Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Direct nitration of aromatic sulfonamides with sodium nitrite

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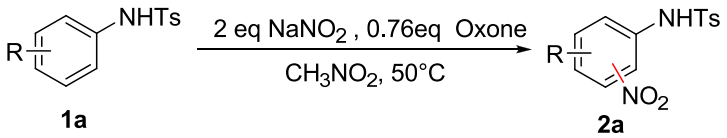
1. General Remarks

Column chromatography was carried out on silica gel. ^{1}H NMR spectra were Recorded on 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 400 MHz in $CDCl_3$. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All compounds were further characterized by HRMS; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided in the Supporting Information. Room temperature is 20–25°C. Commercially available reagents and solvents were used without further purification.

2. General experimental procedure

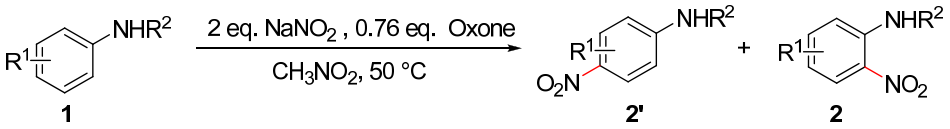


1a **2a**

A mixture of aromatic sulfonamide derivative (0.3 mmol) **1a**, 2 eq $NaNO_2$ (41.4 mg, 0.6 mmol), 2 eq KHS_2O_8 (139.2 mg, 0.6 mmol) and nitromethane (3.0 mL) was stirred at 50ºC under air for 3 h. The reaction was concentrated. The residue was purified by flash column chromatography using mixture of petroleum ether and ethyl acetate as eluent to afford the corresponding product **2** as a yellow solid.

3. Optimization of the reaction conditions

Table SI Optimization of the reaction conditions [a]



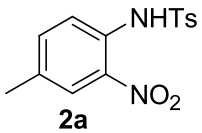
R^1 = H, CH_3, X, NO_2, OCF_3, OR

R^2 = Ts, Ac, Boc, COPh, $CO(CH_3)_3$, Bn, CH_3

Entry	R^2	Oxidant [eq.]	Solvent	Temp. [ºC]	t [h]	Yield [%] [b]
1	-TS	$PhI(OAc)_2$ (3)	DCM	r.t	3	82
2	-TS	DDQ (3)	DCM	r.t	36	67
3	-TS	BQ (3)	DCM	r.t	36	NR
4	-TS	PPTS (3)	DCM	r.t	36	8
5	-TS	$(NH_4)_2S_2O_8$ (2)	DCM	r.t	36	30
6	-TS	Oxone (0.76)	DCM	r.t	36	86
7	-TS	Oxone (0.76)	DCE	r.t	36	42
8	-TS	Oxone (0.76)	CH_3NO_2	r.t	36	83
9	-TS	Oxone (0.76)	CH_3CN	r.t	36	48
10	-TS	Oxone (0.76)	Toluene	r.t	36	41
11	-TS	Oxone (0.76)	THF	r.t	36	NR
12	-TS	Oxone (0.76)	1,4-Dioxane	r.t	36	26
13	-TS	Oxone (0.76)	DMF	r.t	36	19
14	-TS	Oxone (0.76)	DMSO	r.t	28	NR
15	-TS	Oxone (0.76)	CH_3OH	r.t	36	28
16	-TS	Oxone (0.76)	CH_3NO_2	r.t	36	98
17	-Ac	Oxone (0.76)	CH_3NO_2	r.t	36	52
18	-Boc	Oxone (0.76)	CH_3NO_2	r.t	36	26
19	-COPh	Oxone (0.76)	CH_3NO_2	r.t	36	58
20	$-COC(CH_3)_3$	Oxone (0.76)	CH_3NO_2	r.t	36h	52
21	-Bn	Oxone 0.76)	CH_3NO_2	r.t	36	48
22	$-CH_3$	Oxone (0.76)	CH_3NO_2	r.t	36	41
23	**-TS**	**Oxone (0.76)**	**CH_3NO_2**	**50**	**2**	**98**

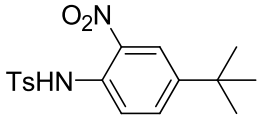
[a] Conditions: 0.3 mmol **1a**, 0.6 mmol $NaNO_2$ and oxidant in nitrommehtane (3 mL) at RT to 50 ºC. [b] Isolated yield.

4. Characterization Data of 2a-2v



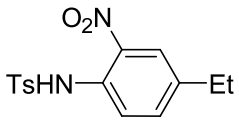
2a

4-Methyl-*N*-(4-methyl-2-nitrophenyl)benzenesulfonamide (2a): 98% yield; yellow solid; mp: 99–101 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.64 (s, 1H), 7.87 (s, 1H), 7.74-7.67 (m, 3H), 7.40-7.38 (d, J = 8.8 Hz, 3H)，7.27-7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.6, 137.2, 136.7, 135.6, 134.5, 131.2, 129.9, 127.1, 125.9, 121.4; IR (KBr, cm^{-1}) 3292, 1533, 1348, 1168; HRMS (ESI) Calcd for $C_{14}H_{14}N_2O_4S$: M+Na = 329.0566; found: 329.0561.



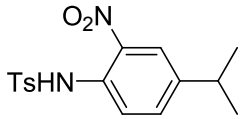
2b

***N*-(4-*tert*-butyl-2-nitrophenyl)-4-methylbenzenesulfonamide (2b):** 63% yield; yellow solid; mp: 121–123 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.75 (s, 1H), 8.09-8.08 (d, J = 4.0 Hz, 1H), 7.75-7.73 (d, 3H), 7.63-7.60 (dd, J_1 = 2.4 Hz, J_2 = 6.4 Hz, 1H), 7.28-7.26 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H),1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 147.5, 144.6, 136.7, 135.9, 133.3, 131.3, 129.9, 127.2, 122.5, 120.7, 34.5, 30.8, 21.5; IR (KBr, cm^{-1}) 3289, 1158, 543; HRMS (ESI) Calcd for $C_{17}H_{20}N_2O_4S$: M+Na = 371.1036; found: 371.1031.



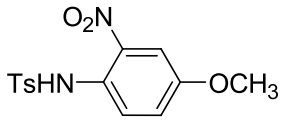
2c

***N*-(4-ethyl-2-nitrophenyl)-4-methylbenzenesulfonamide (2c):** 97% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.69 (s, 1H), 7.91-7.90 (d, J = 1.2 Hz, 1H), 7.76-7.70 (m, 3H),7.44-7.41 (dd, J_1 = 2.0 Hz, J_2 = 6.4 Hz, 1H), 7.27-7.24 (m, 2H), 2.67-2.61 (q, J = 3.6 Hz, 2H), 2.38 (s, 3H),1.24-1.20 (t, J = 3.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.6, 140.5, 137.2, 135.7, 135.6, 131.4, 129.9, 127.1, 124.7, 121.4, 27.7, 21.5, 14.8; IR (KBr, cm^{-1}) 3292, 1169, 548; HRMS (ESI) Calcd for $C_{15}H_{16}N_2O_4S$: M+Na = 343.0723; found: 343.0716.



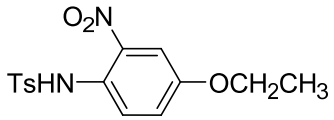
2d

***N*-(4-isopropyl-2-nitrophenyl)-4-methylbenzenesulfonamide (2d):** 97% yield; yellow solid; mp: 176–178 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.23 (s, 1H), 7.98 (s, 2H), 7.49-7.43 (d, *J* = 8.4 Hz, 2H), 7.24-7.22 (d, *J* = 8.4 Hz, 2H), 3.13-3.03 (m, 1H), 2.43 (s, 3H),1.33 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.8, 146.5, 145.3, 134.4, 130.1, 127.6, 126.9, 122.4, 33.6, 23.1, 21.6; IR (KBr, cm^{-1}) 3326, 1536, 545; HRMS (ESI) Calcd for $C_{16}H_{18}N_2O_4S$: M+ = 334.0982; found: 334.0976.



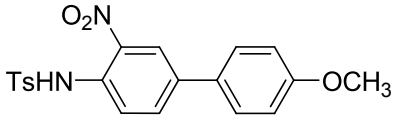
2e

***N*-(4-methoxy-2-nitrophenyl)-4-methylbenzenesulfonamide (2e):** 63% yield; yellow solid; mp: 71–73 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.27 (s, 1H), 7.81-7.78 (m, 1H), 7.62-7.59 (m, 2H), 7.49-7.48 (d, *J* = 4.0 Hz, 1H), 7.27-7.17 (m, 3H), 3.82 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.1, 144.6, 138.9, 135.4, 129.9, 127.1, 126.5, 124.7, 123.0, 109.0, 55.9, 21.5; IR (KBr, cm^{-1}) 3299, 1167, 551; HRMS (ESI) Calcd for $C_{14}H_{14}N_2O_5S$: M+Na = 345.0518; Found: 345.0508.



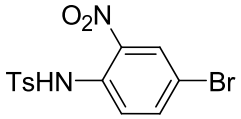
2f

***N*-(4-ethoxy-2-nitrophenyl)-4-methylbenzenesulfonamide (2f):** 62% yield; yellow solid; mp: 91–93 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.27 (s, 1H), 7.81-7.78 (m, 1H), 7.62-7.59 (m,2H), 7.49-7.48 (d, *J* = 4.0 Hz, 1H), 7.23-7.17 (m, 3H), 3.82 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.5, 144.5, 139.0, 135.4, 129.9, 127.0, 126.2, 124.7, 123.3, 109.5, 64.4, 21.5, 14.5; IR (KBr, cm^{-1}) 3299, 1166, 554; HRMS (ESI) Calcd for $C_{15}H_{16}N_2O_5S$: M+Na = 359.0672; found: 359.0665.



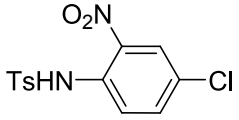
2g

***N*-(4'-methoxy-3-nitrobiphenyl-4-yl)-4-methylbenzenesulfonamide (2g):** 62% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.40 (s, 1H), 7.79-7.76 (d, *J* = 8.8 Hz, 1H), 7.66-7.64 (d, *J* = 8.4 Hz, 2H),7.52-7.51 (d, *J* = 3.2 Hz, 1H),7.25-7.20 (m, 3H), 6.95-6.88 (m, 4H), 3.80 (m, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.7, 155.0, 148.1, 144.6, 138.4, 135.4, 129.9, 127.6, 124.0, 124.7, 123.9, 121.1, 115.1, 112.9, 55.5, 21.5; IR (KBr, cm^{-1}) 3297, 1490, 549; HRMS (ESI) Calcd for $C_{20}H_{18}N_2O_6S$: M+Na = 437.0778; fFound: 437.0768.



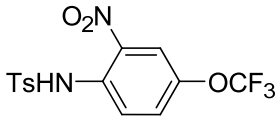
2h

***N*-(4-bromo-2-nitrophenyl)-4-methylbenzenesulfonamide (2h):** 92% yield; yellow solid; mp: 99–101 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.77 (s, 1H), 8.24-8.23 (d, *J* = 2.4 Hz, 1H), 7.77-7.66 (m, 4H), 7.29-7.27 (d, *J* = 8.4 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.1, 138.7, 137.1, 135.3, 133.0, 130.1, 128.6, 127.2, 122.2, 116.0, 21.6; IR (KBr, cm^{-1}) 3299, 1170, 547; HRMS (ESI) Calcd for $C_{13}H_{11}BrN_2O_4S$: M+Na = 394.9495; Found: 394.9506.



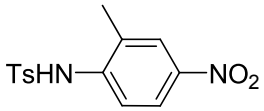
2i

***N*-(4-chloro-2-nitrophenyl)-4-methylbenzenesulfonamide (2i):** 90% yield; yellow solid; mp: 110–112 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.76 (s, 1H), 8.11-8.10 (d, *J* = 2.4 Hz, 1H), 7.85-7.83 (d, *J* = 5.2 Hz, 1H), 7.75-7.73 (d, *J* = 2.4 Hz, 2H), 7.75-7.73 (dd, J_1 = 2.4 Hz, J_2 = 6.8 Hz, 1H), 7.30-7.28 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.1, 137.0, 135.8, 135.3, 132.5, 130.1, 129.2, 127.2, 125.7, 122.2, 21.6; IR (KBr, cm^{-1}) 3299, 1170, 547; HRMS (ESI) Calcd for $C_{13}H_{11}ClN_2O_4S$: M+Na = 349.0020; found: 349.0010.



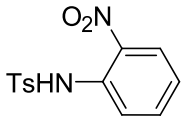
2j

4-Methyl-*N*-(2-nitro-4-(trifluoromethoxy)phenyl)benzenesulfonamide (2j): 90% yield; yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.86 (s, 1H), 8.02 (s, 1H), 7.94-7.92 (d, *J* = 9.2 Hz, 1H), 7.78-7.76 (d, *J* = 8.0 Hz, 2H), 7.50-7.48 (d, *J* = 9.2 Hz, 1H), 7.33-7.31 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.2, 143.7, 136.5, 135.3, 132.7, 130.1, 128.7, 127.2, 124.0, 122.1, 121.4, 118.8, 118.7, 21.5, 21.6; IR (neat, cm^{-1}) 3297, 2925, 1265, 741; HRMS (ESI) Calcd for $C_{14}H_{11}F_3N_2O_5S$: M+Na = 399.0233; found: 399.0223.



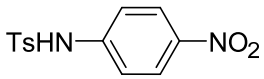
2k

4-Methyl-*N*-(2-methyl-4-nitrophenyl)benzenesulfonamide (2l): 83% yield; yellow solid; mp: 158–160 ºC; ^{1}HNMR (400 MHz, $CDCl_3$) δ ppm 8.46-8.45 (d, *J* = 0.8 Hz, 2H), 8.00 (s, 1H), 7.43-7.41 (d, *J* = 8.4 Hz, 2H), 7.27-7.25 (d, *J* = 8.8 Hz, 2H), 2.79 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.6, 145.5, 145.0, 144.2, 134.5, 134.0, 130.6, 130.3, 127.2, 118.1, 21.7, 20.4; IR (KBr, cm^{-1}) 3295, 1543, 1345, 1167; HRMS (ESI) Calcd for $C_{14}H_{14}N_2O_4S$: M+Na = 329.0566; 329.0576.



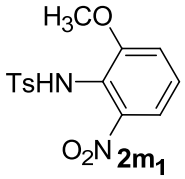
$2l_1$

4-Methyl-*N*-(2-nitrophenyl)benzenesulfonamide ($2k_1$): 31% yield; yellow solid; mp: 113–115 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.87 (s, 1H), 8.12-8.10 (dd, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 1H), 7.85-7.82 (d, *J* = 8.8 Hz, 1H), 7.75-7.73 (d, *J* = 8.4 Hz, 2H), 7.61-7.56 (m, 1H), 7.27-7.25 (d, *J* = 8.0 Hz, 2H), 7.17-7.13 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.0, 142.6, 130.1, 127.3, 125.4, 118.6, 21.6; IR (KBr, cm^{-1}) 3288, 1186, 546; HRMS (ESI) Calcd for $C_{13}H_{12}N_2O_4$: M+Na = 315.0410; found: 315.0404.



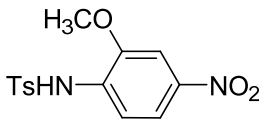
2l$_2$

4-Methyl-*N*-(4-nitrophenyl)benzenesulfonamide (2k$_2$): 62% yield; yellow solid; mp: 113–115 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.14-8.12 (d, *J* = 8.8 Hz, 2H), 7.78-7.76 (d, *J* = 8.4 Hz, 2H), 7.31-7.29 (d, *J* = 4.0 Hz, 2H), 7.23-7.19 (m, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 135.5, 132.3, 131.1, 130.3, 125.9, 124.4 (q, *J* = 276.0 Hz, CF_3), 123.4, 117.9, 39.5 (q, *J* = 30.0 Hz, CH_2CF_3), 30.8 (q, *J* = 3.0 Hz, CHCN); ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.97 (s, 3F); IR (KBr, cm^{-1}) 3330, 2924, 1159; HRMS (ESI) Calcd for $C_{13}H_{12}N_2O_4S$: M+Na = 315.0410; found: 315.0421.



2m$_1$

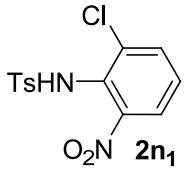
***N*-(2-methoxy-6-nitrophenyl)-4-methylbenzenesulfonamide (2m$_1$):** 50% yield; yellow solid; mp: 138–140 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.84-7.81 (m, 1H), 7.78-7.76 (d, *J* = 8.4 Hz, 2H), 7.65-7.64 (d, *J* = 2.4 Hz, 1H), 7.61-7.59 (d, *J* = 8.8 Hz, 1H), 7.51 (s, 1H), 7.28-7.26 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 147.7, 144.7, 143.6, 135.6, 132.6, 129.9, 127.2, 117.4, 116.7, 105.8, 56.4, 21.6; IR (KBr, cm^{-1}) 3286, 2923, 741; HRMS (ESI) Calcd for $C_{14}H_{14}N_2O_5S$: M+Na = 345.0516; found: 345.0508.



2m$_2$

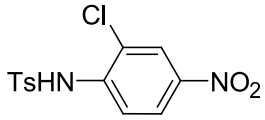
***N*-(2-methoxy-4-nitrophenyl)-4-methylbenzenesulfonamide (2m$_2$):** 32% yield; yellow solid; mp: 157–159 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.74 (s, 1H), 8.56-8.55 (d, *J* = 4.0 Hz, 1H), 7.90-7.89 (d, *J* = 4.0 Hz, 1H), 7.77-7.75 (d, *J* = 8.0 Hz, 2H), 7.36-7.34 (d, *J* = 8.0 Hz, 2H), 3.70 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.6, 135.5, 124.6 (q, *J* = 276.0 Hz, CF_3), 118.4, 105.3, 100.4, 55.4, 39.5 (q, *J* = 30.0 Hz, CH_2CF_3), 31.3 (q, *J* = 3.0 Hz, CHCN); ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.18 (s, 3F); IR (KBr, cm^{-1}) 3285, 2924, 1546, 1345; HRMS (ESI) Calcd

for $C_{14}H_{14}N_2O_5S$: M+Na = 345.0516; found: 345.0507.



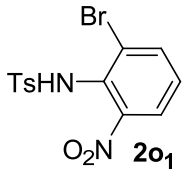
2n1

***N*-(2-chloro-6-nitrophenyl)-4-methylbenzenesulfonamide (2n$_1$):** 82% yield; yellow solid; mp: 163–165 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.21-8.20 (d, *J* = 8.8 Hz, 1H), 8.20-8.08 (m, 1H), 7.78-7.76 (m, 3H), 7.56-7.49 (m, 1H), 7.31-7.29 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.3, 143.5, 139.5, 135.2, 130.1, 127.3, 125.2, 123.5, 123.2, 118.7, 21.6; IR (KBr, cm^{-1}) 3295, 2926, 742, 547; HRMS (ESI) Calcd for $C_{13}H_{11}ClN_2O_4S$: M+Na = 349.0020; found: 349.0011.



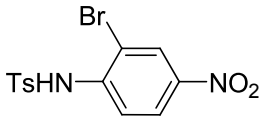
2n2

***N*-(2-chloro-4-nitrophenyl)-4-methylbenzenesulfonamide (2n$_2$):** 17% yield; yellow solid; mp: 116–118 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.78-7.76 (d, *J* = 8.0 Hz, 1H), 7.72-7.70 (d, *J* = 8.0 Hz, 1H), 7.55-7.53 (d, *J* = 8.0 Hz, 2H), 7.39-7.35 (m, 1H), 7.26-7.24 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 147.4, 144.9, 135.8, 135.4, 135.3, 129.9, 128.1, 128.0, 127.3, 123.8, 21.6; IR (KBr, cm^{-1}) 3267, 2925, 571; HRMS (ESI) Calcd for $C_{13}H_{11}ClN_2O_4S$: M+Na = 349.0020; found: 349.0033.



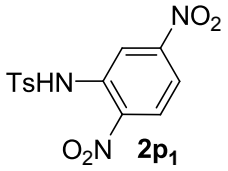
2o1

***N*-(2-bromo-6-nitrophenyl)-4-methylbenzenesulfonamide (2o$_1$)**: 76% yield; yellow solid; mp: 134–136 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.35-8.34 (d, *J* = 2.4 Hz 1H), 8.14-8.11 (m, 1H), 7.79-7.75 (m, 3H), 7.53 (s, 1H), 7.31-7.29 (d, *J* = 8.4 Hz 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.2, 143.6, 140.6, 135.1, 130.0, 128.3, 127.3, 124.0, 118.8, 113.1, 21.6; IR (KBr, cm^{-1}) 3284, 1167, 663; HRMS (ESI) Calcd for $C_{13}H_{11}BrN_2O_4S$: M+Na = 392.9515; found: 392.9510.



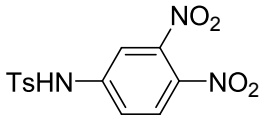
2o$_2$

***N*-(2-bromo-4-nitrophenyl)-4-methylbenzenesulfonamide (2o$_2$)**: 21% yield; yellow solid; mp: 136–138 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.89-7.87 (d, J = 8.0 Hz, 1H), 7.81-7.79 (dd, J_1= 0.8 Hz, J_2= 8.0 Hz, 1H), 7.53-7.51 (d, J = 8.0 Hz, 2H), 7.33-7.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 147.6, 144.9, 138.3, 135.3, 130.0, 129.0, 128.6, 127.4, 126.0, 124.5, 21.7; IR (KBr, cm^{-1}) 3269, 1168, 570; HRMS (ESI) Calcd for $C_{13}H_{11}BrN_2O_4S$: M+Na = 392.9515; found: 392.9506.



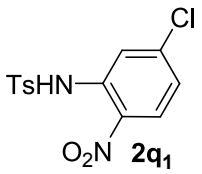
2p$_1$

***N*-(2,5-dinitrophenyl)-4-methylbenzenesulfonamide (2p$_1$):** 44% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.97 (s, 1H) 8.70-8.69 (d, J = 2.0 Hz, 1H), 8.35-8.32 (d, J = 9.2 Hz, 1H), 7.93-7.90 (m, 1H), 7.87-7.85 (d, J = 8.4 Hz, 2H), 7.36-7.34 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.1, 145.7, 138.5, 135.2, 134.9, 130.4, 127.8, 127.5, 117.1, 115.1, 21.7; IR (KBr, cm^{-1}) 3422, 1027; HRMS (ESI) Calcd for $C_{13}H_{11}N_3O_6S$: M+Na = 360.0261; found: 360.0253.



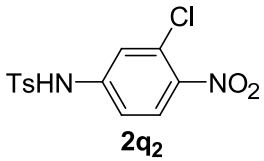
2p$_2$

***N*-(3,4-dinitrophenyl)-4-methylbenzenesulfonamide (2p$_2$):** 32% yield; yellow solid; mp: 125–127 ºC; ^{1}H NMR (400 MHz, DMSO) δ ppm 11.70 (s, 1H) 8.17-8.14 (d, J = 2.4 Hz, 1H), 7.82-7.80 (d, J = 8.0 Hz, 2H), 7.68-7.67 (d, J = 2.4 Hz, 1H), 7.52-7.43 (s, 2H), 2.36(s, 3H); ^{13}C NMR (100 MHz, DMSO) δ ppm 145.1, 144.5, 144.3, 136.1, 135.9, 130.7, 128.5, 127.4, 120.9, 113.7, 21.5; IR (KBr, cm^{-1}) 3293, 1167, 735; HRMS (ESI) Calcd for $C_{13}H_{11}N_3O_6S$: M+Na = 360.0261; found: 360.0253.



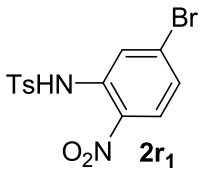
2q1

***N*-(5-chloro-2-nitrophenyl)-4-methylbenzenesulfonamide (2q$_1$):** 35% yield; yellow solid; mp: 166–168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.28 (s, 1H), 8.88 (s, 1H), 8.05 (s, 1H), 7.87-7.84 (d, *J* = 8.4 Hz, 1H), 7.39-7.37 (d, *J* = 8.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 146.2, 140.8, 137.7, 135.7, 134.6, 132.7, 130.5, 127.5, 124.9, 121.5, 21.7; IR (KBr, cm^{-1}) 3238, 1164, 543; HRMS (ESI) Calcd for $C_{13}H_{11}ClN_2O_4S$: M+Na = 349.0020; found: 349.0014.



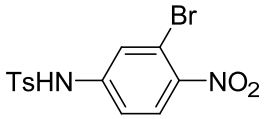
2q2

***N*-(3-chloro-4-nitrophenyl)-4-methylbenzenesulfonamide (2q$_2$):** 24% yield; yellow solid; mp: 166–168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.00 (s, 1H), 8.10-8.07 (d, *J* = 8.8 Hz, 1H), 7.87-7.86 (d, *J* = 2.4 Hz, 1H), 7.79-7.77 (d, *J* = 8.4 Hz, 2H), 7.32-7.30 (d, *J* = 8.0 Hz,2H), 7.11-7.08 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.2, 142.6, 135.3, 135.1, 134.7, 130.1, 127.4, 127.3, 123.8, 120.0, 21.6; IR (KBr, cm^{-1}) 3238, 1164, 543; HRMS (ESI) Calcd for $C_{13}H_{11}ClN_2O_4S$: M+Na = 349.0021; found: 349.0031.



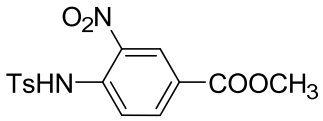
2r1

***N*-(5-bromo-2-nitrophenyl)-4-methylbenzenesulfonamide (2r$_1$):** 43% yield; yellow solid; mp: 147–149 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.06 (s, 1H), 8.81 (s, 1H), 8.26 (s, 1H), 7.86-7.84 (d, *J* = 8.4 Hz, 2H), 7.39-7.37 (d, *J* = 8.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 146.2, 142.8, 137.3, 134.7, 133.3, 130.5, 127.5, 125.0, 124.5, 123.6, 21.7; IR (KBr, cm^{-1}) 3237, 2923, 1165; HRMS (ESI) Calcd for $C_{13}H_{11}BrN_2O_4S$: M+Na = 392.9515; found: 392.9507.



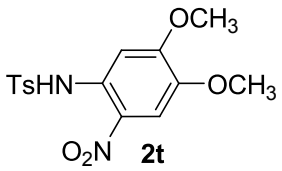
2r$_2$

***N*-(3-bromo-4-nitrophenyl)-4-methylbenzenesulfonamide (2r$_2$):** 20% yield; yellow solid; mp: 126–128 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.96 (s, 1H) 8.04-7.98 (m, 2H), 7.78-7.76 (d, *J* = 8.4 Hz, 2H), 7.32-7.30 (d, *J* = 2.0 Hz, 2H), 7.27-7.24 (dd, J_1= 2.0 Hz, J_2 = 7.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.2, 135.3, 135.0, 131.2, 130.1, 127.3, 126.8, 123.1, 21.6; IR (KBr, cm^{-1}) 3252, 2925, 743; HRMS (ESI) Calcd for $C_{13}H_{11}BrN_2O_4S$: M+Na = 394.9495; found: 394.9505.



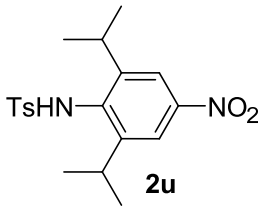
2s

Methyl 4-(4-methylphenylsulfonamido)-3-nitrobenzoate (2s): 83% yield; yellow solid; mp: 139–141ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.20 (s, 1H), 8.81-8.80 (d, *J* = 4.0 Hz, 1H), 8.19-8.17 (m, 1H), 7.89-7.87 (d, *J* = 8.0 Hz, 1H), 7.82-7.79 (d, *J* = 12.0 Hz, 2H), 7.31-7.27 (m, 2H), 3.92 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 164.4, 145.3, 137.6, 136.3, 135.6, 135.3, 130.1, 128.0, 127.4, 125.1, 119.3, 52.6, 21.6; HRMS (ESI) Calcd for $C_{15}H_{14}F_3N_2O_6S$: M+Na = 373.0465; found: 373.0469.



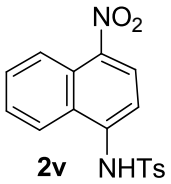
2t

***N*-(4,5-dimethoxy-2-nitrophenyl)-4-methylbenzenesulfonamide (2t):** 32% yield; yellow solid; mp: 192–194 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.10 (s, 1H) 7.70-7.68 (d, *J* = 8.0 Hz, 2H), 7.54 (s,1H), 7.35 (s, 1H), 7.27-7.24 (m, 2H), 3.98 (s, 3H), 3.87 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ ppm 155.4, 145.2, 144.8, 135.5, 130.2, 130.0, 127.1, 107.2, 103.0, 56.7, 56.3, 21.6; IR (KBr, cm^{-1}) 3231, 2922, 1248，1160; HRMS (ESI) Calcd for $C_{15}H_{16}N_2O_6S$: M+Na = 375.0621; found: 375.0616.



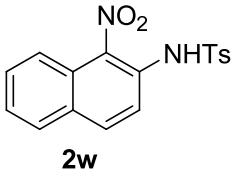
2u

***N*-(2,6-diisopropyl-4-nitrophenyl)-4-methylbenzenesulfonamide (2u):** 43% yield; yellow solid; mp: 172–174 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.00-7.98 (m, 2H) 7.60-7.58 (m, 2H), 7.30-7.27 (m, 2H), 6.32 (s, 1H), 3.22-3.17 (m, 2H), 2.44 (s, 3H), 1.07-1.05 (m, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ ppm150.2, 147.8, 145.2, 144.4, 136.6, 135.2, 129.8, 127.3, 119.3, 29.0, 23.5, 21.5; IR (KBr, cm^{-1}) 3250, 2968, 1161, 739; HRMS (ESI) Calcd for $C_{19}H_{24}N_2O_4S$: M+Na = 399.0233; found: 399.0225.



2v

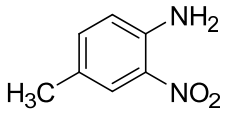
4-Methyl-*N*-(4-nitronaphthalen-1-yl)benzenesulfonamide (2v): 76% yield; yellow solid; mp: 159–161 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.97-8.95 (d, *J* = 8.8 Hz, 1H), 8.83 (s, 1H), 8.58-8.55 (d, *J* = 11.2 Hz, 2H), 8.01-7.97 (m, 1H), 7.91-7.87 (m, 1H), 7.35-7.32 (d, *J* = 8.4 Hz, 2H), 7.23-7.21 (d, *J* = 8.4 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.6, 144.7, 138.8, 134.6, 133.6, 133.5, 132.4, 130.2, 129.9, 129.1, 127.6, 127.2, 122.7, 118.1, 21.7; IR (KBr, cm^{-1}) 3281, 2925, 1168, 544; HRMS (ESI) Calcd for $C_{17}H_{14}N_2O_4S$: M+Na = 365.0566; found: 365.0562.



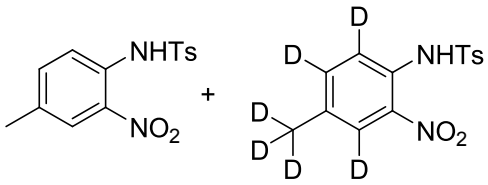
2w

4-Methyl-N-(1-nitronaphthalen-2-yl)benzenesulfonamide (2w): 85% yield; yellow solid; mp: 159–161 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.48 (s, 1H), 8.00-7.91 (m, 3H), 7.85-7.83 (d, *J* = 8.4 Hz, 1H), 7.64-7.53 (m, 4H), 7.22-7.20 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.8, 137.6, 135.5, 134.1, 131.0, 130.0, 129.9, 129.7, 128.3, 127.0, 126.9, 125.5, 122.3, 120.7, 21.6; HRMS

(ESI) Calcd for $C_{17}H_{14}N_2O_4S$: M+Na = 365.0566; found: 365.0565.

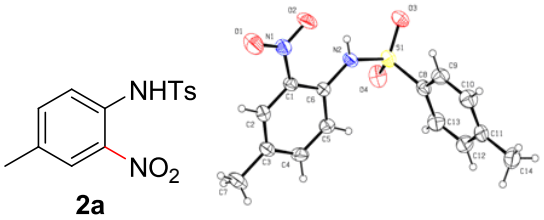


4-Methyl-2-nitroaniline: 86% yield; yellow solid; mp: 107–109 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.90 (s, 1H), 7.20-7.18 (dd, J_1 = 2.0 Hz, J_2 = 6.4 Hz, 1H), 6.75-6.73 (d, J = 8.4 Hz, 1H), 5.94 (s, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.7, 137.2, 131.8, 126.5, 125.2, 118.7, 20.0; IR (KBr, cm^{-1}) 3340.8, 2923.1, 2367, 1243, 1165; HRMS (ESI) Calcd for $C_7H_8N_2O_2$: M+Na = 153.0659; found: 153.0662.



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.66 (s, 2H), 7.88 (s, 1H), 7.74-7.68 (m, 5H), 7.41-7.39 (d, J = 8.8 Hz, 1H), 7.28-7.23 (m, 4H), 2.38, (s, 6H), 2.34, (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.6, 137.1, 137.0, 136.7, 135.5, 134.4, 134.1, 131.1, 130.1, 130.0, 129.8, 127.1, 126.9, 125.8, 125.8, 121.3, 21.5, 20.4.

5. Crystallographic data of 2a



2a

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

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Bond precision: C-C = 0.0038 A Wavelength=0.71070

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alpha=92.665(13) beta=97.218(15) gamma=107.79(2)
Temperature: 293 K

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Hall group	-P 1	-P 1
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Sum formula	C14 H14 N2 O4 S	C14 H14 N2 O4 S
Mr	306.34	306.33
Dx,g cm-3	1.393	1.393
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F000'	320.40	
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Tmin,Tmax	0.911,0.920	0.635,1.000
Tmin'	0.911	

Correction method= MULTI-SCAN

Data completeness= 0.998 Theta(max)= 26.010

R(reflections)= 0.0517(2076) wR2(reflections)= 0.1545(2864)

S = 1.084 Npar= Npar = 203

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

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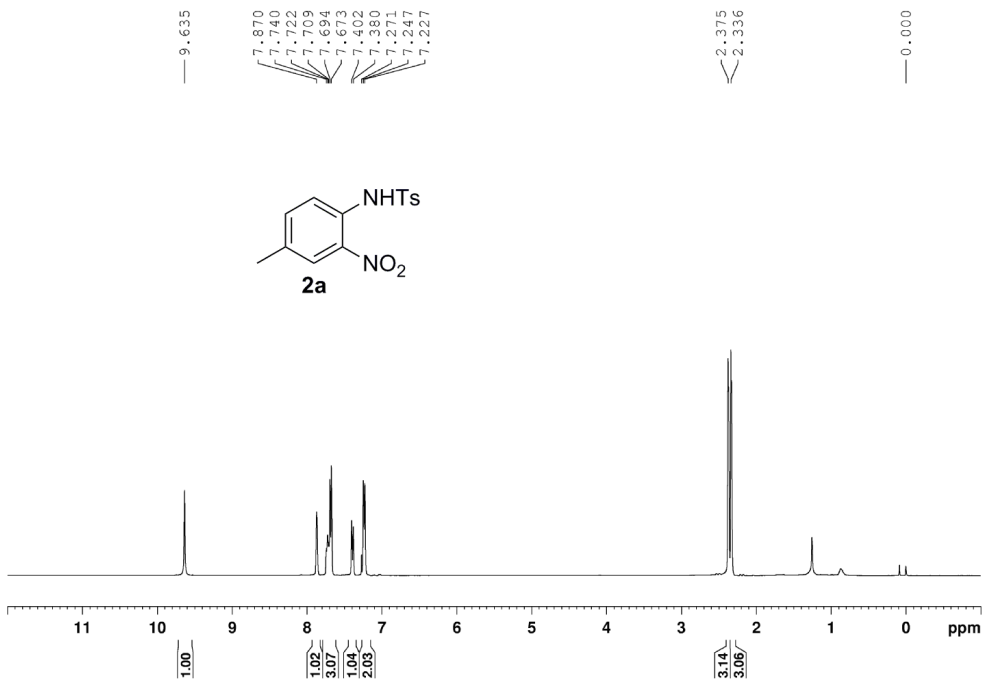
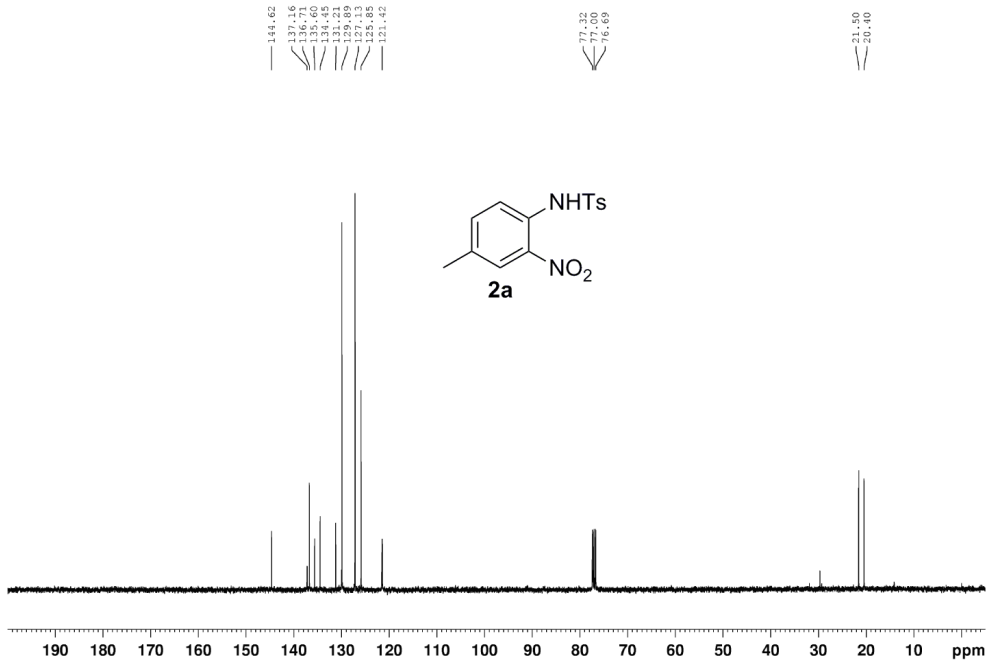
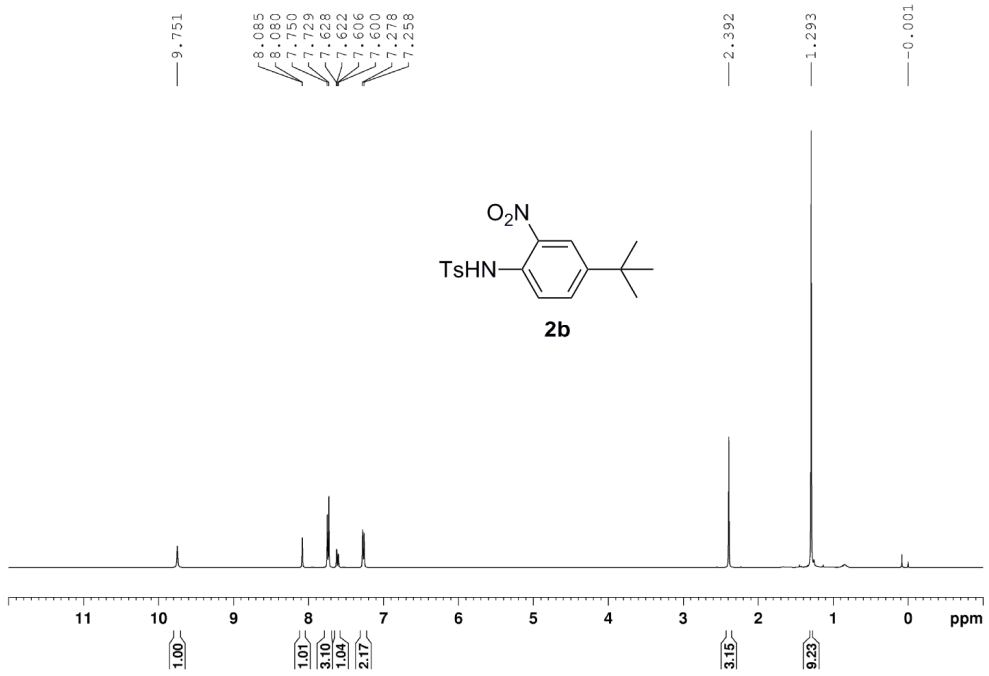
6. ^{1}H NMR、^{13}C NMR、Spectra for Substrates 2a-3v



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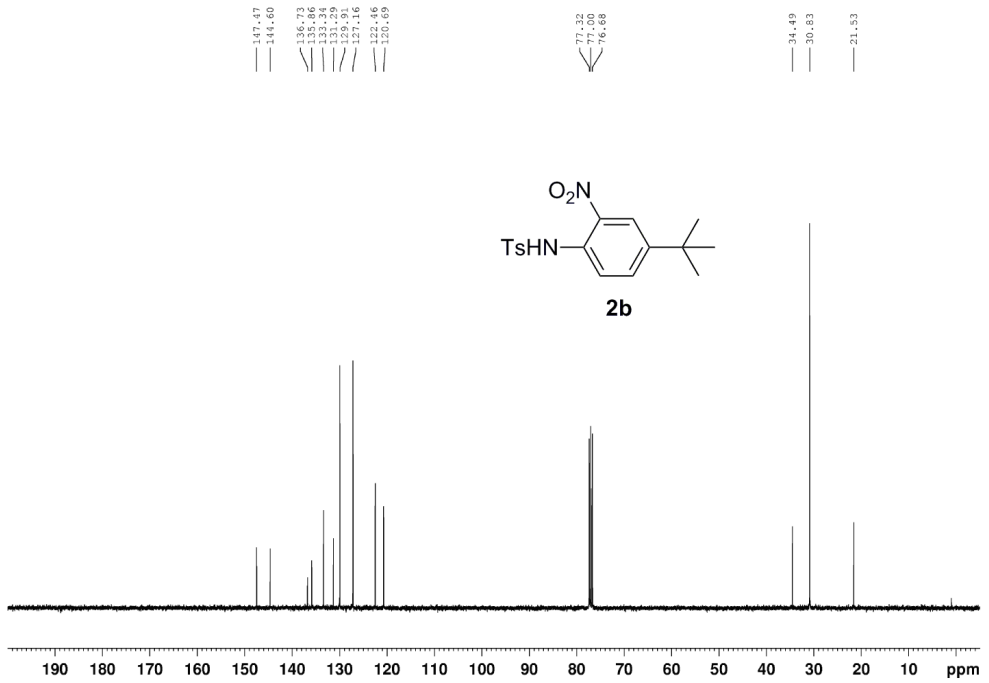
8.085
8.080
7.750
7.729
7.628
7.622
7.606
7.600
7.278
7.258
2.392
1.293
0.001
O2N
TsHN
2b
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.01
3.10
1.04
2.17
3.15
9.23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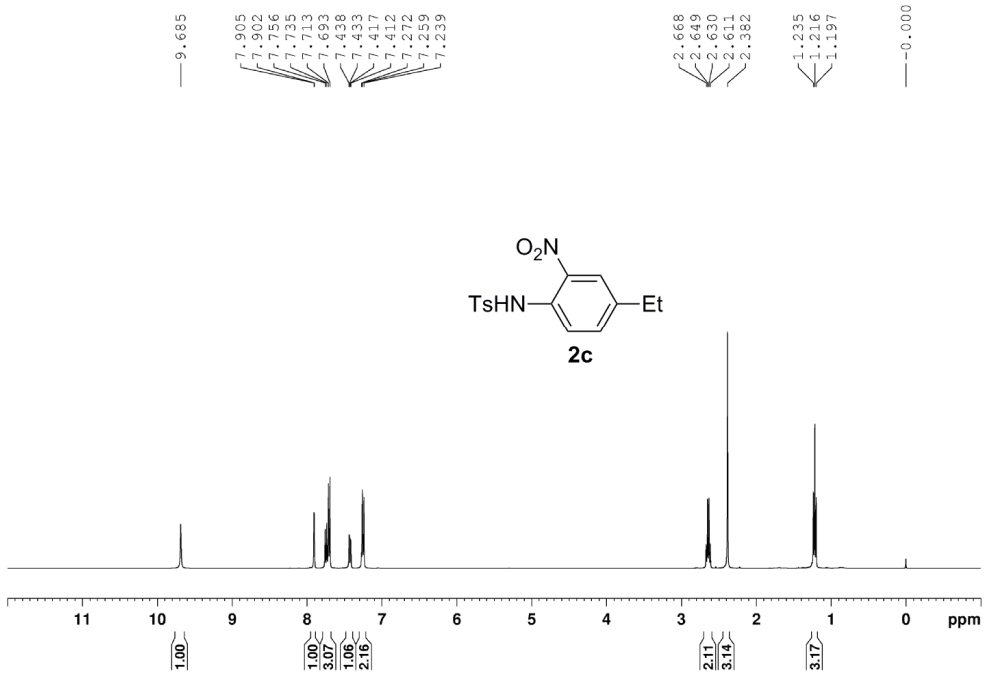
144.60
136.73
135.86
133.34
131.29
129.91
127.16
122.46
120.89
77.32
77.00
76.68
34.49
30.83
21.53
O2N
TsHN
2b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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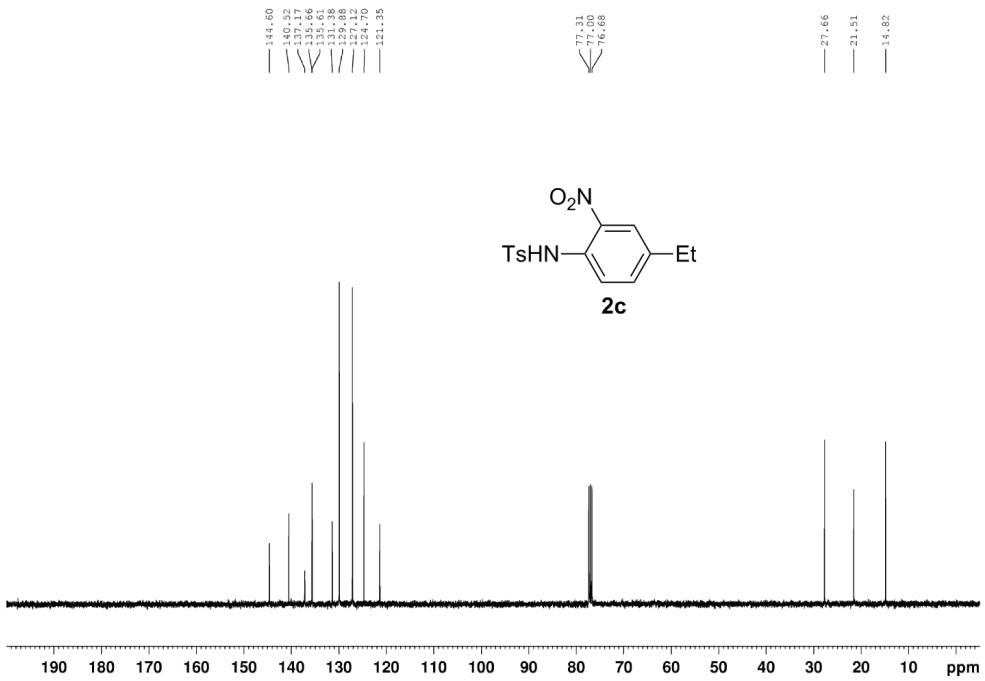
7.905
7.902
7.756
7.735
7.713
7.693
7.438
7.433
7.417
7.412
7.272
7.259
7.239
2.668
2.649
2.630
2.611
2.382
1.235
1.216
1.197
0.000
O2N
TsHN
Et
2c
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
3.07
1.06
2.16
2.11
3.14
3.17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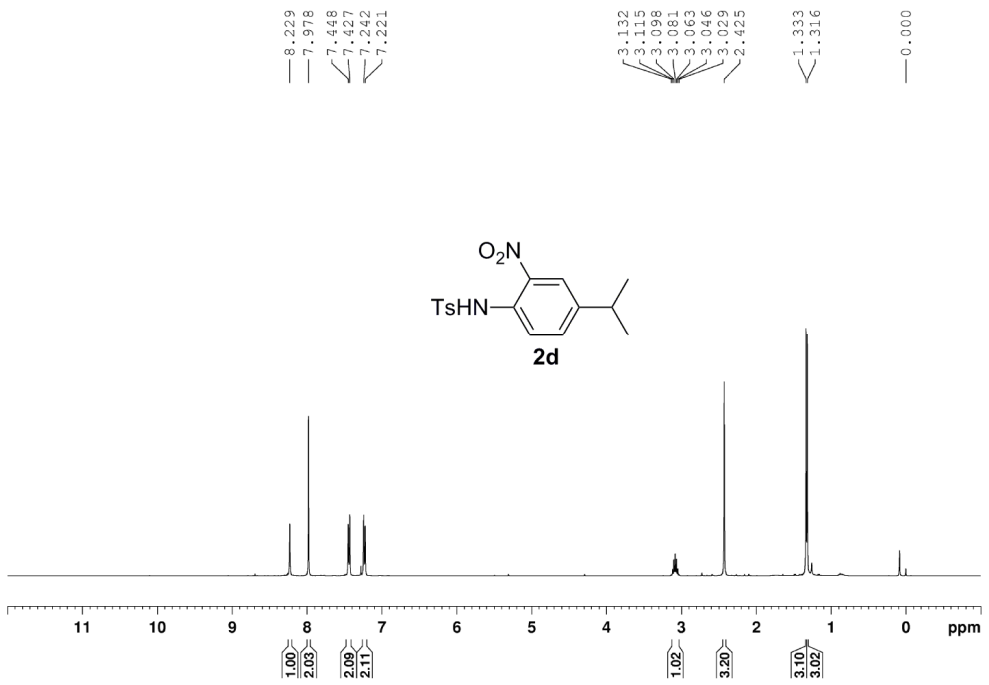
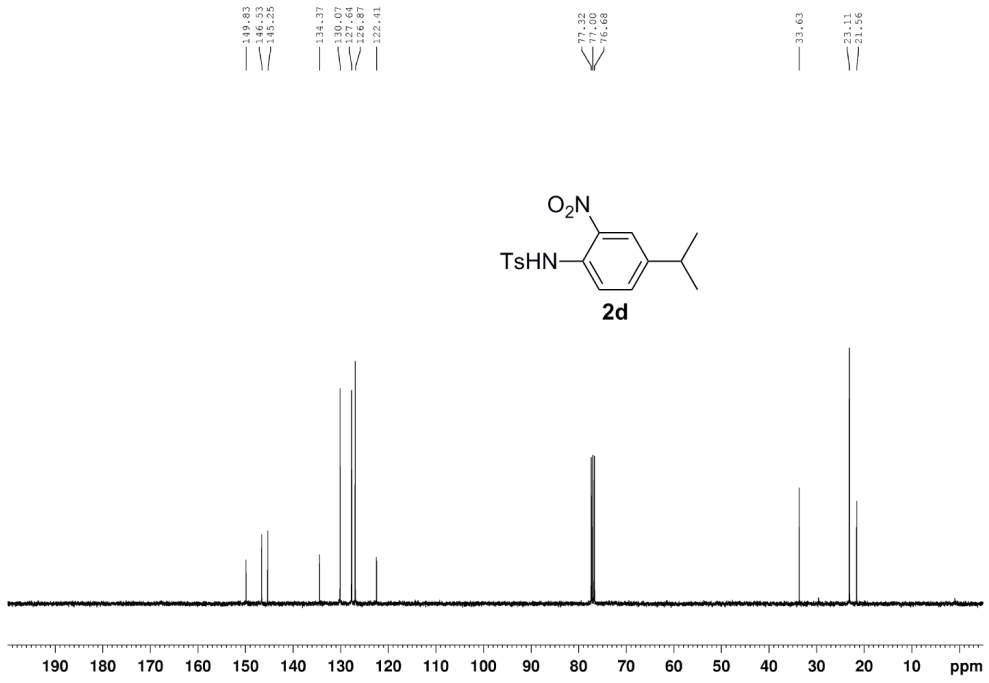
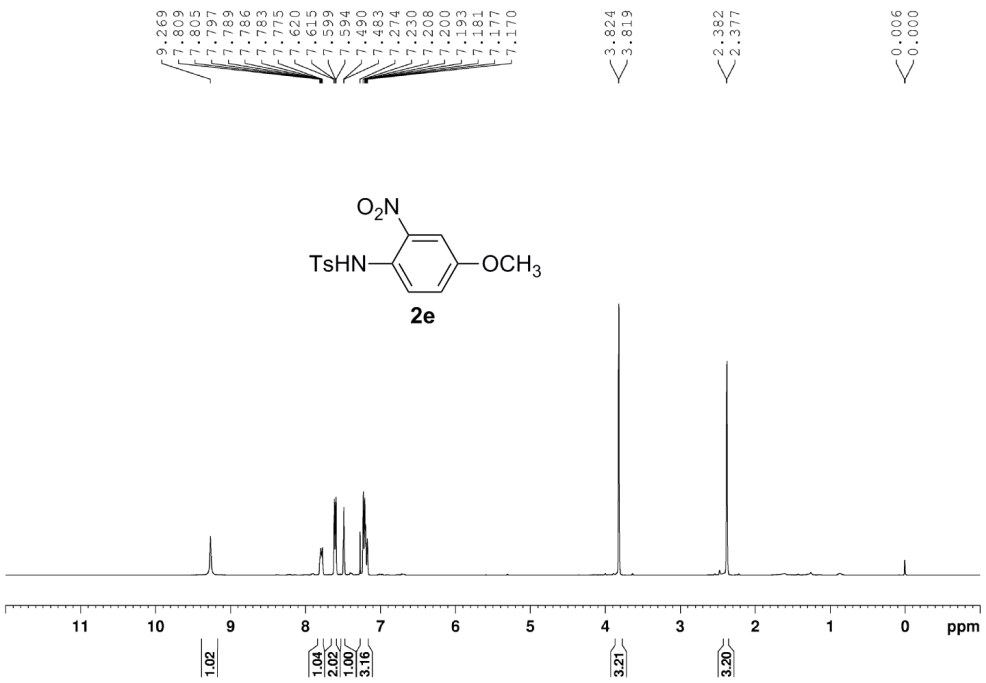
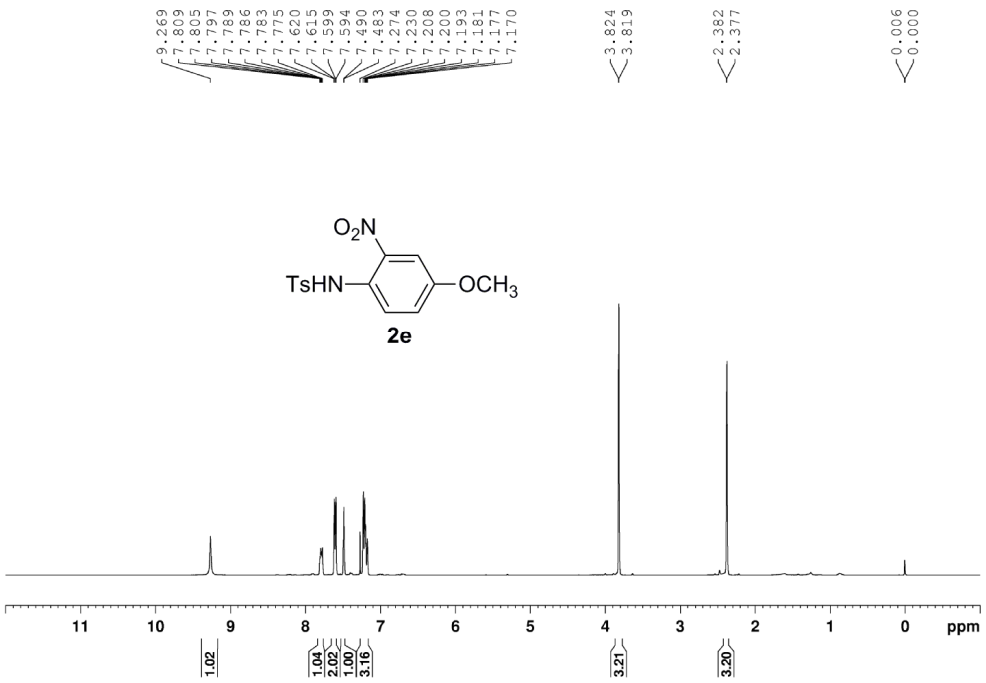
140.52
137.17
135.66
135.61
131.38
129.48
127.12
124.70
121.35
77.31
77.00
76.68
27.66
21.51
14.82
O2N
TsHN
Et
2c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.229
7.978
7.448
7.427
7.242
7.221
3.132
3.115
3.098
3.081
3.063
3.046
3.029
2.425
1.333
1.316
0.000
O2N
TsHN
2d
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.03
2.09
2.11
1.02
3.20
3.10
3.02


149.83
146.53
145.25
134.37
130.07
127.64
126.87
122.41
77.32
77.00
76.68
33.63
23.11
21.56
O2N
TsHN
2d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


9.269
7.809
7.805
7.797
7.789
7.786
7.783
7.775
7.620
7.615
7.599
7.594
7.490
7.483
7.274
7.230
7.208
7.200
7.193
7.181
7.177
7.170
3.824
3.819
2.382
2.377
0.006
0.000
O2N
TsHN
OCH3
2e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.04
2.02
1.00
3.16
3.21
3.20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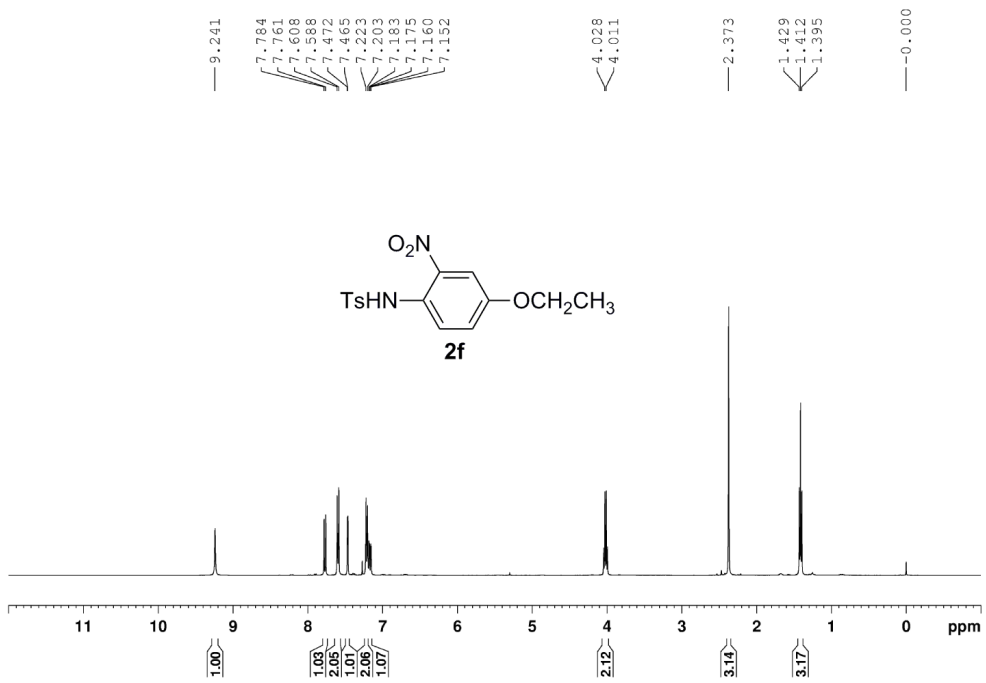
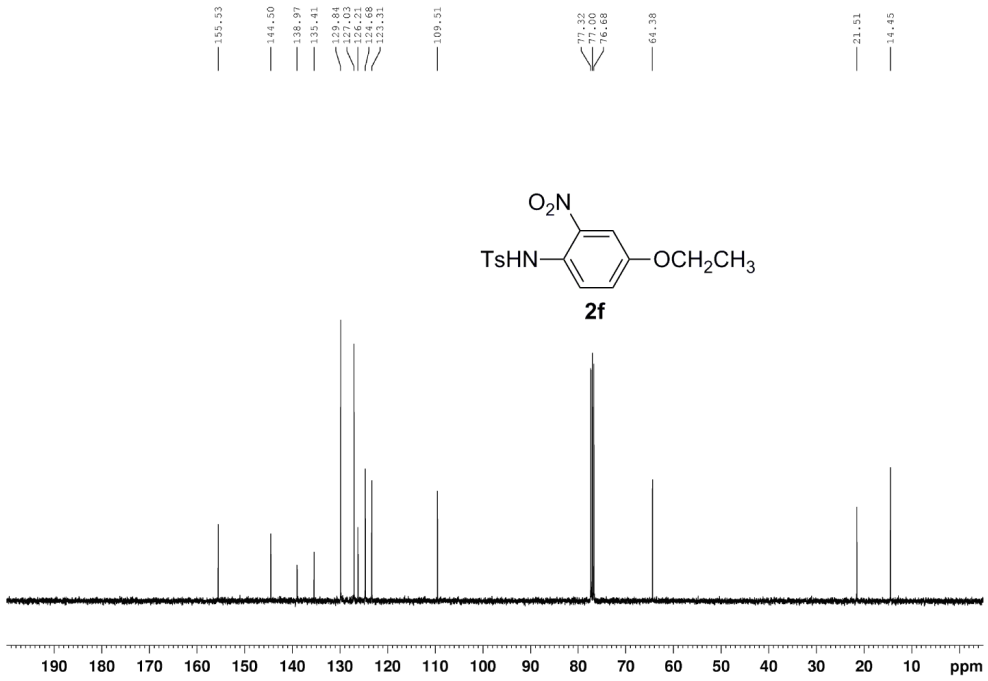
7.809
7.805
7.797
7.789
7.786
7.783
7.775
7.620
7.615
7.599
7.594
7.490
7.483
7.274
7.230
7.208
7.200
7.193
7.181
7.177
7.170
3.824
3.819
2.382
2.377
0.006
0.000
O2N
TsHN
OCH3
2e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.04
2.02
1.00
3.16
3.21
3.20


9.241
7.784
7.761
7.608
7.588
7.472
7.465
7.223
7.203
7.183
7.175
7.160
7.152
4.028
4.011
2.373
1.429
1.412
1.395
0.000
O2N
TsHN
OCH2CH3
2f
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.03
2.05
1.01
2.06
1.07
2.12
3.14
3.17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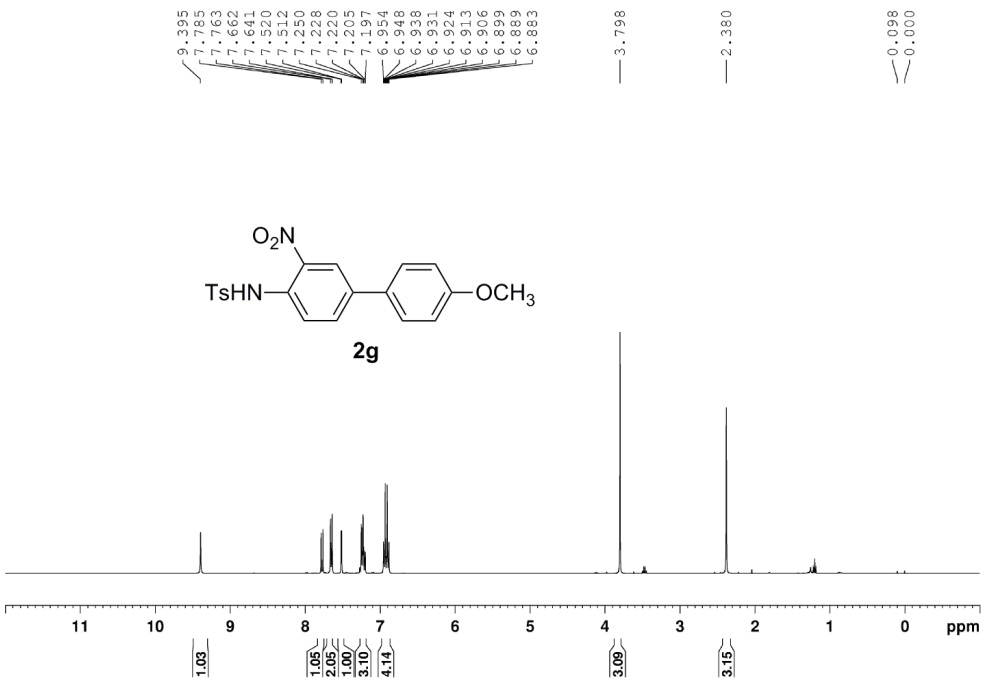
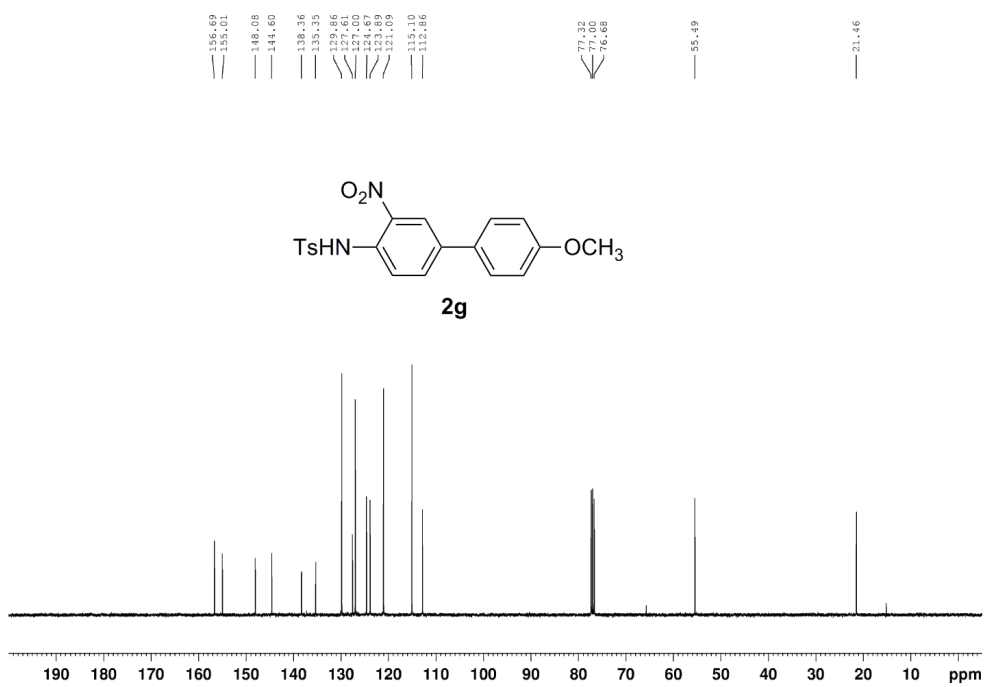
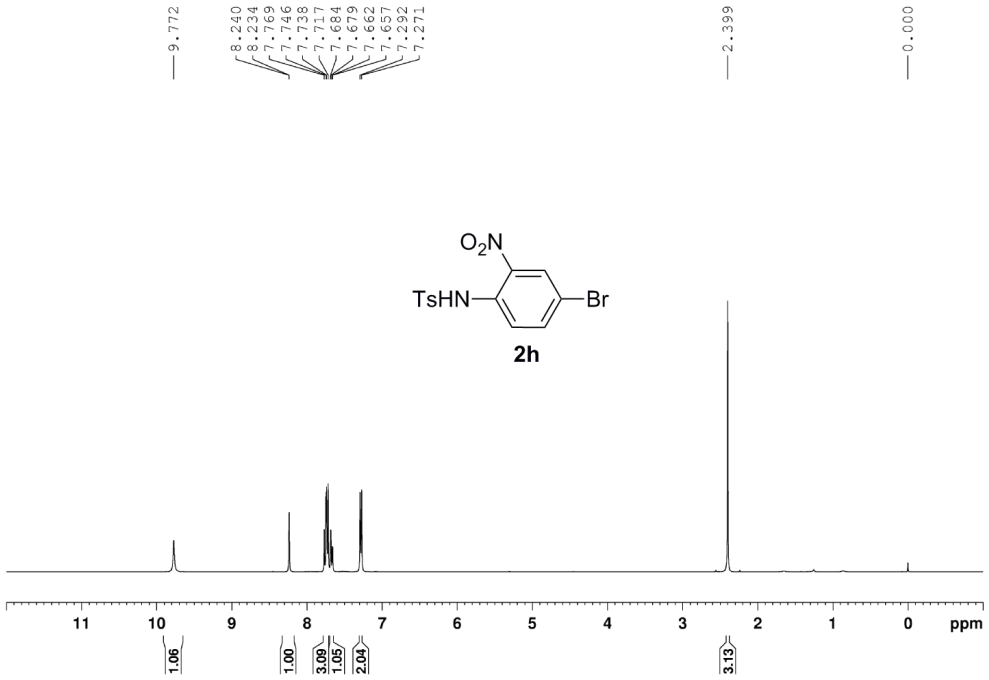
144.50
138.97
135.41
129.84
127.03
126.21
124.68
123.31
109.51
77.32
77.00
76.68
64.38
21.51
14.45
O2N
TsHN
OCH2CH3
2f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


9.395
7.785
7.763
7.662
7.641
7.520
7.512
7.250
7.228
7.220
7.205
7.197
6.954
6.948
6.938
6.931
6.924
6.913
6.906
6.899
6.889
6.883
3.798
2.380
0.098
0.000
O2N
TsHN
OCH3
2g
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
1.05
2.05
1.00
3.10
4.14
3.09
3.15


156.69
155.01
148.08
144.60
138.36
135.35
129.86
129.61
127.00
124.67
123.89
121.09
115.10
112.86
77.32
77.00
76.68
55.49
21.46
O2N
TsHN
OCH3
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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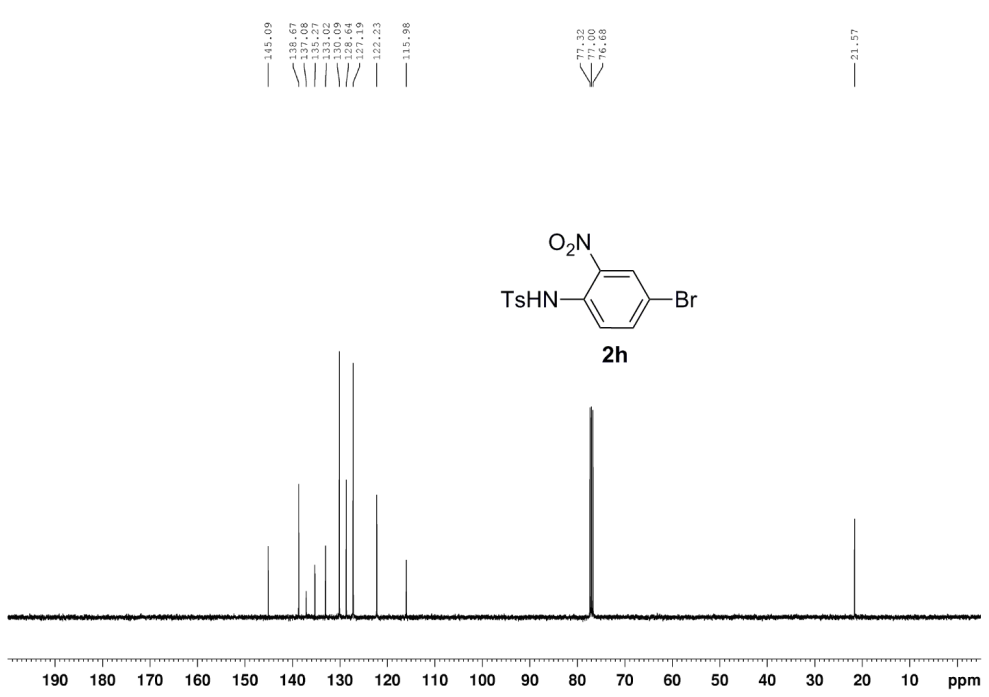
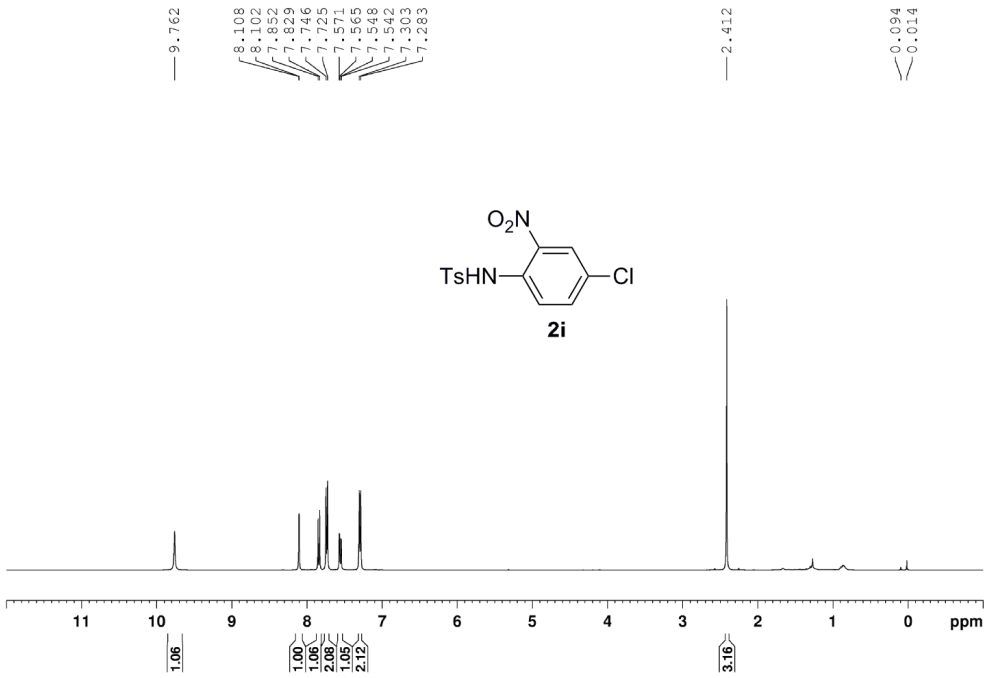
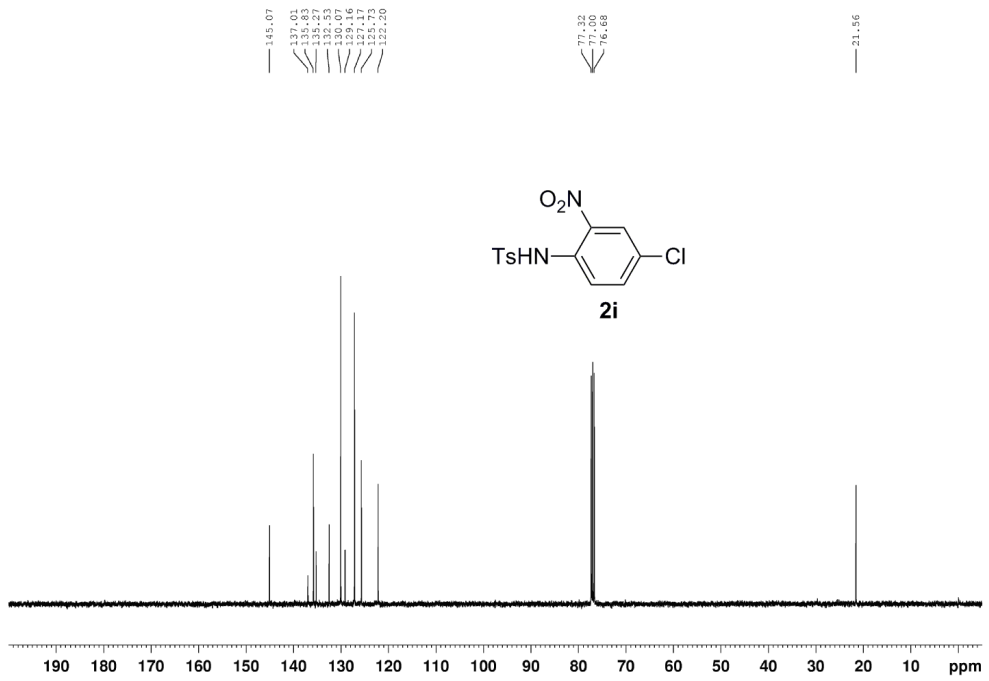
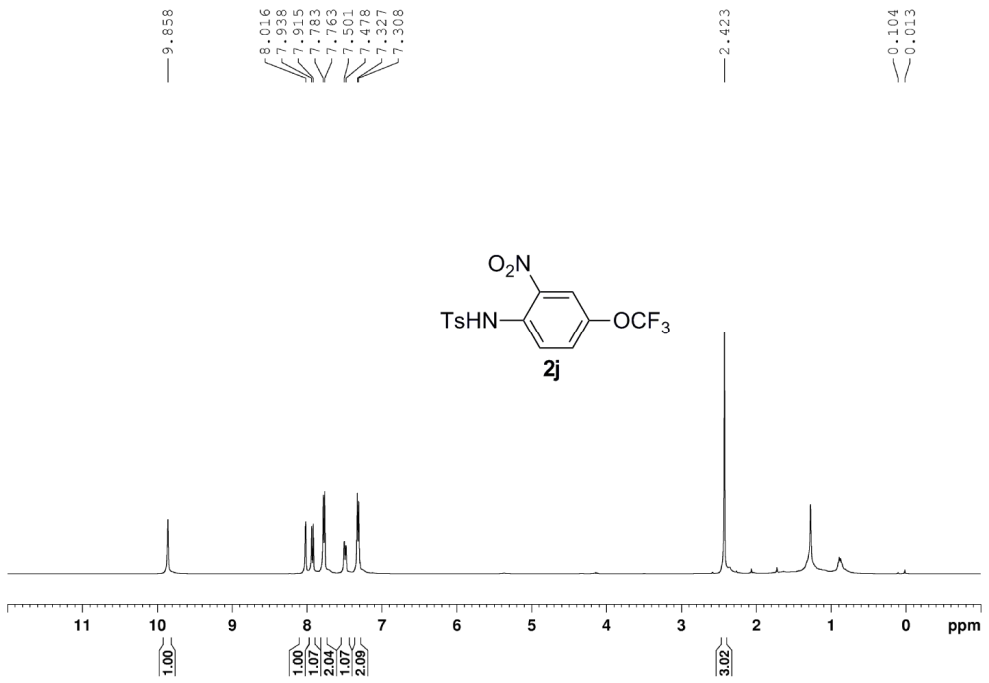
8.240
8.234
7.769
7.746
7.738
7.717
7.684
7.679
7.662
7.657
7.292
7.271
2.399
0.000
O2N
TsHN
Br
2h
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.06
1.00
3.09
1.05
2.04
3.13


145.09
138.67
137.08
135.27
133.02
130.09
128.64
127.19
122.23
115.98
77.32
77.00
76.68
21.57
O2N
TsHN
Br
2h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.762
8.108
8.102
7.852
7.829
7.746
7.725
7.571
7.565
7.548
7.542
7.303
7.283
2.412
0.094
0.014
O2N
TsHN
Cl
2i
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.06
1.00
1.06
2.08
1.05
2.12
3.16


145.07
137.01
135.83
133.27
132.53
130.07
129.16
127.17
125.53
122.20
77.32
77.00
76.68
21.56
O2N
TsHN
Cl
2i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


9.858
8.016
7.938
7.915
7.783
7.763
7.501
7.478
7.327
7.308
2.423
0.104
0.013
O2N
TsHN
OCF3
2j
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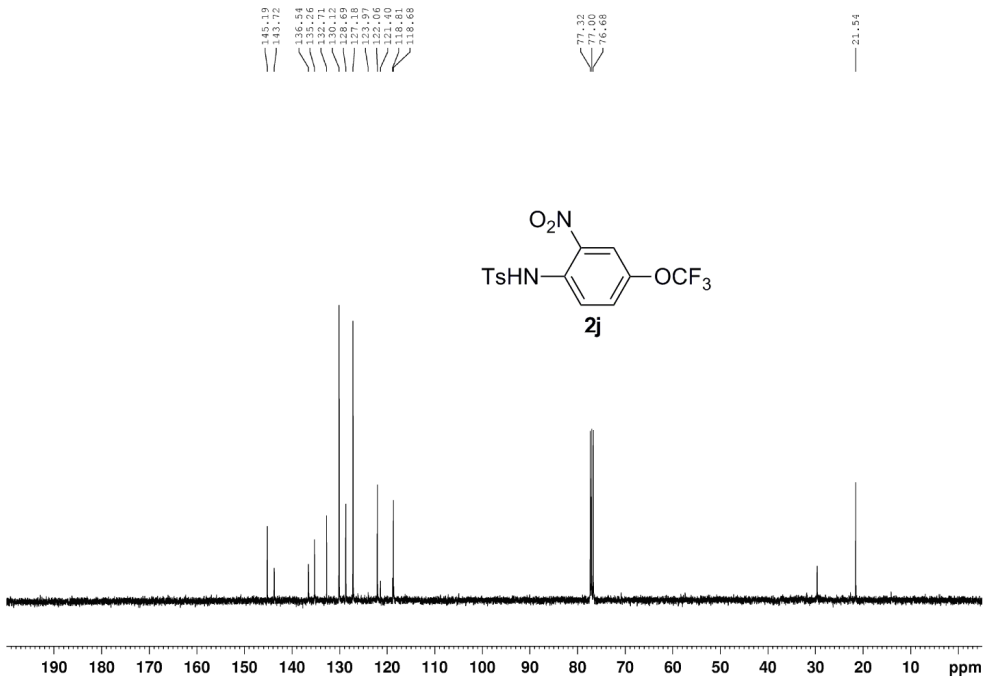
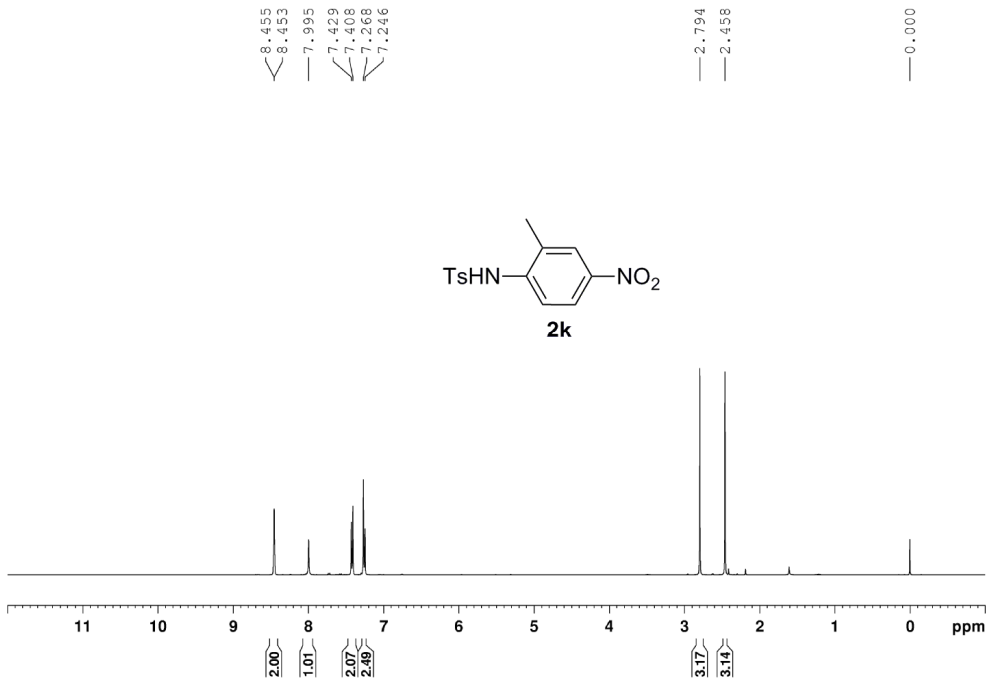
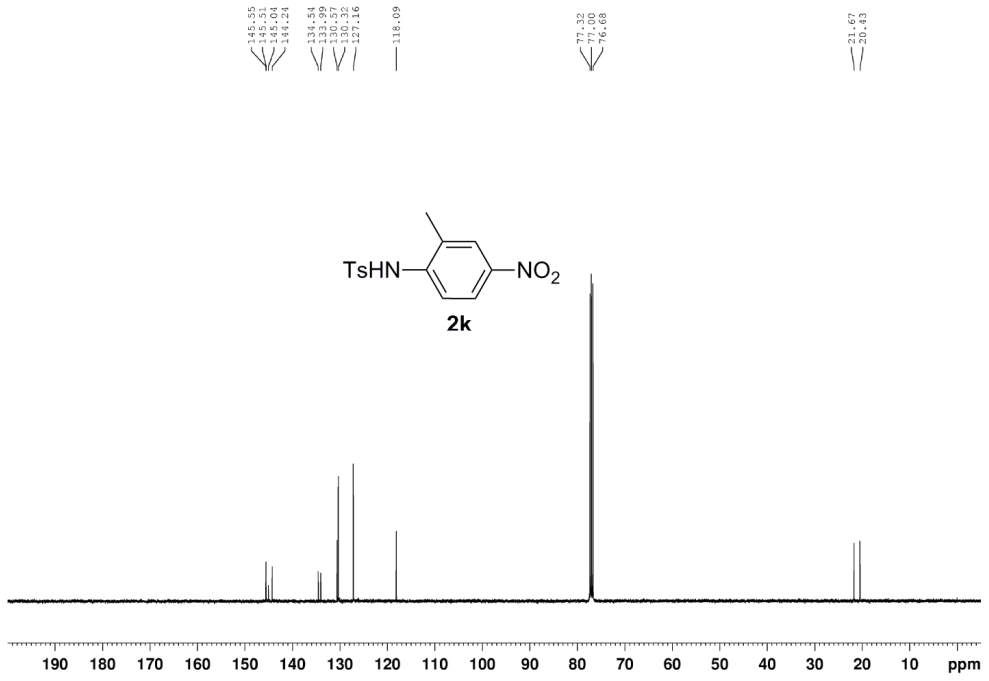
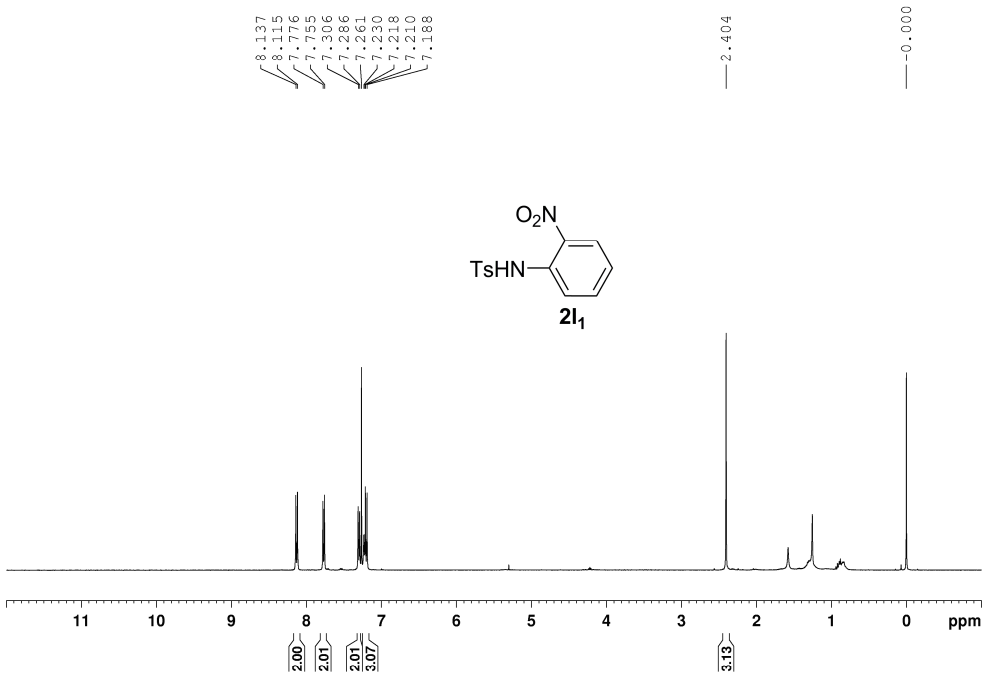
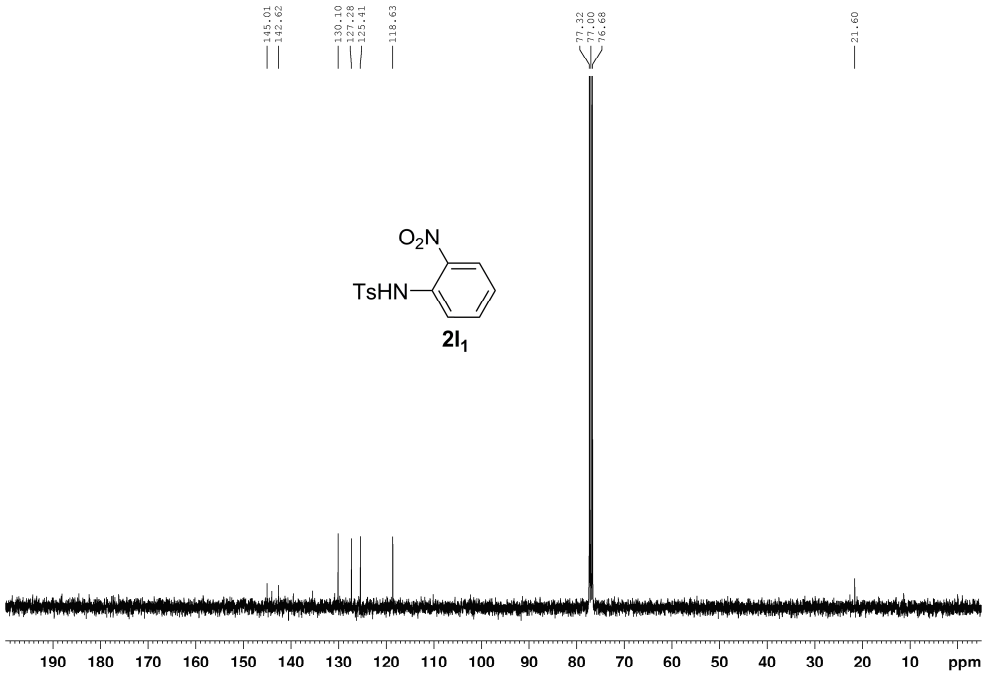
1.00
1.07
2.04
1.07
2.09
3.02

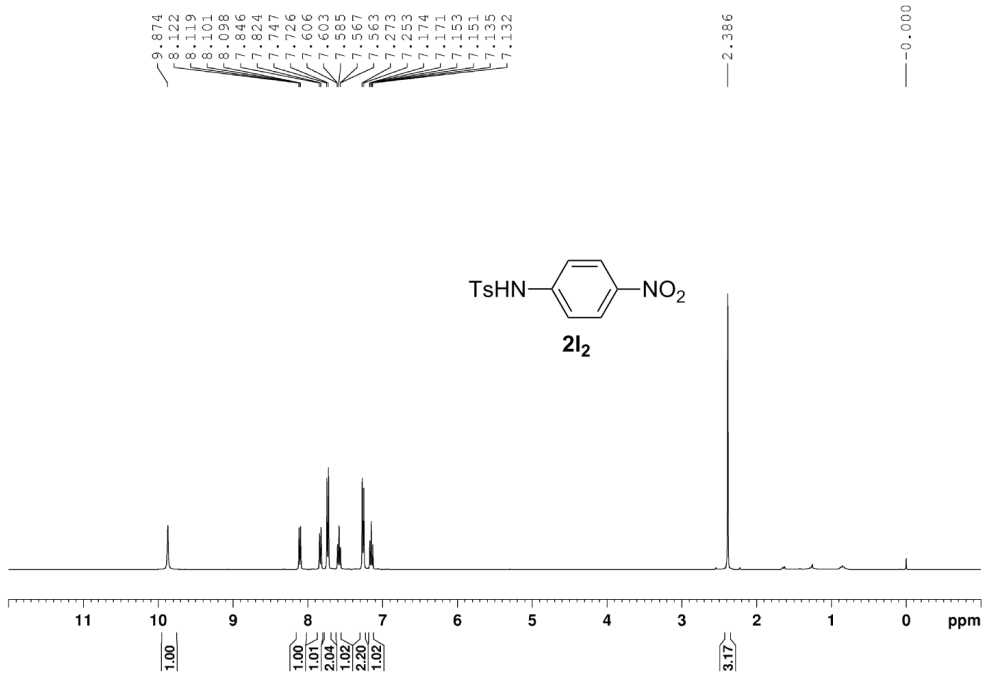

145.19
143.72
136.54
135.26
132.71
130.12
128.68
127.18
123.97
122.06
121.40
118.81
118.68
77.32
77.00
76.68
21.54
O2N
TsHN
OCF3
2j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.455
8.453
7.995
7.429
7.408
7.268
7.246
2.794
2.458
0.000
TsHN
NO2
2k
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.01
2.07
2.49
3.17
3.14


145.55
145.51
144.64
144.24
134.54
133.99
130.57
130.12
127.16
118.09
77.32
77.00
76.68
21.67
20.43
TsHN
NO2
2k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.137
8.115
7.776
7.755
7.306
7.286
7.261
7.230
7.218
7.210
7.188
2.404
0.000
O2N
TsHN
2I1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
2.01
3.07
3.13


145.01
142.62
130.10
127.28
125.41
118.63
77.32
77.00
76.68
21.60
O2N
TsHN
2I1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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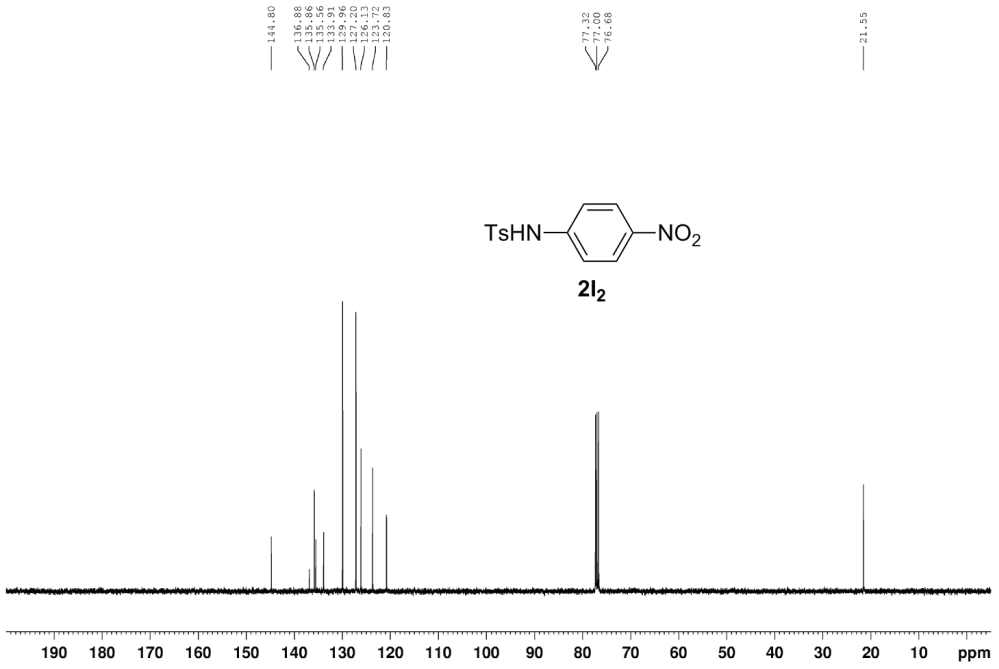
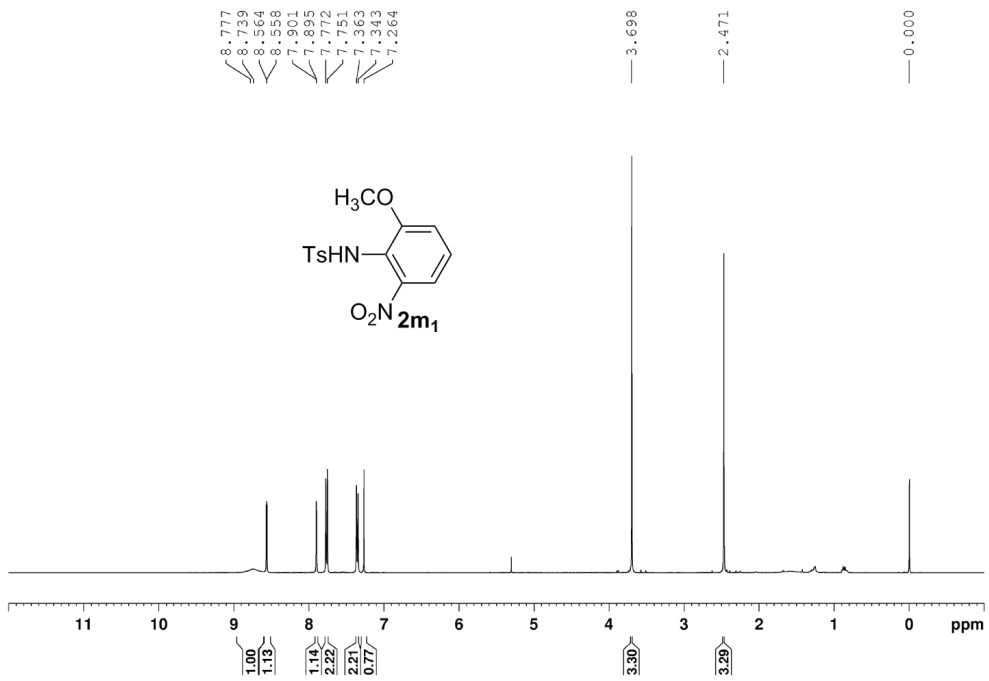
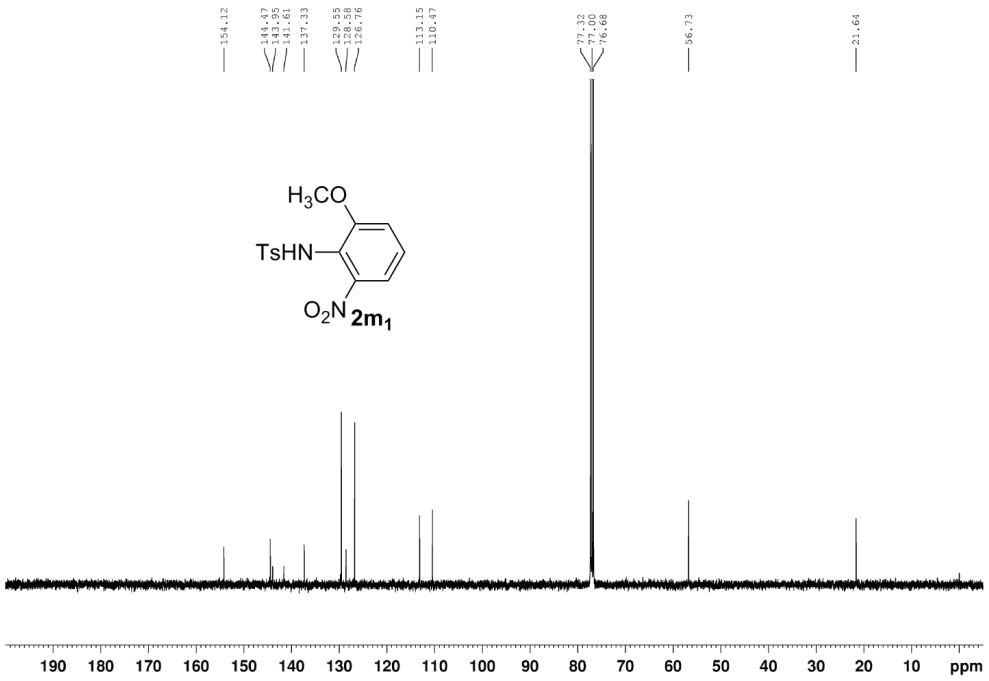
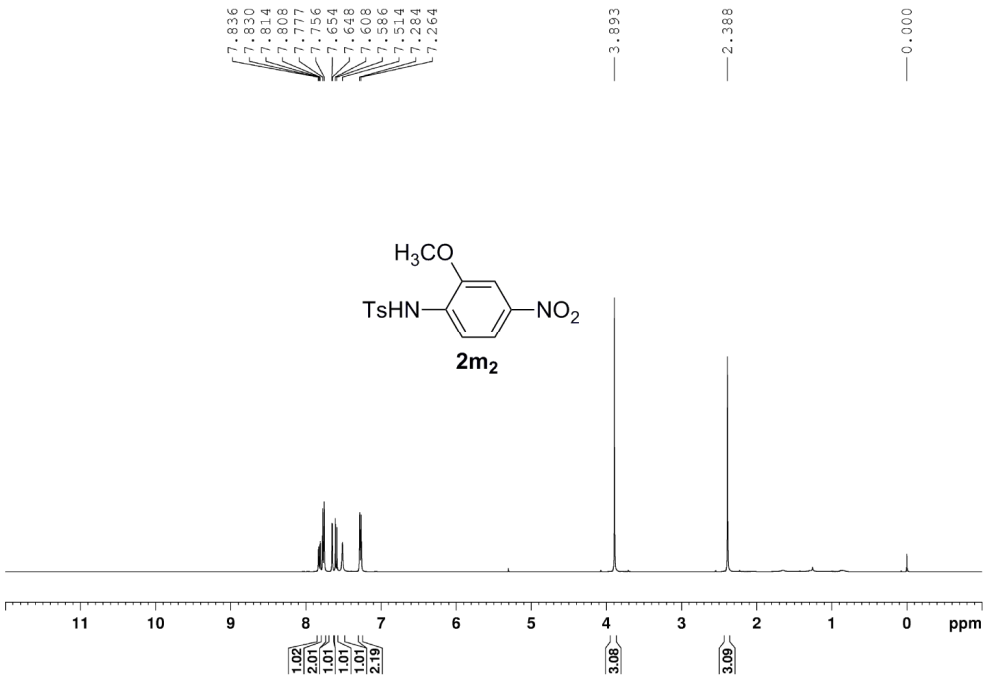
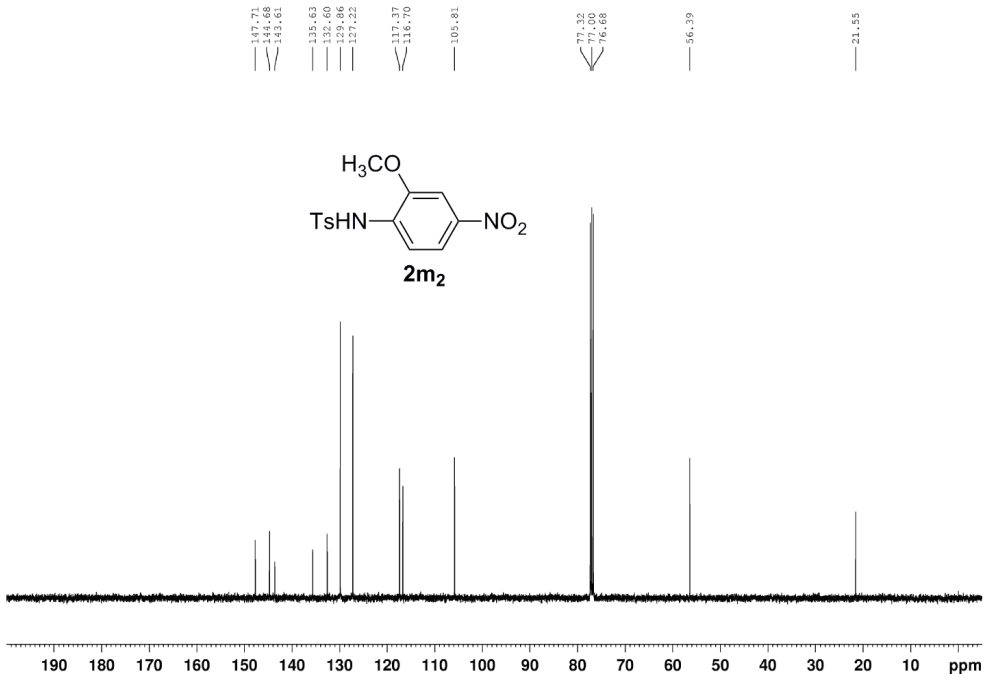
8.122
8.119
8.101
8.098
7.846
7.824
7.747
7.726
7.606
7.603
7.585
7.567
7.563
7.273
7.253
7.174
7.171
7.153
7.151
7.135
7.132
2.386
0.000
TsHN
NO2
2I2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.01
2.04
1.02
2.20
1.02
3.17

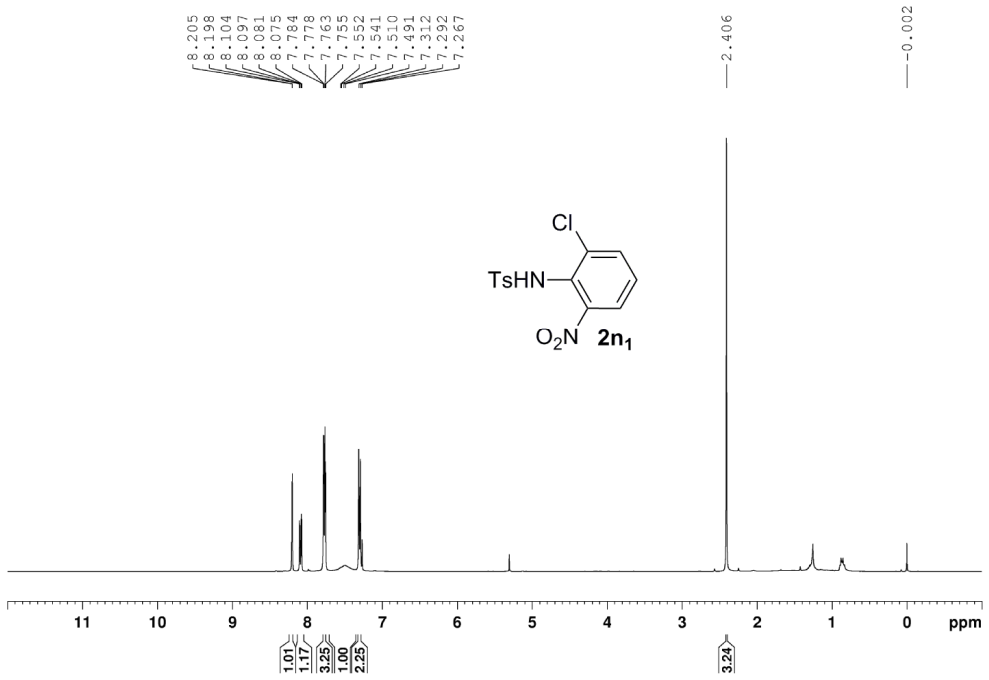

144.80
136.88
135.86
135.56
133.91
129.96
127.30
126.13
123.72
120.83
77.32
77.00
76.68
21.55
TsHN
NO2
2I2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.777
8.739
8.564
8.558
7.901
7.895
7.772
7.751
7.363
7.343
7.264
3.698
2.471
0.000
H3CO
TsHN
O2N
2m1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.13
1.14
2.22
2.21
0.77
3.30
3.29


154.12
144.47
143.95
141.61
137.33
129.55
128.58
126.76
113.15
110.47
77.32
77.00
76.68
56.73
21.64
H3CO
TsHN
O2N
2m1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.836
7.830
7.814
7.808
7.777
7.756
7.654
7.648
7.608
7.586
7.514
7.284
7.264
3.893
2.388
0.000
H3CO
TsHN
NO2
2m2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.02
2.01
1.01
1.01
1.01
2.19
3.08
3.09


147.71
144.68
143.61
135.63
132.60
129.86
127.22
117.37
116.70
105.81
77.32
77.00
76.68
56.39
21.55
H3CO
TsHN
NO2
2m2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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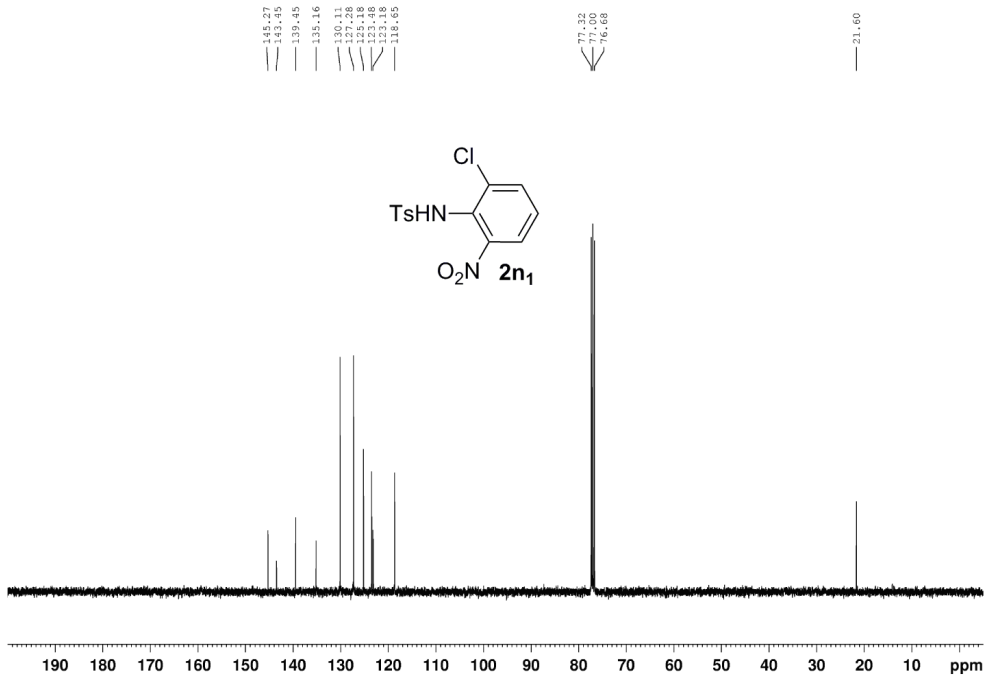
8.198
8.104
8.097
8.081
8.075
7.784
7.778
7.763
7.755
7.552
7.541
7.510
7.491
7.312
7.292
7.267
2.406
0.002
Cl
TsHN
O2N
2n1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.17
3.25
1.00
2.25
3.24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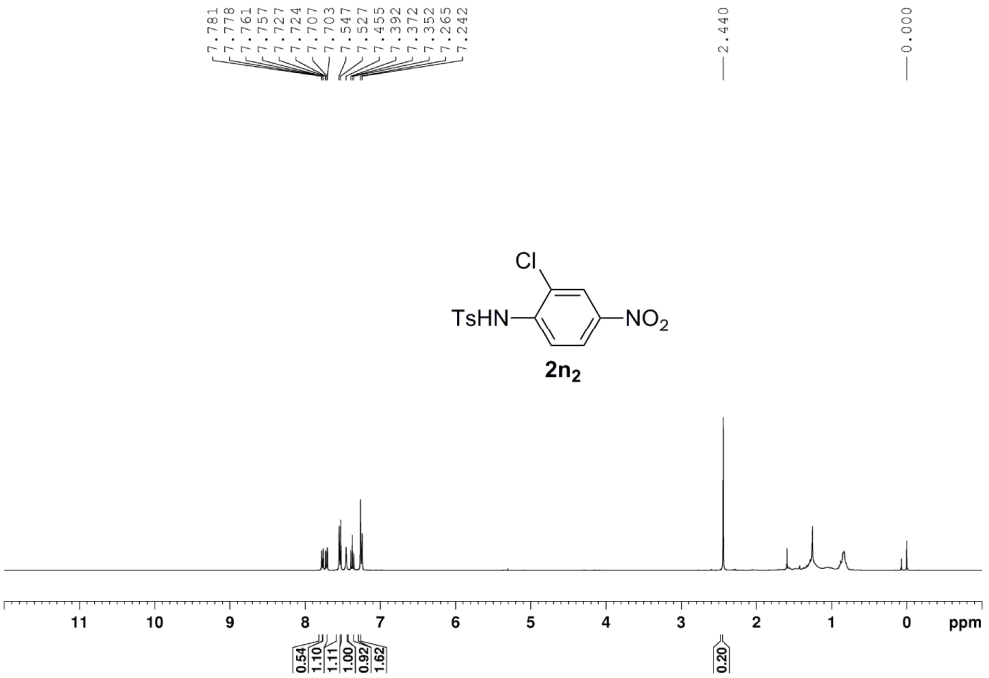
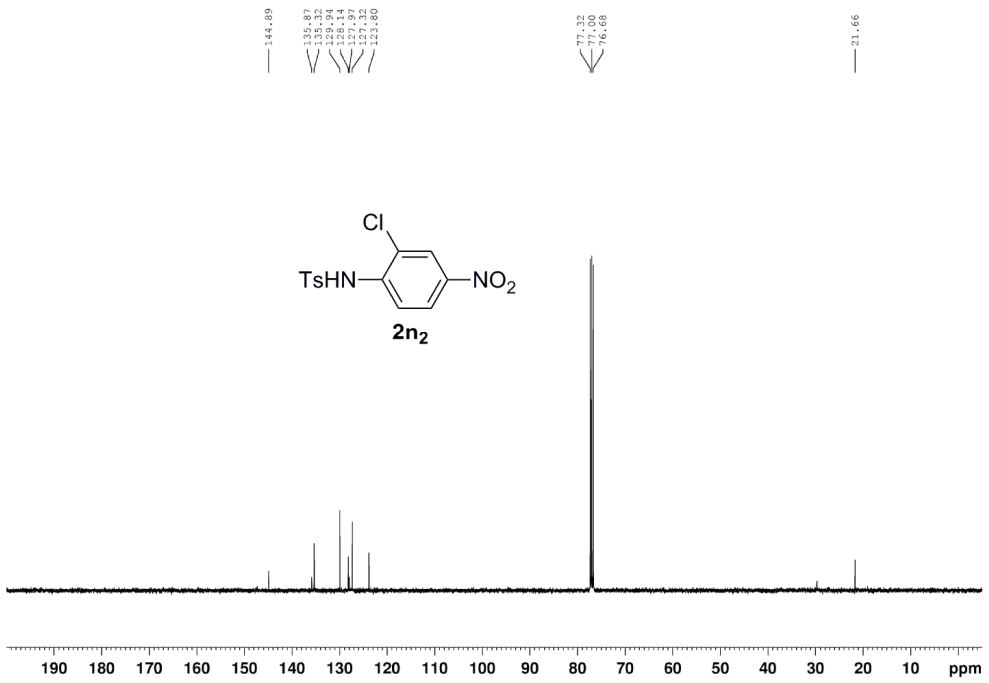
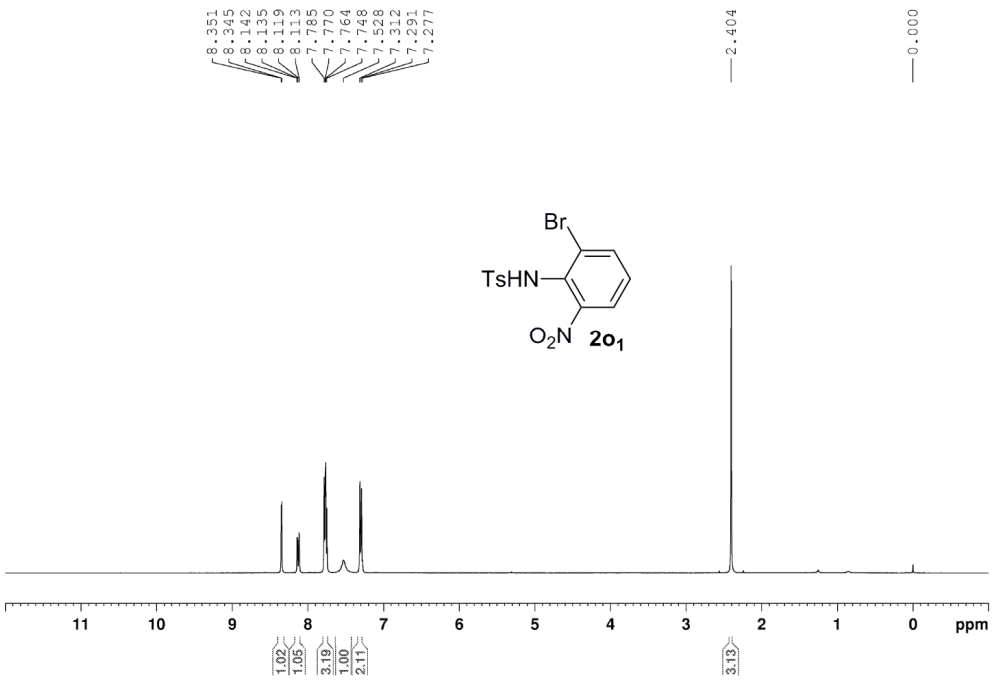
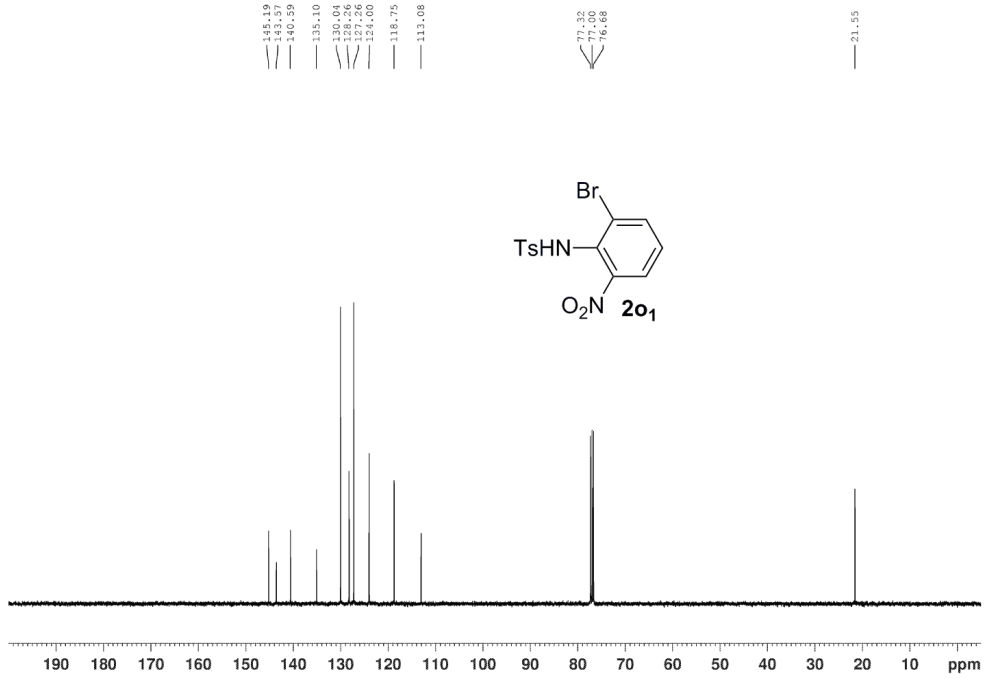
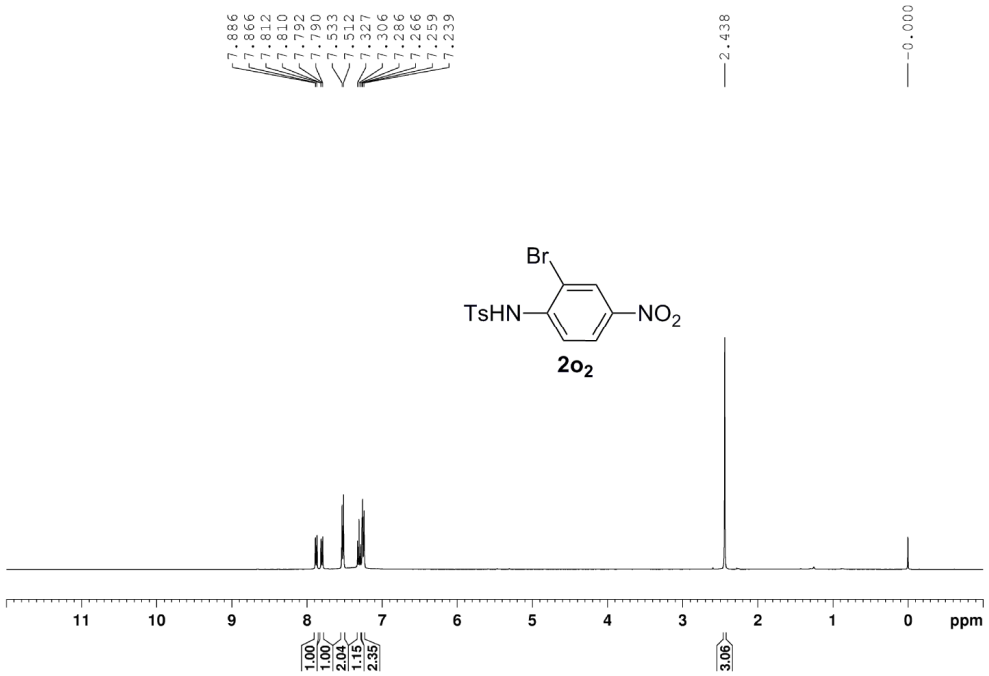
143.45
139.45
135.16
130.11
127.28
125.18
123.18
123.18
118.65
77.32
77.00
76.68
21.60
Cl
TsHN
O2N
2n1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

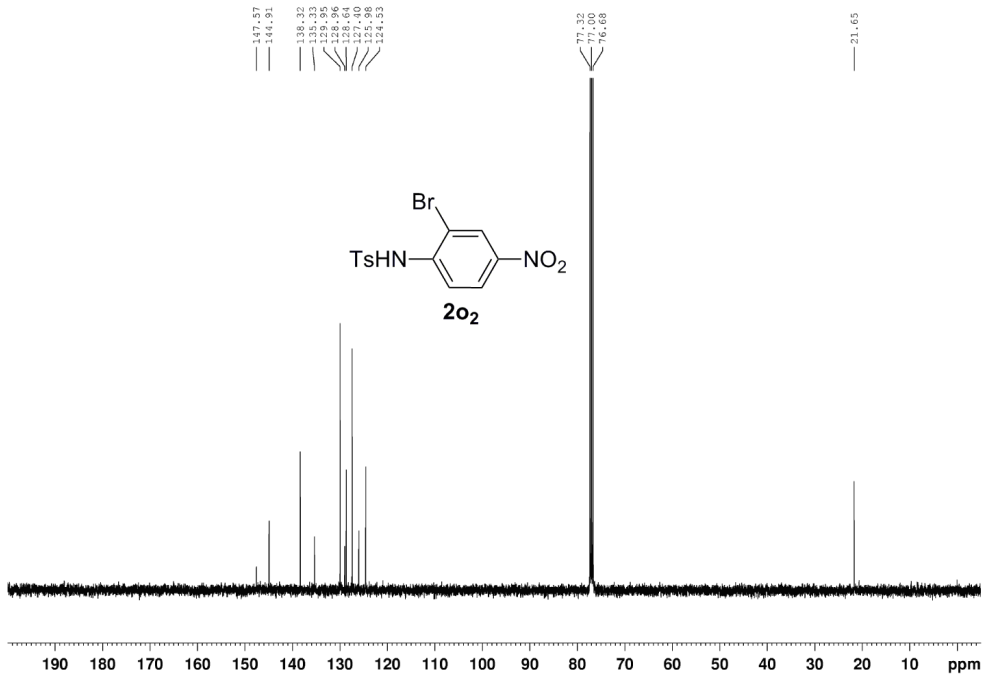

7.781
7.778
7.761
7.757
7.727
7.724
7.707
7.703
7.547
7.527
7.455
7.392
7.372
7.352
7.265
7.242
2.440
0.000
Cl
TsHN
NO2
2n2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.54
1.10
1.11
1.00
0.92
1.62
0.20

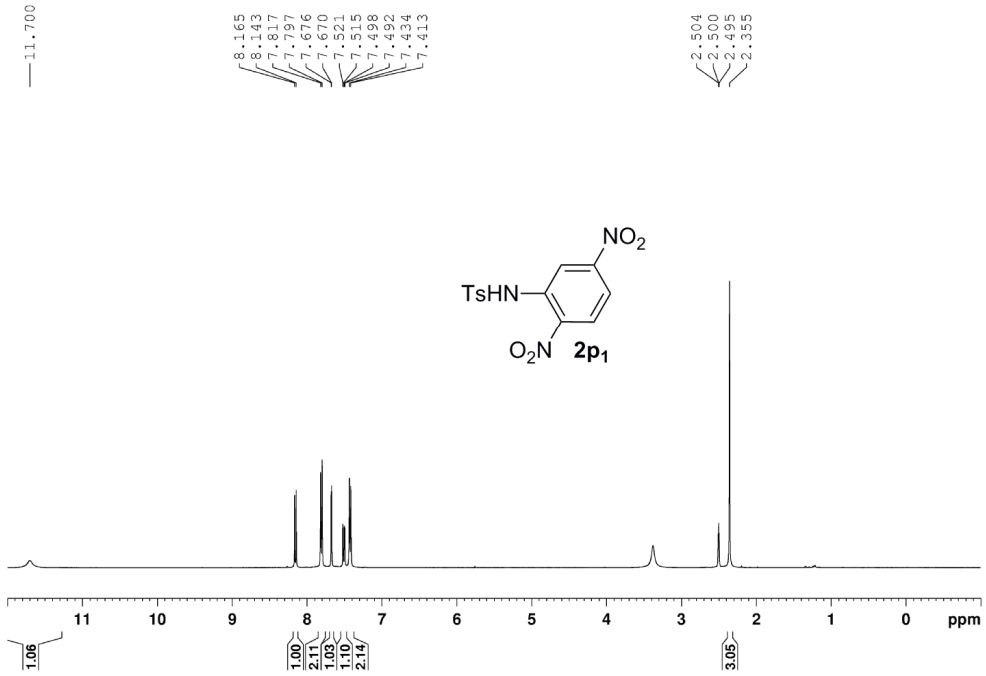

144.89
135.87
135.32
129.84
128.14
127.97
127.32
123.80
77.32
77.00
76.68
21.66
Cl
TsHN
NO2
2n2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

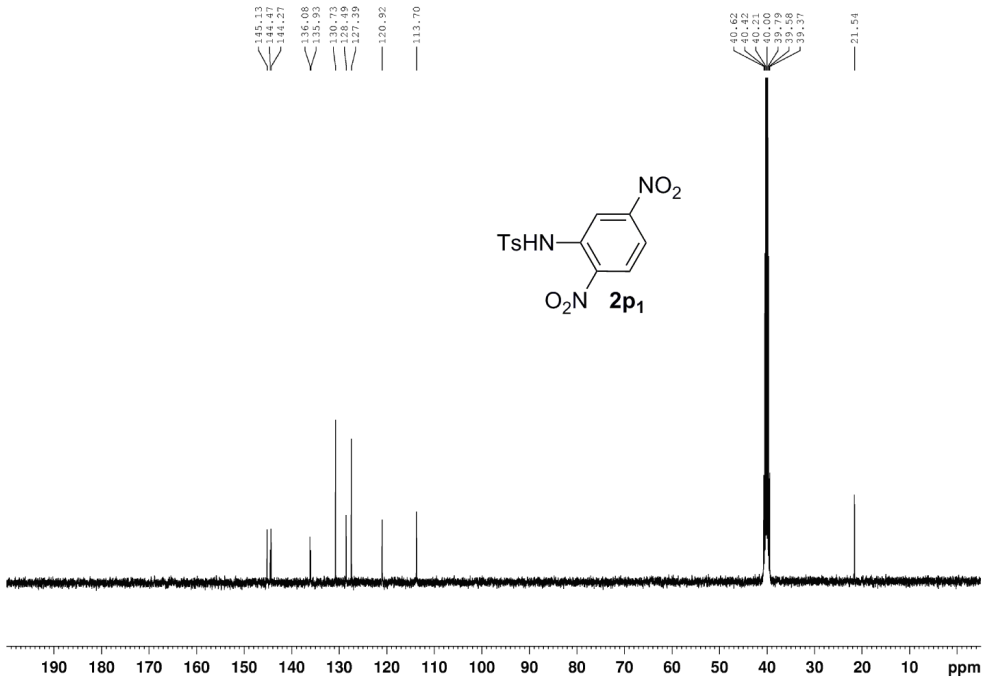

8.351
8.345
8.142
8.135
8.119
8.113
7.785
7.770
7.764
7.748
7.528
7.312
7.291
7.277
2.404
0.000
Br
TsHN
O2N
2o1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.05
3.19
1.00
2.11
3.13

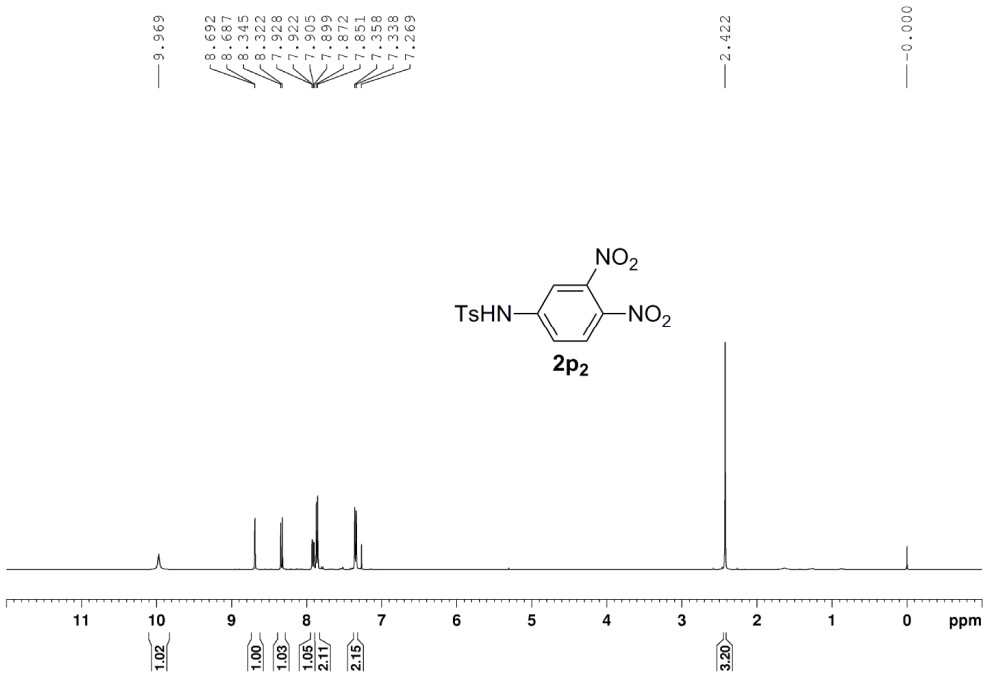

145.19
143.57
140.59
135.10
130.04
128.26
127.76
124.00
118.75
113.08
77.32
77.00
76.68
21.55
Br
TsHN
O2N
2o1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

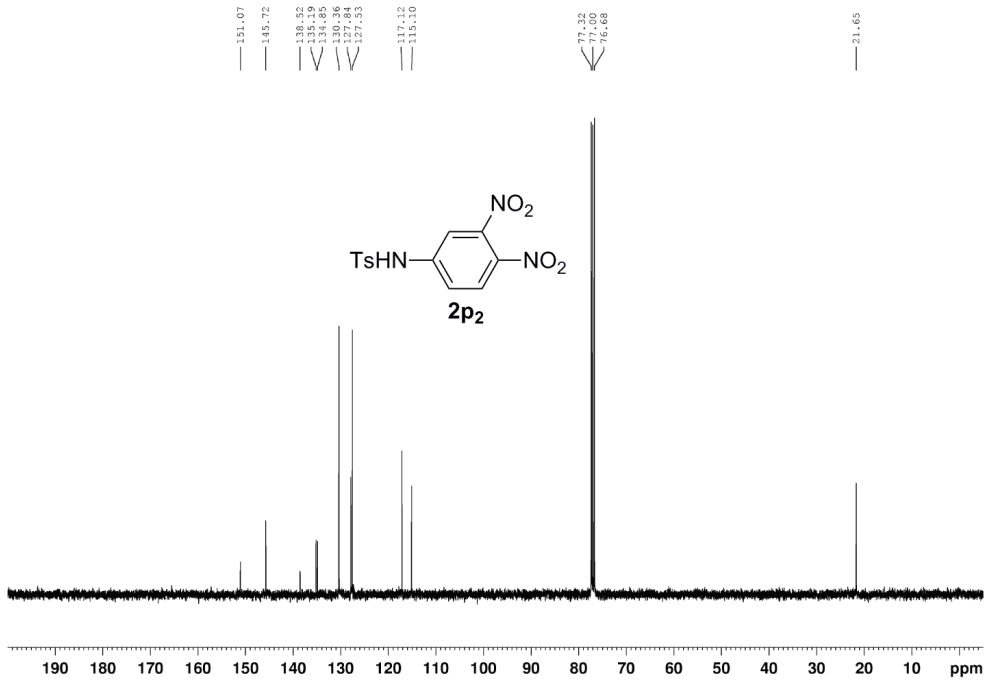

7.886
7.866
7.812
7.810
7.792
7.790
7.533
7.512
7.327
7.306
7.286
7.266
7.259
7.239
2.438
0.000
Br
TsHN
NO2
2o2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.00 2.04 1.15 2.35
3.06

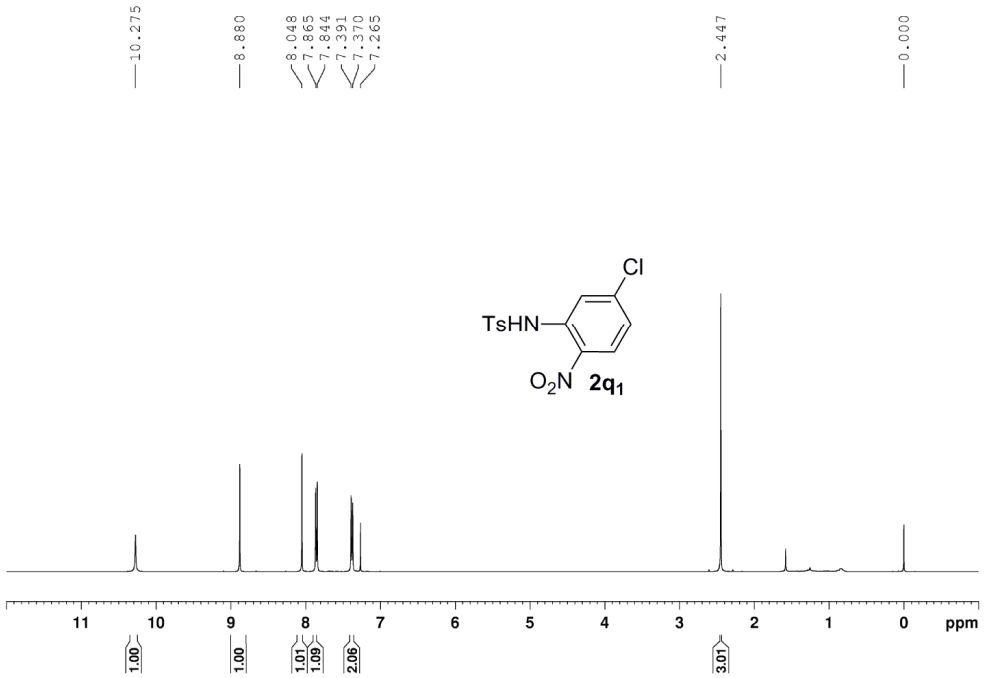

147.57
144.91
138.32
135.33
129.95
128.96
128.64
127.40
125.98
124.53
77.32
77.00
76.68
21.65
Br
TsHN
NO2
2o2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

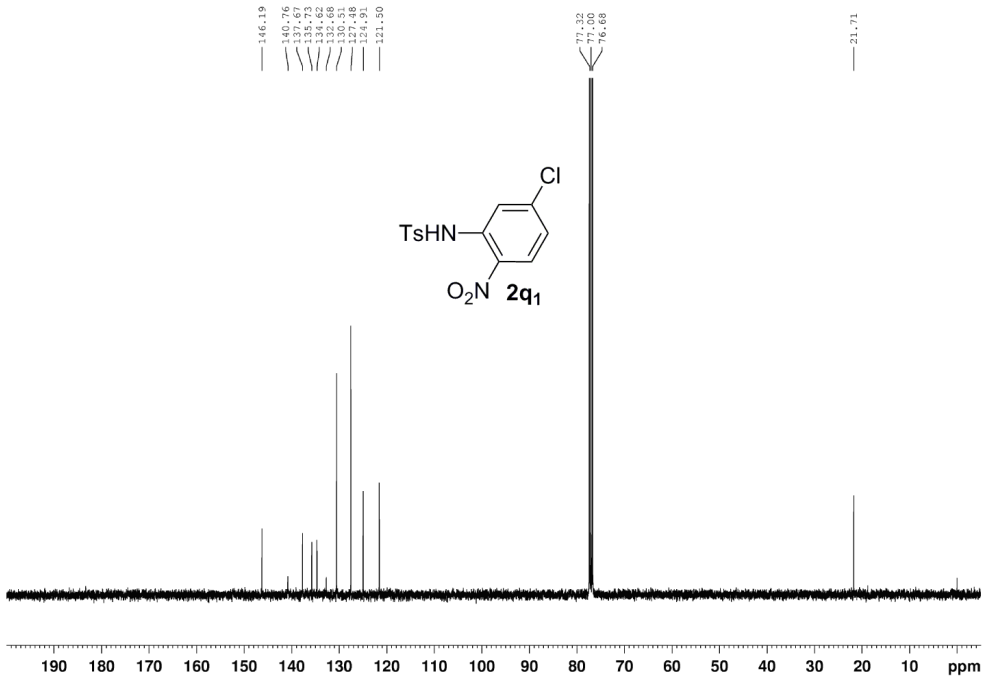

11.700
8.165
8.143
7.817
7.797
7.676
7.670
7.521
7.515
7.498
7.492
7.434
7.413
2.504
2.500
2.495
2.355
NO2
TsHN
O2N
2p1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.06
1.00
2.11
1.03
1.10
2.14
3.05

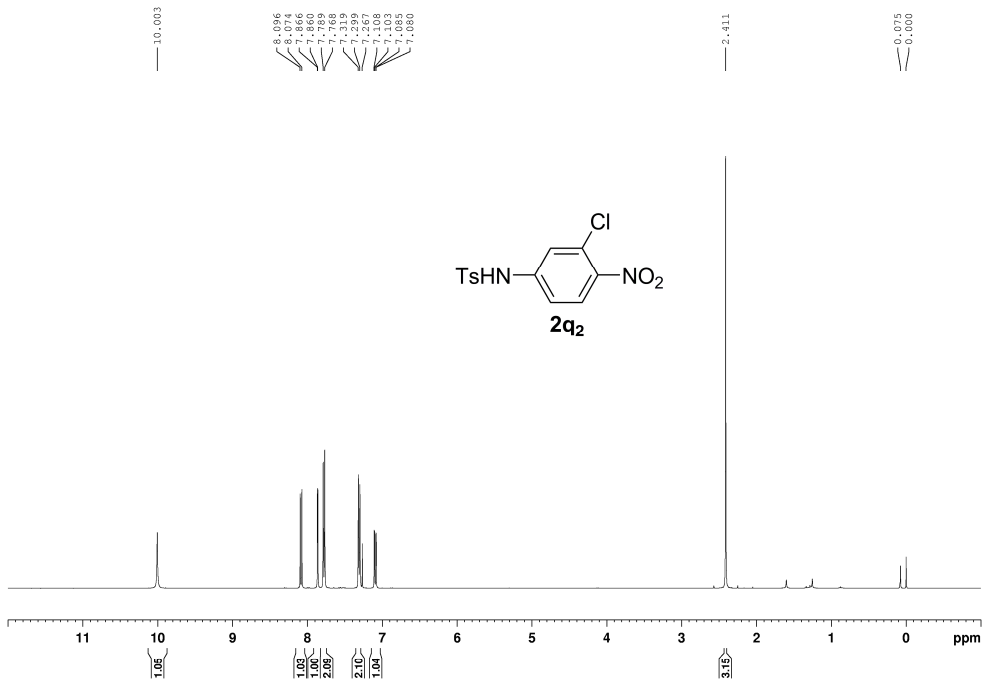

145.13
144.47
144.27
136.08
135.93
130.73
129.58
127.39
120.92
113.70
40.62
40.42
40.21
40.00
39.79
39.58
39.37
21.54
NO2
TsHN
O2N
2p1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

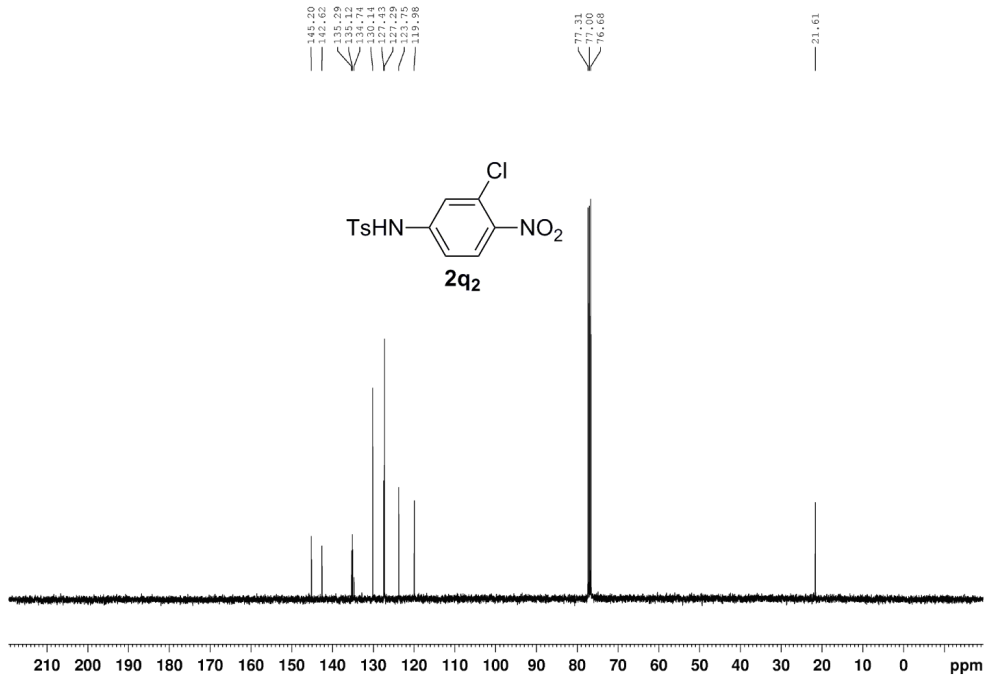

9.969
8.692
8.687
8.345
8.322
7.928
7.922
7.905
7.899
7.872
7.851
7.358
7.338
7.269
2.422
0.000
NO2
TsHN
NO2
2p2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
1.03
1.05
2.11
2.15
3.20

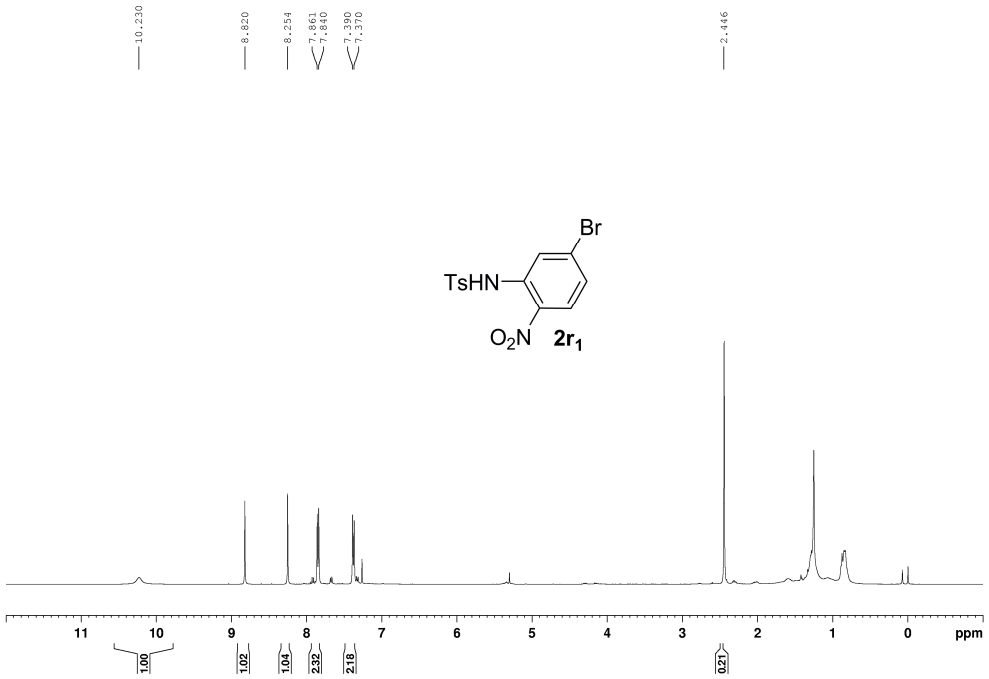

151.07
145.72
138.52
135.19
134.85
130.36
127.84
127.53
117.12
115.10
77.32
77.00
76.68
21.65
NO2
TsHN
NO2
2p2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

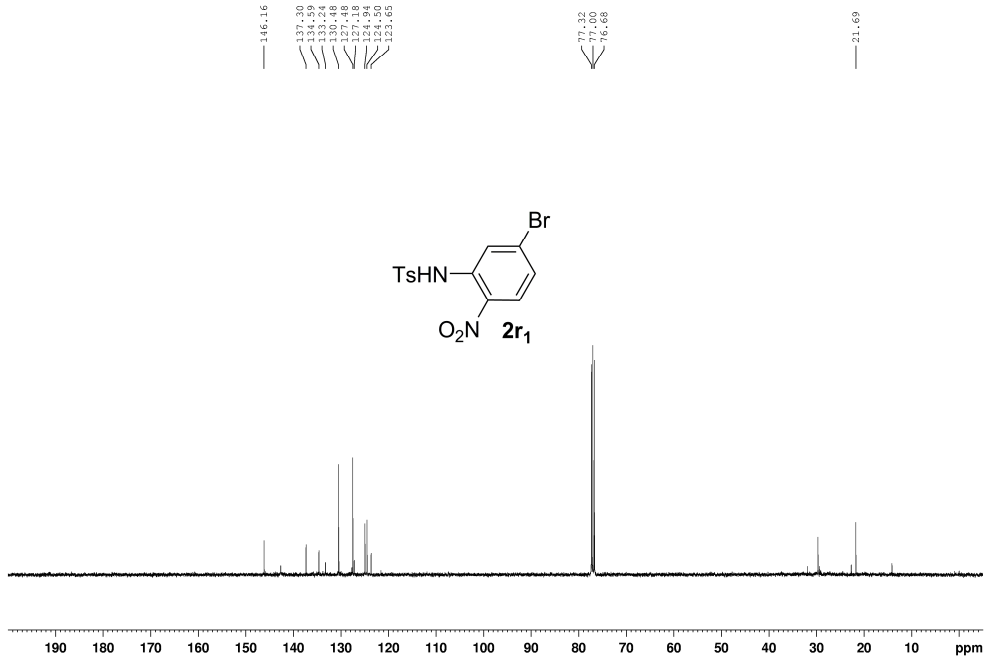

10.275
8.880
8.048
7.865
7.844
7.391
7.370
7.265
2.447
0.000
Cl
TsHN
O2N
2q1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.01
1.09
2.06
3.01

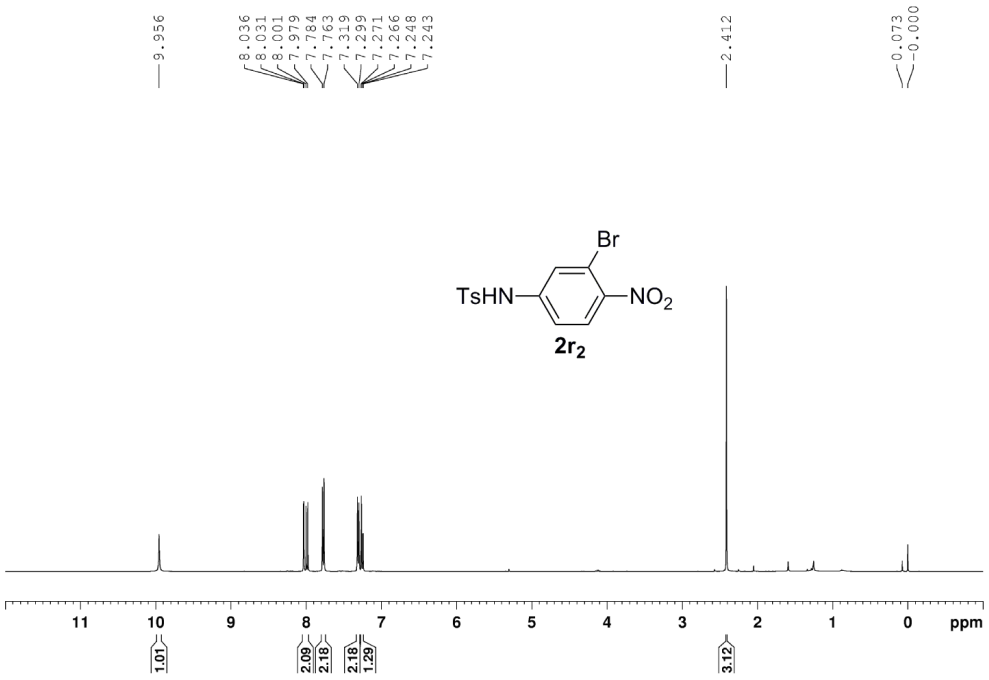

146.19
140.76
137.67
135.73
134.62
132.68
130.51
127.48
124.91
121.50
77.32
77.00
76.68
21.71
Cl
TsHN
O2N
2q1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

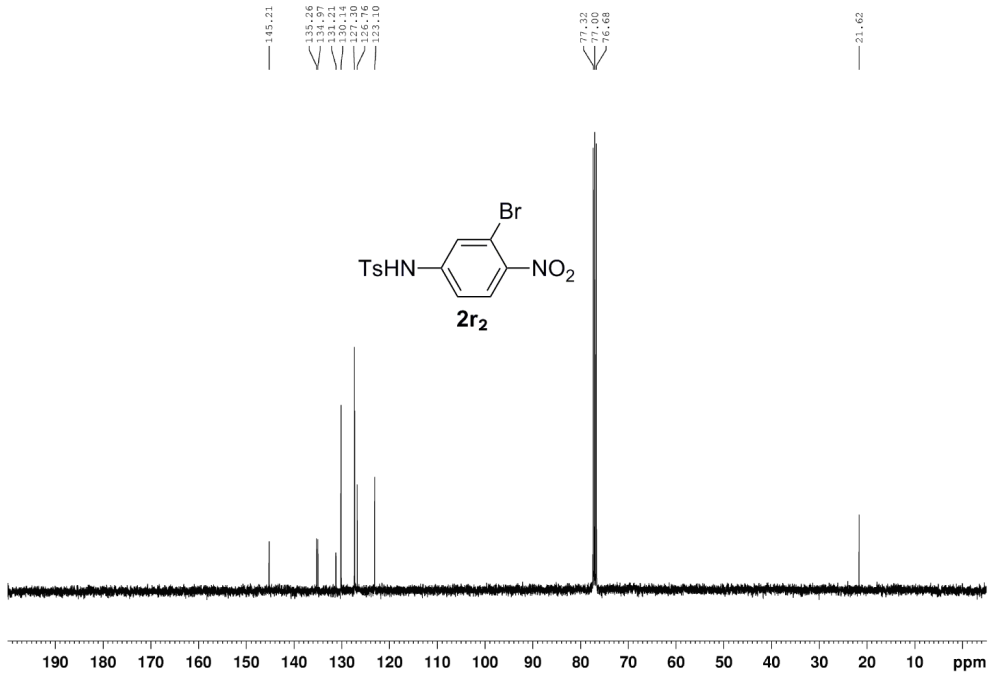

10.003
8.096
8.074
7.866
7.860
7.789
7.768
7.313
7.299
7.267
7.108
7.103
7.085
7.080
2.411
0.075
0.000
Cl
TsHN
NO2
2q2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.06
1.03
1.00
2.09
2.10
1.04
3.15

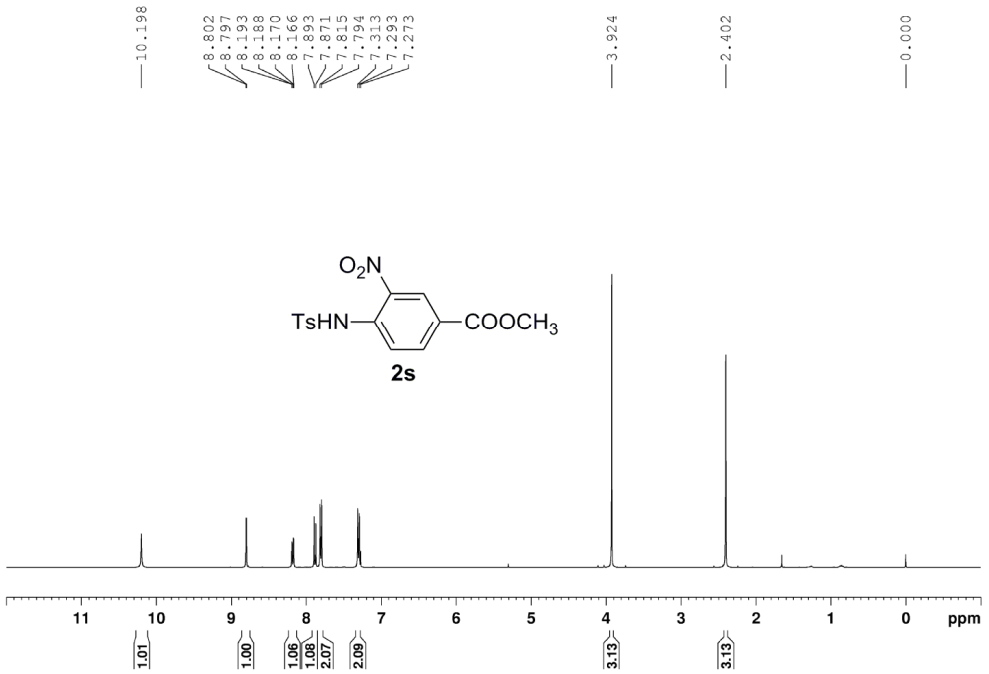

145.20
142.62
135.29
135.12
134.74
130.34
127.43
127.29
123.75
119.98
77.31
77.00
76.68
21.61
Cl
TsHN
NO2
2q2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

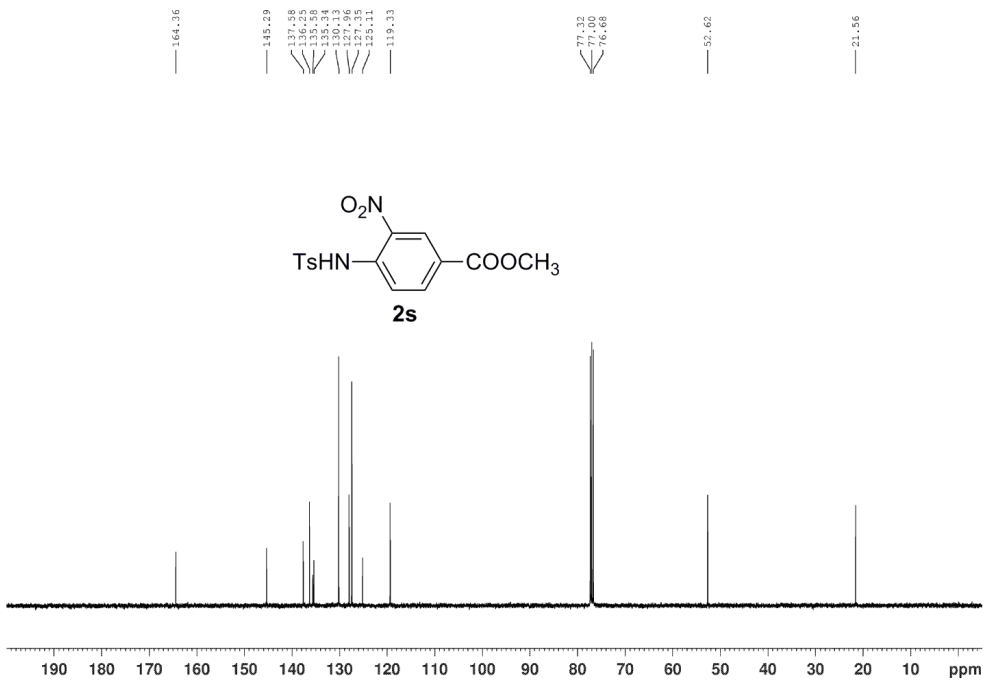

10.230
8.820
8.254
7.861
7.840
7.390
7.370
2.446
Br
TsHN
O2N
2r1
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.04
2.32
2.18
0.21

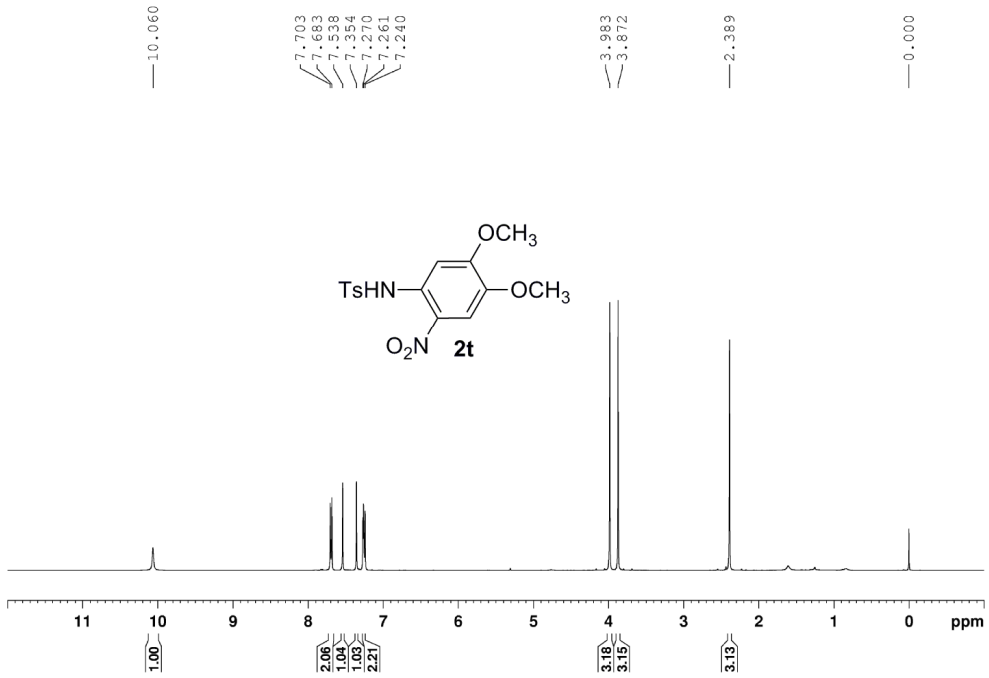

146.16
137.30
134.59
133.24
130.48
129.48
127.18
125.10
124.94
124.50
123.65
77.32
77.00
76.68
21.69
Br
TsHN
O2N
2r1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

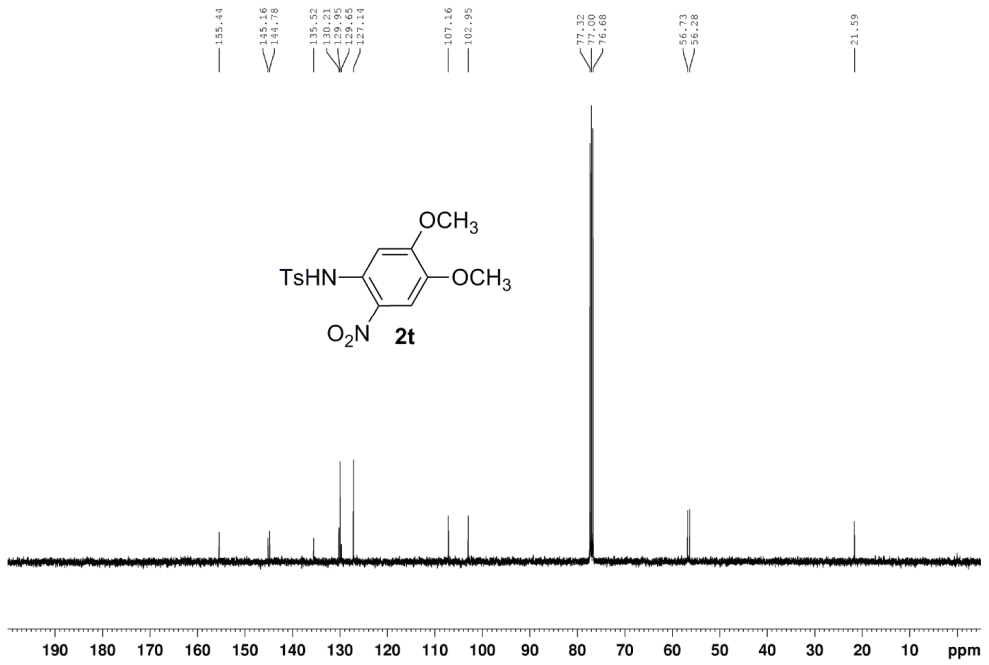

9.956
8.036
8.031
8.001
7.979
7.784
7.763
7.319
7.299
7.271
7.266
7.248
7.243
2.412
0.073
0.000
Br
TsHN
NO2
2r2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
2.09
2.18
2.18
1.29
3.12

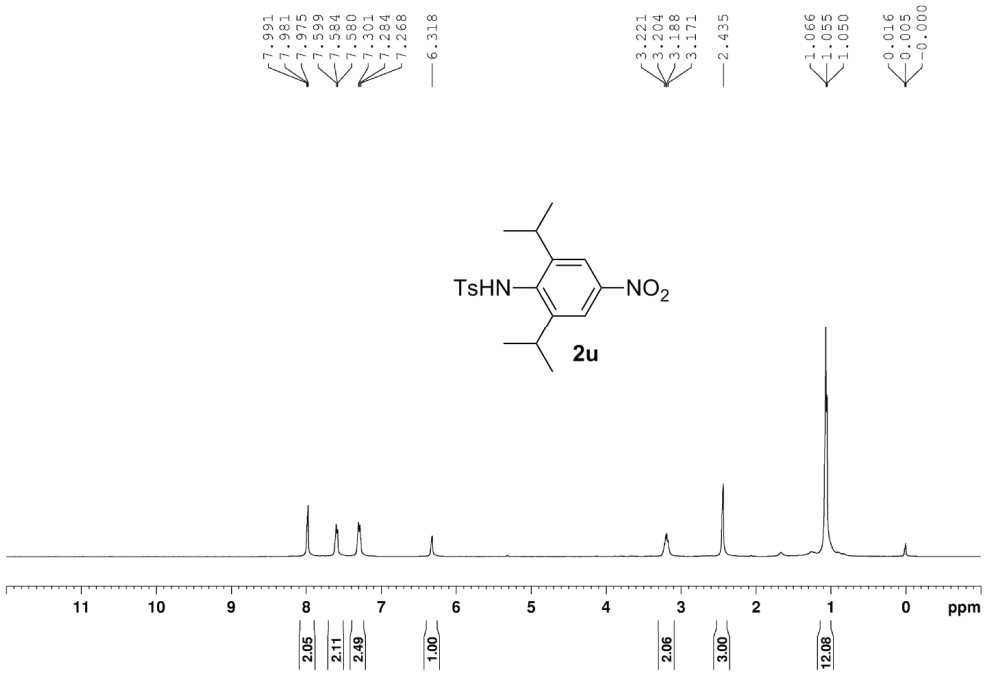

145.21
135.26
134.97
131.21
130.14
127.30
126.76
123.10
77.32
77.00
76.68
21.62
Br
TsHN
NO2
2r2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

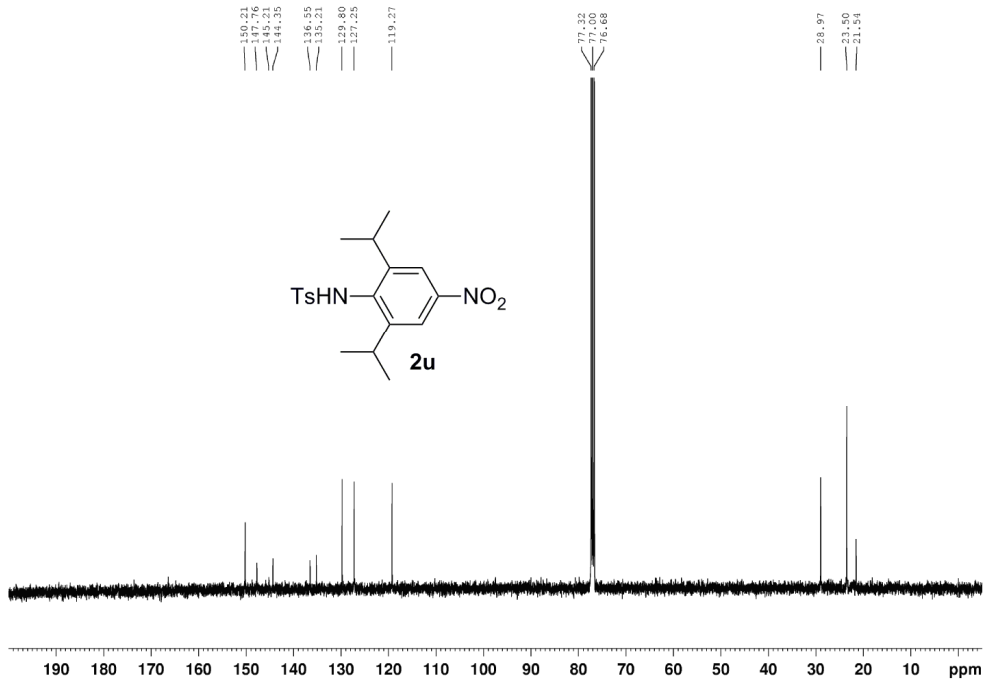

10.198
8.802
8.797
8.193
8.188
8.170
8.166
7.893
7.871
7.815
7.794
7.313
7.293
7.273
3.924
2.402
0.000
O2N
TsHN
COOCH3
2s
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.01
1.00
1.06
1.08
2.07
2.09
3.13
3.13

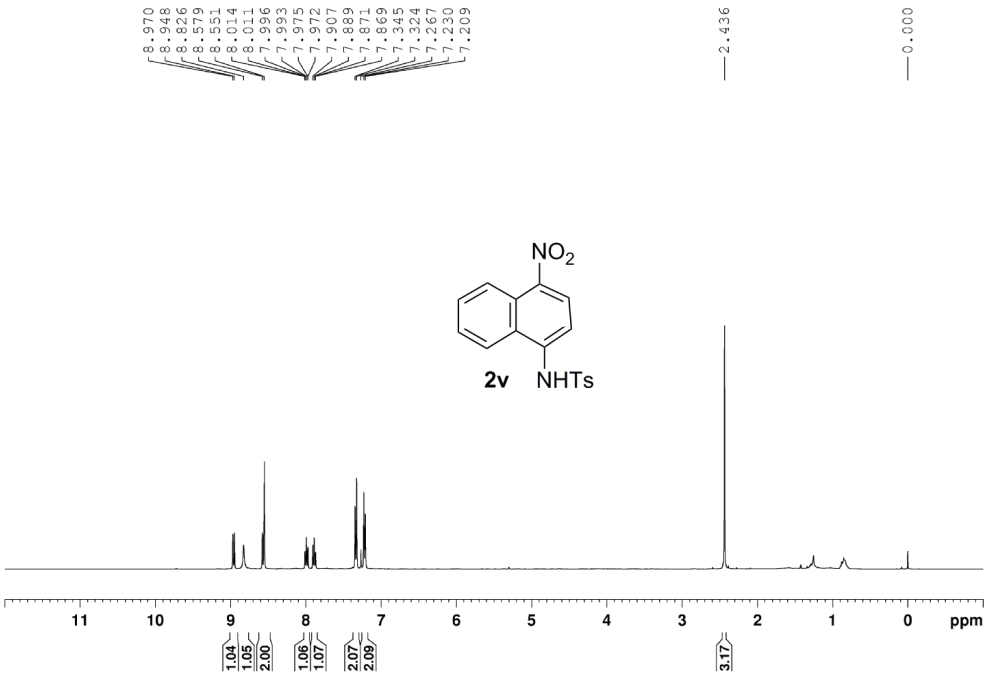

164.36
145.29
137.58
136.65
135.60
135.34
130.13
127.96
127.35
125.11
119.33
77.32
77.00
76.68
52.62
21.56
O2N
TsHN
COOCH3
2s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

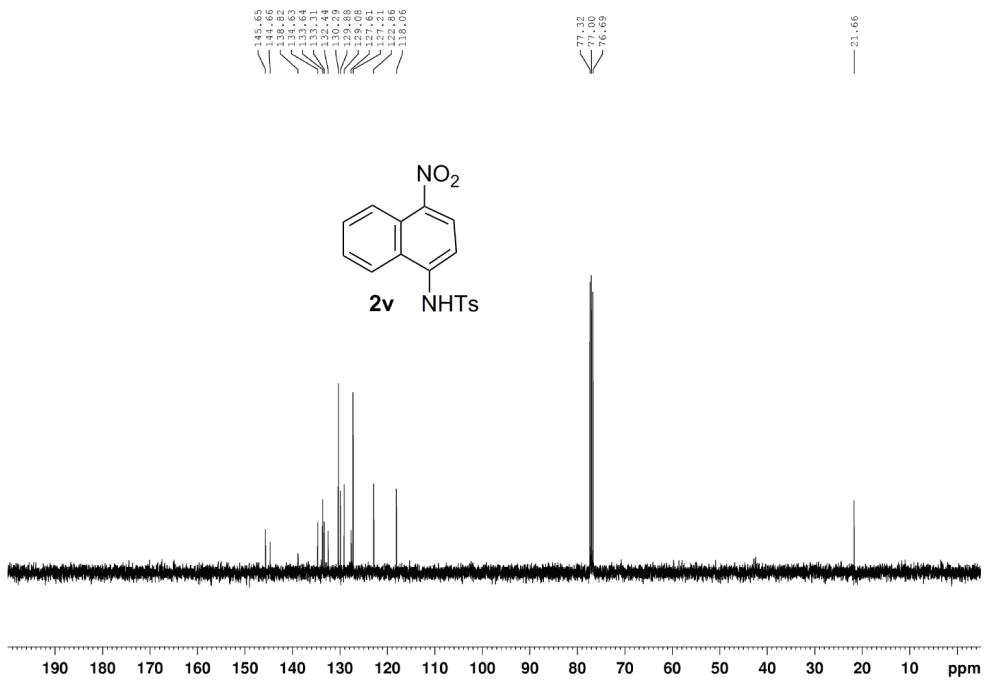

10.060
7.703
7.683
7.538
7.354
7.270
7.261
7.240
3.983
3.872
2.389
0.000
OCH3
TsHN
OCH3
O2N
2t
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.06
1.04
1.03
2.21
3.18
3.15
3.13

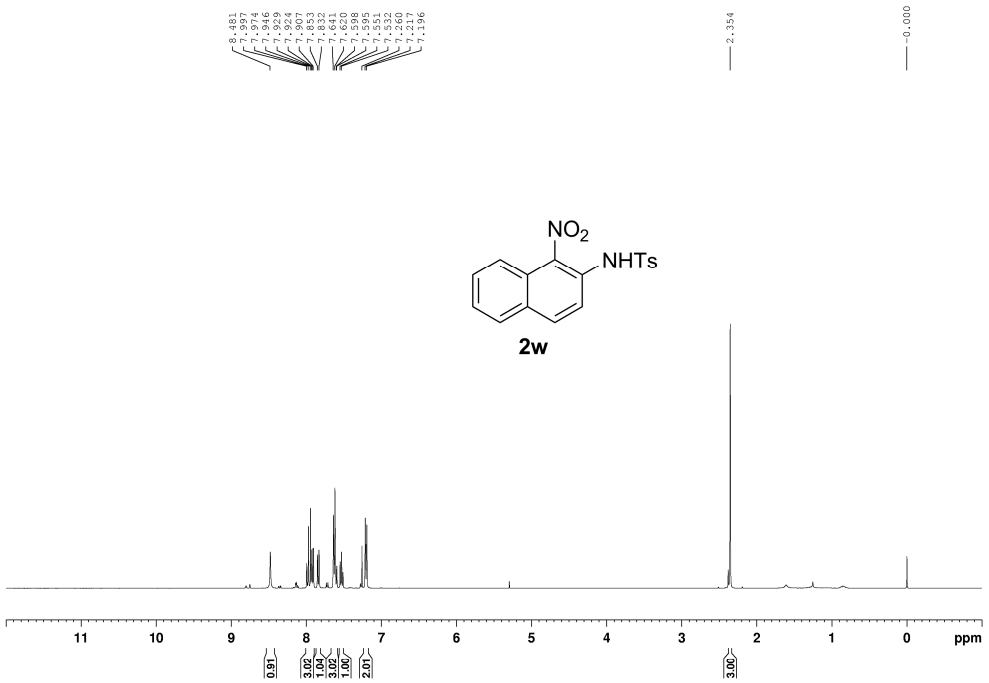

155.44
145.16
144.78
135.52
130.21
129.95
129.65
127.14
107.16
102.95
77.32
77.00
76.68
56.73
56.28
21.59
OCH3
TsHN
OCH3
O2N
2t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

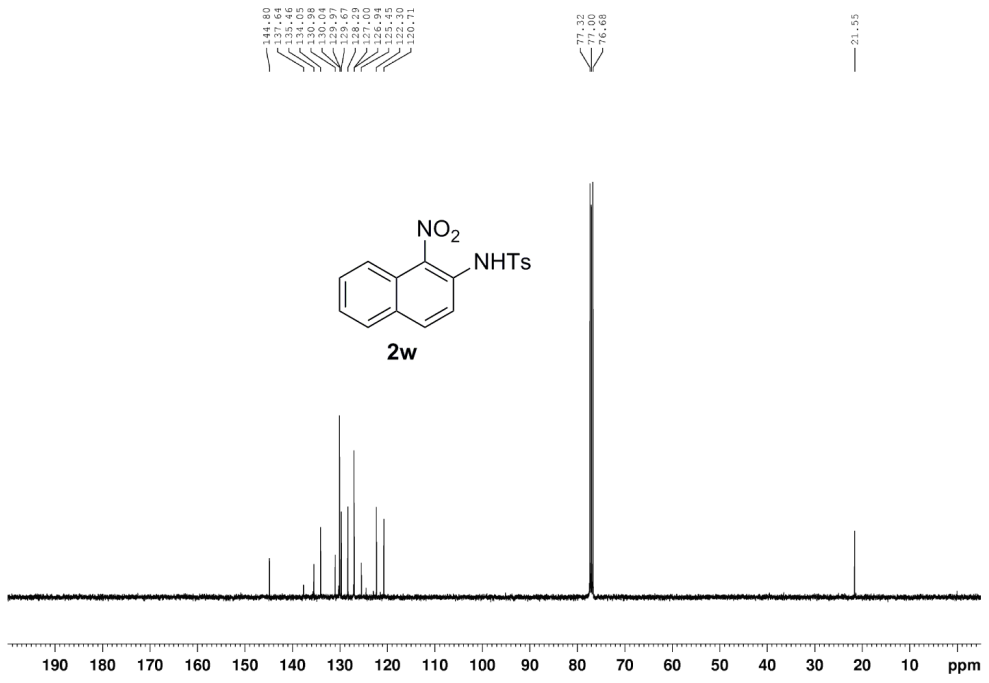

7.991
7.981
7.975
7.599
7.584
7.580
7.301
7.284
7.268
6.318
3.221
3.204
3.188
3.171
2.435
1.066
1.055
1.050
0.016
0.005
-0.000
TsHN
NO2
2u
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.05
2.11
2.49
1.00
2.06
3.00
12.08

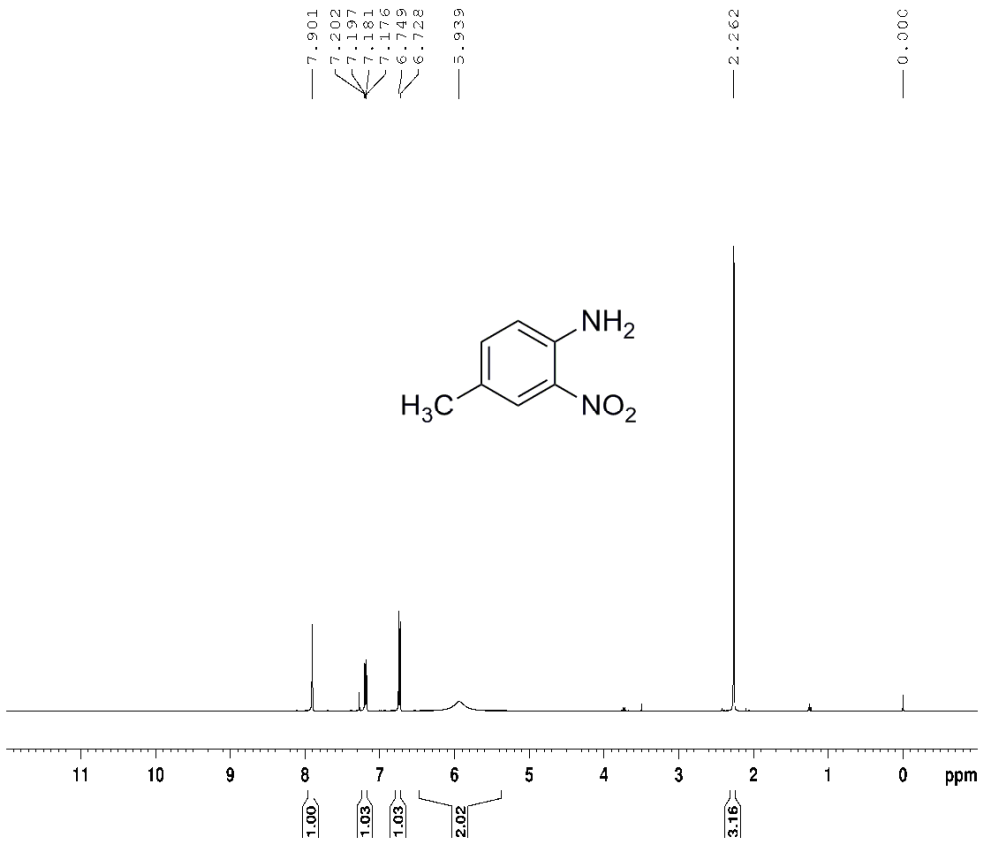

150.21
147.76
145.21
144.35
136.55
135.21
129.80
127.25
119.27
77.32
77.00
76.68
28.97
23.50
21.54
TsHN
NO2
2u
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

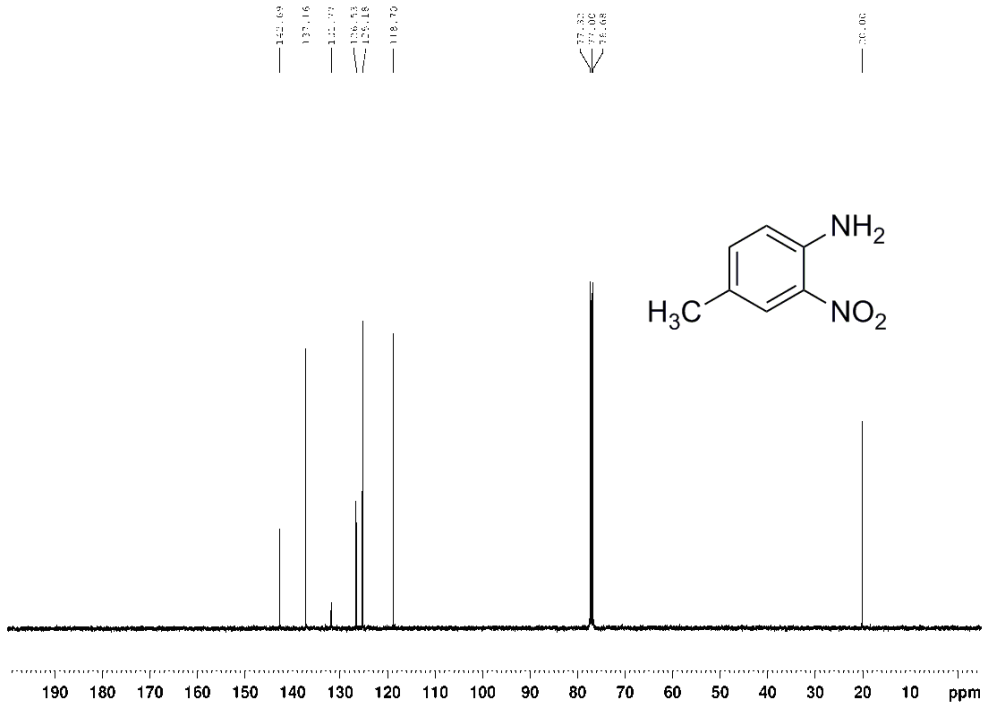

8.970
8.948
8.826
8.579
8.551
8.014
8.011
7.996
7.993
7.975
7.972
7.907
7.889
7.871
7.869
7.345
7.324
7.267
7.230
7.209
2.436
0.000
NO2
2v NHTs
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.04 1.05 2.00 1.06 1.07 2.07 2.09 3.17

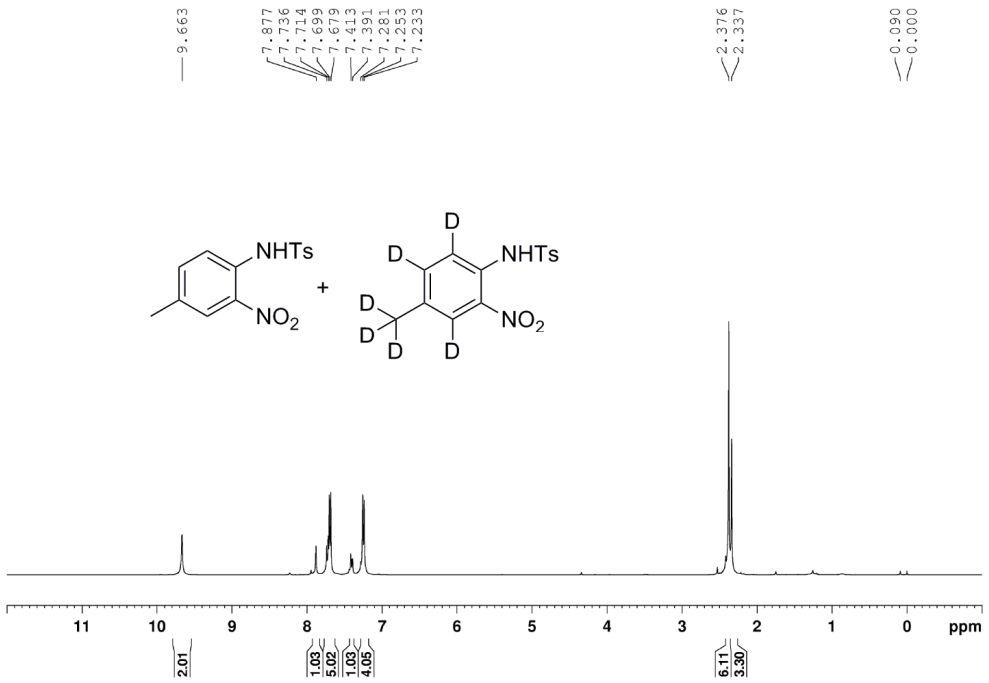

145.65
144.66
138.82
134.63
133.54
133.11
132.44
130.29
129.88
129.68
127.61
127.21
122.86
118.06
77.32
77.00
76.69
21.66
NO2
2v NHTs
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

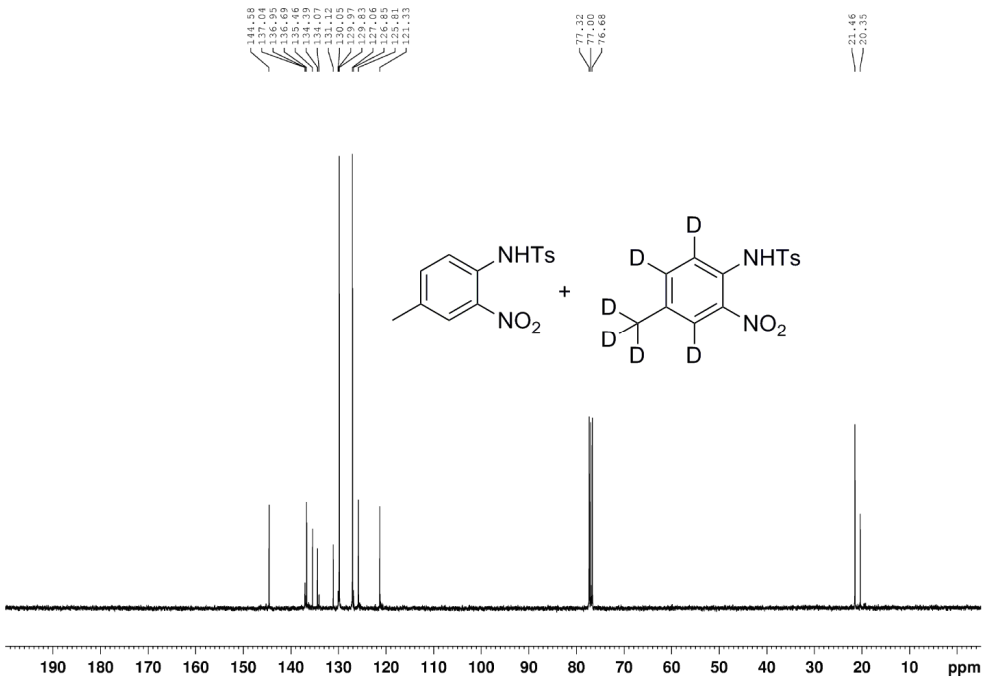

8.481
7.997
7.974
7.946
7.929
7.904
7.907
7.853
7.832
7.641
7.620
7.598
7.595
7.551
7.532
7.260
7.217
7.196
2.354
-0.000
NO2
NHTs
2w
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.91
3.02
1.04
3.02
1.00
2.01
3.00


144.80
137.64
133.66
134.45
130.98
130.04
129.97
128.67
128.29
127.00
126.94
125.45
123.30
120.71
77.32
77.00
76.68
21.55
NO2
NHTs
2w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

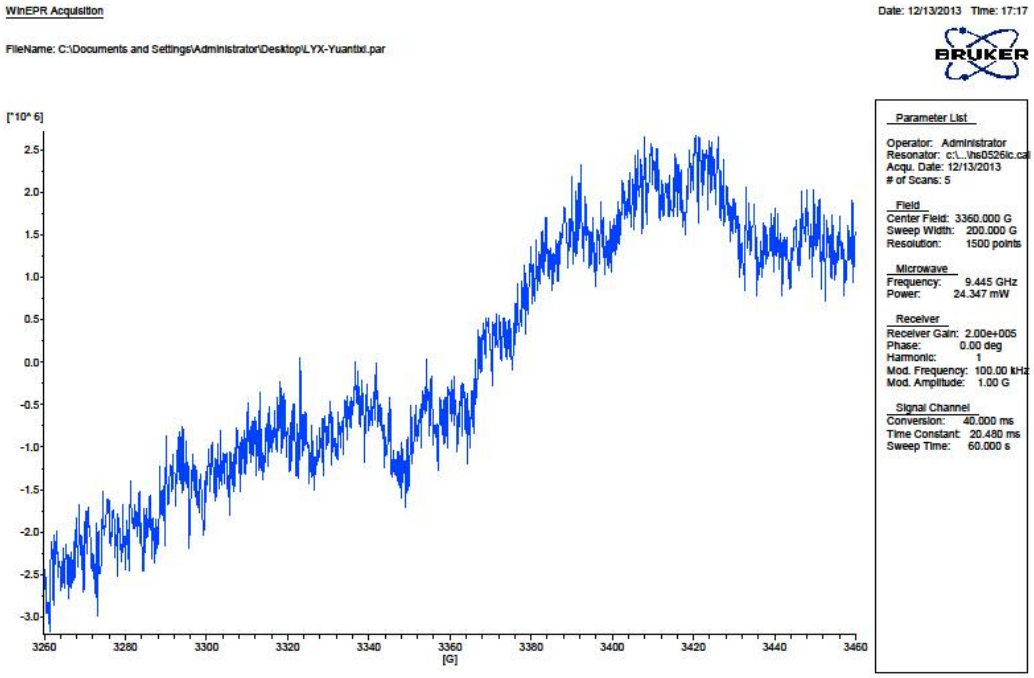

7.901
7.202
7.197
7.181
7.176
6.749
6.728
5.939
2.262
0.000
NH2
H3C
NO2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.03
1.03
2.02
3.16

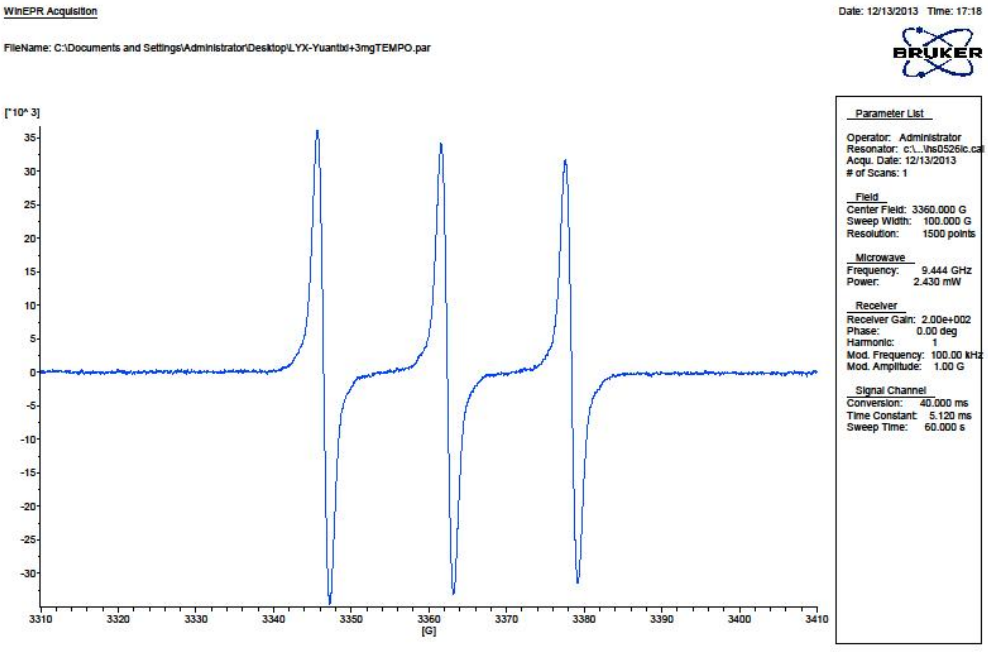

142.69
137.16
122.77
126.53
125.18
118.76
77.32
77.00
76.68
20.06
NH2
H3C
NO2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

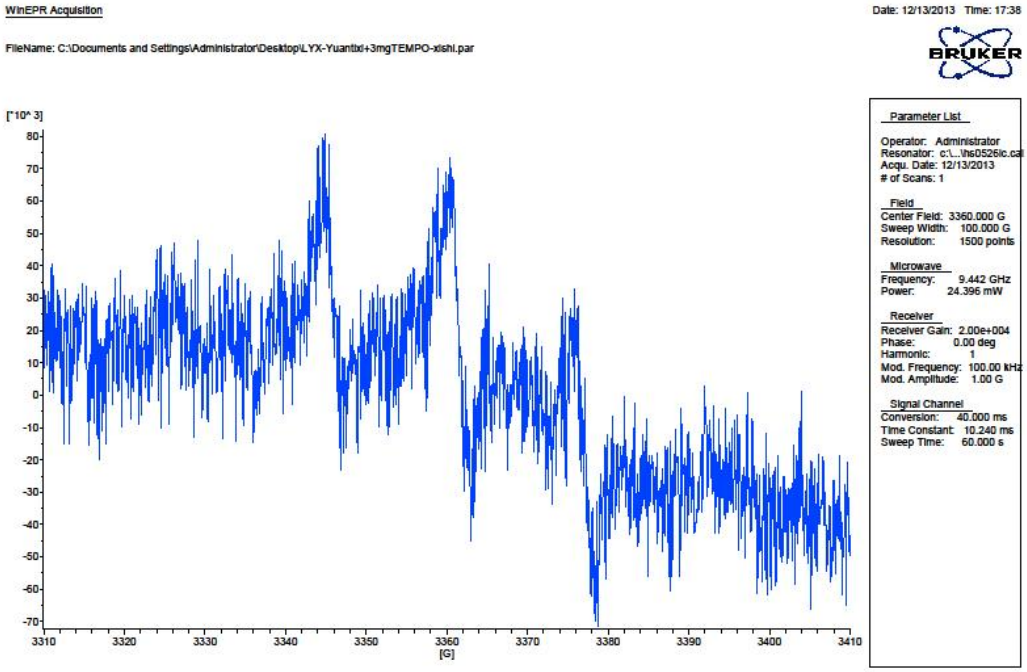

9.663
7.877
7.736
7.714
7.699
7.679
7.413
7.391
7.281
7.253
7.233
2.376
2.337
0.090
0.000
NHTs
NO2
+
D
NHTs
NO2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.03
5.02
1.03
4.05
6.11
3.30

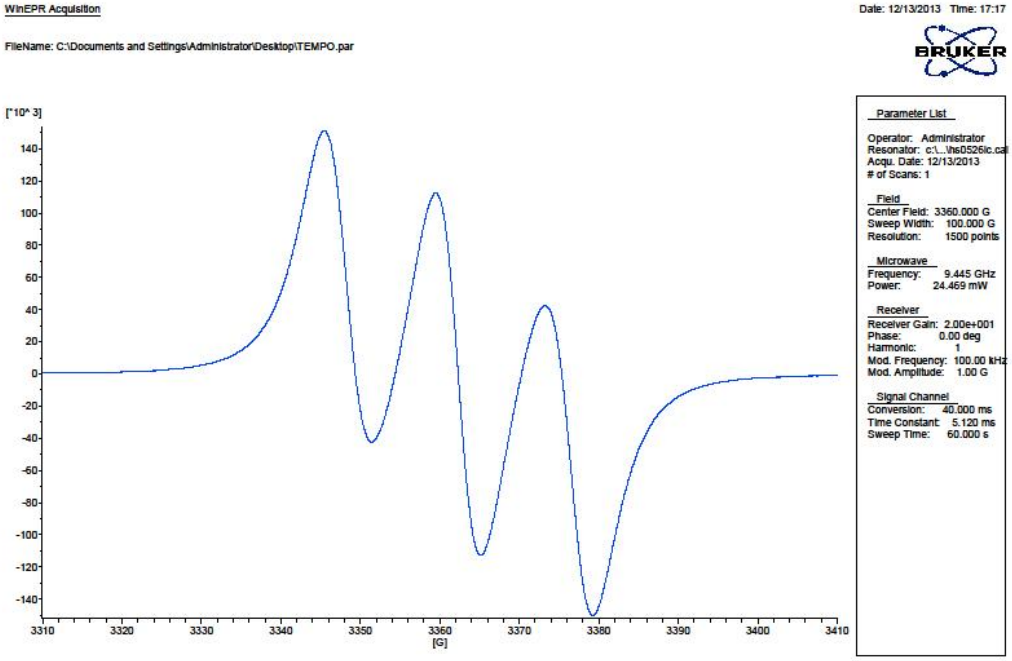

144.58
137.04
136.65
136.69
135.46
134.39
134.07
131.22
130.05
129.97
129.83
127.86
126.89
125.81
121.33
77.32
77.00
76.68
21.46
20.35
NHTs
NO2
+
D
NHTs
NO2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

7. Electron paramagnetic resonance (EPR) for 2a.






WinEPR Acquisition
Date: 12/13/2013 Time: 17:38
FileName: C:\Documents and Settings\Administrator\Desktop\LYX-Yuantbl+3mgTEMPO-xishl.par
BRUKER
[*10^ 3]
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
3310
3320
3330
3340
3350
3360
3370
3380
3390
3400
3410
[G]
Parameter List
Operator: Administrator
Resonator: c:\...\hs0526lc.cal
Acqu. Date: 12/13/2013
# of Scans: 1
Field
Center Field: 3360.000 G
Sweep Width: 100.000 G
Resolution: 1500 points
Microwave
Frequency: 9.442 GHz
Power: 24.396 mW
Receiver
Receiver Gain: 2.00e+004
Phase: 0.00 deg
Harmonic: 1
Mod. Frequency: 100.00 kHz
Mod. Amplitude: 1.00 G
Signal Channel
Conversion: 40.000 ms
Time Constant: 10.240 ms
Sweep Time: 60.000 s


WinEPR Acquisition
Date: 12/13/2013 Time: 17:17
FileName: C:\Documents and Settings\Administrator\Desktop\TEMPO.par
BRUKER
[*10^ 3]
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
3310
3320
3330
3340
3350
3360
3370
3380
3390
3400
3410
[G]
Parameter List
Operator: Administrator
Resonator: c:\...\hs0526lc.cal
Acqu. Date: 12/13/2013
# of Scans: 1
Field
Center Field: 3360.000 G
Sweep Width: 100.000 G
Resolution: 1500 points
Microwave
Frequency: 9.445 GHz
Power: 24.469 mW
Receiver
Receiver Gain: 2.00e+001
Phase: 0.00 deg
Harmonic: 1
Mod. Frequency: 100.00 kHz
Mod. Amplitude: 1.00 G
Signal Channel
Conversion: 40.000 ms
Time Constant: 5.120 ms
Sweep Time: 60.000 s