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

Silver-catalyzed nitrosation and nitration of aromatic amides using $NOBF_4$

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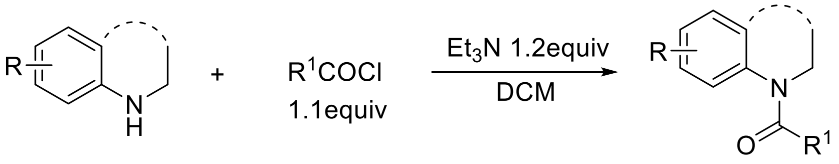
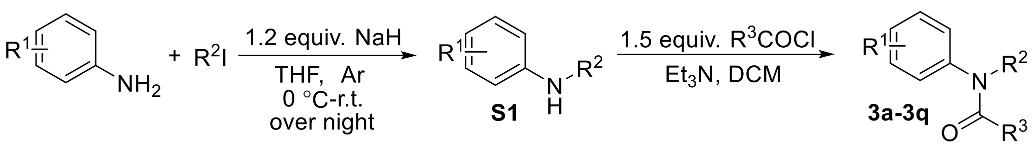
I. General Remarks: Column chromatography was carried out on silica gel. Unless noted ^1H NMR spectra were recorded on 400 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$, ^{19}F NMR spectra were recorded on 376 MHz in $CDCl_3$. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1} . Melting points were determined on a microscopic apparatus and were uncorrected. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra was obtained on a micrOTOF-Q instrument equipped with an ESI source; copies of their ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra are provided. All solvents were distilled from appropriate drying agents prior to use or directly taken from commercial sealed bottles. All reagents were used as received unless otherwise stated. Coupling constants are quoted in Hz (J). ^1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q) as they appeared in the spectrum. If the appearance of a signal differs from the expected splitting pattern, the observed pattern is designated as apparent (app)

II. Preparation of Starting Materials 1a-1f, 3a-3q, 5a-5p



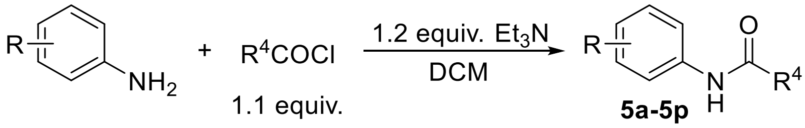
1a-1f

For preparation of **1a-1f** from the corresponding arylamines and acyl chloride. To a solution of arylamine (5 mmol) and triethylamine (0.83 mL, 6 mmol) in dichloromethane (10 mL), acyl chloride (1.1equiv) was added dropwise at 0 °C. After stirring at room temperature for 5 h, the reaction mixture was quenched with water and extracted by DCM for three times. The combined extracts were washed with brine and dried over Na_2SO_4, After removal of the solvent under reduced pressure, the residue was purified by recrystallization with petroleum ether/CH_2Cl_2, to obtain the desired products.



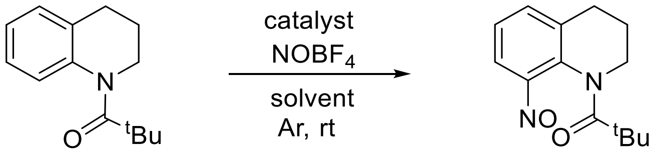
Under Ar atmosphere，aniline (5.0 mmol, 1.0 equiv) dissolved in 5 mL THF was added to a suspension of sodium hydride (144 mg, 6.0 mmol, 1.2 equiv.) in 10 mL THF at 0℃ and stirred for 30 min at 50°C. Then alkyl iodide (6.0 mmol, 1.2 equiv.) in THF (5 mL) was added at 0°C, and the mixture was stirred overnight at 50°C. The reaction mixture was cooled in an ice bath and was slowly quenched with water (10-15 mL). The aqueous phase was extracted with ethyl acetate (3 x 20 mL) and the combined organic phases were dried over Na_2SO_4 and volatiles were removed under reduced pressure. The crude oil obtained was further purified by silica gel column chromatography to obtain raw material **S1**.

To the solution of **S1** (1.0 equiv.) in DCM (0.5 M) was added R^3COCl (1.5 equiv.) and Et_3N (1.5 equiv.) at 0°C. After stirring for 6 h, the reaction mixture was quenched with water and extracted by DCM for three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by recrystallization with petroleum ether/CH_2Cl_2, to obtain the desired products **3a-3q**.



For preparation of **5a-5p** from the corresponding arylamines and acyl chloride. To a solution of arylamine (10 mmol) and triethylamine (1.66 mL, 12 mmol) in dichloromethane (20 mL), acyl chloride (1.1equiv) was added dropwise at 0 °C. After stirring at room temperature for 5 h, the reaction mixture was quenched with water and extracted by ethyl acetate for three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by recrystallization with petroleum ether/CH_2Cl_2, to obtain the desired products.

III. Table S1. Screening of reaction conditions [a]



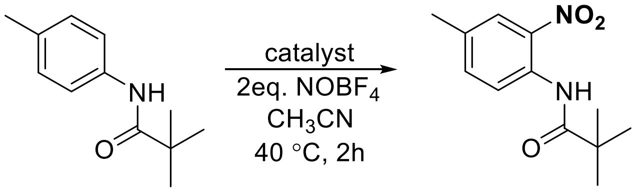
1 **2**

Entry	Catalyst	Solvent	Yield (%)[b]
1	CuBr	CH_3CN (2.0 mL)	<5%
2	CuCl	CH_3CN (2.0 mL)	<5%
3	$FeBr_2$	CH_3CN (2.0 mL)	<5%
4	$AgNO_3$	CH_3CN (2.0 mL)	68%
5	AgOTf	CH_3CN (2.0 mL)	11%
6	AgOAc	CH_3CN (2.0 mL)	12%
7	$AgBF_4$	CH_3CN (2.0 mL)	43%
8[c]	$AgNO_3$	CH_3CN (2.0 mL)	<5%
9[d]	$AgNO_3$	CH_3CN (2.0 mL)	20%
10	$AgNO_3$	CH_3CN (1.0 mL)	43%
11	$AgNO_3$	CH_3CN (3.0 mL)	60%
12[e]	$AgNO_3$	CH_3CN (2.0 mL)	69%
13[f]	**$AgNO_3$**	**CH_3CN** (2.0 mL)	**71%**
14[f]	$AgNO_3$	DCE (2.0 mL)	<5%
15[f]	$AgNO_3$	THF (2.0 mL)	<5%
16[f]	$AgNO_3$	CH_3NO_2 (2.0 mL)	10%

17[f]	$AgNO_3$	EtOAc (2.0 mL)	33%

[a]Reaction conditions: **1** (0.1 mmol), catalyst (20 mmol%), $NOBF_4$ (2eq, dropwise added in 10 min), solvent (2.0 mL), rt, under Ar atmosphere, 1-2 h. [b] Isolated yield. [c]$NOBF_4$ was added directly. [d]10 mmol% catalyst was used. [e]dropwise added in 30 min. [f]dropwise added in 60 min.

Table S2. Screening of reaction conditions [a]

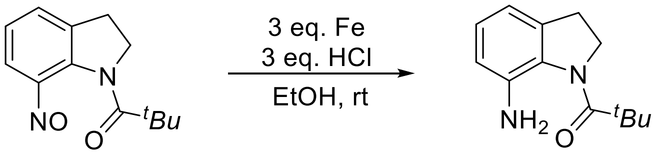


5a **6a**

Entry	Catalyst	Solvent	Yield (%)[b]
1	$AgNO_3$ (20%)	CH_3CN (2.0 mL)	77%
2	$AgNO_3$ (15%)	CH_3CN (2.0 mL)	65%
3	$AgNO_3$ (10%)	CH_3CN (2.0 mL)	55%

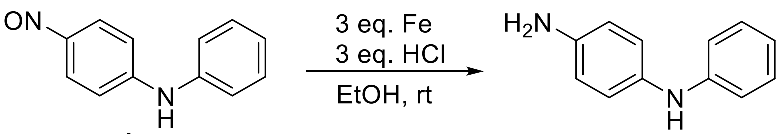
[a]Reaction conditions: **5a** (0.1 mmol), catalyst (10-20 mmol%), $NOBF_4$ (2eq, dropwise added in 1 h), solvent (2.0 mL), 40℃, 2 h. [b] Isolated yield.

IV. Reduction experiment



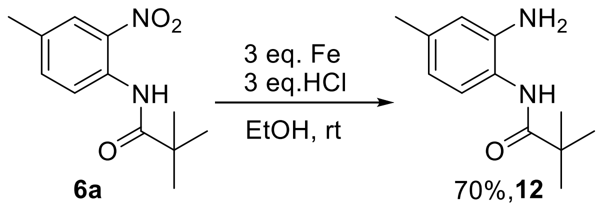
2e 71%,**10**

Under Ar atmosphere, substrate **2e** (0.3 mmol) and Fe powder (3 equiv.) were added to the reaction tube, 3mL EtOH was added, and finally HCl (3 equiv.) was slowly added under an ice water bath. The reaction was stirred for 4 h. The solution was transferred into a separatory funnel and sequentially washed with H_2O and brine. The combined organic extracts dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the desired reduce product **10** (47 mg, 71%).



4m 80% **11**

Under Ar atmosphere, substrate **4m** (0.3 mmol) and Fe powder (3 equiv.) were added to the reaction tube, 3mL EtOH was added, and finally HCl (3 equiv.) was slowly added under an ice water bath. The reaction was stirred for 4 h. The solution was transferred into a separatory funnel and sequentially washed with H_2O and brine. The combined organic extracts dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the desired reduce product **11** (44mg, 80%).



Under Ar atmosphere, substrate **6a** (0.3 mmol) and Fe powder (3 equiv.) were added to the reaction tube, 3mL EtOH was added, and finally HCl (3 equiv.) was slowly added under an ice water bath. The reaction was stirred for 4 h. The solution was transferred into a separatory funnel and sequentially washed with H_2O and brine. The combined organic extracts dried over Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography afforded the desired reduce product **12** (43mg, 70%).

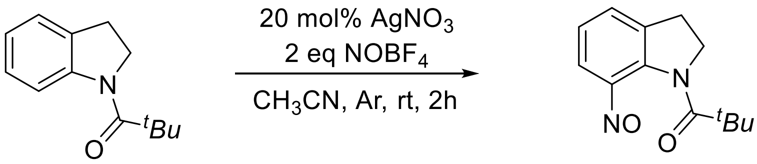
V. General Procedure for the synthesis of products 2, 4, 6, 7a, 8a, 9a

Under Ar atmosphere, Substrate **1** (0.3 mmol) and 20%mmol silver nitrate were added to the reaction tube, and then 2.0 equiv. of $NOBF_4$ was dissolved in CH_3CN (6 mL) and slowly added to the reaction tube at room temperature for one hour. After the reaction, the reaction system was quenched with water, extracted three times with ethyl acetate (3×10 mL), and dried with anhydrous sodium sulfate. Combined with the organic layer, the crude product was concentrated under reduced pressure and purified by silica gel column chromatography to give product **2**.

Under Ar atmosphere, substrate **3** (0.3 mmol) and 20%mmol silver nitrate were added to the reaction tube, and then 2.0 equiv. of $NOBF_4$ was dissolved in CH_3CN (6 mL) and slowly added to the reaction tube at room temperature for one hour. After the reaction, the reaction system was quenched with water, extracted three times with ethyl acetate (3×10 mL), and dried with anhydrous sodium sulfate. Combined with the organic layer, the crude product was concentrated under reduced pressure and purified by silica gel column chromatography to give product **4.**

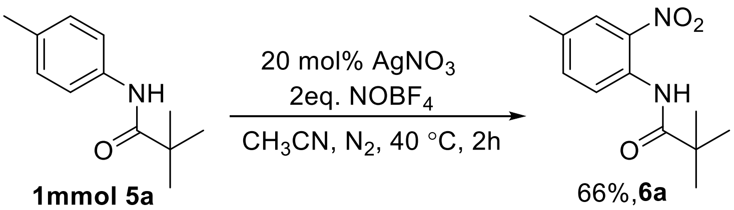
Under N_2 atmosphere, substrate **5** (0.3 mmol) and 20%mmol silver nitrate were added to the reaction tube, and then 2.0 equiv. of $NOBF_4$ was dissolved in CH_3CN (6 mL) and slowly added to the reaction tube at room temperature for 1 hour. After the reaction was carried out in 40 °C for another 1 hour, the reaction system was quenched with water, extracted three times with ethyl acetate (3×10 mL), and dried with anhydrous sodium sulfate. Combined with the organic layer, the crude product was concentrated under reduced pressure and purified by silica gel column chromatography to give product **6, 7a, 8a, 9a**.

Ⅵ. Scale-up experiment



1 mmol, **1e** 73%, **2e**

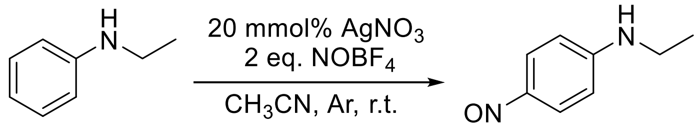
We carried out a scale-up experiment on the basis of the above reaction conditions, with substrate **1e** (1 mmol, 203 mg), silver nitrate (20 mol%, 34 mg), $NOBF_4$ (234 mg), solvent acetonitrile (10 mL) to explore the scale-up experiment. After the reaction, a 73% yield of target product **2e** (170 mg) was obtained.



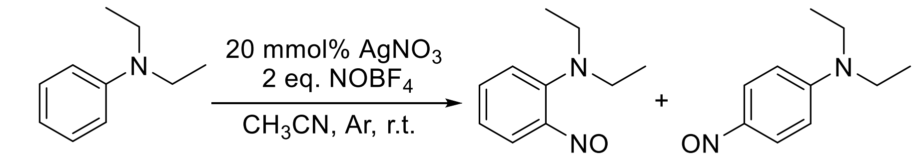
1mmol 5a 66%,**6a**

We also carried out a scale-up experiment on the basis of the above reaction conditions, with substrate **5a** (1 mmol, 191 mg), silver nitrate (20 mol%, 34 mg), $NOBF_4$ (234 mg), solvent acetonitrile (10 mL) to explore the scale-up experiment. After the reaction, a 66% yield of target product **6a** (157 mg) was obtained.

VII. Control experiments



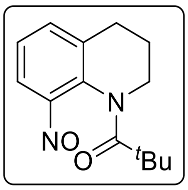
N-ethylaniline **4e**, trace



N,*N*-diethylaniline **13, 32%** **13', 47%**

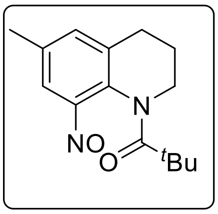
In order to insight into the possible mechanism, some control experiments were carried out. When substrate *N*-ethylaniline was submitted into the standard conditions, only trace amount of **4e** was observed. While, electron-rich substrate *N*,*N*-diethylaniline delivered *ortho*-substituted and *para*-substituted products **13** and **13’** in moderate yields.

VIII. Date of products 2, 4, 6, 7a, 8a, 9a, 10, 11, 12, 13, 13’



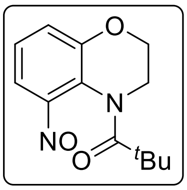
2,2-dimethyl-1-(8-nitroso-3,4-dihydroquinolin-1(2H)-yl)propan-1-one, **2a**, 70%, M.P.= 90-92 °C, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (d, J = 2.8 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.60 (d, J = 9.2 Hz, 1H), 3.87 – 3.83 (m, 2H), 2.93 (t, J = 7.0 Hz, 2H), 2.10 – 2.01 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 178.85, 146.35, 143.59, 130.64, 126.14, 124.55, 120.74, 45.49, 40.41, 28.56, 26.38, 23.25. IR(cm^{-1}): 2930, 1659, 1583, 1515, 1479, 1400, 1337, 1279, 1261, 1153, 1109, 956, 924, 869, 801. HRMS (ESI) m/z calcd for $C_{14}H_{19}N_2O_2^+$ (M+H)$^+$ 247.1441, found 247.1442.



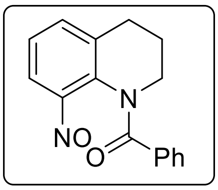
2,2-dimethyl-1-(6-methyl-8-nitroso-3,4-dihydroquinolin-1(2H)-yl)propan-1-one, **2b**, 75%, M.P. = 126-128 °C, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.54 – 7.49 (m, 1H), 7.18 – 7.12 (m, 1H), 4.61 – 3.24 (m, 2H), 2.83 (t, J = 7.2 Hz, 2H), 2.34 (s, 3H), 2.07 (s, 2H), 1.35 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$): 177.30, 145.01, 134.97, 134.32, 133.39, 131.23, 122.64, 44.65, 39.24, 27.93, 25.89, 23.92, 20.56. IR (cm^{-1}): 2926, 1693, 1533, 1449, 1476, 1401, 1356, 1201, 1154, 1102, 978, 954, 869, 757, 580. HRMS (ESI) m/z calcd for $C_{15}H_{21}N_2O_2^+$ (M+H)$^+$ 261.1598, found 261.1597.



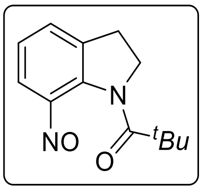
2,2-dimethyl-1-(5-nitroso-2,3-dihydro-4H-benzo[b][1,4]oxazin-4-yl)propan-1-one, **2c**, 76%, M.P. = 127-129 °C, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (d, J = 9.2 Hz, 1H), 7.76 – 7.70 (m, 2H), 4.40 – 4.35 (m, 2H), 4.06 – 4.01 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$): 176.97, 146.46, 144.20, 132.71, 125.49, 115.07, 112.79, 66.08, 44.03, 40.05, 28.26. IR(cm^{-1}): 3072, 2968, 1667, 1609, 1588, 1518, 1492, 1388, 1338, 1319, 1290, 1251, 1170, 1083, 1054, 944, 900, 818, 765, 748, 722, 560. HRMS (ESI) m/z calcd for $C_{13}H_{17}N_2O_3^+$ (M+H)$^+$ 249.1234, found 249.1235.

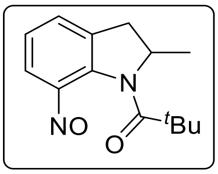


(8-nitroso-3,4-dihydroquinolin-1(2H)-yl)(phenyl)methanone, **2d**, 60%, M.P. = 131-133 °C, white solid.

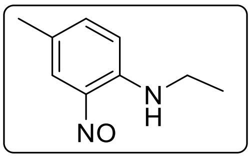
^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, J = 2.7 Hz, 1H), 7.76 (dd, J = 9.0, 2.7 Hz, 1H), 7.51 – 7.30 (m, 5H), 6.98 (d, J = 9.0 Hz, 1H), 3.93 (t, J = 6.3 Hz, 2H), 2.96 (t, J = 6.6 Hz, 2H), 2.09 (p, J = 6.5 Hz, 2H). ^{13}C NMR (100MHz, $CDCl_3$): 170.87, 145.14, 143.53, 135.26, 131.19, 131.06, 128.55, 128.49, 125.14, 124.23, 121.23, 45.42, 27.24, 23.27. IR(cm^{-1}): 2922, 1653, 1611, 1583, 1546, 1513, 1490, 1331, 1280, 1195, 1179, 1131, 1076, 791, 723, 705. HRMS (ESI) m/z calcd for $C_{16}H_{15}N_2O_2^+$ (M+H)$^+$ 267.1128, found 267.1129.



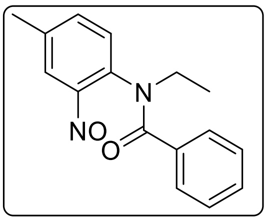
2,2-dimethyl-1-(7-nitrosoindolin-1-yl)propan-1-one, **2e**, 83 %, M.P. = 114-116 °C, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.31 (d, J = 9.0 Hz, 1H), 8.12 – 8.08 (m, 1H), 8.03 (d, J = 2.4 Hz, 1H), 4.37 (t, J = 8.4 Hz, 2H), 3.27 – 3.21 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 177.44, 150.36, 143.37, 131.97, 124.30, 119.80, 117.48, 50.09, 40.53, 28.55, 27.47. IR(cm^{-1}): 2977, 2934, 1650, 1596, 1515, 1476, 1446, 1403, 1370, 1339, 1248, 1159, 1089, 936, 903, 831, 751, 615. HRMS (ESI) m/z calcd for $C_{13}H_{17}N_2O_2^+$ (M+H)$^+$ 233.1285, found 233.1286.



2,2-dimethyl-1-(2-methyl-7-nitrosoindolin-1-yl)propan-1-one, **2f**, 71%, oil.
^{1}H NMR (400 MHz, $CDCl_3$): 8.22 (d, J = 8.9 Hz, 1H), 8.12 (dd, J = 8.8, 2.9 Hz, 1H), 8.09 (s, 1H), 5.08 – 4.92 (m, 1H), 3.39 (dd, J = 15.5, 7.8 Hz, 1H), 2.74 (d, J = 15.5 Hz, 1H), 1.41 (s, 9H), 1.31 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 177.16, 148.88, 143.57, 131.81, 124.09, 120.39, 118.39, 57.04, 40.95, 36.22, 28.21, 21.85. IR(cm^{-1}): 2971, 1657, 1598, 1514, 1497, 1379, 1324, 1297, 1250, 1191, 1159, 1065, 992, 861, 754. HRMS (ESI) m/z calcd for $C_{14}H_{19}N_2O_2^+$ (M+H)$^+$247.1441, found 247.1442.

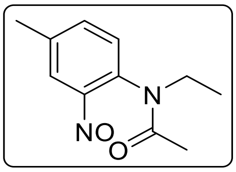


N-ethyl-4-methyl-2-nitrosoaniline, 4a, 61 %, M.P. = 109-111 °C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): 7.9 – 7.9 (m, 1H), 7.8 (s, 1H), 7.2 (dd, J = 8.8, 2.3 Hz, 1H), 6.7 (d, J = 8.7 Hz, 1H), 3.3 – 3.2 (m, 2H), 2.2 (s, 3H), 1.3 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 142.78, 136.72, 130.35, 125.03, 123.59, 112.73, 36.68, 18.91, 13.42. IR(cm^{-1}): 3382, 2958, 2922, 2853, 1631, 1568, 1525, 1477, 1425, 1406, 1347, 1272, 1233, 1166, 1076, 966, 913, 801, 765, 529. HRMS (ESI) m/z calcd for $C_9H_{12}N_2O^+$ (M+H)$^+$ 165.1028, found 165.1025.

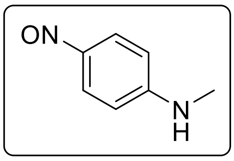


N-ethyl-N-(4-methyl-2-nitrosophenyl)benzamide, **4b**, 80%, oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.08 (m, 8H), 3.91 (m, 2H), 2.36 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 169.51, 145.75, 139.01 135.67, 134.52, 131.60, 129.82, 127.91, 125.93, 45.38, 20.81, 12.79. IR(cm^{-1}): 3058, 2976, 2933, 2872, 1651, 1615, 1600, 1567, 1530, 1498, 1445,

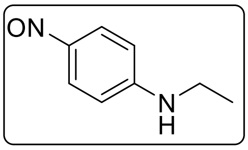
1384, 1350, 1309, 1146, 1122, 1082, 1033, 831, 803, 788, 761, 725, 699, 673, 632, 588. HRMS (ESI) m/z calcd for $C_{16}H_{17}N_2O_2^+$ $(M+H)^+$ 269.1285, found 269.1286.



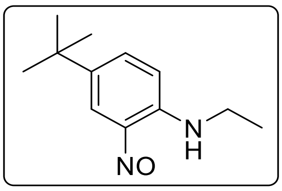
N-ethyl-N-(4-methyl-2-nitrosophenyl)acetamide, **4c**, 56%, oil.
^{1}H NMR (400 MHz, $CDCl_3$): 7.80 (d, J = 2.1 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 3.98 – 3.34 (m, 2H), 2.50 (s, 3H), 1.83 (s, 3H), 1.07 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 169.87, 146.94, 140.36, 134.70, 133.32, 131.58, 125.80, 43.90, 22.55, 20,95, 12.87. IR(cm-1): 2976, 2933, 1670, 1615, 1532, 1532, 1500, 1442, 1395, 1442, 1395, 1353, 1299, 1142, 1107, 1069, 835, 803, 564. HRMS (ESI) m/z calcd for $C_{11}H_{15}N_2O_2^+$ $(M+H)^+$ 207.1128, found 207.1129.



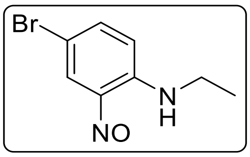
N-methyl-4-nitrosoaniline, **4d**, 59 %, M.P. = 94-96 °C, yellow solid. CAS:10595-51-4[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 – 8.26 (m, 2H), 7.72 – 7.67 (m, 2H), 3.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.05, 145.94, 125.27, 117.85, 30.06. IR (cm^{-1}): 3380, 2986, 2899, 1607, 1594, 1514, 1467, 1403, 1399, 1193, 1180, 1075, 939, 855, 813, 750.



N-ethyl-4-nitrosoaniline, **4e**, 70 %, M.P. = 98-101 °C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 9.2 Hz, 2H), 6.51 (d, J = 9.2 Hz, 2H), 3.26 (q, J = 7.2 Hz, 2H), 1.30 (d, J = 8.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 142.78, 136.72, 130.35, 125.03, 123.59, 112.73, 36.68, 18.91, 13.42. IR(cm^{-1}): 3368, 2955, 2924, 2852, 1600, 1525, 1499, 1466, 1319, 1304, 1183, 1108, 995, 831, 752. HRMS (ESI) m/z calcd for $C_8H_{11}N_2O^+$ $(M+H)^+$151.0866, found 151.0866.

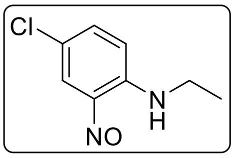


4-(tert-butyl)-N-ethyl-2-nitrosoaniline, **4f**, 56%, M.P. = 83-86 ℃, yellow solid
^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, J = 2.4 Hz, 1H), 7.83 (s, 1H), 7.44 (dd, J = 9.0, 2.4 Hz, 1H), 6.74 (d, J = 9.1 Hz, 1H), 3.28 (dd, J = 7.2, 5.1 Hz, 2H), 1.28 (d, J = 7.2 Hz, 3H), 1.22 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$): 143.70, 138.31, 134.38, 131.19, 122.50, 113.68, 37.69, 33.90, 31.05, 14.49. IR(cm^{-1}): 3383, 2962, 2868, 1631, 1564, 1521, 1477, 1425, 1404, 1362, 1348, 1280, 1256, 1234, 1204, 1172,1135, 1116, 1075, 922, 896, 806, 765, 518. HRMS (ESI) m/z calcd for $C_{12}H_{19}N_2O^+$ $(M+H)^+$ 207.1492, found 207.1493.



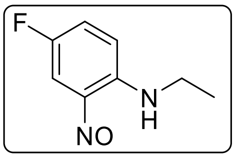
4-bromo-N-ethyl-2-nitrosoaniline, **4g**, 42%, M.P. = 85-88℃, yellow solid

^{1}H NMR (400 MHz, $CDCl_3$): 8.31 (d, J = 2.4 Hz, 1H), 7.94 (s, 1H), 7.49 (dd, J = 9.2, 2.4 Hz, 1H), 6.76 (d, J = 9.2 Hz, 1H), 3.37 – 3.31 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 144.37, 138.91, 132.14, 128.94, 115.48, 106.22, 37.84, 14.28. IR(cm-1): 3374, 2976, 2912, 2879,1616, 1560, 1501, 1469, 1450, 1421, 1387, 1346, 1299, 1262, 1233, 1158, 1073, 882, 873, 810, 758, 519. HRMS (ESI) m/z calcd for $C_8H_{10}BrN_2O^+$ (M+H) $^+$ 228.9971, found 228.9970.



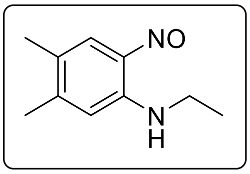
4-chloro-N-ethyl-2-nitrosoaniline, **4h**, 40%, M.P = 84-88 ℃, yellow solid

^{1}H NMR (400 MHz, $CDCl_3$): 8.08 (d, J = 2.6 Hz, 1H), 7.86 (s, 1H), 7.30 (dd, J = 9.2, 2.6 Hz, 1H), 6.73 (d, J = 9.2 Hz, 1H), 3.31 – 3.22 (m, 2H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 144.37, 138.91, 132.14, 128.94, 115.48, 106.22, 37.84, 14.28. IR (cm^{-1}): 3372, 3093, 2923, 1617, 1563, 1511, 1471, 1451, 1404, 1382, 1348, 1260, 1235, 1157, 1134, 1095, 1022, 881, 812, 759, 653, 519. HRMS (ESI) m/z calcd for $C_8H_{10}ClN_2O^+$ (M+H) $^+$ 185.0476, found 185.0477.



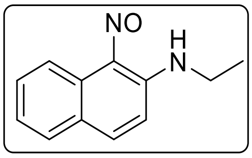
4-fluoro-N-ethyl-2-nitrosoaniline, **4i**, 42%, M.P. = 55-59 ℃ yellow solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 3.1 Hz, 1H), 7.77 (d, J = 3.1 Hz, 1H), 7.20 – 7.13 (m, 1H), 6.74 (dd, J = 9.5, 4.5 Hz, 1H), 3.26 (dd, J = 7.2, 5.1 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100MHz，$CDCl_3$): 152.47, 150.11, 141.65, 124.09, 123.86, 114.05, 113.98, 110.99, 110.73, 36.95, 13.34. ^{19}F NMR (376MHz，$CDCl_3$): -128.56. IR (cm-1): 3378, 2982, 2871, 1617, 1580, 1521, 1508, 1478, 1449, 1410, 1349, 1296, 1269, 1238, 1184, 1148, 1120, 1051, 946, 926, 876, 830, 801, 783, 758, 677, 493. HRMS (ESI) m/z calcd for $C_8H_{10}FN_2O^+$ (M+H) $^+$ 169.0772, found 169.0771.



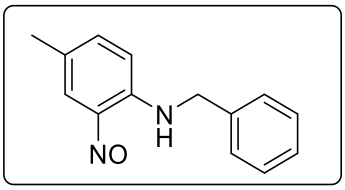
N-ethyl-4,5-dimethyl-2-nitrosoaniline, **4j**, 40%. M.P. = 66-69 ℃, yellow solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.80 (s, 1H), 6.54 (s, 1H), 3.25 (dd, J = 7.2, 5.1 Hz, 2H), 2.19 (s, 3H), 2.10 (s, 3H), 1.28 (s, 3H). ^{13}C (100 MHz, $CDCl_3$): 146.22, 143.15, 125.41, 113.21, 113.07, 36.65, 19.70, 17.51, 13.45. IR(cm^{-1}): 3375, 2967, 2922, 1630, 1571, 1504, 1407, 1385, 1428, 1332, 1300, 1270, 1238, 1197, 1157, 1074, 1038, 763. HRMS (ESI) m/z calcd for $C_{10}H_{15}N_2O^+$ (M+H) $^+$ 179.1179, found 179.1179.



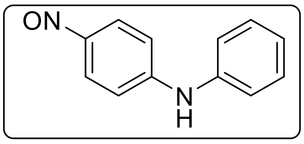
N-ethyl-1-nitrosonaphthalen-2-amine, **4k**, 44% M.P. = 84-87℃, yellow solid. CAS: 76145-81-3[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 9.3 Hz, 1H), 7.58 (d, J = 6.4 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.25 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 9.4 Hz, 1H), 3.41 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 146.55, 137.23, 130.18, 128.93, 128.73, 126.37, 123.88, 123.25, 124.01, 38.24, 14.70. IR (cm^{-1}): 2970, 2926, 2874, 1633, 1560, 1518, 1481, 1470, 1438, 1416, 1378, 1356, 1322, 1303, 1206, 964, 798, 778, 754, 655, 604, 491.



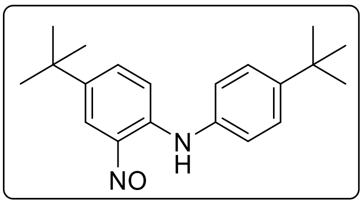
N-benzyl-4-methyl-2-nitrosoaniline, **4l**, 56%, M.P. = 88-90℃, yellow solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.92 (s, 1H), 7.27 (d, J = 6.7 Hz, 5H), 7.13 (dd, J = 8.7, 2.2 Hz, 1H), 6.65 (d, J = 8.7 Hz, 1H), 4.45 (d, J = 5.7 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.51, 137.70, 137.64, 131.94, 128.90, 127.62, 127.02, 126.12, 125.31, 114.22, 47.14, 19.96. IR(cm^{-1}): 3400, 2919, 2849, 1632, 1568, 1522, 1495, 1452, 1424, 1399, 1348, 1320, 1303, 1271, 1229,1195, 1154, 1055, 809, 764, 726, 696, 581, 531. HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2O^+$ (M+H)$^+$ 227.1179, found 227.1180.



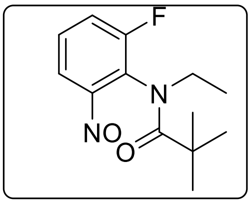
4-nitroso-N-phenylaniline, **4m**, 71%, oil. CAS:156-10-5[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 9.2 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.21 (dd, J = 21.8, 14.4 Hz, 3H), 6.97 – 6.91 (m, 2H), 6.30 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.22, 139.55, 129.75, 126.23, 124.68, 121.95, 113.71. IR(cm^{-1}): 3341, 2971, 2899, 1603, 1584, 1540, 1495, 1405, 1303, 1249, 1185, 1076, 1065, 1049, 879, 841, 747, 690, 565, 496.

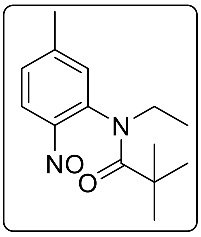


4-(*tert*-butyl)-N-(4-(*tert*-butyl)phenyl)-2-nitrosoaniline, **4n**, 42%, oil

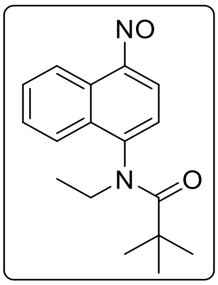
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (s, 1H), 8.09 (d, J = 2.4 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.11 (dd, J = 8.8, 2.8 Hz, 3H), 1.25 (d, J = 15.8 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.55, 141.39, 140.60, 136.31, 133.70, 132.56, 126.51, 123.94, 122.28, 116.14, 34.53, 34.08, 31.39, 31.02. IR(cm^{-1}): 3356, 2960, 2866, 1629, 1607, 1564, 1520, 1464, 1435, 1407, 1364, 1345, 1256, 1227, 1203, 1159, 1113, 1076, 828, 554. HRMS (ESI) m/z calcd for $C_{20}H_{27}N_2O^+$ (M+H)$^+$ 311.2118, found 311.2117.



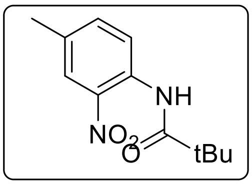
N-ethyl-N-(2-fluoro-6-nitrosophenyl)pivalamide, **4o**, 15%, M.P. = 60-63℃, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.05 – 7.96 (m, 2H), 7.39 – 7.33 (m, 1H), 3.62 (q, *J* = 7.1 Hz, 2H), 1.04 (s, 12H). ^{13}C NMR (100MHz, $CDCl_3$): 177.34, 159.63, 157.10, 137.77, 137.64, 132.17, 119.59, 112.76, 112.76, 112.50, 46.90, 40.94, 28.61, 12.83. ^{19}F NMR (376MHz，$CDCl_3$): -112.99. IR (cm^{-1}): 2969, 1649, 1601, 1530, 1497, 1480, 1397, 1351, 1284, 1199, 1117, 1131, 1073, 1021, 883, 809, 745, 731. HRMS (ESI) m/z calcd for $C_{13}H_{18}FN_2O_2^+$ $(M+H)^+$ 253.1347, found 253.1348.



N-ethyl-N-(5-methyl-2-nitrosophenyl)pivalamide, **4p**, 31%, M.P.= 86-89 °C, yellow solid
^{1}H NMR (400 MHz, $CDCl_3$): 8.17 (d, *J* = 2.7 Hz, 1H), 8.08 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.29 – 7.25 (m, 1H), 3.60 (m, 2H), 2.36 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.07 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$): 177.12, 148.07, 146.99, 138.45, 131.43, 126.33, 121.51, 46.10, 40.92, 28.88, 18.22, 12.51. IR(cm^{-1}): 2968, 2933, 1638, 1611, 1582, 1522, 1480, 1381, 1289, 1203, 1121, 1090, 802. HRMS (ESI) m/z calcd for $C_{16}H_{17}N_2O_2^+$ $(M+H)^+$ 249.1598, found 249.1597.

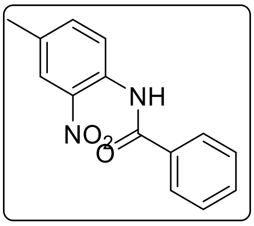


N-ethyl-N-(4-nitrosonaphthalen-1-yl)pivalamide, **4q**, 70%, M.P. = 106-109°C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.58 (d, *J* = 9.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.76 (dd, *J* = 14.7, 8.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 3.74 (m, 2H), 1.19 (t, *J* = 7.0 Hz, 3H), 0.99 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$): 117.87, 146.34, 145.23, 132.06, 129.87, 128.55, 126.36, 125.69, 124.20, 123.86, 123.14, 47.38, 41.33, 29.23, 12.98. IR(cm^{-1}): 2968, 2933, 1641, 1597, 1572, 1522, 1507, 1479, 1459, 1421, 1398, 1364, 1343, 1286, 1266, 1201, 1171, 1147, 1122, 1071, 886, 815, 770. HRMS (ESI) m/z calcd for $C_{17}H_{21}N_2O_2^+$ $(M+H)^+$ 285.1598, found 285.1597.

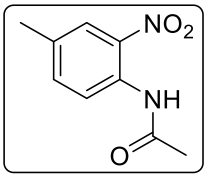


N-(4-methyl-2-nitrophenyl)pivalamide, **6a**, 77%, M.P. = 58-60 °C, yellow solid.

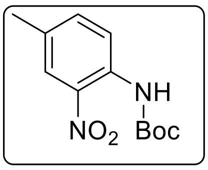
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.61 (d, J = 8.7 Hz, 1H), 7.94 (s, 1H), 7.38 (s, 1H), 2.31 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.74, 136.86, 136.24, 133.18, 133.03, 125.49, 122.07, 40.49, 27.47, 20.49. IR(cm $^{-1}$):3373, 2962, 2926, 2870, 1694, 1626, 1578, 1513, 1477, 1441, 1398, 1342, 1302, 1274, 1147, 1081, 1028, 935, 833, 807, 760, 677, 536 HRMS (ESI) m/z calcd for $C_{12}H_{17}N_2O_3^+$ (M+H) $^+$ 237.1239, found 237.1232



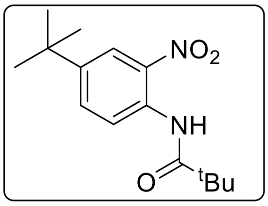
N-(4-methyl-2-nitrophenyl)benzamide, **7a**, 80%, M.P. = 136-138 °C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.86 (d, J = 8.6 Hz, 1H), 8.06 (s, 1H), 7.98 (d, J = 7.0 Hz, 2H), 7.59 – 7.50 (m, 4H), 2.41 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.64, 137.07, 136.38, 134.18, 133.62, 132.96, 132.53, 129.01, 127.33, 125.68, 122.08, 20.58. IR(cm-1): 3355, 2986, 2899, 1688, 1580, 1521, 1450, 1405, 1381, 1250, 1221, 1065, 1056, 925, 891, 834, 758, 682, 640, 534. HRMS (ESI) m/z calcd for $C_{14}H_{13}N_2O_3^+$ (M+H) $^+$ 257.0926, found 257.0923



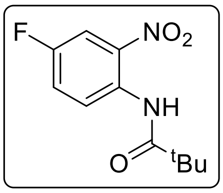
N-(4-methyl-2-nitrophenyl)acetamide, **8a**, 65%, M.P. = 85-87 °C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.62 (d, J = 8.7 Hz, 1H), 8.00 (s, 1H), 7.45 (d, J = 8.7 Hz, 1H), 2.38 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.90, 136.80, 136.28, 133.49, 132.44, 125.46, 122.18, 25.51, 20.51. IR(cm^1): 3363, 2987, 2899, 1708, 1617, 1576, 1512, 1481, 1407, 1381, 1303, 1271, 1228, 1075, 849, 825, 759, 590, 530. HRMS (ESI) m/z calcd for $C_9H_{11}N_2O_3^+$ (M+H) $^+$ 195.0770, found 195.0764.



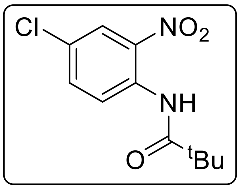
tert-butyl (4-methyl-2-nitrophenyl)carbamate, **9a**, 37%, M.P. = 66-69°C, yellow solid, CAS: 866005-25-6.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.33 (d, J = 8.7 Hz, 1H), 7.90 (s, 1H), 7.33 (d, J = 8.7 Hz, 1H), 2.28 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.30, 135.65, 134.88, 132.49, 130.93, 124.48, 119.68, 80.57, 27.20, 19.32. IR(cm-1): 3374, 2978, 2927, 1736, 1629, 1576, 1521, 1442, 1393, 1367, 1340, 1303, 1277, 1250, 1222, 1145, 1086, 1048, 919, 899, 828, 761, 736, 675, 536.



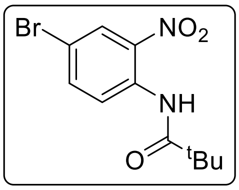
N-(4-(tert-butyl)-2-nitrophenyl)pivalamide, **6b**, 75%, M.P. = 42-44 °C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.64 (d, J = 8.9 Hz, 1H), 8.12 (d, J = 2.4 Hz, 1H), 7.59 (s, 1H), 1.27 (d, J = 5.4 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.76, 145.65, 135.20, 132.44, 131.92, 121.02, 120.96, 39.46, 33.53, 29.96, 26.45. IR(cm^{-1}): 3373, 2964, 1699, 1622, 1579, 1534, 1510, 1477, 1442, 1394, 1338, 1281, 1263, 1232, 1148, 1076, 928, 896, 841, 762, 587. HRMS (ESI) m/z calcd for $C_{15}H_{23}N_2O_3^+$ (M+H)$^+$ 279.1709, found 279.1701



N-(4-fluoro-2-nitrophenyl)pivalamide, **6c**, 53%, M.P. = 52-55°C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.89 – 8.85 (m, 1H), 7.94 (dd, J = 8.5, 3.1 Hz, 1H), 7.43 – 7.38 (m, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.79, 158.06, 155.60, 132.04, 124.06, 123.99, 123.59, 123.37, 112.35, 112.08, 40.53, 27.24. ^{19}F NMR (376MHz, $CDCl_3$): -116.50. IR(cm^{-1}): 3376, 2969, 2899, 1695, 1591, 1511, 1478, 1451, 1403, 1393, 1355, 1288, 1266, 1143, 1065, 1057, 1027, 948, 878, 832, 810, 787. HRMS (ESI) m/z calcd for $C_{11}H_{14}FN_2O_3^+$ (M+H)$^+$ 241.0988, found 241.0982.

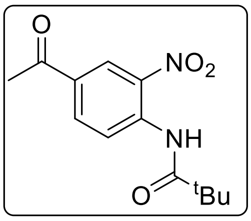


N-(4-chloro-2-nitrophenyl)pivalamide, **6d**, 52%, M.P. = 61-63°C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.76 (d, J = 9.2 Hz, 1H), 8.13 (s, 1H), 7.52 (d, J = 6.6 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.80, 135.40, 134.88, 133.12, 127.05, 124.28, 122.35, 39.61, 26.38. IR(cm^{-1}): 3372, 2966, 1700, 1610, 1578, 1542, 1493, 1441, 1367, 1339, 1262, 1149, 1107, 1073, 925, 886, 832, 761, 728, 657, 533. HRMS (ESI) m/z calcd for $C_{11}H_{14}ClN_2O_3^+$ (M+H)$^+$ 257.0693, found 241.0687.

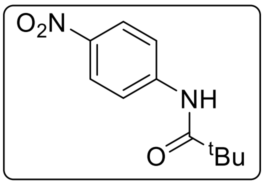


N-(4-bromo-2-nitrophenyl)pivalamide, **6e**, 54%, M.P. = 74-76°C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.68 (s, 1H), 8.79 (d, J = 9.1 Hz, 1H), 8.37 (s, 1H), 7.74 (d, J = 6.8 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.85, 138.77, 136.59, 134.57, 128.23, 123.56, 114.96, 40.66, 27.39. IR(cm^{-1}): 3371, 2969, 2900, 1700, 1606, 1576, 1492, 1441, 1393,

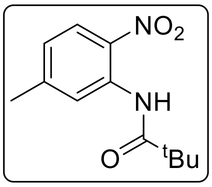
1336, 1261, 1149, 1075, 1065, 1056, 923, 877. HRMS (ESI) m/z calcd for $C_{11}H_{14}BrN_2O_3^+$ (M+H) $^+$ 301.0188, found 301.0181.



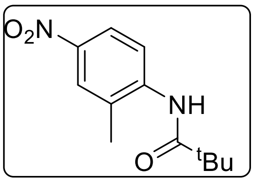
N-(4-acetyl-2-nitrophenyl)pivalamide, **6f**, 38%, M.P. = 87-89°C, yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.95 (s, 1H), 8.99 (d, *J* = 8.9 Hz, 1H), 8.83 (s, 1H), 8.21 (d, *J* = 6.8 Hz, 1H), 2.64 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.79, 178.09, 138.98, 135.65, 135.20, 131.47, 126.34, 121.79, 40.85, 27.38, 26.35. IR(cm^{-1}): 3364, 2963, 1690, 1615, 1577, 1512, 1477, 1443, 1398, 1358, 1340, 1283, 1260, 1220, 1188, 1138, 1080,1026, 974, 924, 844, 763, 596. HRMS (ESI) m/z calcd for $C_{13}H_{17}N_2O_4^+$ (M+H)$^+$ 265.1183, found 265.1181.



N-(4-nitrophenyl)pivalamide, **6g**, 55%, M.P. = 72-76 °C, oil, CAS: 56619-95-5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.83 (d, *J* = 10.0 Hz, 1H), 8.23 (d, *J* = 6.8 Hz, 1H), 7.65 (d, *J* = 14.2 Hz, 1H), 7.17 (d, *J* = 14.3 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.88, 136.36, 135.99, 135.45, 125.76, 122.95, 122.12, 40.59, 27.45. IR(cm^{-1}): 3370, 2968, 2900, 1700, 1608, 1585, 1499, 1451, 1429, 1393, 1337, 1272, 1229, 1147, 1065, 1056, 741.

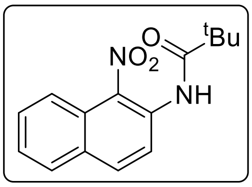


N-(5-methyl-2-nitrophenyl)pivalamide, **6h**, 40%, M.P. = 71-74°C, yellow solid, CAS: 1707681-15-9.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.69 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 2.43 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.04, 148.04, 135.40, 134.24, 125.80, 123.95, 122.00, 40.61, 27.45, 22.09. IR(cm^{-1}): 3348, 2973, 2899, 1703, 1615, 1588, 1495, 1480, 1447, 1407, 1393, 1381, 1323, 1262, 1229, 1158, 1073, 1065, 1056, 885, 815, 750.



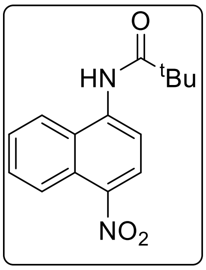
N-(2-methyl-4-nitrophenyl)pivalamide, **6i**, 27%, M.P. = 125-128°C, yellow solid, CAS: 404352-86-9.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.97 (s, 1H), 8.88 (s, 1H), 8.53 (s, 1H), 6.31 (t, *J* = 1.4 Hz, 1H), 2.48 (d, *J* = 1.3 Hz, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.93, 159.04, 158.05,

150.80, 138.12, 123.37, 115.45, 109.14, 40.84, 27.35, 18.36. IR(cm^{-1}): 3302, 2964, 2927, 2870, 1662, 1586, 1529, 1501, 1400, 1346, 1274, 1161, 1093, 808, 744, 734.



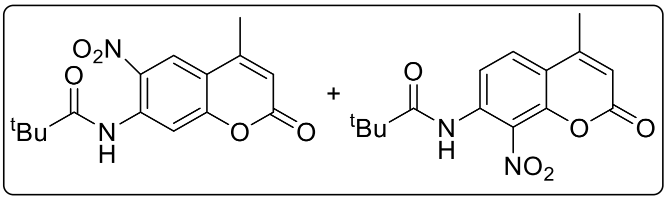
N-(1-nitronaphthalen-2-yl)pivalamide, **6j**, 45%, oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.47 (d, J = 9.1 Hz, 1H), 8.06 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 9.1 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.1 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.59, 135.95, 133.74, 131.86, 130.31, 129.36, 128.24, 126.33, 125.67, 122.30, 120.82, 40.31, 27.44. IR(cm^{-1}): 3290, 2969, 2900, 1662, 1623, 1595, 1532, 1495, 1495, 1428, 1401, 1349, 1264, 1218, 1611, 1074, 1065, 1056, 826, 799, 756. HRMS (ESI) m/z calcd for $C_{15}H_{17}N_2O_3^+$ $(M+H)^+$ 273.1234, found 273.1231.



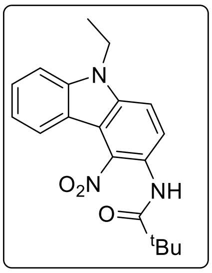
N-(4-nitronaphthalen-1-yl)pivalamide, **6k**, 60%, M.P. = 136-139°C, yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.79 (d, J = 9.1 Hz, 1H), 7.66 – 7.60 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.87, 135.87, 131.00, 129.62, 129.15, 128.20, 127.58, 127.29, 126.91, 126.64, 120.21, 39.88, 27.51. IR(cm^{-1}): 3409, 2966, 1694, 1628, 1601, 1574, 1530, 1491, 1443, 1428, 1330, 1276, 1216, 1172, 1155, 1065, 865, 814, 794, 779, 745. HRMS (ESI) m/z calcd for $C_{15}H_{17}N_2O_3^+$ $(M+H)^+$ 273.1234, found 273.1231.

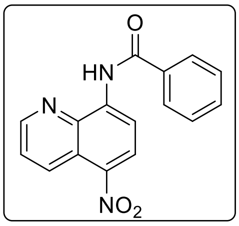


N-(4-methyl-6-nitro-2-oxo-2H-chromen-7-yl)pivalamide, **6l**, 38%, M.P.=122-126℃, yellow solid, r.r = 1:1.

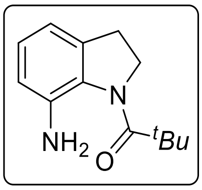
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.33 (d, J = 8.8 Hz, 1H), 8.07 (d, J = 9.9 Hz, 3H), 7.84 (d, J = 8.3 Hz, 1H), 7.53 (s, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.26 (d, J = 7.2 Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 1.36 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.72, 176.69, 144.78, 143.35, 142.11, 138.26, 136.09, 130.35, 127.50, 127.45, 126.03, 125.51, 122.86, 122.82, 120.82, 120.79, 40.25, 39.56, 27.56, 27.42, 18.84, 17.54. IR(cm^{-1}): 3357, 2968, 2899, 1755, 1662, 1626,1568, 1532, 1506, 1481, 1449, 1384, 1298, 1361, 1298, 1275, 1255, 1190, 1160, 1065, 1055, 903, 878, 745. HRMS (ESI) m/z calcd for $C_{15}H_{17}N_2O_5^+$ $(M+H)^+$ 305.1132, found 305.1135.



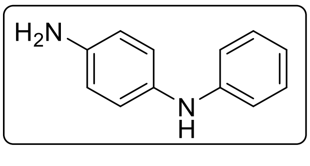
N-(9-ethyl-2-nitro-9H-carbazol-3-yl)pivalamide, **6m**, 32%, M.P.=164-167°C, brown solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 2.1 Hz, 1H), 8.01 – 7.97 (m, 2H), 7.68 (s, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.39 (s, 9H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.14, 142.45, 135.02, 129.25, 128.42, 128.36, 127.64, 122.16, 120.70, 120.50, 117.98, 115.75, 109.93, 40.72, 39.64, 27.64, 14.15. IR(cm^{-1}): 3320, 2965, 2924, 1656, 1605, 1576, 1522, 1479, 1449, 1400, 1381, 1331, 1296, 1260, 1210, 1163, 1124, 1078, 966, 936, 869, 766, 744. HRMS (ESI) m/z calcd for $C_{19}H_{22}N_3O_3^+$ $(M+H)^+$ 340.1656, found 340.1651.



N-(5-nitroquinolin-8-yl)benzamide, **6n**, 52%, M.P.=76-79°C, yellow solid, CAS: 62802-76-0.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.97 (s, 1H), 9.20 (d, *J* = 8.9 Hz, 1H), 8.93 – 8.85 (m, 2H), 8.51 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 7.0 Hz, 2H), 7.66 (dd, *J* = 8.9, 4.2 Hz, 1H), 7.55 – 7.48 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.66, 149.08, 140.85, 138.70, 137.77, 134.15, 133.41, 132.63, 129.03, 127.86, 127.46, 124.71, 121.82, 113.72. IR(cm^{-1}): 3353, 2986, 2899, 1570,1534, 1505, 1483, 1450, 1381, 1322, 1257, 1229, 1197, 1165, 1065, 1056, 891, 854, 839, 812, 791, 739, 691,683, 642.

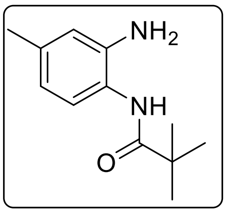


1-(7-aminoindolin-1-yl)-2,2-dimethylpropan-1-one, **10**, 71%, oil.
^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (d, *J* = 8.5 Hz, 1H), 6.55 (s, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 4.17 (t, *J* = 8.0 Hz, 2H), 3.55 (s, 2H), 3.04 (t, *J* = 8.0 Hz, 2H), 1.35 (s, 9H).^{13}C NMR (100MHz, $CDCl_3$): 175.48, 142.72, 136.96, 132.12, 119.12, 113.63, 111.31, 49.33, 39.85, 29.42, 27.74. IR(cm^{-1}): 3433, 3348, 2962, 1618, 1590, 1487, 1440, 1404, 1378, 1363, 1331, 1192, 1092, 903, 818, 746. HRMS (ESI) m/z calcd for $C_{13}H_{19}N_2O^+$ $(M+H)^+$ 219.1492, found 219.1494.



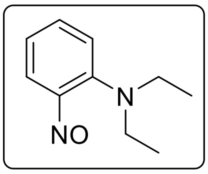
N^1-phenylbenzene-1,4-diamine, **11**, 80%, M.P. = 69-73°C, gray solid CAS:101-54-2[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.15 (m, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 7.5 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 2H), 5.38 (s, 1H), 3.44 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.94, 142.15, 133.86, 129.32, 123.36, 119.03, 116.21, 115.12. IR (cm^{-1}): 3458, 3370, 2361, 2343, 1594, 1507, 1281, 812, 744.



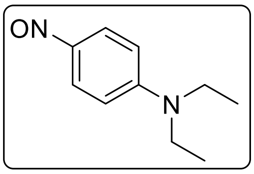
N-(2-amino-4-methylphenyl)pivalamide, **12**, 70%, white solid, M.P. = 196-199 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 5.6 Hz, 2H), 3.71 (s, 2H), 2.23 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.32, 140.97, 137.03, 125.37, 121.84, 120.25, 118.67, 39.29, 27.78, 21.00. IR (cm^{-1}): 3455, 3290, 2969, 2900, 1640, 1607, 1501, 1451, 1401, 1366, 1301, 1231, 1182, 1076, 1065, 1050, 789.



***N,N*-diethyl-2-nitrosoaniline**, **13**, 32%, oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.7 Hz, 1H), 3.07 (t, *J* = 7.1 Hz, 4H), 1.01 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.48, 143.24, 131.38, 124.43, 121.51, 119.49, 45.69, 11.55. IR (cm^{-1}): 2971, 2937, 1602, 1564, 1520, 1484, 1443, 1379, 1347, 1297, 1258, 1187, 1141, 1079, 1046, 848, 798, 772, 746, 710.



***N,N*-diethyl-4-nitrosoaniline**, **13'**, 47%, yellow solid, M.P. = 67-69°C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 9.5 Hz, 2H), 6.49 (d, *J* = 9.5 Hz, 2H), 3.37 (q, *J* = 7.1 Hz, 4H), 1.15 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.26, 136.27, 126.46, 109.85, 44.95, 12.38. IR (cm^{-1}): 2980, 2936, 2906, 1598, 1574, 1522, 1481, 1437, 1412, 1380, 1302, 1273, 1192, 1163, 1110, 1074, 1008, 826, 793, 753, 728.

IX. References

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[2] D. A. Fletcher, B. G. Gowenlock, K. G. Orrell, V. Šik. Dynamic NMR study of the factors governing nitroso group rotation in p-nitrosoanilines in the solution and solid states [J]. *Magnetic Resonance in Chemistry*, 1995, 33: 561-569.

[3] E. Toja, D. Selva, and P. Schiatti. 3-Alkyl-2-aryl-3H-naphth[1,2-d] imidazoles, a novel class of nonacidic antiinflammatory agents.[J] *Journal of Medicinal Chemistry*, 1984, 27 (5): 610-616.

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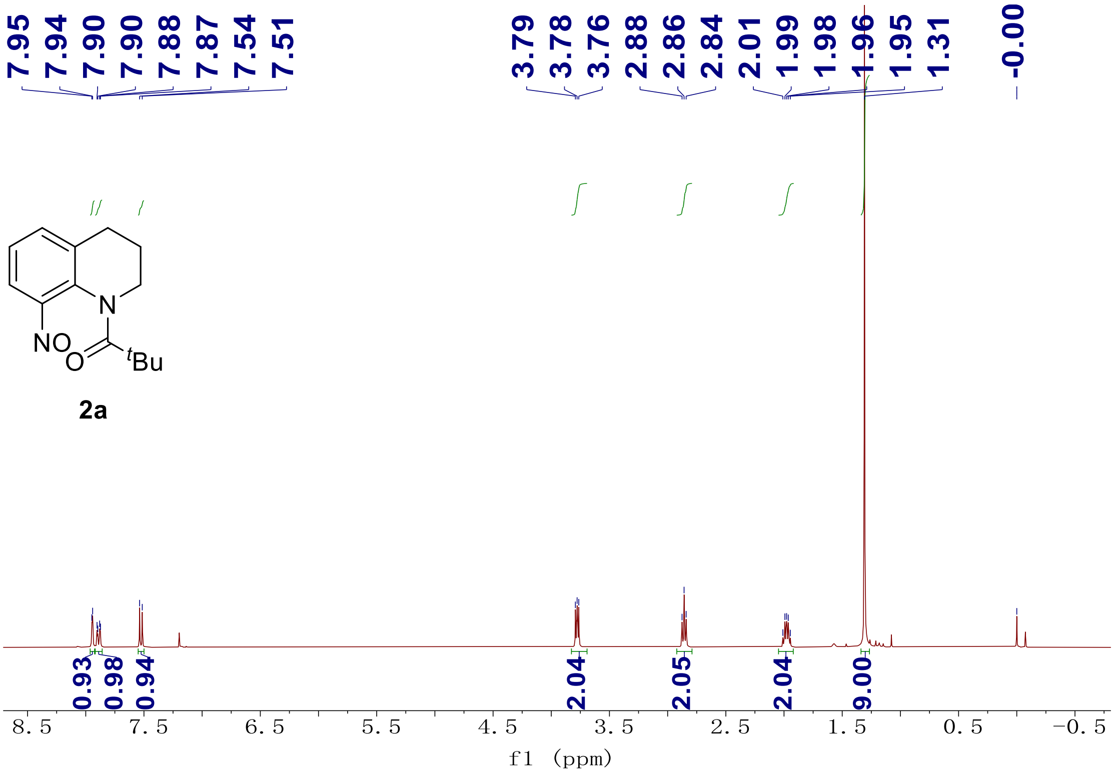
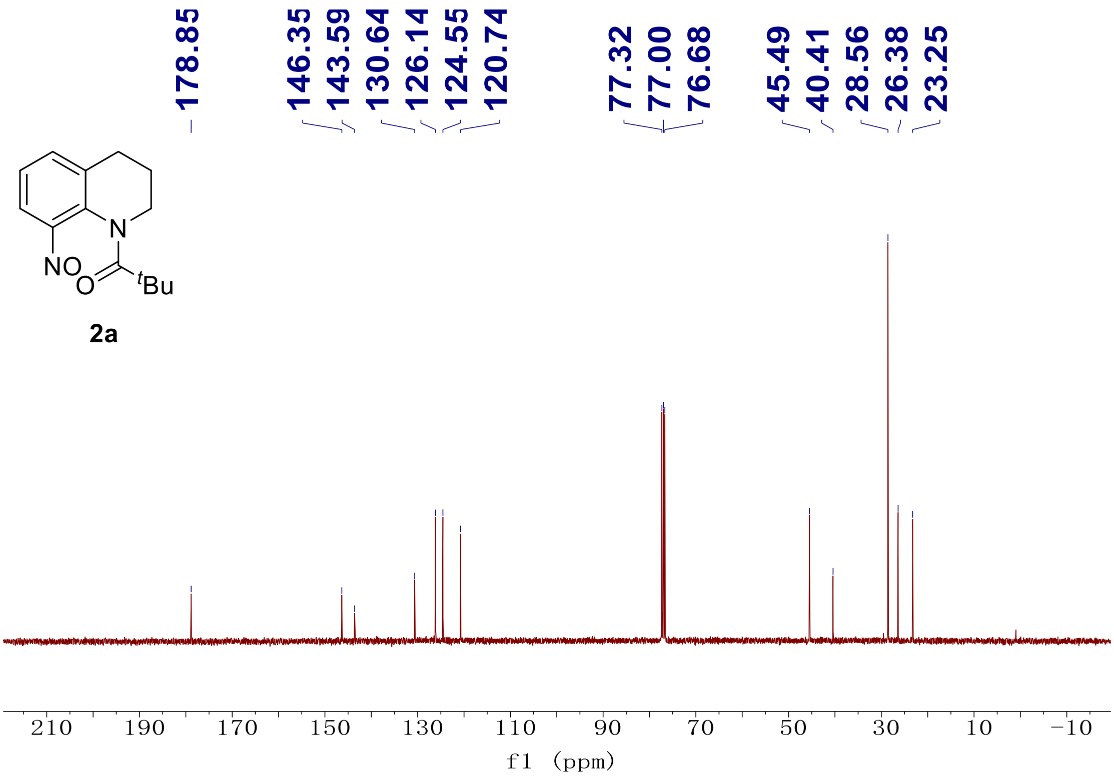
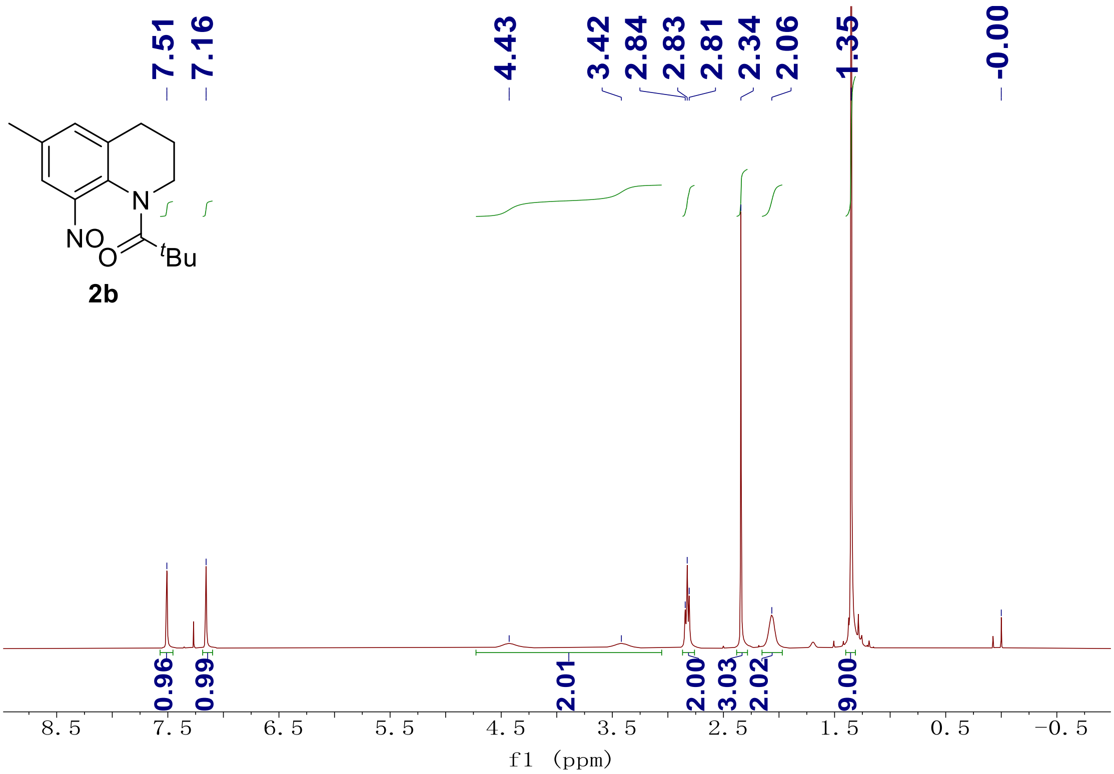
X. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound 2, 4, 6, 7a, 8a, 9a, 10, 11, 12, 13, 13'



2a



2a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2.83
2.81
2.34
2.06
1.35
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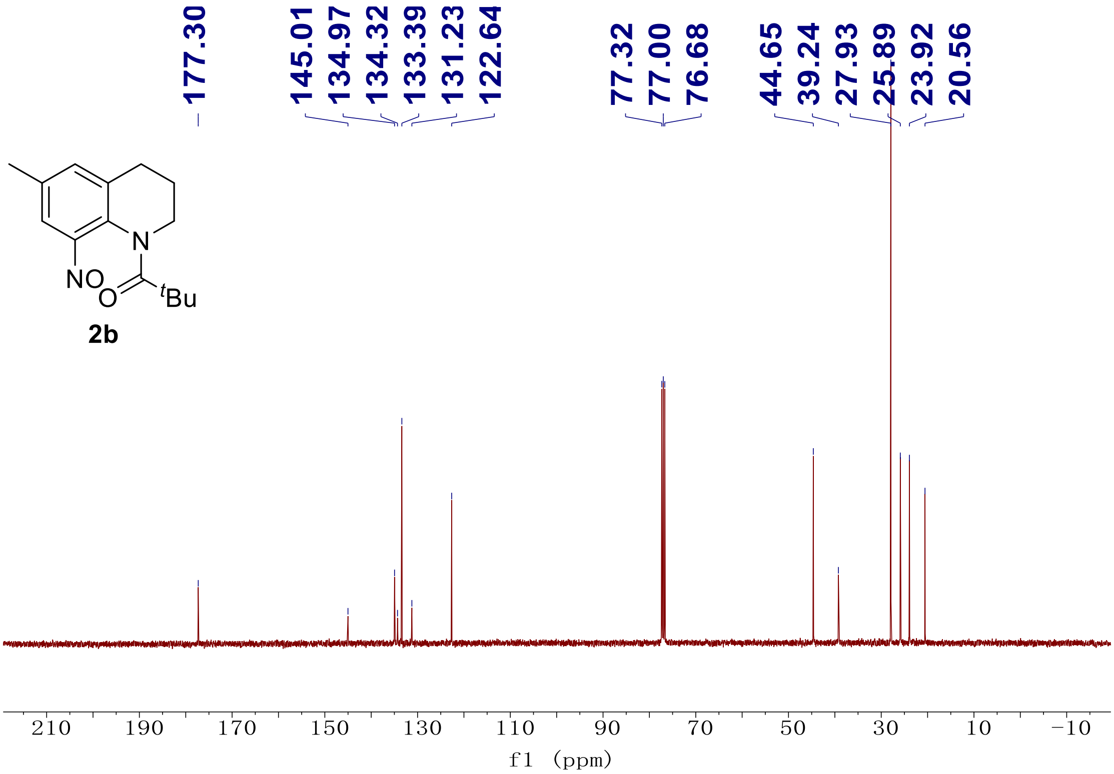
N
O
tBu
2b
0.96
0.99
2.01
2.00
3.03
2.02
9.00
f1 (ppm)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NO
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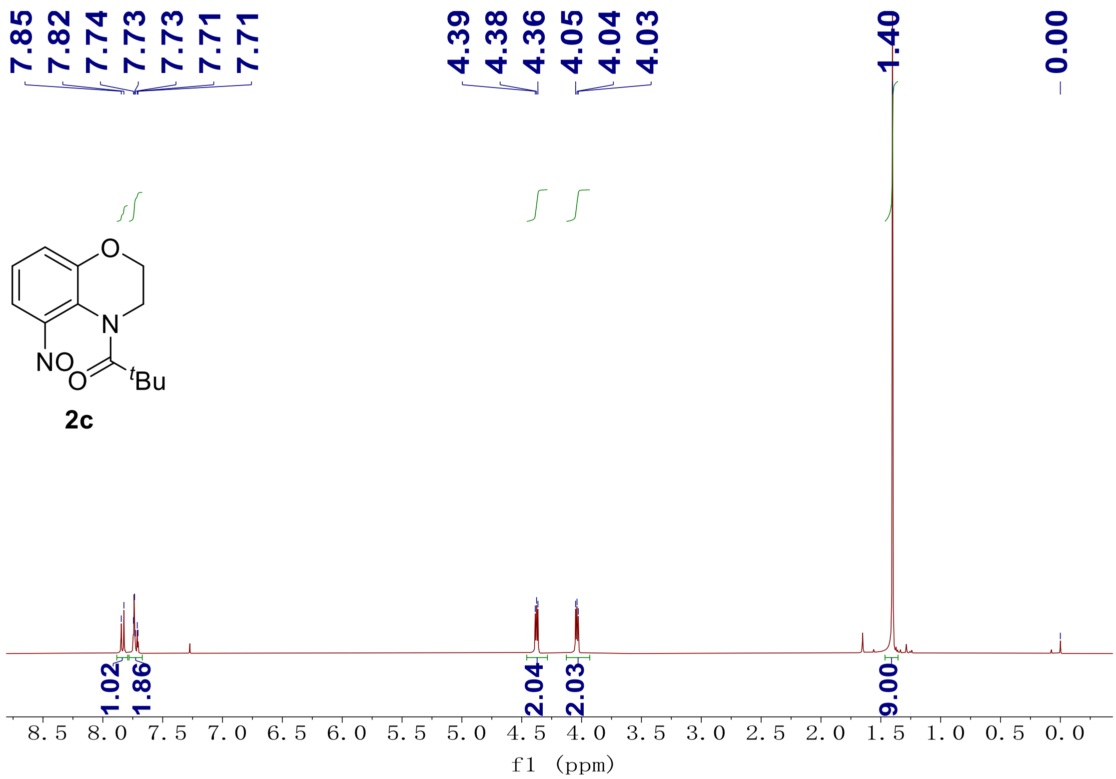
O
tBu
2b
f1 (ppm)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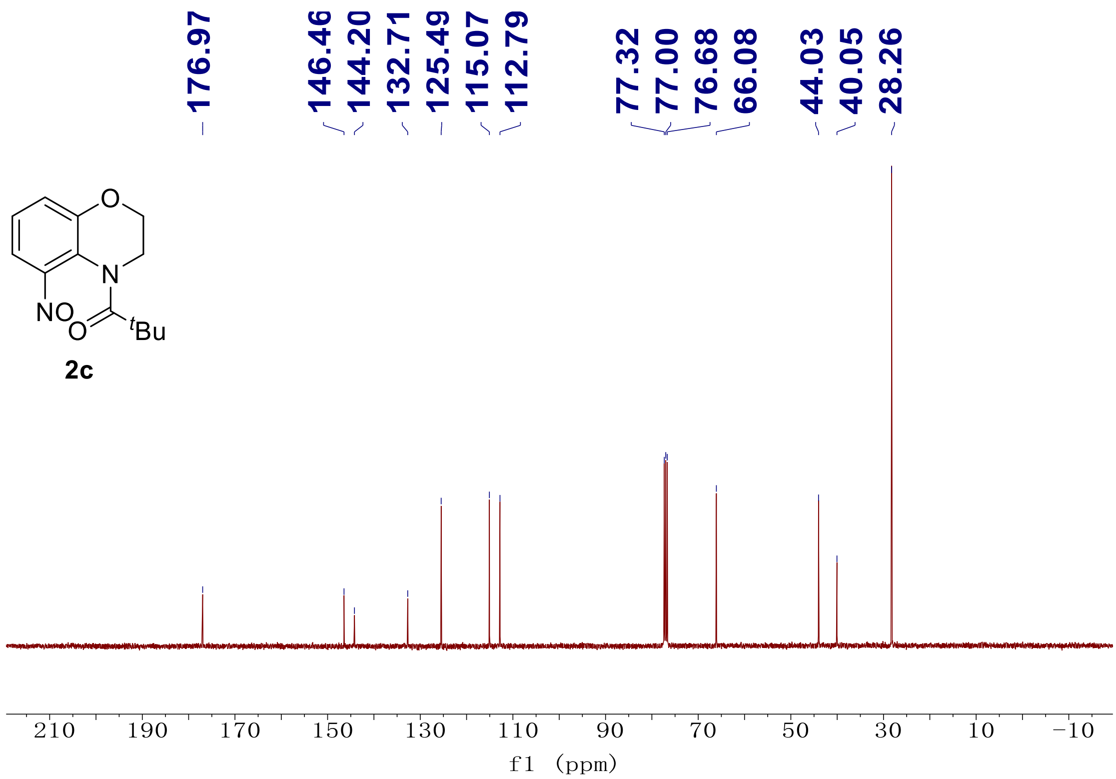
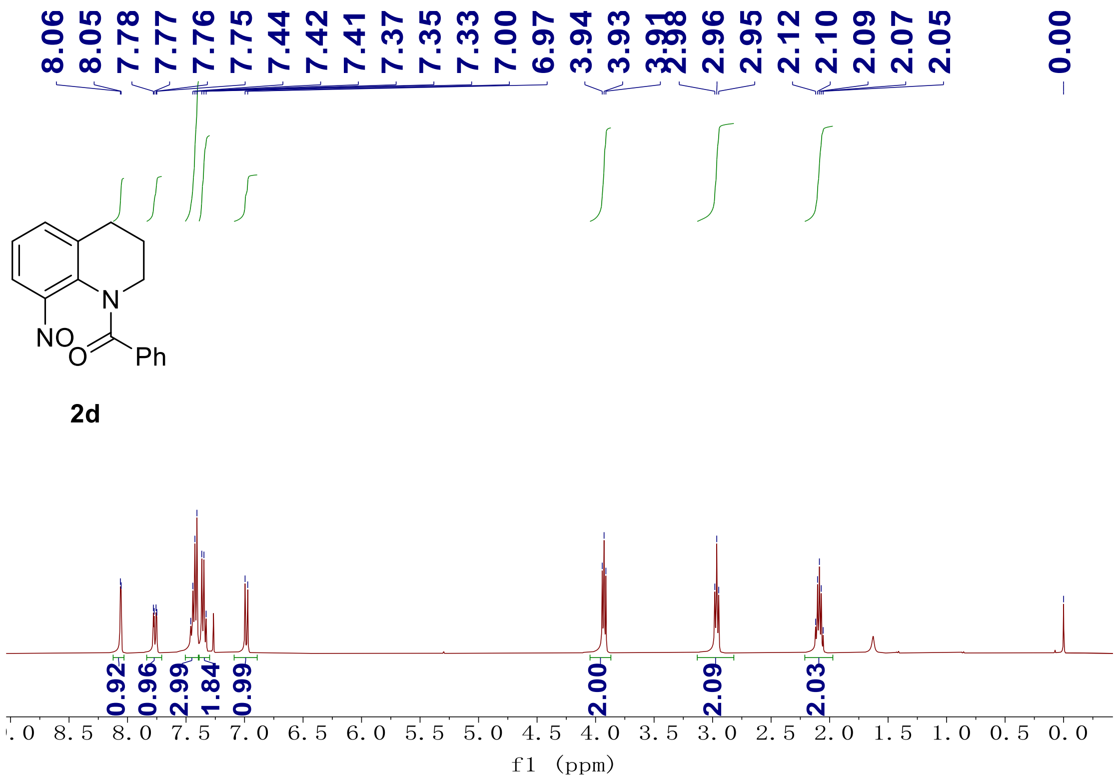
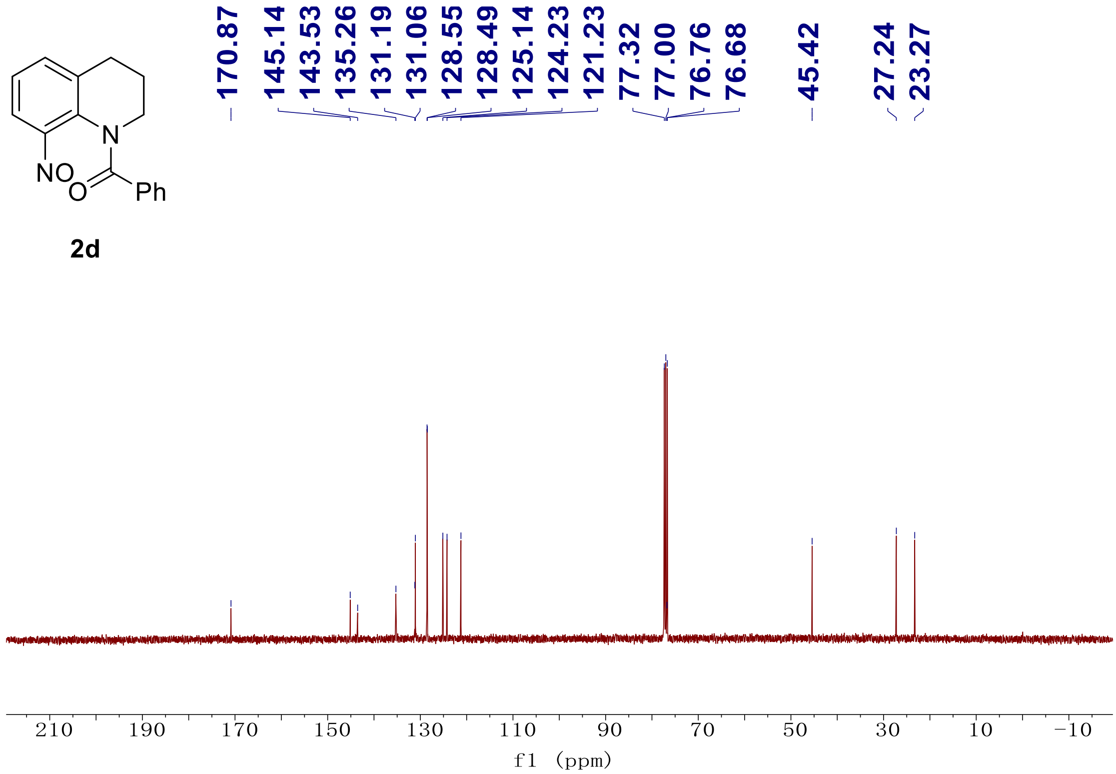
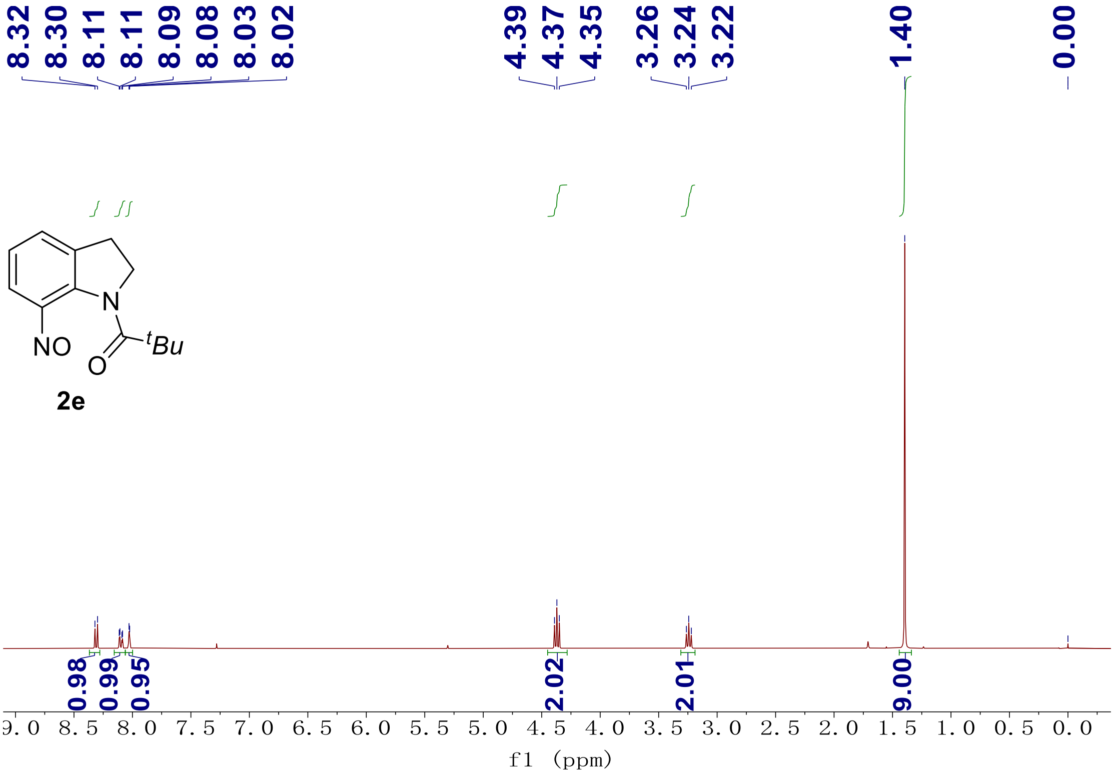
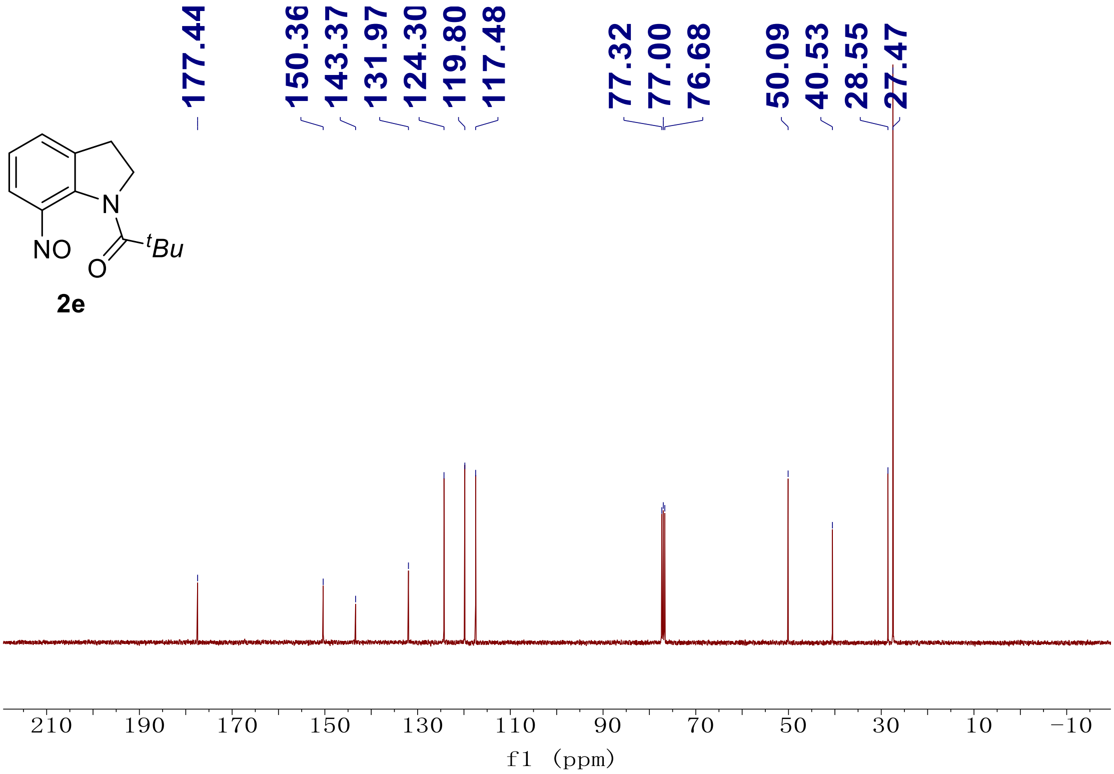
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

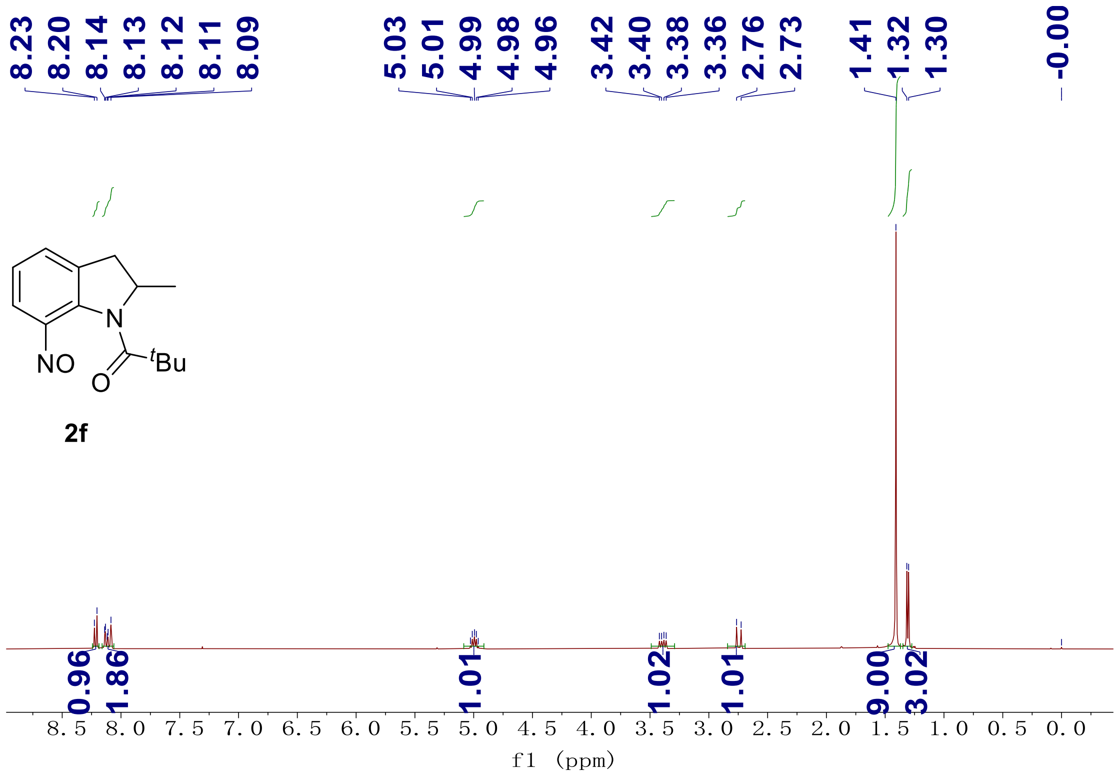

176.97
146.46 144.20 132.71 125.49 115.07 112.79
77.32 77.00 76.68 66.08
44.03 40.05 28.26
NO
O
N
O
tBu
2c
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

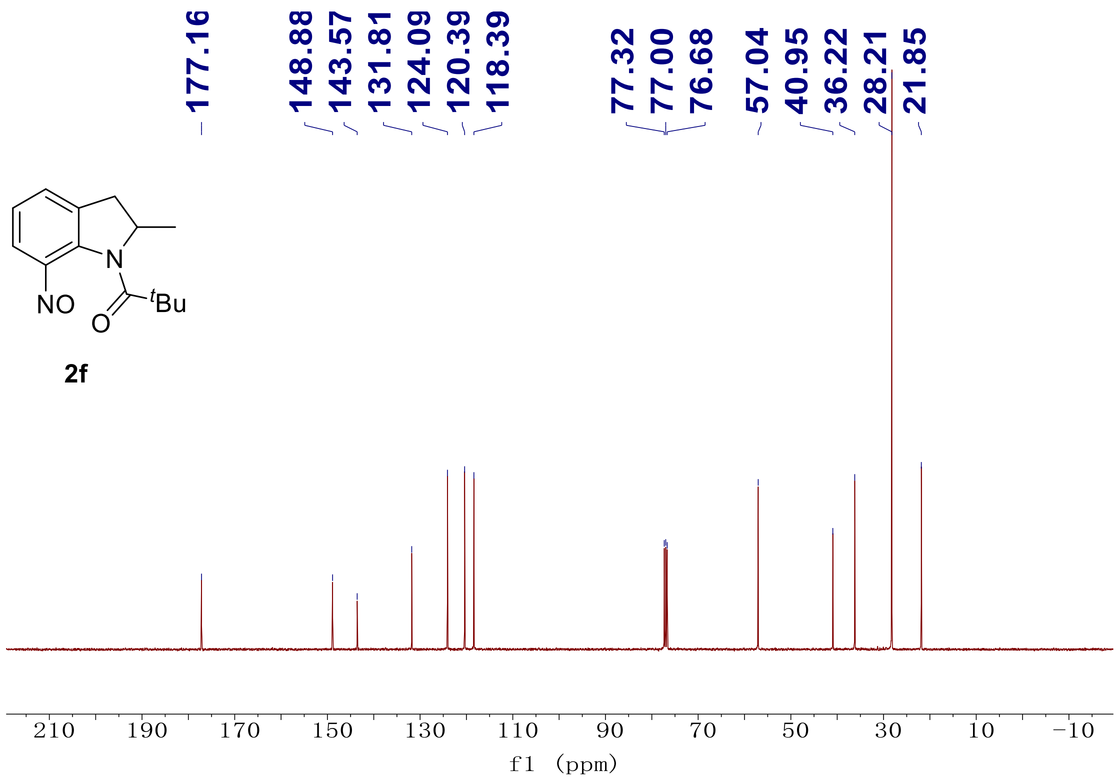

8.06 8.05 7.78 7.77 7.76 7.75 7.44 7.42 7.41 7.37 7.35 7.33 7.00 6.97 3.94 3.93 3.91 2.98 2.96 2.95 2.12 2.10 2.09 2.07 2.05 0.00
NO
N
O
Ph
2d
0.92 0.96 2.99 1.84 0.99 2.00 2.09 2.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

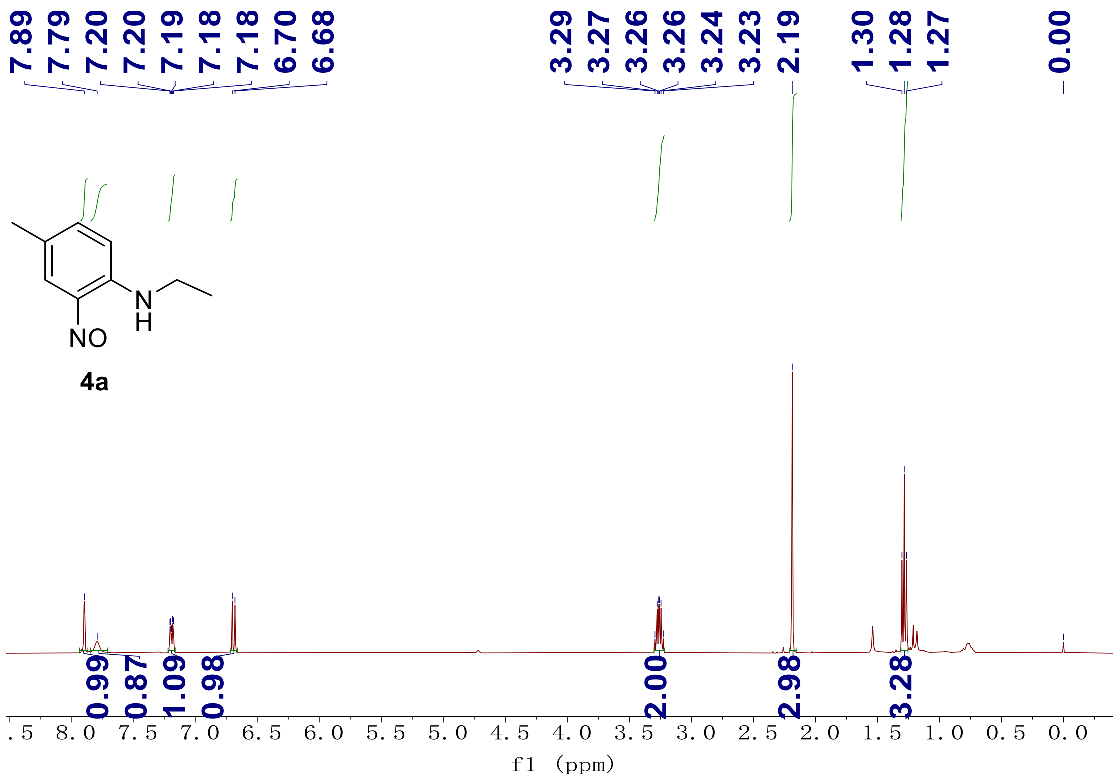

170.87 145.14 143.53 135.26 131.19 131.06 128.55 128.49 125.14 124.23 121.23 77.32 77.00 76.76 76.68 45.42 27.24 23.27
NO
N
O
Ph
2d
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

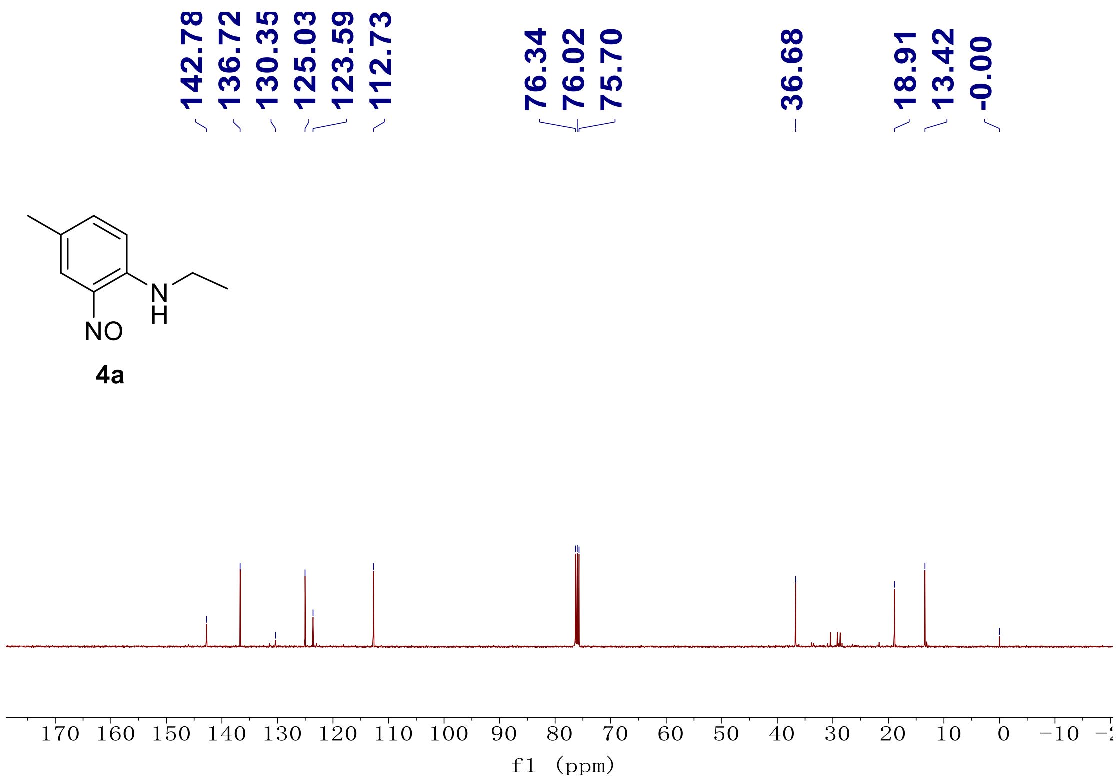

8.32 8.30 8.11 8.11 8.09 8.08 8.03 8.02
4.39 4.37 4.35 3.26 3.24 3.22
1.40
0.00
NO
N
O
tBu
2e
0.98 0.99 0.95
2.02
2.01
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

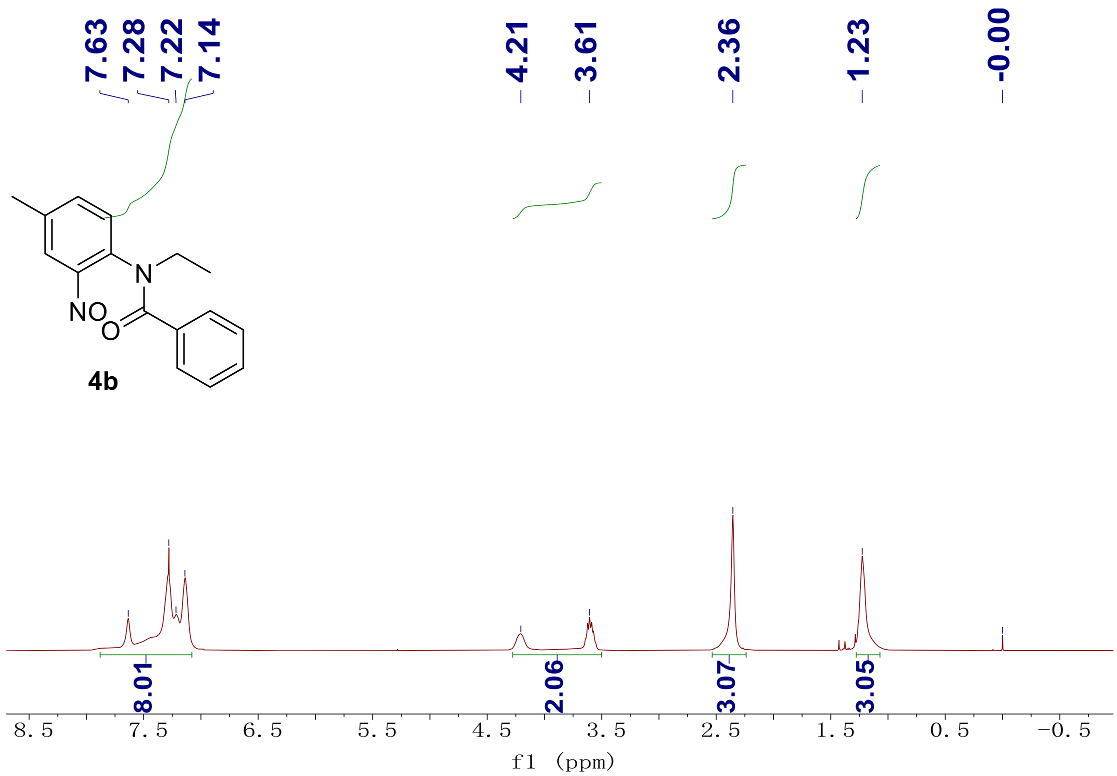

177.44
150.36 143.37 131.97 124.30 119.80 117.48
77.32 77.00 76.68
50.09 40.53 28.55 27.47
NO
N
O
tBu
2e
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

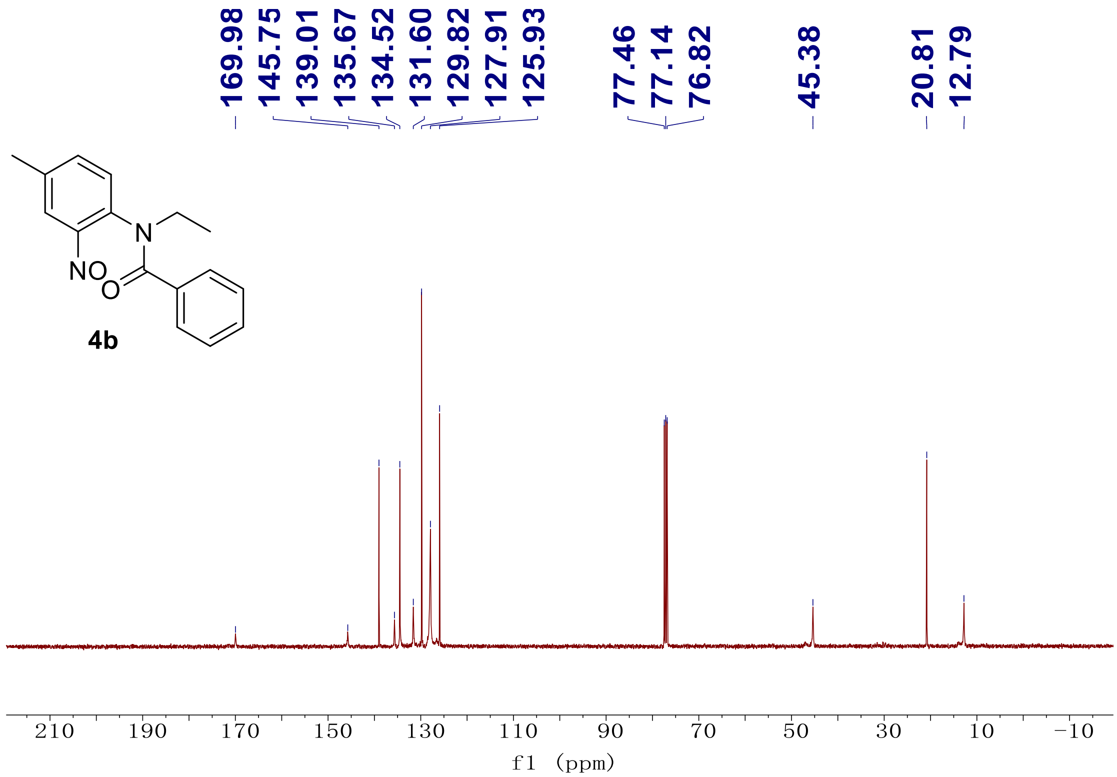

8.23
8.20
8.14
8.13
8.12
8.11
8.09
5.03
5.01
4.99
4.98
4.96
3.42
3.40
3.38
3.36
2.76
2.73
1.41
1.32
1.30
-0.00
NO
N
O
tBu
2f
0.96
1.86
1.01
1.02
1.01
9.00
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

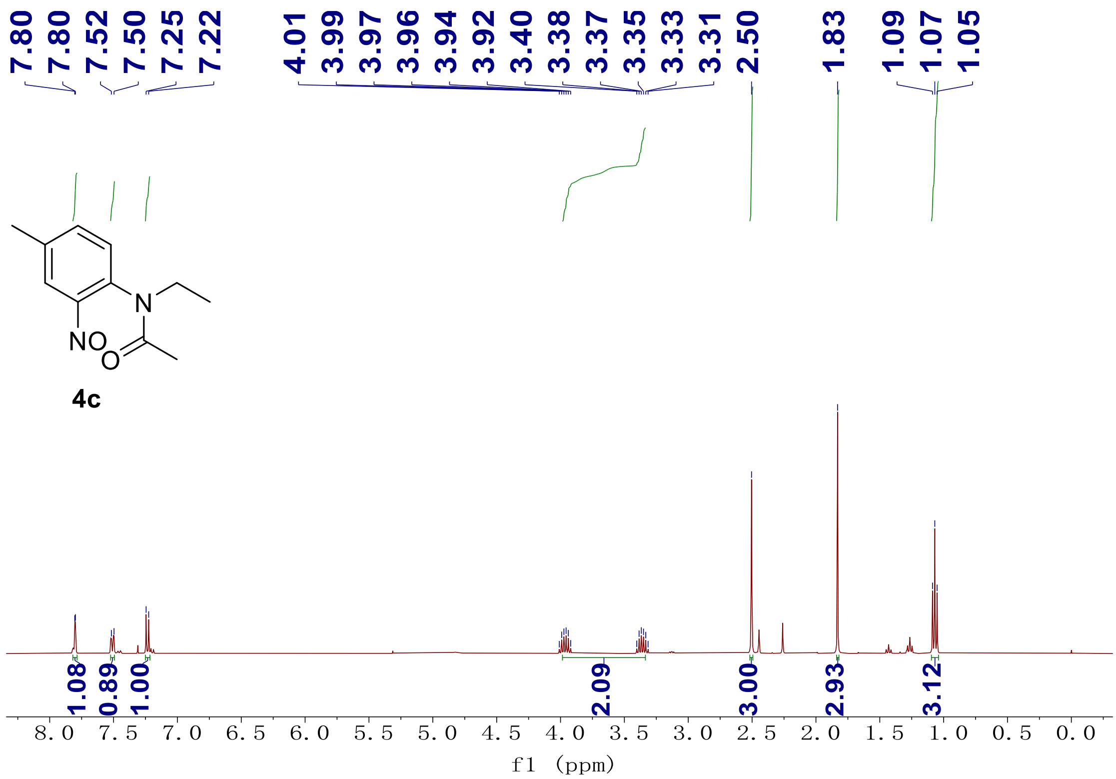

177.16
148.88
143.57
131.81
124.09
120.39
118.39
77.32
77.00
76.68
57.04
40.95
36.22
28.21
21.85
NO
N
O
tBu
2f
210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)

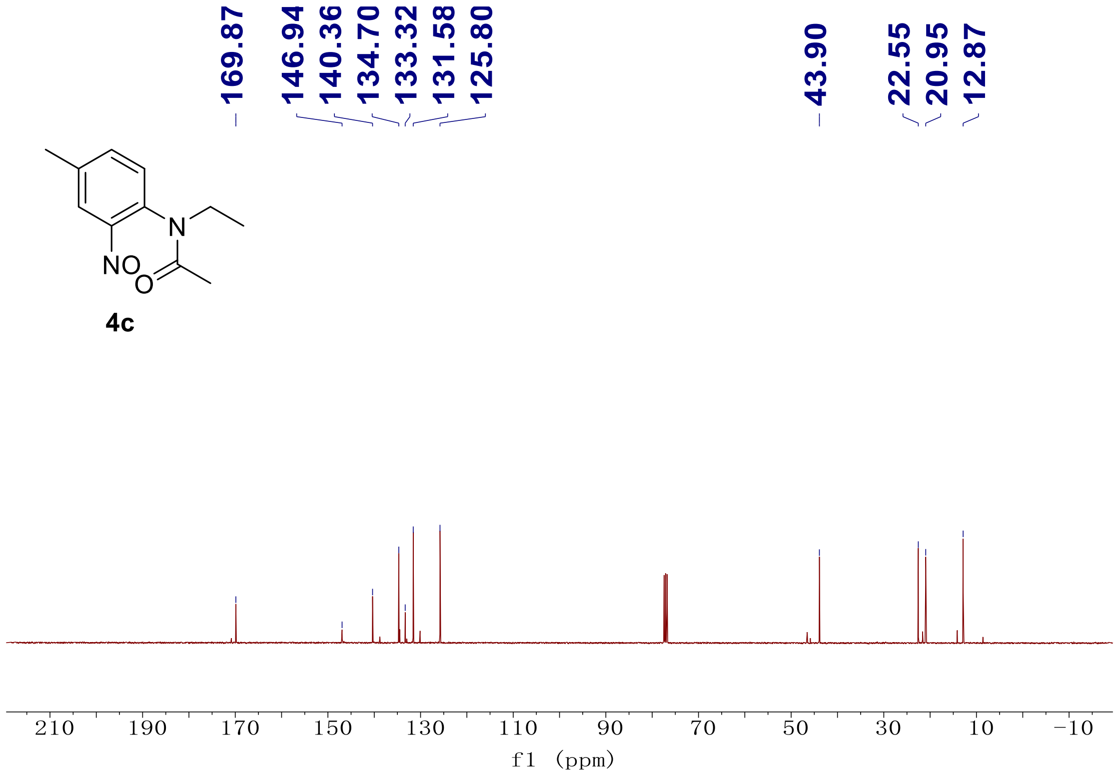

7.89
7.79
7.20
7.20
7.19
7.18
7.18
6.70
6.68
3.29
3.27
3.26
3.26
3.24
3.23
2.19
1.30
1.28
1.27
0.00
NO
N
H
4a
0.99
0.87
1.09
0.98
2.00
2.98
3.28
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

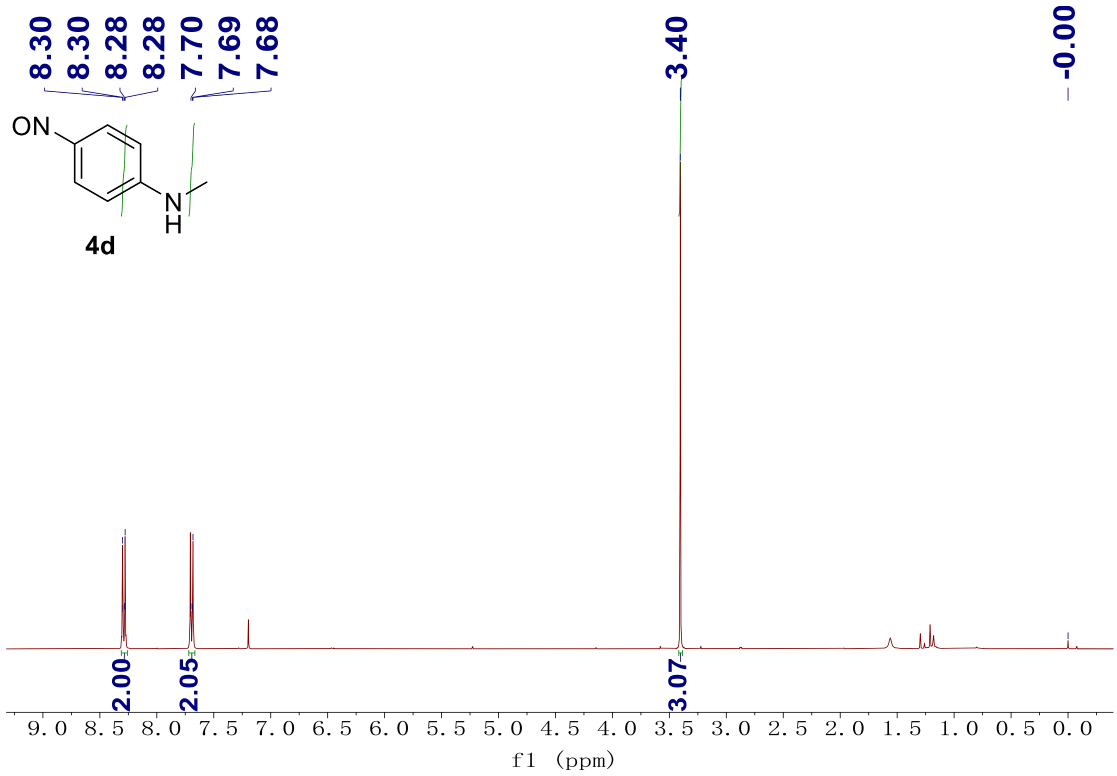

142.78
136.72
130.35
125.03
123.59
112.73
76.34
76.02
75.70
36.68
18.91
13.42
-0.00
NO
N
H
4a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

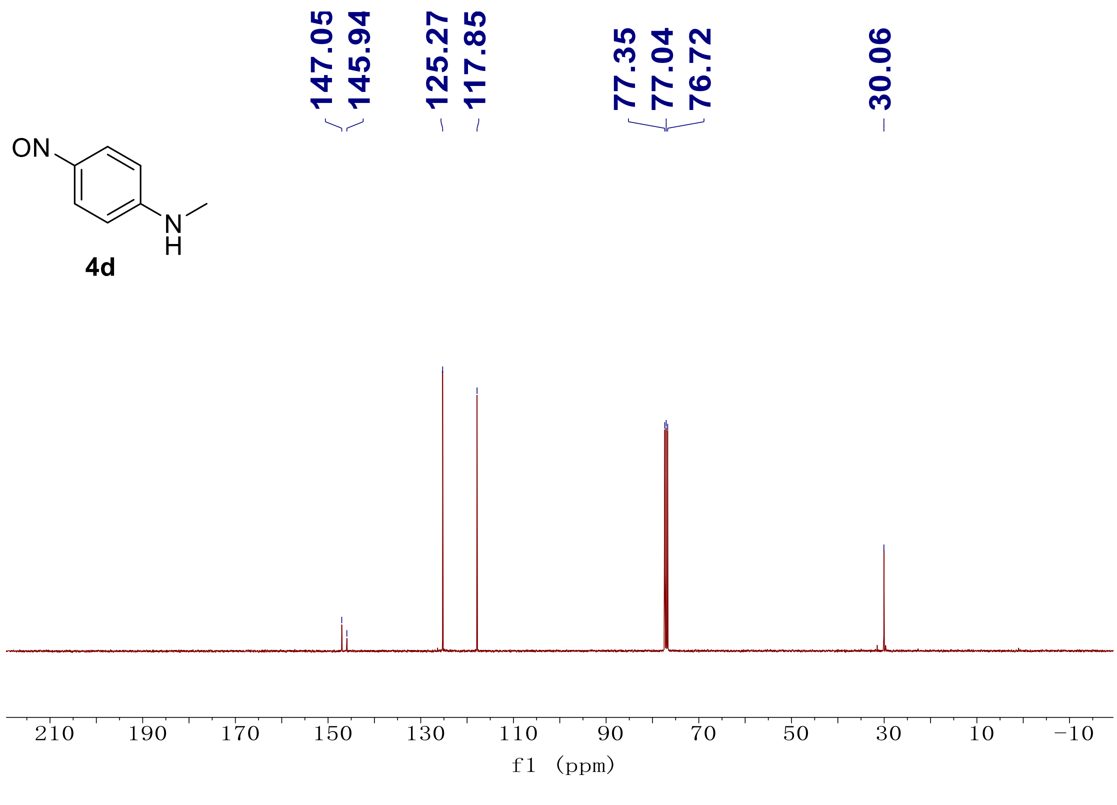

7.63
7.28
7.22
7.14
4.21
3.61
2.36
1.23
-0.00
NO
N
O
4b
8.01
2.06
3.07
3.05
8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

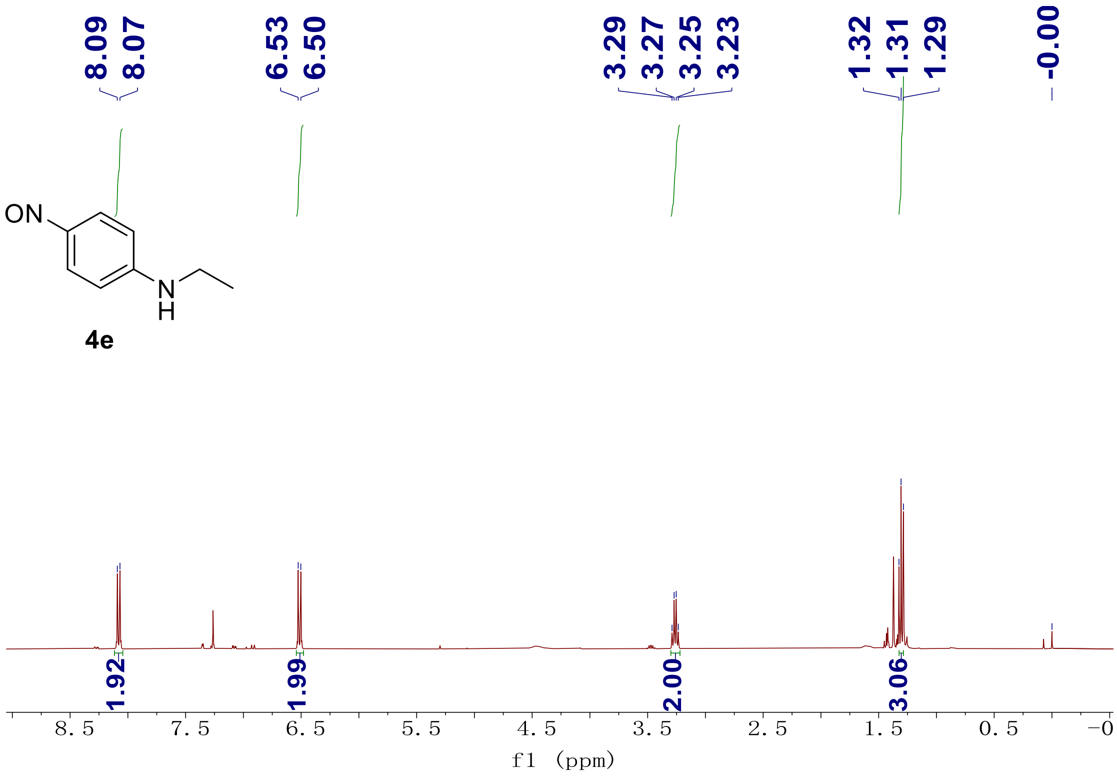

169.98
145.75
139.01
135.67
134.52
131.60
129.82
127.91
125.93
77.46
77.14
76.82
45.38
20.81
12.79
NO
N
O
4b
210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)

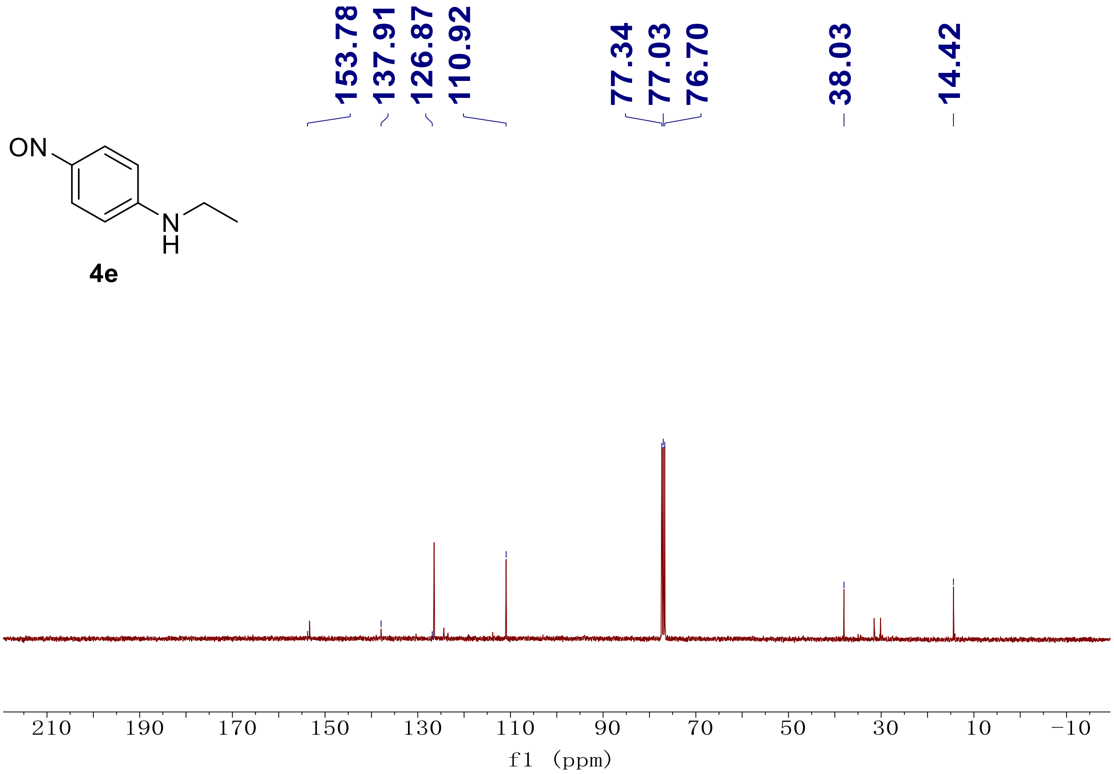

7.80 7.80 7.52 7.50 7.25 7.22
4.01 3.99 3.97 3.96 3.94 3.92 3.40 3.38 3.37 3.35 3.33 3.31 2.50
1.83
1.09 1.07 1.05
NO
N
O
4c
1.08 0.89 1.00
2.09
3.00
2.93
3.12
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

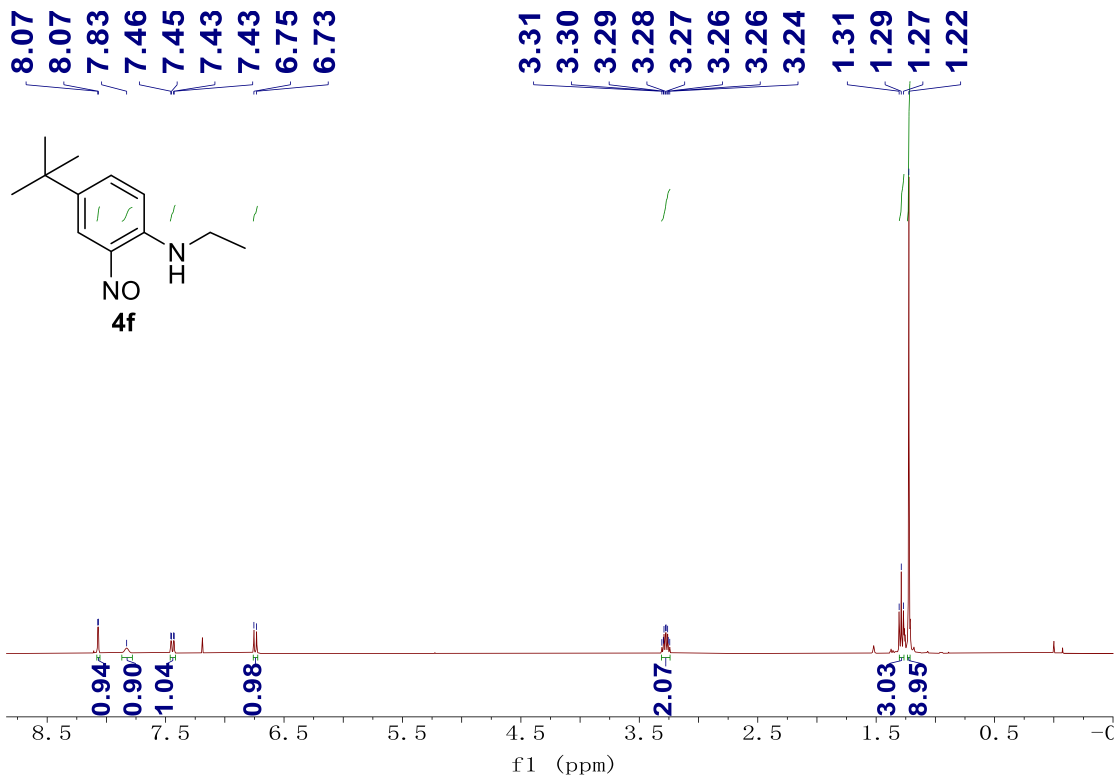

169.87
146.94 140.36 134.70 133.32 131.58 125.80
43.90
22.55 20.95 12.87
NO
N
O
4c
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

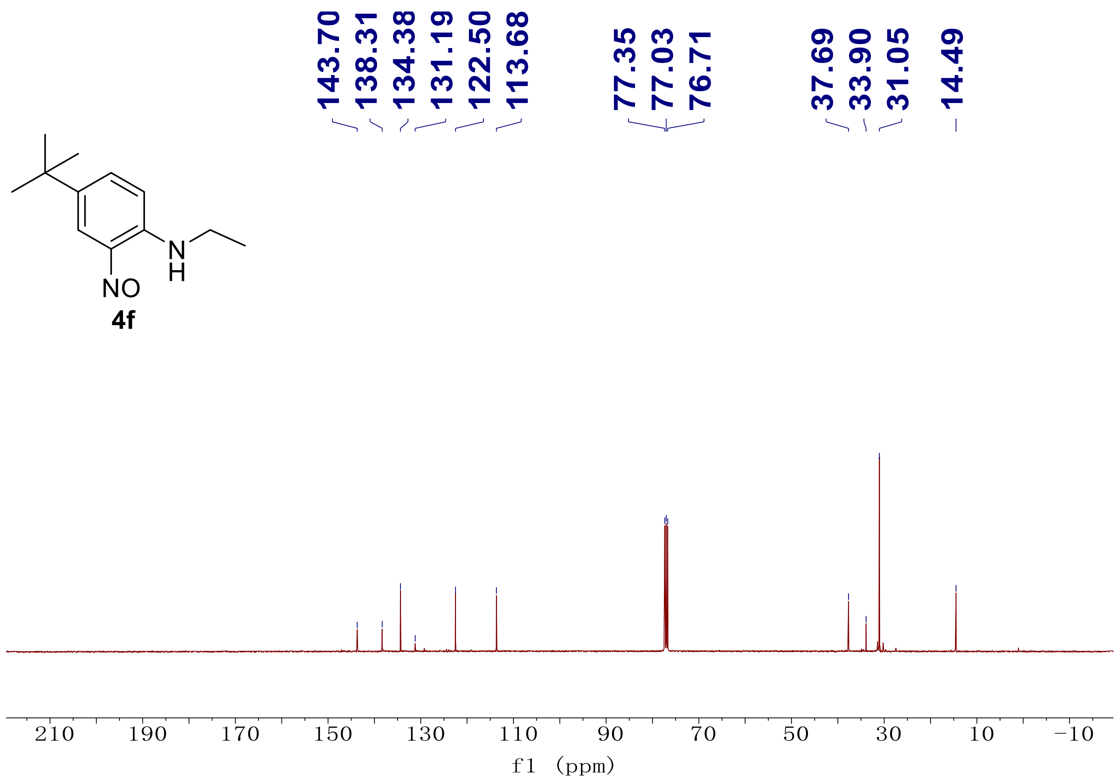

8.30
8.30
8.28
8.28
7.70
7.69
7.68
3.40
-0.00
ON
N
H
4d
2.00
2.05
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

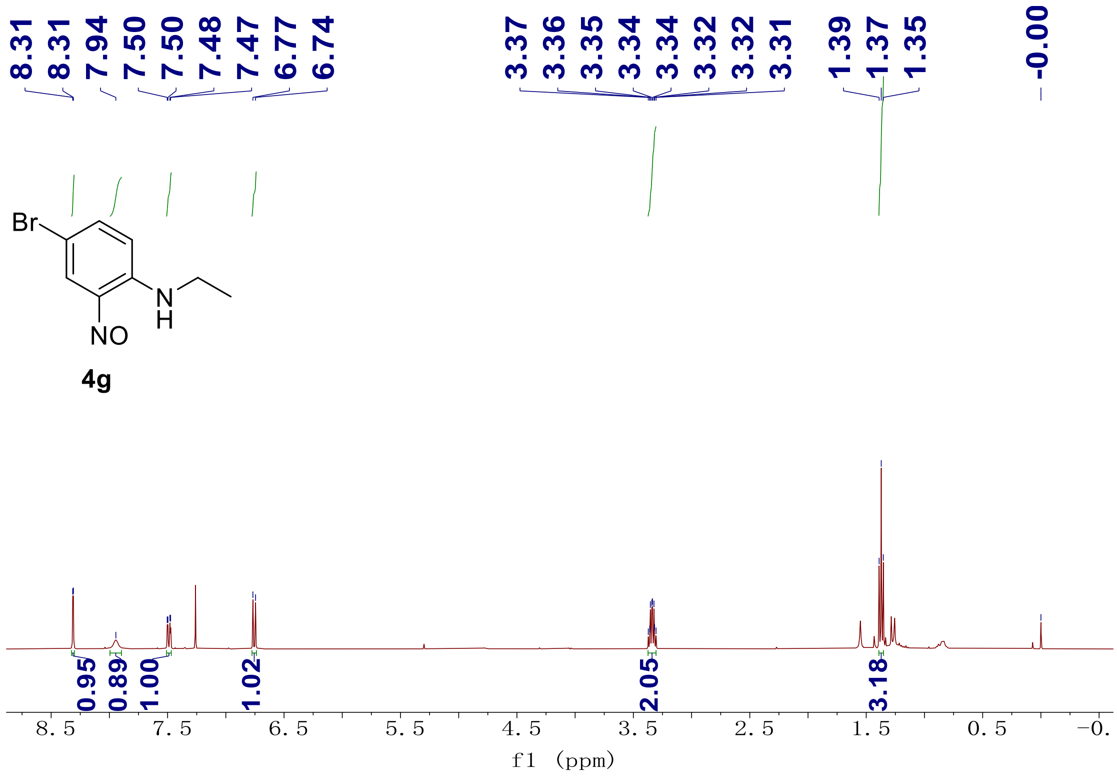

147.05
145.94
125.27
117.85
77.35
77.04
76.72
30.06
ON
N
H
4d
210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)


8.09
8.07
6.53
6.50
3.29
3.27
3.25
3.23
1.32
1.31
1.29
-0.00
ON
N
H
4e
1.92
1.99
2.00
3.06
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
f1 (ppm)

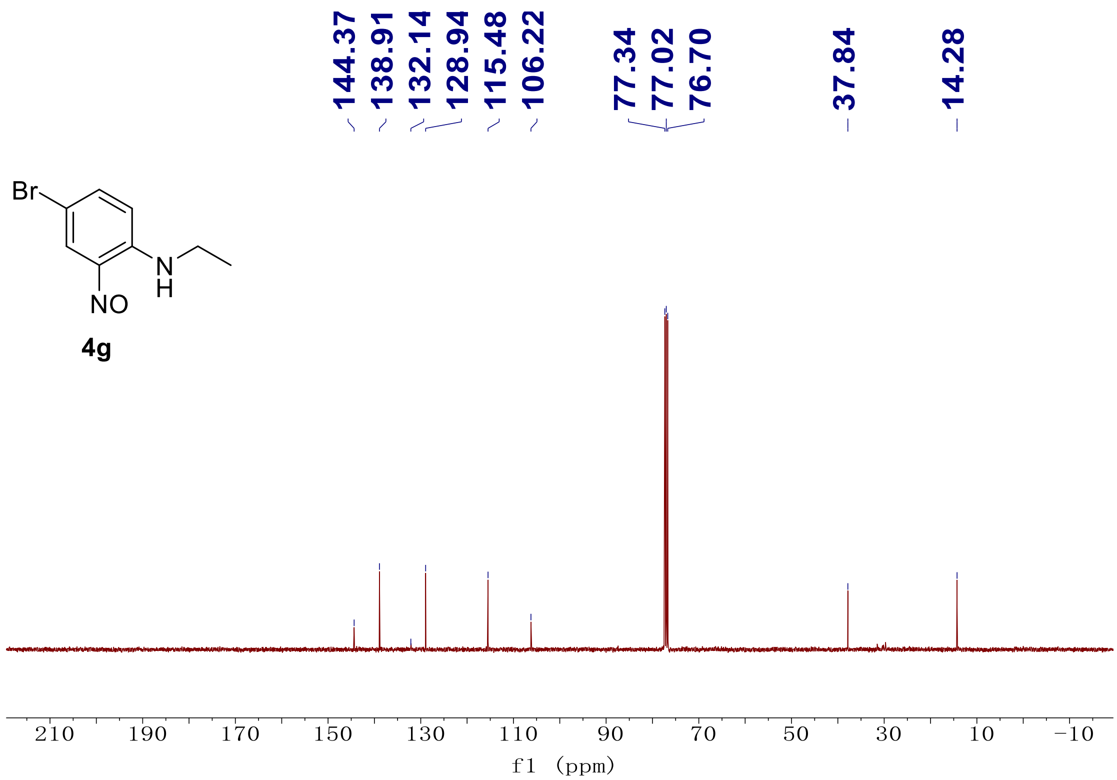

153.78
137.91
126.87
110.92
77.34
77.03
76.70
38.03
14.42
ON
N
H
4e
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)


8.07 8.07 7.83 7.46 7.45 7.43 7.43 6.75 6.73
3.31 3.30 3.29 3.28 3.27 3.26 3.26 3.24
1.31 1.29 1.27 1.22
NO
N
H
4f
0.94 0.90 1.04 0.98 2.07 3.03 8.95
8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

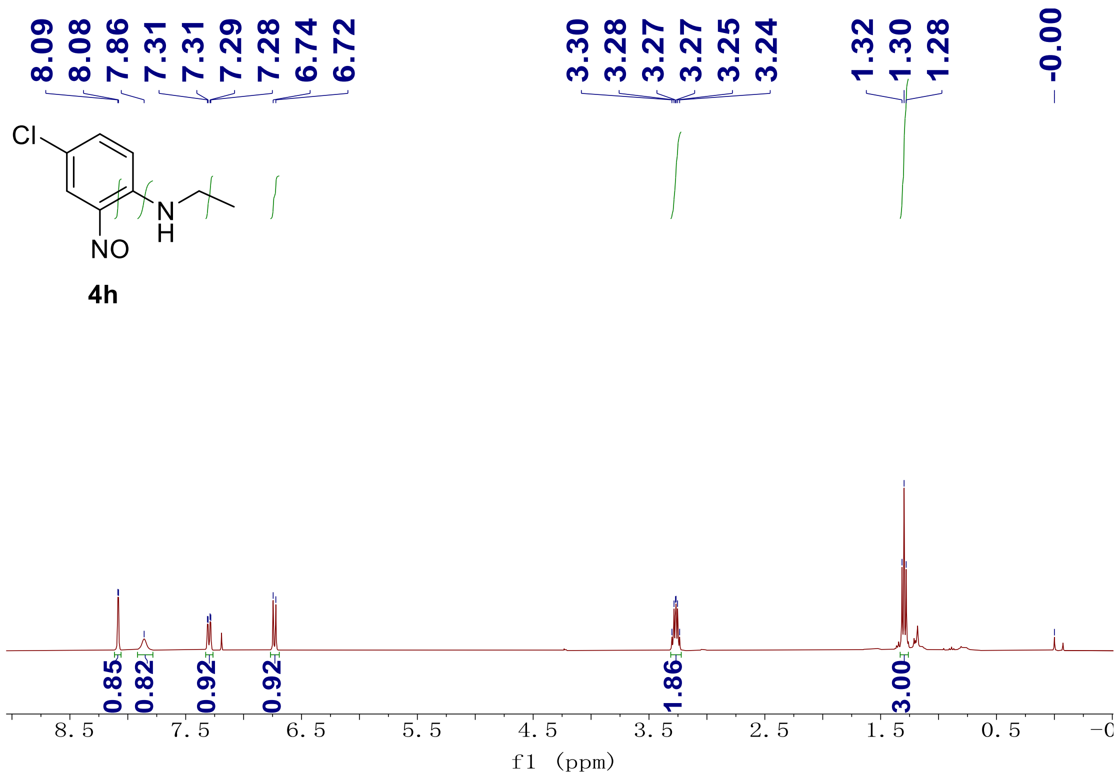

143.70 138.31 134.38 131.19 122.50 113.68
77.35 77.03 76.71
37.69 33.90 31.05
14.49
NO
N
H
4f
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

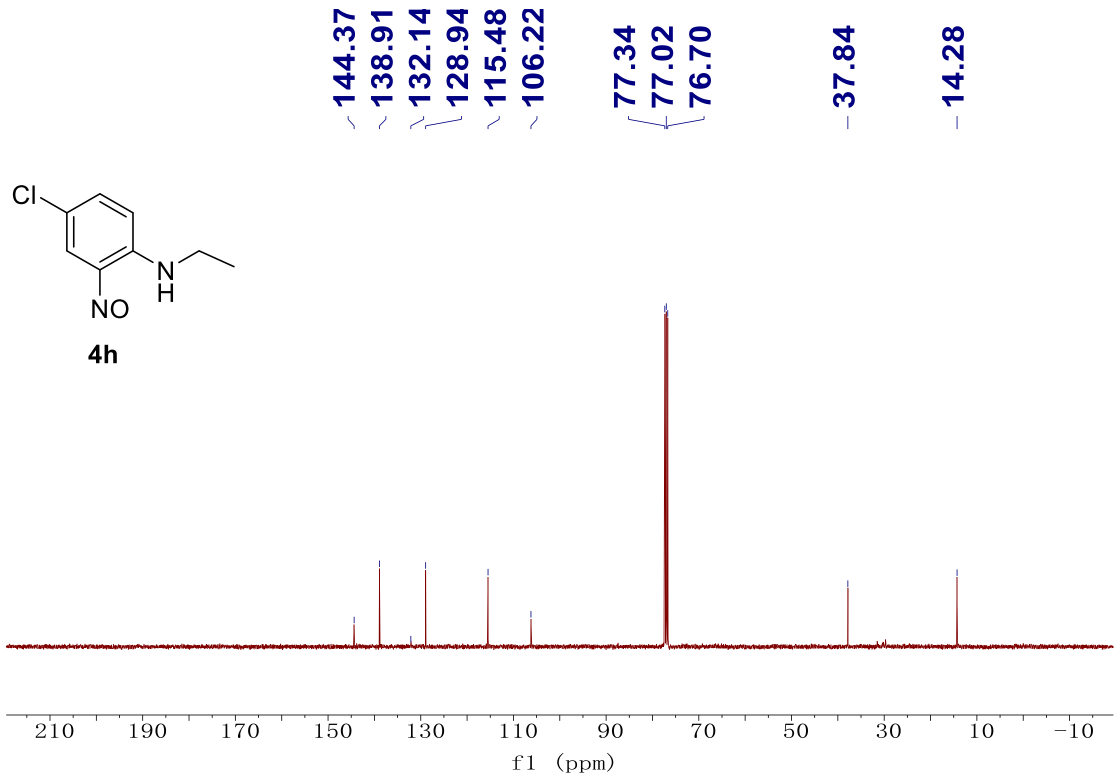


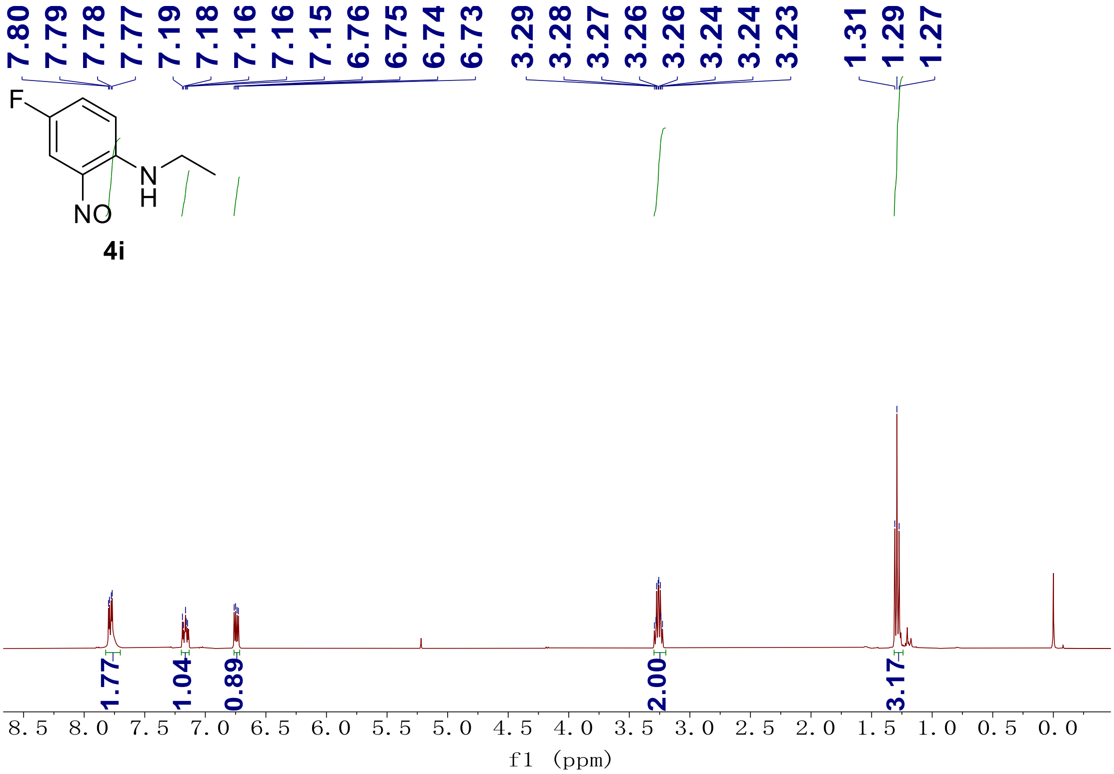
8.31
8.31
7.94
7.50
7.50
7.48
7.47
6.77
6.74
3.37
3.36
3.35
3.34
3.34
3.32
3.32
3.31
1.39
1.37
1.35
-0.00
Br
N
H
NO
4g
0.95
0.89
1.00
1.02
2.05
3.18
8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.
f1 (ppm)



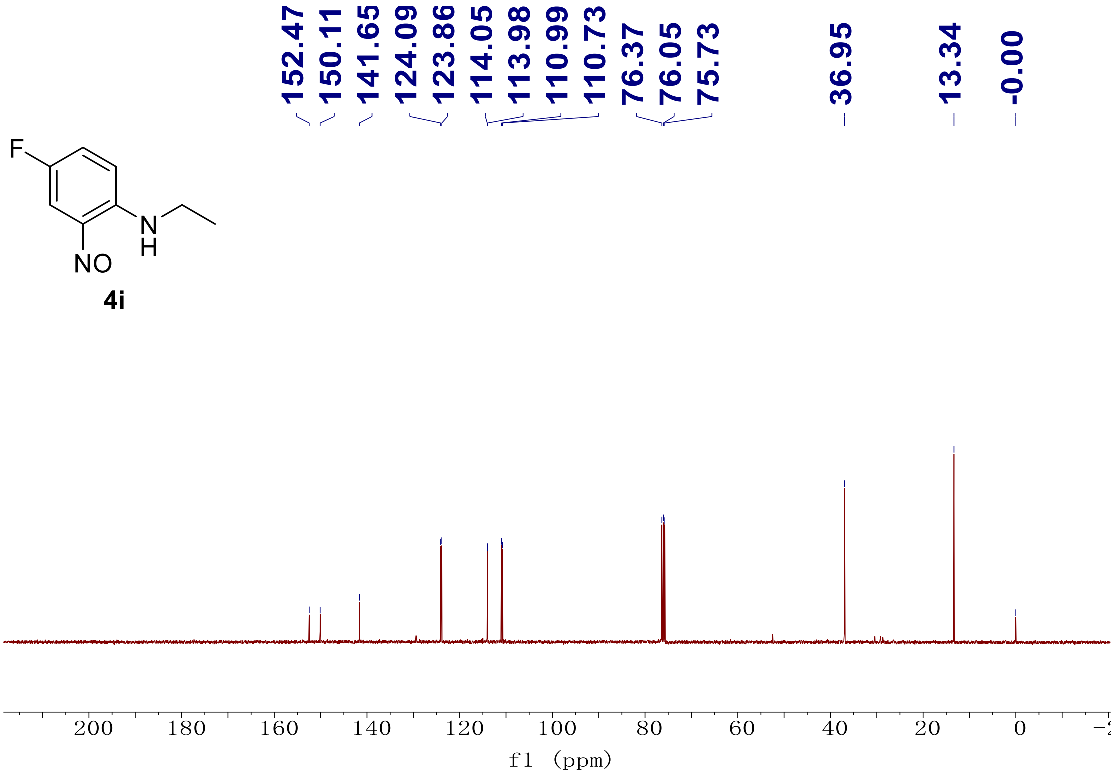
144.37
138.91
132.14
128.94
115.48
106.22
77.34
77.02
76.70
37.84
14.28
Br
N
H
NO
4g
210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)


8.09 8.08 7.86 7.31 7.31 7.29 7.28 6.74 6.72
3.30 3.28 3.27 3.27 3.25 3.24
1.32 1.30 1.28
-0.00
Cl
N
H
NO
4h
0.85 0.82 0.92 0.92 1.86 3.00
8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

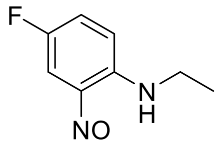

144.37 138.91 132.14 128.94 115.48 106.22
77.34 77.02 76.70
37.84
14.28
Cl
N
H
NO
4h
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)


7.80
7.79
7.78
7.77
7.19
7.18
7.16
7.16
7.15
6.76
6.75
6.74
6.73
3.29
3.28
3.27
3.26
3.26
3.24
3.24
3.23
1.31
1.29
1.27
F
N
H
NO
1.77
1.04
0.89
2.00
3.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

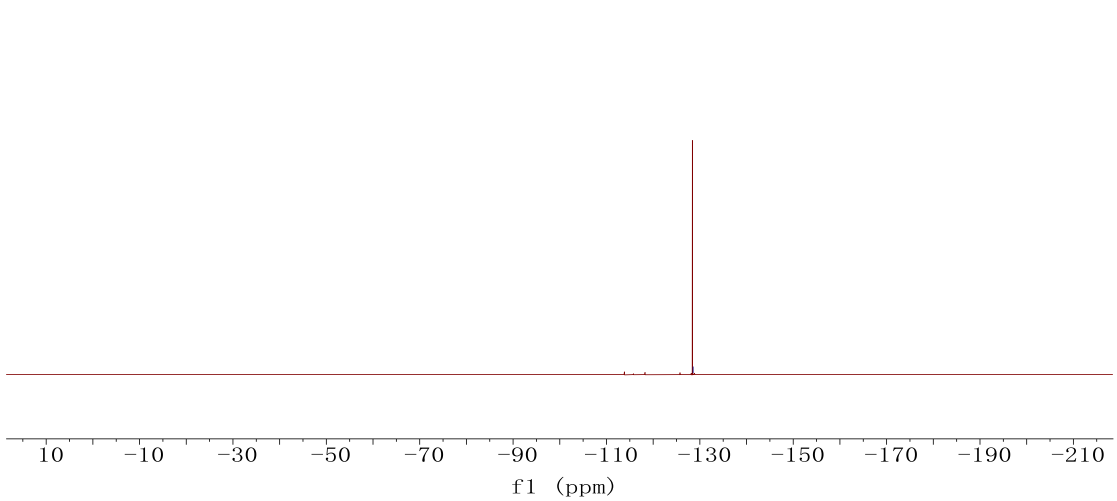
4i

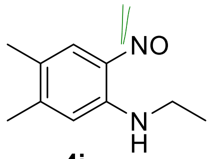

152.47
150.11
141.65
124.09
123.86
114.05
113.98
110.99
110.73
76.37
76.05
75.73
36.95
13.34
-0.00
F
N
H
NO
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

4i

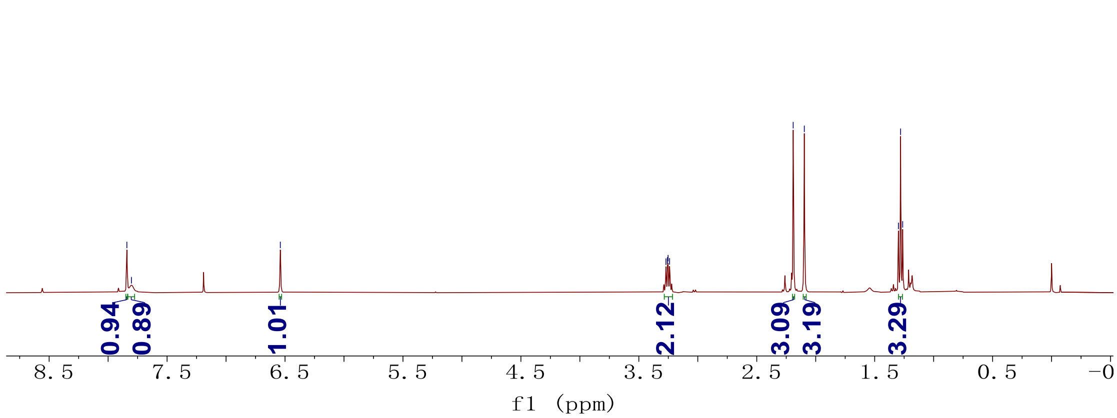


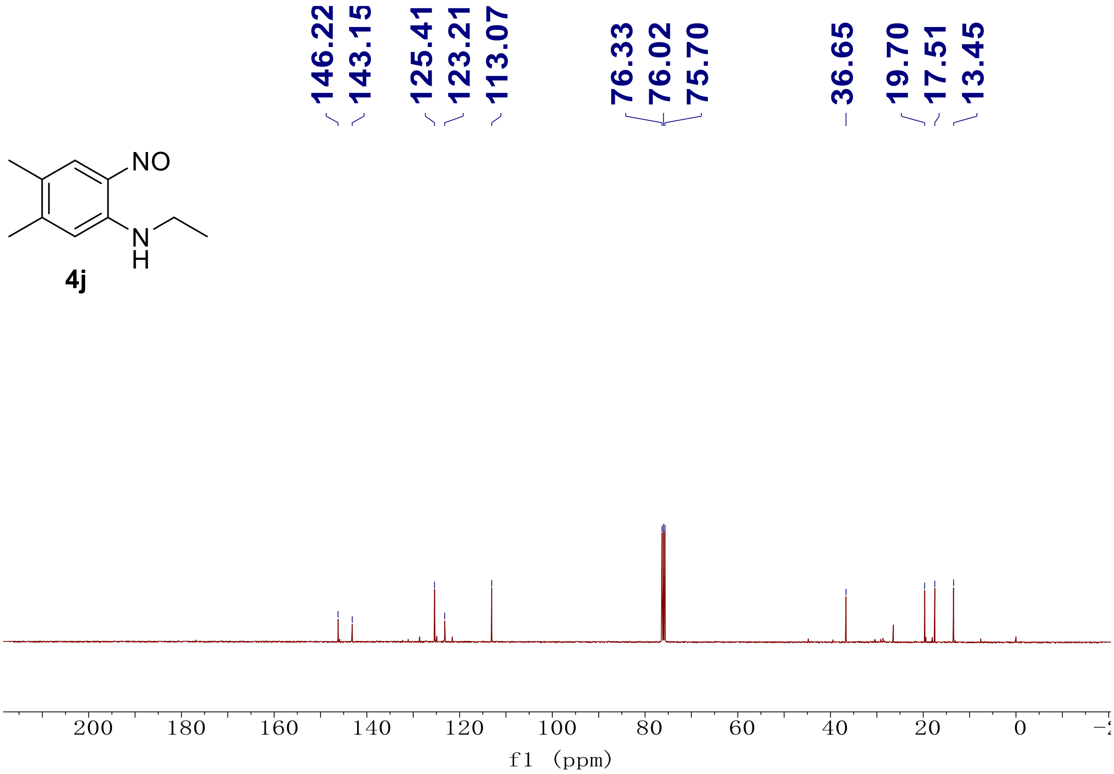
4i


-128.56
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

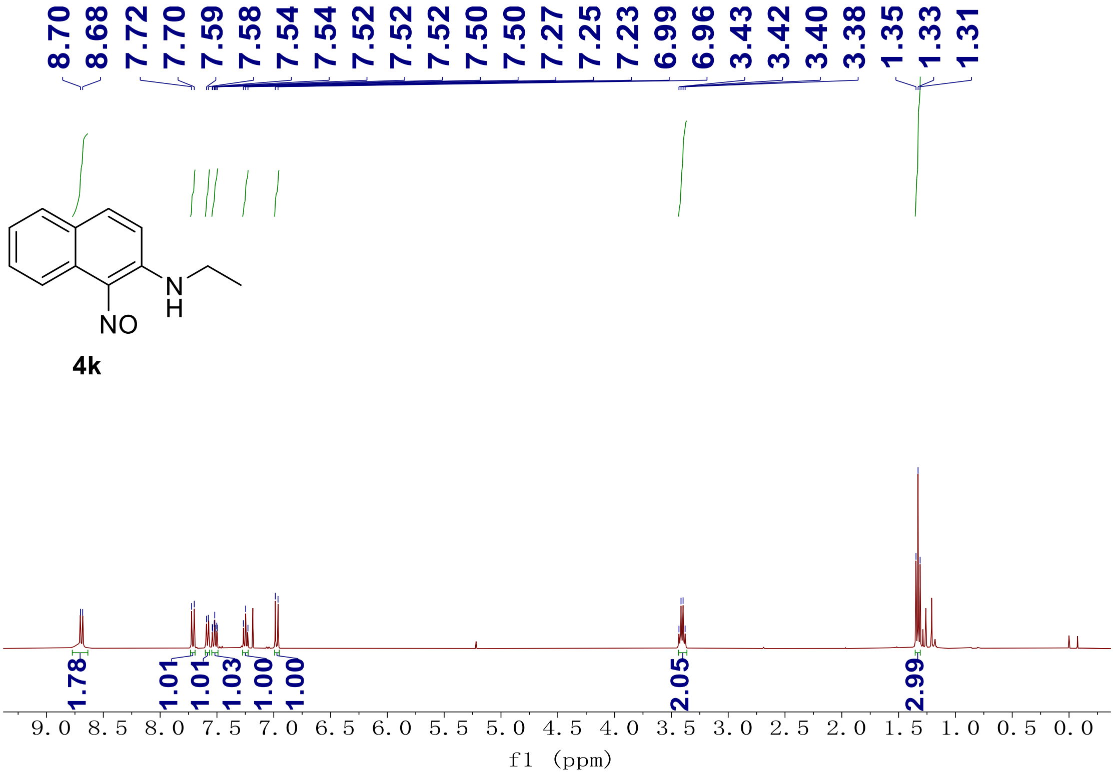


4j

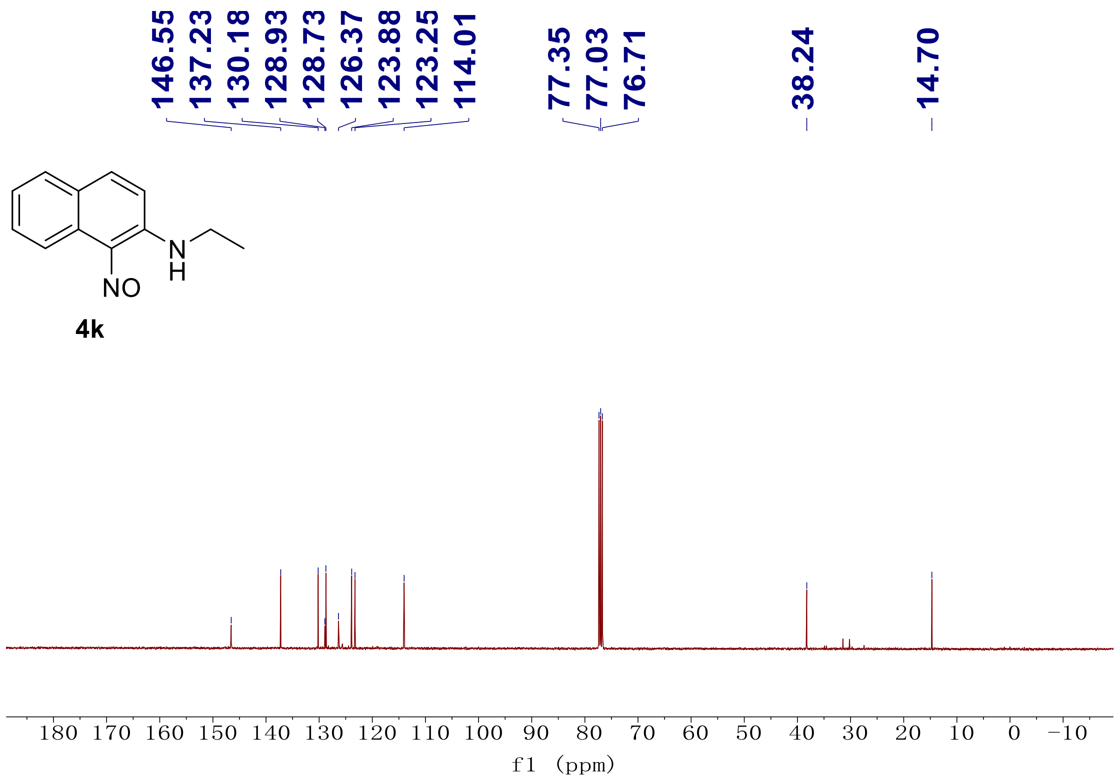

7.84
7.80
6.54
3.27
3.26
3.25
3.24
2.19
2.10
1.30
1.28
1.26
0.94
0.89
1.01
2.12
3.09
3.19
3.29
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0
f1 (ppm)



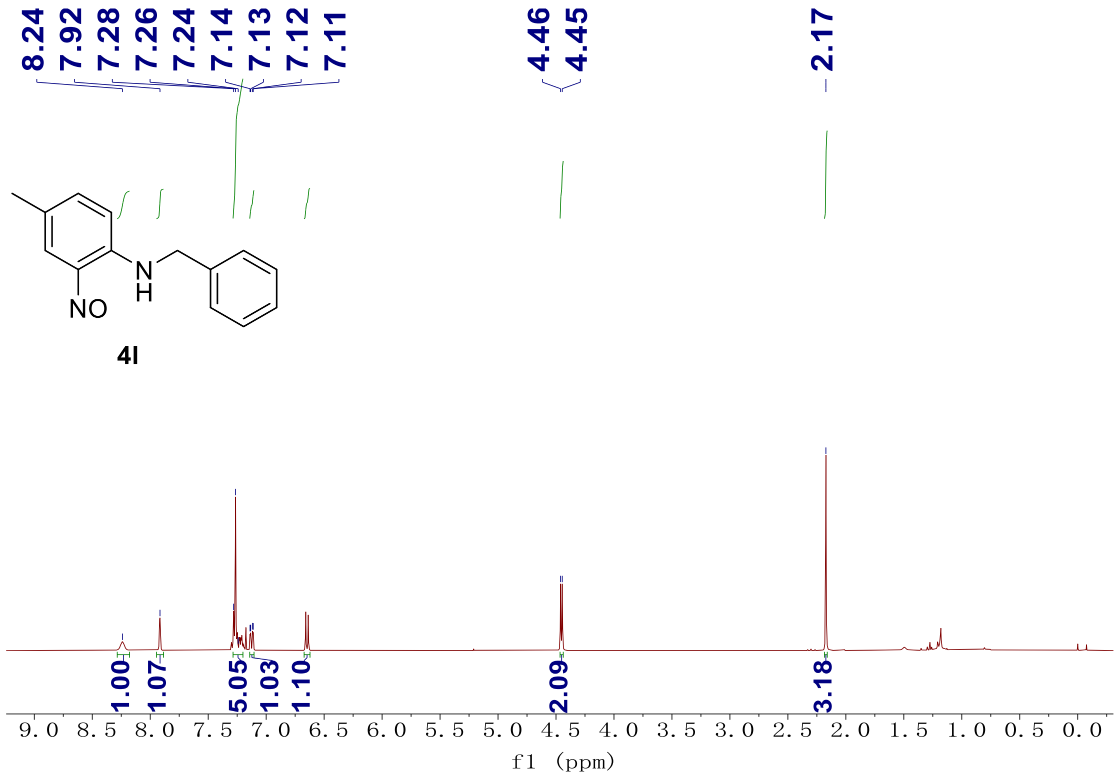
146.22
143.15
125.41
123.21
113.07
76.33
76.02
75.70
36.65
19.70
17.51
13.45
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)
4j



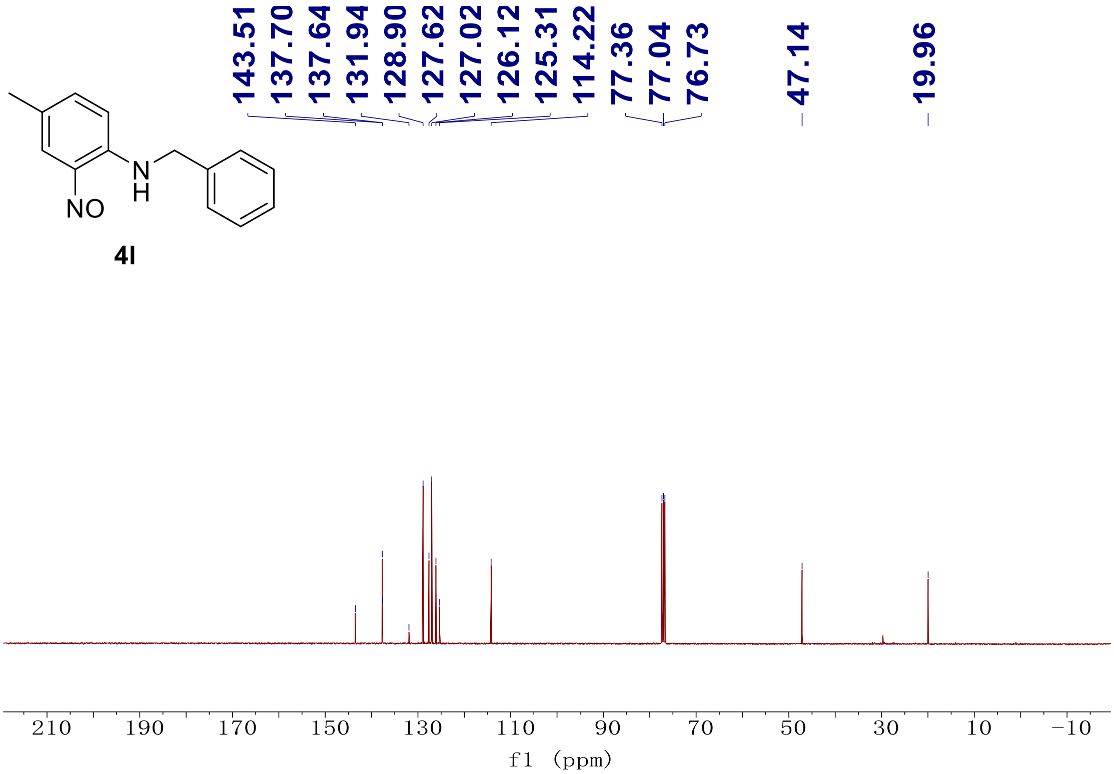
8.70
8.68
7.72
7.70
7.59
7.58
7.54
7.54
7.52
7.52
7.52
7.50
7.50
7.27
7.25
7.23
6.99
6.96
3.43
3.42
3.40
3.38
1.35
1.33
1.31
1.78
1.01
1.01
1.03
1.00
1.00
2.05
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
4k


146.55
137.23
130.18
128.93
128.73
126.37
123.88
123.25
114.01
77.35
77.03
76.71
38.24
14.70
NO
N
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

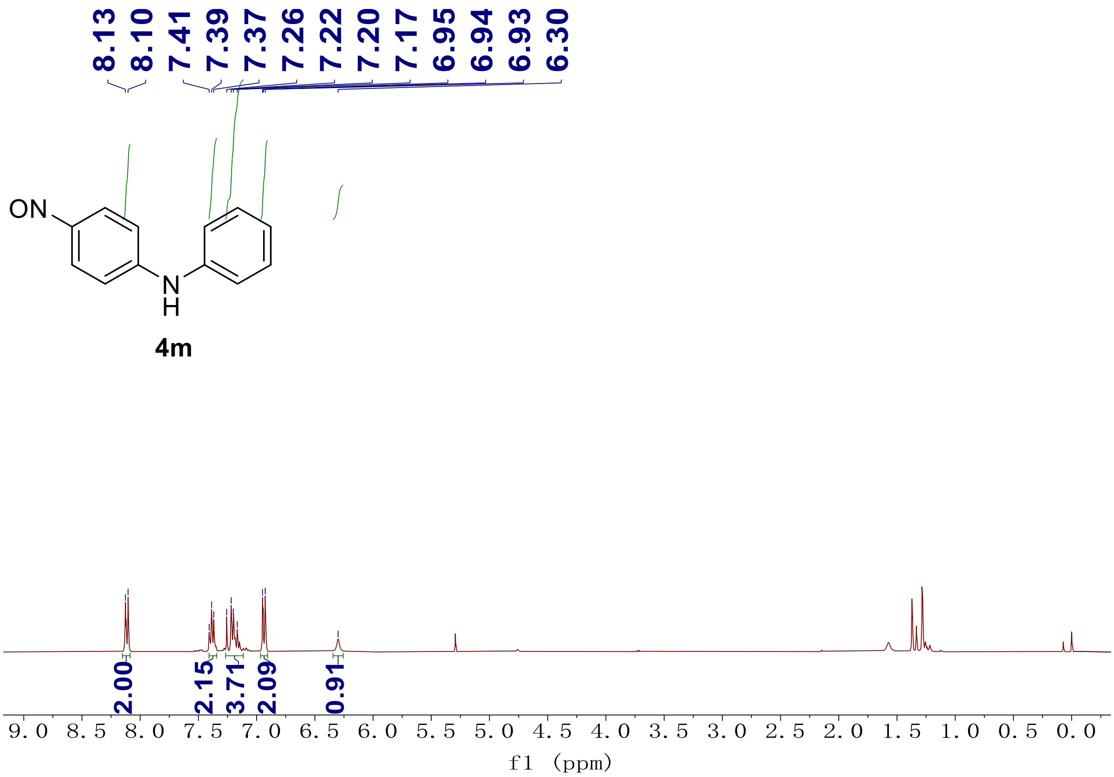
4k


8.24
7.92
7.28
7.26
7.24
7.14
7.13
7.12
7.11
4.46
4.45
2.17
NO
N
H
1.00
1.07
5.05
1.03
1.10
2.09
3.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

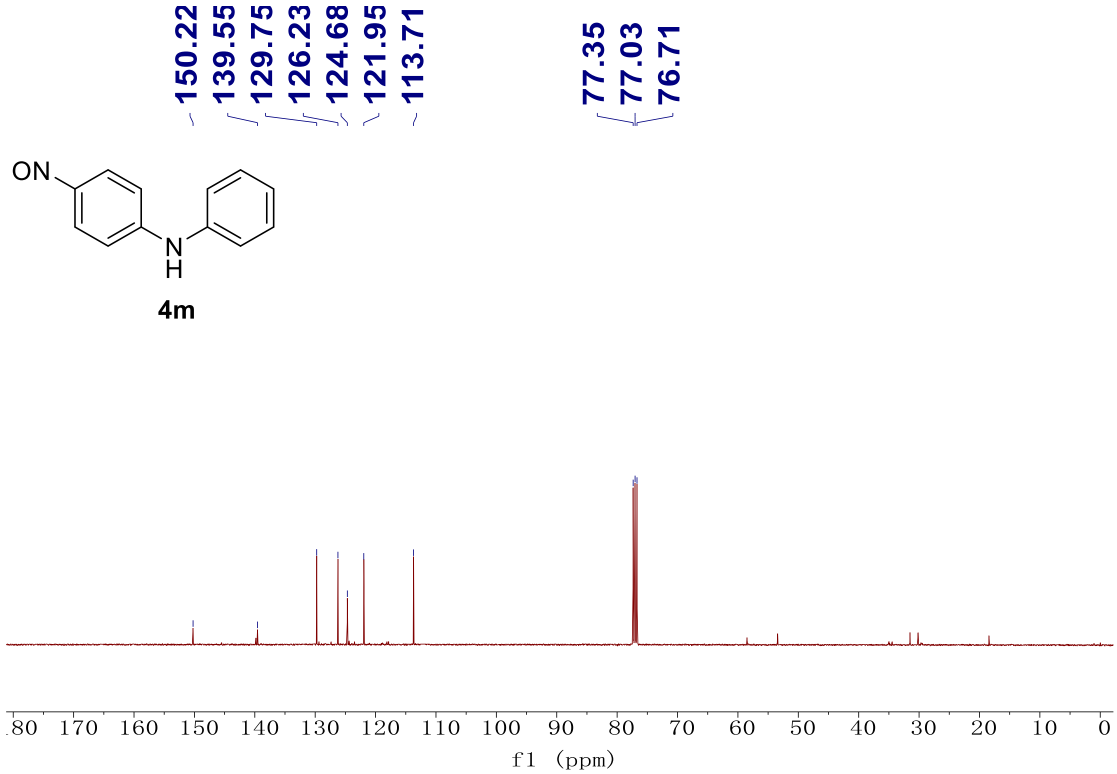
4l

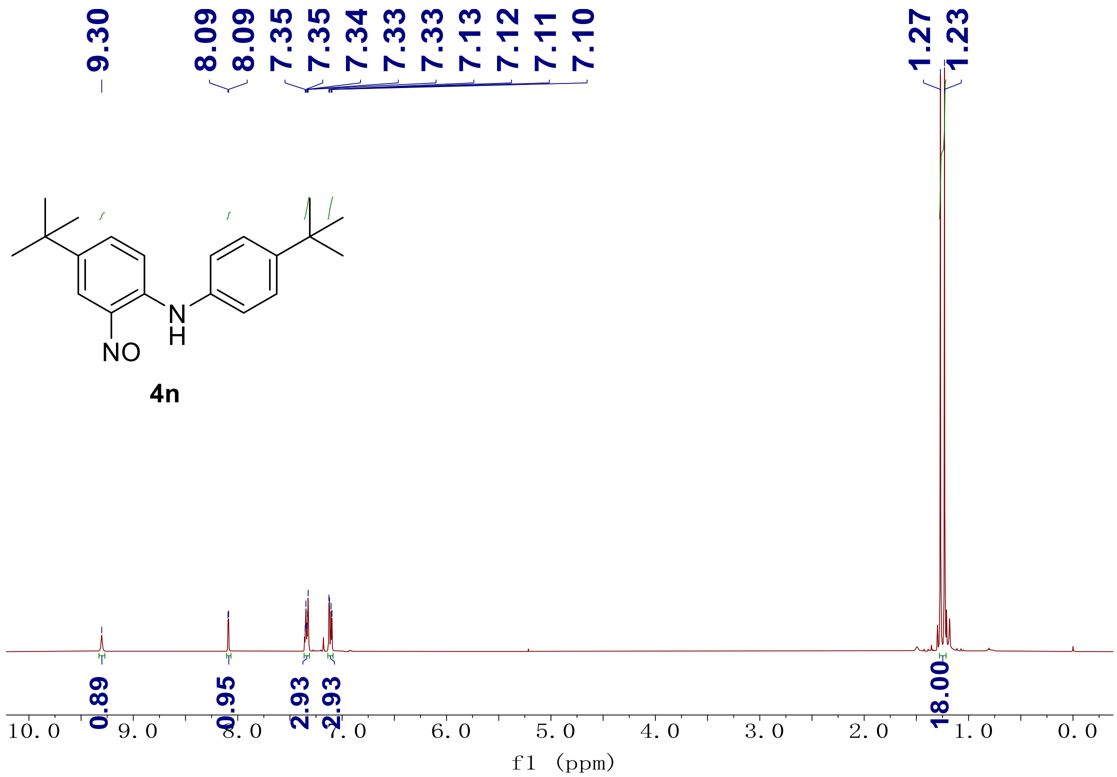

NO
N
H
143.51
137.70
137.64
131.94
128.90
127.62
127.02
126.12
125.31
114.22
77.36
77.04
76.73
47.14
19.96
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

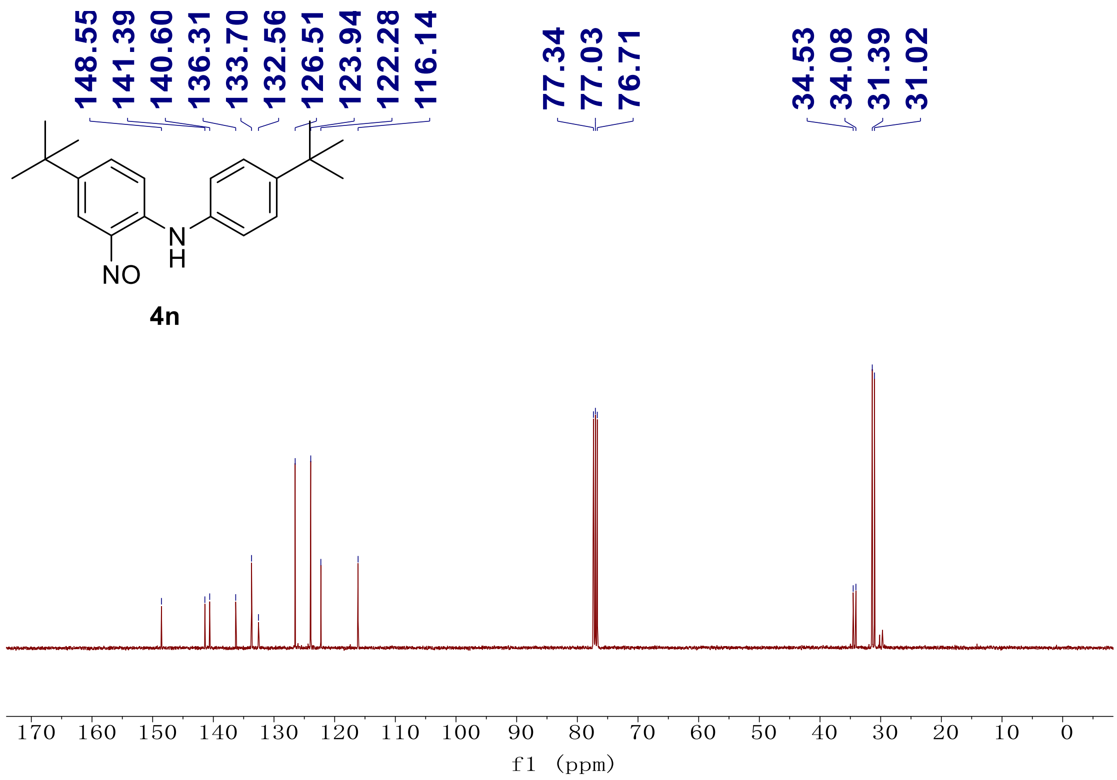
4l

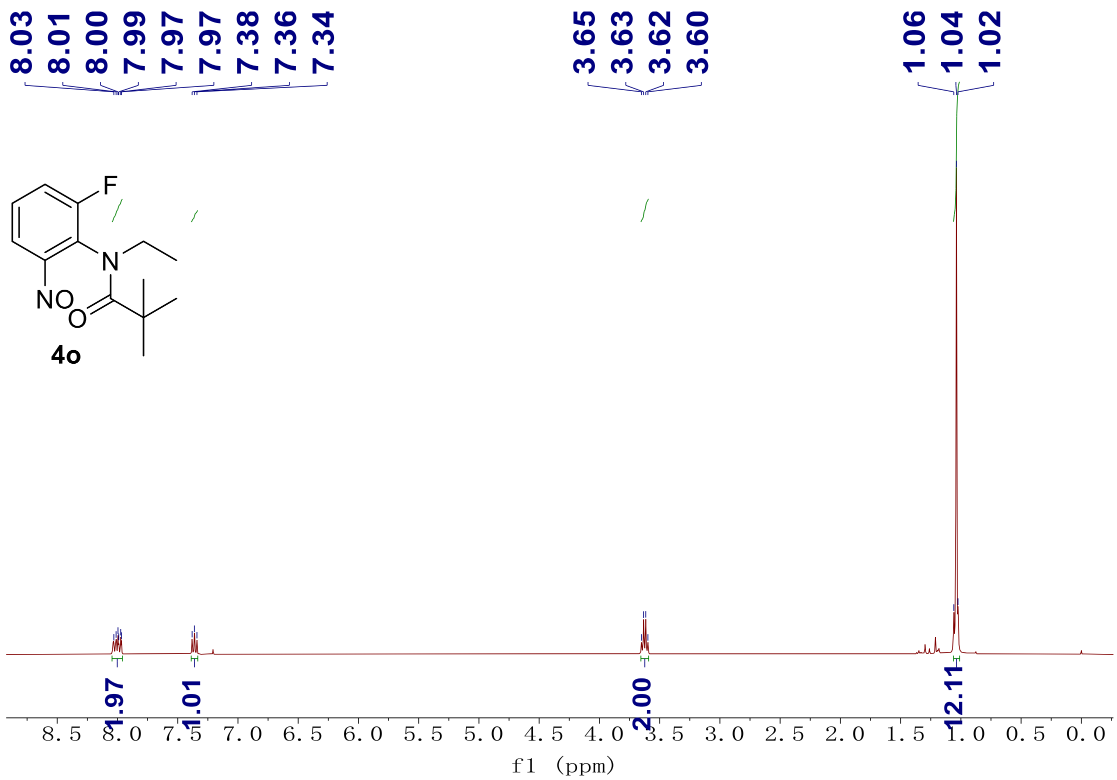

ON
N
H
8.13
8.10
7.41
7.39
7.37
7.26
7.22
7.20
7.17
6.95
6.94
6.93
6.30
2.00
2.15
3.71
2.09
0.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

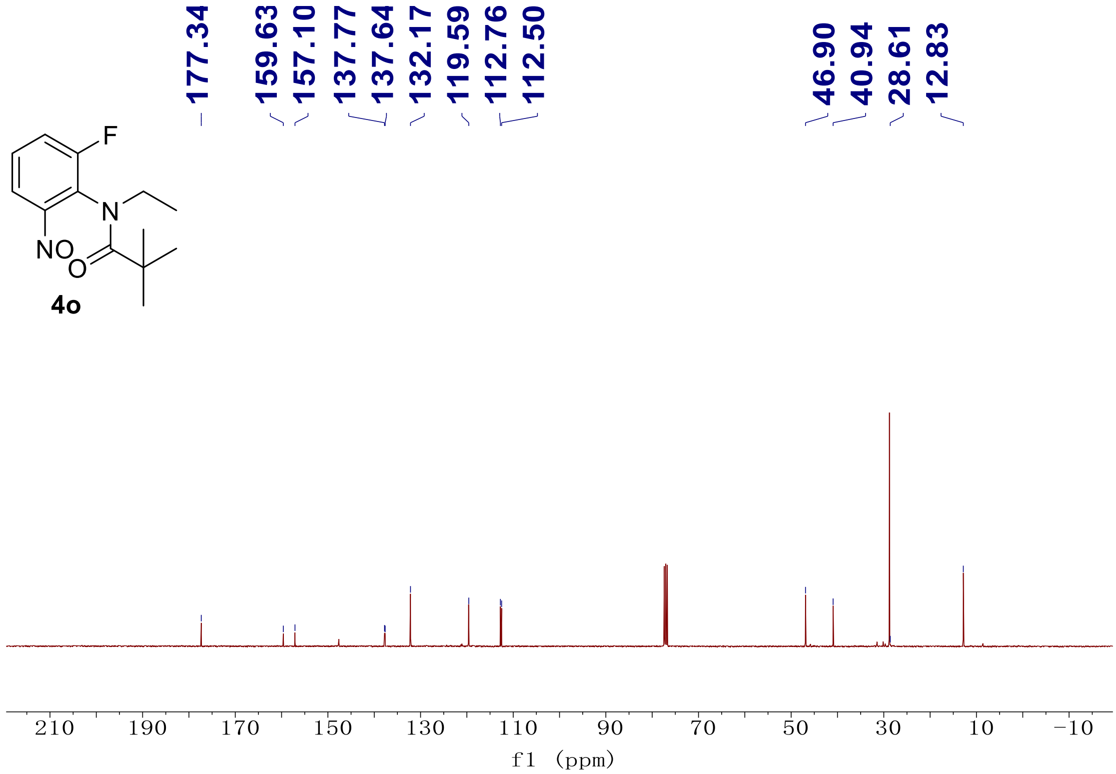
4m

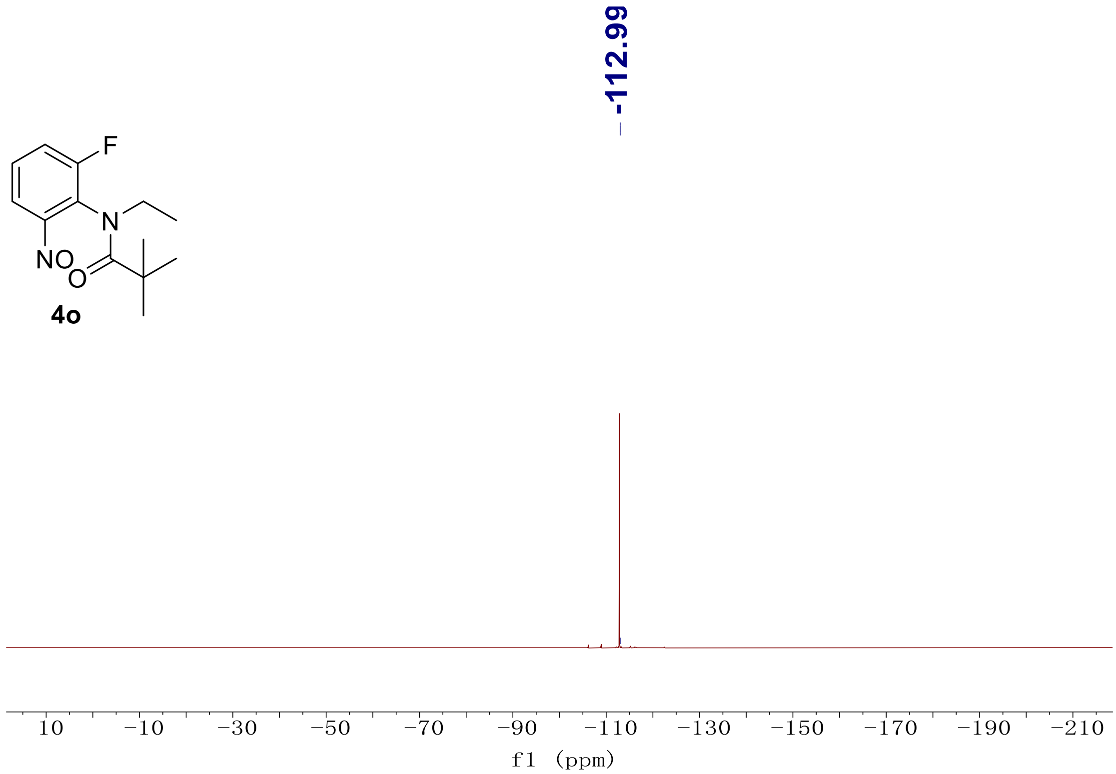

150.22
139.55
129.75
126.23
124.68
121.95
113.71
77.35
77.03
76.71
ON
N
H
4m
f1 (ppm)

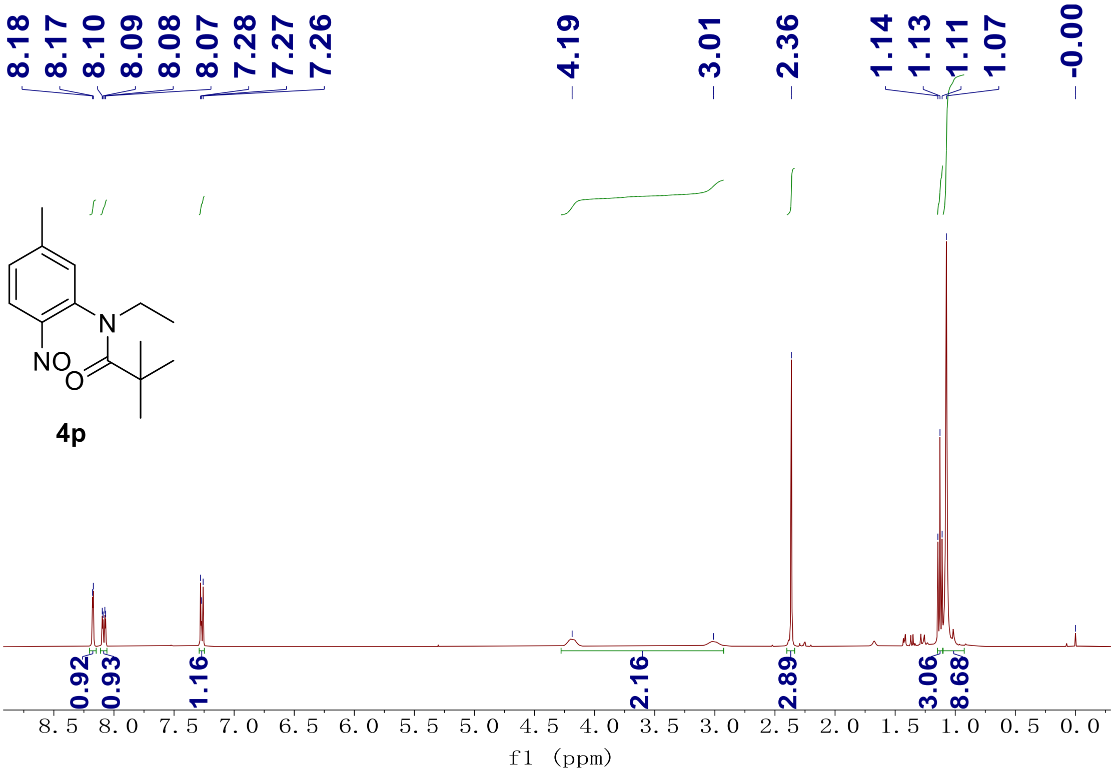

9.30
8.09
8.09
7.35
7.35
7.34
7.33
7.33
7.13
7.12
7.11
7.10
1.27
1.23
NO
N
H
4n
0.89
0.95
2.93
2.93
18.00
f1 (ppm)

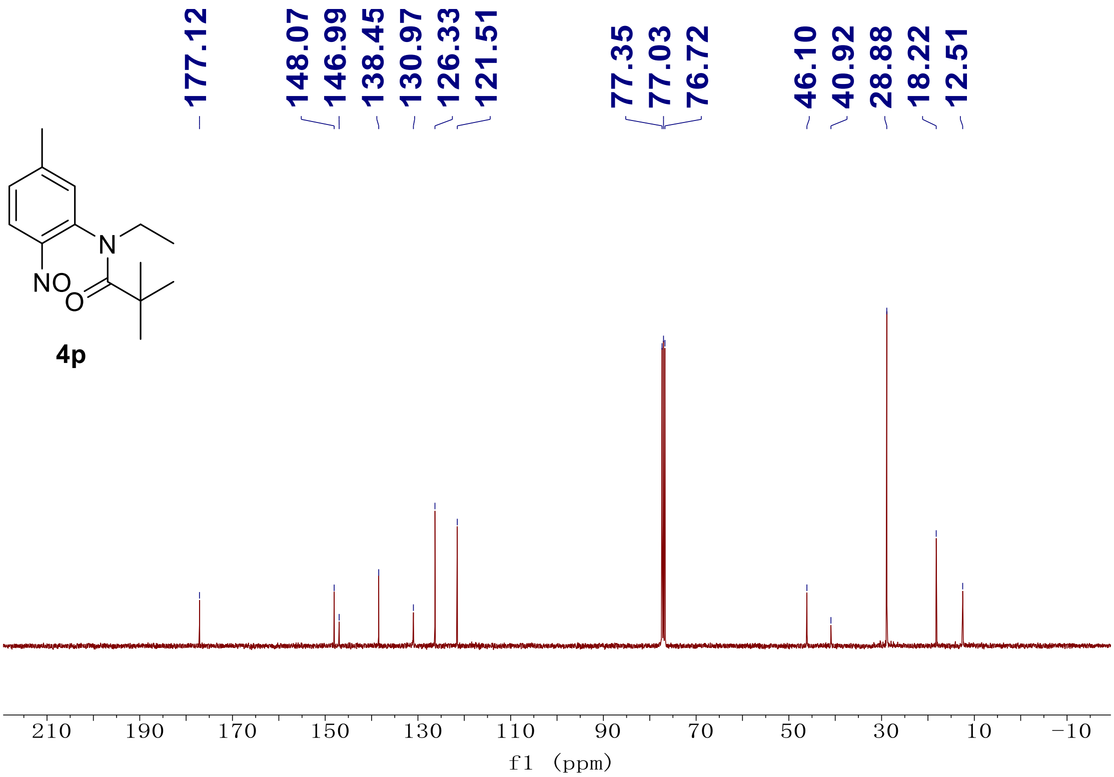

148.55
141.39
140.60
136.31
133.70
132.56
126.51
123.94
122.28
116.14
77.34
77.03
76.71
34.53
34.08
31.39
31.02
NO
N
H
4n
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.03
8.01
8.00
7.99
7.97
7.97
7.38
7.36
7.34
3.65
3.63
3.62
3.60
1.06
1.04
1.02
F
N
NO
O
4o
1.97
1.01
2.00
12.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


177.34
159.63
157.10
137.77
137.64
132.17
119.59
112.76
112.50
46.90
40.94
28.61
12.83
F
N
NO
O
4o
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)


-112.99
F
N
NO
O
4o
10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210
f1 (ppm)


8.18
8.17
8.10
8.09
8.08
8.07
7.28
7.27
7.26
4.19
3.01
2.36
1.14
1.13
1.11
1.07
-0.00
NO
N
O
4p
0.92
0.93
1.16
2.16
2.89
3.06
8.68
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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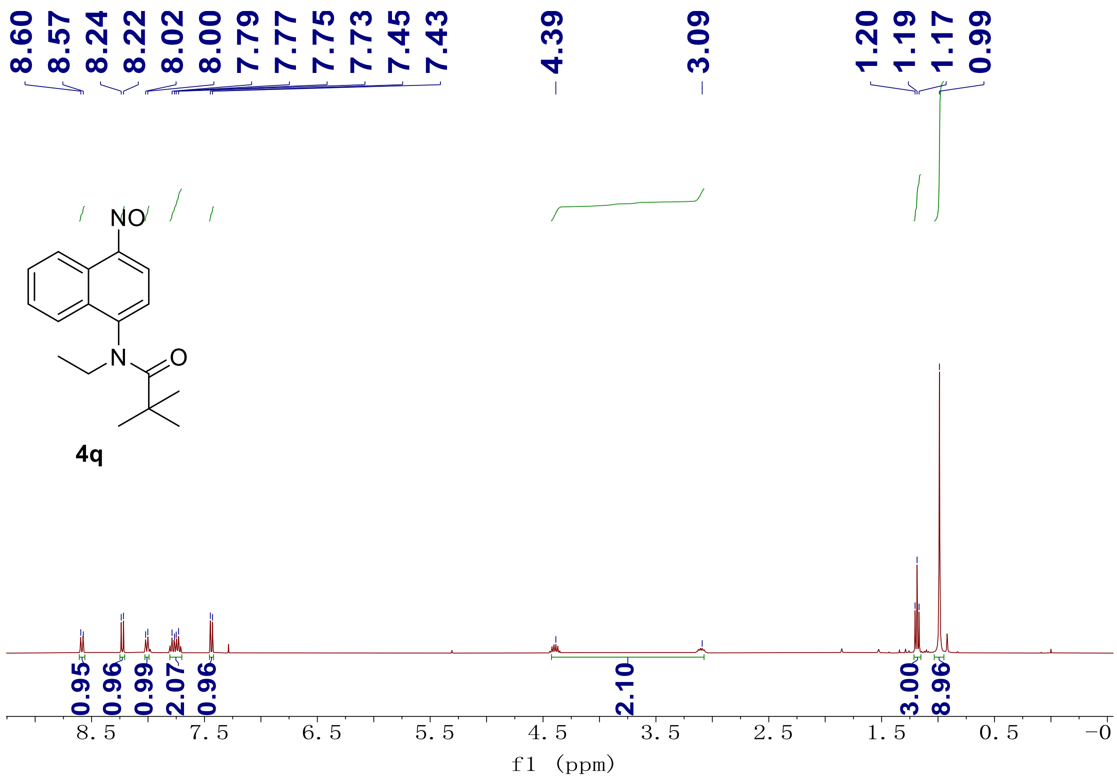
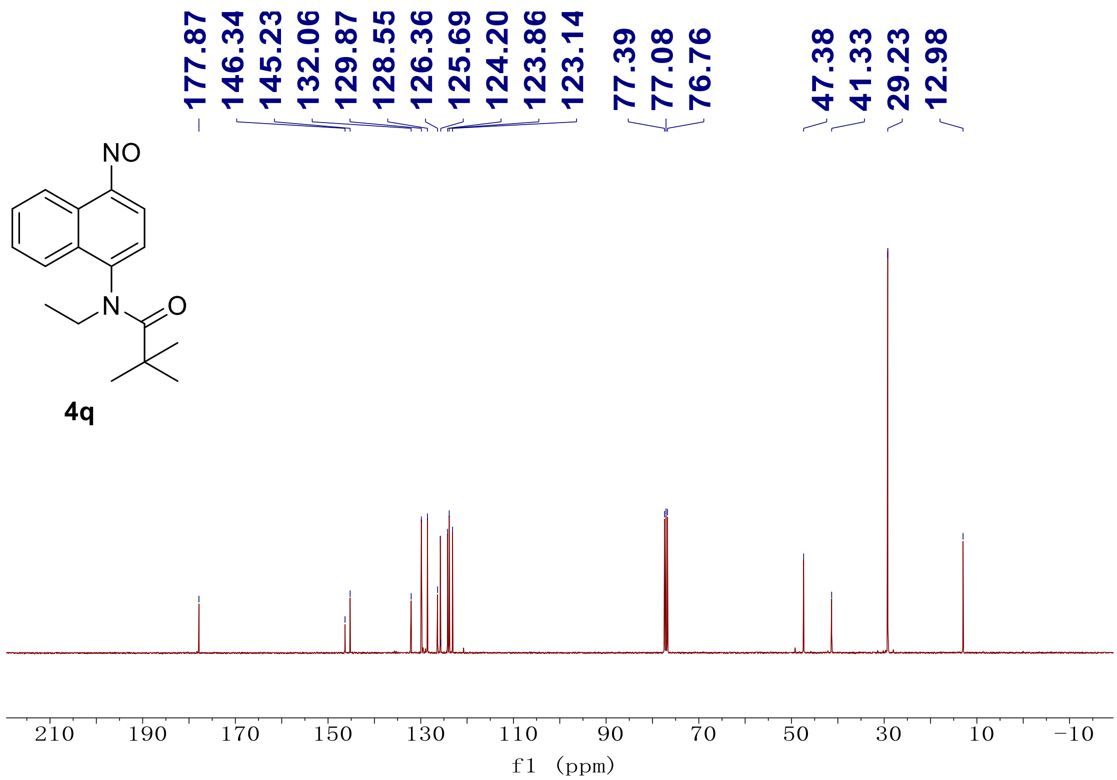
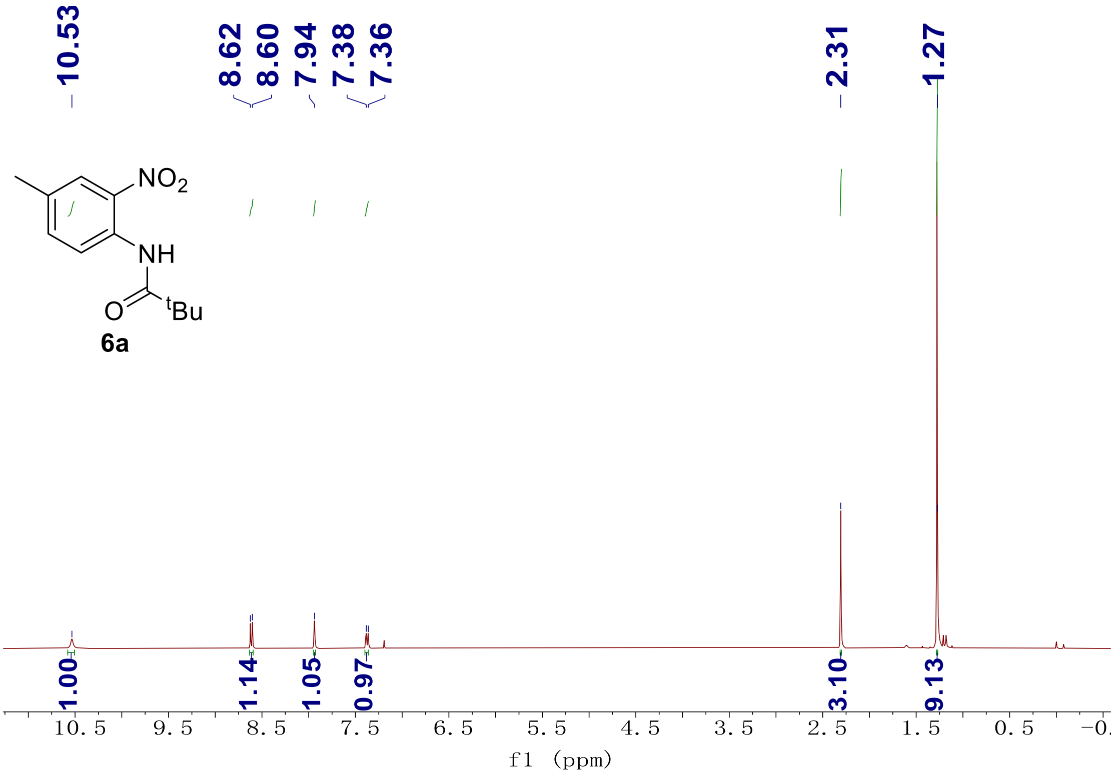
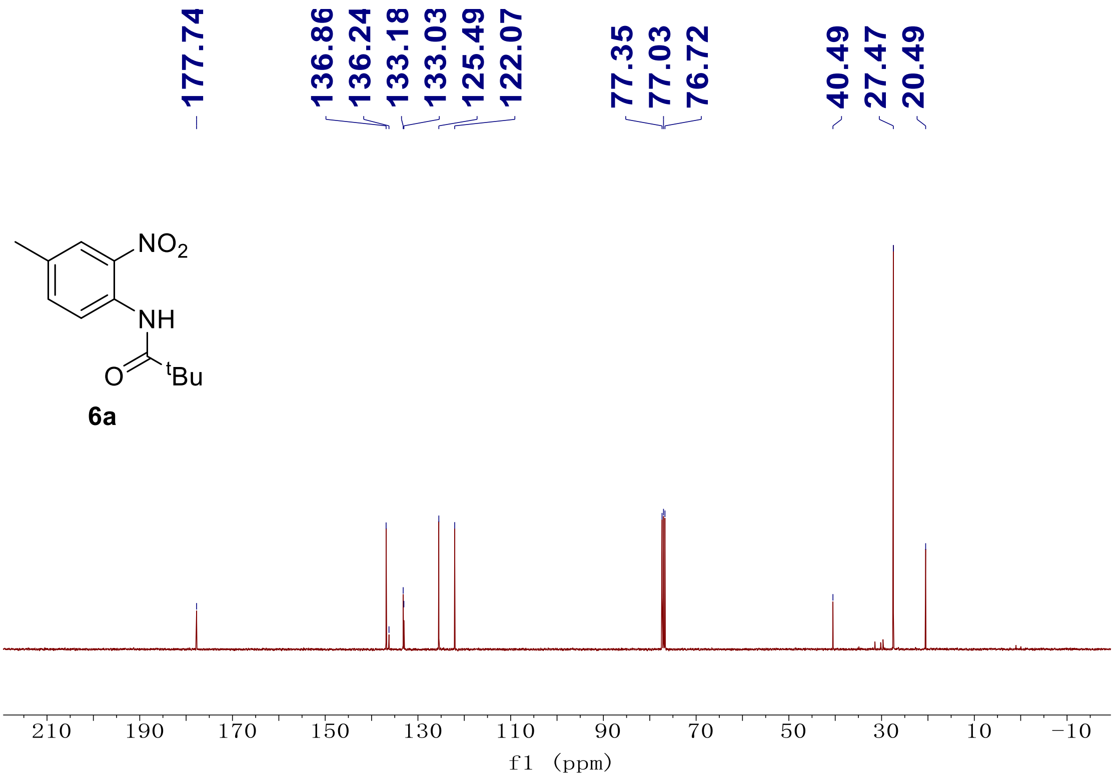
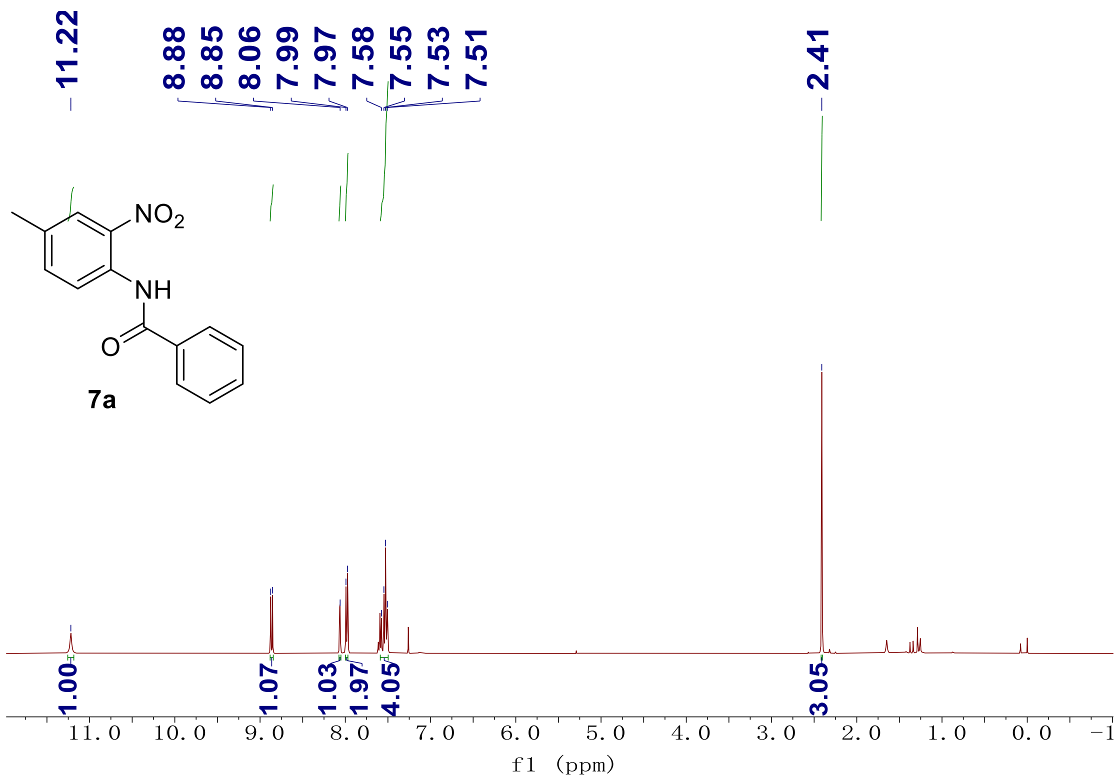
148.07
146.99
138.45
130.97
126.33
121.51
77.35
77.03
76.72
46.10
40.92
28.88
18.22
12.51
NO
N
O
4p
210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)

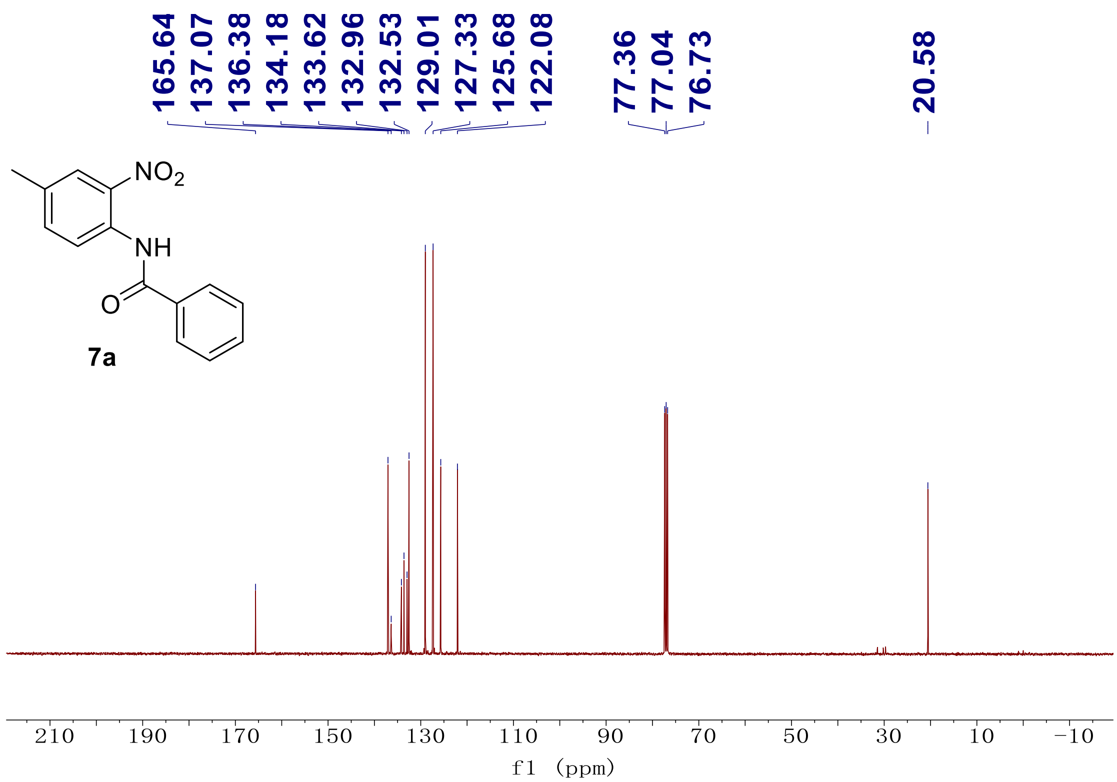

8.60
8.57
8.24
8.22
8.02
8.00
7.79
7.77
7.75
7.73
7.45
7.43
4.39
3.09
1.20
1.19
1.17
0.99
NO
N
O
4q
0.95
0.96
0.99
2.07
0.96
2.10
3.00
8.96
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
f1 (ppm)

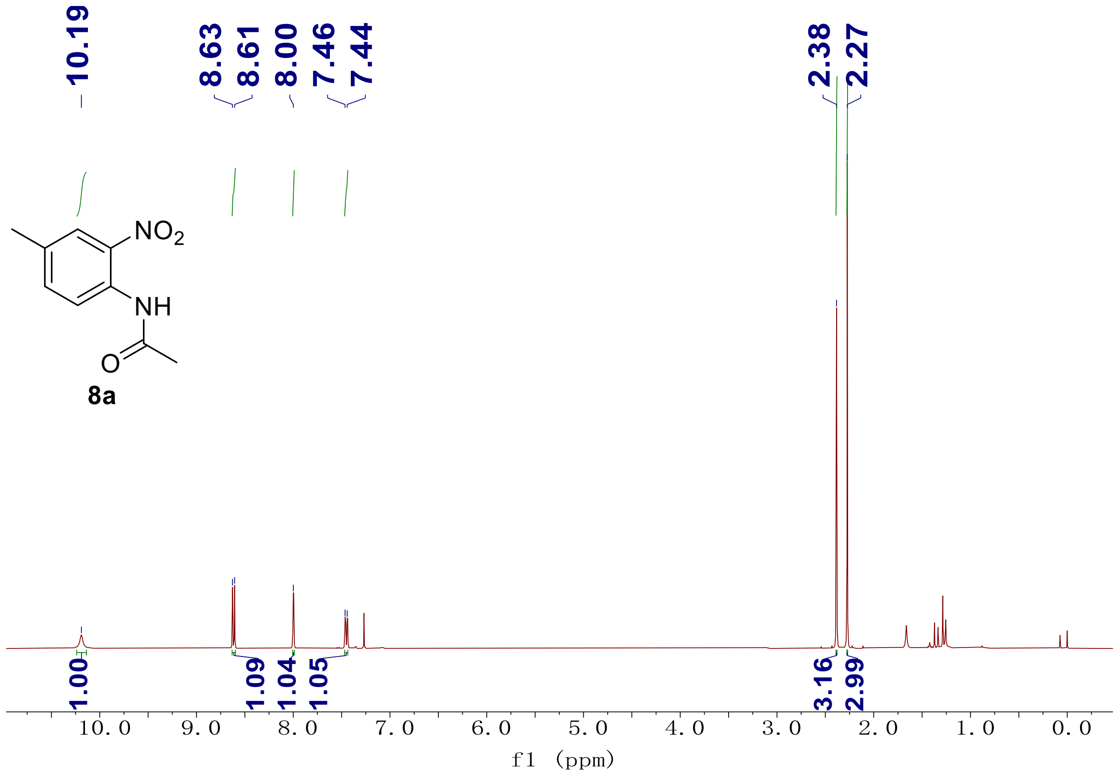

177.87
146.34
145.23
132.06
129.87
128.55
126.36
125.69
124.20
123.86
123.14
77.39
77.08
76.76
47.38
41.33
29.23
12.98
NO
N
O
4q
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)

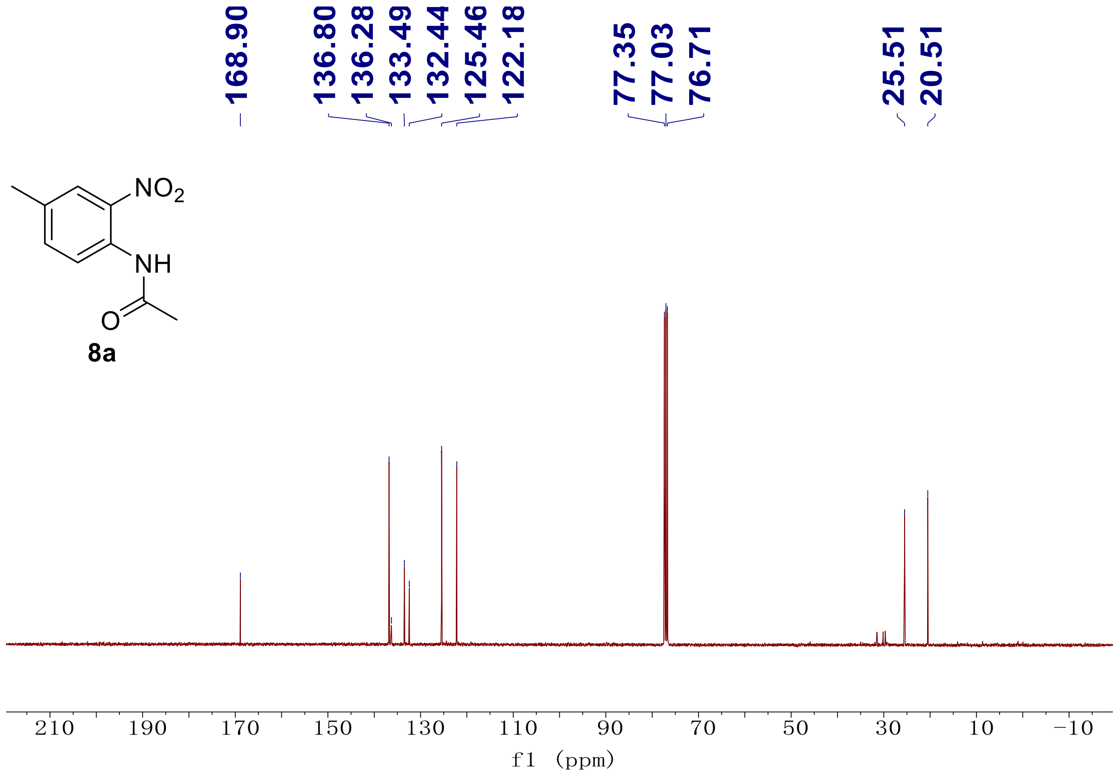

10.53
8.62
8.60
7.94
7.38
7.36
2.31
1.27
NO2
NH
O
tBu
6a
1.00
1.14
1.05
0.97
3.10
9.13
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.
f1 (ppm)

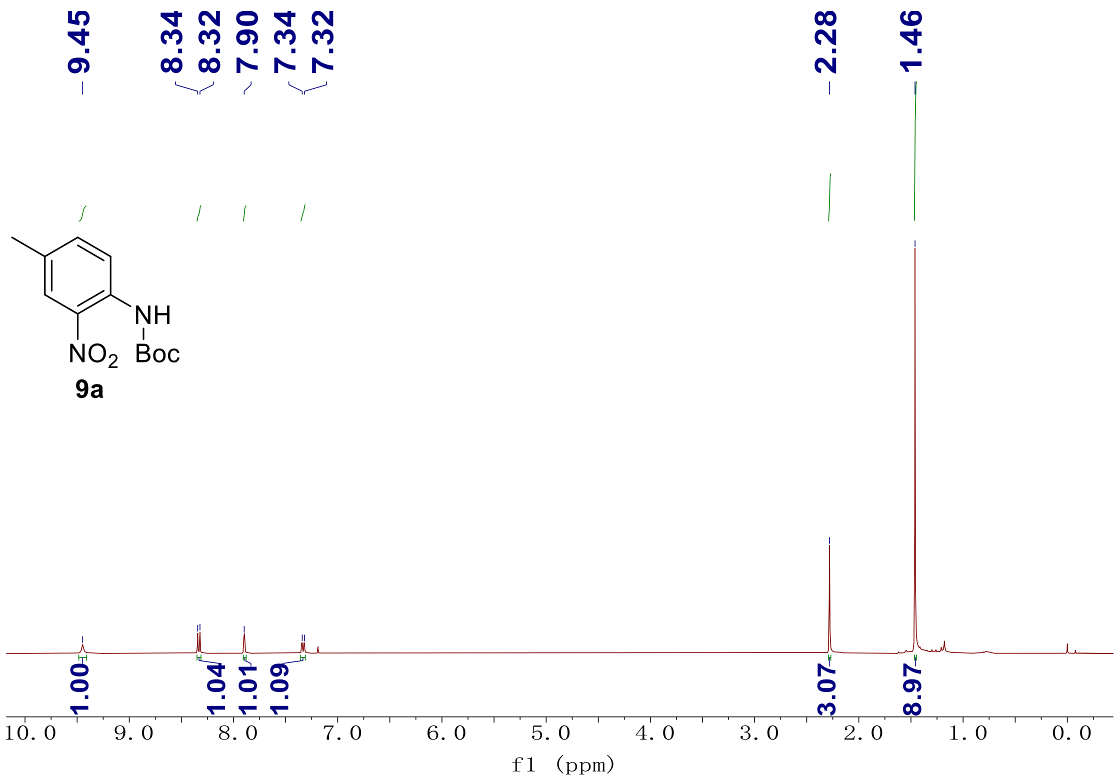

177.74
136.86
136.24
133.18
133.03
125.49
122.07
77.35
77.03
76.72
40.49
27.47
20.49
NO2
NH
O
tBu
6a
210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)

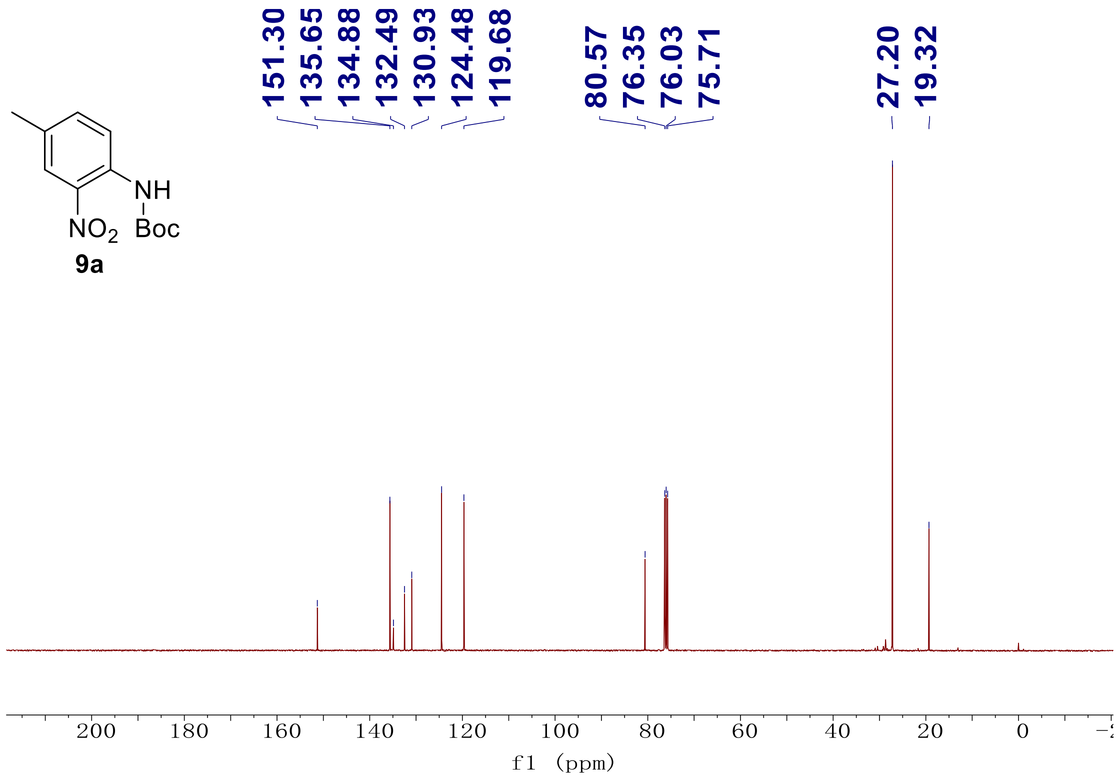

11.22
8.88 8.85 8.06 7.99 7.97 7.58 7.55 7.53 7.51
2.41
NO2
NH
O
7a
1.00 1.07 1.03 1.97 4.05 3.05
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1
f1 (ppm)

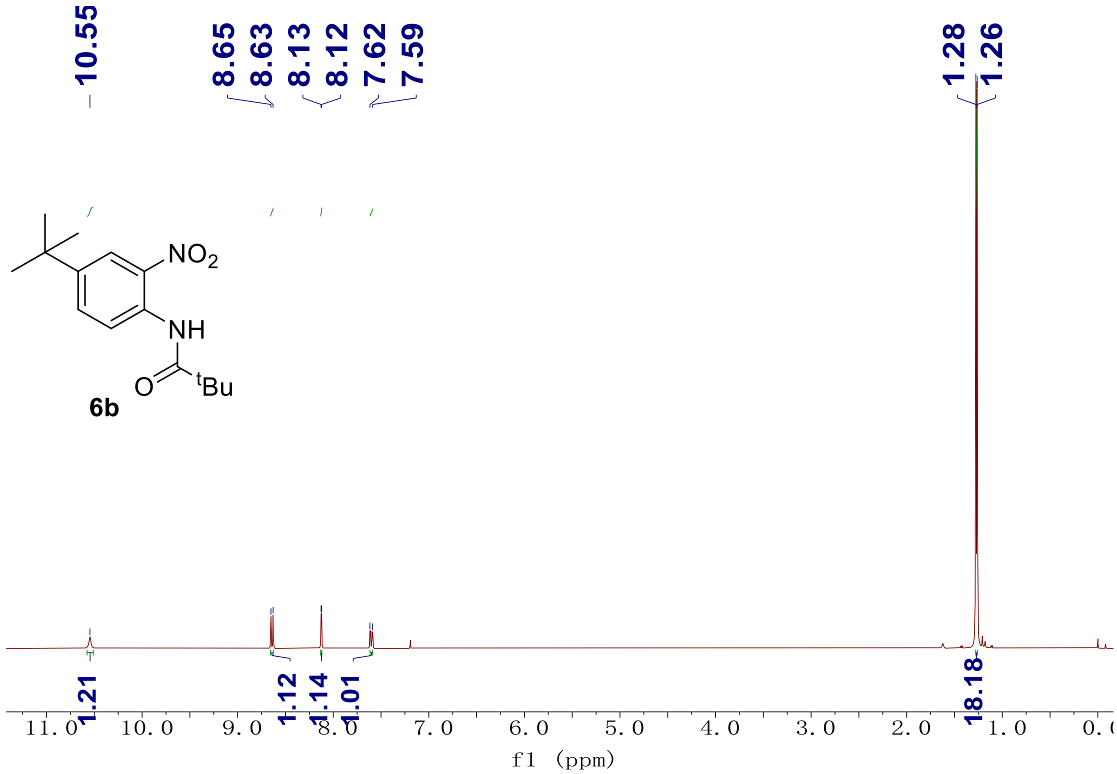

165.64 137.07 136.38 134.18 133.62 132.96 132.53 129.01 127.33 125.68 122.08
77.36 77.04 76.73
20.58
NO2
NH
O
7a
210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)

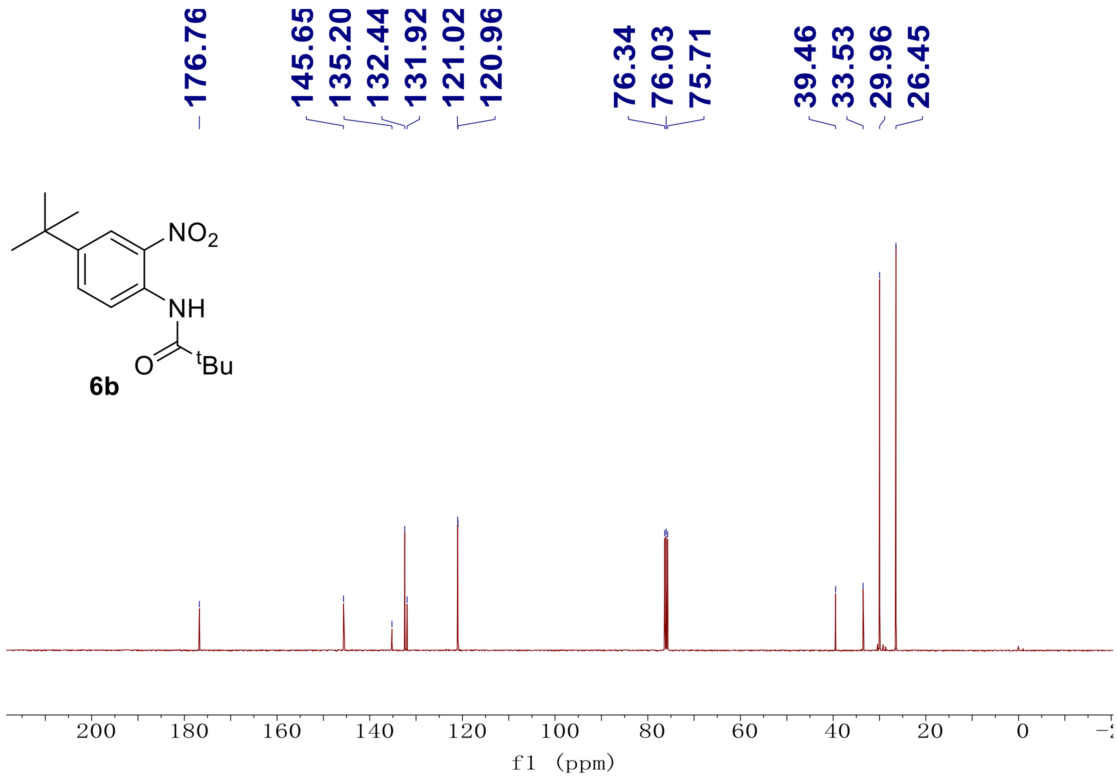

10.19
8.63
8.61
8.00
7.46
7.44
2.38
2.27
NO2
NH
O
8a
1.00
1.09
1.04
1.05
3.16
2.99
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

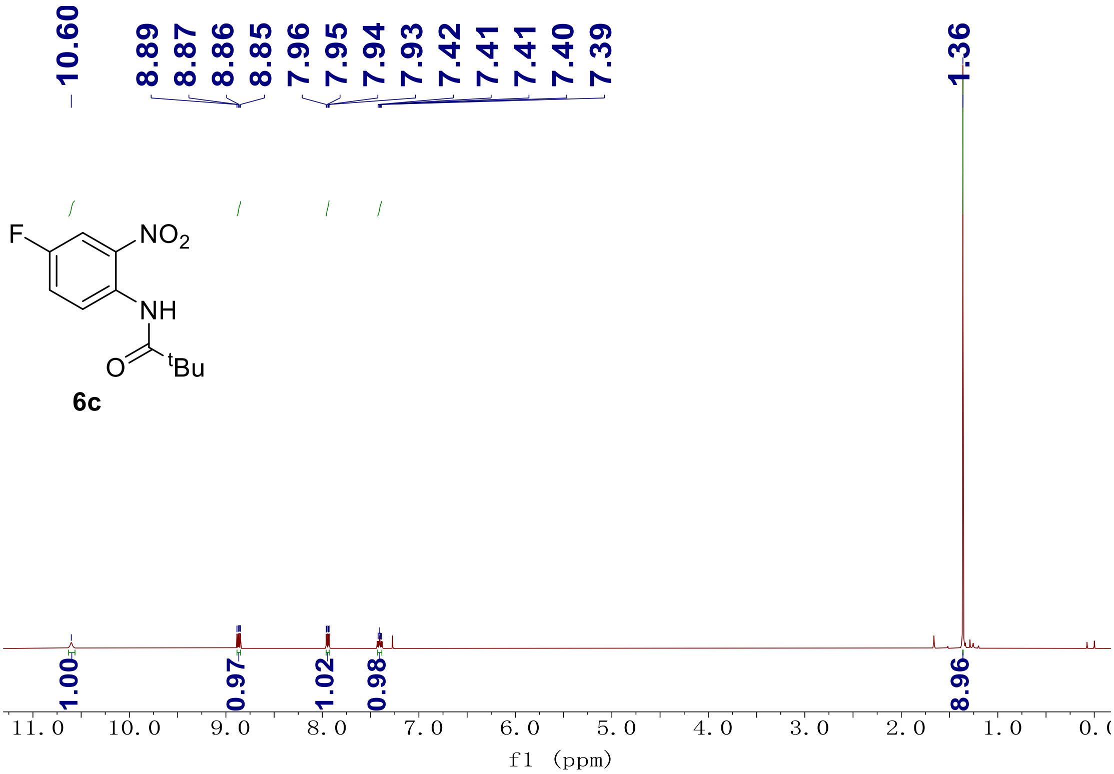

168.90
136.80
136.28
133.49
132.44
125.46
122.18
77.35
77.03
76.71
25.51
20.51
NO2
NH
O
8a
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

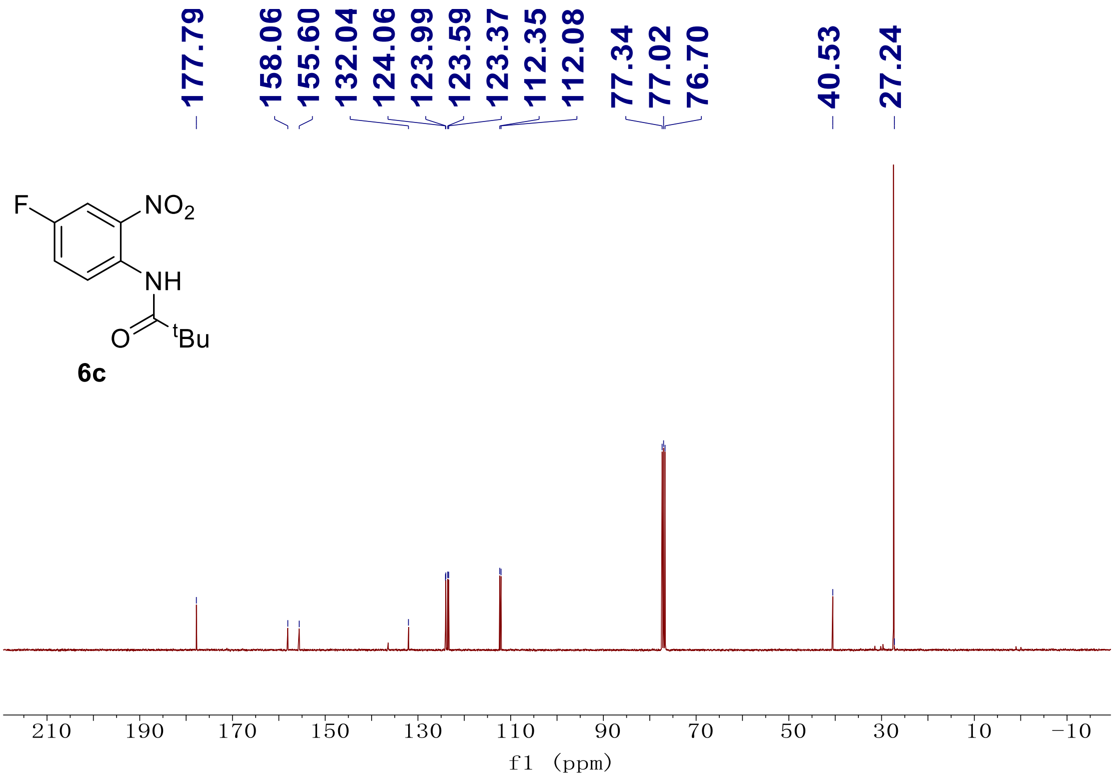

9.45
8.34
8.32
7.90
7.34
7.32
2.28
1.46
NH
NO2
Boc
9a
1.00
1.04
1.01
1.09
3.07
8.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

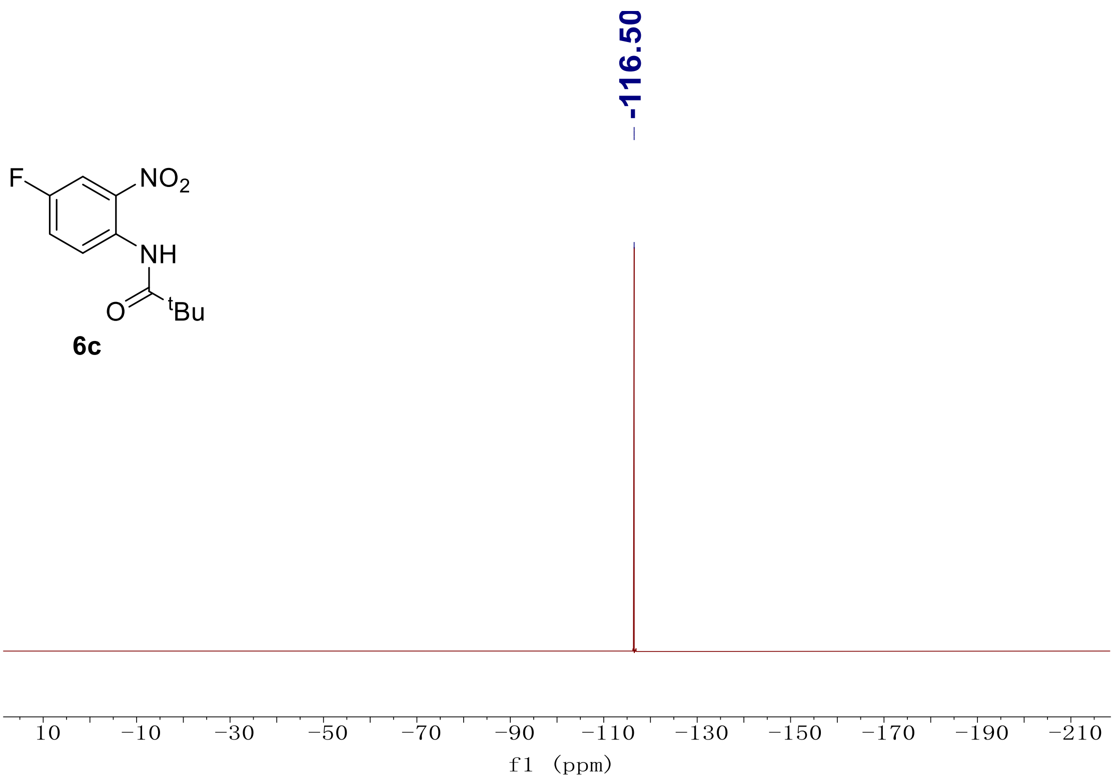

151.30
135.65
134.88
132.49
130.93
124.48
119.68
80.57
76.35
76.03
75.71
27.20
19.32
NH
NO2
Boc
9a
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


10.55
8.65 8.63 8.13 8.12 7.62 7.59
1.28 1.26
NO2
NH
O
tBu
6b
1.21 1.12 1.14 1.01 18.18
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
f1 (ppm)

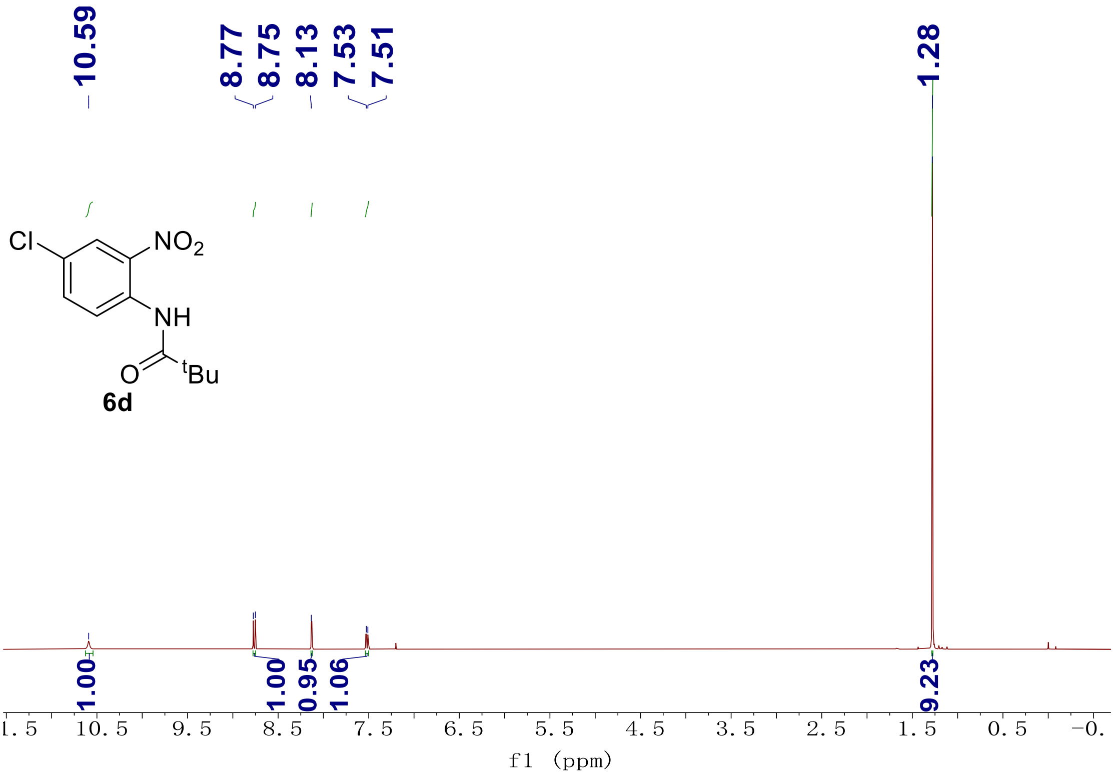

176.76
145.65 135.20 132.44 131.92 121.02 120.96
76.34 76.03 75.71
39.46 33.53 29.96 26.45
NO2
NH
O
tBu
6b
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


10.60
8.89 8.87 8.86 8.85 7.96 7.95 7.94 7.93 7.42 7.41 7.41 7.40 7.39
1.36
F
NO2
NH
O
tBu
6c
1.00
0.97
1.02
0.98
8.96
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

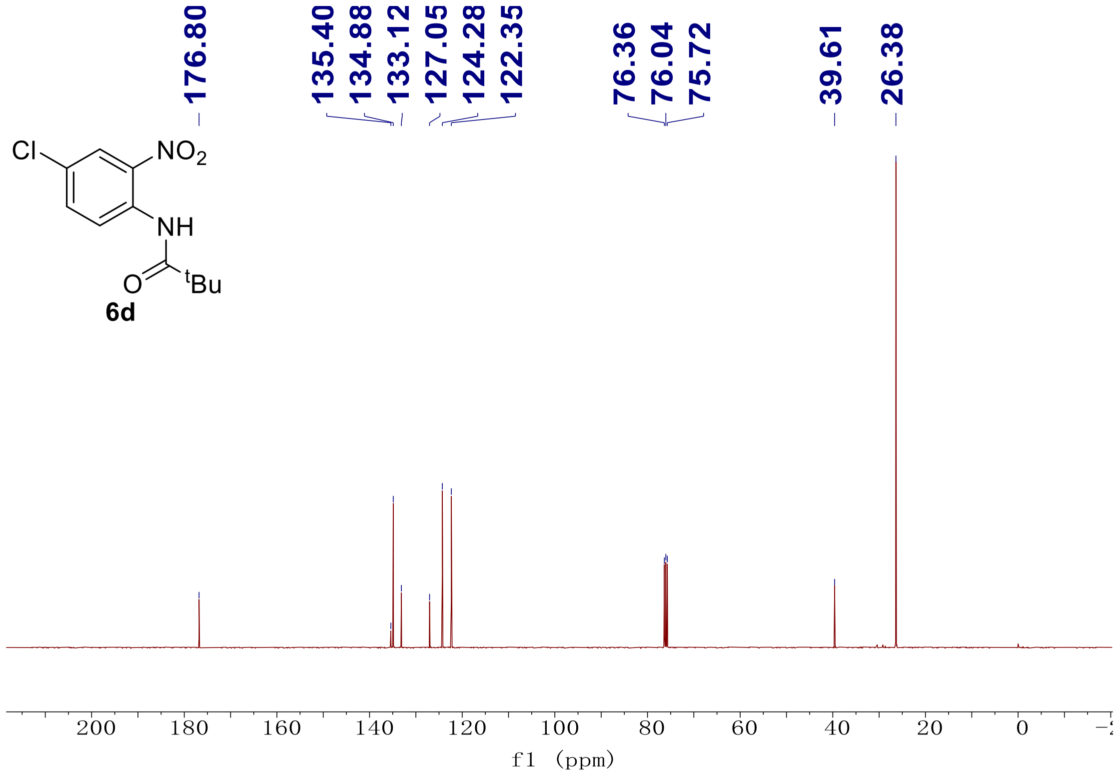

177.79
158.06 155.60 132.04 124.06 123.99 123.59 123.37 112.35 112.08
77.34 77.02 76.70
40.53
27.24
F
NO2
NH
O
tBu
6c
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

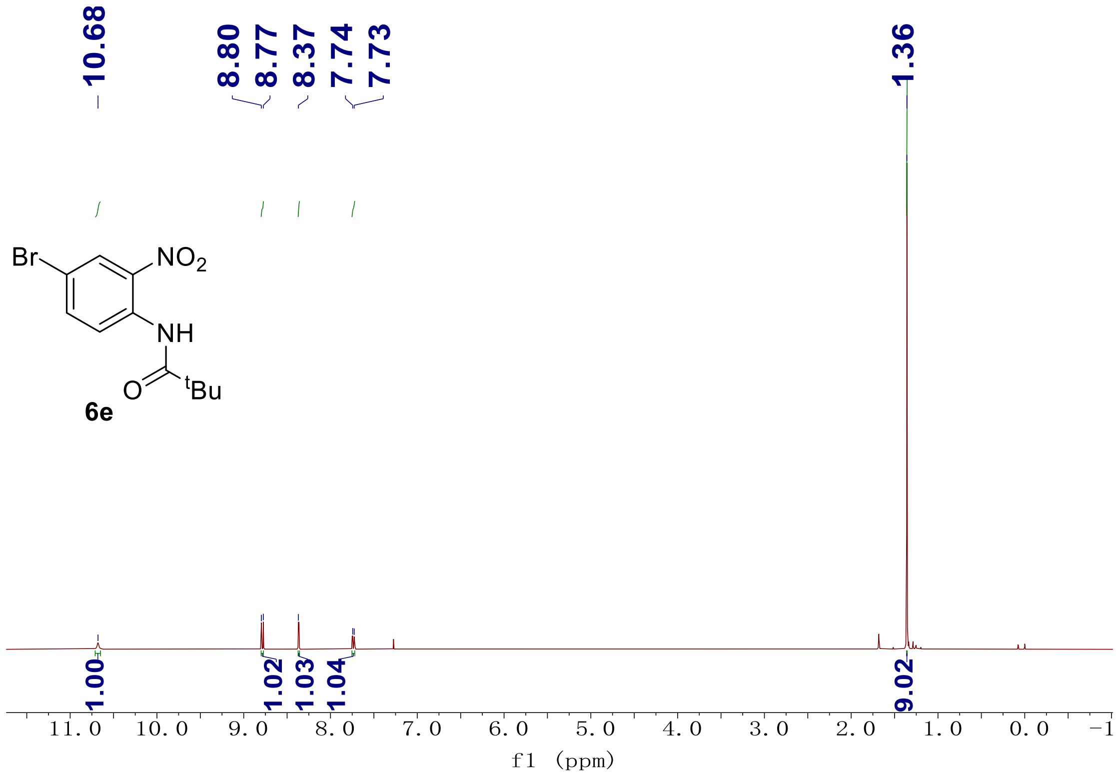

-116.50
F
NO2
NH
O
tBu
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

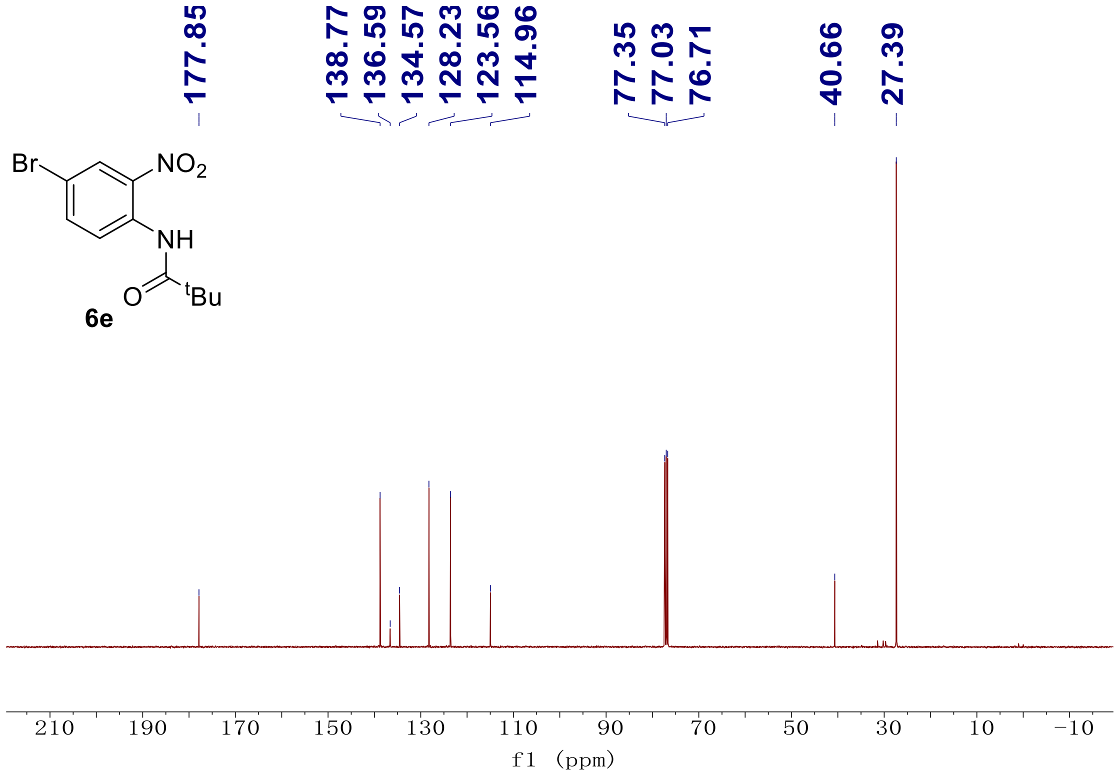
6c

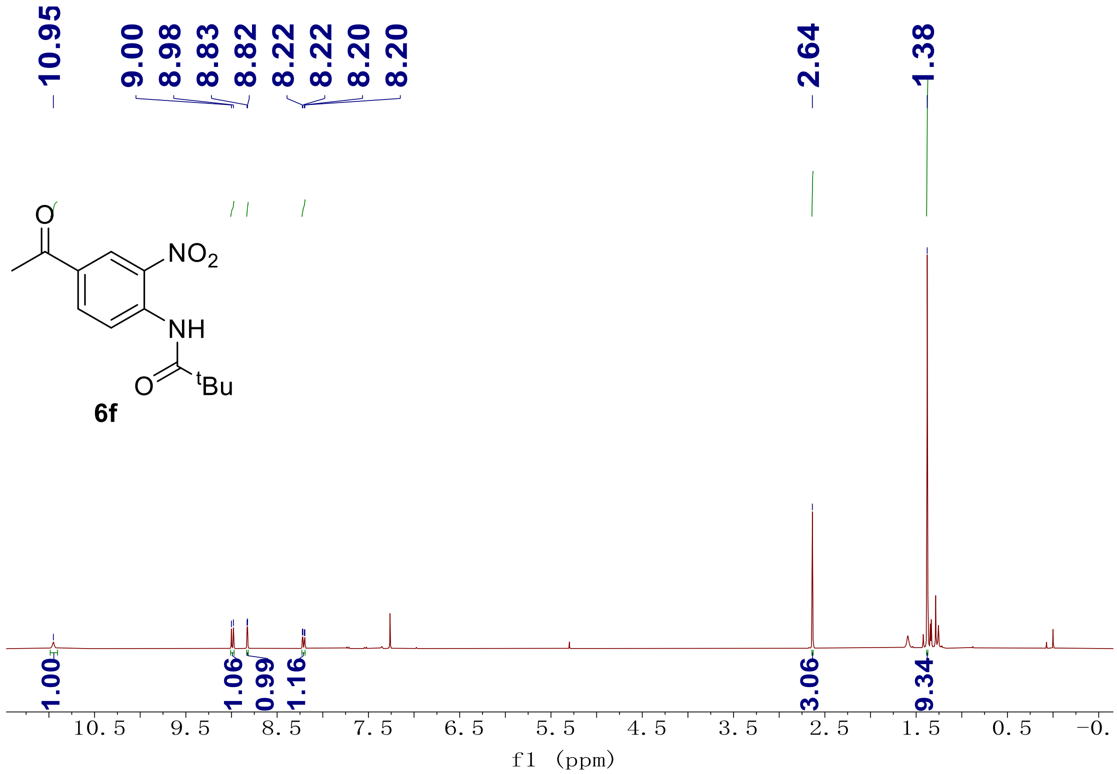

10.59
8.77
8.75
8.13
7.53
7.51
1.28
Cl
NO2
NH
O
tBu
1.00
1.00
0.95
1.06
9.23
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

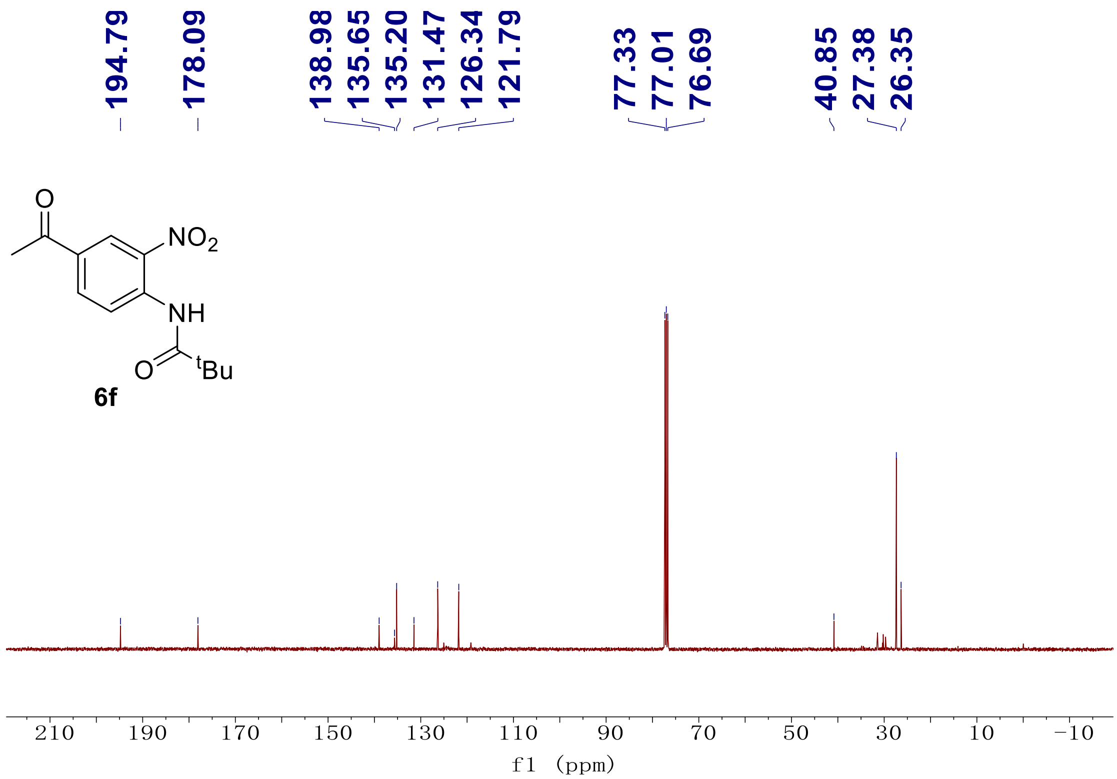
6d

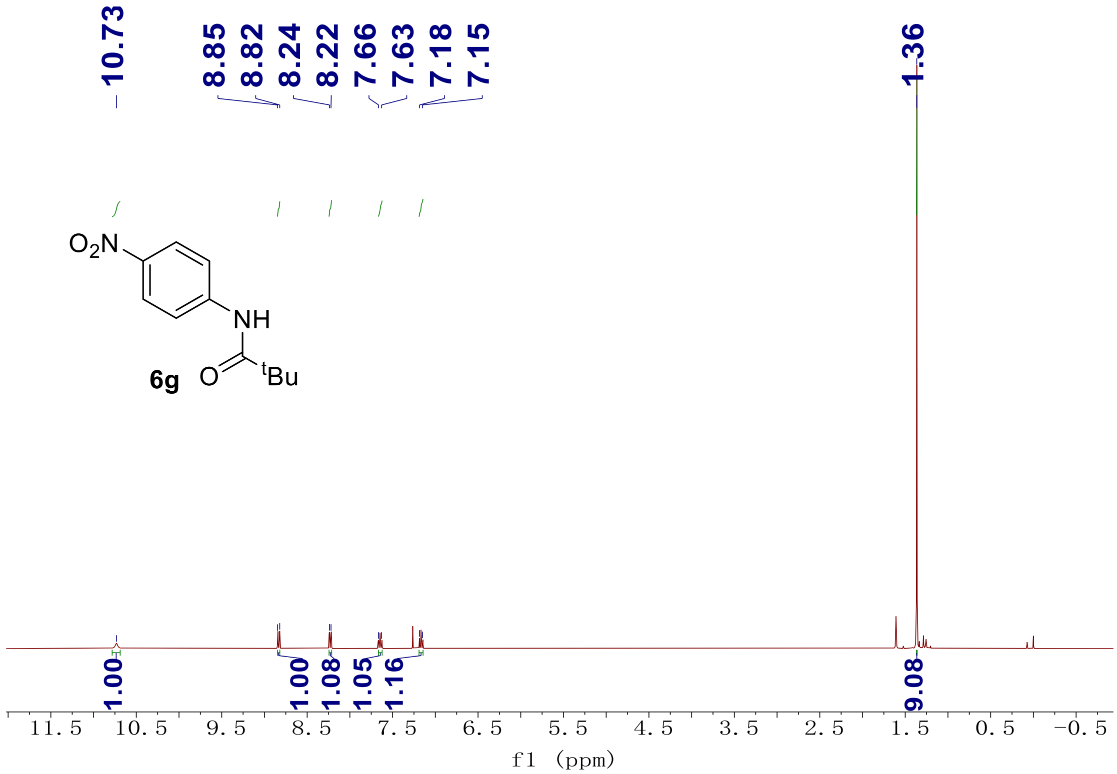

176.80
135.40
134.88
133.12
127.05
124.28
122.35
76.36
76.04
75.72
39.61
26.38
Cl
NO2
NH
O
tBu
6d
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

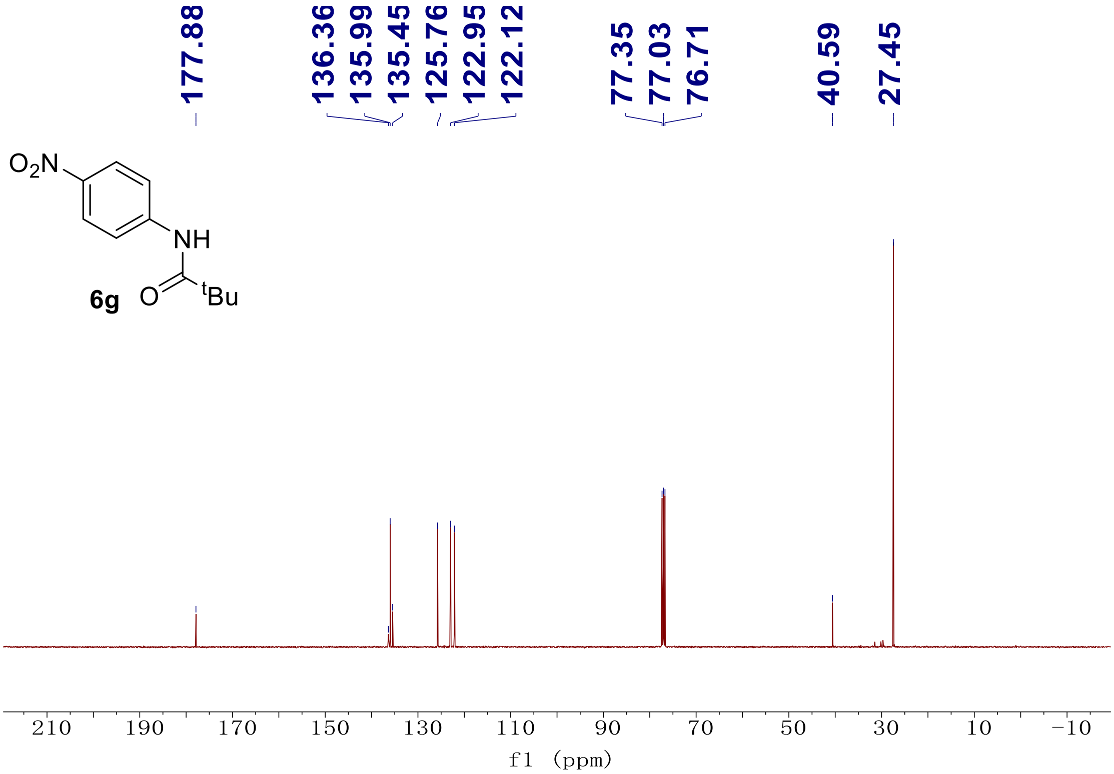

10.68
8.80
8.77
8.37
7.74
7.73
1.36
Br
NO2
NH
O
tBu
6e
1.00
1.02
1.03
1.04
9.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)

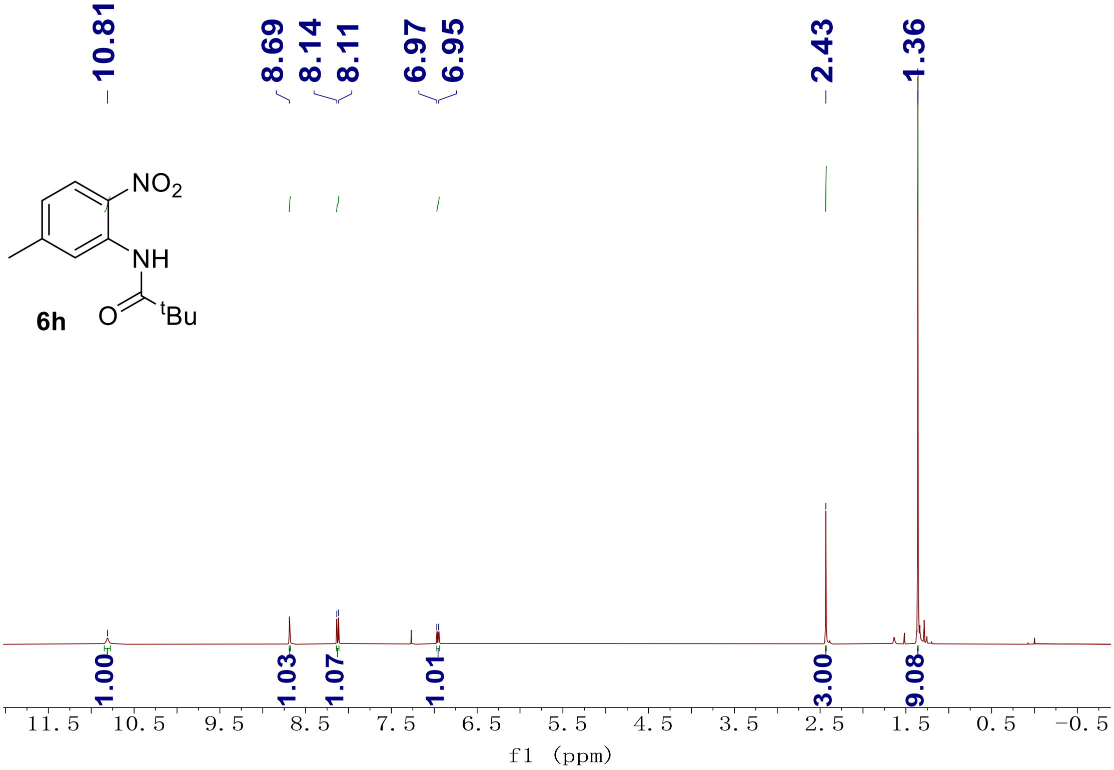

177.85
138.77
136.59
134.57
128.23
123.56
114.96
77.35
77.03
76.71
40.66
27.39
Br
NO2
NH
O
tBu
6e
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)

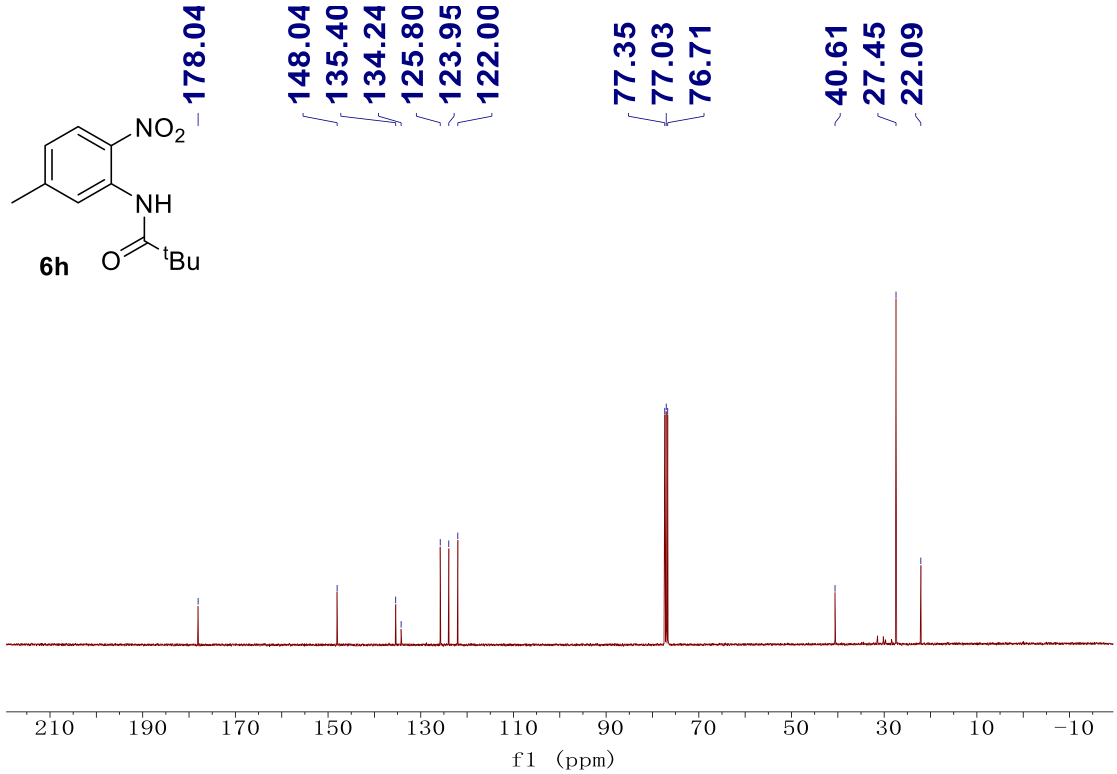

10.95
9.00
8.98
8.83
8.82
8.22
8.22
8.20
8.20
2.64
1.38
O
NO2
NH
O
tBu
6f
1.00
1.06
0.99
1.16
3.06
9.34
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.
f1 (ppm)

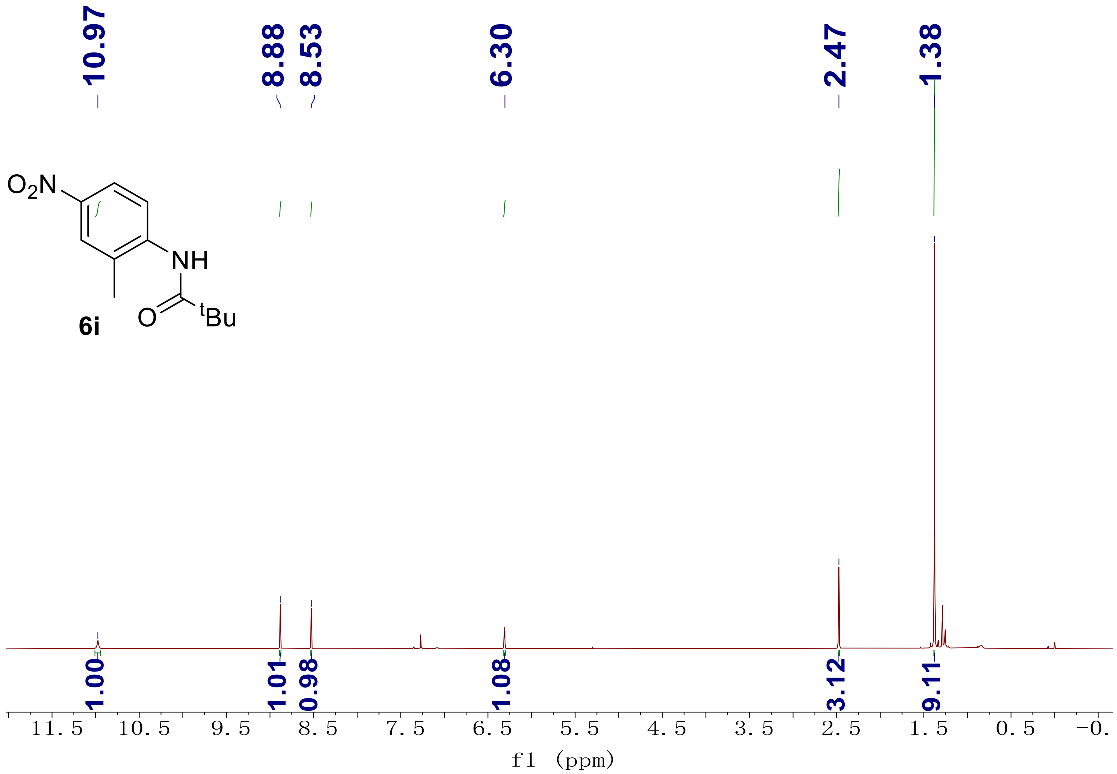

194.79
178.09
138.98
135.65
135.20
131.47
126.34
121.79
77.33
77.01
76.69
40.85
27.38
26.35
O
NO2
NH
O
tBu
6f
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

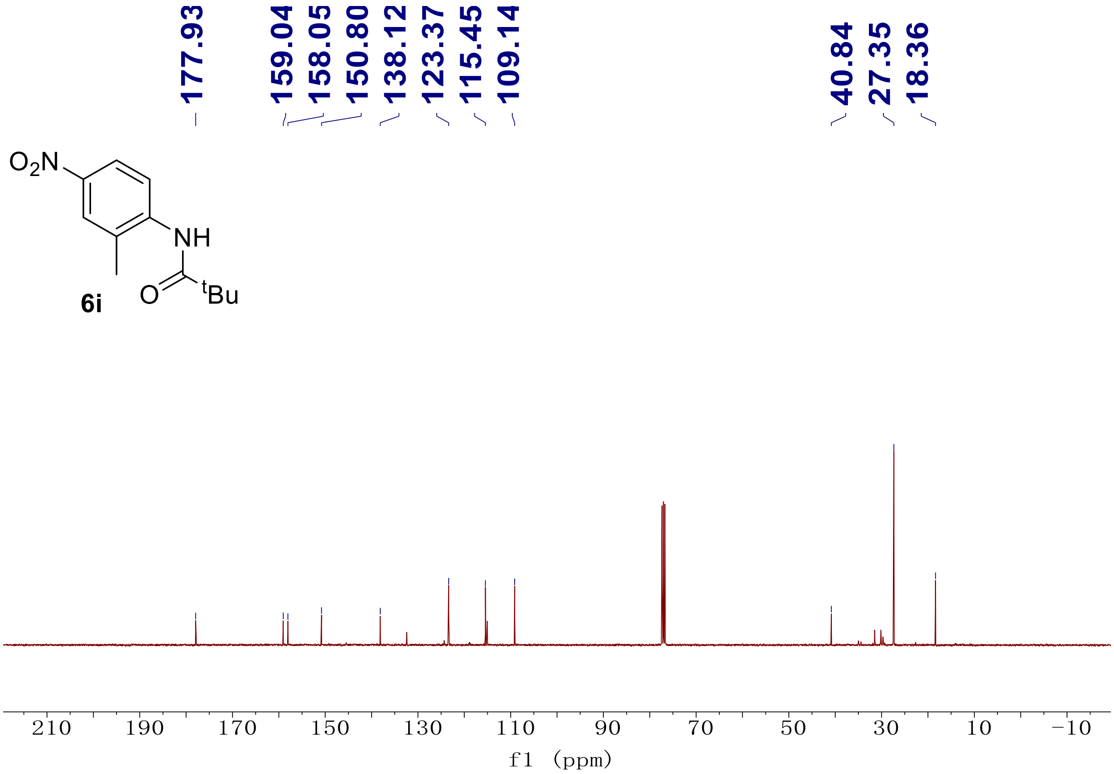

10.73
8.85
8.82
8.24
8.22
7.66
7.63
7.18
7.15
1.36
O2N
NH
6g
O
tBu
1.00
1.00
1.08
1.05
1.16
9.08
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)


177.88
136.36
135.99
135.45
125.76
122.95
122.12
77.35
77.03
76.71
40.59
27.45
O2N
NH
O
tBu
6g
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

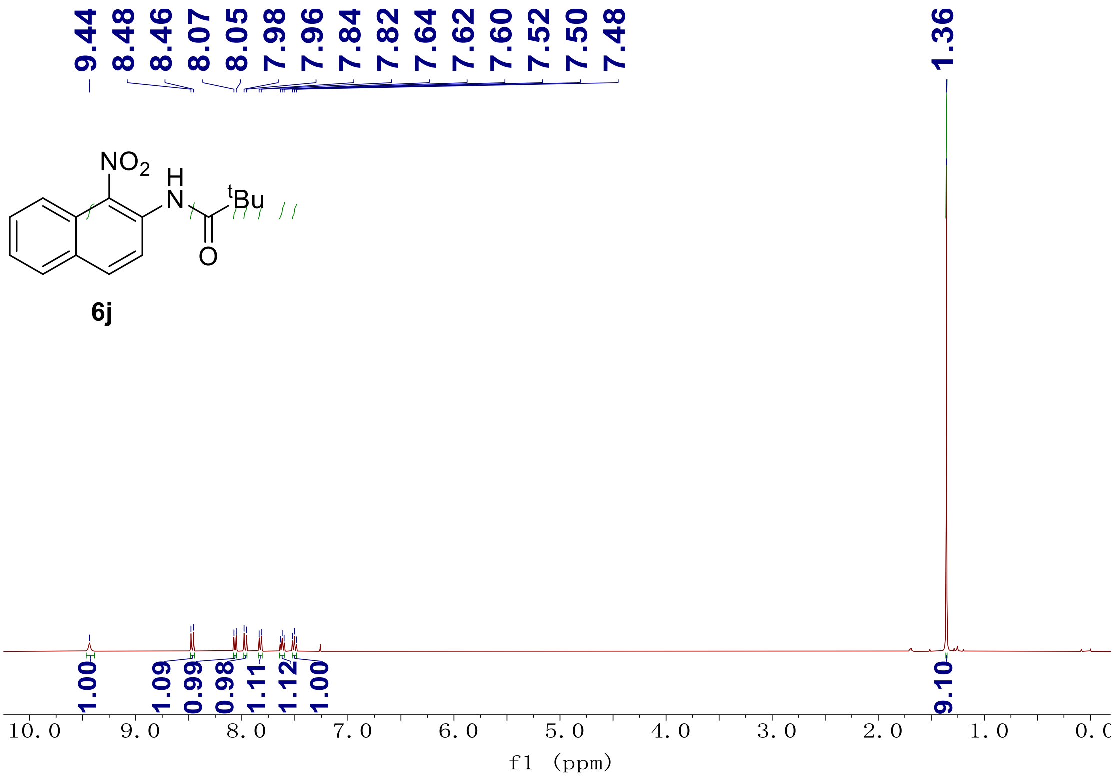

10.81
8.69
8.14
8.11
6.97
6.95
2.43
1.36
NO2
NH
O
tBu
6h
1.00
1.03
1.07
1.01
3.00
9.08
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)


178.04
148.04
135.40
134.24
125.80
123.95
122.00
77.35
77.03
76.71
40.61
27.45
22.09
NO_2
NH
O
^tBu
6h
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

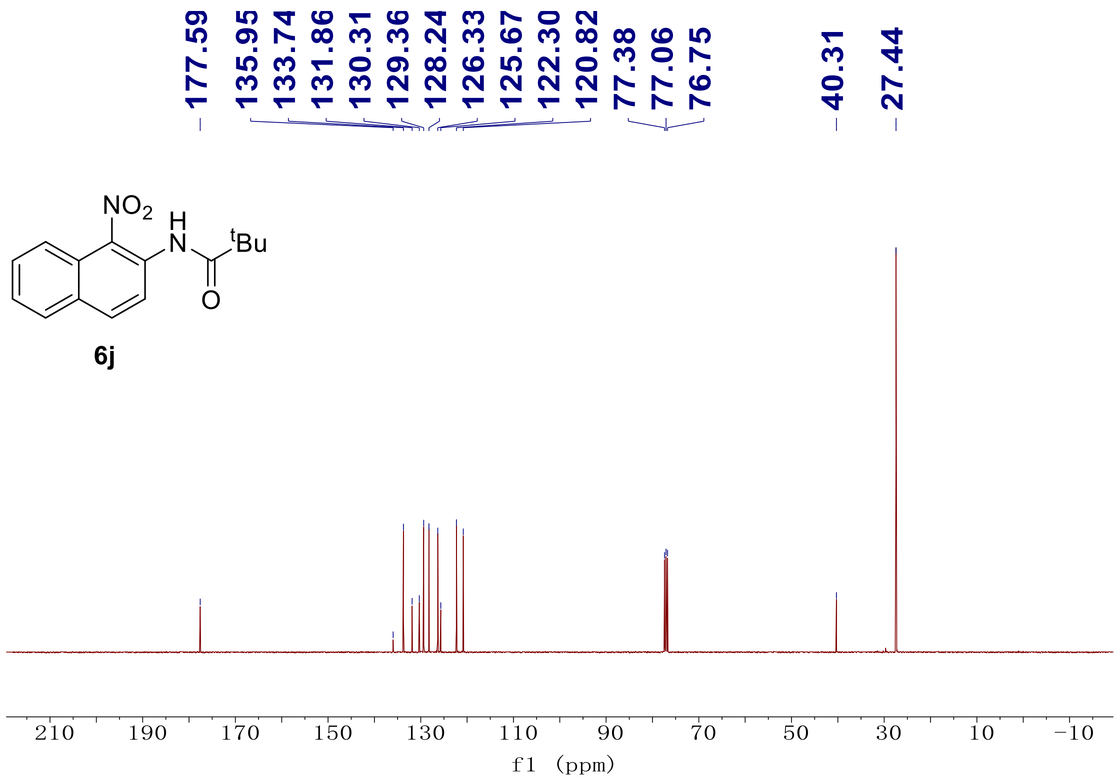

10.97
8.88
8.53
6.30
2.47
1.38
O_2N
NH
O
^tBu
6i
1.00
1.01
0.98
1.08
3.12
9.11
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.
f1 (ppm)

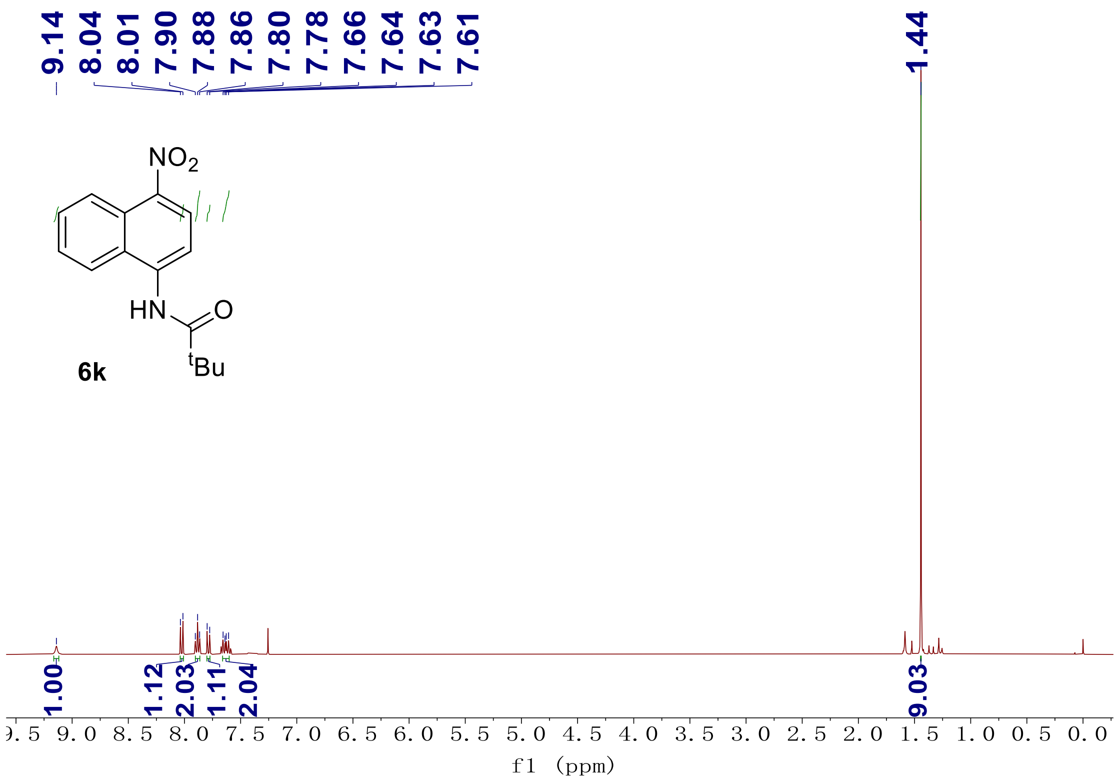

177.93
159.04
158.05
150.80
138.12
123.37
115.45
109.14
40.84
27.35
18.36
O_2N
NH
O
^{t}Bu
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

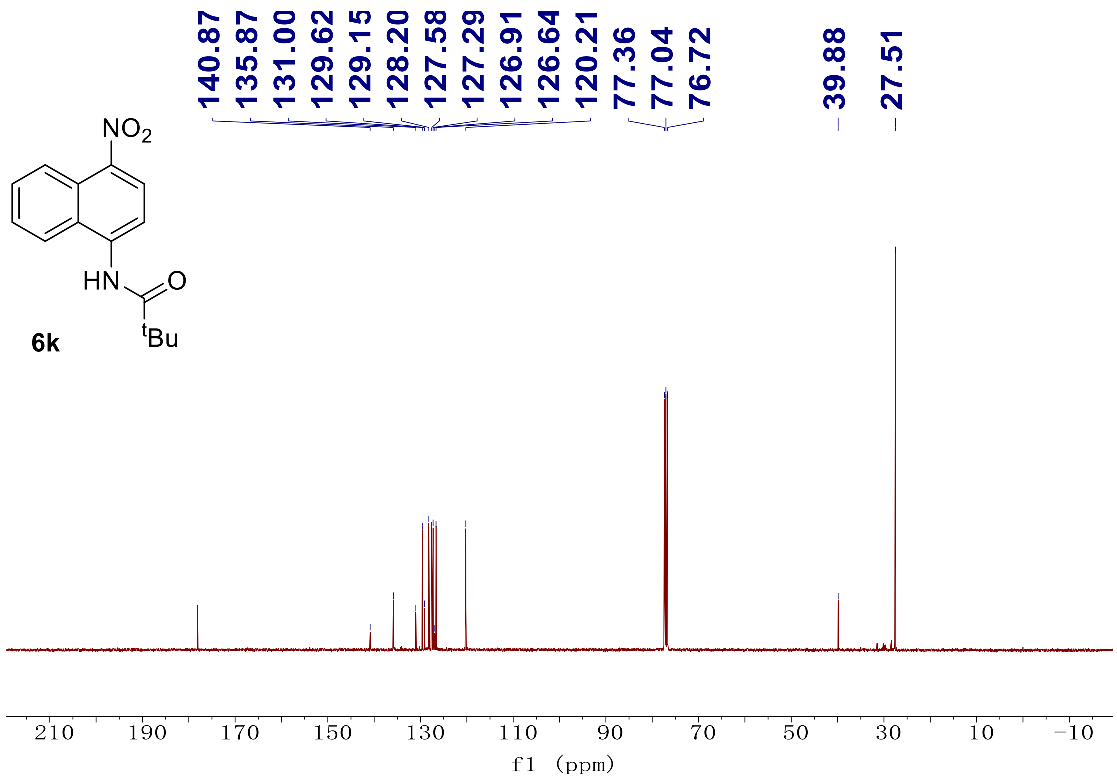
6i

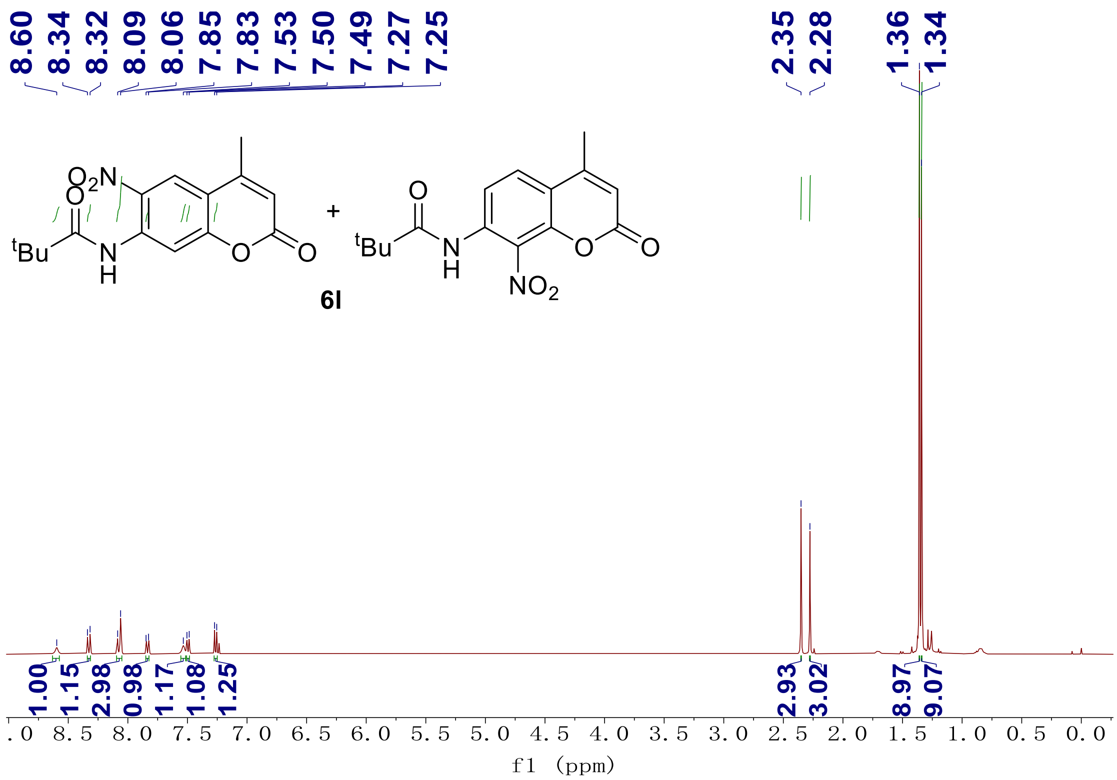

9.44
8.48
8.46
8.07
8.05
7.98
7.96
7.84
7.82
7.64
7.62
7.60
7.52
7.50
7.48
1.36
NO_2
H
N
^{t}Bu
O
1.00
1.09
0.99
0.98
1.11
1.12
1.00
9.10
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

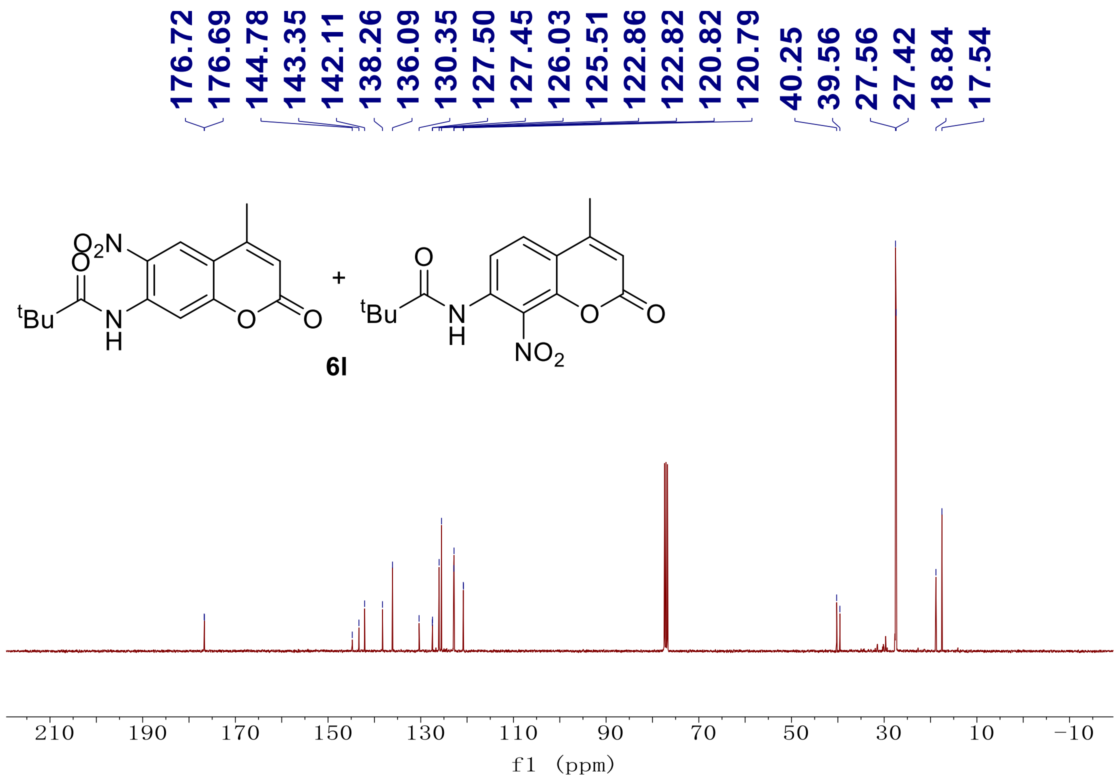
6j

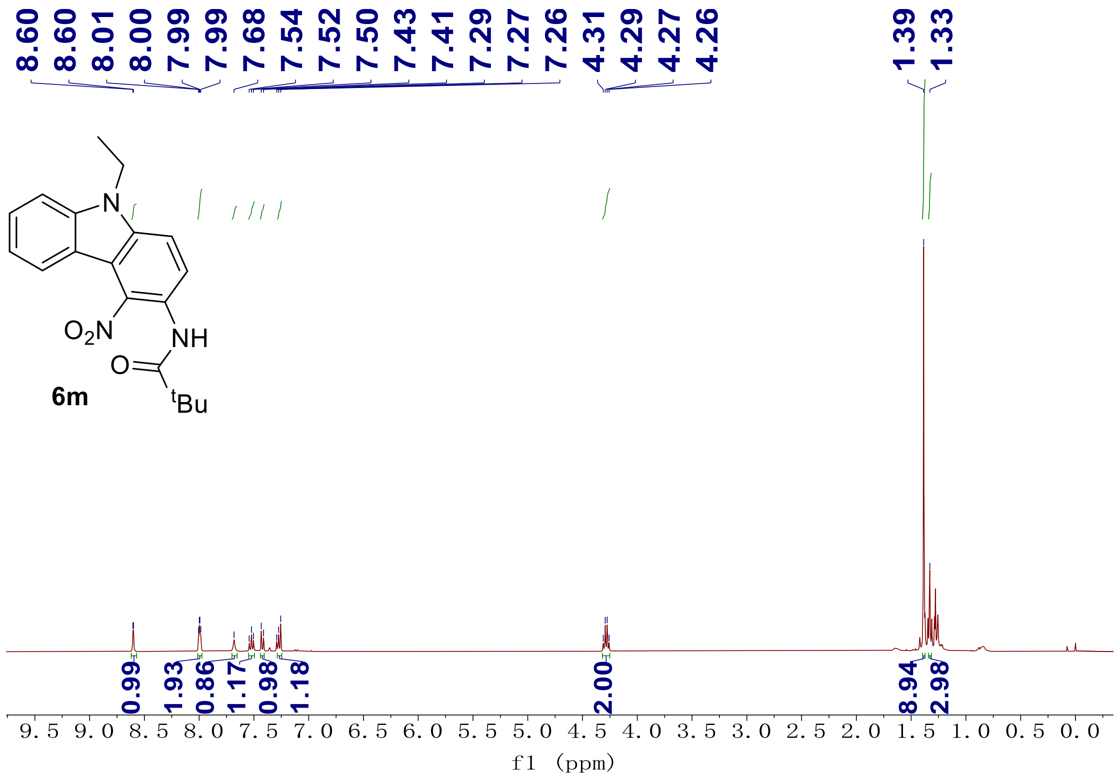

177.59
135.95
133.74
131.86
130.31
129.36
128.24
126.33
125.67
122.30
120.82
77.38
77.06
76.75
40.31
27.44
NO2
H
N
tBu
O
6j
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

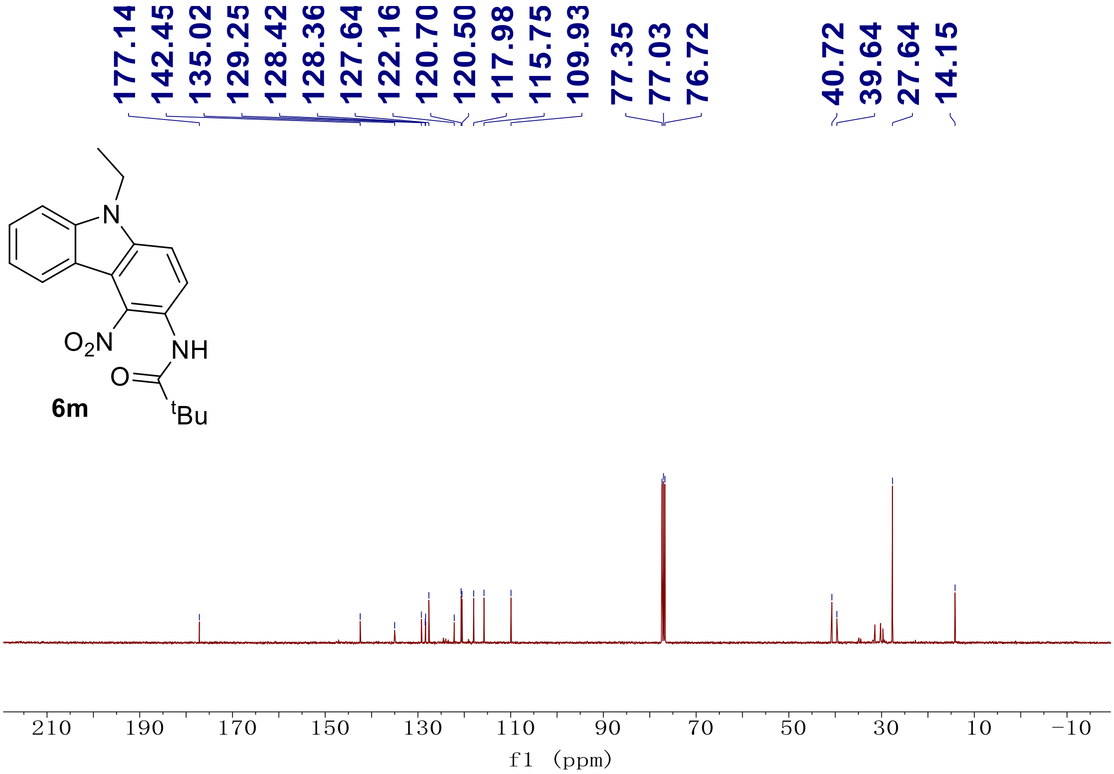

9.14
8.04
8.01
7.90
7.88
7.86
7.80
7.78
7.66
7.64
7.63
7.61
1.44
NO2
HN
O
tBu
6k
1.00
1.12
2.03
1.11
2.04
9.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.87
135.87
131.00
129.62
129.15
128.20
127.58
127.29
126.91
126.64
120.21
77.36
77.04
76.72
39.88
27.51
NO2
HN
O
tBu
6k
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

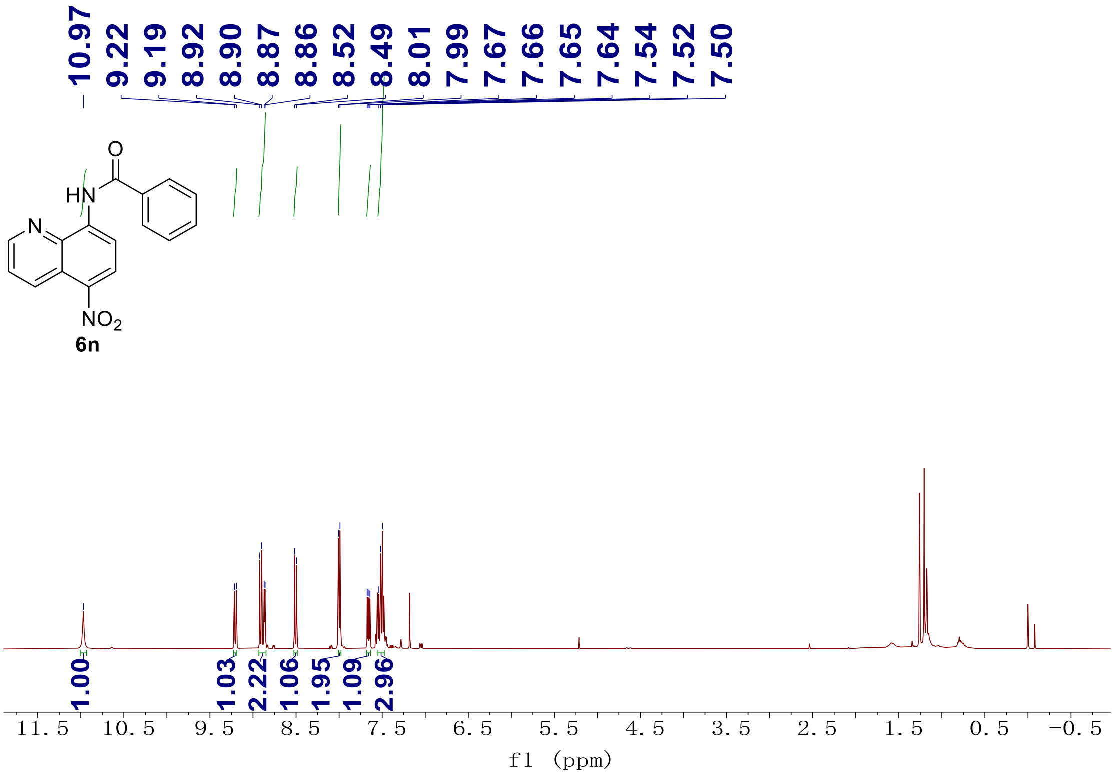

8.60
8.34
8.32
8.09
8.06
7.85
7.83
7.53
7.50
7.49
7.27
7.25
2.35
2.28
1.36
1.34
O2N
O
tBu
N
H
O
O
+
6l
NO2
1.00
1.15
2.98
0.98
1.17
1.08
1.25
2.93
3.02
8.97
9.07
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.72 176.69 144.78 143.35 142.11 138.26 136.09 130.35 127.50 127.45 126.03 125.51 122.86 122.82 120.82 120.79 40.25 39.56 27.56 27.42 18.84 17.54
O2N
O
tBu
N
H
O
O
6l
+
O
tBu
N
H
O
O
NO2
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

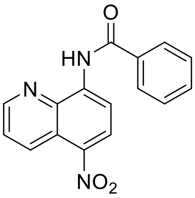

8.60 8.60 8.01 8.00 7.99 7.99 7.68 7.54 7.52 7.50 7.43 7.41 7.29 7.27 7.26 4.31 4.29 4.27 4.26 1.39 1.33
N
O2N
NH
O
tBu
6m
0.99 1.93 0.86 1.17 0.98 1.18 2.00 8.94 2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


177.14
142.45
135.02
129.25
128.42
128.36
127.64
122.16
120.70
120.50
117.98
115.75
109.93
77.35
77.03
76.72
40.72
39.64
27.64
14.15
N
O_2N
NH
O
^{t}Bu
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

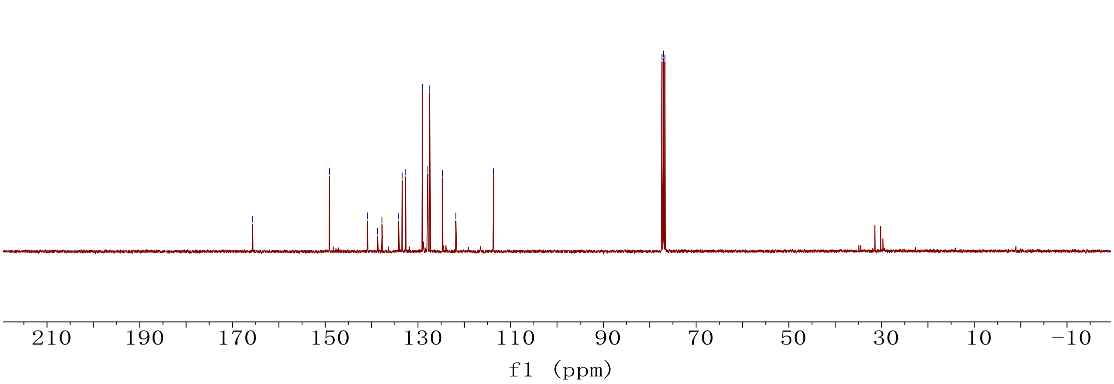
6m

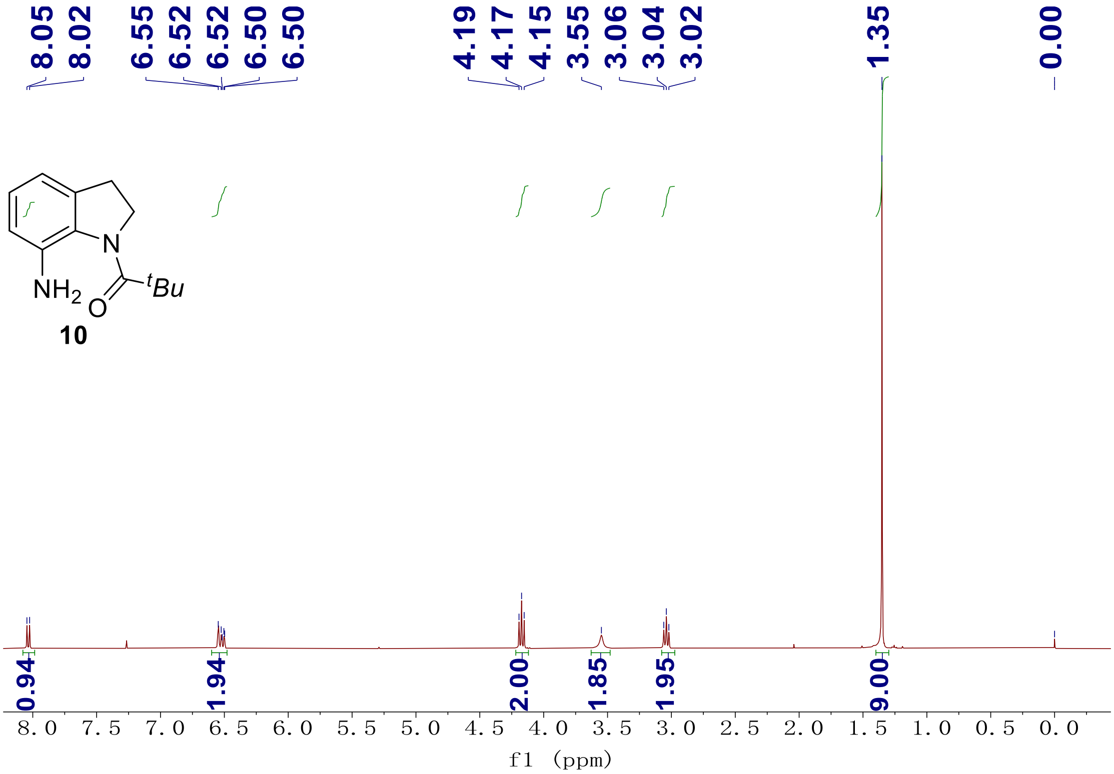

10.97
9.22
9.19
8.92
8.90
8.87
8.86
8.52
8.49
8.01
7.99
7.67
7.66
7.65
7.64
7.54
7.52
7.50
O
HN
N
NO_2
1.00
1.03
2.22
1.06
1.95
1.09
2.96
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)

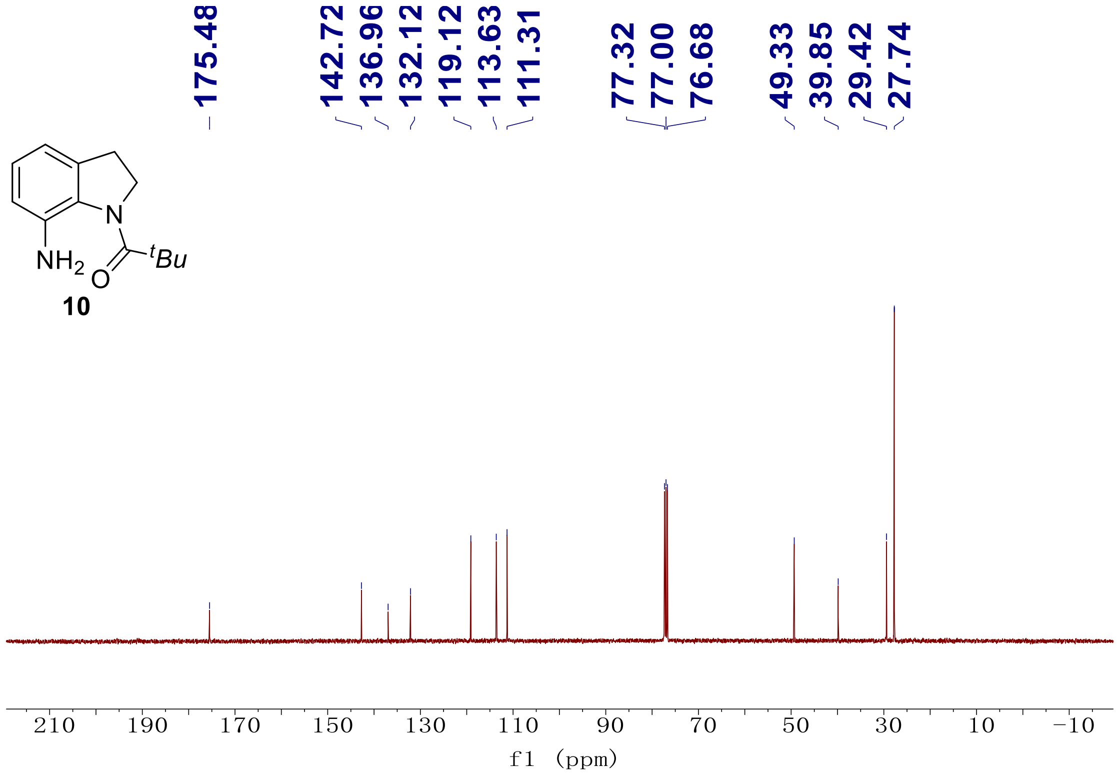
6n


NO2

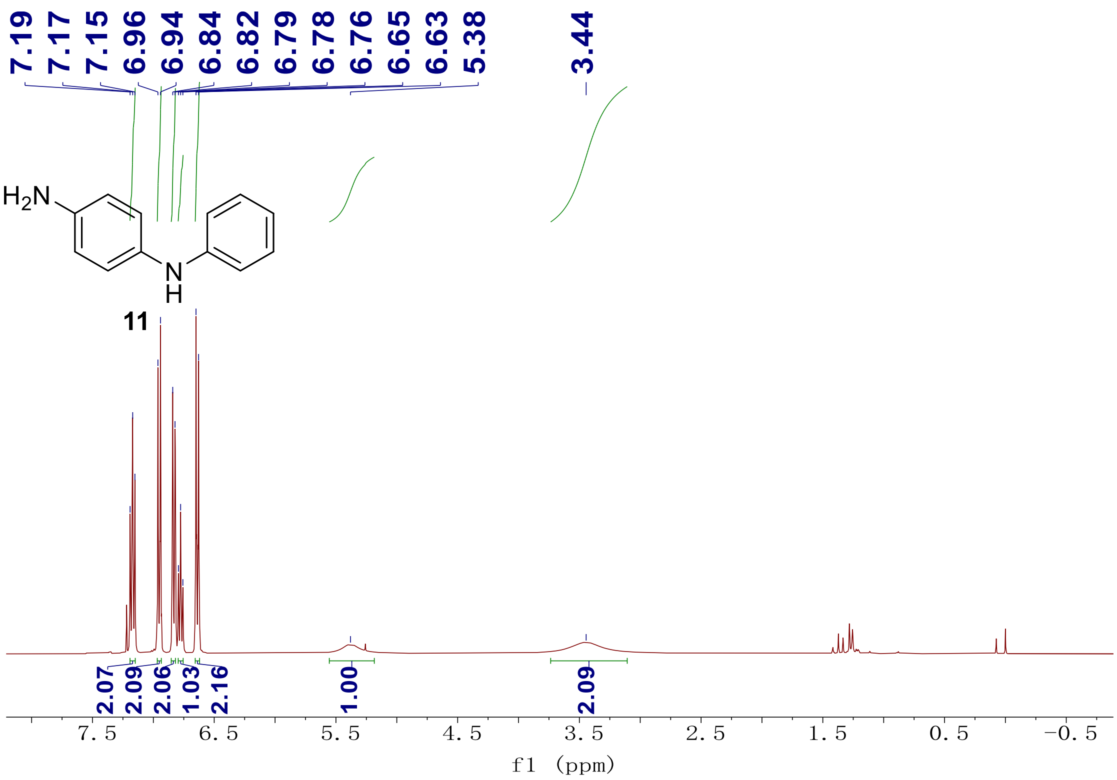
6n


165.66
149.08
140.85
138.70
137.77
134.15
133.41
132.63
129.03
127.86
127.46
124.71
121.82
113.72
77.35
77.03
76.72
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

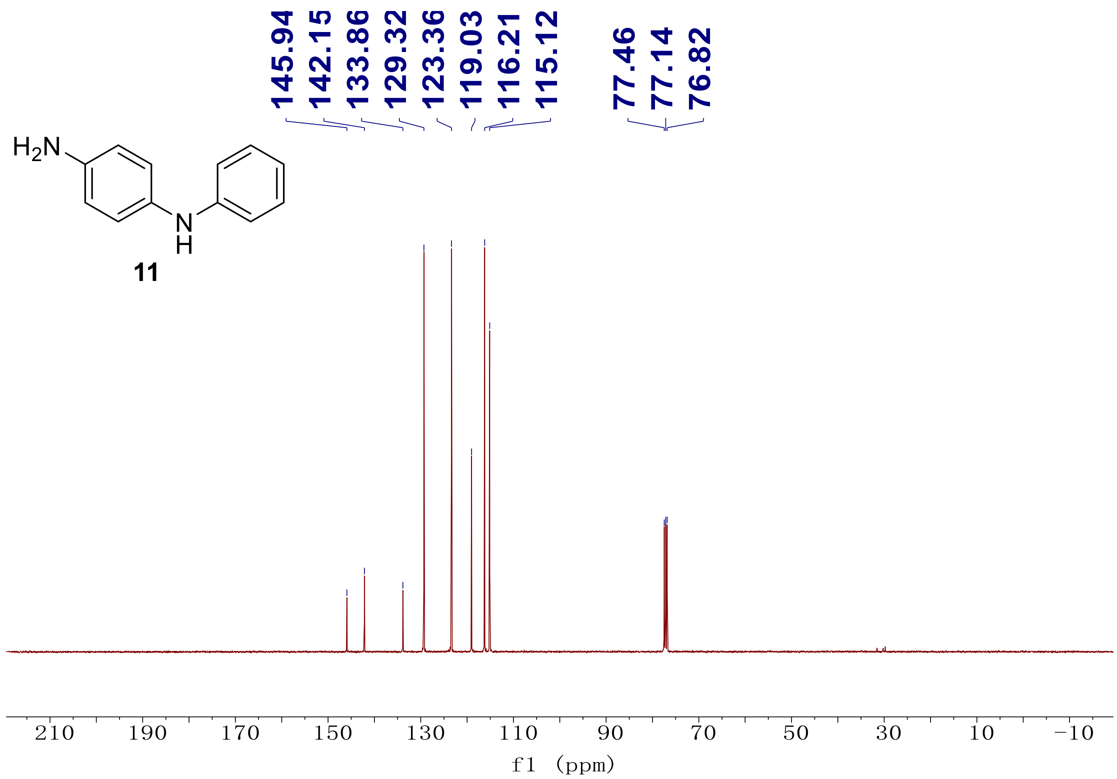

8.05
8.02
6.55
6.52
6.52
6.50
6.50
4.19
4.17
4.15
3.55
3.06
3.04
3.02
1.35
0.00
NH2
tBu
10
0.94
1.94
2.00
1.85
1.95
9.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

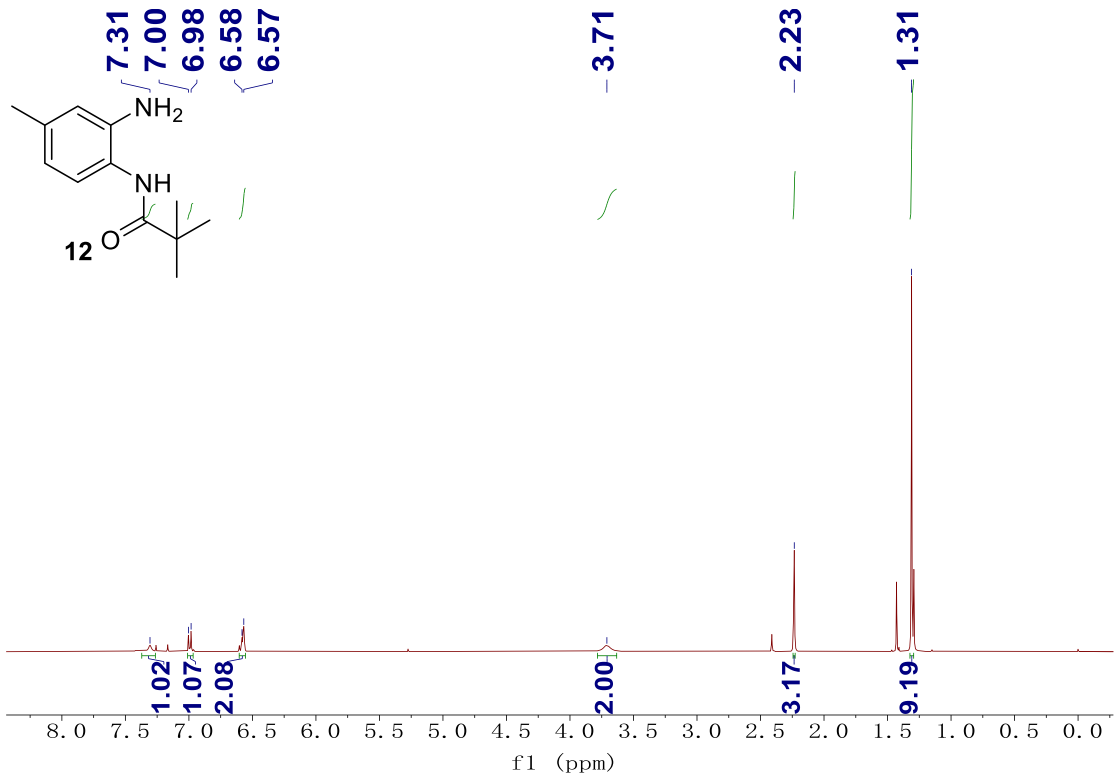


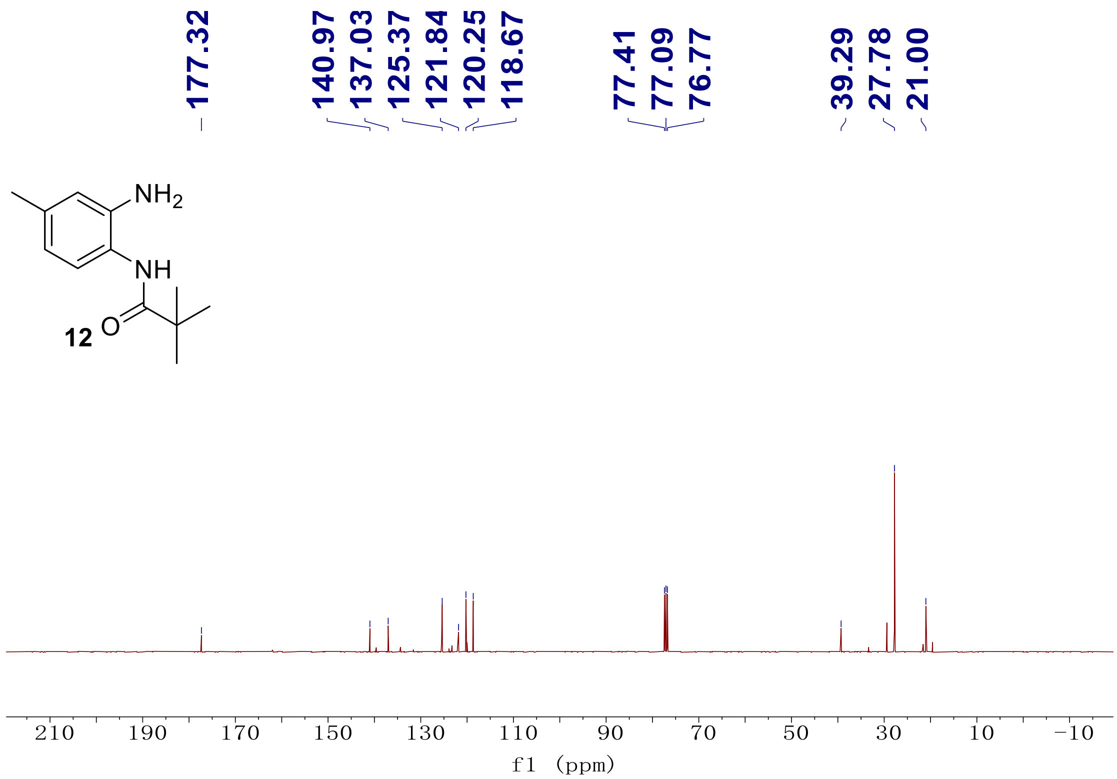
175.48
142.72
136.96
132.12
119.12
113.63
111.31
77.32
77.00
76.68
49.33
39.85
29.42
27.74
NH_2
N
O
^tBu
10
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

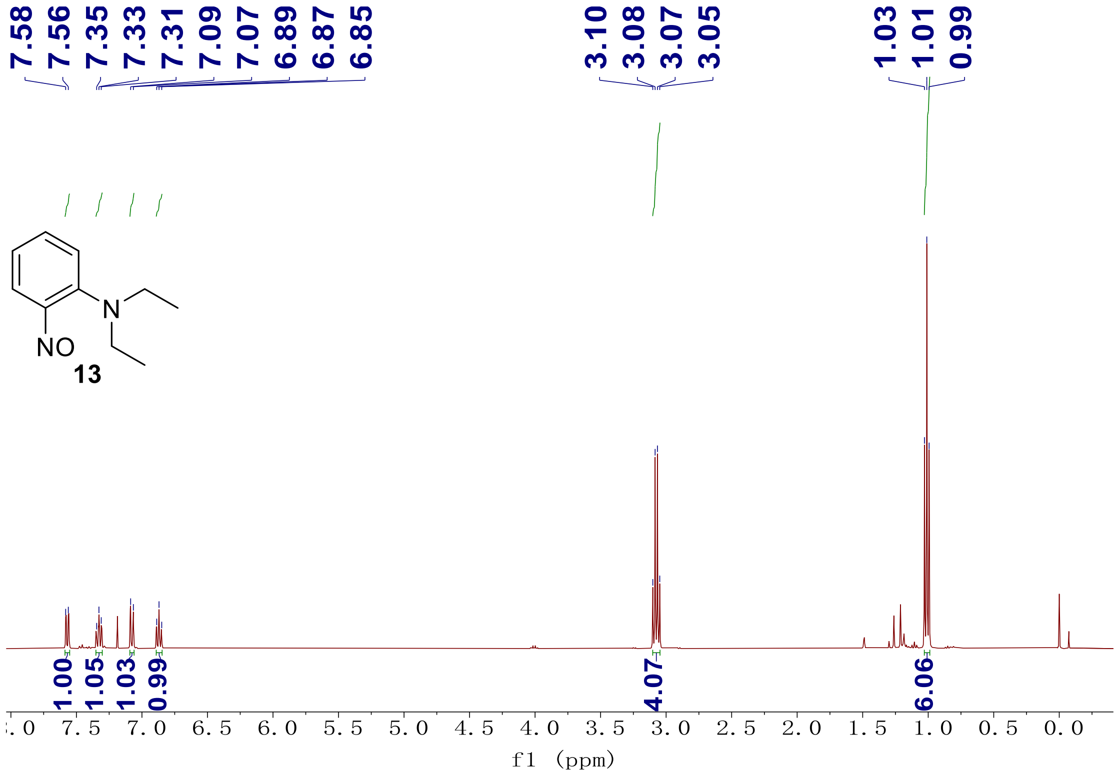


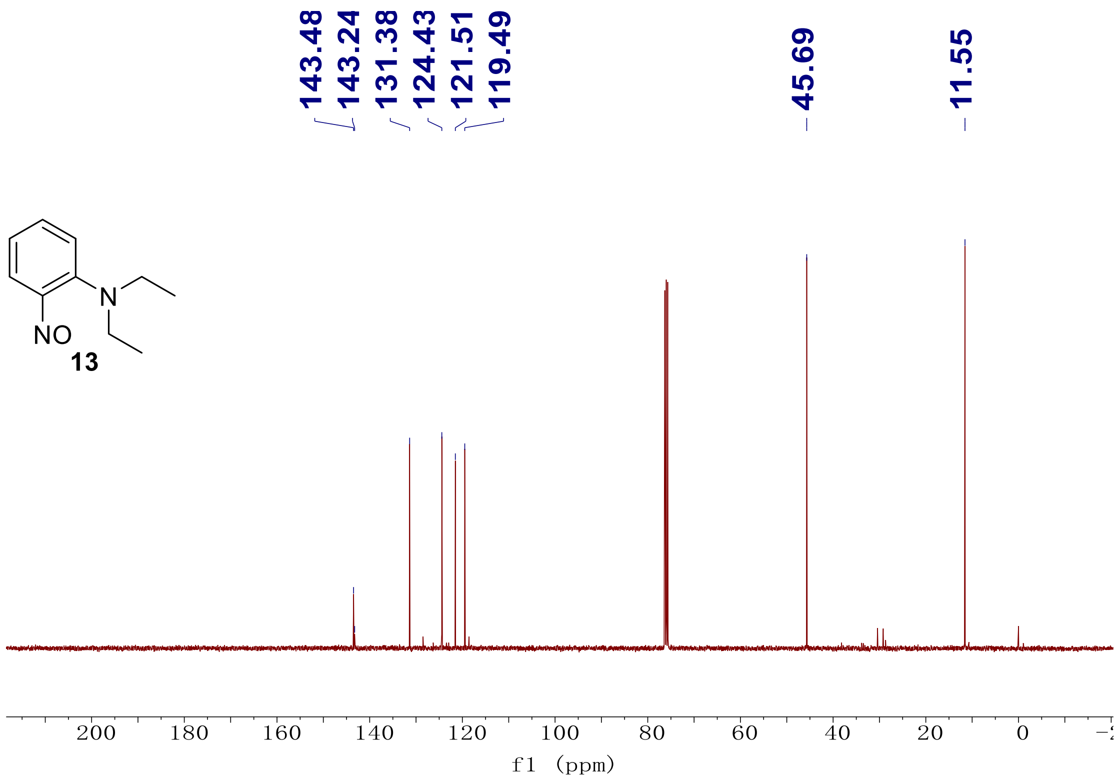
7.19
7.17
7.15
6.96
6.94
6.84
6.82
6.79
6.78
6.76
6.65
6.63
5.38
3.44
H_2N
N
H
11
2.07
2.09
2.06
1.03
2.16
1.00
2.09
7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)

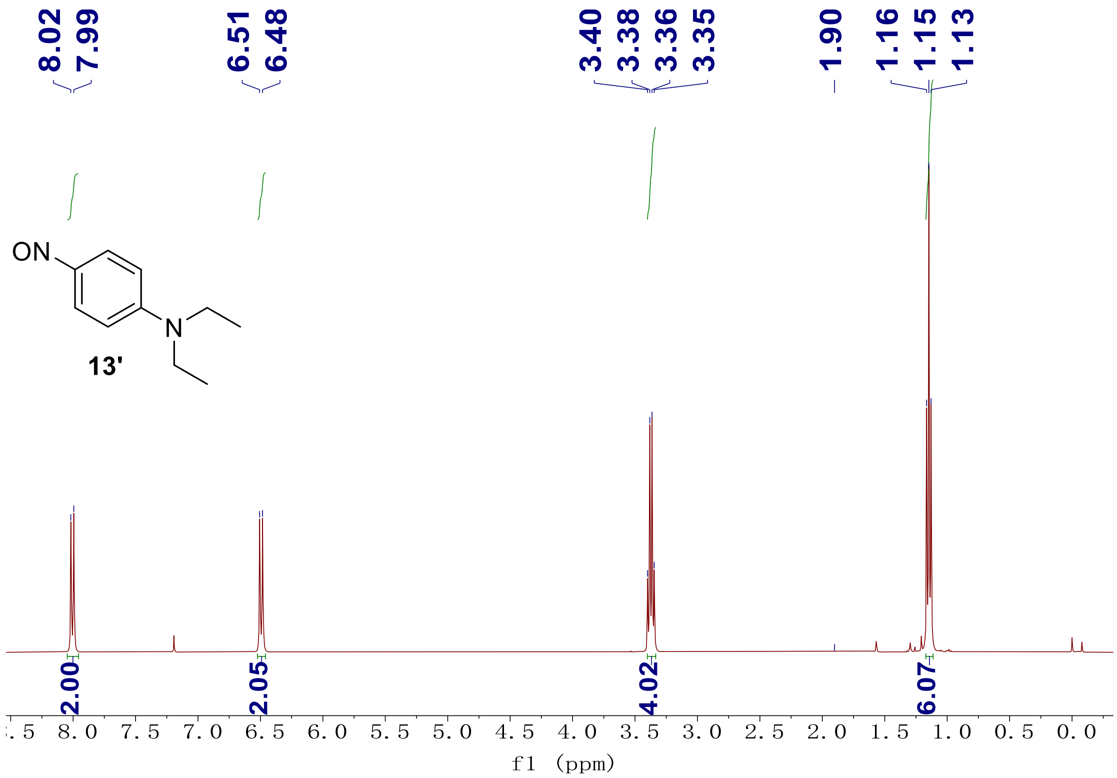

145.94
142.15
133.86
129.32
123.36
119.03
116.21
115.12
77.46
77.14
76.82
H_2N
N
H
11
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)

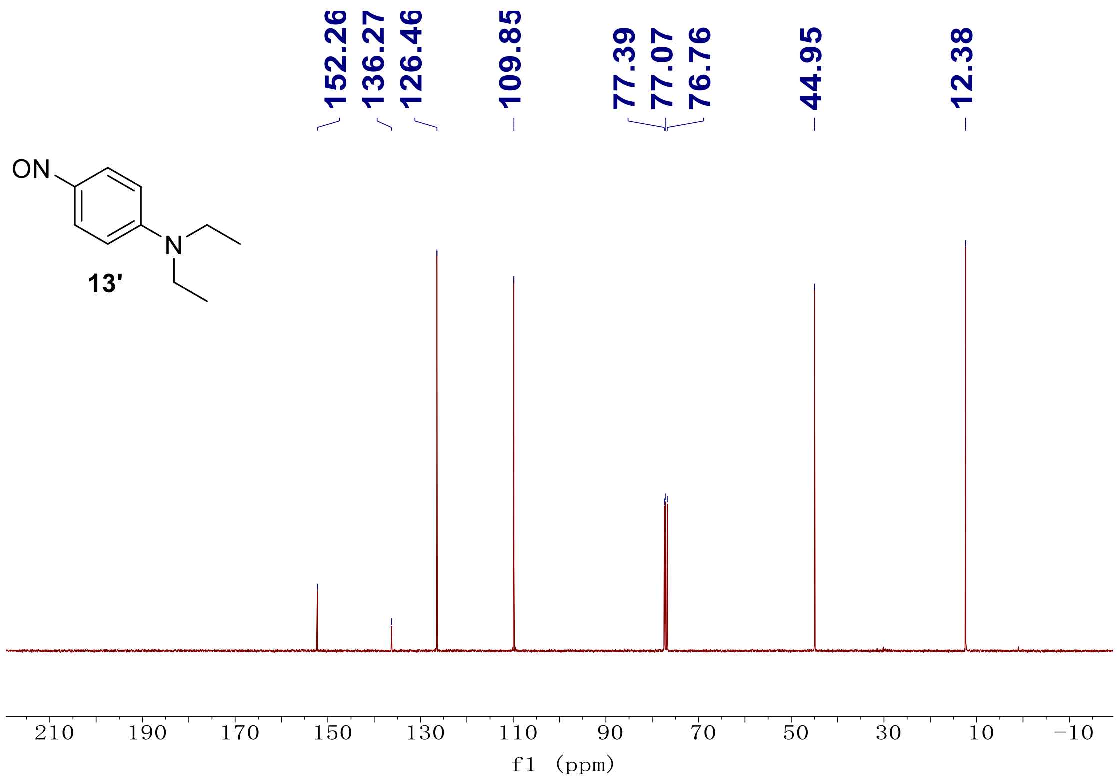

7.31
7.00
6.98
6.58
6.57
3.71
2.23
1.31
NH_2
NH
O
12
1.02
1.07
2.08
2.00
3.17
9.19
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


177.32
140.97
137.03
125.37
121.84
120.25
118.67
77.41
77.09
76.77
39.29
27.78
21.00
NH_2
NH
O
12
210 190 170 150 130 110 90 70 50 30 10 −10
f1 (ppm)


7.58
7.56
7.35
7.33
7.31
7.09
7.07
6.89
6.87
6.85
3.10
3.08
3.07
3.05
1.03
1.01
0.99
N
NO
13
1.00
1.05
1.03
0.99
4.07
6.06
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


143.48
143.24
131.38
124.43
121.51
119.49
45.69
11.55
NO
N
13
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


8.02
7.99
6.51
6.48
3.40
3.38
3.36
3.35
1.90
1.16
1.15
1.13
ON
N
13'
2.00
2.05
4.02
6.07
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



152.26
136.27
126.46
109.85
77.39
77.07
76.76
44.95
12.38
ON
N
13'
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)