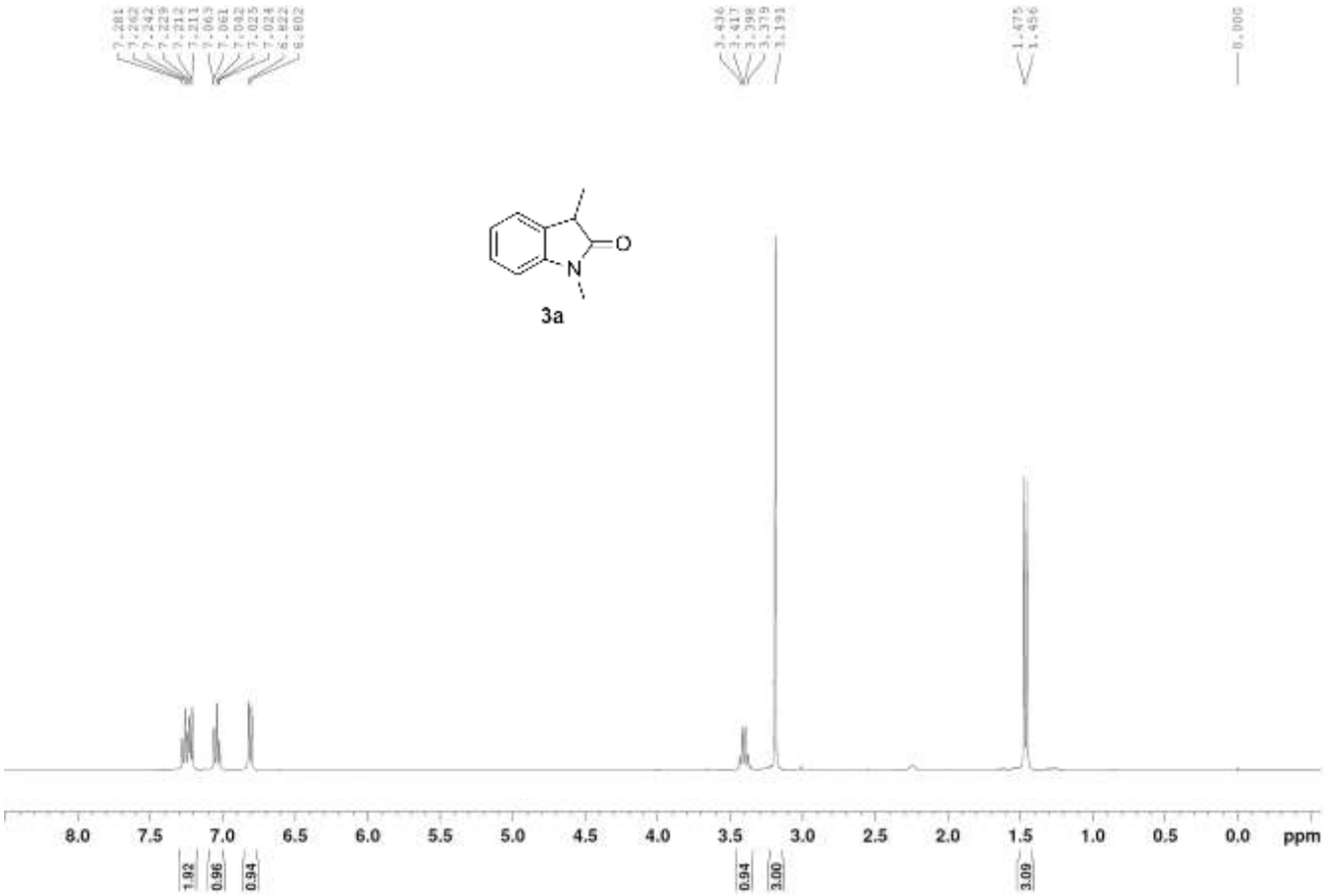

170.39
142.98
139.64
133.53
129.76
128.61
113.71
42.90
37.33
22.59
Cl
N
O
1v
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

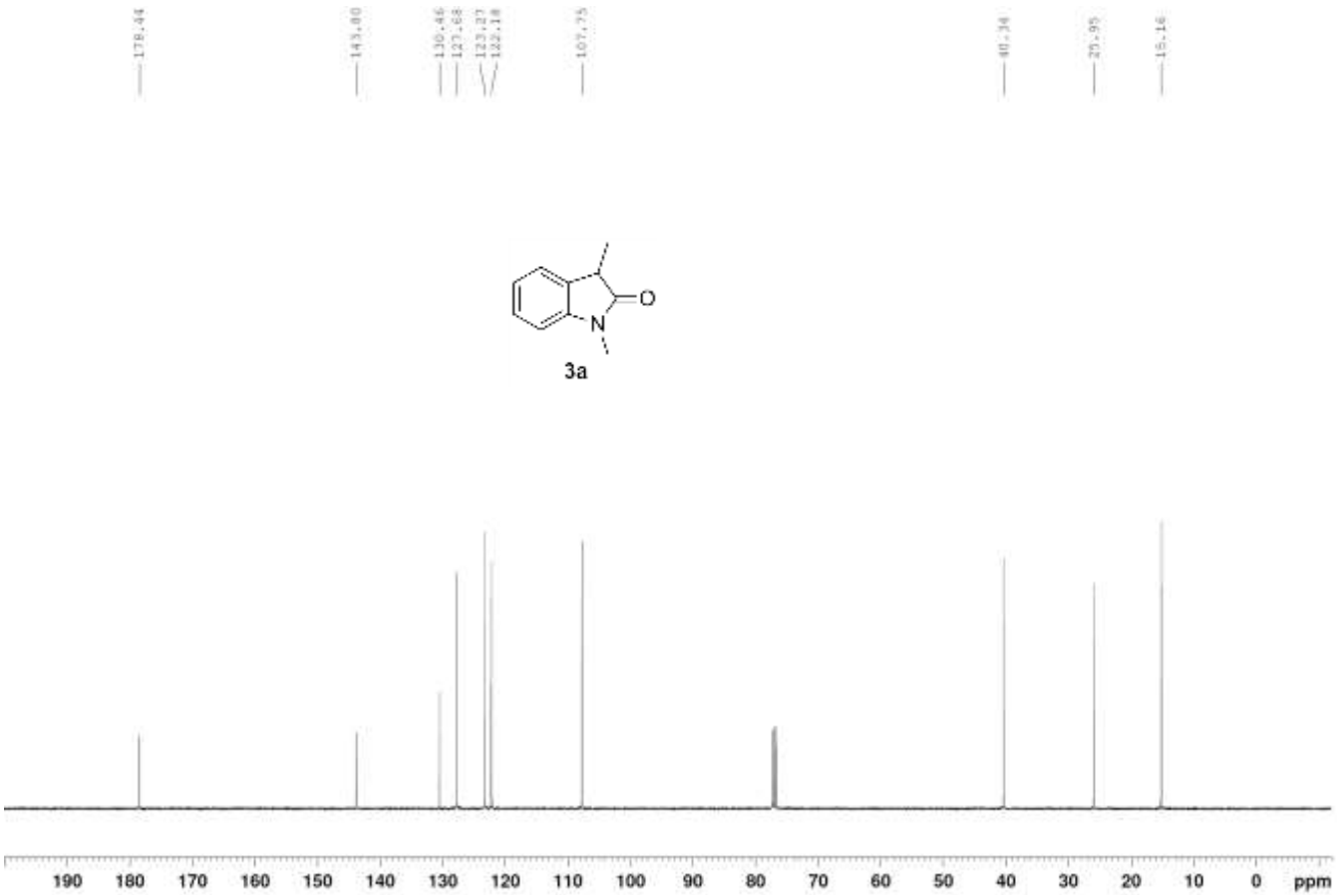

7.549
7.537
7.115
7.094
4.631
4.628
3.261
2.845
1.702
0.000
Br
N
O
1w
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.05
2.02
1.00
0.96
2.92
1.90
3.00


170.22
143.02
139.56
132.69
128.89
121.37
113.67
42.83
37.22
22.53
Br
N
O
1w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.746
7.725
6.979
6.957
4.832
4.628
3.258
2.845
1.702
0.000
I
N
O
1x
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
ppm
2.03
2.05
1.04
0.97
2.97
1.92
3.00


170.30
143.81
139.65
138.78
129.20
113.77
92.79
42.90
37.29
22.63
I
N
O
1x
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.281
7.262
7.242
7.229
7.212
7.211
7.063
7.061
7.042
7.025
7.024
6.822
6.802
3.436
3.417
3.398
3.379
3.191
1.475
1.456
0.000
O
N
3a
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
ppm
1.92
0.96
0.94
0.94
3.00
3.09


178.44
143.60
130.46
127.68
123.27
122.18
107.75
40.34
25.95
15.16
O
N
3a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm