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

Aryne Generation vs Truce-Smiles and Fries Rearrangements during the Kobayashi Fragmentation Reaction: A New Bi-Aryl Synthesis

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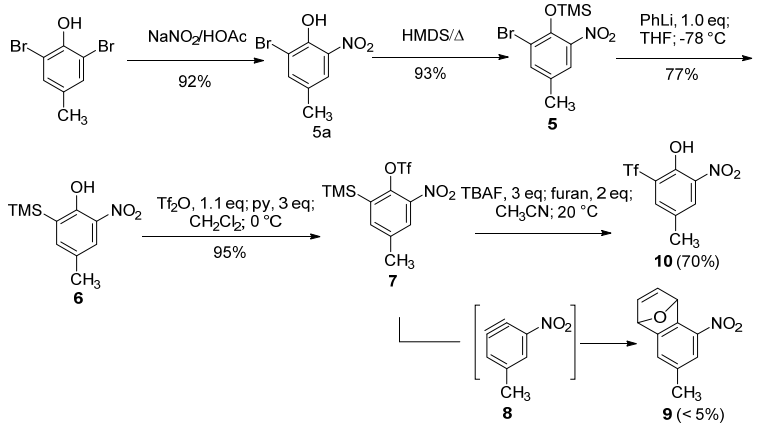
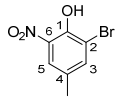
NOTE OF CAUTION: Many of the compounds prepared and utilised in this study are poly-nitroaramtics. While we have not tested the thermal/shock stability of these compouds we do suggest that every precaution be taken in their handling in order to avoid detonation.

All reactions were conducted in dry glassware under a nitrogen atmosphere, unless otherwise stated. All chemicals were purchased from a chemical supplier and used as received unless otherwise stated. THF was distilled from sodium wire and acetonitrile and DCM were redistilled from calcium hydride; methanol was dried over molecular sieves (4 Å). *n*-BuLi was purchased as a 1.6M solution in hexane from Aldrich Chemicals. PhLi was purchased as 1.8M solution in dibutylether from Aldrich Chemicals. Tetrabutylammonium fluoride was purchased as 1M solution in THF from Aldrich chemicals. Sodium hydride was purchased as 80% dispersion in mineral oil from Aldrich chemicals. ^{1}H NMR spectra were recorded at 300, 400 or 500 MHz and ^{13}C NMR spectra at 75, 100 or 125 MHz on a Bruker AC300, AC400 or AC500 spectrometer. The splitting patterns for NMR spectra are designated as follows: s (singlet), br.s (broad singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), or combinations thereof. Assignments were made with the aid of DEPT135, COSY, HMBC and HMQC experiments. Mass spectra were recorded on one of the following: Waters QTOF (ES, HRMS), Thermo Finnigan MAT95XP (GC/MS, EI, and HRMS) or a Hewlett Packard 5971 MSD (GC/MS). Infrared spectra were recorded on a Bruker Alpha FT-IR. A Sanyo Gallenkamp melting point apparatus was used for melting points. Chromatographic purifications were performed using silica gel SDS (particle size 0.04-0.06 mm).

i. Attempted generation and trapping of benzyne (9).

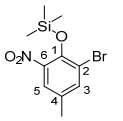


Synthesis of 2-bromo-4-methyl-6-nitrophenol (5a):[1]

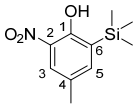


To the stirred mixture of 2,6-dibromo-4-methylphenol (30.8 g, 0.12 mol) in glacial acetic acid (300 mL), sodium nitrite (88 g, 0.13 mol) was added. The reaction mixture was stirred overnight at rt. The mixture was poured into water (1.5 L). The product was precipitated out which was then filtered. The *title compound* was obtained as deep yellow solid (26.81 g, 93%, **mp** 66-68 °C, Lit[1] 67-69 °C). **^{1}H NMR** (500 MHz, *CDCl$_3$*) δ ppm 2.33 (3H, s, CH_3) 7.67 (1H, d, *J* = 1.5 Hz, Ar-**H**$_3$) 7.86 (1H, d, *J* = 1 Hz, Ar-**H**$_5$) 10.90 (1H, br. s., OH).**^{13}C NMR** (125 MHz, *CDCl$_3$*) δ ppm 20.0(CH_3), 112.6, 123.9 (**C**$_5$), 130.5, 137.5, 141.6 (**C**$_3$), 149.9. **MS** (ES-): $[M]^-$ 230. **Accurate Mass** (ES-): $[C_7H_6O_3N_1{}^{79}Br_1{}^{-1}H]^-$ requires 229.9458 found 229.9449. **υ$_{max}$**(ATR): 1534, 1620, 1734, 3440 cm^{-1}.

Synthesis of (2-bromo-4-methyl-6-nitrophenoxy)trimethylsilane (5): The phenol (1.1 mmol, 1.1 eq.) was refluxed with 1,1,1,3,3,3-hexamethyldisilazane (3.3 mmol, 3 eq.) for 3 hours. After cooling down the reaction mixture was concentrated *in vacuo* to give pure *title compound* as an orange oil. 93% yield. **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.33 (9H, s, Si-CH_3) 2.33 (3H, s, CH_3) 7.54 (1H, d, *J* = 1 Hz, Ar-**H**$_3$) 7.58 (1H, d, *J* = 2 Hz, Ar-**H**$_5$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm 0.88 (Si-**C**H_3), 20.1 (**C**H_3), 117.7, 124.5(**C**$_5$), 132.3, 138.0, 142.7 (**C**$_3$), 144.6. **MS** (EI+): $[M]^+$ 303.0. **Accurate Mass** (EI+): $C_{10}H_{14}O_3{}^{79}Br_1Si_1N_1$ requires 302.9925 found 302.9928. **υ$_{max}$**(ATR): 1252, 1353, 1473, 1527, 2956 cm^{-1}.



Synthesis of 2-nitro-4-methyl-6-(trimethylsilyl)phenol (6):[1]

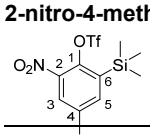


Phenyllithium (5 mL, 2 M, 10 mmol) was added to the (2-bromo-4-methyl-6-nitrophenoxy)trimethylsilane (3.04 g, 10 mmol, 1 eq.) in THF (50 mL) at -78 °C over 10 min. The reaction mixture was stirred for 2 hrs and then quenched with water. After this allowed the reaction mixture to warm to room temperature poured into ether (50 mL) and washed with brine (3 x 50 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (silica; ether : petroleum ether 5 : 95) to afford the *title compound* as bright yellow solid. (1.75 g, 77.7 %; **mp** 94.2-94.6 °C).**^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.36 (9H, s, Si-CH_3) 2.34 (3H, s, C-CH_3) 7.47 (1H, d, *J* = 2 Hz, Ar-**H**$_5$) 7.88 (1H, dd, *J* = 1.5 Hz, Ar-**H**$_3$) 10.88 (1H, s, OH). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -1.3 (Si-CH_3), 20.2 (C-CH_3), 125.2 (**C**$_3$), 127.1, 129.6, 131.4, 144.4 (**C**$_5$), 157.1. **MS** (EI+): $[M^+]$ 225.1. **Accurate Mass** (EI+): $C_{10}H_{15}O_3N_1Si_1$ requires 225.0821 found 225.0816. □**$_{max}$**(ATR): 1542, 1590, 1607, 1639, 2961, 3409 cm^{-1}.

General procedure for triflate synthesis:

To the stirred mixture of substituted trimethylsilyl phenol (1 eq.), dry pyridine (3 eq.) in DCM (5 mL), Trifluoromethanesulphonic anhydride (1.1 eq.) was added slowly at 0 °C. The reaction mixture was then stirred for sixteen hours and then poured into ether (30 mL). The organic phase was washed with water (3 x 30 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give the *title compound*,

2-nitro-4-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (7) as an orange oil, 95 % yeild. **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ ppm 0.43 (9H, s, Si-CH_3) 2.47 (3H, s, CH_3) 7.57 (1H, dd, *J* = 2, 1 Hz, Ar-**H**$_5$) 7.78 (1H, dd, *J* = 2, 1 Hz, Ar-**H**$_3$). **^{13}C NMR** (125 MHz, *CDCl$_3$*) δ ppm -0.16 (Si-CH_3), 20.8 (CH_3), 127.5 (**C**$_3$), 138.6, 139.3, 139.8, 141.1 (**C**$_5$), 143.2. **MS**

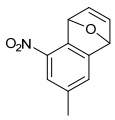


[1] I. R. Hardcastle, R. F. Hunter, P. Quayle and P. N. Edwards, *Tetrahedron lett*. 1994, **35**, 3805.b) I. R. Hardcastle, *University of Manchester*, PhD thesis, 1990**.** c) L. C. Railford, *J. Am. Chem. Soc.* 1919**, 41**, 2068.

(ES+): [M^+] 380.0. **Accurate Mass**(ES+): $C_{11}H_{14}O_5Si_1N_1S_1{}^{19}F_3$ requires 380.0206 found 380.0206.**υ** $_{max}$(ATR): 1254, 1353, 1404, 1539, 1575, 2957 cm^{-1}.

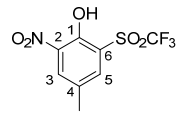
Attempted aryne generation

Synthesis of 4-methyl-2-nitro-6-((trifluromethyl)sulfonyl)phenol (10)

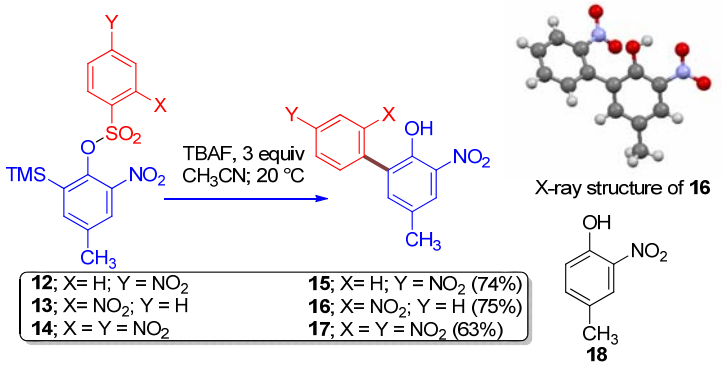


Tetrabutylammonium fluoride (3 mL, 1 M, 3 mmol) was added to the stirred mixture of 2-nitro-4-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.32 g, 1 mmol), furan (0.1 mL, 2 mmol) and acetonitrile (5 mL). The reaction mixture was stirred for 16 hours and then poured into ether (30 mL). The organic layer was washed with HCl (2 M, 20 mL) and then with water (2 x 20 mL). The organic layer was dried and concentrated *in vacuo*. The crude product was purified by column chromatography (5-100% ether-petroleum ether) and afforded **7-methyl-5-nitro-1,4-dihydro-1,4-epoxynaphthalene (9)**, yield 9.9 mg (5%), as a viscous yellow oil. **^{1}H NMR** (80 MHz, *$CDCl_3$*) δppm 2.4 (3H, s, CH_3) 5.75 (1H, s) 6.4 (1H, s) 7.1 (2H, s) 7.3 (1H, s) 7.55 (1H, s). **MS** (EI): m/e = 203 (M^+) . **Accurate Mass** (+EI): $C_{11}H_9O_3N_1$ requires 203.0582 found 203.0579. **υ_{max}**(liq.): 1413, 1526, 1413 cm^{-1}.

The major product from this reaction, a yellow-coloured, crystalline solid (0.15 g, 69.7 %; **mp** 100.8-101 °C) was identified as **4-methyl-2-nitro-6-((trifluromethyl)sulfonyl)phenol (10)**. **^{1}H NMR** (400 MHz, *$CDCl_3$*) δppm 2.50 (3H, s, CH_3) 8.17 (1H, d, *J* = 2 Hz, Ar-**H**$_3$) 8.38 (1H, d, *J* = 2 Hz, Ar-**H**$_5$) 11.47 (1H, s, OH). **^{13}C NMR** (400 MHz, *$CDCl_3$*) δppm 20.3(CH_3), 112.8, 124.1, 130.7 (**C**$_5$), 133.5, 141.6 (**C**$_3$), 150.0. **MS** (EI+): 285. **Accurate Mass** (+EI): $C_8H_6O_5N_1{}^{19}F_3S_1$ requires 284.9913 found 284.9907. **Microanalysis:** $C_8H_6N_1F_1O_5S$ requires C 33.7; H 2.1; N 4.9%. Found C 33.7; H 2.2; N 4.9%. **υ_{max}**(ATR): 1304, 1570, 1625, 3076, 3188 cm^{-1}.



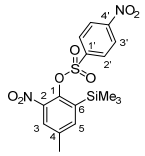
ii. Truce Smiles rearrangement: initial observations



General procedure for preparation of Arene sulfonate esters:[1]

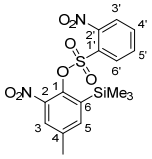
To the stirred solution of sodium hydride (0.288 g, 12.12 mmol, 4.12 eq.) in dry THF (50 mL), substituted *o*-trimethylsilylphenol (3.01 mmol, 1 eq) was added. The reaction mixture was stirred for thirty minutes and then substituted benzenesulphonyl chloride (3.31 mmol, 1.1 eq.) was added. The reaction mixture was stirred for one hour and then poured it into ether (50 mL). The organic phase was washed with water, brine, and dried over $MgSO_4$ and the reaction mixture taken to dryness *in vacuo.* The product was purified by column chromatography.

Synthesis of 2-nitro-4-methyl-6-(trimethylsilyl)phenyl-4'-nitrobenzenesulfonate (12):



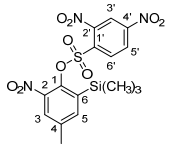
Column chromatography (silica, 10% ether, petroleum ether) afforded the compound as yellow oil (1.1 g, 81 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.44 (9H, s) 2.46 (3H, s, CH_3) 7.57 (1H, d, *J* = 2 Hz, Ar-**H**$_5$) 7.67 (1H, d, *J* = 2 Hz, Ar-**H**$_3$) 8.17 (2H, d, *J* = 8 Hz, Ar-**H**$_{2'}$) 8.45 (2H, d, *J* = 8 Hz, Ar-**H**$_{3'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm 0.06 (Si-CH_3), 30.7 (CH_3), 124.5 (**C**$_{2'}$), 127.0 (**C**$_3$), 128.5, 129.9 (**C**$_{3'}$), 138.3, 139.1, 140.9, 141.1 (**C**$_5$), 143.5, 151.2. **MS (EI+):** $[M+Na]^+$ 433.0. **Accurate Mass** (ES+): $[C_{16}H_{18}O_7S_1Si_1N_2Na_1]^+$ requires 433.0497 found 433.0508. **υ$_{max}$**(ATR): 1203, 1229, 1358, 1511, 1560, 1601, 2984 cm^{-1}.

Synthesis of 2-nitro-4-methyl-6-(trimethylsilyl)phenyl-2'-nitrobenzenesulfonate (13):



Column chromatography (silica, 10% ether, petroleum ether) afforded the compound as oil (1.13 g, 83 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.47 (9H, s, Si-CH_3) 2.45 (3H, s, CH_3) 7.57 (1H, d, *J*=2.2 Hz, Ar-**H**$_5$) 7.63 (1H, d, *J* = 2.2 Hz, Ar-**H**$_3$) 7.76 - 7.89 (2H, m, Ar-**H**$_{5',6'}$) 7.93 (1H, td, *J* = 8, 1.5 Hz, Ar-**H**$_{4'}$) 8.07 (1H, dd, *J* = 7.8, 1.5 Hz, Ar-**H**$_{3'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.24 (Si-**C**H_3), 20.7 (C-CH_3), 125.5 (**C**$_{4'}$), 126.8 (**C**$_3$), 130.5 (**C**$_{3'}$), 131.0 (**C**$_{6'}$), 132.6 (**C**$_{5'}$), 135.4, 138.0, 139.2, 141.1 (**C**$_5$), 142.6, 142.9, 148.0. **MS** (ES+): $[M+Na]^+$ 433.0. **Accurate Mass** (ES+): $C_{16}H_{18}O_7S_1Si_1N_2Na_1$ requires 433.0502. found 433.0499. □**$_{max}$**(ATR): 1213, 1235, 1347, 1507, 1569, 1621, 3001 cm^{-1}.

Synthesis of 2-nitro-4-methyl-6-(trimethylsilyl)phenyl 2',4'-dinitrobenzenesulfonate (14):

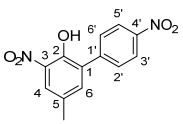


Column chromatography (silica, 10% ether, petroleum ether) afforded the compound as oil (0.91 g, 74 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.49 (9H, s, Si-CH_3) 2.46 (3H, s, C-CH_3) 7.59 (1H, d, *J* = 2.2 Hz, Ar-**H**$_5$) 7.68 (1H, d, *J* = 2.2 Hz, Ar-**H**$_3$) 8.30 (1H, d, *J* = 8.5 Hz, Ar-**H**$_{6'}$) 8.60 (1H, dd, *J*=8.5, 2.2 Hz, Ar-**H**$_{5'}$) 8.79 (1H, d, *J* = 2.2 Hz, Ar-**H**$_{3'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.33 (Si-**C**H_3), 20.8 (C-CH_3), 120.7 (**C**$_{3'}$), 126.9 (**C**$_3$), 127.0 (**C**$_{5'}$), 132.5 (**C**$_{6'}$), 136.1, 138.6, 139.1, 141.5 (**C**$_5$), 142.2, 142.6, 150.7, 163.8. □**$_{max}$**(ATR): 1133, 1197, 1220, 1348, 1519, 1540, 1556, 1608, 2980 cm^{-1}.

General method for Truce-Smiles reacrrangement leading to bi-aryl synthesis:

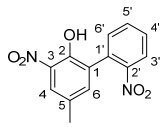
To a stirred solution of trimethylsilylsulfonate ester (1 eq.) and furan (3 eq.) in dry acetonitrile (12 mL), Tetrabutylammonium fluroide (1 M, 3 eq.) was added slowly. The reaction mixture was stirred at rt for sixteen hours and then poured into ether. The resulting mixture was washed with dilute HCl (3 N, 10 mL) and then with water (2 x 10 mL), dried over $MgSO_4$ and the reaction mixture taken to dryness *in vacuo.* Coloumn chromatography (silica, ether : petrol) afforded the *pure compound*.

Synthesis of 5-methyl-3,4'-dinitro-[1,1'-biphenyl]-2-ol (15):



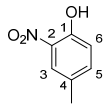
Coloumn chromatography (silica, 10% ether,petroleum ether) afforded the *title compound* as bright yellow solid (0.349 g, 74.4% ; **mp** 196-197 C°). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 2.43 (3H, s, CH_3) 7.50 (1H, d, *J* = 2 Hz, Ar-**H**$_6$) 7.75 (2H, d, *J* = 9 Hz, Ar-**H**$_{2'6'}$) 8.03 (1H, d, *J* = 1.5 Hz, Ar-**H**$_4$) 8.32 (2H, d, *J* = 9 Hz, Ar-**H**$_{3'5'}$) 10.96 (1H, s, OH). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm 20.4 (CH_3), 123.5 (**C**$_{3'5'}$), 125.1(**C**$_4$), 127.9, 130.2, 130.3(**C**$_{2'6'}$), 133.9, 139.3, 142.5 (**C**$_6$), 146.5, 150.5. **MS** (EI+): [M˙] 273. **Accurate Mass** (ES-): $[C_{13}H_{10}O_5N_2$-$^1H]^-$ requires 273.0511 found 273.0516. **Microanalysis:** $C_{13}H_{10}N_2O_5$ requires C 57.0; H 3.7; N 10.2%. Found C 57.0; H 3.3; N 10.1%. **υ**$_{max}$(ATR):1138, 1253, 1346, 1518, 1535 2968, 3087 cm^{-1}.

Synthesis of 5-methyl-2',3-dinitro-[1,1'-biphenyl]-2-ol (16):



Coloumn chromatography (silica, 10% ether,petroleum ether) afforded the *title compound* as bright yellow solid (0.359 g, 75 % ; mp 193-194 C°). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 2.42 (3H, s, CH_3) 7.39 - 7.45 (2H, m, Ar-**H**$_{3',6}$) 7.59 (1H, td, *J* = 8, 1.5 Hz, Ar-**H**$_{4'}$) 7.72 (1H, td, *J* = 8, 2 Hz, Ar-**H**$_{5'}$) 7.98 (1 H, s, Ar-**H**$_4$) 8.10 (1 H, dd, *J* = 8, 1 Hz, Ar-**H**$_{3'}$) 10.73 (1H, s, OH). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm 20.4 (CH_3), 124.5 (**C**$_{3'}$), 124.6(**C**$_4$), 129.3 (**C**$_{4'}$), 129.7, 130.0, 130.1, 132.4, 133.2, 138.2 (**C**$_{5'}$), 149.1 (**C**$_6$), 150.3. **MS** (ES+): $[M+Na]^+$ 297.3. **Accurate Mass** (ES+): $C_{13}H_{10}O_5N_2Na_1$ requires 297.0494 found 297.0487. **Microanalysis:** $C_{13}H_{10}N_2O_5$ requires C 56.9; H 3.6; N 10.2%. Found C 56.1; H 3.3; N 10.1%.**υ** $_{max}$(ATR):1126, 1344, 1401, 1458, 1517, 2915, 3228 cm^{-1}.

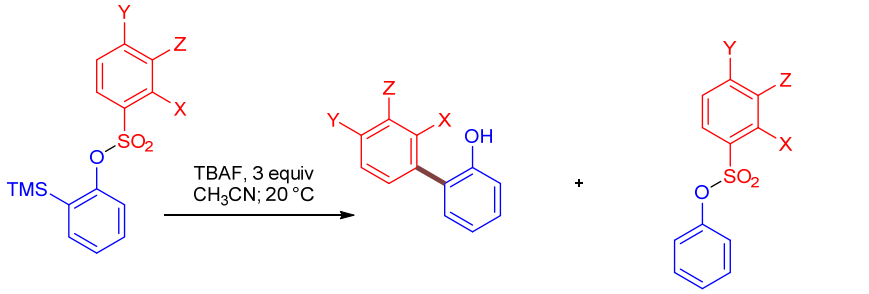
Synthesis of 5-methyl-2',3,4'-trinitro-[1,1'-biphenyl]-2-ol (17):



4-methyl-2-nitrophenol (18):[2] Column chromatography (silica, 5% ether : petroleum ether) afforded the *title compound* as an yellowish oil (0.023 g, 13 %). **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 2.35 (3H, s, CH_3) 7.06 (1H, d, *J* = 8.5 Hz, Ar-**H_5**) 7.41 (1H, dd, *J*=8.5, 2Hz, Ar-**H_6**) 7.91 (1H, s, Ar-**H_3**) 10.46 (1H, s, OH). **^{13}C NMR** (300 MHz, $CDCl_3$) δ ppm 20.3(**C**H_3), 119.3 (**C_6**), 124.5 (**C_3**), 130.1, 133.2, 138.8 (**C_5**), 153.2. Further elution (10% ether,petroleum ether) afforded **5-methyl-2',3,4'-trinitro-[1,1'-biphenyl]-2-ol (17)** as bright yellow solid (0.401 g, 63 % ; **mp** 177-179 C°). **^{1}H NMR** (400 MHz, *$CDCl_3$*) δppm 2.49 (3H, s, CH_3) 7.46 (1H, d, *J* = 2 Hz, Ar-**H_6**) 7.66 (1 H, d, *J* = 8 Hz, Ar-**$H_{6'}$**) 8.07 (1H, d, *J* = 1 Hz, Ar-**H_4**) 8.56 (1H, dd, *J* = 8, 2 Hz, Ar-**$H_{5'}$**) 8.94 (1 H, d, *J* = 2 Hz, Ar-**$H_{3'}$**) 10.75 (1H, s, OH). **^{13}C NMR** (125 MHz, *$CDCl_3$*) δ ppm 20.5(**C**H_3), 120.1 (**$C_{3'}$**), 125.8 (**C_4**), 127.3 (**$C_{5'}$**), 127.5, 130.6, 133.4, 133.7 (**$C_{6'}$**), 136.9, 137.8 (**C_6**), 147.3, 149.2, 149.8. **MS** (ES+): $[M]^+$ 320.1. **Accurate Mass** (ES+): $C_{13}H_9O_7N_3Na_1$ requires 343.0441found 343.0452. **υ** $_{max}$(ATR): 1527, 1548, 1640, 2930, 3101 cm^{-1}.

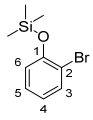
[2] Y. Zhou, E. Lindback, C. M. Pedersen and M. Bols, *Tetrahedron Lett.* 2014, **55**, 2304.

iii. Synthesis of substrtates for Truce-Smile rearrangements – electronic effects



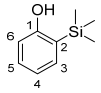
19; X = Z = H; Y = NO_2	**25**; X = Z = H; Y = NO_2 (44%)[a]	**31**; X = Z = H; Y = NO_2 (19%)
20; X = NO_2; Y = Z = H	**26**; X= NO_2; Y = Z = H (39%)[a]	**32**; X= NO_2; Y = Z = H (nd)
21; X = Y = NO_2; Z=H	**27**; X = Y = NO_2; Z = H (49%)	
22; X = Y = H; Y = Cl	**28**; X = Y = H; Y = Cl (0%)	**33**; X = Z = H; Y = Cl (75%)
23; X = Y = Z = H	**29**; X = Y = Z = H (0%)	**34**; X = Y = H (88%)
24; X,Z = $(CH)_4$	**30**; X,Z = $(CH)_4$ (0%)	**35**; X,Z = $(CH)_4$ (84%)

Synthesis of (2-bromophenoxy)trimethylsilane:[3]



1,1,1,3,3,3-hexamethyldisilazane (12.18 mL, 61.96 mmol) was added slowly to *o*-bromophenol (17.15 g, 99.14 mmol) at rt. The reaction mixture was refluxed for three hours. The product was isolated by distillation as colourless oil (12.6 g, 84 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.33 (9H, s, CH_3) 6.82 - 6.93 (2H, m, Ar-**$H_{6,4}$**) 7.18 (1H, t, *J* = 8 Hz, Ar-**H_5**) 7.54 (1H, dd, *J* = 8, 1.5 Hz, Ar-**H_3**). **^{13}C NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.35(CH_3), 115.6, 120.7 (**C_3**), 122.6 (**C_5**), 128.3 (**C_4**), 133.3 (**C_6**), 152.4. **MS** (EI+): [M^+] 244. **Accurate Mass** (EI+): $C_9H_{13}O_1Si_1{}^{79}Br_1$ requires 243.9914 found 243.9913.**υ max**(ATR): 1284, 1474, 1583, 2959 , 3064 cm^{-1}.

Synthesis of 2-(trimethylsilyl)phenol:[4]



A solution of 2-bromo-1-trimethylsilyloxybenzene (7.6 g, 30.96 mmol, 1 eq.) in dry THF (10 mL) was added slowly to the stirred solution of *n*-BuLi (26.5 mL, 46.44 mmol, 1.5 eq.) in dry THF (10 mL) at -78 °C under nitrogen. At -78 °C stirred the reaction mixture for three hours and then at rt for one hour. Upon recooling to -78 °C the reaction mixture quenched by adding saturated ammonium chloride (3 mL). The reaction mixture was allowed to room temperature and then extracted it with ethyl acetate (2 x 15 mL). The organic phase was washed with water, brine, and dried over $MgSO_4$ and the reaction mixture taken to dryness *in vacuo.* The product obtained as light brown oil in colour which is used without further purification (4.54 g, 83%). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.37 (s, 9H, CH_3) 5.09 (1H, br. s., OH) 6.70 (1H, d, *J* = 8 Hz, Ar-**H_6**) 6.98 (1H, td, *J* = 7, 1 Hz, Ar-**H_4**) 7.28 (1H, td, *J* = 8, 2 Hz, Ar-**H_5**) 7.43 (1H, dd, J=7, 2 Hz, Ar-**H_3**) **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.99 (CH_3), 114.4 (**C_6**), 120.4 (**C_4**), 128.4, 130.6 (**C_5**), 135.3 (**C_3**), 160.4. **MS** (EI+): [$M]^+$ 166. **Accurate Mass** (EI+): $C_9H_{14}O_1Si_1$ requires 166.0808 found 166.0813. **υmax**(ATR): 1270, 1368, 1592, 3067, 2953 cm^{-1}

Sulfonate esters (19)-(24) were prepared using the general methid as described above.

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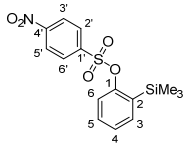
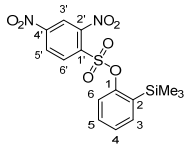
Synthesis of 2-(trimethylsilyl)phenyl-4'-nitrobenzenesulfonate (19):



The product was purified by recrystallisation (ether : petroleum ether) as white crystalline powder (1.05 g , 90.6 %; **mp** 134-134.4 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.28 (9H, s, CH_3) 7.04 (1H, dd, *J* = 8, 1 Hz, Ar-**H_6**) 7.27 - 7.36 (2H, m, Ar-**$H_{4,5}$**) 7.50 (1H, dd, *J* = 7, 1 Hz, Ar-**H_3**) 8.19 (2H, d, *J* = 9 Hz, Ar-**$H_{2',6'}$**) 8.44 (2H, d, *J* = 9 Hz, Ar-**$H_{3',5'}$**). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.62 (Si-CH_3), 119.1 (**C_4**), 124.5 (**$C_{3',5'}$**), 126.6 (**C_6**), 129.6 (**C_3**), 130.7 (**$C_{2',6'}$**), 132.6, 136.3 (**C_5**), 142.5, 150.9, 154.8. **Microanalysis:** $C_{15}H_{17}O_5SiSN$ requires C 51.3; H 4.9, N 4.0 %. Found C 51.0; H 4.8 %; N 4.0%. **MS** (ES+): $[M+Na]^+$ 374. **Accurate Mass** (+EI): $[C_{15}H_{17}N_1O_5S_1Si_1Na_1]^+$ requires 374.0489 found 374.0481.; **(EI+):** $[C_{15}H_{17}N_1O_5S_1Si_1\text{-}CH_3]^+$ requires 336.0356 found 336.0351. **υmax**(ATR): 1176, 1311, 1348, 1528, 2956 cm^{-1}.

Synthesis of 2-(trimethylsilyl)phenyl-2',4'-dinitrobenzenesulfonate (21):

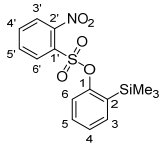


The product was purified by recrystallisation (DCM : hexane) as light yellow powder (1 g, 76%; **mp** 134-135 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.34 (9H, s, CH_3) 6.88 - 6.93 (1H, m, Ar-**H_6**) 7.28 - 7.34 (2H, m, Ar-**$H_{4,5}$**) 7.53 - 7.58 (1H, m, Ar-**H_3**) 8.38 (1H, d, *J* = 8.5 Hz, Ar-**$H_{6'}$**) 8.61 (1H, dd, *J* = 8.5, 2.1 Hz, Ar-**$H_{5'}$**) 8.72 (1H, d, *J* = 2.2 Hz, Ar-**$H_{3'}$**). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.63 (Si-**C**H_3), 119.6 (**C_4**), 120.8 (**$C_{3'}$**), 126.7 (**C_6**), 127.1 (**$C_{5'}$**), 130.8 (**C_3**), 132.9 (**$C_{6'}$**), 133.1, 135.6, 136.4 (**C_5**), 148.7, 150.7, 154.7. **Microanalysis:** $C_{15}H_{16}N_2O_7SSi$ requires C 45.4; H 4.1; N 7.1%; S 8.1%. Found C 45.1; H 4.1; N 7.1%; S 8.0% **MS** (ES+): $[M+Na]^+$ 419. **Accurate Mass** (EI+): $[C_{15}H_{16}N_2O_7S_1Si_1\text{-}CH_3]^+$ requires 381.0213 found 381.0217. **υmax**(ATR): 1184, 1348, 1382, 1537, 1557, 3099 , 3105, 3312 cm^{-1}.

[3] D. Pena, A. Cobas, D. Perez and E. Guitian, *Synthesis,* 2002, **10,** 1454. b) G. M. Tierney, Third Year Undergraduate Project Report, *University of Manchester*, 1990-1991**.** c) T. Ikawa, A. Takagi, Y. Kurita, K. Saito, K. Azechi, M. Egi, K. Kakiguchi, Y. Kita and S. Akai, *Angew. Chem. Int. Ed*. 2010, **49,** 5563.

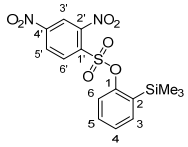
[4] T. Ikawa, T. Nishiyama, T. Nosaki, A. Takagi and S. Akai, *Org. Lett*. 2011, **13**, 1730.

Synthesis of 2-(trimethylsilyl)phenyl-2'-nitrobenzenesulfonate (20):



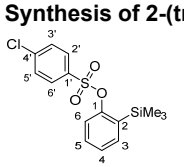
The product was purified by recrystallisation (DCM : petroleum ether) as white crystalline powder (1 g, 86.2 %; **mp** 98-100 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.32 (9H, s, CH_3) 6.94 - 6.99 (1H, m, Ar-**H**$_4$) 7.24 - 7.30 (2H, m, Ar-**H**$_{3,6}$) 7.49 - 7.53 (1H, m, Ar-**H**$_5$) 7.80 (1H, dd, *J* = 7.5, 2.0 Hz, Ar-**H**$_{6'}$) 7.83 - 7.90 (2H, m, Ar-**H**$_{4',5'}$) 8.15 (1 H, d, *J* = 8 Hz, Ar-**H**$_{3'}$).**^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.85 (Si-CH_3), 119.5(**C**$_4$), 124.9 (**C**$_{4'}$), 126.4(**C**$_6$), 130.4 (**C**$_3$), 130.5, 130.9(**C**$_{3'}$), 132.1 (**C**$_{6'}$), 135.9 (**C**$_5$), 134.9 (**C**$_{5'}$), 137.2, 148.3, 154.7. **MS** (EI+): $[M]^+$ 336. **Accurate Mass** (EI+): $[C_{15}H_{17}N_1O_5S_1Si_1\text{-}CH_3]^+$ requires 336.0356 found 336.0351. **Microanalysis:** $C_{15}H_{17}NO_5SSi$ requires C 51.3; H 4.9; N 4.0%; S 9.1%. Found C 51.0; H 5.1; N 3.9%; S 9.0%. □**$_{max}$**(ATR): 1192, 1364, 1375, 1432, 1538, 2951 cm^{-1}.

Synthesis of 2-(trimethylsilyl)phenyl-2',4'-dinitrobenzenesulfonate (21):



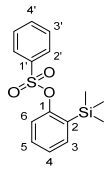
The product was purified by recrystallisation (DCM : hexane) as light yellow powder (1 g, 76%; **mp** 134-135 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.34 (9H, s, CH_3) 6.88 - 6.93 (1H, m, Ar-**H**$_6$) 7.28 - 7.34 (2H, m, Ar-**H**$_{4,5}$) 7.53 - 7.58 (1H, m, Ar-**H**$_3$) 8.38 (1H, d, *J* = 8.5 Hz, Ar-**H**$_{6'}$) 8.61 (1H, dd, *J* = 8.5, 2.1 Hz, Ar-**H**$_{5'}$) 8.72 (1H, d, *J* = 2.2 Hz, Ar-**H**$_{3'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.63 (Si-**C**H_3), 119.6 (**C**$_4$), 120.8 (**C**$_{3'}$), 126.7 (**C**$_6$), 127.1 (**C**$_{5'}$), 130.8 (**C**$_3$), 132.9 (**C**$_{6'}$), 133.1, 135.6, 136.4 (**C**$_5$), 148.7, 150.7, 154.7. **Microanalysis:** $C_{15}H_{16}N_2O_7SSi$ requires C 45.4; H 4.1; N 7.1%; S 8.1%. Found C 45.1; H 4.1; N 7.1%; S 8.0% **MS** (ES+): $[M+Na]^+$ 419. **Accurate Mass** (EI+): $[C_{15}H_{16}N_2O_7S_1Si_1\text{-}CH_3]^+$ requires 381.0213 found 381.0217. **υ$_{max}$**(ATR): 1184, 1348, 1382, 1537, 1557, 3099 , 3105, 3312 cm^{-1}.

Synthesis of 2-(trimethylsilyl)phenyl-4'-chlorobenzenesulfonate (22):



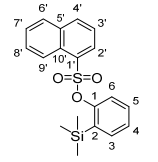
The product was purified by recrystallisation (ether : petroleum ether) as white crystalline powder (1 g, 89.9%, **mp** 114-115 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.28 (9H, s, CH_3) 7.08 (1H, dd, *J* = 8, 1 Hz, Ar-**H**$_6$) 7.20 - 7.27 (1 H, m, Ar-**H**$_4$) 7.27 - 7.34 (1H, m, Ar-**H**$_5$) 7.48 (1H, dd, *J* = 7, 2 Hz, Ar-**H**$_3$) 7.56 (2H, d, *J* = 8 Hz, Ar-**H**$_{3',5'}$) 7.92 (2H, d, *J* = 8 Hz, Ar-**H**$_{2',6'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.64 (Si-CH_3), 119.2 (**C**$_4$), 126.3 (**C**$_6$), 129.6 (**C**$_3$), 130.5 (**C**$_{2',6'}$), 132.5 (**C**$_{3',5'}$), 135.5, 136.0 (**C**$_5$), 140.6, 150.1, 155.0. **GC/MS** (EI+): $[M]^+$ 325. **Accurate Mass** (EI+): $[C_{15}H_{17}O_3S_1Si_1{}^{35}Cl_1\text{-}CH_3]^+$ requires 325.0116 found 325.0108. **υ$_{max}$**(ATR): 1176, 1376, 1442, 1589, 2954 cm^{-1}.

Synthesis of 2-(trimethylsilyl)phenyl benzenesulfonate (23):



Colourless oil (0.9 g, 89.9 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.28 (9H, s, CH_3) 7.10 (1 H, dd, *J* = 8, 1 Hz, Ar-**H**$_6$) 7.19 - 7.34 (2H, m, Ar-**H**$_4$) 7.48 (1H, dd, *J* = 7, 2 Hz, Ar-**H**$_3$) 7.56 - 7.63 (2H, m, Ar-**H**$_{3'}$) 7.68 - 7.74 (1H, m, Ar-**H**$_{4'}$) 8.00 (2H, dd, *J* = 7, 1 Hz, Ar-**H**$_{2'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.67 (Si-CH_3), 119.3 (**C**$_4$), 126.1(**C**$_6$), 128.2 (**C**$_{2'}$), 129.2 (**C**$_{3'}$), 130.5 (**C**$_3$), 132.5, 134.1 (**C**$_{4'}$), 135.8(**C**$_5$), 137.1, 155.1. **MS** (EI+): $[M]^+$ 307. **Accurate Mass** (EI+): $[C_{15}H_{17}O_3S_1Si_1\text{-}CH_3]^+$. requires 291.0506 found 291.0504 **Microanalysis:** $C_{15}H_{18}O_3SSi$ requires C 58.7; H 6.0; S 10.4%. Found C 58.7; H 6.4; S 10.4%. **υ$_{max}$**(ATR): 1193, 1371, 1431, 2954 cm^{-1}.

Synthesis of 2-(trimethylsilyl)phenyl naphthalene-1-sulfonate (24):



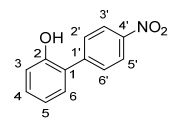
The product was purified by recrystallisation (DCM : petroleum ether) as white crystalline powder.(1.0 g, 85.5 %; **mp** 114-115 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δppm 0.34 (9H, s, CH_3) 6.67 (1H, dd, *J* = 7, 1.5 Hz, Ar-**H**$_6$) 7.11 - 7.23 (2H, m, Ar-**H**$_{4,5}$) 7.49 (1H, dd, *J* = 7, 2 Hz, Ar-**H**$_3$) 7.61 (1H, t, *J* = 8, Ar-**H**$_{7'}$) 7.69 (1H, t, *J* = 8, Ar-**H**$_{8'}$), 7.75 (1H, t, *J* = 7.00 Hz, Ar-**H**$_{3'}$) 8.01 (1H, d, *J* = 8 Hz, Ar-**H**$_{2'}$) 8.20 (1H, d, *J* = 8 Hz, Ar-**H**$_{4'}$) 8.31 (1 H, dd, *J* = 8, 1 Hz, Ar-**H**$_{6'}$) 8.81 (1H, d, *J* = 8 Hz, Ar-**H**$_{9'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.62 (Si-CH_3), 119.2 (**C**$_4$), 124.0, 125.1, 126.1 (**C**$_6$), 127.4 (**C**$_{3'}$), 128.4 (**C**$_{7'}$), 128.8 (**C**$_{2'}$), 129.9 (**C**$_{6'}$), 130.4, 132.9 (**C**$_3$), 133.3, 134.2, 135.5 (**C**$_{4'}$), 135.8 (**C**$_5$), 155.0. **MS** (EI+): $[M^+]$ 341. **Accurate Mass** (EI+): $[C_{19}H_{20}O_3S_1Si_1\text{-}CH_3]^+$ requires 341.0662 found 341.0655. **υ**$_{max}$(ATR): 1192, 1367, 1434, 1562, 2952 cm^{-1}.

General method for synthesis of bi-aryls:

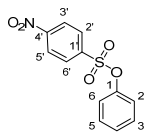
To a stirred solution of the sulfonate ester compound (1 eq.) and furan (3 eq.) in dry acetonitrile (12 mL), Tetrabutylammonium fluroide (1 M, 3 eq.) was added slowly. The reaction mixture was stirred at rt for sixteen hours and then poured into ether. The resulting mixture was washed with dilute HCl (3 N, 10 mL) and then with water (2 x 10 mL), dried over $MgSO_4$ and the reaction mixture taken to dryness *in vacuo.* Coloumn chromatography (silica, ether : petrol) afforded the *pure compound*.

Synthesis of 4'-nitro-[1,1'-biphenyl]-2-ol (25):[5]

The *title compound* was prepared by using general procedure using 2-(trimethylsilyl)phenyl-4'-nitrobenzenesulfonate **19**.



Fraction A: Column chromatography (silica, 10% ether,petroleum ether) afforded the *title compound* as bright yellow solid (44.4 %; **mp** 110.5-113 °C, Lit 107-108 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 5.28 (1H, s, OH) 6.97 (1H, dd, *J* = 8, 1 Hz, Ar-**H**$_3$) 7.03 - 7.10 (1 H, m, Ar-**H**$_4$) 7.28 - 7.37 (2H, m, Ar-**H**$_{5,6}$) 7.73 (2H, dd, *J* = 8, 2 Hz, Ar-**H**$_{2'6'}$) 8.31 (2H, dd, *J*=8, 2 Hz, Ar-**H**$_{3'5'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm 116.5 (**C**$_3$), 121.5 (**C**$_4$), 123.8 (**C**$_{3'5'}$), 126.1, 130.1 (**C**$_{2'6'}$), 130.2 (**C**$_5$), 130.5 (**C**$_6$), 144.6, 144.9, 152.4. **MS** (ES-): $[M^-]$: 214. **Accurate Mass** (ES-): $[C_{12}H_9O_3N_1\text{-}^1H]^-$ requires 214.0502 found 214.0509. **Microanalysis:** $C_{12}H_9N_1O_3$ requires C 66.9; H 4.2; N 6.5%. Found C 66.9; H 4.4; N 6.5%. **υ$_{max}$**(ATR): 1332, 1455, 1503, 1592, 3473 cm^{-1}.

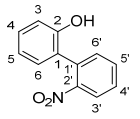


Fraction B: phenyl-4'-nitrobenzenesulfonate (31):[6]Coloumn chromatography (silica, 20% ether,petroleum ether) afforded the *title compound* as bright yellow solid (19%-36%**; **mp** 77-78 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 6.98 - 7.02 (2H, m, Ar-**H**$_{2,6}$) 7.29 - 7.38 (3H, m, Ar-**H**$_{3,4,5}$) 8.04 (2H, dd, *J* = 8, 2 Hz, Ar-**H**$_{2'6'}$) 8.38 (2H, dd, *J* = 8, 2 Hz, Ar-**H**$_{3'5'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm 122.1 (**C**$_{2,6}$), 124.3 (**C**$_{3'5'}$), 127.7(**C**$_4$), 129.8 (**C**$_{2'6'}$), 129.9 (**C**$_{3,5}$), 133.7, 141.0, 149.2. **υ**$_{max}$(ATR):1185, 1364, 1350, 1531, 1495, 1605 cm^{-1}

[5] J. C. Colbert and D. P. Denny, *J. Org. Chem*. 1959, **24,** 348. b) J. H. Chu, P. S. Li and M. J. Wu, *Organometallics* 2010, **29,** 4058.

Synthesis of 2'-nitro-[1,1'-biphenyl]-2-ol (26):[6]

The *title compound* was prepared by using general procedure using 2-(trimethylsilyl)phenyl-2'-nitrobenzenesulfonate (20)**.**



Coloumn chromatography (silica, 10% ether,petroleum ether) afforded the *title compound* as bright yellow solid (38.8 % ; **mp** 141-143 C°; Lit[8] 142-144 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 4.97 (1 H, br. s., OH), 6.85 (1 H, dd, J=8, 1 Hz, Ar-**H**$_3$), 7.06 (1 H, td, *J* = 7.5, 1 Hz, Ar-**H**$_5$), 7.22 - 7.34 (2H, m, Ar-**H**$_{4,6}$), 7.46 (1H, dd, *J* = 8, 1.5 Hz, Ar-**H**$_{6'}$), 7.53 (1H, td, *J* = 8, 1.5 Hz, Ar-**H**$_{5'}$), 7.68 (1H, t, *J* = 8 Hz, Ar-**H**$_{4'}$), 7.99 (1H, dd, J = 8, 1 Hz, Ar-**H**$_{3'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm 115.4 (**C**$_4$), 121.3 (**C**$_5$), 124.6 (**C**$_{5'}$), 125.1 (**C**$_{4'}$), 128.9 (**C**$_{3'}$), 130.1 (**C**$_6$), 132.4(**C**$_3$), 133.5 (**C**$_{6'}$), 149.2, 152.6. **MS (ES+):** $[M + Na]^+$ 238. MS (ES-): $[M^-]$ 214. **Accurate Mass** (ES-): $[C_{12}H_9O_3N_1\text{-}^1H]^-$ requires 214.0509 found 214.0515. **Microanalysis:** $C_{12}H_9N_1O_3$ requires C 66.9; H 4.2; N 6.5%. Found C 66.6; H 4.1; N 6.5%. **υ**$_{max}$(ATR): 1336, 1450, 1513, 1591, 3470 cm^{-1}

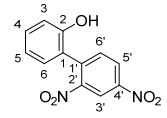
Table 1: Optimized reaction conditions for synthesis of bi-aryls (25), (26) and (15).

These bi-aryl forming reactions were optimised as follows:

Reactant	**Reaction conditions**	**%age Yield**	**%age Yield**
		biaryl (25)	**disylation (31)**
19 (1.0 eq)	TBAF (1.1 eq), dry acetonitrile, rt, 16 h	32%	36%
	TBAF (1.1 eq), furan (2 eq.), dry acetonitrile, rt, 16 h	33%	26.5%
	TBAF (2 eq), dry acetonitrile, rt, 16 h	35%	27%
	TBAF (3 eq), furan (3 eq.), dry acetonitrile, rt, 16 h	43%	17%
	TBAF (3 eq), dry acetonitrile, rt, 16 h	45%	19%
	TBAF (4 eq), dry acetonitrile, rt, 16 h	42.5%	21%
	CsF (2 eq), dry acetonitrile, rt, 16 h	nr	nr
	CsF (5 eq), dry acetonitrile, rt, 16 h	nr	nr
	CsF (5 eq), dry acetonitrile, reflux, 16 h	nr	nr
	TBAF (15% wt on alumina; 3 eq), , dry acetonitrile, rt, 16 h	nr	nr
	TBAT (2 eq.), dry acetonitrile, rt, 16 h	nr	nr
20 (1.0 eq)		**(26)**	**(32)**
	TBAF (1.1 eq), dry acetonitrile, rt, 16 h	26%	-
	TBAF (3 eq), dry acetonitrile, rt, 16 h	38.8%	-
	TBAF (3 eq), furan (3 eq.)dry acetonitrile, rt, 16 h	34.2%	-
	CsF (2 eq), dry acetonitrile, rt, 16 h	nr	nr
	CsF (5 eq), dry acetonitrile, rt, 16 h	nr	nr
	CsF (5 eq), dry acetonitrile, reflux, 16 h	nr	nr
12 (1.0 eq)		**(15)**	
	TBAF (1 eq), furan (3 eq.)dry acetonitrile, rt, 16 h	53%	-
	TBAF (2 eq), furan (3 eq.)dry acetonitrile, rt, 16 h	60%	-
	TBAF (3 eq), furan (3 eq.)dry acetonitrile, rt, 16 h	66%	-
	TBAF (3 eq),dry acetonitrile, rt, 16 h	74%	-

Synthesis of 2',4'-dinitro-[1,1'-biphenyl]-2-ol (27):[3b]

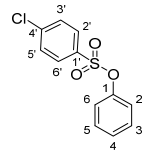
The *title compound* was prepared by using general procedure using 2-(trimethylsilyl)phenyl-2'-nitrobenzenesulfonate (21).



Coloumn chromatography (silica, 5% ether,petroleum ether) afforded the *title compound* as yellow solid (49 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 5.15 (1H, br. s., OH), 6.85 (1H, dd, J=8, 1 Hz, Ar-**H**$_3$), 7.15 (1H, td, *J* = 7.5, 1 Hz, Ar-**H**$_5$), 7.30 - 7.44 (2H, m, Ar-**H**$_{4,6}$), 7.68 (H, d, *J* = 8, Ar-**H**$_{6'}$), 8.5 (1H, dd, *J* = 8, 2 Hz, Ar-**H**$_{5'}$), 8.85 (1H, d, *J* = 2 Hz, Ar-**H**$_{3'}$). **υ**$_{max}$(ATR): 1346, 1528, 1607, 3465 cm^{-1}

4-Chlorophenylbenzenesulfonate (33):[7]

The *title compound* was prepared by using general procedure using **2**-(trimethylsilyl)phenyl-4'-chlorobenzenesulfonate (22**)**.



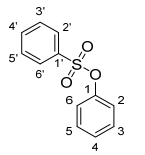
Coloumn chromatography (silica, 15% ether,petroleum ether) afforded the compound as white solid.(0.400 g, 74.6%; mp 97-98 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δppm 6.98 - 7.03 (2H, d, *J* = 7, Ar-**H**$_{2,6}$) 7.28 - 7.34 (3H, m, Ar-**H**$_{3,4,5}$) 7.52 (2H, d, *J* = 8 Hz, Ar-**H**$_{3,'5'}$) 7.78 (2H, d, *J* = 8 Hz, Ar-**H**$_{2'6'}$). **^{13}C NMR** (300 MHz, *CDCl$_3$*) δ ppm 122.2 (**C**$_{2,6}$), 127.3 (**C**$_{3,5}$), 129.5 (**C**$_{3',5'}$), 129.7 (**C**$_4$), 129.8(**C**$_{2'6'}$) , 133.8, 140.9, 149.4. **υ**$_{max}$(ATR): 1377, 1397, 1455, 1585, 3057 cm^{-1}. **MS** (EI+):$[M^+]$ 268. **Accurate Mass** (EI+): $C_{12}H_9O_3{}^{35}Cl_1S_1$ requires 267.9955 found 267.9951.

[6] J. H. Choi, B. C. Lee, H. W. Lee and I. Lee, *J. Org. Chem*. 2002, **67**, 1277.

[7] W. Cabri, S. D. Bernardinis, F. Francalanci, S. Penco, R. Santi, *J. Org. Chem*. 1990, **55**, 350.

Phenyl benzenesulfonate (34):[5]

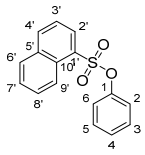
The *title compound* was prepared by using general procedure using 2-(trimethylsilyl)phenyl benzenesulfonate (23).



Column chromatography (silica, 15% ether : petroleum ether) afforded the *title compound* as an oil (0.410, 87.6%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.01 (2H, dd, *J* = 8, 2 Hz, Ar-$\mathbf{H}_{2,6}$) 7.27 - 7.32 (4H, m, Ar-$\mathbf{H}_{3,5,\ 3',5'}$) 7.54 (1H, t, *J* = 8 Hz, Ar-$\mathbf{H}_4$) 7.69 (1H, t, *J* = 7.5 Hz, Ar-$\mathbf{H}_{4'}$) 7.85 (2H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{2',6'}$). **^{13}C NMR** (300 MHz, $CDCl_3$) δ ppm 122.3($\mathbf{C}_{2,6}$), 127.1($\mathbf{C}_4$), 128.4($\mathbf{C}_{2',6'}$), 129.0($\mathbf{C}_{3',5'}$), 129.6 ($\mathbf{C}_{3,5}$), 134.1($\mathbf{C}_{4'}$), 135.4, 149.6. **MS** (EI+): [M^+] 234.1. **Accurate Mass** (EI+): $C_{12}H_{10}O_3S_1$ requires 234.0345 found 234.0347.**υ** $_{max}$(ATR): 1197, 1371, 1448, 1487, 3067 cm^{-1}.

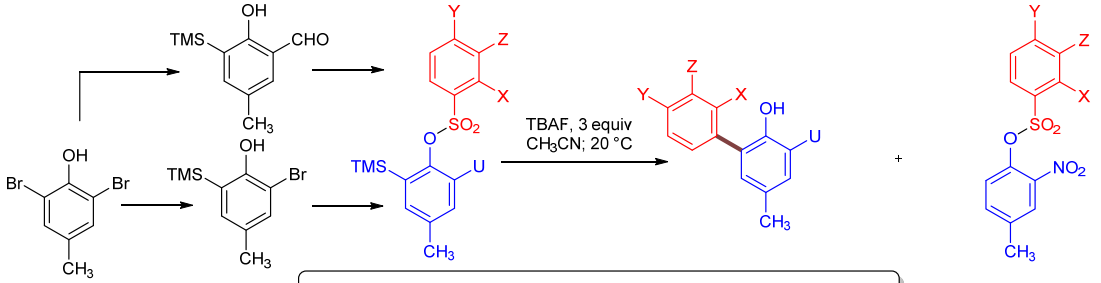
Phenyl naphthalene-1'-sulfonate (35):[6]

The *title compound* was prepared by using general procedure using 2-(trimethylsilyl)phenyl naphthalene-1-sulfonate (24).



Column chromatography (silica, 15% ether,petroleum ether) afforded the *title compound* as white solid (0.285, 84%; mp 114-116 °C). **^{1}H NMR** (300 MHz, *$CDCl_3$*) δ ppm 6.85 - 6.90 (2H, m, Ar-$\mathbf{H}_{2,6}$) 7.17 - 7.20 (3H, m, Ar-$\mathbf{H}_{3,4,5}$) 7.47 (1H, t, *J* =8 Hz, Ar-$\mathbf{H}_{8'}$) 7.69 (1H, t, *J* = 7.5 Hz, Ar-$\mathbf{H}_{3'}$) 7.80 (1H, t, *J* = 8 Hz, Ar-$\mathbf{H}_{7'}$) 8.00 (1H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{2'}$) 8.10 (1 H, dd, *J* = 7.5, 1 Hz, Ar-$\mathbf{H}_{6'}$) 8.14 (1 H, d, *J* = 8 Hz, Ar-$\mathbf{H}_{4'}$) 8.85 (1 H, d, *J*=8.5 Hz, Ar-$\mathbf{H}_{9'}$). **^{13}C NMR** (75 MHz, *$CDCl_3$*) δ ppm 122.0 ($\mathbf{C}_{2,6}$), 123.9 ($\mathbf{C}_{8'}$), 125.1 ($\mathbf{C}_{9'}$), 127.1 ($\mathbf{C}_4$), 127.3 ($\mathbf{C}_{3'}$), 128.5 ($\mathbf{C}_{2'}$), 128.9 ($\mathbf{C}_{7'}$), 129 ($\mathbf{C}_{3,5}$), 129.5, 130.8 ($\mathbf{C}_{6'}$), 131.2, 134, 135.6 ($\mathbf{C}_{4'}$). **MS** (EI+): [M^+] 284.1. **Accurate Mass**(+EI): $C_{16}H_{12}O_3S_1$ requires 284.0502 found 284.050.**υ** $_{max}$(ATR): 1133, 1365, 1586, 1485, 3063 cm^{-1}.

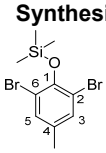
iv. Truce-Smile rearrangements – more highly functionalised substrates



36; X = Z = H; Y = NO_2; U = Br
37; X = Z = H; Y = NO_2; U = CHO
41; X = Z = H; Y = NO_2; U = Br (63%)
42; X = Z = H; Y = NO_2; U = CHO (71%)

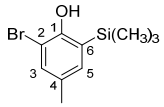
38; X = Z = H; Y = CF_3; U = NO_2
39; Y = Z = H; X = CO_2Me; U = NO_2
40; X = Y = H; Z = NO_2; U = NO_2
43 X = Z = H; Y = CF_3; U = NO_2 (0%)
44; Y = Z = H; X = CO_2Me; U = NO_2 (0%)
45; X = Y = H; Z = NO_2; U = NO_2 (0%)
46 X = Z = H; Y = CF_3 (nd)[a]
47; Y = Z = H; X = CO_2Me (nd)[a]

Synthesis of (2,6-dibromo-4-methylphenoxy)trimethylsilane:



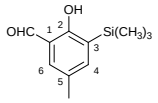
The phenol (1.1 mmol, 1.1 eq.) was refluxed with 1,1,1,3,3,3-hexamethyldisilazane (3.3 mmol, 3 eq.) for 3 hours. After cooling down the reaction mixture was concentrated *in vacuo* to give pure *title compound* as a pale yellow oil. 97.8% yield. **^{1}H NMR** (500 MHz, *CDCl$_3$*) δ ppm 0.38 (9H, s, Si-CH_3) 2.25 (3H, s, **C**-CH_3) 7.29 (2H, s, Ar-**H**$_{3,5}$). **^{13}C NMR** (125 MHz, *CDCl$_3$*) δ ppm 1.25 (Si-CH_3), 19.9 (**C**-CH_3), 115.6, 132.8 (**C**$_{3,5}$), 133.3, 148.3. **MS** (EI+): [M^+] 335.9, 337.8. **Accurate Mass** (+EI): $C_{10}H_{14}O_1{}^{79}Br_2Si_1$ requires 335.9175 found 335.9165. **υ$_{max}$**(ATR): 1534, 1580, 1604, 2962, 3401 cm^{-1}.

Synthesis of 2-bromo-4-methyl-6-(trimethylsilyl)phenol:[8]



To the stirred solution of (2,6-dibromo-phenoxy)trimethylsilane (0.507 g, 1.5 mmol, 1 eq.) in THF (50 mL), *t*-Butyllithium (1.7 M in pentane, 3.53 mL, 6 mmol, 4 eq.) was added at -78 °C over 10 min. The reaction mixture was stirred for 2 hrs and upon recooling to -78 °C quenched with water. The reaction mixture was allowed to warm to room temperature and then poured into ether (50 mL) and washed with brine (3 x 50 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (silica; ether : petroleum ether 20 : 80) to afford the *title compound* as oil (0.29 g, 74.4 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.32 (9H, s, Si-CH_3), 2.28 (3H, s, C-CH_3), 5.56 (1H, s, OH), 7.10 (1H, s, Ar-H_3), 7.30 (1H, s, Ar-H_5). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -1.1 (Si-CH_3), 20.2 (C-CH_3), 110.0, 126.6, 130.9, 133.1 (**C**$_5$), 135.1 (**C**$_3$), 153.6. **υ$_{max}$**(ATR): 1268, 1301, 1386, 1417, 1650, 3101 cm^{-1}

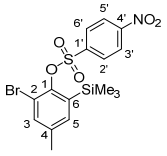
Synthesis of 2-hydroxy-5-methyl-3-(trimethylsilyl)benzaldehyde:[9]



A solution of (2,6-dibromo-4-methylphenoxy)trimethylsilane (1.0 g, 3.0 mmol, 1 eq.) in dry THF (10 mL) was cooled to -78 °C and treated slowly with *t*-BuLi (7.6 mL,12.0 mmol, 4 eq.) under nitrogen. At -78 °C stirred the reaction mixture for two hours and then at rt for one hour. Upon recooling the reaction mixture to -78 °C DMF (1.0 mL, 12 mmol, 4 eq.) was added all at once. The reaction mixture was stirred for 1 hour while warming to 0 °C and then quenched by adding saturated ammonium chloride (3 mL). The reaction mixture was allowed to room temperature and then extracted it with ethyl acetate (2 x 15 mL). The organic phase was washed with water, brine, and dried over $MgSO_4$ and the reaction mixture taken to dryness *in vacuo*. The product obtained as light yellow colour solid which is used without further purification (0.504, 80.4%; **mp** 60-61 °C, Lit[9] 61 °C). **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ ppm 0.32 (9H, s, Si-C**H**$_3$) 2.34 (3H, s, C-C**H**$_3$) 7.33 (1H, d, *J* = 2 Hz, Ar-**H**$_4$) 7.42 (1H, d, *J* = 2 Hz, Ar-**H**$_6$) 9.84 (1H, s, C**H**O) 11.14 (1H, s, OH). **^{13}C NMR** (125 MHz, *CDCl$_3$*) δ ppm -0.96 (Si-CH_3), 20.6 (C-CH_3), 119.5, 128.8, 134.8 (**C**$_4$), 144.0(**C**$_6$), 164.6, 192.1. **MS** (ES-): [M$^-$] 207.06. **Accurate Mass** (EI-): $C_{11}H_{16}O_2Si_1$–^{1}H requires 207.0840 found 207.0841. **Microanalysis:** $C_{11}H_{16}O_2Si_1$ requires C 63.4; H 7.7%. Found C 63.2; H 7.7%. **υ$_{max}$**(ATR): 3147, 2946, 2831, 2739, 1640, 1619, 1586, 1400, 1319,cm^{-1}.

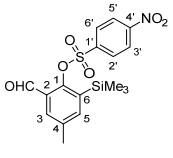
Sulfonate esters (36)-(40) were prepared using the general methid as described above.

2-Bromo-4-methyl-6-(trimethylsilyl)phenyl-4'-nitrobenzenesulfonate (36):



Column chromatography (silica, 10% ether, Petrol) afforded the compound as oil (1.18 g, 89 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.45 (9H, s, Si-CH_3) 2.34 (3H, s, C-CH_3) 7.29 (1H, s, Ar-**H**$_3$) 7.31 (1H, s, Ar-**H**$_5$) 8.15 (2H, d, *J* = 8 Hz, Ar-**H**$_{2'6'}$) 8.40 (2H, d, *J* = 8 Hz, Ar-**H**$_{3',5'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm 0.26 (Si-CH_3), 20.5 (C-CH_3), 116.3, 124.1(**C**$_{3',5'}$), 130.1(**C**$_{2'6'}$), 135.4(**C**$_3$), 136.3, 138.1, 138.5, 142.8 (**C**$_5$), 148.1, 150.9. **MS** (ES+): [M+Na]$^+$ 466. **Accurate Mass** (ES+): $C_{16}H_{18}O_5$ $^{79}Br_1S_1Si_1Na_1$ requires 465.9777 found 465.8956. **υ**$_{max}$(ATR): 1233, 1369, 1501, 1574, 1599, 3012 cm^{-1}.

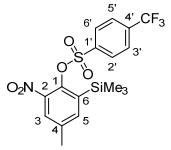
2-Formyl-2-6-(trimethylsilyl)phenyl-4'-nitrobenzenesulfonate (37):



Column chromatography (silica, 10% ether, Petrol) afforded the compound as yellow solid (1.0 g, 77 %, **mp** 107-109 °C). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.41 (9H, s, Si-CH_3) 2.43 (3H, s, CH_3) 7.60 (1H, s, Ar-**H**$_5$) 7.62 (1H, s, Ar-**H**$_3$) 8.08 (2H, d, *J* = 9 Hz, Ar-**H**$_{2',6'}$) 8.43 (2H, d, *J* = 9 Hz, Ar-**H**$_{3',5'}$) 9.67 (s, 1H, CHO). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.25(Si-CH_3), 20.36 (CH_3), 124.2 (**C**$_{3',5'}$), 129.6 (**C**$_{2',6'}$), 130.4 (**C**$_3$), 130.8, 136.9, 137.8, 140.2, 142.8(**C**$_5$), 151.1, 151.6, 186.7. **MS** (ES+): [M+Na]$^+$ 416.4; [M+NH_4]$^+$ 411.1. **Accurate Mass** (ESI+): [$C_{17}H_{19}O_6S_1Si_1N_1$ + NH_4]$^+$ requires 411.1046 found 411.1040. **υ$_{max}$**(ATR): 1161, 1237, 1460, 1585, 1681, 2829 cm^{-1}.

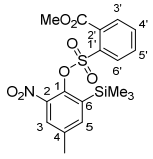
[8] F.i. Carroll, T. P. Robinson, L. E. Brieaddy, R. N. Atkinson, S. Wayne, M. I. Damaj, B.R. Martin and H. A. Navarro, *J. Med. Chem*, 2007, **50,** 6383.
[9] A. N. Thandi, Y. Huang and V. H. Rawal, *Org. Lett.* 2007, **9**, 3873.

2-Nitro-4-methyl-6-(trimethylsilyl)phenyl-4'-(trifluoromethyl)benzenesulfonate (38):



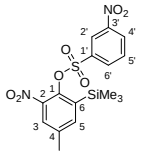
Column chromatography (silica, 10% ether, Petrol) afforded the compound as oil (1.25 g, 85 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.43 (9H, s, Si-CH$_3$) 2.45 (3H, s, CH$_3$) 7.56 (1H, dd, *J* = 1.5, 0.75 Hz, Ar-**H**$_5$) 7.67 (1H, s, Ar-**H**$_3$) 7.88 (2H, d, *J* = 8 Hz, Ar-**H**$_{2',6'}$) 8.11 (2H, d, *J* = 8 Hz, Ar-**H**$_{3',5'}$). **^{13}C NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.06 (Si-CH$_3$), 20.7 (C-CH$_3$), 126.5, 126.6 (**C**$_3$), 126.9 (**C**$_{2',6'}$), 127.0, 129.2(**C**$_{3',5'}$), 138.1, 140.9, , 141.1(**C**$_5$), 143.7, 144.4. **MS** (ES+): [M$^+$] 455.9. **Accurate Mass**(+ESI): $C_{17}H_{18}O_5S_1Si_1N_1{}^{19}F_3Na_1$ requires 456.0519 found 456.0508. **υ$_{max}$**(ATR): 1130, 1234, 1257, 1307, 1569, 1581, 1601, 2921 cm^{-1}.

Methyl 2-((4-methyl-2-nitro-6-(trimethylsilyl)phenoxy)sulfonyl)benzoate (39):



Column chromatography (silica, 10% ether, Petrol) afforded the compound as oil (1.05 g, 80 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.42 (9H, s, Si-CH$_3$) 2.43 (3H, s, C-CH$_3$) 3.85 (3H, s, OCH$_3$) 7.54 (1H, d, *J* = 2 Hz, Ar-**H**$_5$) 7.58 (1H, d, *J* = 2 Hz, Ar-**H**$_3$) 7.64 - 7.80 (3H, m, Ar-**H**$_{4',5',6'}$) 7.99 (1H, dd, *J* = 8, 0.75 Hz, Ar-**H**$_{3'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.07 (Si-CH$_3$), 20.7 (C-CH$_3$), 53.2 (OCH$_3$), 126.7 (**C**$_3$), 127.1, 129.7, 130.0 (**C**$_{3'}$), 131.1, 133.3, 134.3, 137.6, 139.4, 139.3, 140.8 (**C**$_5$), 142.8, 143.6, 166.6. **MS** (ES+): [M$^+$] 445.9. **Accurate Mass**(+ESI): $C_{18}H_{21}O_7S_1Si_1N_1Na_1$ requires 446.0757 found 446.0689. **υ$_{max}$**(ATR): 1131, 1230, 1470, 1595, 1701, 2835 cm^{-1}

4-Methyl-2-nitro-6-(trimethylsilyl)phenyl 3-nitrobenzenesulfonate (40):

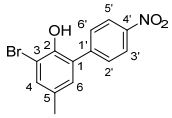


Column chromatography (silica, 10% ether, Petrol) afforded the compound as oil (1.1 g, 83 %). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 0.45 (9H, s, Si-CH$_3$) 2.45 (3H, s, C-CH$_3$) 7.57 (1H, d, *J* = 2 Hz, Ar-**H**$_5$) 7.64 (1H, d, *J* = 2 Hz, Ar-**H**$_3$) 7.85 (1H, t, Ar-**H**$_{5'}$) 8.30 (1H, dd, *J* = 8, 1.5 Hz, Ar-**H**$_{6'}$) 8.60 (1H, dd, *J* = 8, 1.5 Hz, Ar-**H**$_{4'}$) 8.76 (1H, t, *J* = 2 Hz, Ar-**H**$_{2'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm -0.08 (Si-CH$_3$), 20.7 (C-CH$_3$), 126.9 (**C**$_3$), 129.1 (**C**$_{2'}$), 130.9, 133.9(**C**$_{4'}$), 137.5(**C**$_{5'}$), 138.3(**C**$_{6'}$), 139.2, 141.1,141.2 (**C**$_5$), 143.4, 148.2.

General method for synthesis of bi-aryls:

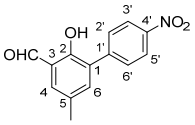
To a stirred solution of the sulfonate ester compound (1 eq.) and furan (3 eq.) in dry acetonitrile (12 mL), Tetrabutylammonium fluroide (1 M, 3 eq.) was added slowly. The reaction mixture was stirred at rt for sixteen hours and then poured into ether. The resulting mixture was washed with dilute HCl (3 N, 10 mL) and then with water (2 x 10 mL), dried over $MgSO_4$ and the reaction mixture taken to dryness *in vacuo.* Coloumn chromatography (silica, ether : petrol) afforded the *pure compound*.

Synthesis of 3-bromo-5-methyl-4'-nitro-[1,1'-biphenyl]-2-ol (41):



Column chromatography (silica, 10% ether,petroleum ether) afforded the compound as bright yellow solid (0.401 g, 63 % ; **mp** 177-179 C°). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δ ppm 2.34 (3H, s, CH$_3$) 5.65 (1H, s, OH) 7.10 (1H, d, *J* = 1.5 Hz, Ar-**H**$_6$) 7.36 (1H, d, *J* = 1.5 Hz, Ar-**H**$_4$) 7.73 (2H, d, *J* = 8.5 Hz, Ar-**H**$_{2'6'}$) 8.27 (2H, d, *J* = 8.5 Hz, Ar-**H**$_{3'5'}$). **^{13}C NMR** (75 MHz, *CDCl$_3$*) δ ppm 20.2 (CH$_3$), 111.3, 123.4 (**C**$_{3'5'}$), 126.7 (**C**$_4$), 130.0 (**C**$_{2'6'}$), 130.1, 131.6, 132.6, 144.3 (**C**$_6$), 146.9, 147.0. **MS** (ES-): [M$^-$] 306.0. **Accurate Mass** (ESI-): $C_{13}H_9O_3N_1{}^{79}Br_1{}^{-1}H$ requires 305.9771 found 305.9760. **Microanalysis:** $C_{13}H_{10}N_2O_3Br$ requires C 50.7; H 3.3; N 4.5%. Found C 50.7; H 3.5; N 4.5%. **υ**$_{max}$(ATR): 1237, 1348, 1468, 1514, 1573 cm^{-1}.

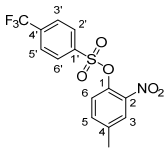
Synthesis of 2-hydroxy-5-methyl-4'-nitro-[1,1'-biphenyl]-3-carbaldehyde (42):



Column chromatography (silica, 10% ether,petroleum ether) afforded the compound as bright yellow solid (0.364 g, 71 % ; **mp** 167-169 C°). **^{1}H NMR** (300 MHz, *CDCl$_3$*) δppm 2.43 (3H, s, CH$_3$) 7.43 - 7.48 (2H, m, Ar-**H**$_{4,6}$) 7.78 (2H, d, *J* = 8.5 Hz, Ar-**H**$_{2'6'}$) 8.29 (2H, d, *J* = 8.5 Hz, Ar-**H**$_{3'5'}$) 9.94 (1H, s, CHO) 11.47 (1 H, s, OH). **^{13}C NMR** (300 MHz, *CDCl$_3$*) δ ppm 20.3 (CH$_3$), 120.8, 123.4 (**C**$_{3'5'}$), 127.7 (**C**$_4$), 129.5 (**C**$_{2'6'}$), 130.1, 134.4, 138.5, 143.2 (**C**$_6$), 147.1, 156.7, 196.7 (CHO). **MS** (ES-): [M$^-$] 256.0. **Accurate Mass** (ESI-): $C_{14}H_{10}O_4N_1$ requires 256.0615 found 256.0604. **υ**$_{max}$(ATR): 1245, 1334, 1376, 1530, 1544, 1597, 1650, 2961, 3112 cm^{-1}.

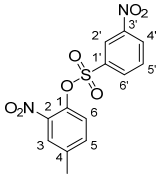
The following protodesilylated products compounds were isolated/observed from failed Truce-Smiles rearrangements.

4-Methyl-2-nitrophenyl 4'-(trifluoromethyl)benzenesulfonate (46):



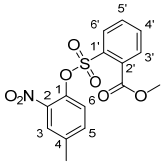
^{1}H NMR (300 MHz, *CDCl$_3$*) δppm **(crude)** 2.33 (3H, s, CH$_3$) 7.08 (1H, d, *J* = 8.5 Hz, Ar-**H**$_6$) 7.38 (1H, dd, *J* = 8.5, 2 Hz, Ar-**H**$_5$) 7.57 (2H, d, *J* = 8 Hz, Ar-**H**$_{2',6'}$) 7.87 (1 H, s, Ar-**H**$_3$) 8.02 (2 H, d, *J* = 8 Hz, Ar-**H**$_{3',5'}$).

4-Methyl-2-nitrophenyl 3'-nitrobenzenesulfonate:



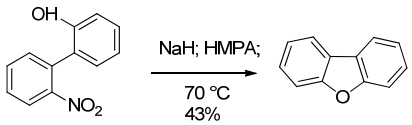
^{1}H NMR (300 MHz, *CDCl$_3$*) δppm **(crude)** 2.39 (3 H, s, CH$_3$) 7.10 (1H, d, *J* = 8.5 Hz, Ar-**H**$_6$) 7.44 (1H, dd, *J* = 8.5, 2 Hz, Ar-**H**$_5$) 7.56 (1H, t, *J* = 8 Hz, Ar-**H**$_{5'}$) 7.94 (1H, s, Ar-**H**$_3$) 8.22 (1H, d, *J* = 9 Hz, Ar-**H**$_{6'}$) 8.33 (1H, d, *J* = 8 Hz, Ar-**H**$_D$) 8.79 (1H, t, *J* = 2 Hz, Ar-**H**$_{2'}$).

Methyl 2-((4-methyl-2-nitrophenoxy)sulfonyl)benzoate (47):



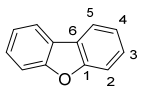
^{1}H NMR (300 MHz, *CDCl$_3$*) δ ppm **(crude)** 2.34 (3H, s, C-C**H**$_3$) 3.90 (3H, s, O-C**H**$_3$) 7.06 (1H, d, *J* = 8.5 Hz, Ar-**H**$_6$) 7.30 - 7.44 (4H, m, Ar-**H**$_{5,4',5',6'}$) 7.89 (1H, s, Ar-**H**$_3$) 8.05 (1H, d, *J* = 8 Hz, Ar-**H**$_3$').

v. Synthesis of dibenzofuran, (48)



26 **48**

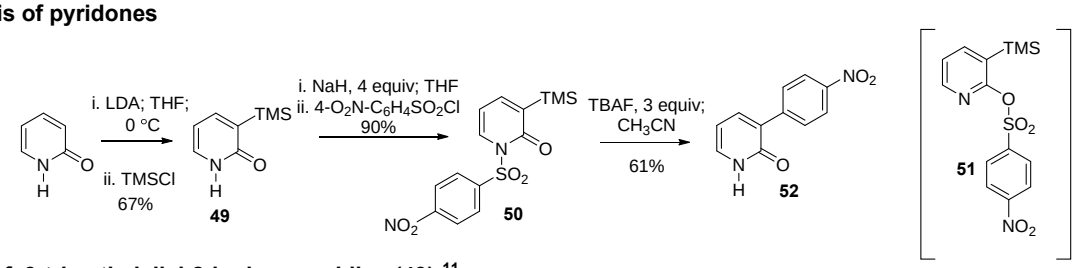
Synthesis of Dibenzofuran (48):[10]



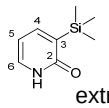
A solution of 2'-nitro-[1,1'-biphenyl]-2-ol, (**26**), (0.215 g, 1.0 mmol) in hexamethylphosphoric triamide (1.5 mL) was added to a stirred solution of sodium hydride (0.072 g, 3.0 mmol) in hexamethylphosphoric triamide (2.0 mL). The reaction mixture was heated at 70 °C for 24 hrs and then allawed to cool to room temperature. 5% HCl was added to the reaction mixture and then extracted with diethyl ether. The organic layer was dried and concentrated *in vacuo*. The crude product was purified by column chromatography (20:80 ether-petroleum ether) afforded the *title compound,* (**48**)*,* as white powder (43%; **mp** 80-81°C Lit[10] **mp** 83.5). **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ ppm 7.37 (2H, td, *J* = 8, 1 Hz, Ar-**H**$_4$) 7.49 (2H, td, *J* = 8, 1 Hz, Ar-**H**$_3$) 7.61 (2H, d, *J* = 8 Hz, Ar-**H**$_2$) 7.99 (2H, dd, *J* = 7.5, 0.76 Hz, Ar-**H**$_5$).**^{13}C NMR** (125 MHz, *CDCl$_3$*) δ ppm 111.6 (**C**$_2$), 120.6 (**C**$_5$), 122.6 (**C**$_4$), 124.2 (**C**$_3$), 127.1, 156.2.

[10] A. F. Sierakowski*, Aust. J. Chem*. 1983, **36**, 1281.

vi. Synthesis of pyridones

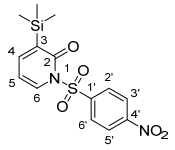


Synthesis of 3-trimethylsilyl-2-hydroxypyridine (49):[11]



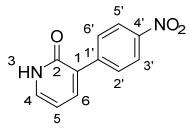
To a stirred solution of 2-hydroxypyridine (10 g, 105 mmol) in THF (250 mL) at 0 °C was added Lithium diisopropylamide (2 M, 115 mL, 231 mmol) over 15 min under nitrogen. The solution was stirred at 0 °C for 15 min and for 1 hour while warming to room temperature. Upon recooling to 0 °C chlorotrimethylsilane (15 mL, 115 mmol) was added dropwise to the reaction mixture. The solution was allowed to stir overnight at room temperature. The THF was evaporated and extracted with ethyl acetate. The organic phase was washed with water, brine, and dried over $MgSO_4$ and the reaction mixture taken to dryness *in vacuo.* The product obtained as off-white solid (11.8 g, 67%; **mp** 93-94 °C; Lit[11] 91-92 °C) after flash chromatography (ethyl acetate). **^{1}H NMR** (400 MHz, *CDCl$_3$*) δ ppm 0.28 (9H, s, CH_3) 6.24 (1H, t, *J* = 6.5 Hz, Ar-**H**$_5$) 7.37 (1H, dd, *J* = 6.5, 2 Hz, Ar-**H**$_4$) 7.55 (1H, dd, *J* = 6.5, 2 Hz, Ar-**H**$_6$) 12.90 (1 H, br. s., OH). **^{13}C NMR** (125 MHz, *CDCl$_3$*) δ ppm -1.55(Si-CH_3), 106.9 (**C**$_5$), 131.8 (**C**$_6$), 135.8 (**C**$_4$), 147.6, 168.0. **MS** (ES+): $[M+Na]^+$ 190.4. **Accurate Mass** (ES+): $C_8H_{13}N_1O_1Si_1Na_1$ requires 190.664 found 190.0670. **υ$_{max}$**(ATR): 1241, 1429, 1465, 1536, 1616, 2951 cm^{-1}.

Synthesis of 3-(trimethylsilyl)pyridin-2-yl-4-nitrobenzenesulfonate (50):



The *title compound* was prepared by using general procedure as above. 4-nitrobenzenesulfonylchloride (0.728 g, 3.31 mmol, 1.1 eq) was added to the reaction mixture of 3-(trimethylsilyl)pyridine-2-ol (0.505 g, 3.01 mmol, 1 eq.) and sodium hydride (0.288 g, 12.04 mmol) in THF (50 mL). Column chromatography (silica, 10% ether, Petrol) afforded the compound as yellow crystalline solid (1.05 g, 90 %; **mp** 164-166 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.16 (9H, s, CH_3) 6.28 - 6.32 (1H, m, Ar-**H**$_5$) 7.45 (1H, dd, *J* = 6, 2 Hz, Ar-**H**$_6$) 8.04 (1 H, dd, *J*=7.57, 2.02 Hz, Ar-**H**$_4$) 8.30 (2H, d, *J* = 9 Hz, Ar-**H**$_{2'6'}$) 8.39 (2H, d, *J* = 9 Hz, Ar-**H**$_{3'5'}$). **^{13}C NMR** (125 MHz, *CDCl$_3$*) δ ppm -1.98 (CH_3), 107.3 (**C**$_5$), 123.9 (**C**$_{3'5'}$), 131.0 (**C**$_{2'6'}$), 132.0 (**C**$_4$), 136.4, 142.5, 147.8, 150.9 (**C**$_6$), 162.1. **MS** (EI+): $[M^+]$ 353.4. **Accurate Mass** (ES+): $C_{14}H_{16}O_5S_1Si_1N_2Na_1$ requires 375.0447 found 375.0431 **Microanalysis:** $C_{14}H_{16}O_5S_1Si_1N_2$ requires C 47.7; H 4.6; N 7.9; S 9.1%. Found C 47.5; H 4.6; N 7.7; S 8.9%.**υ** $_{max}$(ATR): 1162, 1334, 1367, 1530, 1600, 1656, 2953 cm^{-1}.

Synthesis of 3-(4-nitrophenyl)pyridin-2(1H)-one (52):[12]

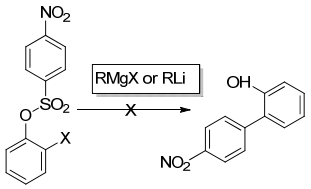


Following the general method for bi-aryl synthesis, column chromatography (silica, 15% ether,petroleum ether) of the reation between (**50**) and TBAF afforded the compound as bright yellow solid (0.266 g, 61.4%; **mp** 187-189 C°). **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ ppm 6.35 - 6.40 (1H, m, Ar-**H**$_5$) 7.52 (1H, dd, *J* = 6.5, 2 Hz, Ar-**H**$_4$) 7.87 (1H, dd, *J* = 7, 2 Hz, Ar-**H**$_6$) 8.07 (2H, d, *J* = 9 Hz, Ar-**H**$_{2'6'}$) 8.24 (2H, d, *J* = 9 Hz, Ar-**H**$_{3'5'}$) 12.06 (1H, br. s.). **^{13}C NMR** (75 MHz, DMSO-*d*$_6$) δ ppm 105.6 (**C**$_5$), 123.1 (**C**$_{3'5'}$), 127.2, 128.9 (**C**$_{2'6'}$), 136.7 (**C**$_5$), 140.6 (**C**$_6$), 143.4, 146.1, 160.8(**C**$_2$). **MS** (ES+): $[M^+]$ 217.4; **Accurate Mass** (ES+): $C_{11}H_9N_2O_3$ requires 217.0613 found 217.0628. **υ**$_{max}$(ATR): 1247, 1328, 1499, 1556, 1591, 1658, 2792 cm^{-1}.

[11] F.I. Carroll, T. P. Robinson, L. E. Brieaddy, R. N. Atkinson, S. Wayne, M. I. Damaj, B.R. Martin and H. A. Navarro, *J. Med. Chem*. 2007, **50**, 6383.

[12] J. Witherington, V. Bordas, A. Gaiba, A. Naylor, N. Parr, D. G. Smith, A. K. Takle and R. W. Ward, *Bioorg and Med. Chem. Lett.* 2006, **16**, 2256.

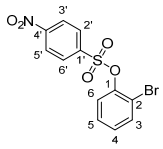
vii. Attempted halogen metal excahnge reactions on (53) and (54).



53; X = Br
54; X = I

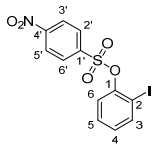
25

Synthesis of 2-bromophenyl 4'-nitrobenzenesulfonate (53)[13]



2-bromophenol (1.5 g, 8.67 mmol) was added to a stirred suspension of sodium hydride (0.550 g, 17.34 mmol) in dry THF (15 mL). After 40 minutes 4-nittrobenzenesulphonylchloride (2.114 g, 9.55 mmol) was slowly added in dry THF (13 mL). the reaction mixture was stirred at room temperature for two hours. After this reaction mixture was poured into ether (50 mL) and washed with water. The organic layer was dried and concentrated *in vacuo.* The crude product was purified by recrystalisation (petroleum ether) afforded the *title compound* as brown solid (2.055 g, 76%).^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.03 - 7.07 (1H, m) 7.40 - 7.43 (2H, m) 7.78 (1 H, d, *J*=8.07 Hz) 8.14 (2 H, dd, *J*=8.83, 1.77 Hz) 8.40 (2 H, dd, *J*=8.83, 2.02 Hz). υ_{max}(ATR): 1390, 1534, 1608, 3109 cm^{-1}.

Synthesis of 2-iodophenyl 4'-nitrobenzenesulfonate (54):[3b]



2-iodophenol (1.89 g, 8.67 mmol) was added to a stirred suspension of sodium hydride (0.550 g, 17.34 mmol) in dry THF (15 mL). After 40 minutes 4-nittrobenzenesulphonylchloride (2.114 g, 9.55 mmol) was slowly added in dry THF (13 mL). the reaction mixture was stirred at room temperature for two hours. After this reaction mixture was poured into ether (50 mL) and washed with water. The organic layer was dried and concentrated *in vacuo.* The crude product was purified by recrystalisation (petroleum ether) afforded the *title compound* as brown solid (1.141 g, 82%).

^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 6.99 - 7.09 (1H, m) 7.38 - 7.45 (2H, m) 7.78 (1H, d, *J* = 7.3 Hz, Ar-**H**$_3$) 8.14 (2H, dd, *J* = 8.8, 2.2 Hz, Ar-**H**$_{2'}$) 8.40 (2H, dd, *J* = 8.8, 2.2 Hz, Ar-**H**$_{3'}$).**^{13}C NMR** (125 MHz, *CDCl$_3$*) δ ppm 89.5, 123.2, 124.3, 129.0, 129.9, 130.3, 140.3, 141.3, 149.5, 151.2. υ_{max}(ATR): 1394, 1578, 1615, 3106 cm^{-1}.

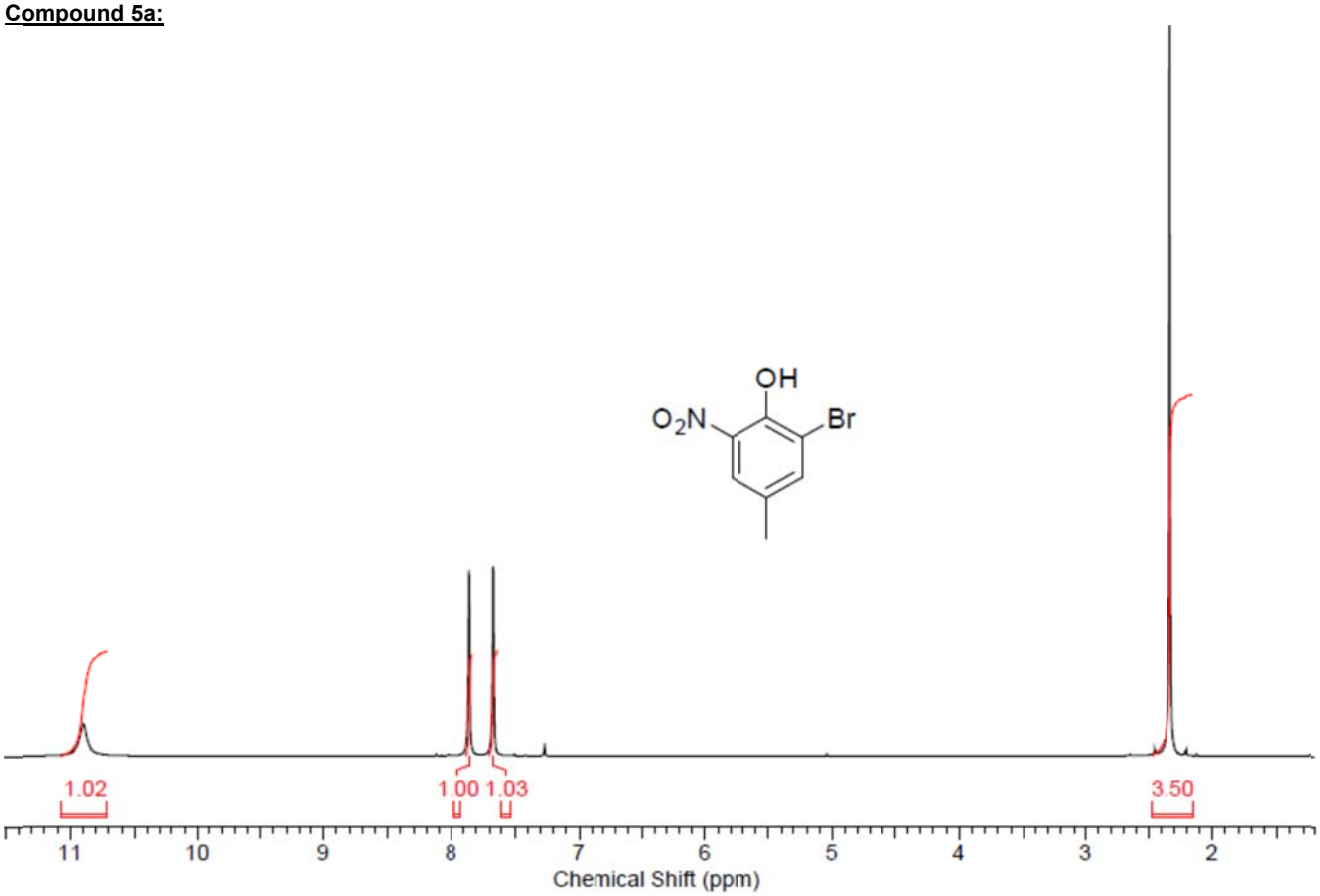
Attempted Truce Smiles reactions using (53) and (54).

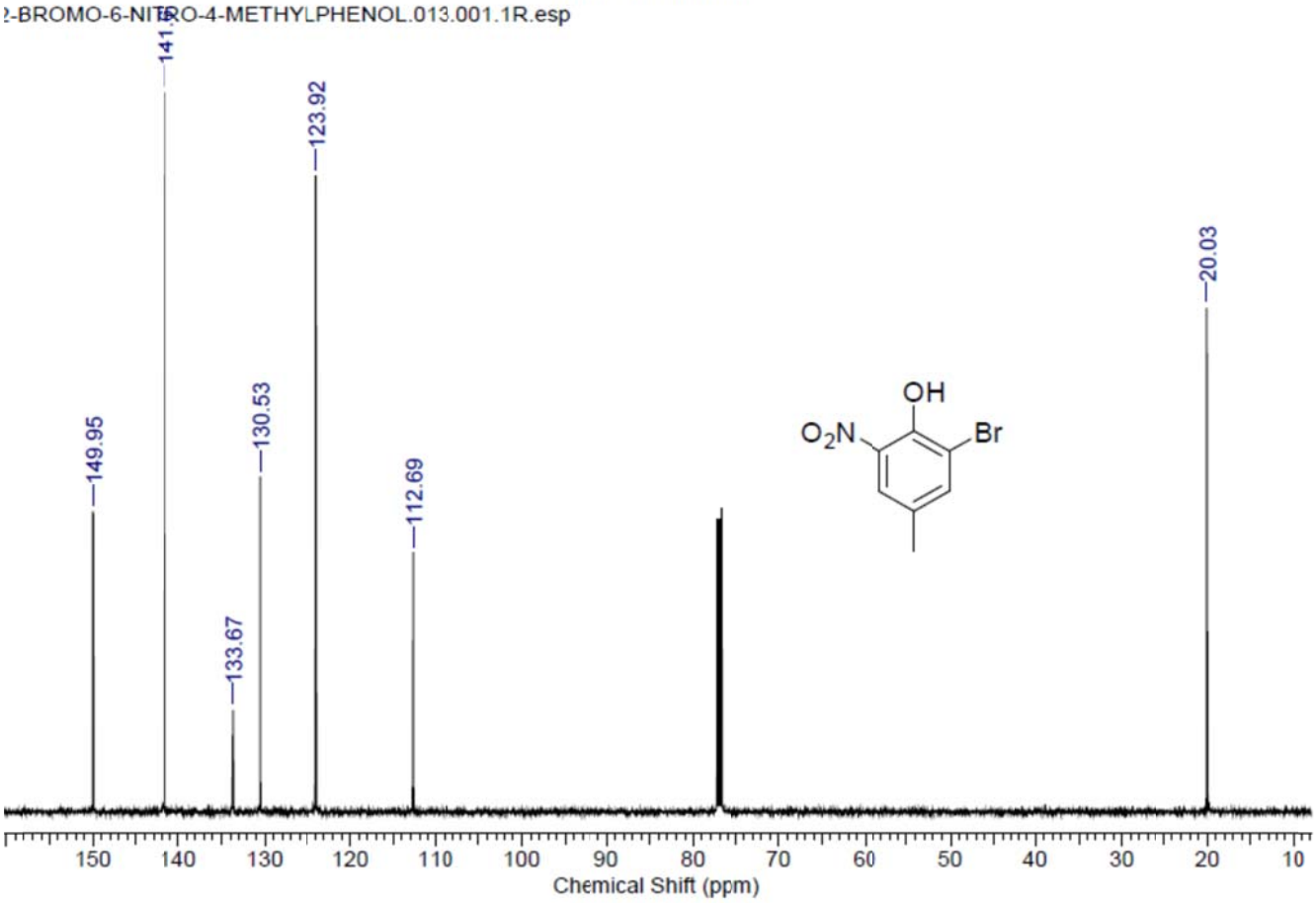
Reaction of either 2-iodophenyl 4'-nitrobenzenesulfonate or 2-bromophenyl 4'-nitrobenzenesulfonate with PhLi (2 eq.) or *iso*-propylmagnesium chloride (1.5 eq. 2M THF solution) at -78 °C in THF, under an atmosphere of nitrogen, for 1 hour afforded none of the desired rearranged products as judged by an examination of the ^{1}H NMR sprectra of the crude reaction mixtures.

[13] R. L. Dannley and W. R. Knipple, *J. Org. Chem.* 1973, **3***8,* 6.

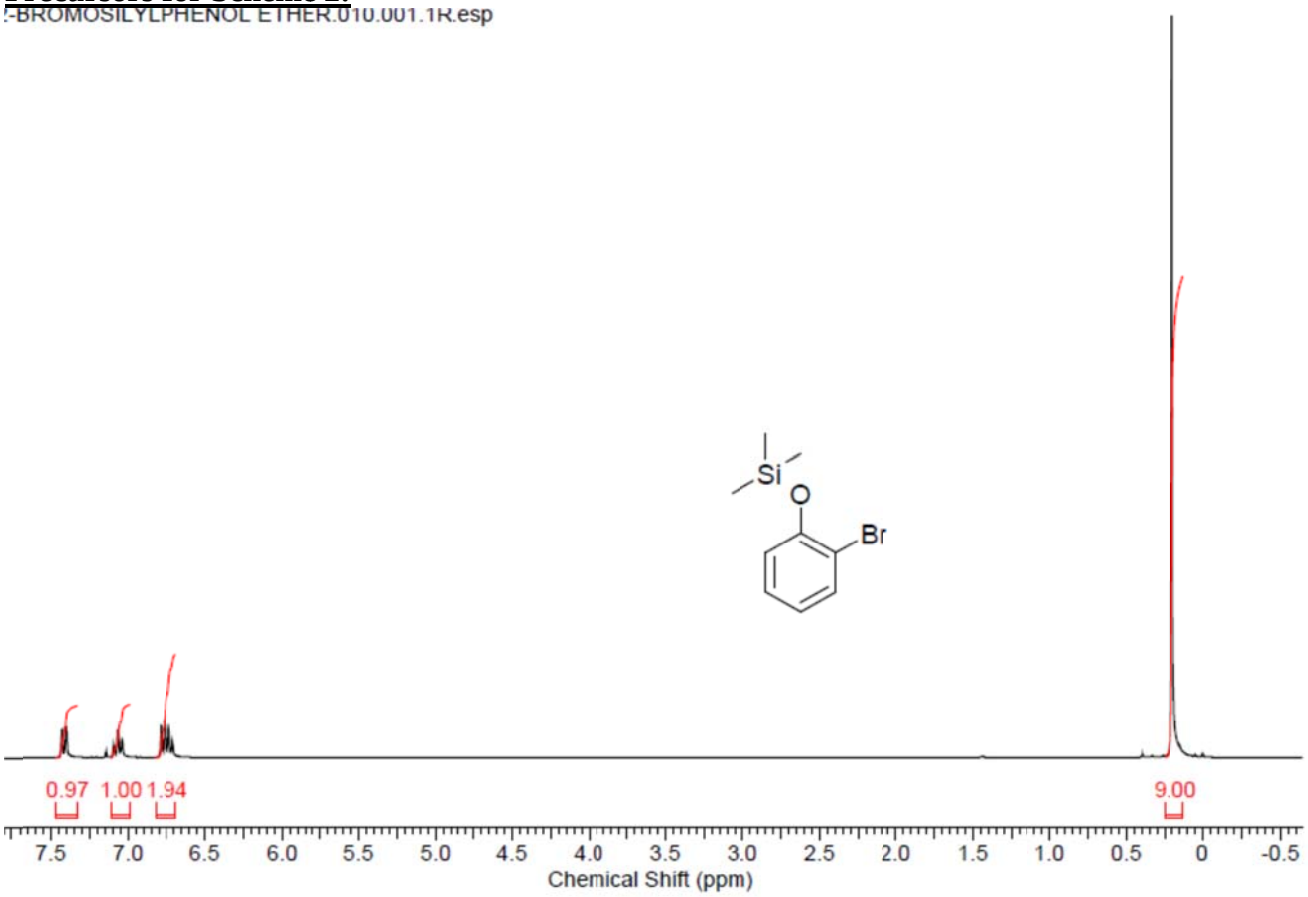
Part B: Spectroscopic data

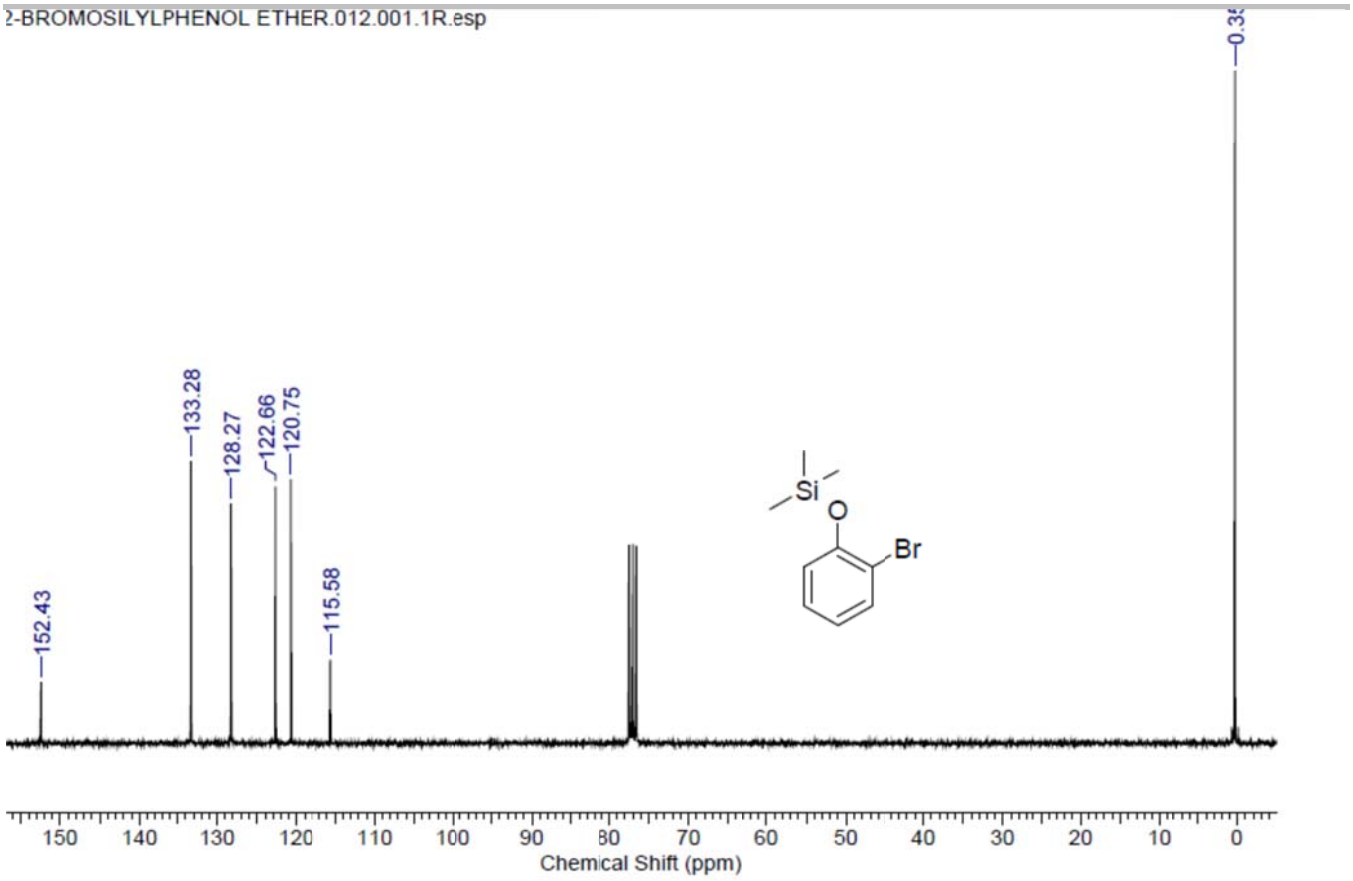
Compound 5a:


OH
O2N
Br
1.02
1.00
1.03
3.50
11
10
9
8
7
6
5
4
3
2
Chemical Shift (ppm)

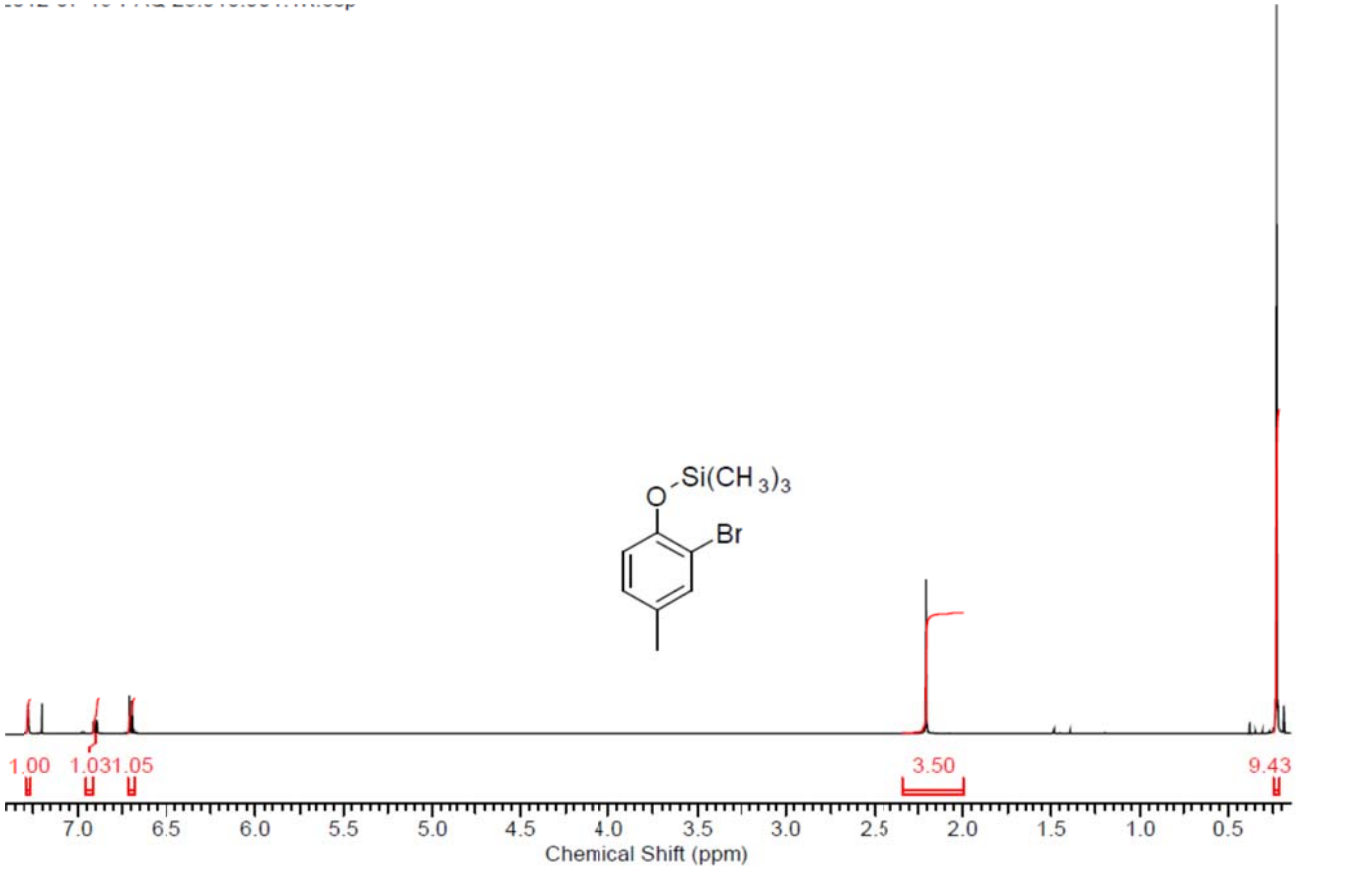

2-BROMO-6-NITRO-4-METHYLPHENOL.013.001.1R.esp
141.
123.92
149.95
130.53
133.67
112.69
20.03
OH
O2N
Br
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

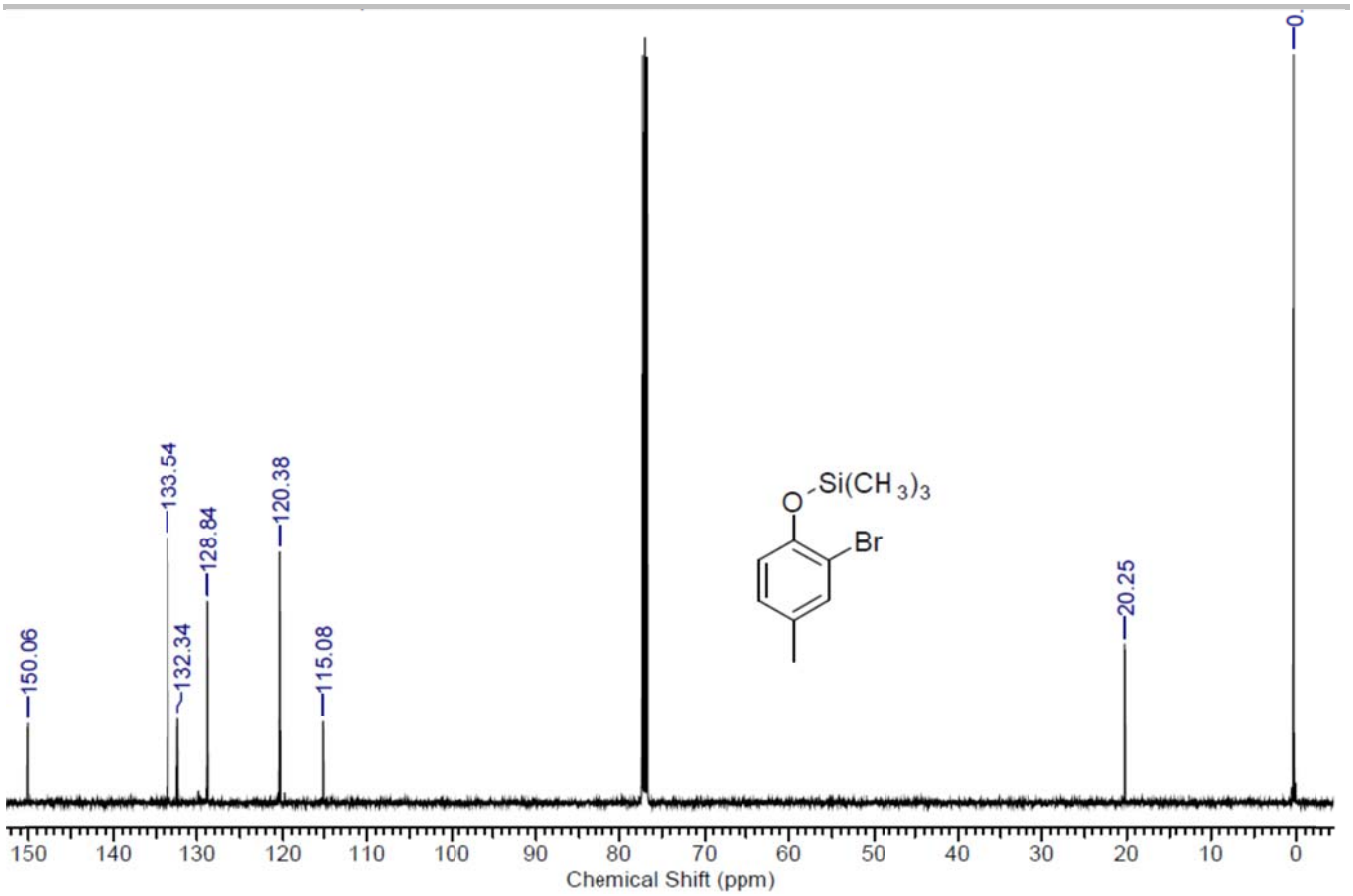
Precursors for Scheme 2:



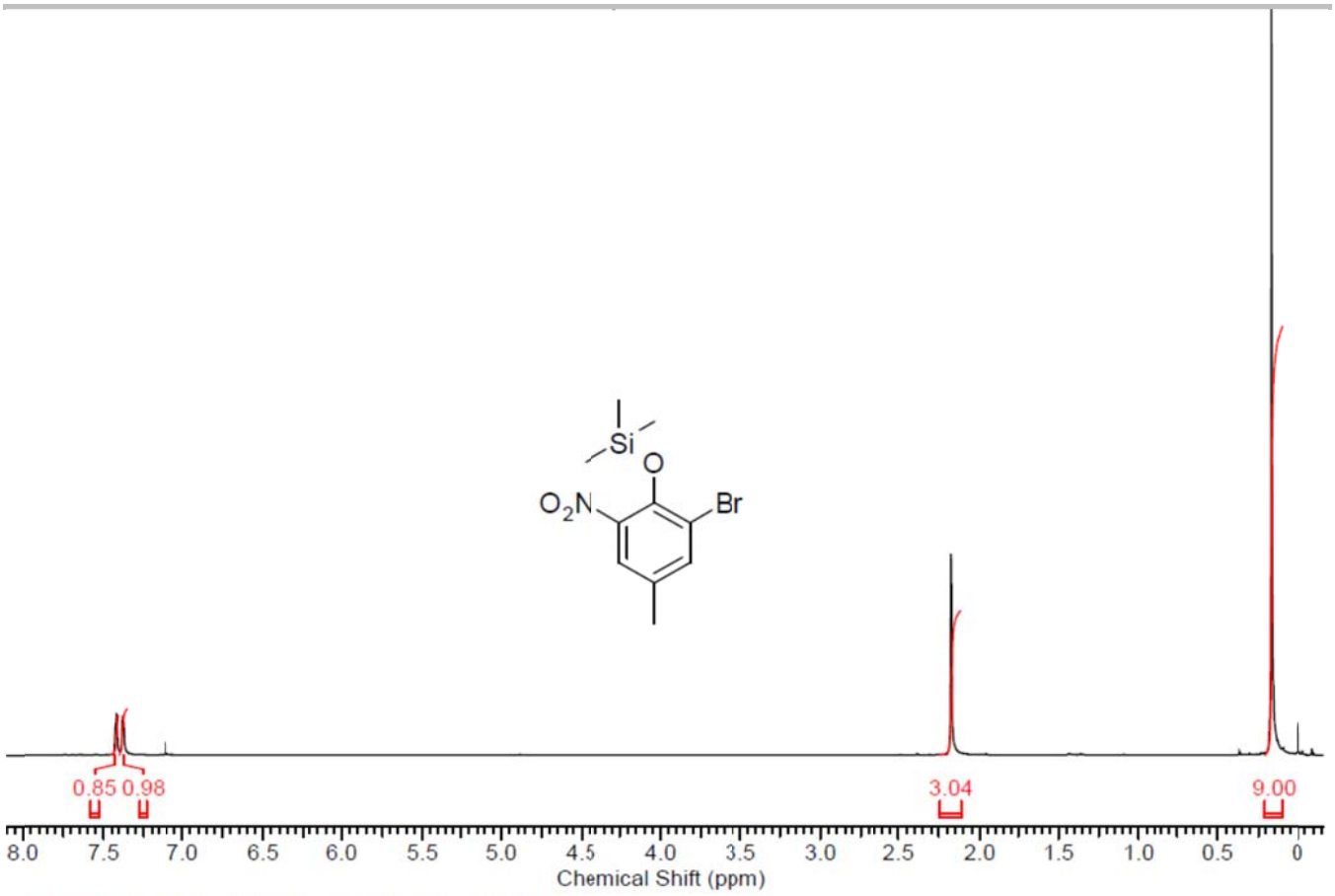


Precursors for Scheme 2:

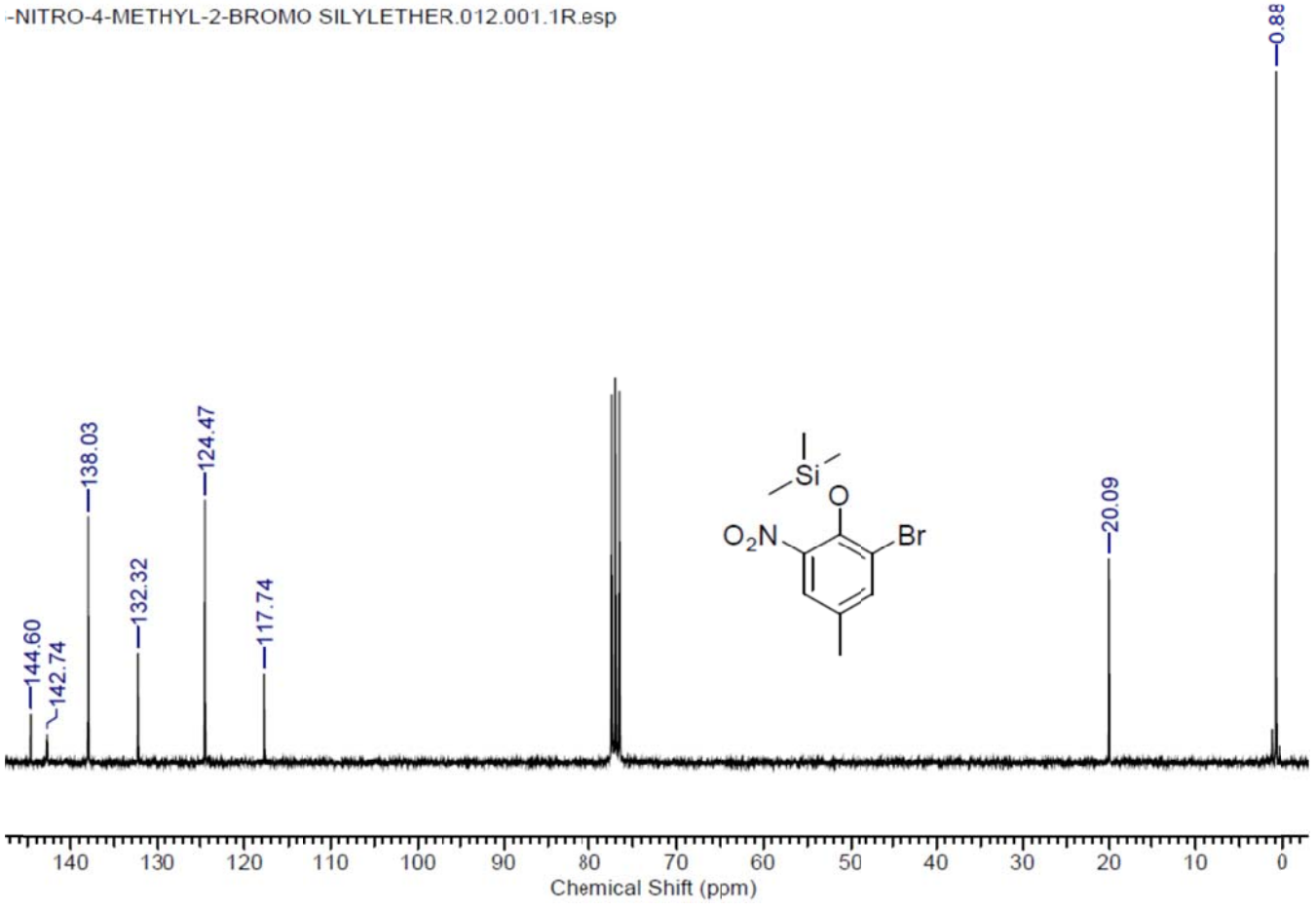



150.06
133.54
132.34
128.84
120.38
115.08
20.25
0
Si(CH3)3
O
Br
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

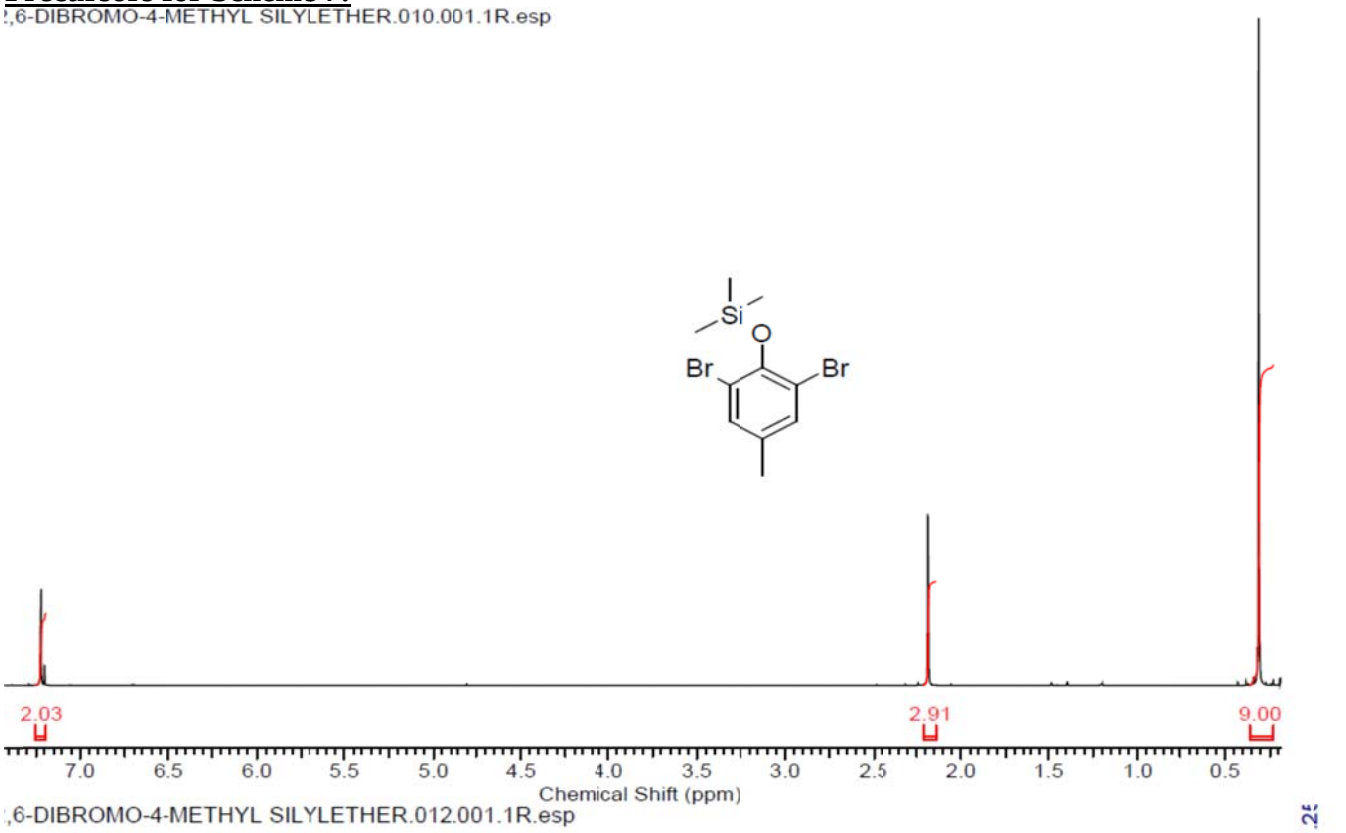
Compound 5:

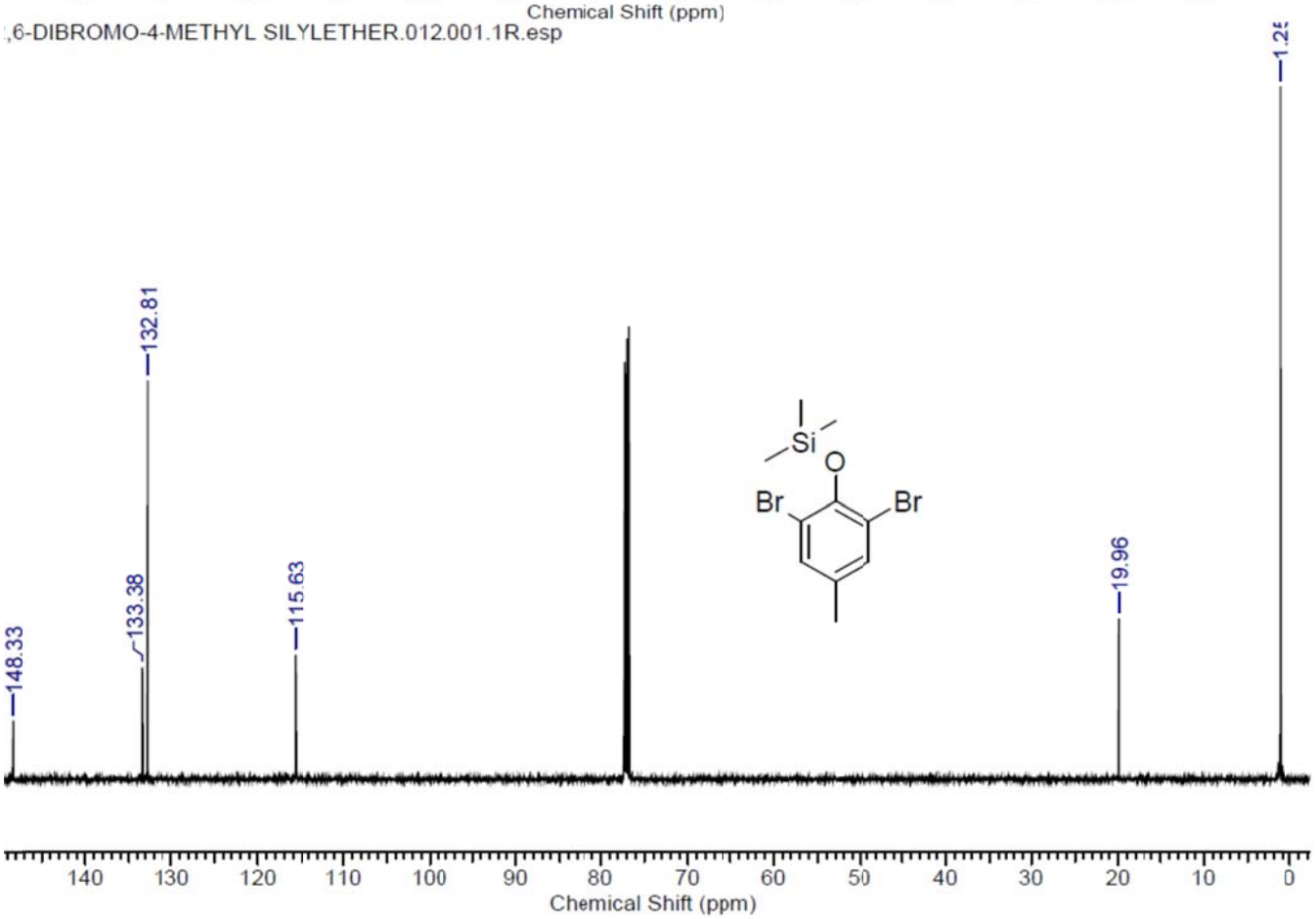


-NITRO-4-METHYL-2-BROMO SILYLETHER.012.001.1R.esp

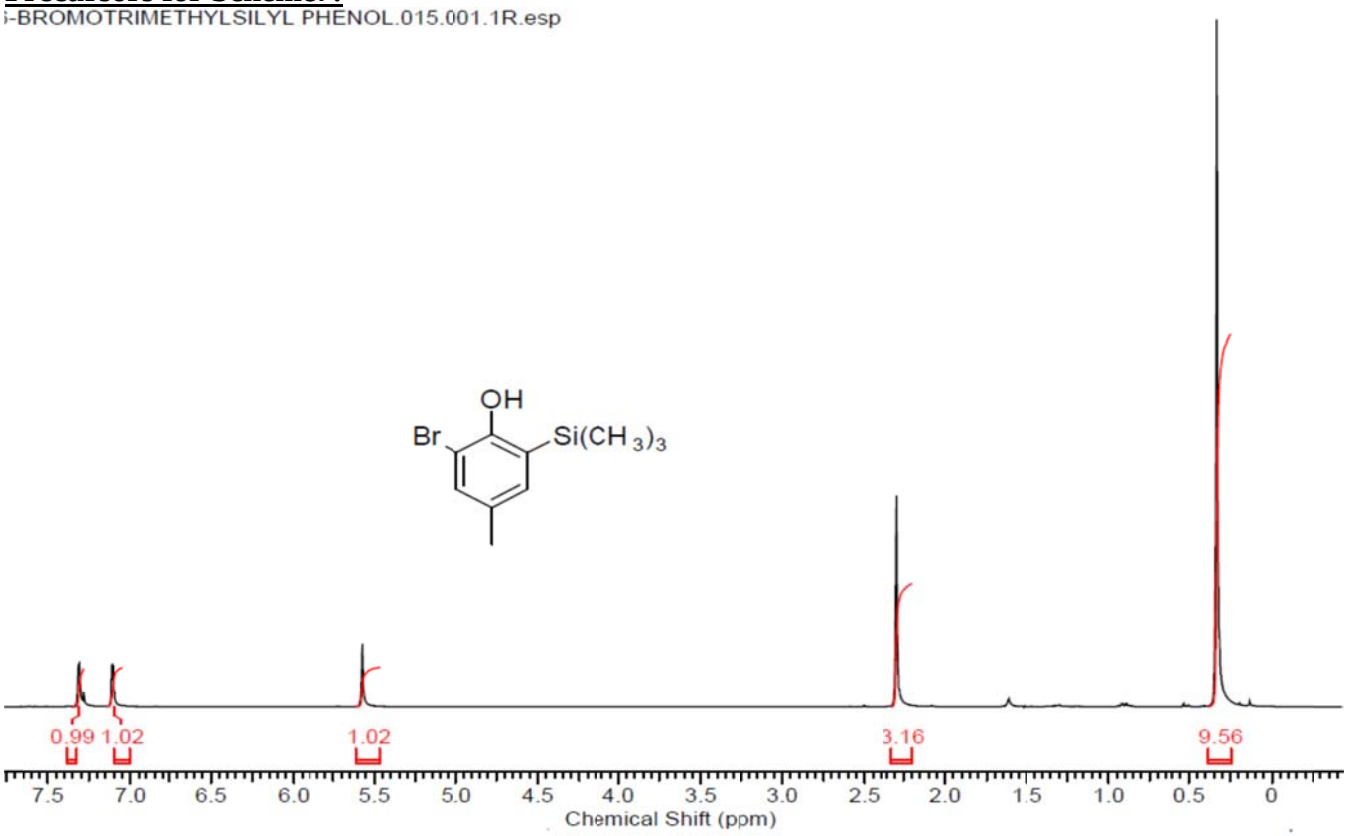


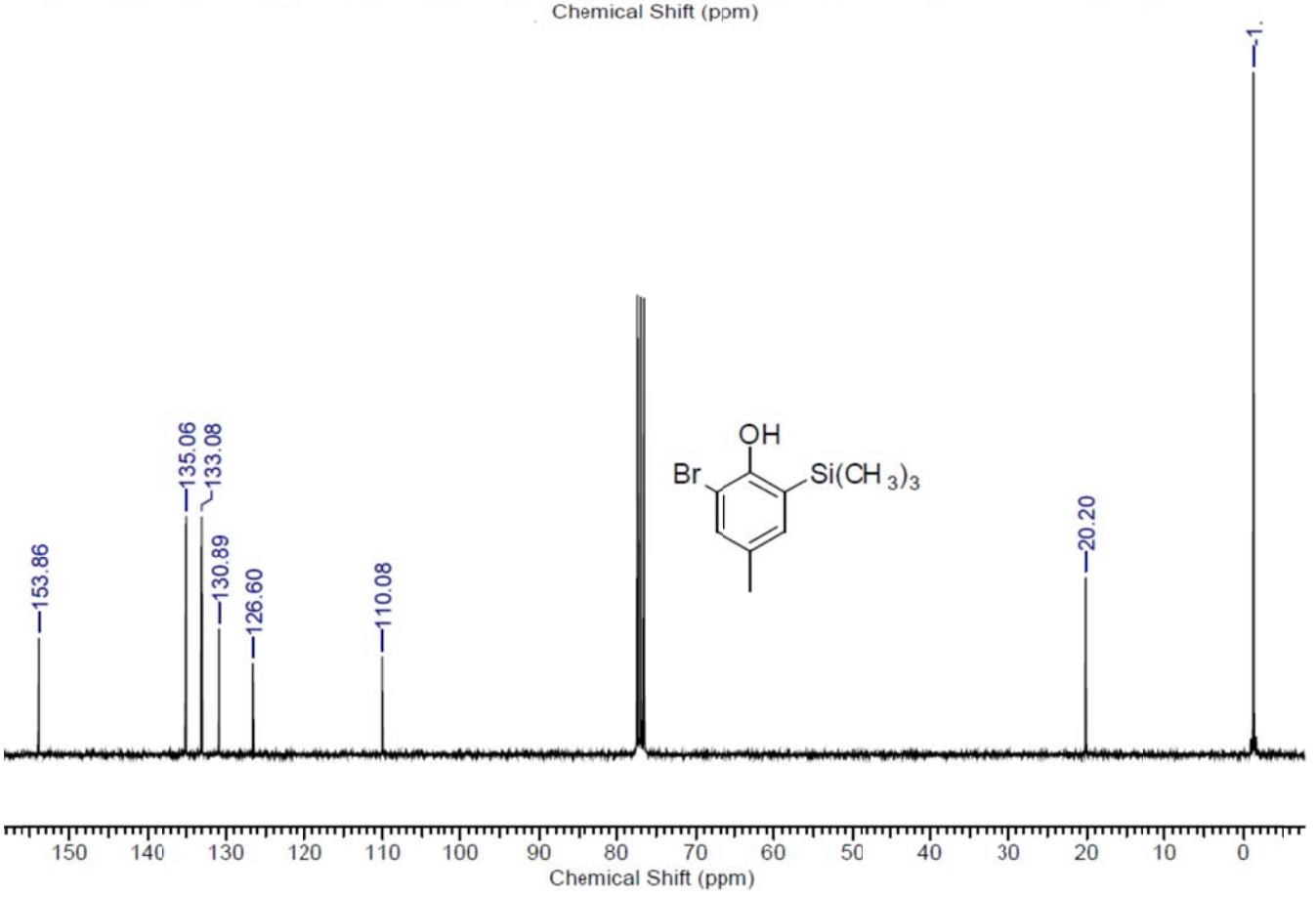
Precursors for Scheme 7:



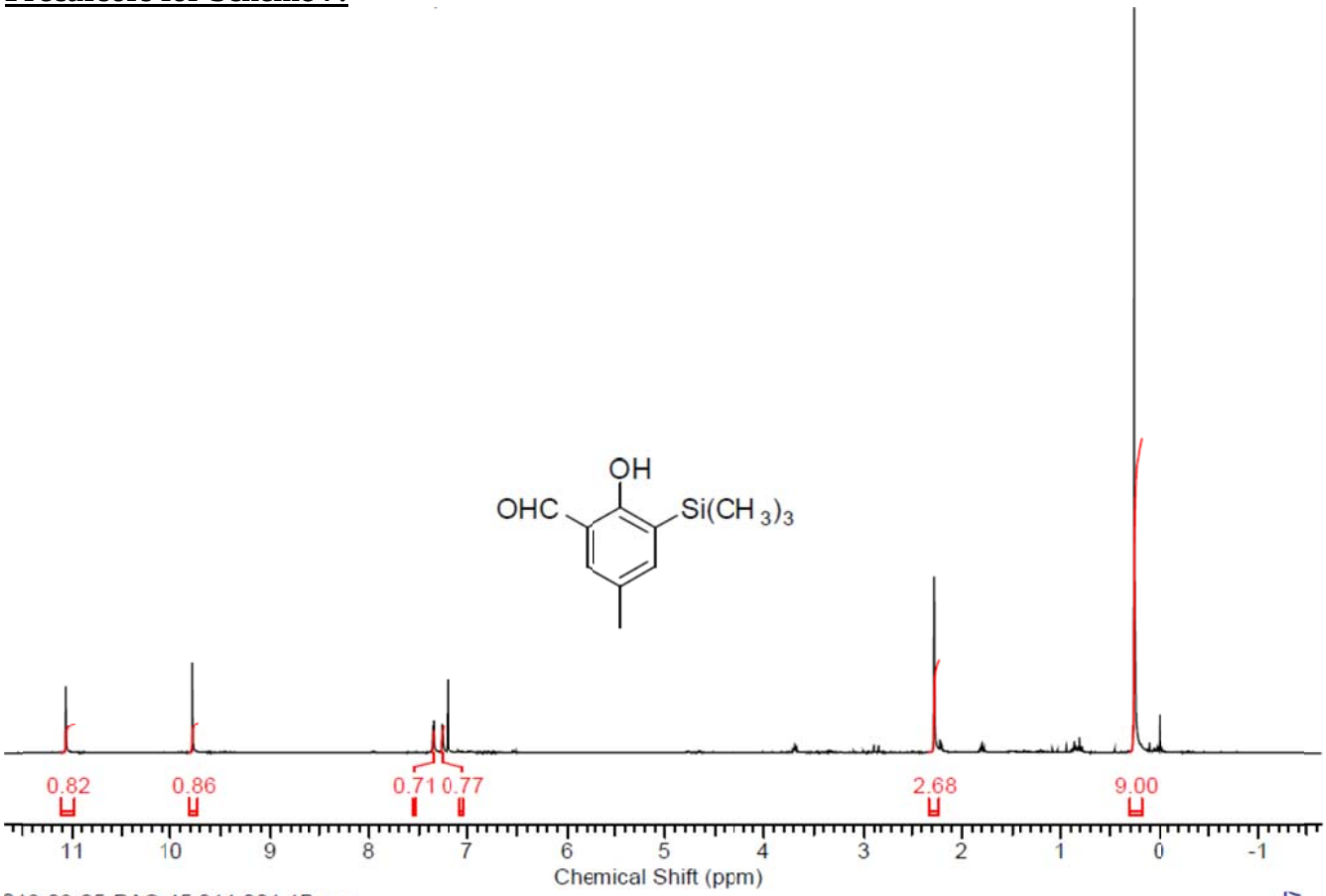


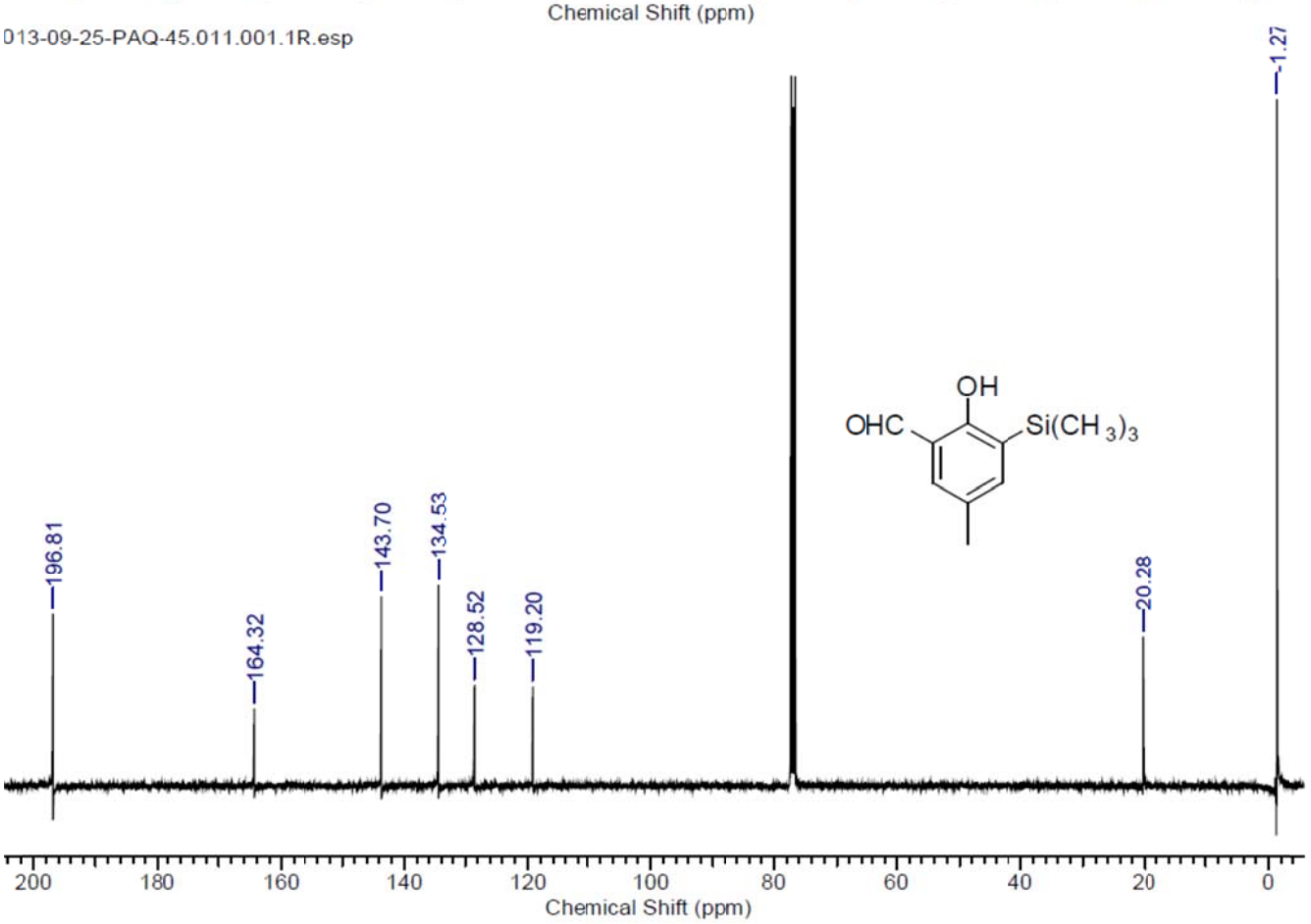
Precursors for Scheme7:



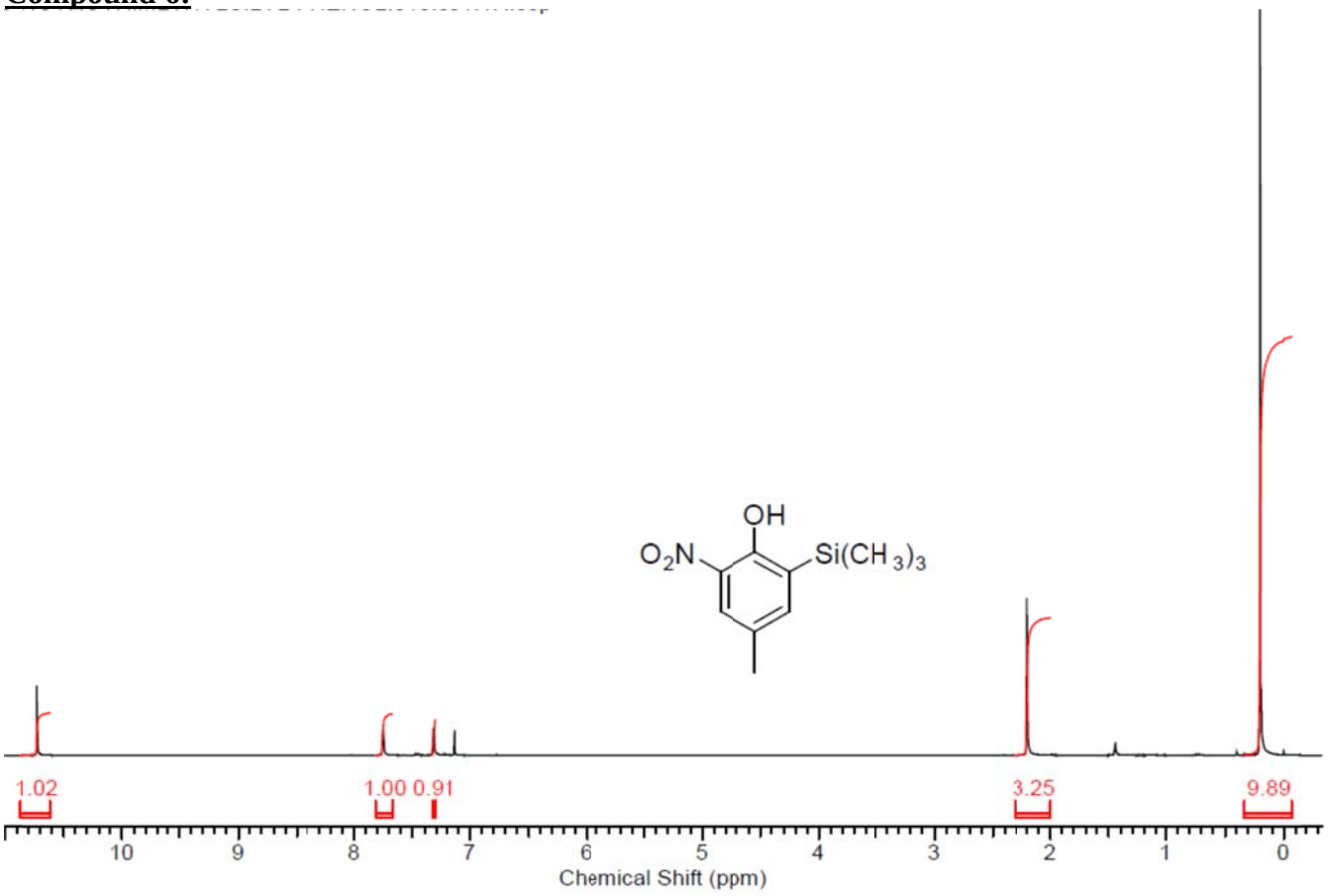


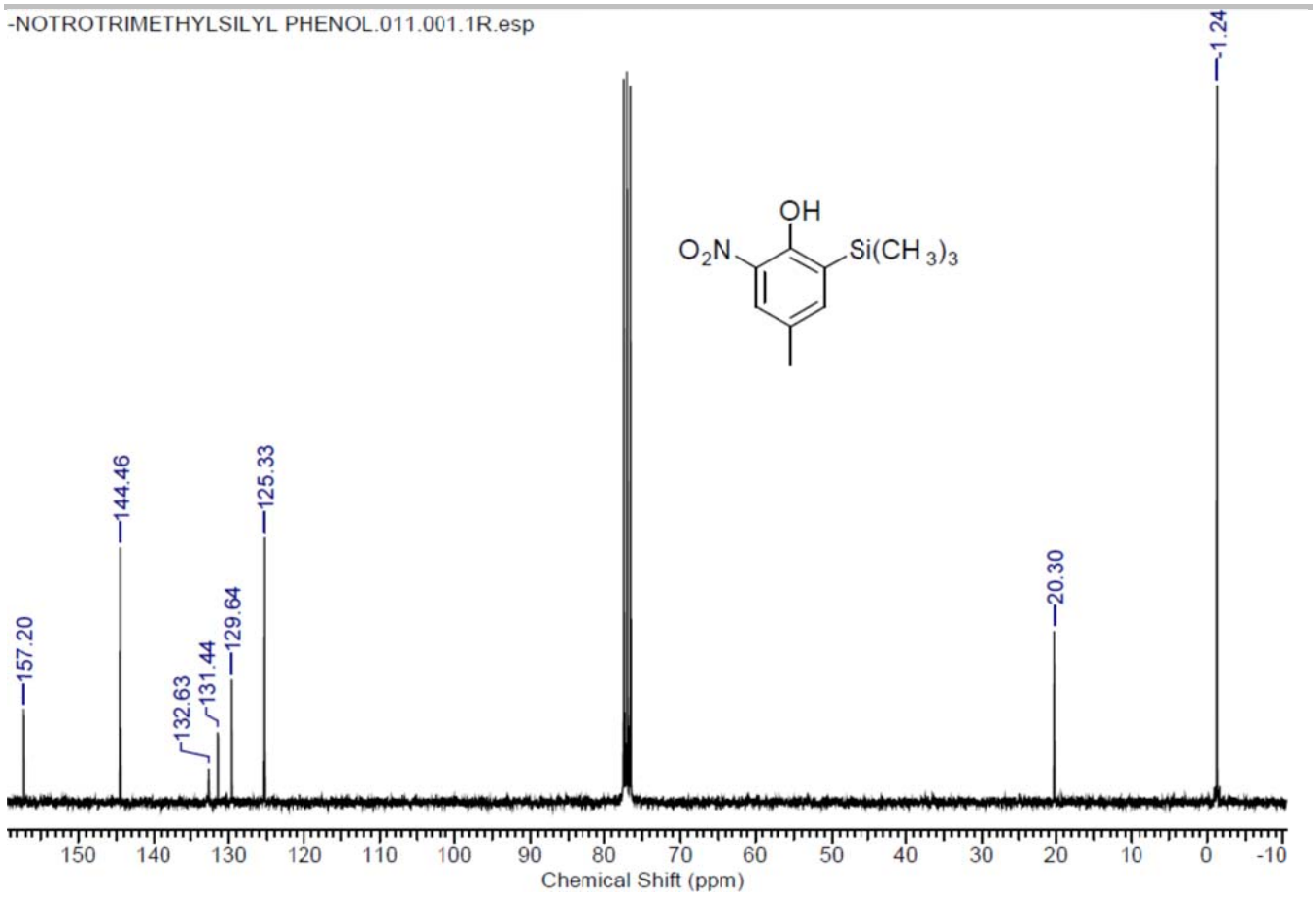
Precursors for Scheme 7:





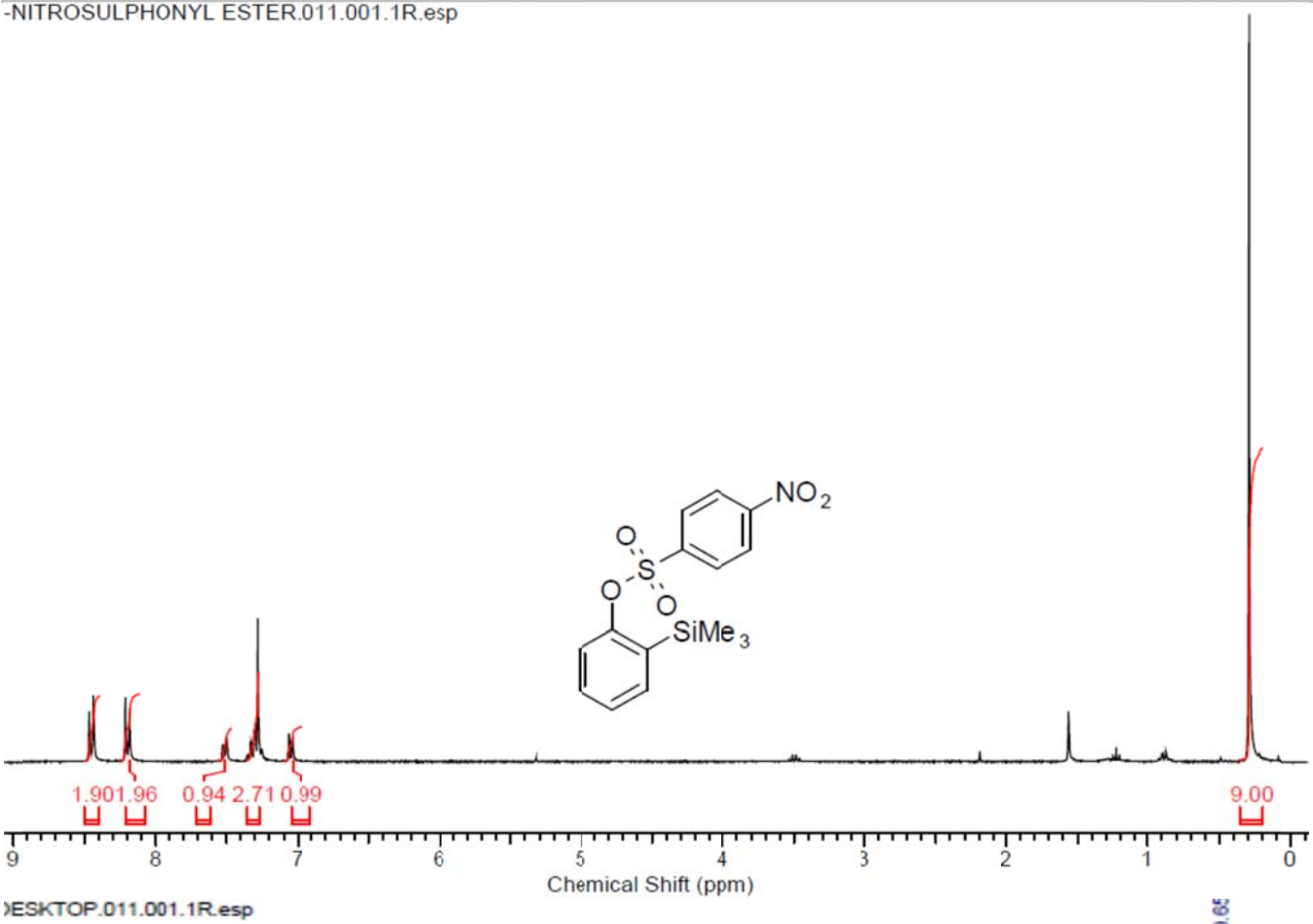
Compound 6:


OH
O2N
Si(CH3)3
1.02
1.00
0.91
3.25
9.89
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

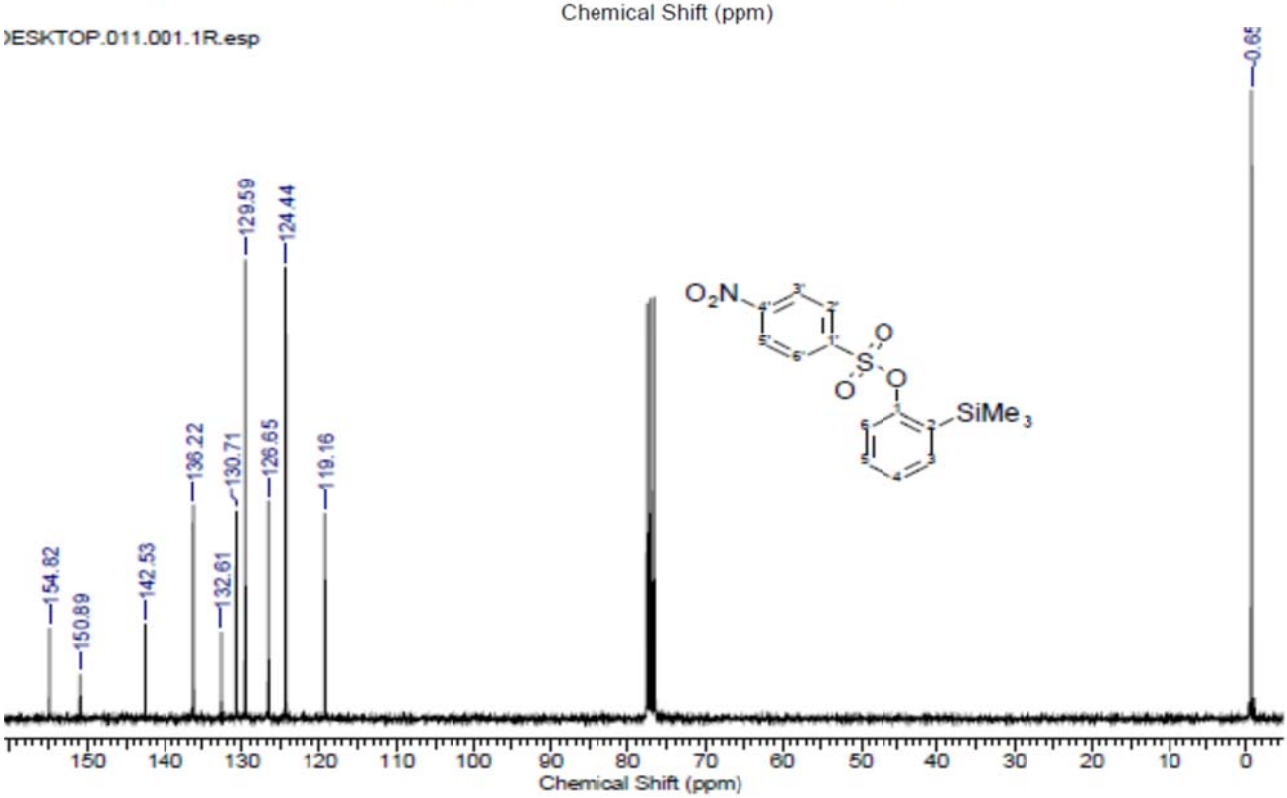

-NOTROTRIMETHYLSILYL PHENOL.011.001.1R.esp
-1.24
OH
O2N
Si(CH3)3
144.46
125.33
20.30
157.20
132.63
131.44
129.64
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

Compound 19:

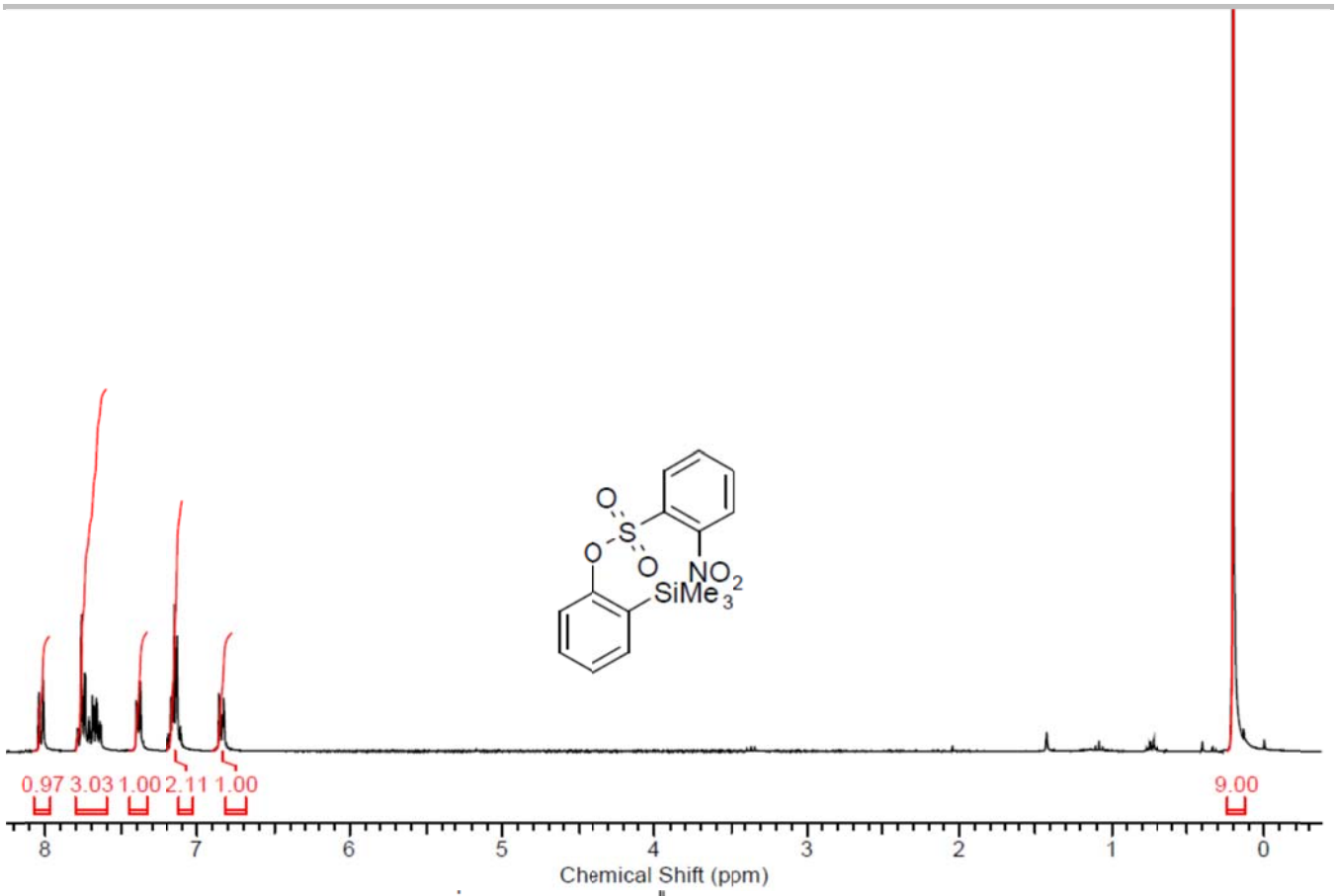
-NITROSULPHONYL ESTER.011.001.1R.esp

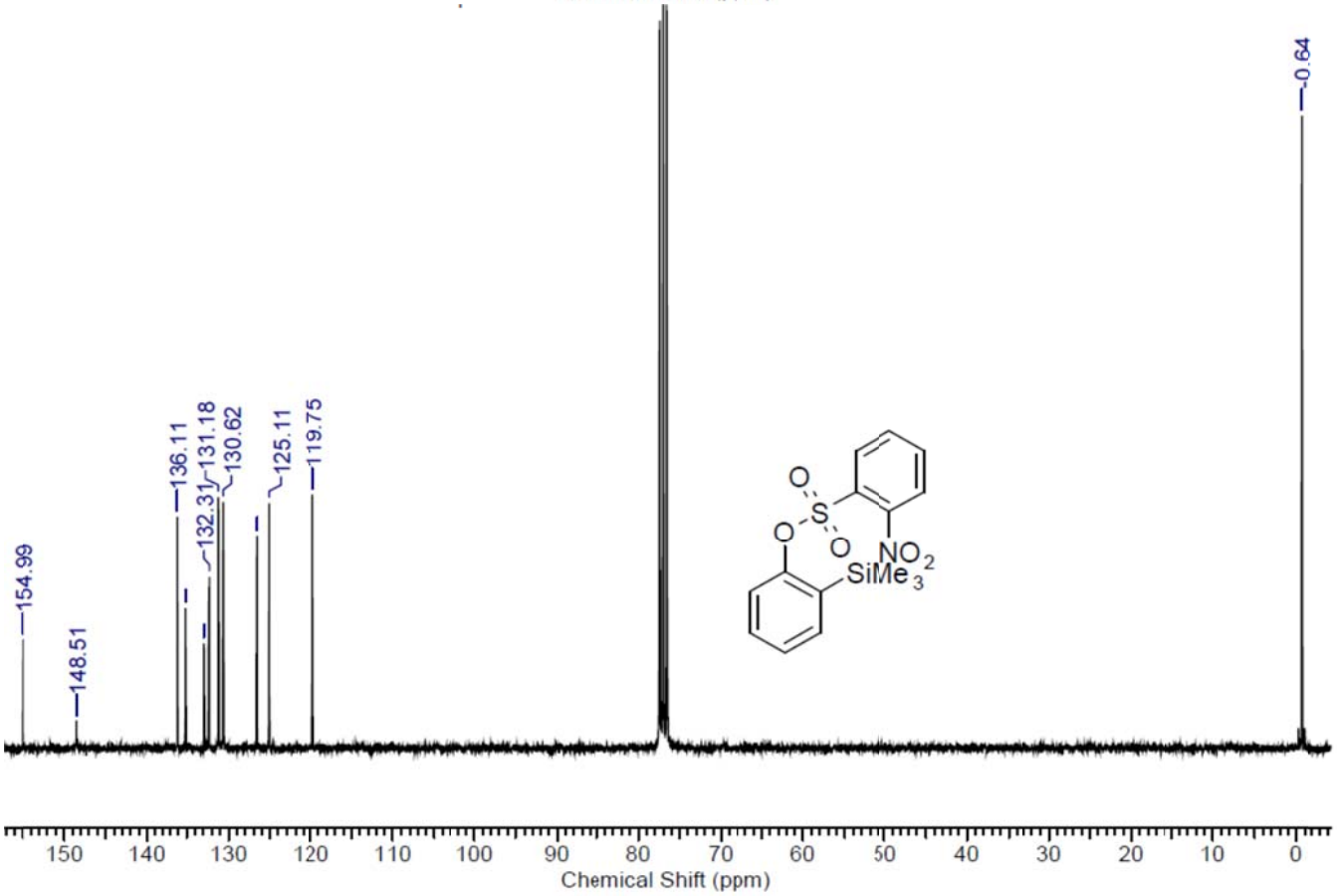


DESKTOP.011.001.1R.esp

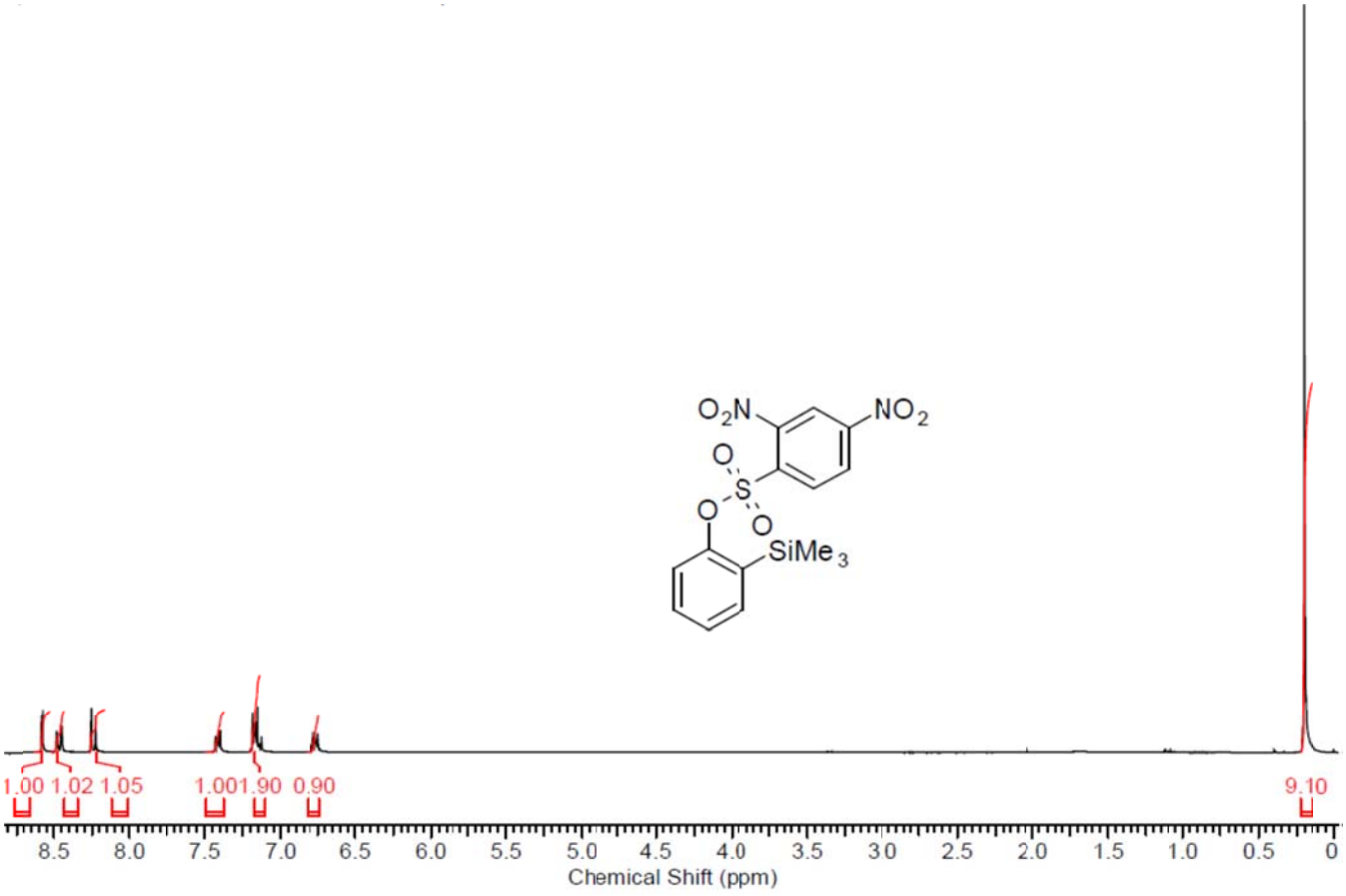


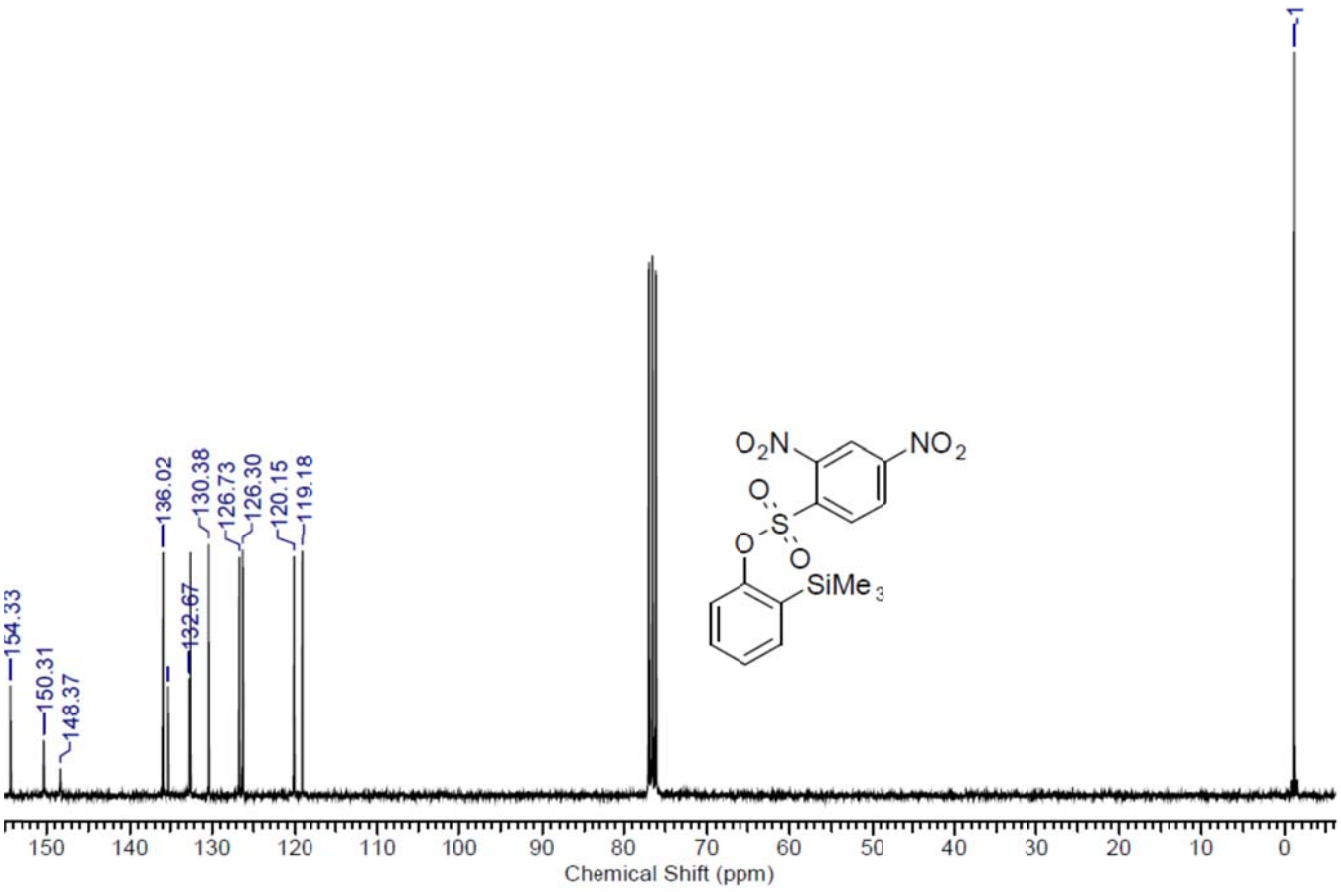
Compound 20:


0.97 3.03 1.00 2.11 1.00
9.00
8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)
O
S
O
O
NO2
SiMe3

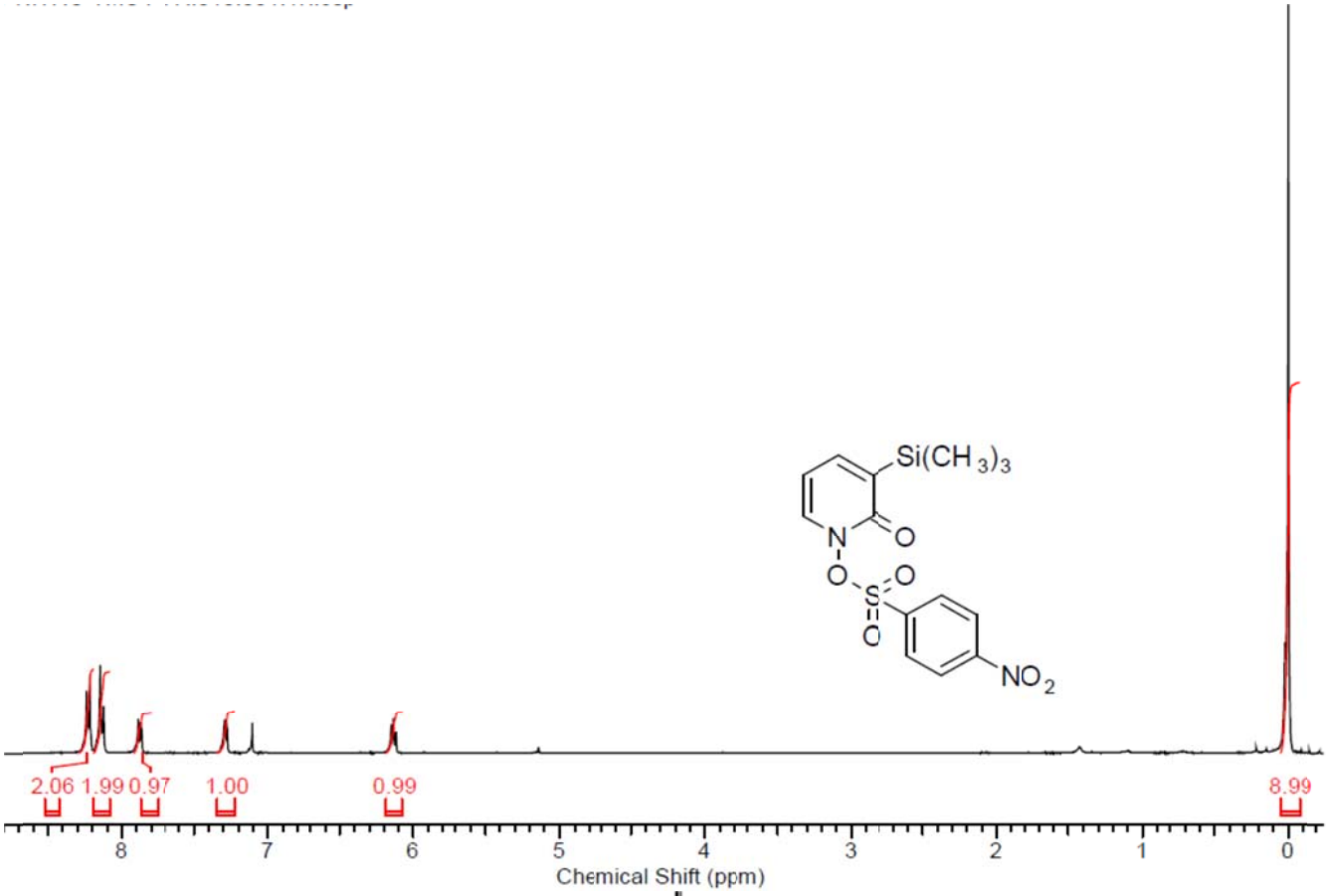

154.99
148.51
136.11
132.31
131.18
130.62
125.11
119.75
0.64
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)
O
S
O
O
NO2
SiMe3

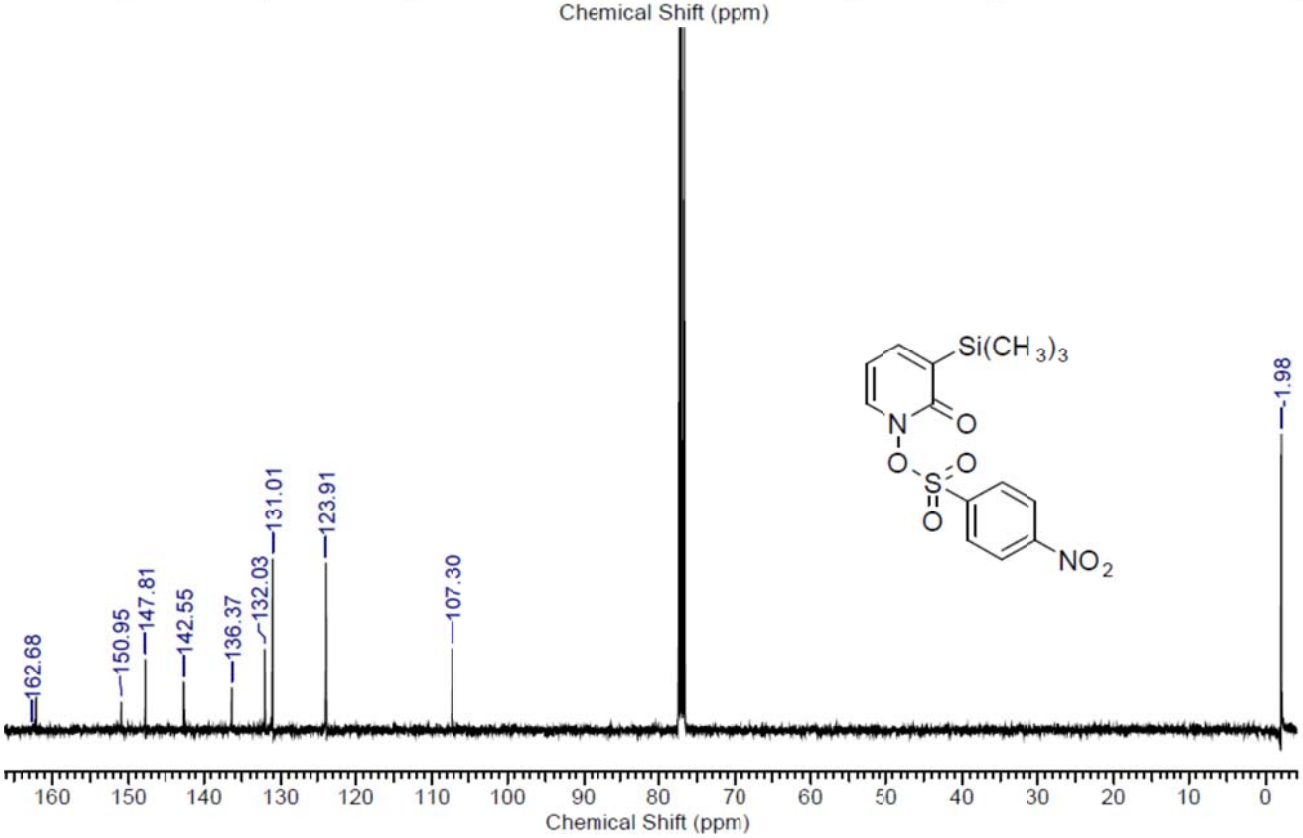
Compound 21:


O2N
NO2
O
S
O
O
SiMe3
1.00 1.02 1.05 1.00 1.90 0.90 9.10
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
Chemical Shift (ppm)

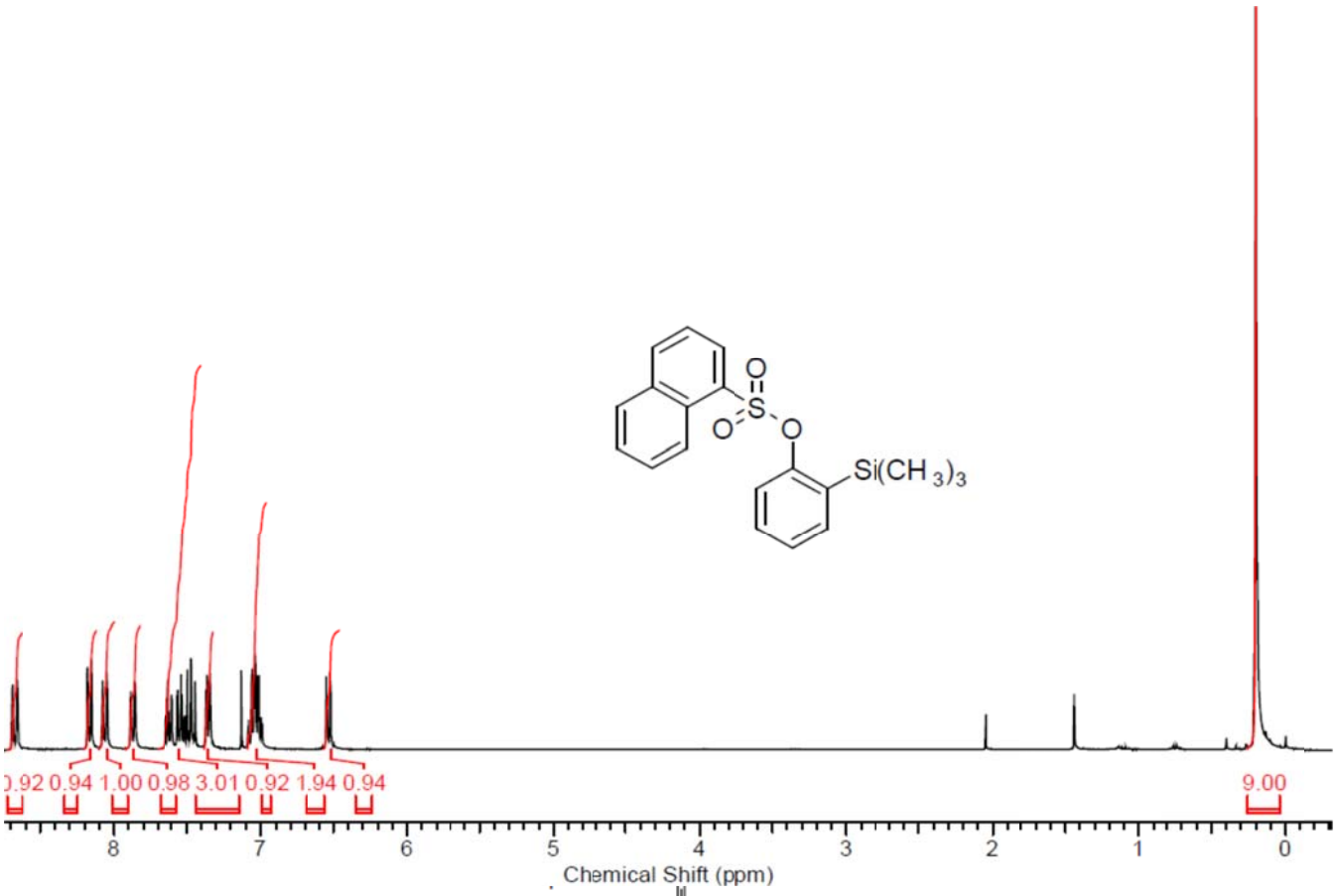

154.33
150.31
148.37
136.02
132.67
130.38
126.73
126.30
120.15
119.18
O2N
NO2
O
S
O
O
SiMe3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

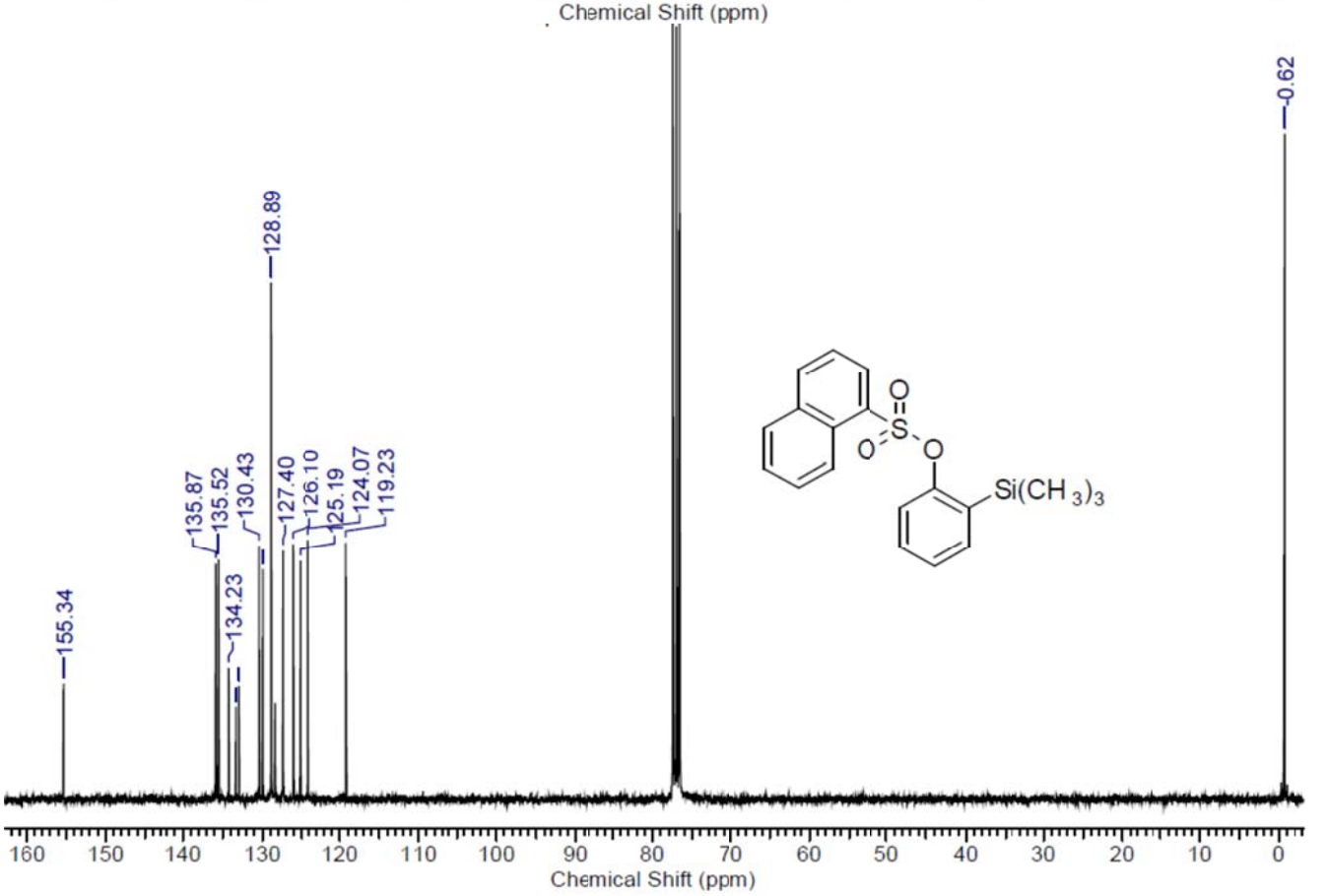
Compound 50:


Si(CH 3)3
N
O
O
S
O
O
NO2
2.06
1.99
0.97
1.00
0.99
8.99
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

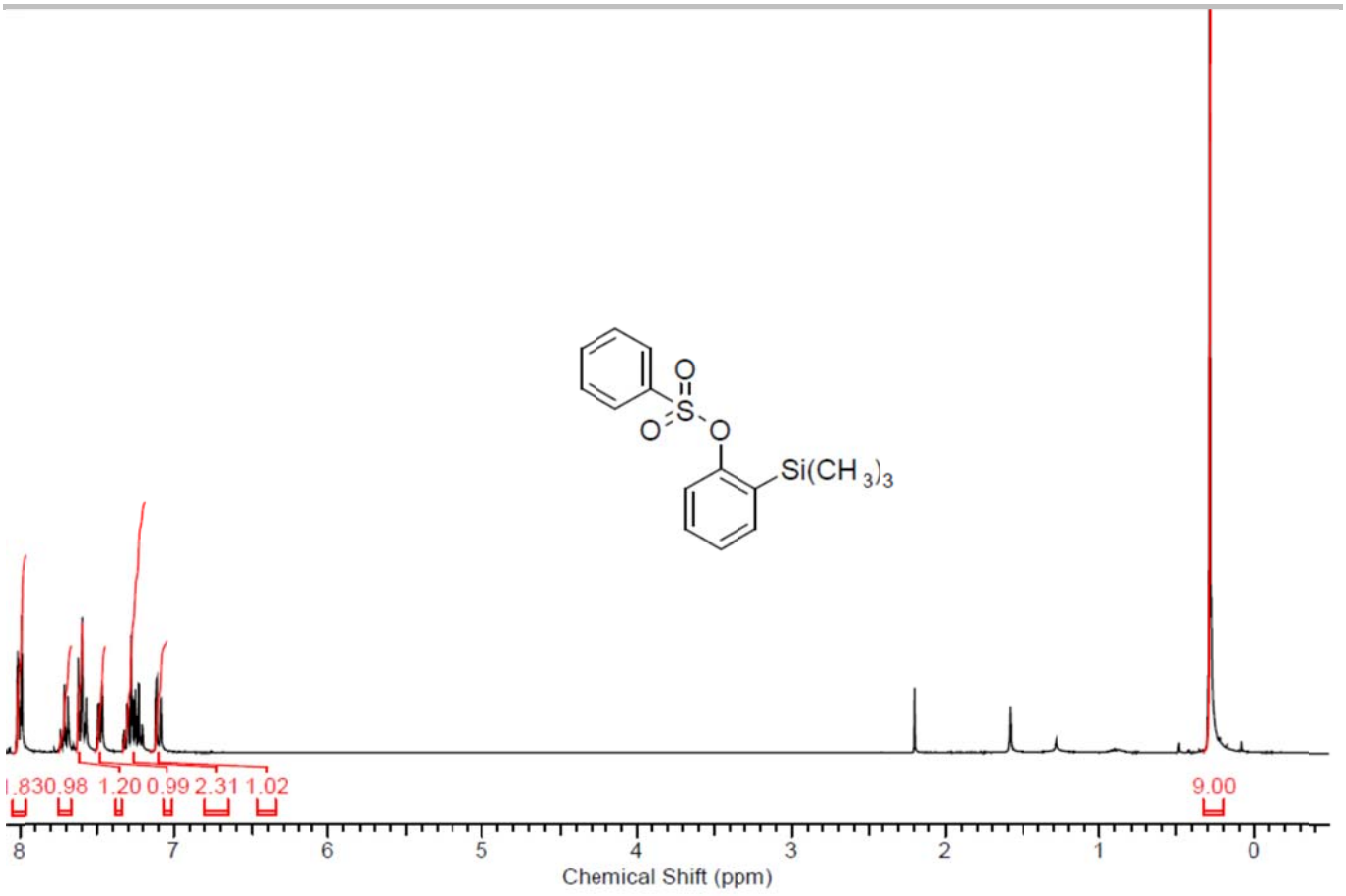

Si(CH 3)3
N
O
O
S
O
O
NO2
1.98
162.68
150.95
147.81
142.55
136.37
132.03
131.01
123.91
107.30
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

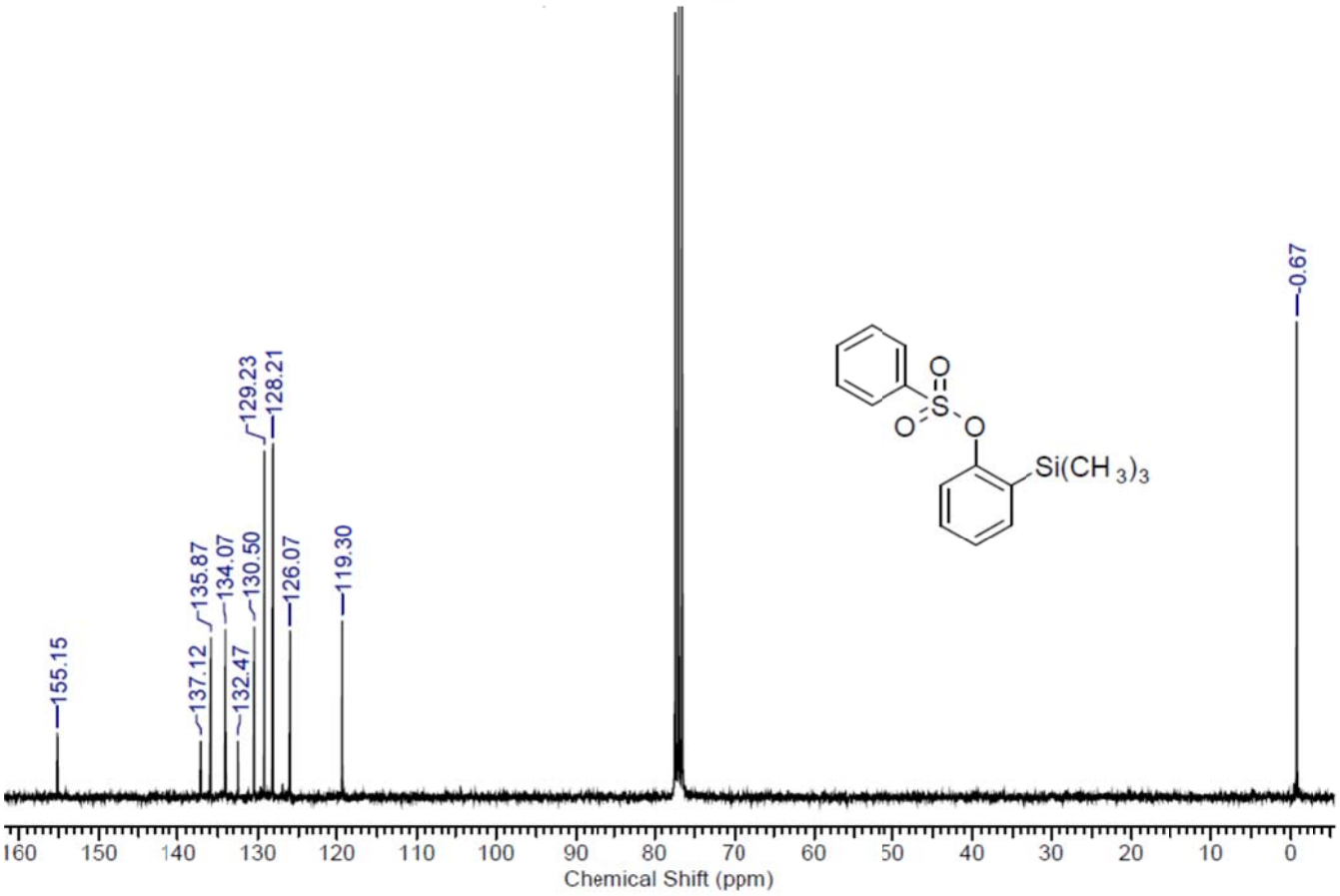
Compound 24:


0.92 0.94 1.00 0.98 3.01 0.92 1.94 0.94
9.00
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
Si(CH3)3

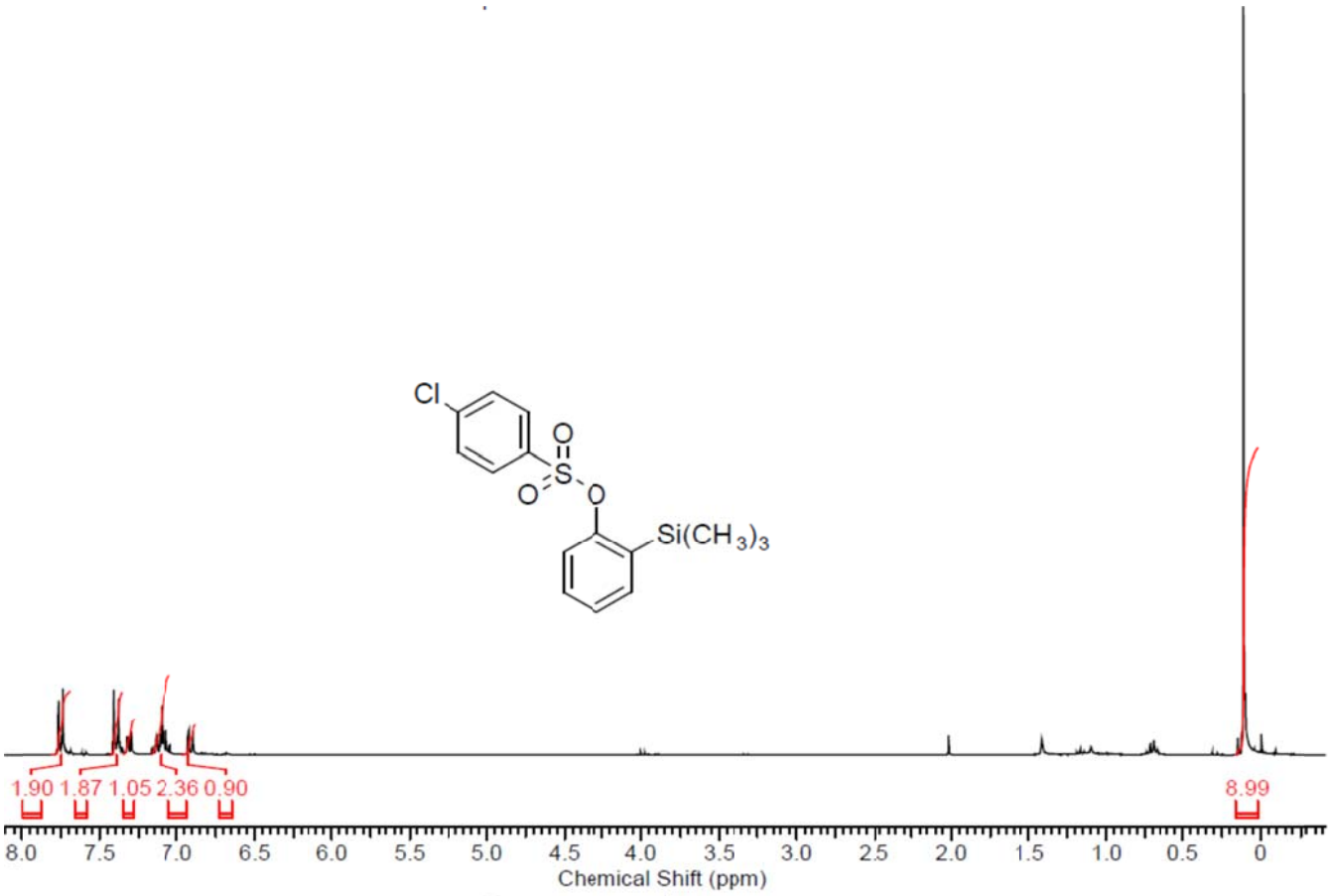

155.34
135.87
135.52
134.23
130.43
128.89
127.40
126.10
125.19
124.07
119.23
0.62
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
Si(CH3)3

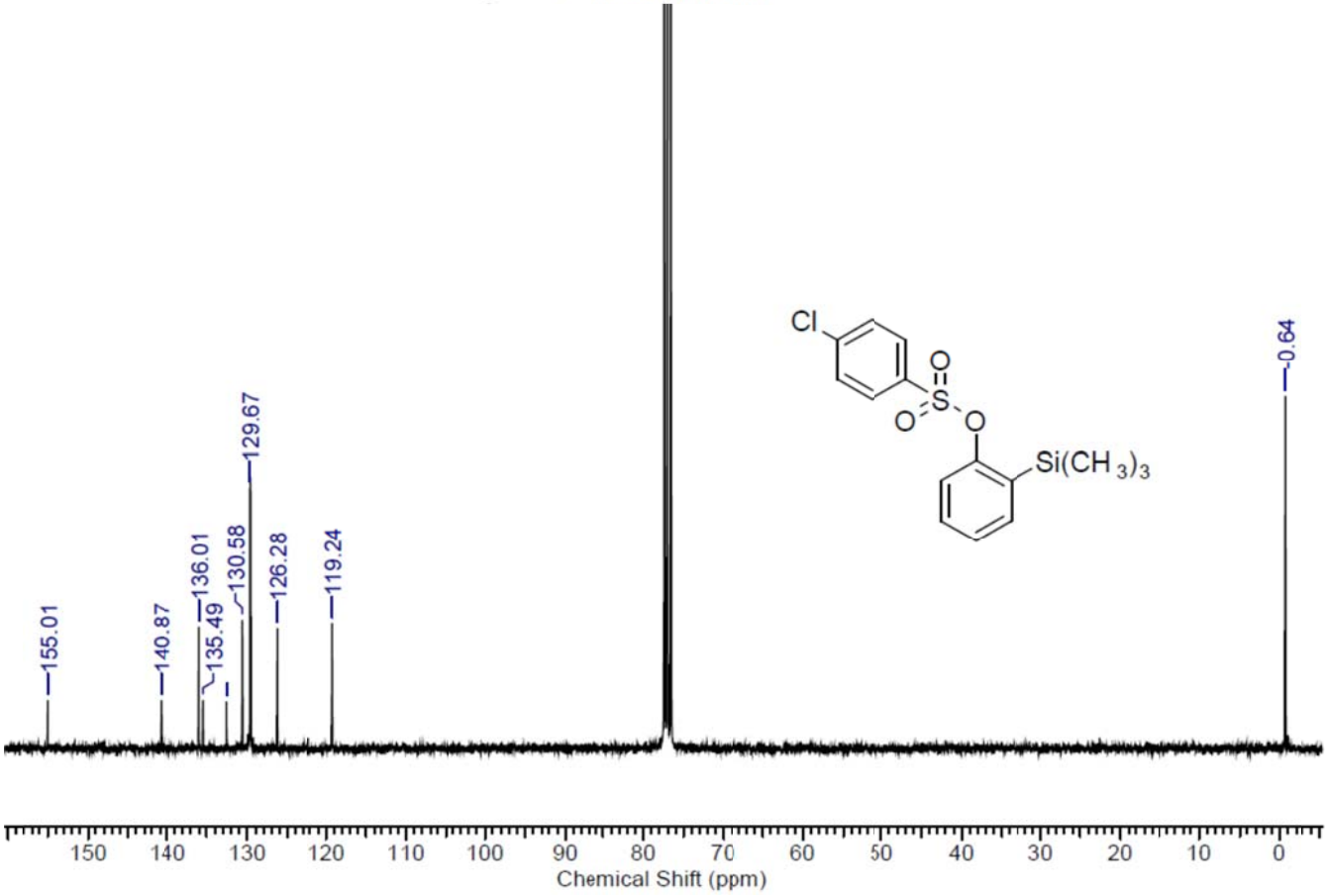
Compound 23:


O
S
O
O
Si(CH3)3
1.83 0.98 1.20 0.99 2.31 1.02
9.00
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

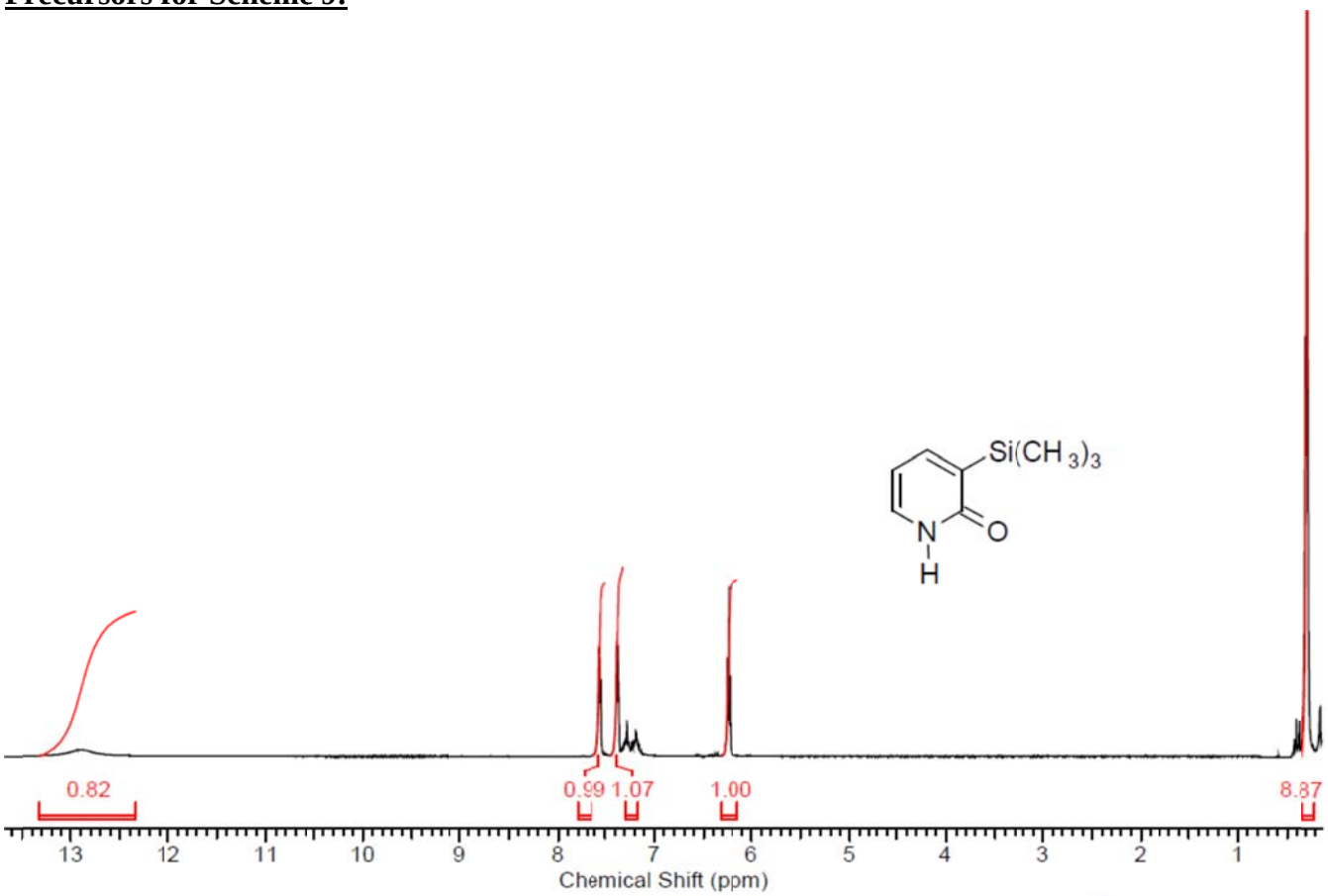

155.15
137.12
135.87
134.07
132.47
130.50
129.23
128.21
126.07
119.30
0.67
O
S
O
O
Si(CH3)3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

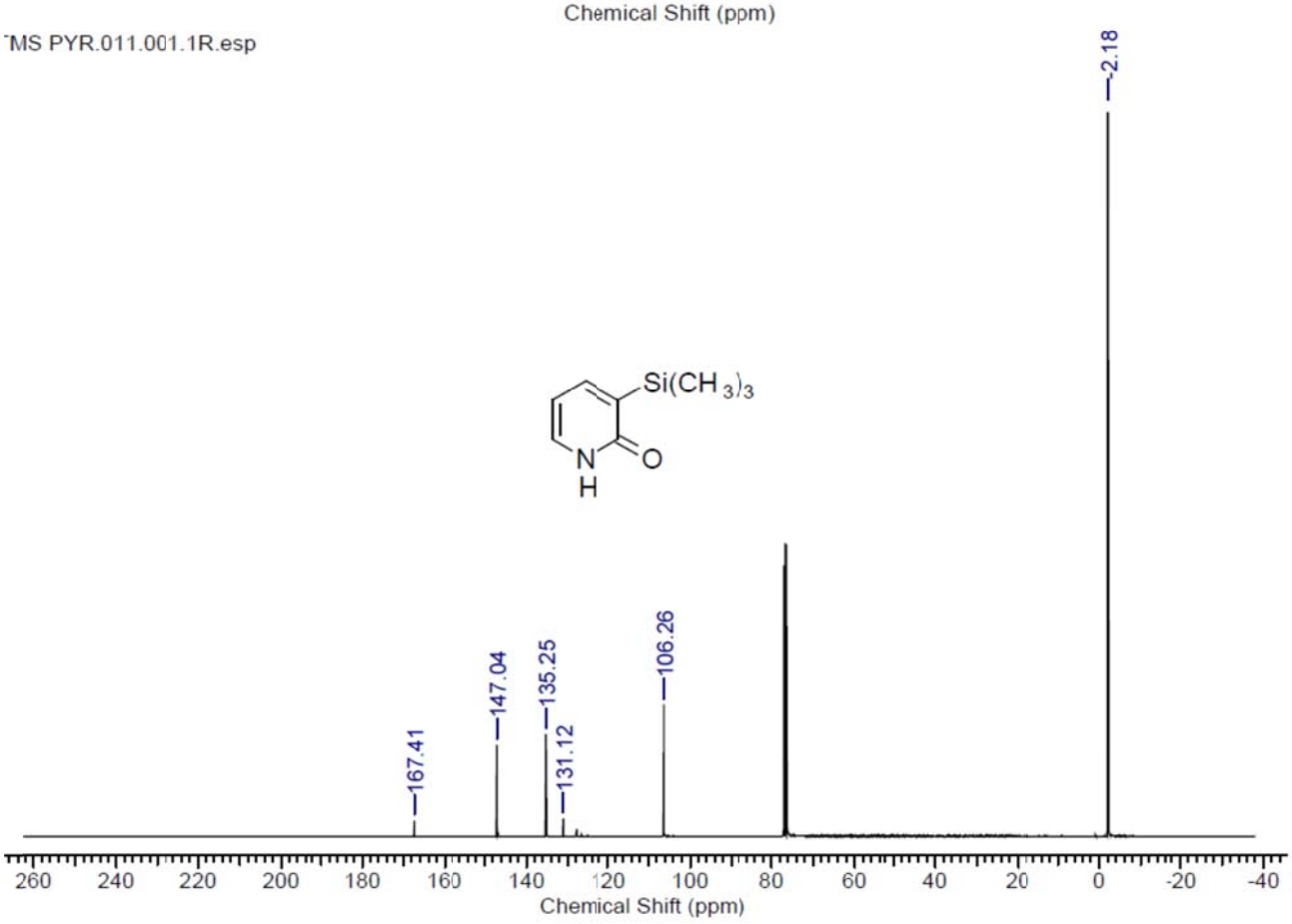
Compound 22:


Cl
O
O
S
O
Si(CH3)3
1.90
1.87
1.05
2.36
0.90
8.99
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
Chemical Shift (ppm)

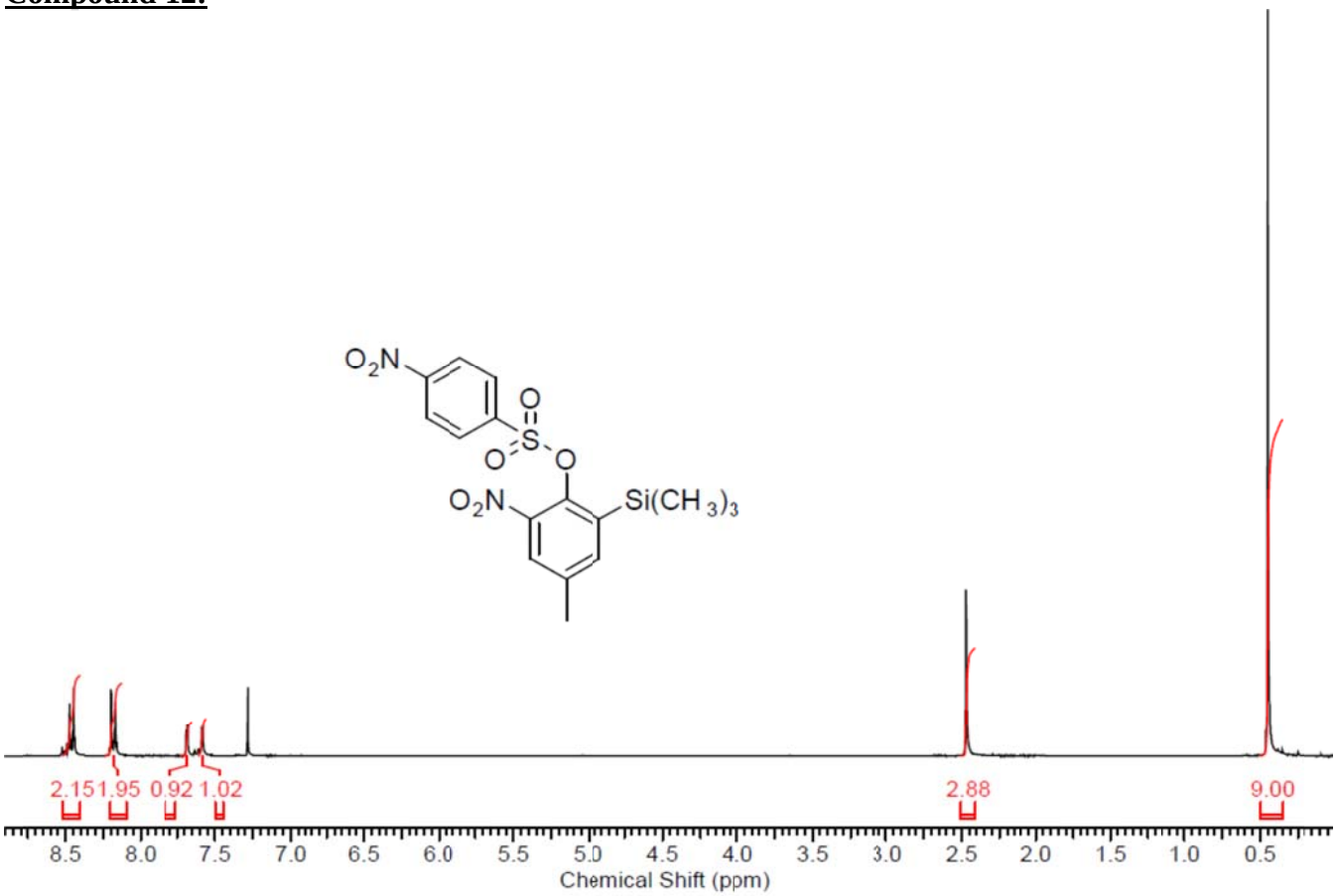

Cl
O
O
S
O
Si(CH3)3
155.01
140.87
135.49
136.01
130.58
129.67
126.28
119.24
0.64
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

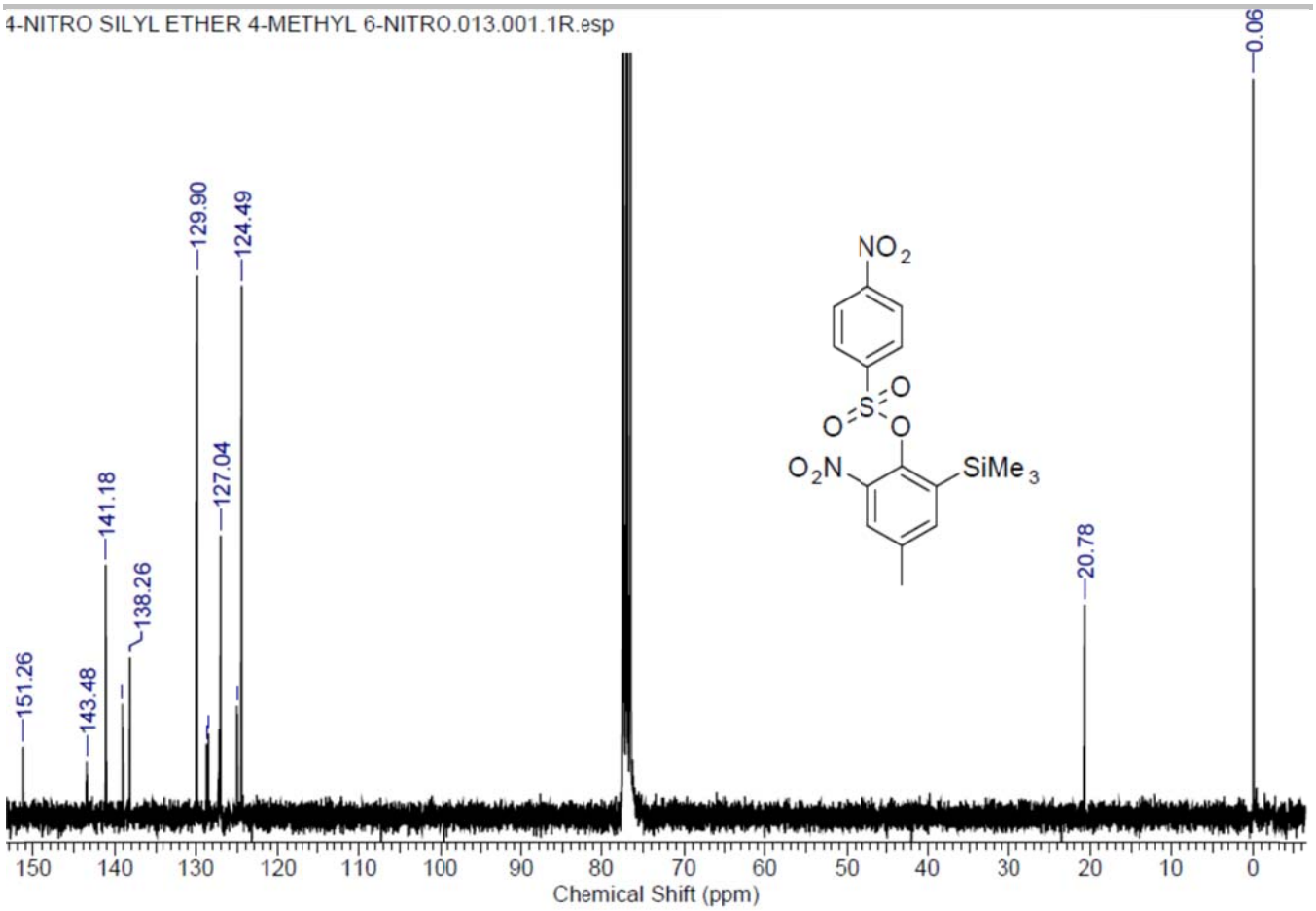
Precursors for Scheme 9:



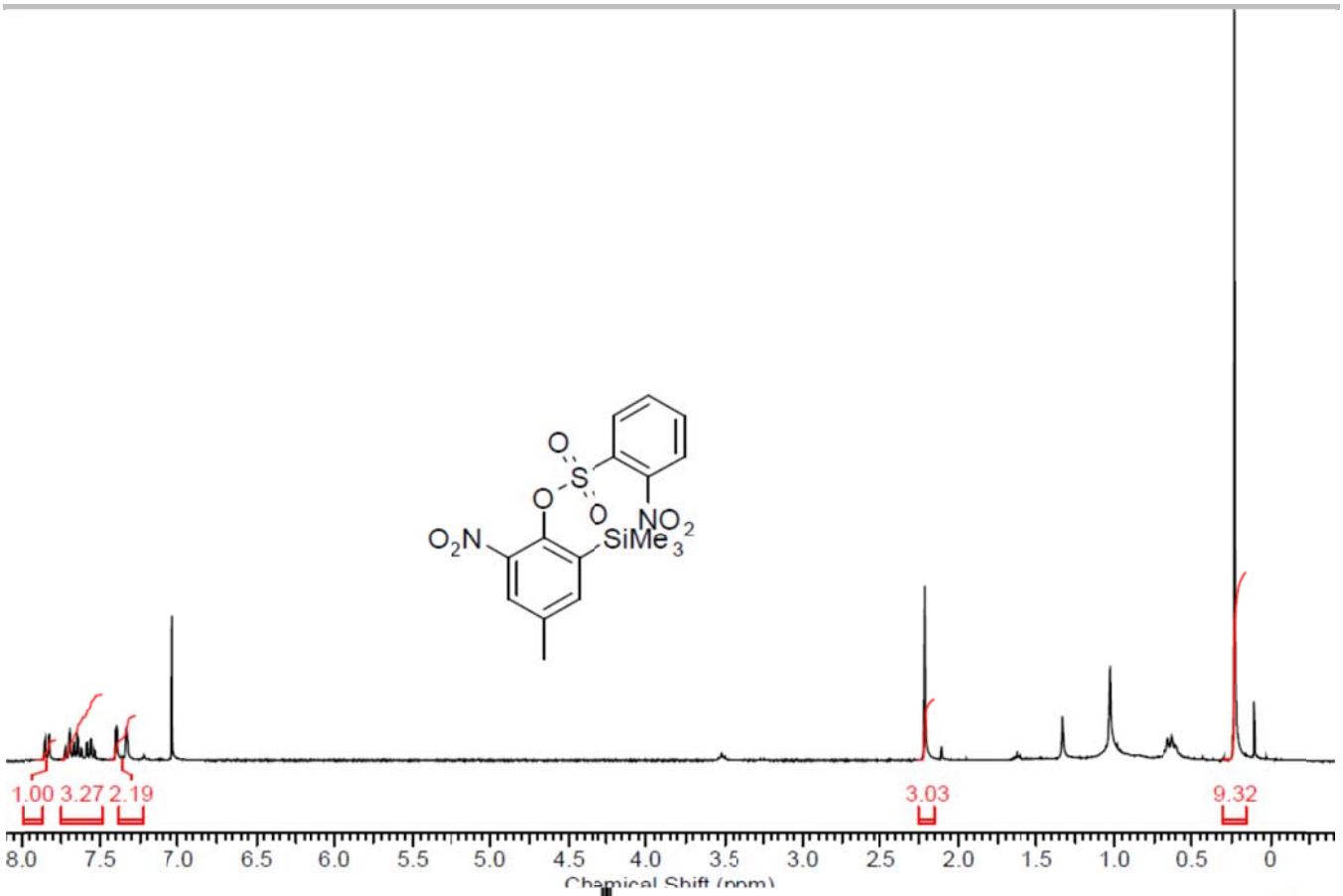


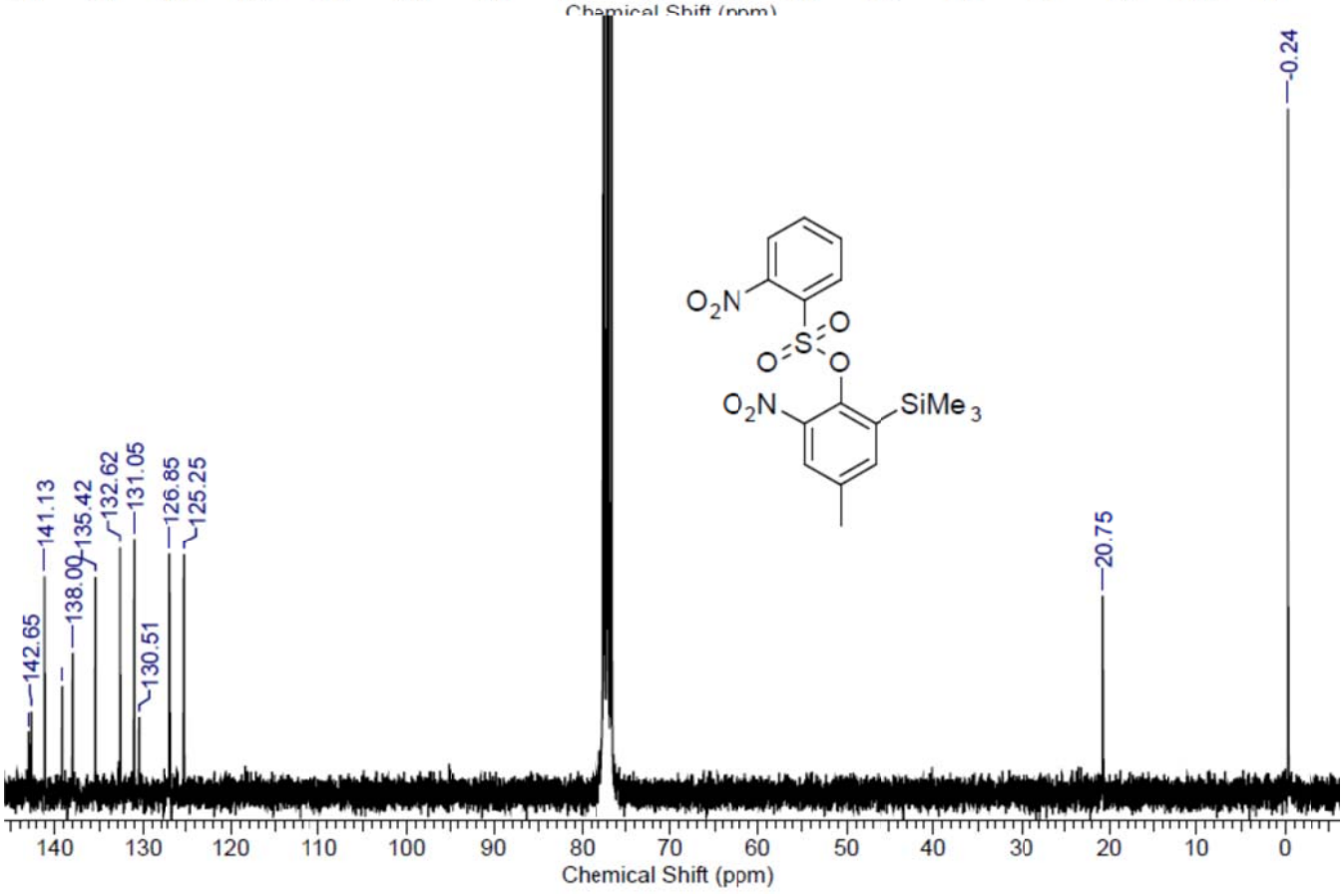
Compound 12:


O2N
O
S
O
O
O2N
Si(CH3)3
2.15
1.95
0.92
1.02
2.88
9.00
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
Chemical Shift (ppm)

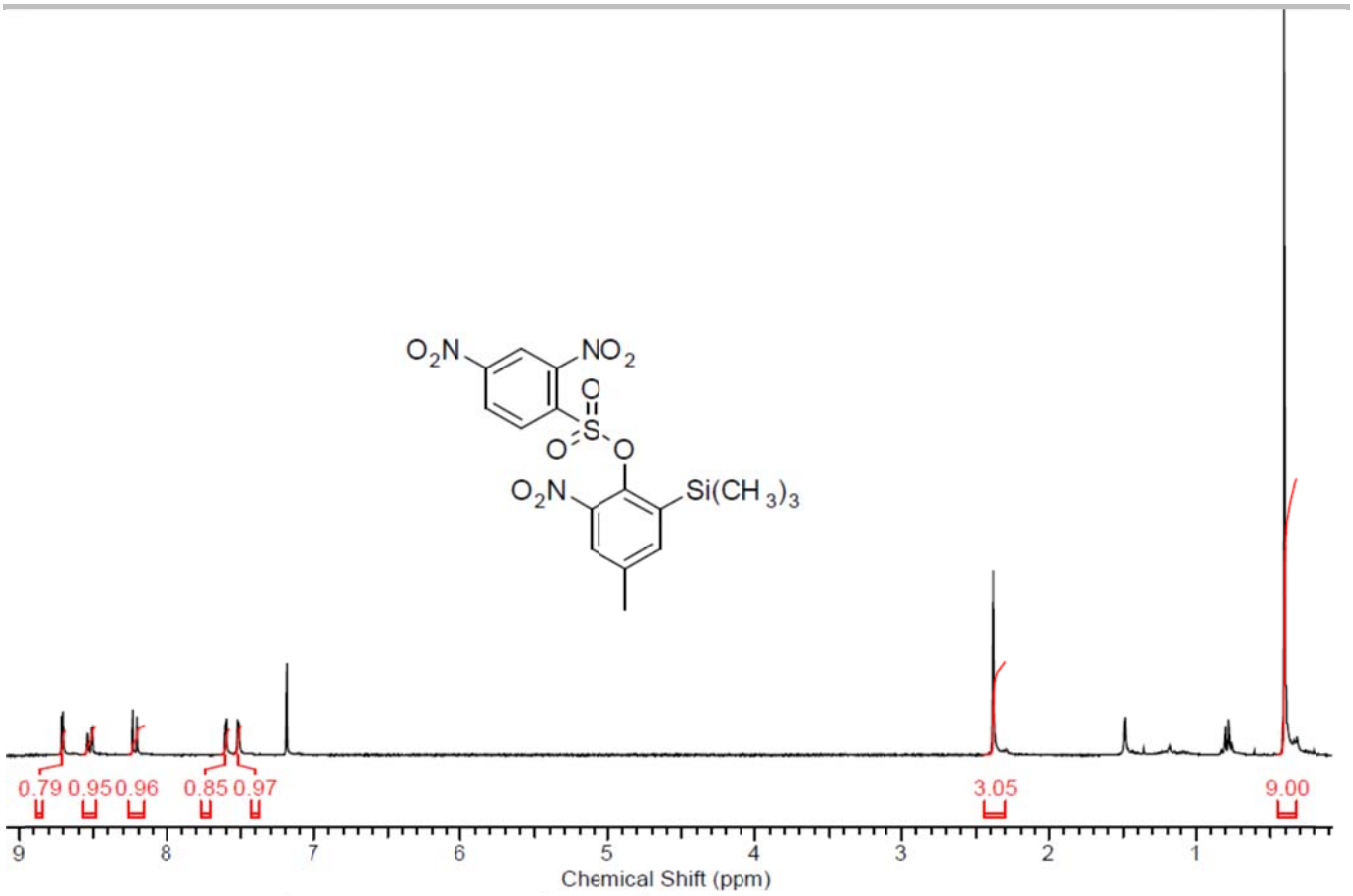

4-NITRO SILYL ETHER 4-METHYL 6-NITRO.013.001.1R.esp
0.06
129.90
124.49
127.04
141.18
138.26
151.26
143.48
20.78
NO2
O
S
O
O
O2N
SiMe3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

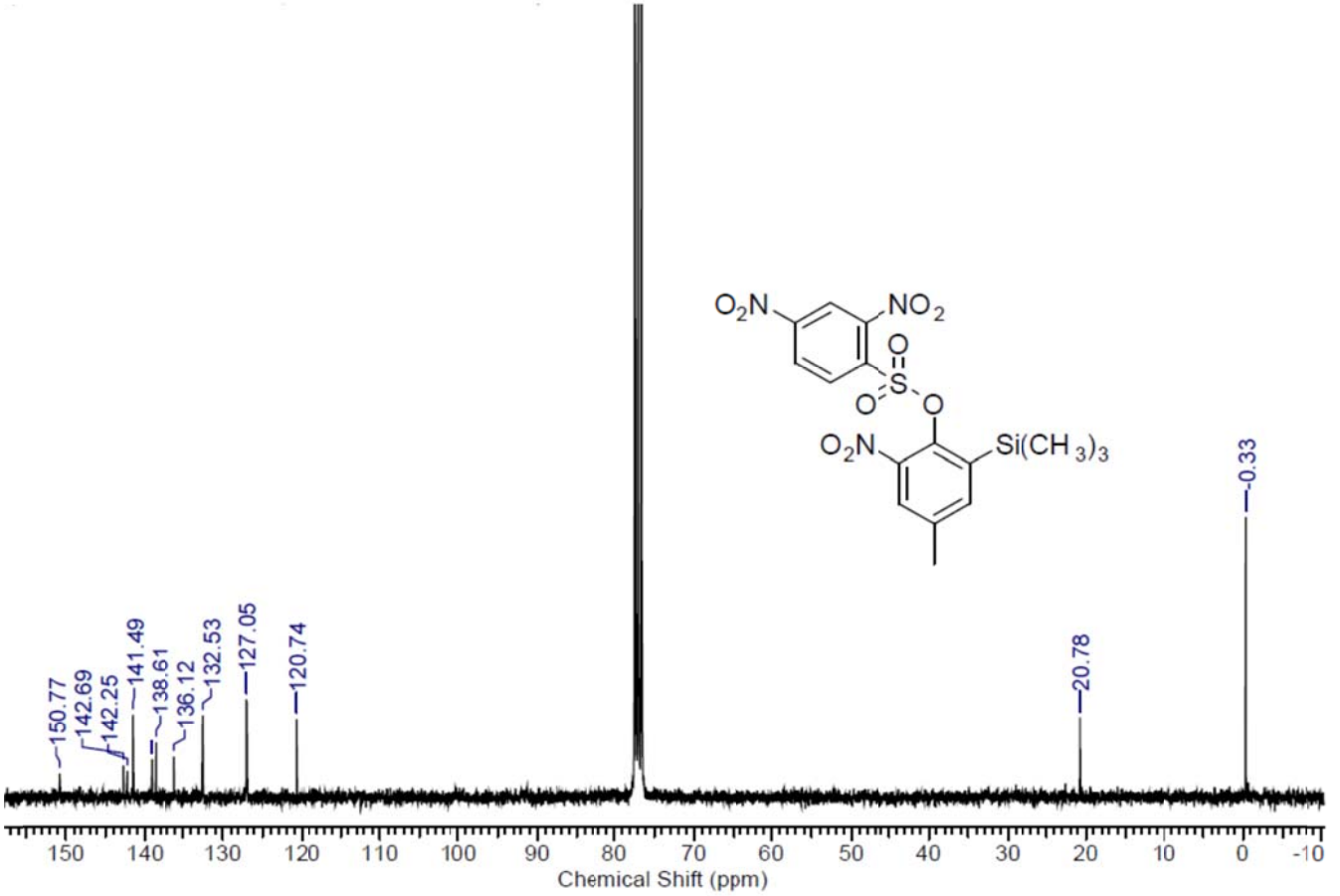
Compound 13:


1.00 3.27 2.19
3.03
9.32
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
Chemical Shift (ppm)

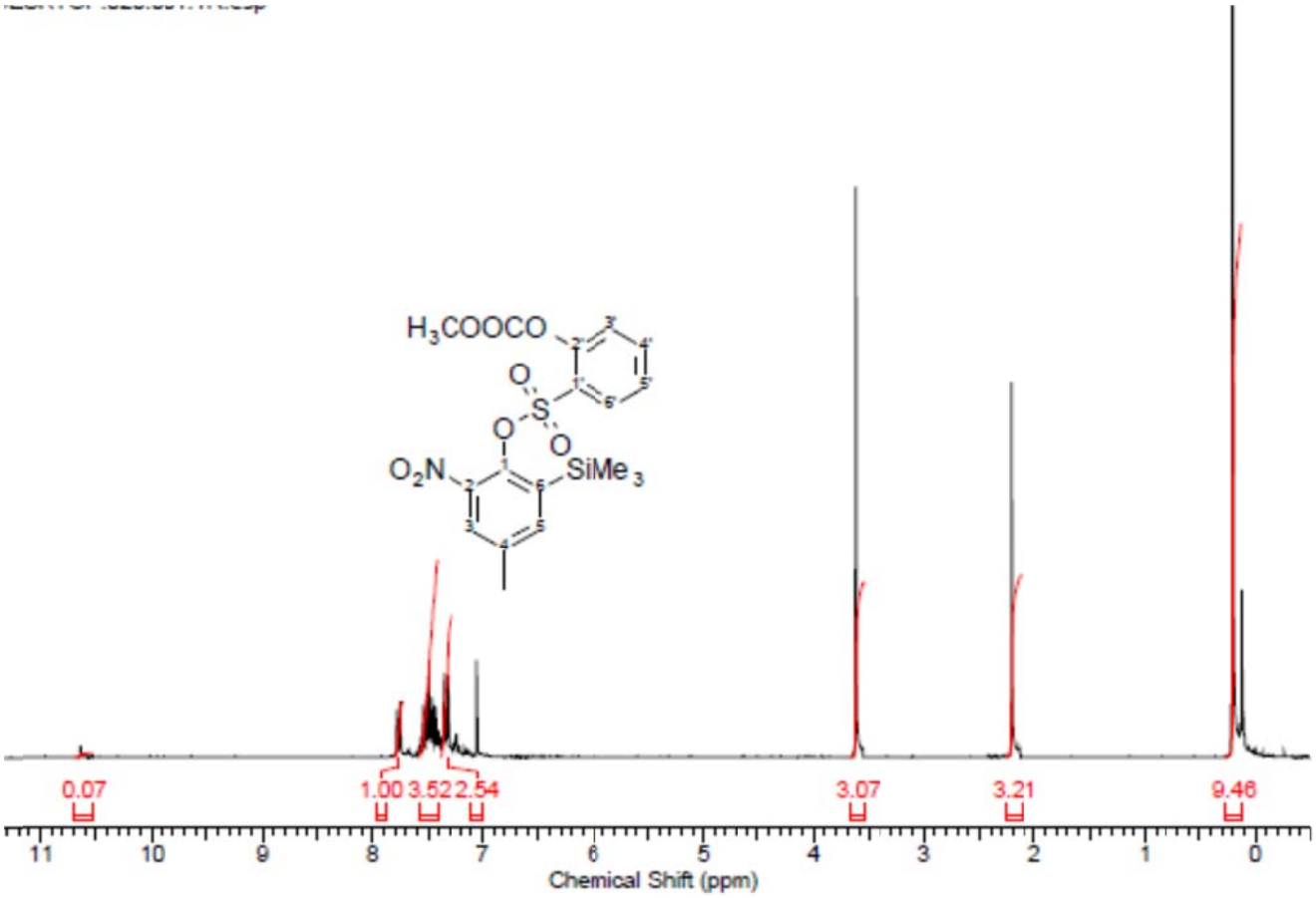

142.65
141.13
138.00
135.42
132.62
131.05
130.51
126.85
125.25
20.75
0.24
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

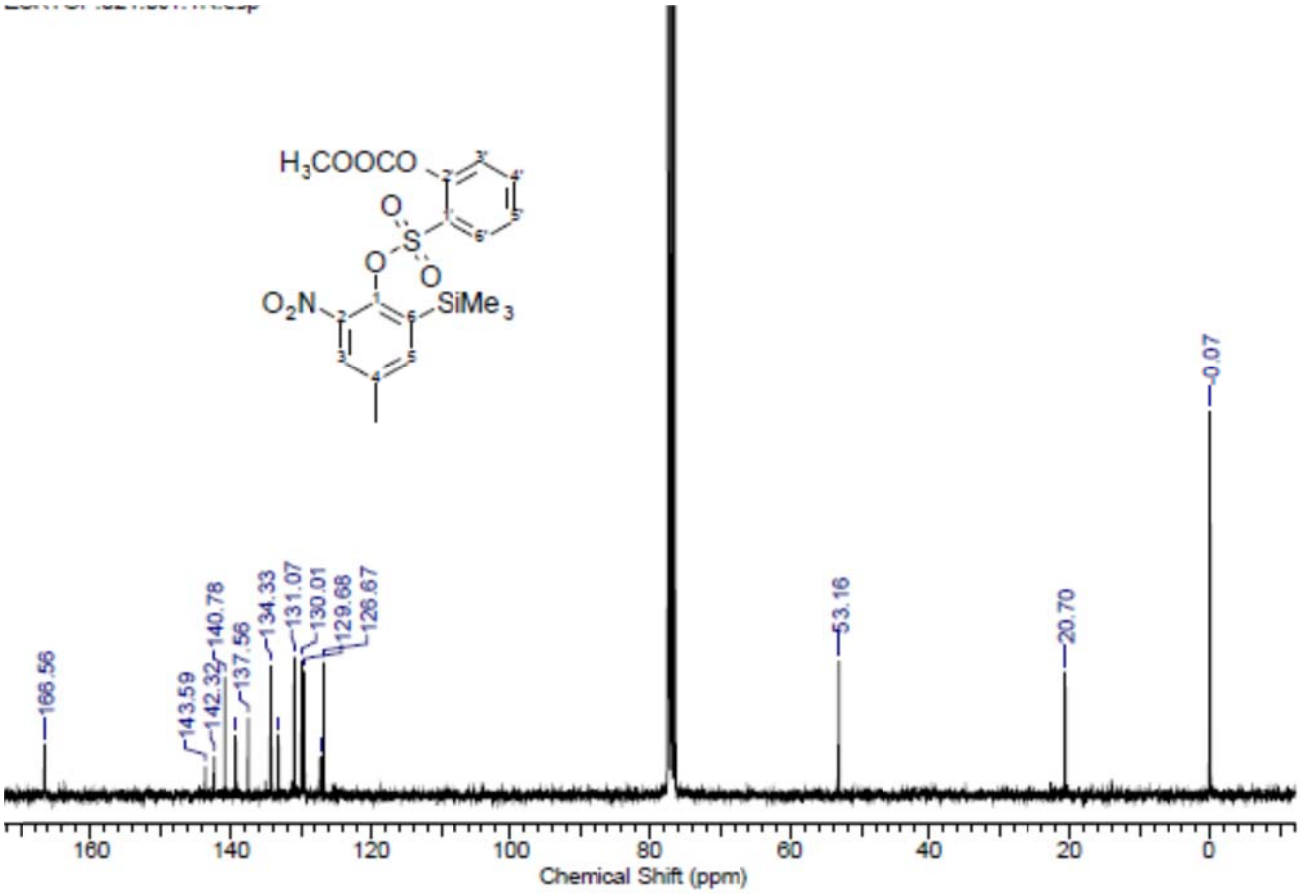
Compound 14:


O2N
NO2
O
S
O
O
O2N
Si(CH3)3
0.79 0.95 0.96 0.85 0.97
3.05
9.00
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

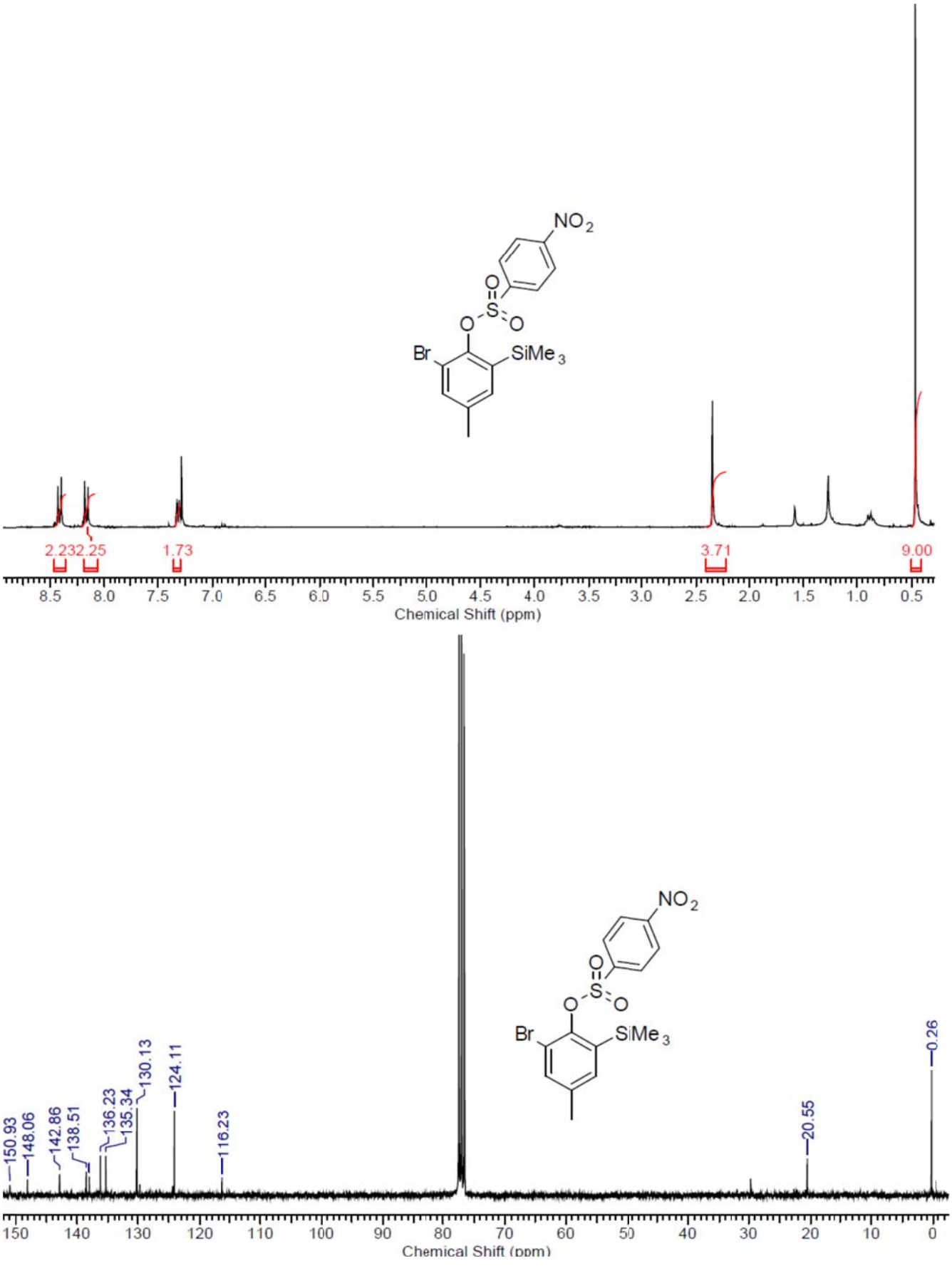

O2N
NO2
O
S
O
O
O2N
Si(CH3)3
150.77
142.69
142.25
141.49
138.61
136.12
132.53
127.05
120.74
20.78
-0.33
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

Compound 39:

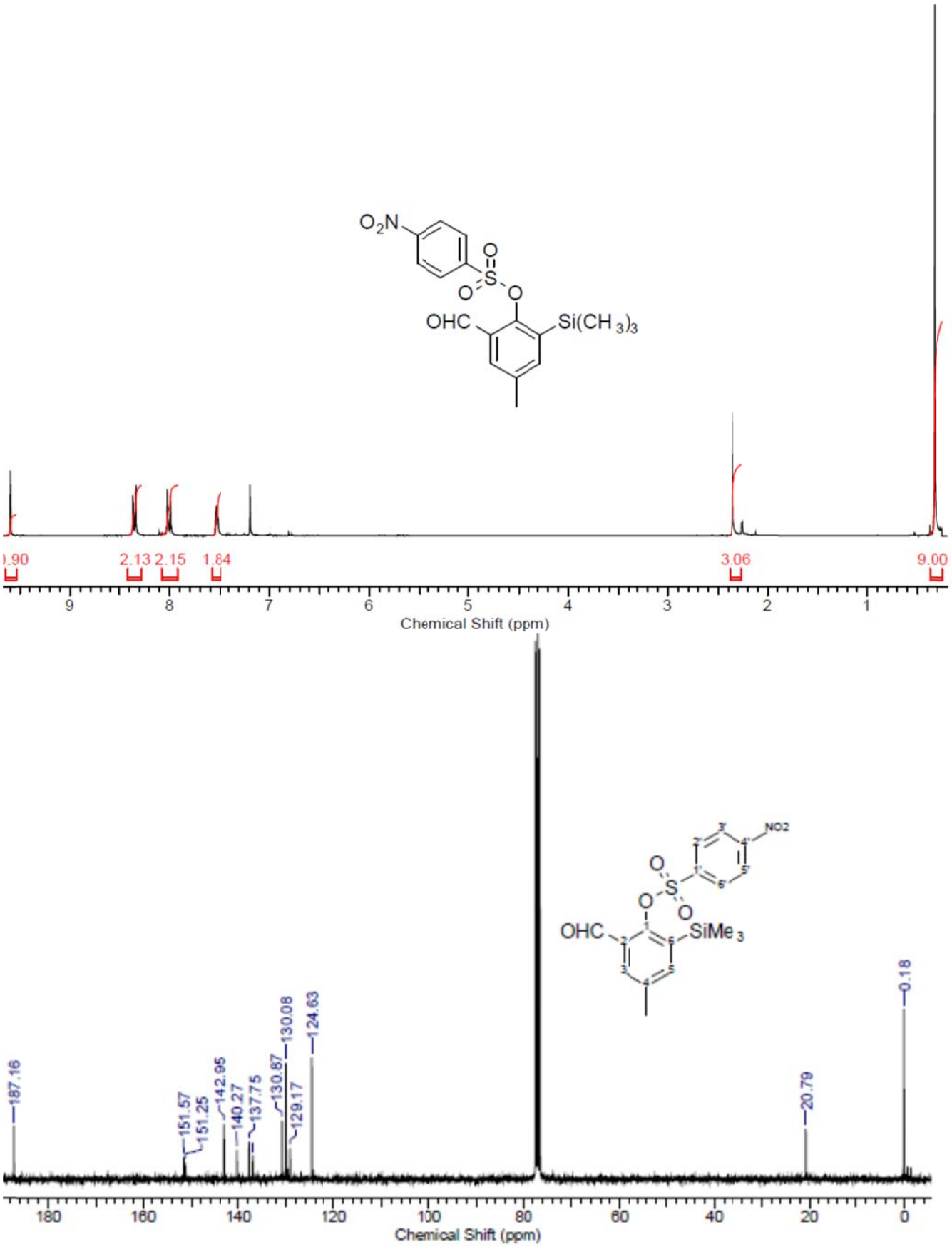

H3COOCO
O2N
SiMe3
0.07
1.00
3.52
2.54
3.07
3.21
9.46
Chemical Shift (ppm)


H3COOCO
O2N
SiMe3
166.56
143.59
142.32
140.78
137.56
134.33
131.07
130.01
129.68
126.67
53.16
20.70
0.07
Chemical Shift (ppm)

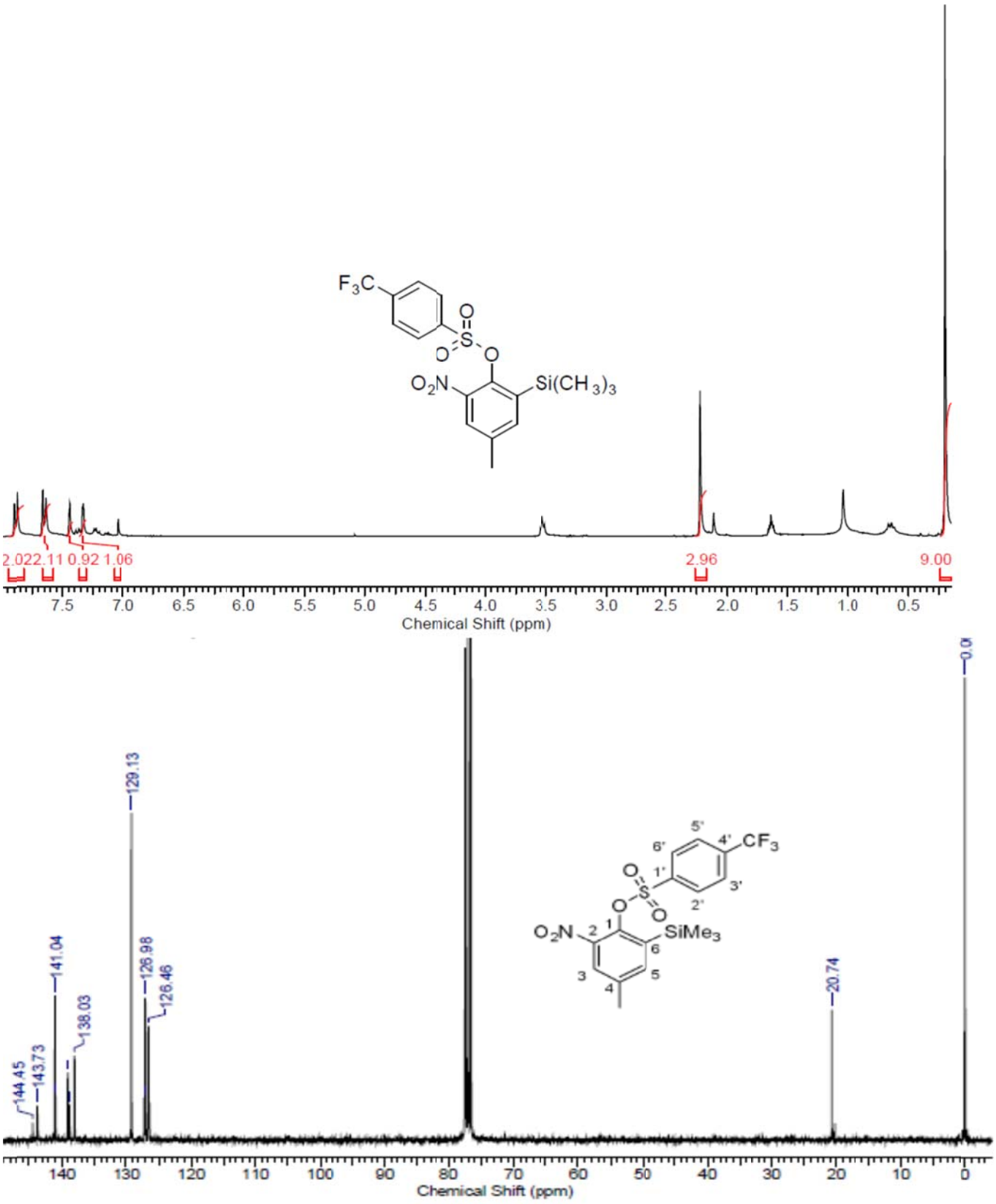
Compound 36:


NO2
O
S
O
O
Br
SiMe3
2.23
2.25
1.73
3.71
9.00
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
Chemical Shift (ppm)
150.93
148.06
142.86
138.51
136.23
135.34
130.13
124.11
116.23
20.55
0.26
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

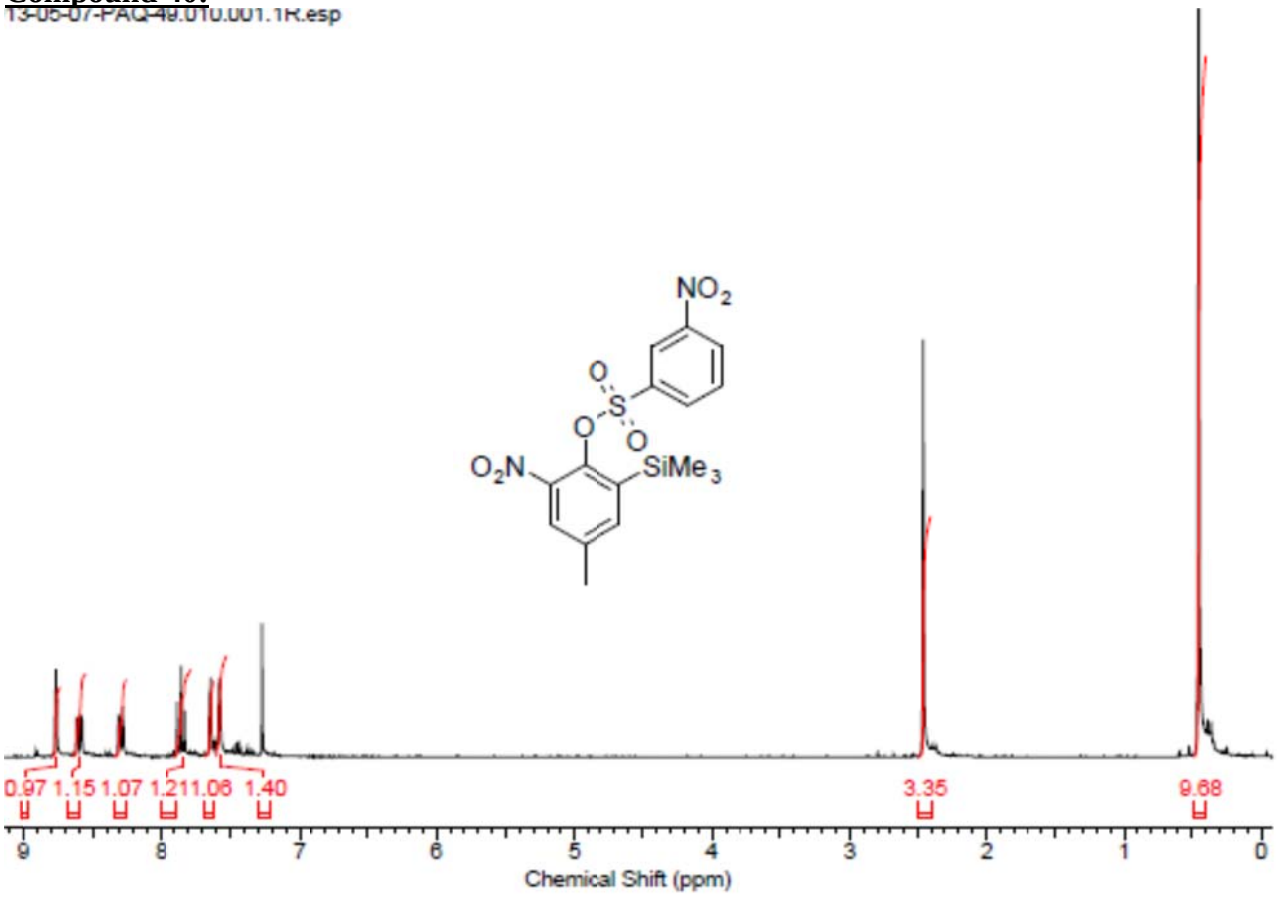
Compound 37:

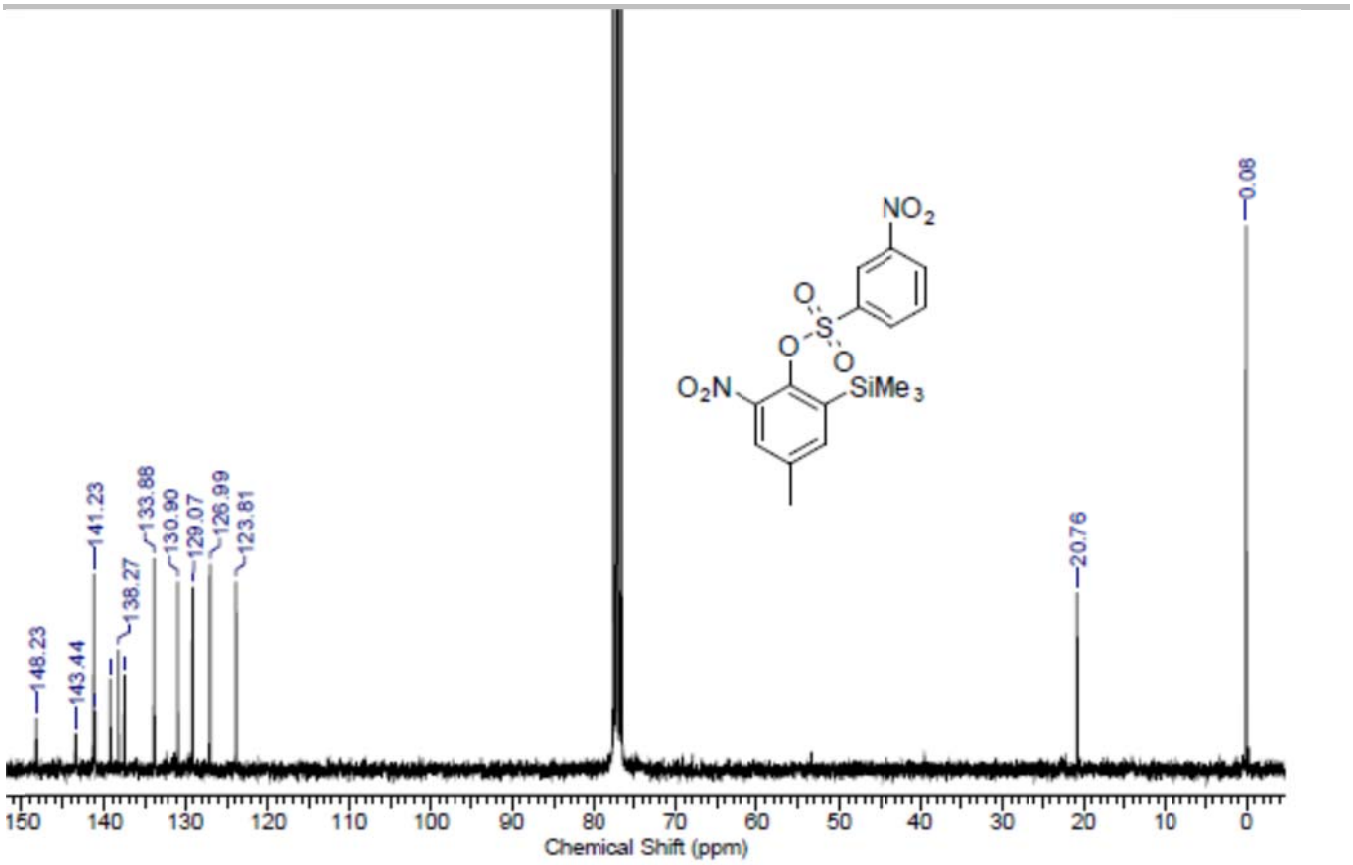

O2N
O
S
O
O
OHC
Si(CH3)3
1.90
2.13
2.15
1.84
3.06
9.00
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)
NO2
OHC
SiMe3
187.16
151.57
151.25
142.95
140.27
137.75
130.87
130.08
129.17
124.63
20.79
0.18
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Compound 38:

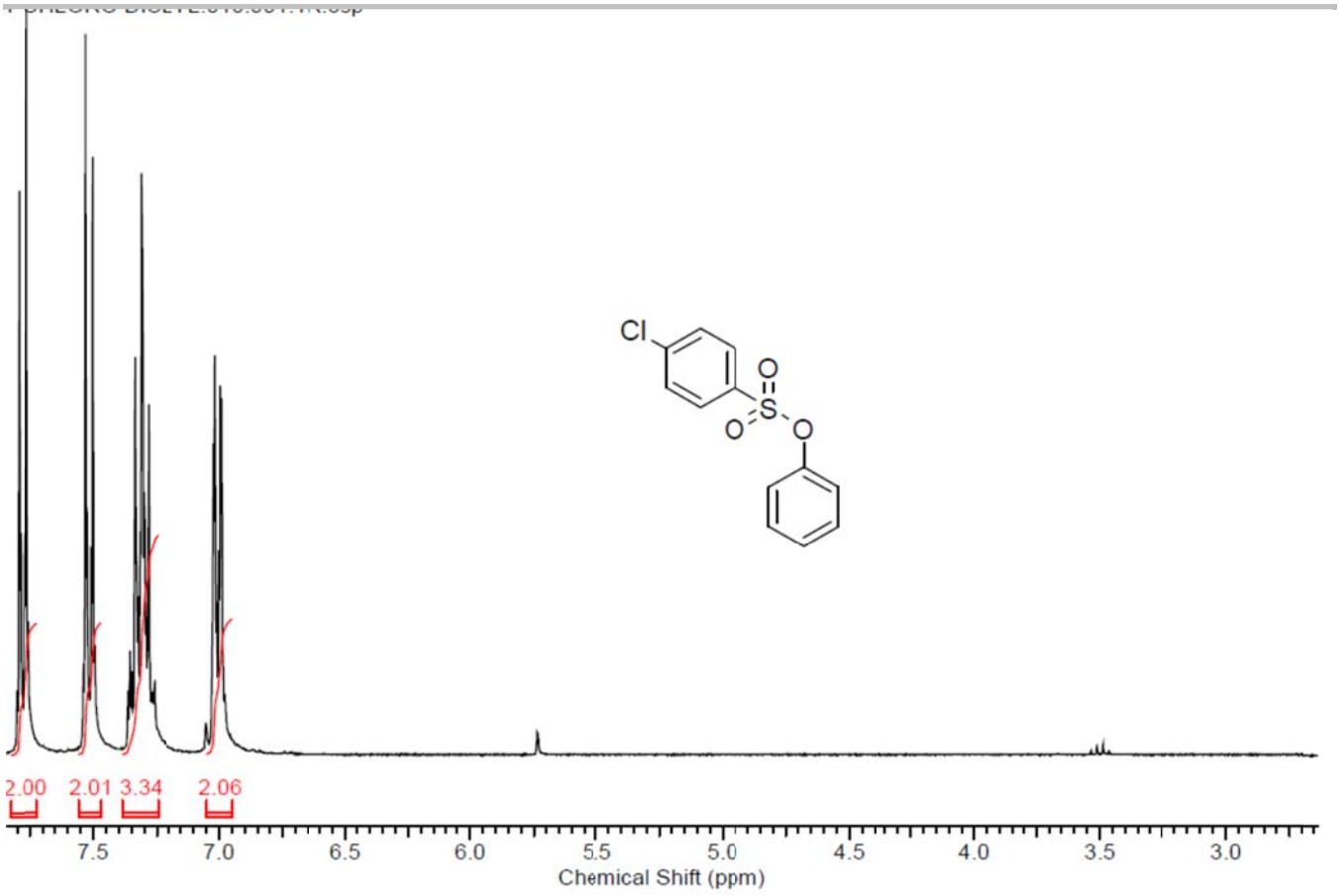

F3C
O2N
Si(CH3)3
2.02 2.11 0.92 1.06
2.96
9.00
Chemical Shift (ppm)
144.45
143.73
141.04
138.03
129.13
126.98
126.46
20.74
CF3
SiMe3
Chemical Shift (ppm)

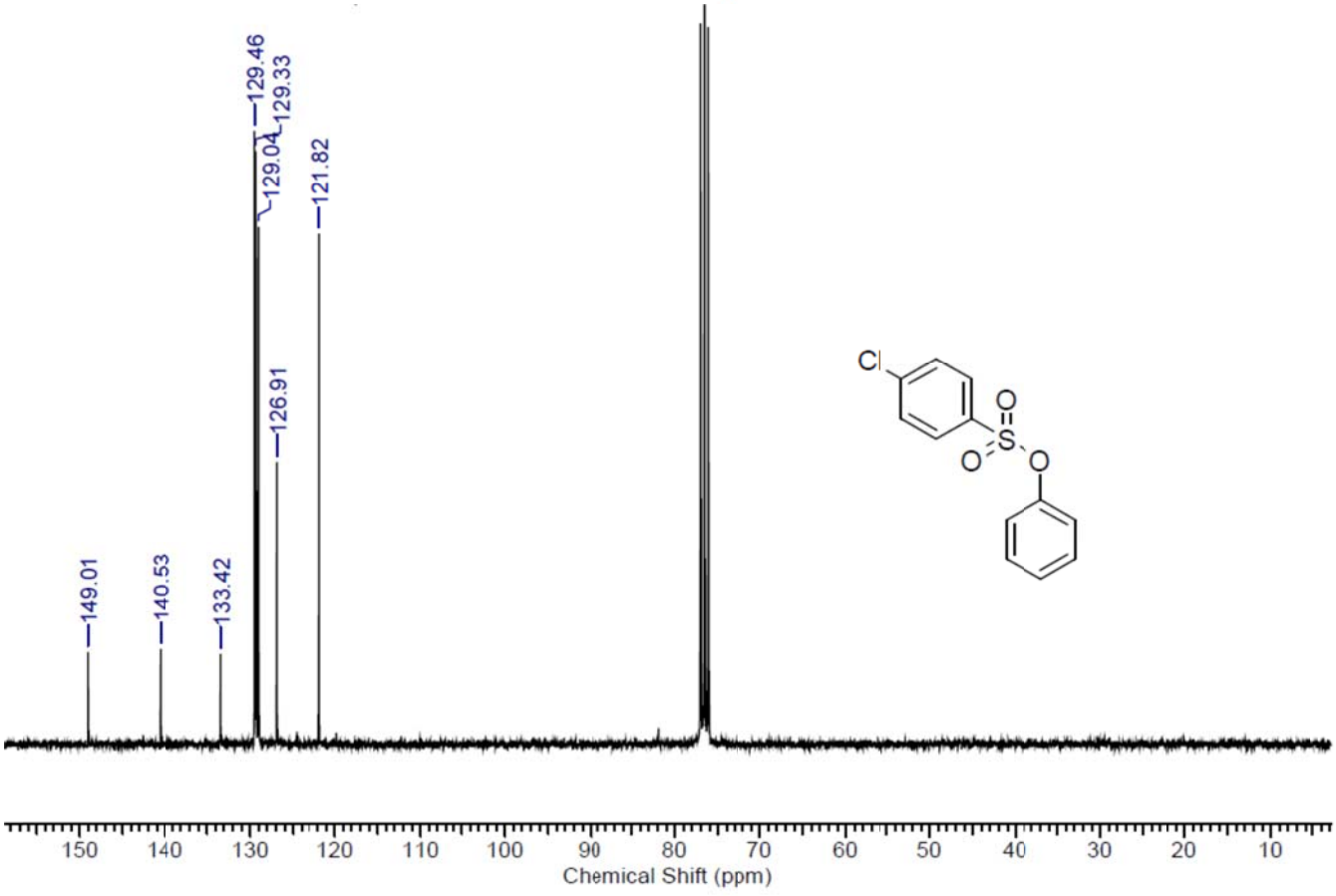
Compound 40:


13-05-07-PAC-48.010.001.1R.esp
NO2
O
S
O
O
O2N
SiMe3
0.97 1.15 1.07 1.21 1.06 1.40
3.35
9.68
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

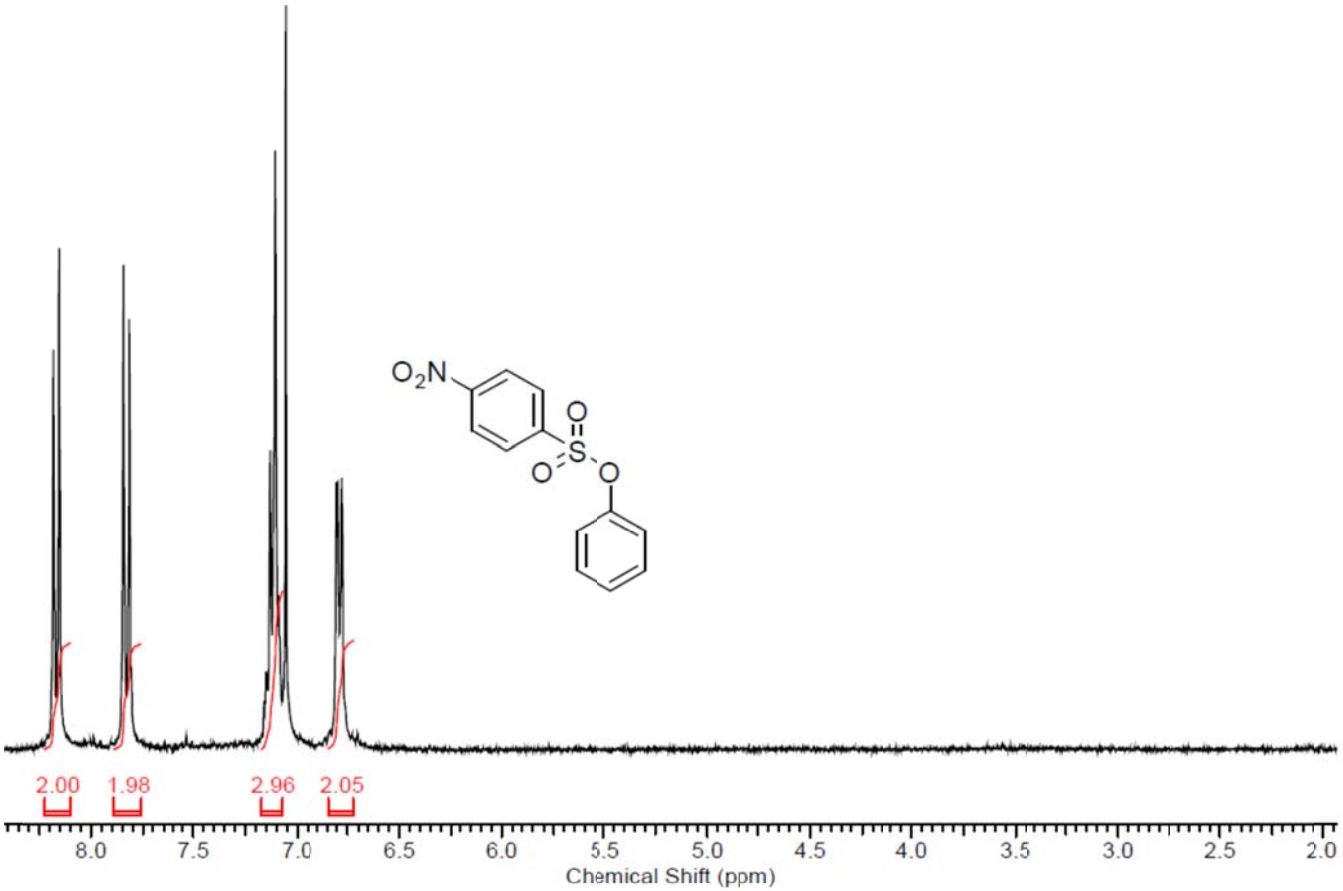

148.23
143.44
141.23
138.27
133.88
130.90
129.07
126.99
123.81
20.76
0.08
NO2
O
S
O
O
O2N
SiMe3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

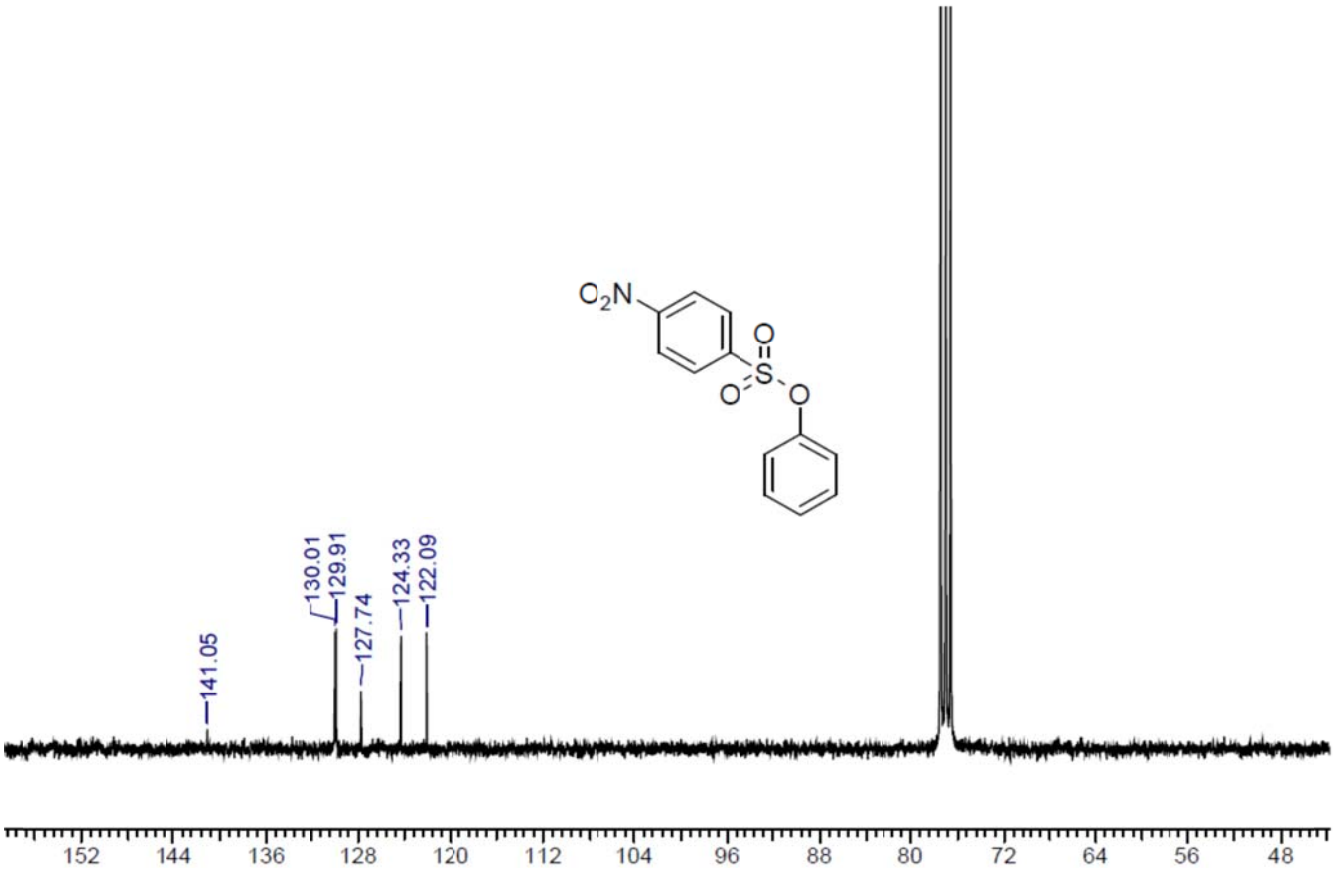
Compound 22:


Cl
O
S
O
O
2.00
2.01
3.34
2.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Chemical Shift (ppm)

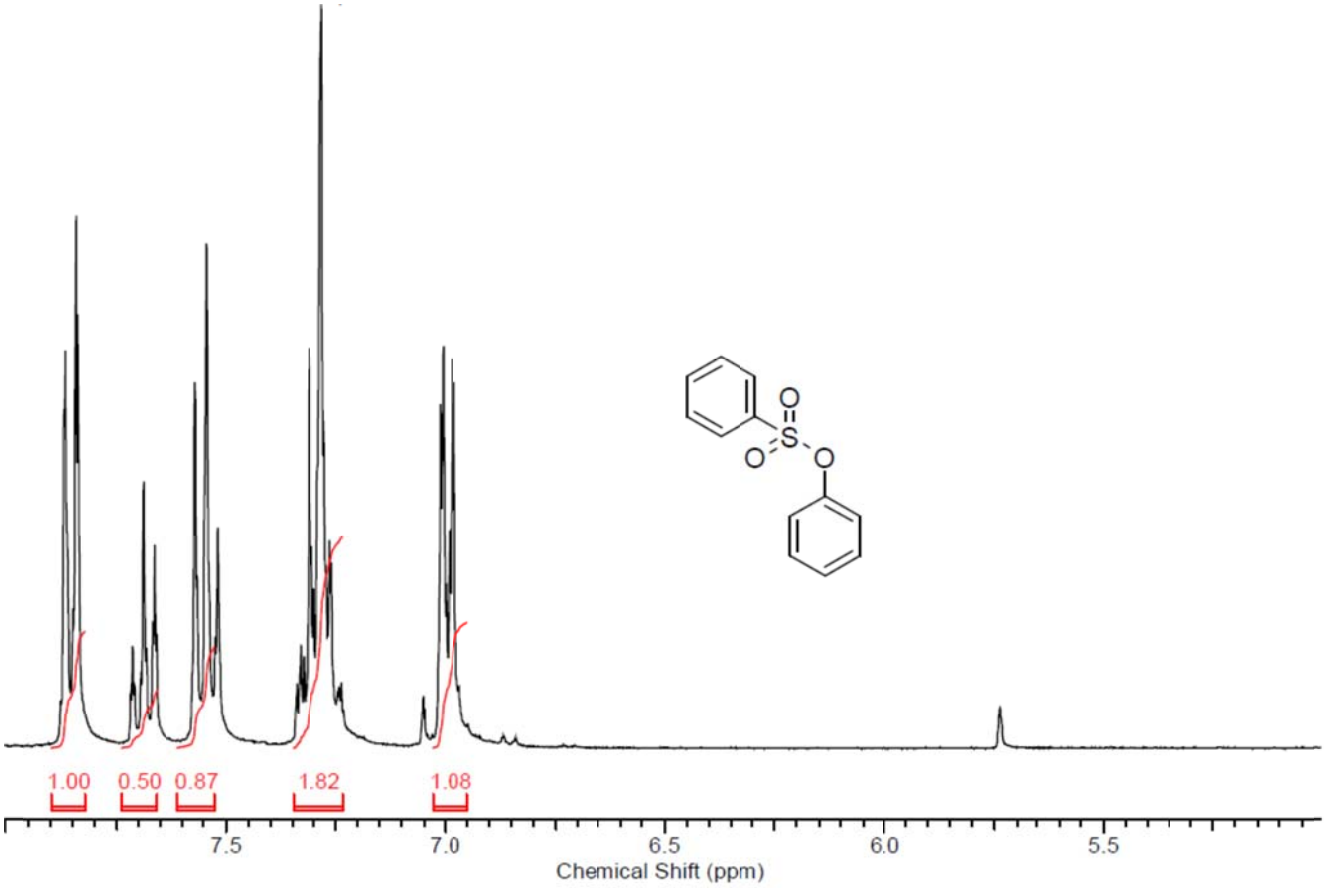

129.46
129.33
129.04
121.82
126.91
149.01
140.53
133.42
Cl
O
S
O
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

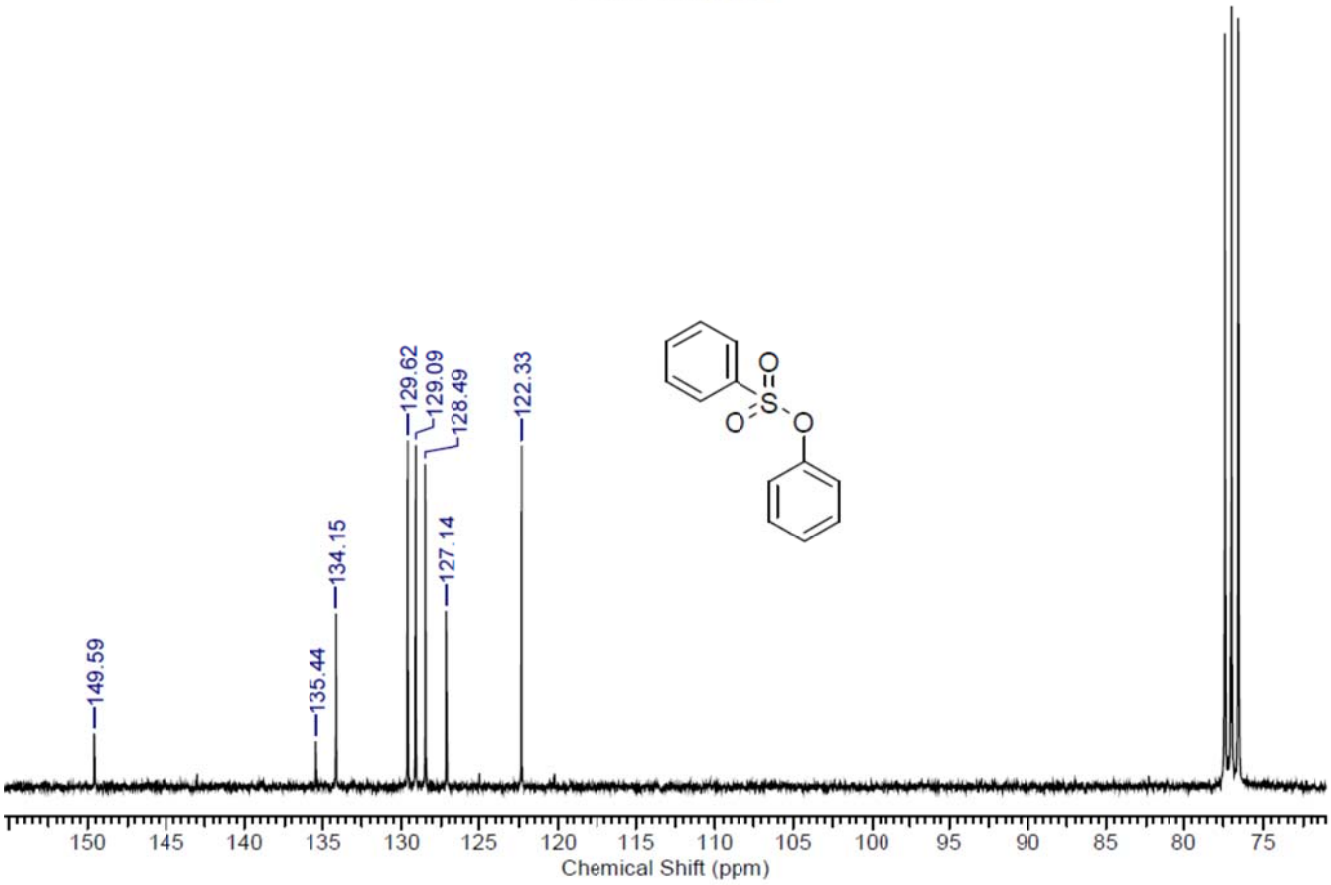
Compound 23:


O2N
O
S
O
O
2.00
1.98
2.96
2.05
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
Chemical Shift (ppm)

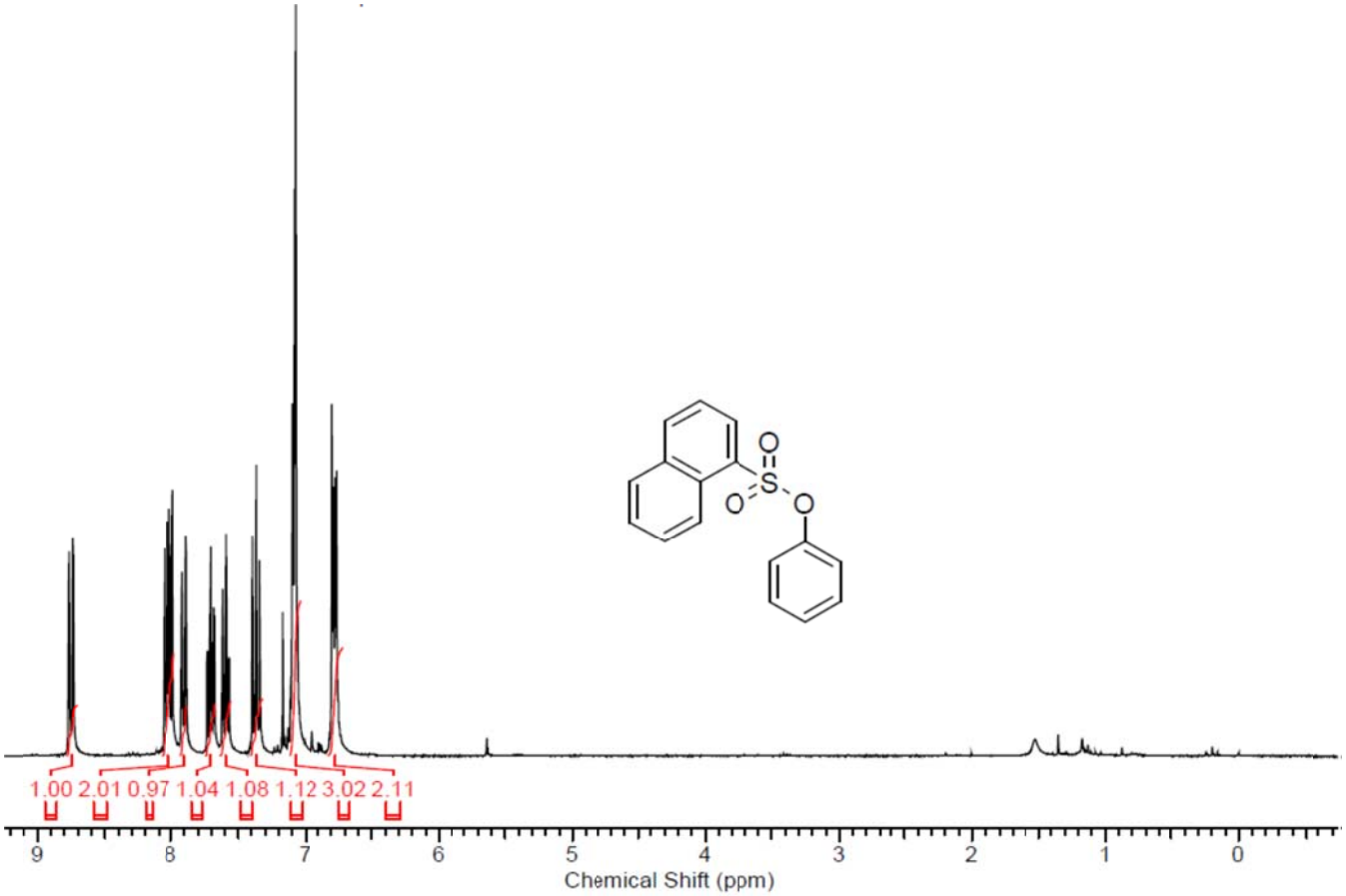

O2N
O
S
O
O
141.05
130.01
129.91
127.74
124.33
122.09
152
144
136
128
120
112
104
96
88
80
72
64
56
48

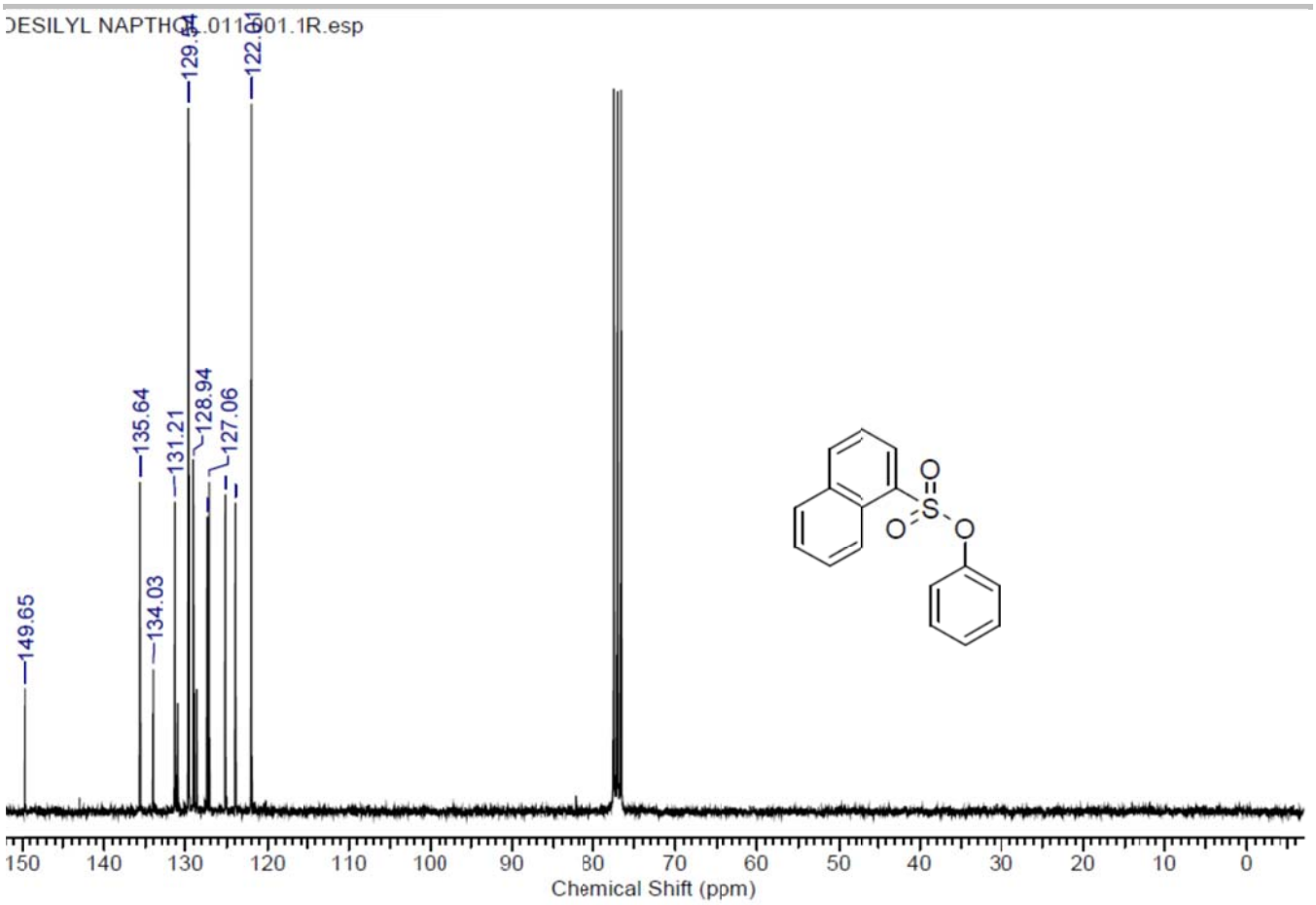
Compound 34:


1.00
0.50
0.87
1.82
1.08
7.5
7.0
6.5
6.0
5.5
Chemical Shift (ppm)

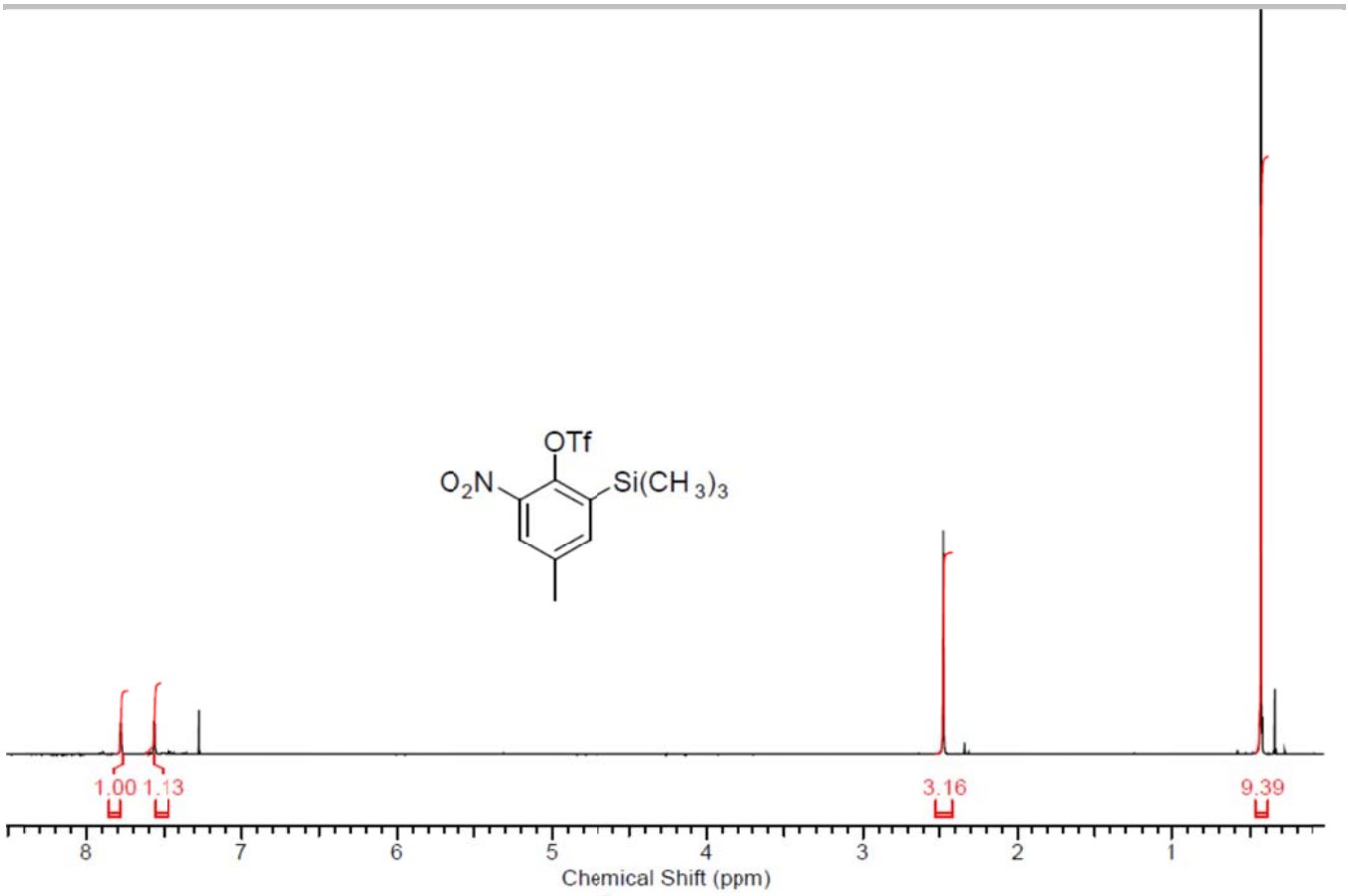

149.59
135.44
134.15
129.62
129.09
128.49
127.14
122.33
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
Chemical Shift (ppm)

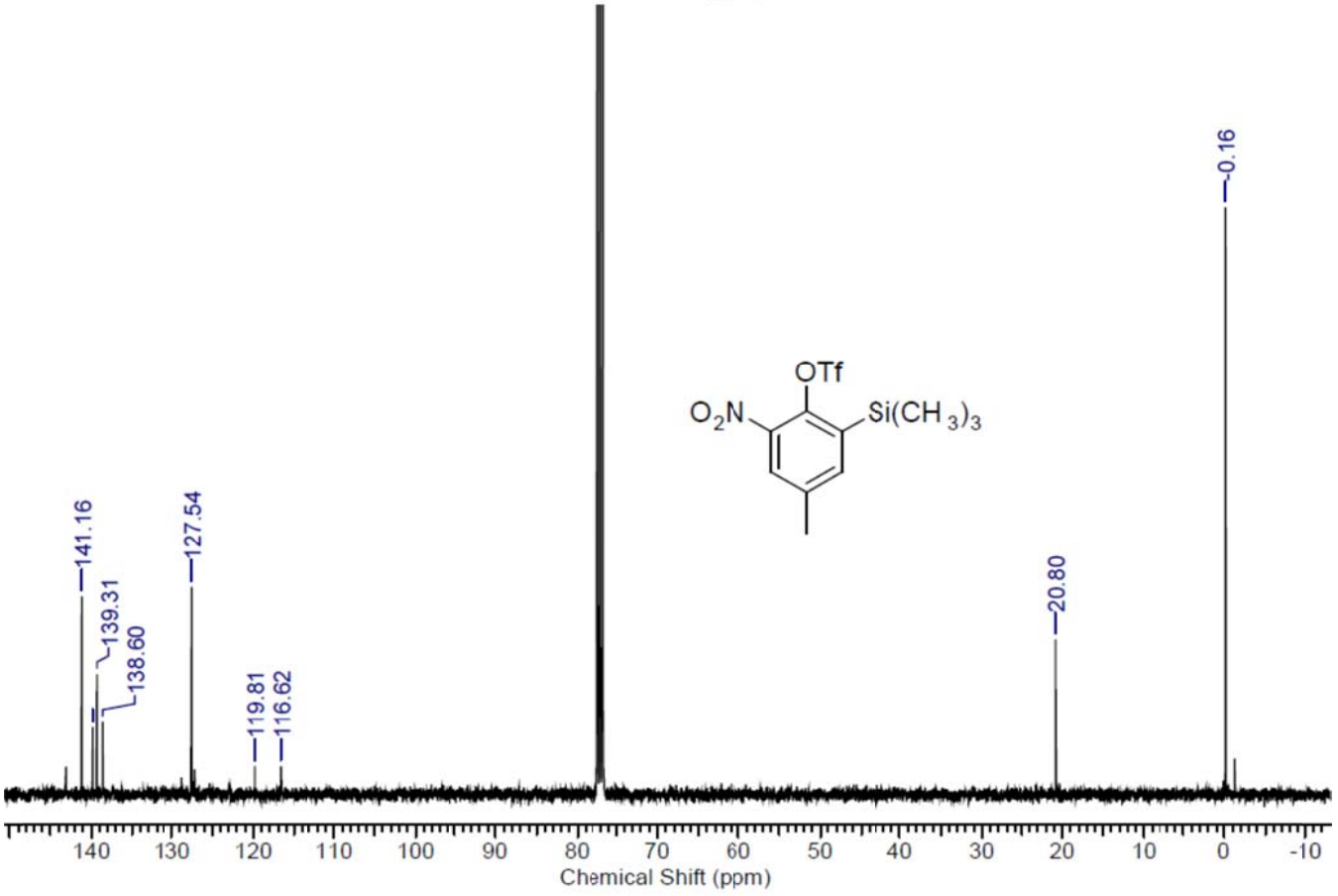
Compound 35:


1.00 2.01 0.97 1.04 1.08 1.12 3.02 2.11
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
O
S
O
O

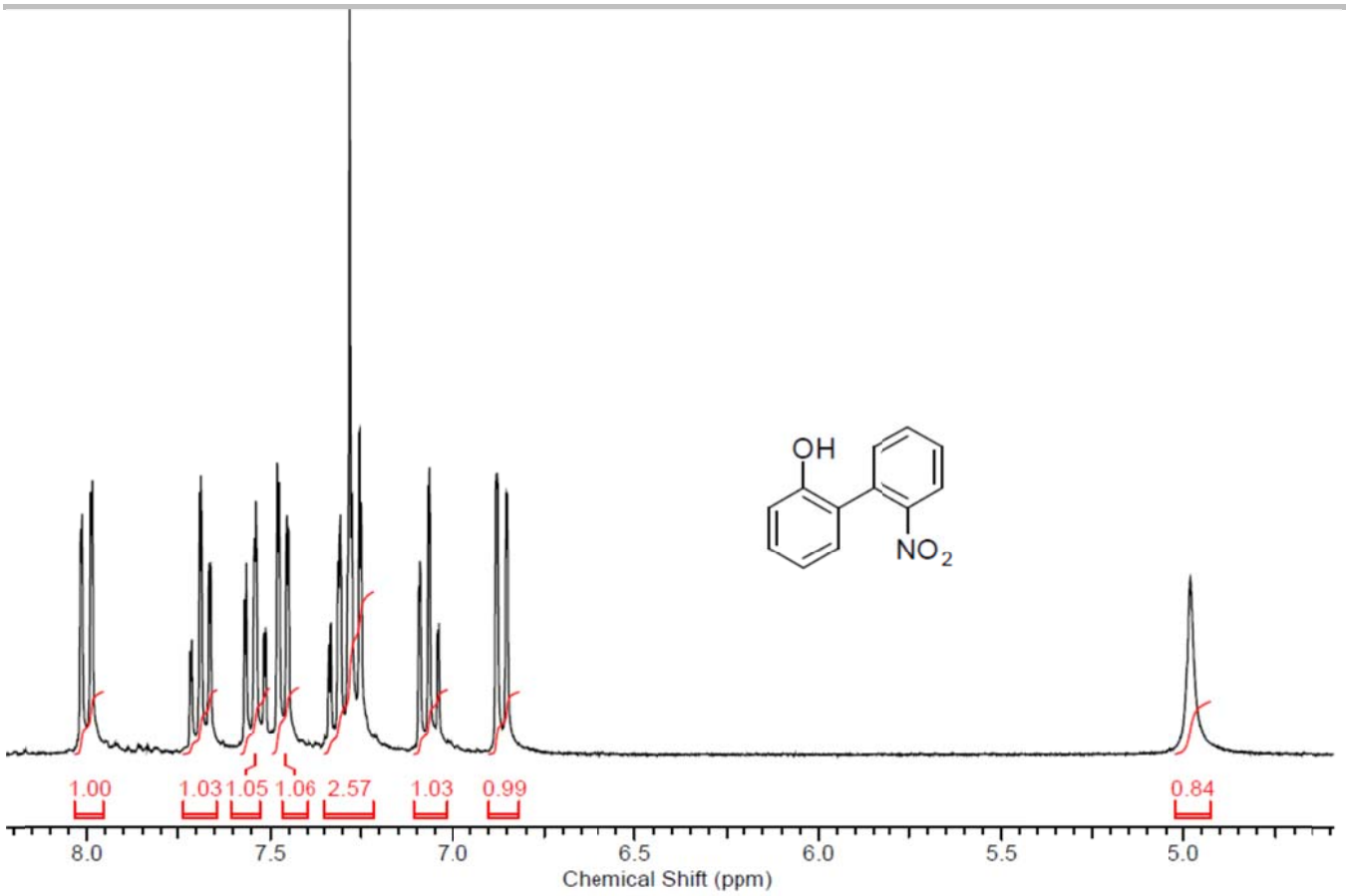

DESILYL NAPTHOL.011501.1R.esp
129.34
122.11
135.64
131.21
128.94
127.06
134.03
149.65
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

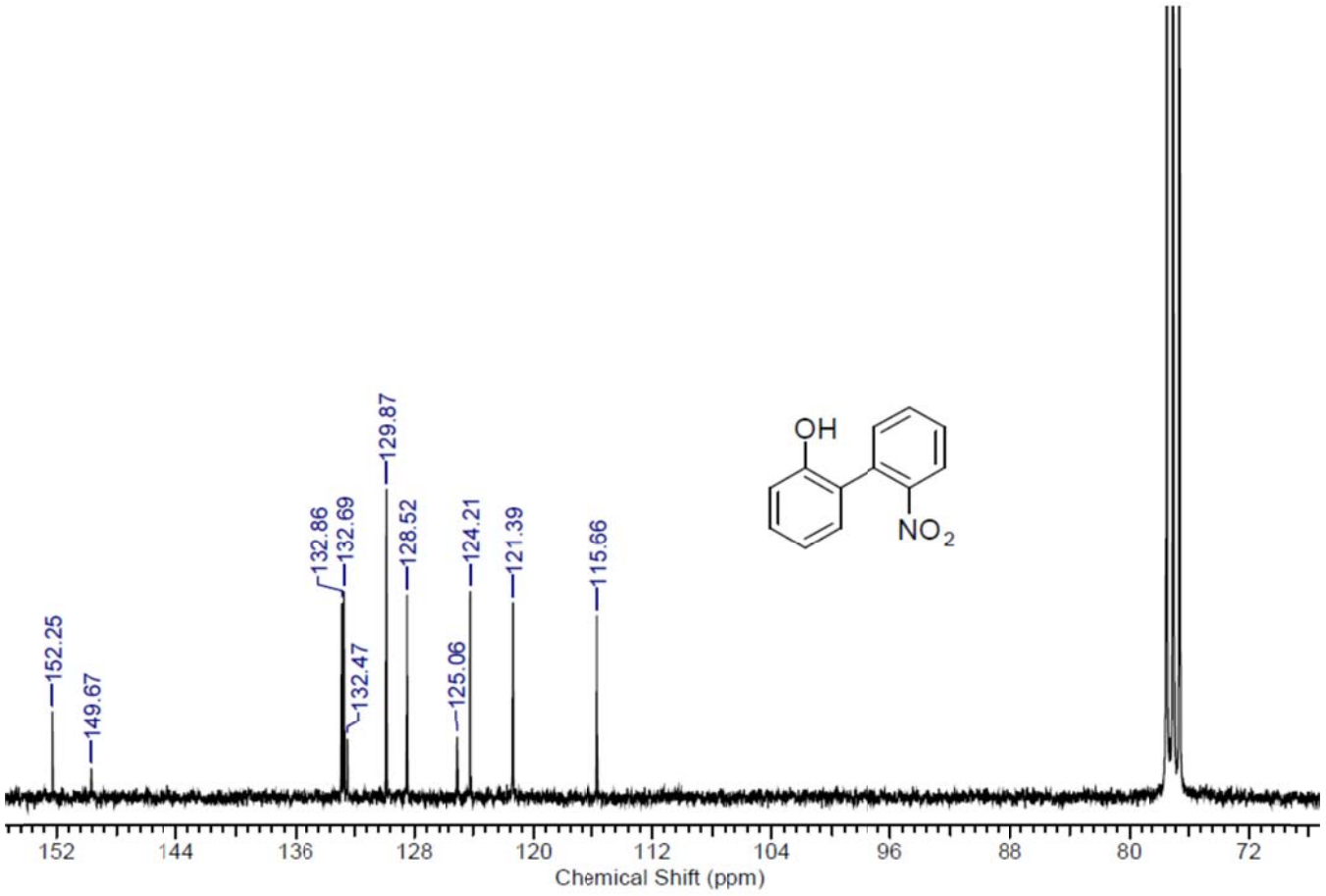
Compound 7:


OTf
O2N
Si(CH3)3
1.00
1.13
3.16
9.39
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

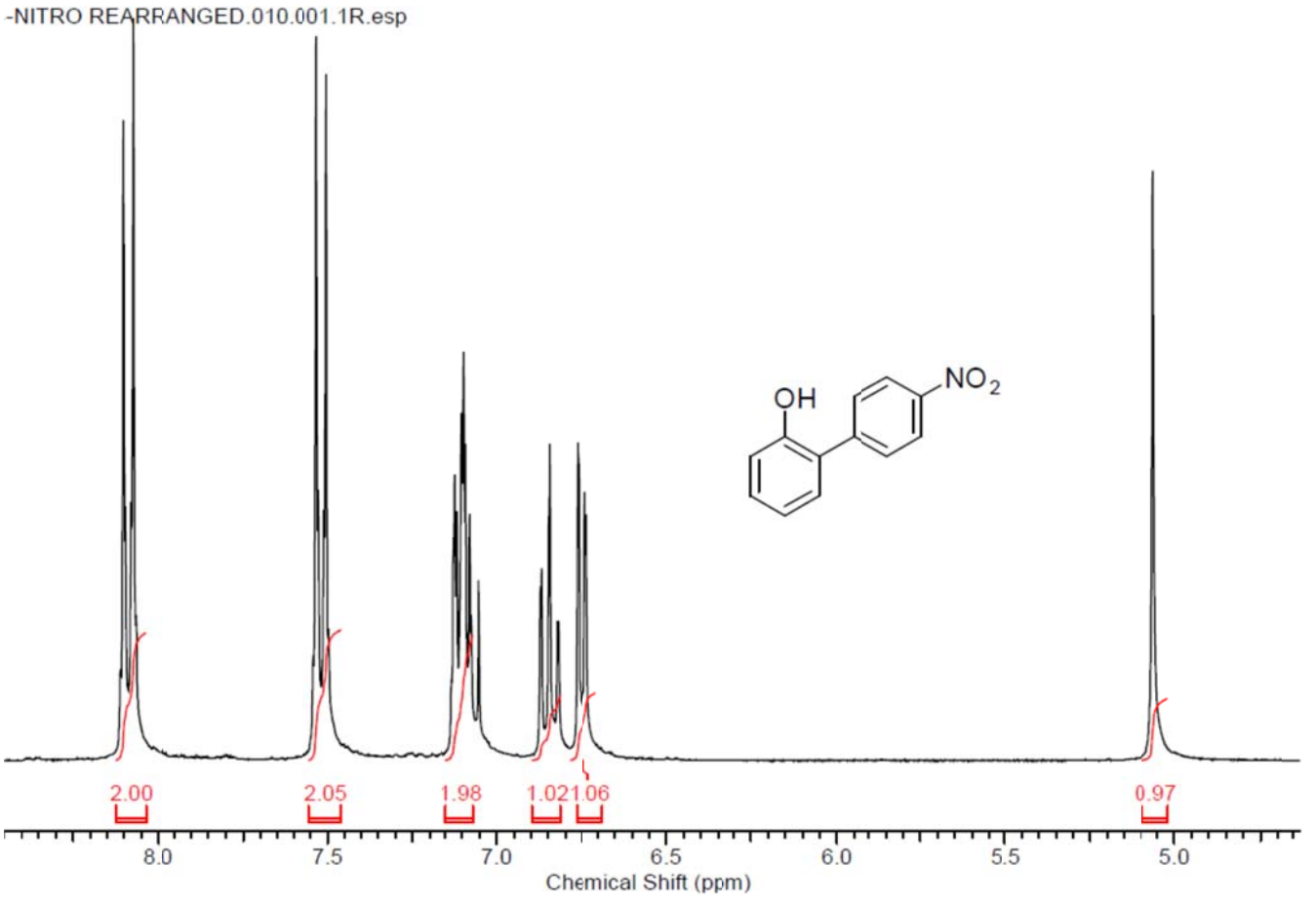

OTf
O2N
Si(CH3)3
141.16
139.31
138.60
127.54
119.81
116.62
20.80
0.16
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

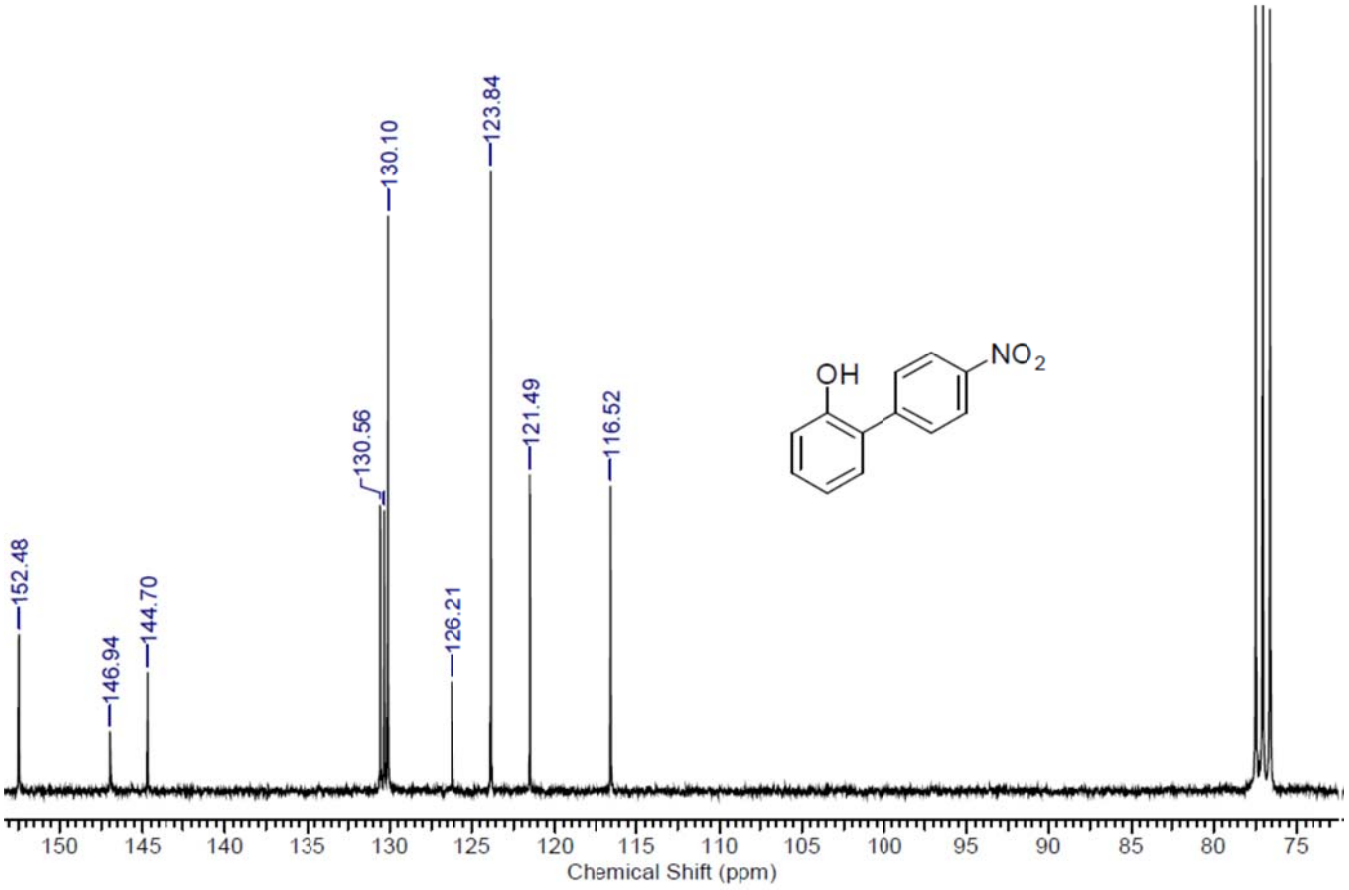
Compound 26:


OH
NO2
1.00
1.03
1.05
1.06
2.57
1.03
0.99
0.84
8.0
7.5
7.0
6.5
6.0
5.5
5.0
Chemical Shift (ppm)

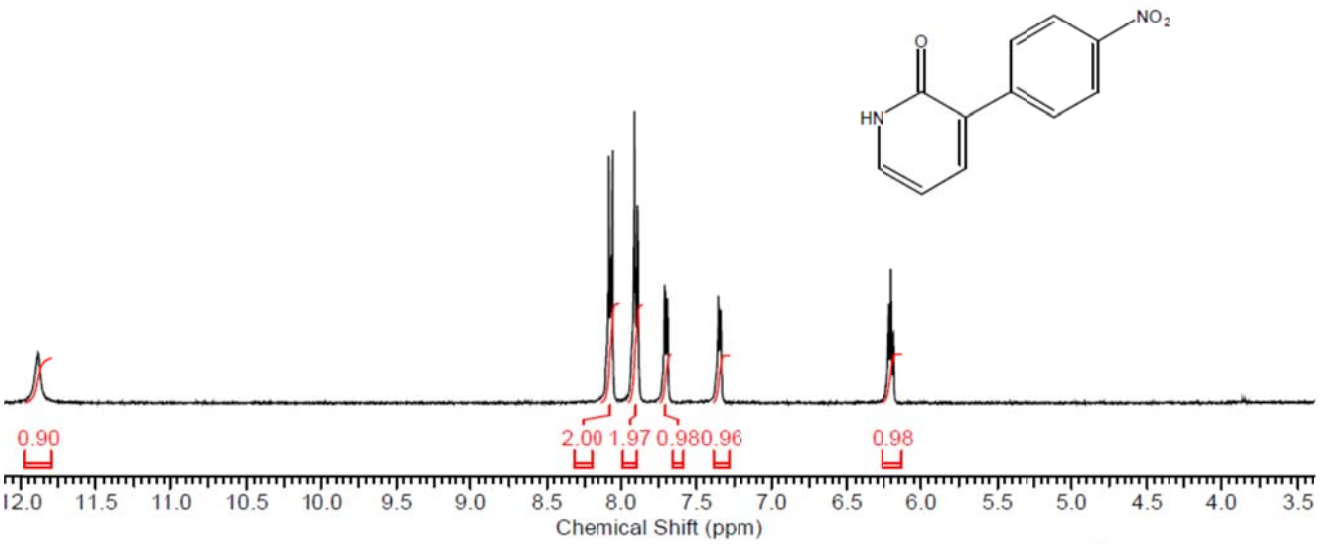

OH
NO2
152.25
149.67
132.86
132.69
132.47
129.87
128.52
125.06
124.21
121.39
115.66
152
144
136
128
120
112
104
96
88
80
72
Chemical Shift (ppm)

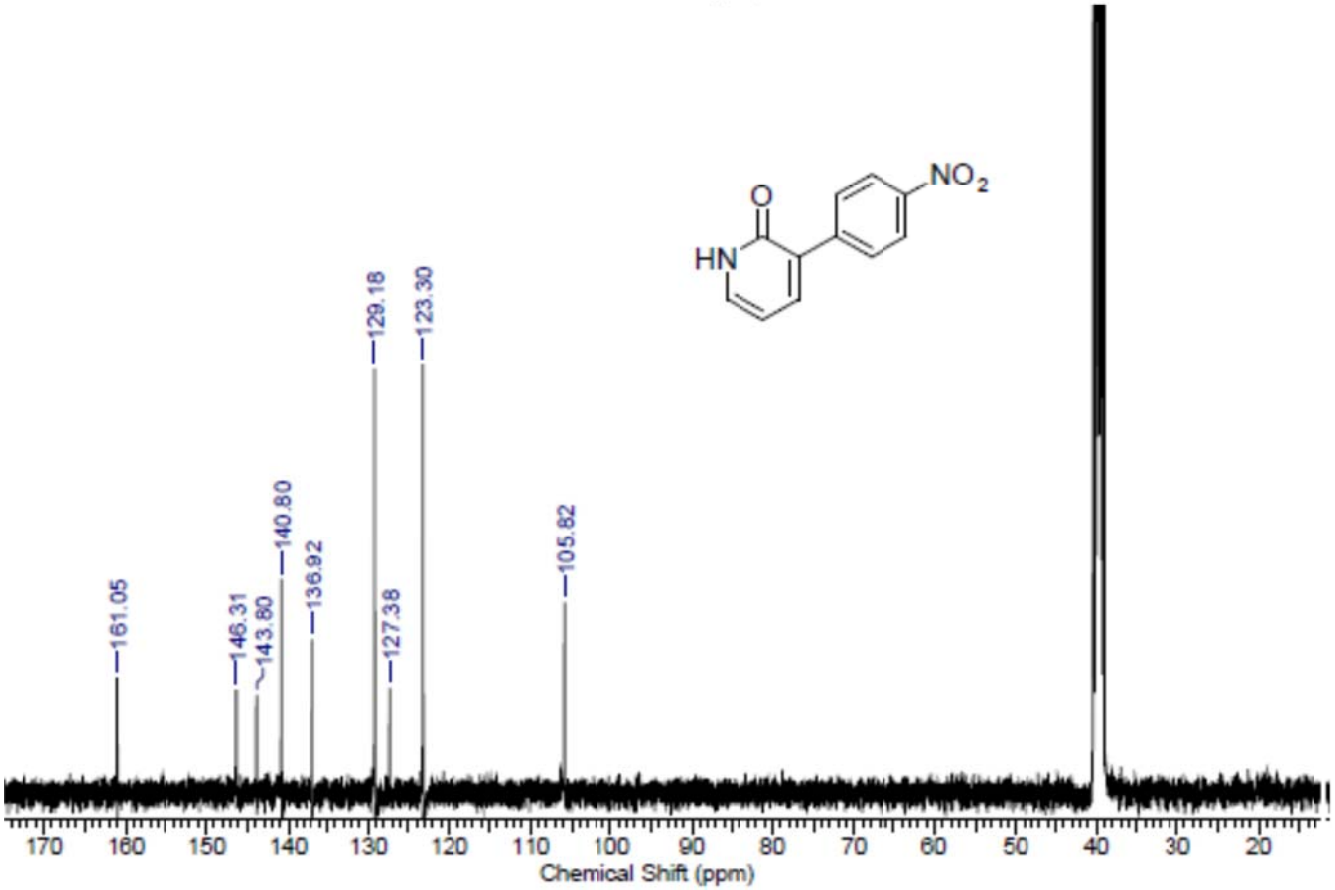
Compound 25:


-NITRO REARRANGED.010.001.1R.esp
OH
NO2
2.00
2.05
1.98
1.02
1.06
0.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
Chemical Shift (ppm)

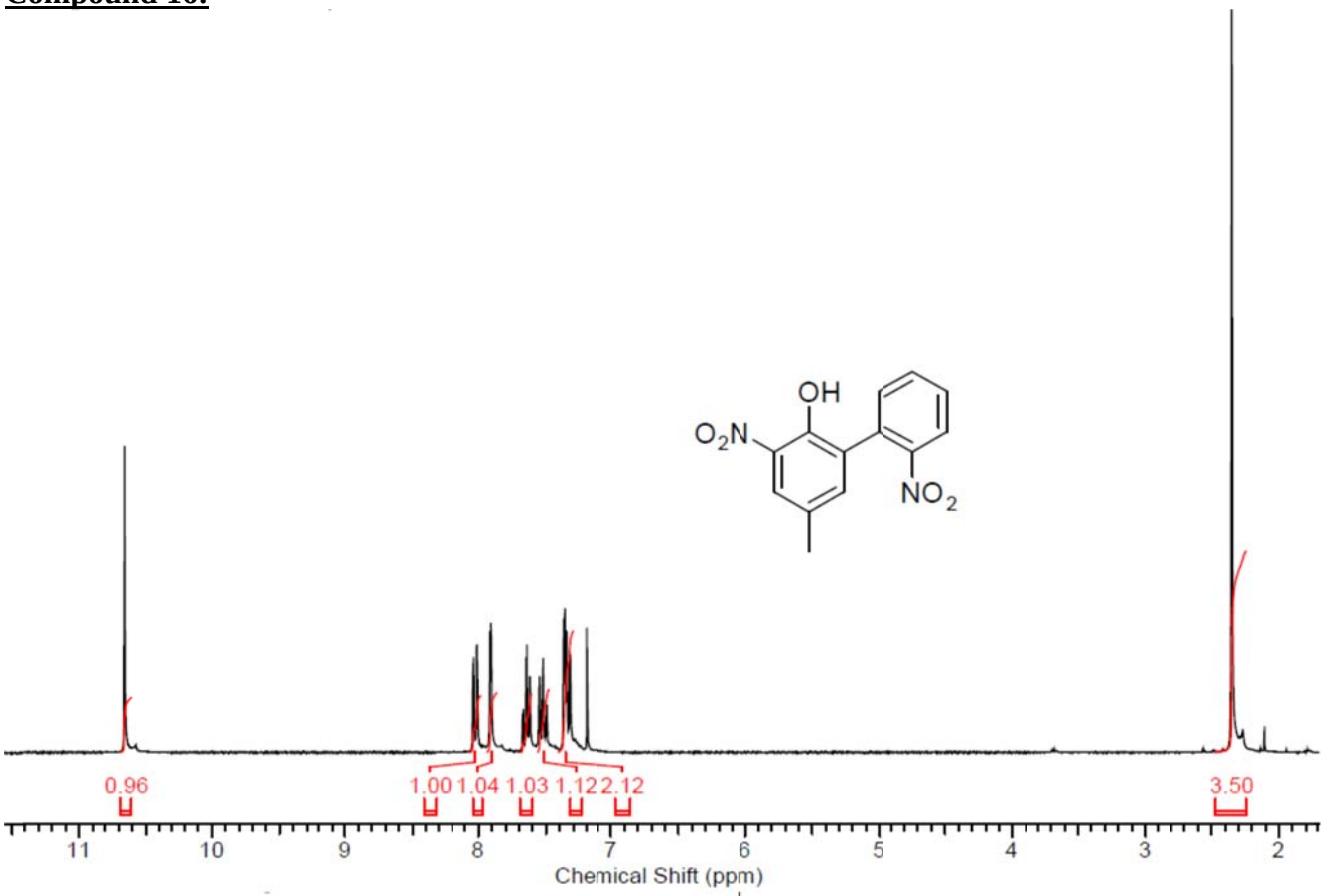

OH
NO2
152.48
146.94
144.70
130.56
130.10
126.21
123.84
121.49
116.52
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
Chemical Shift (ppm)

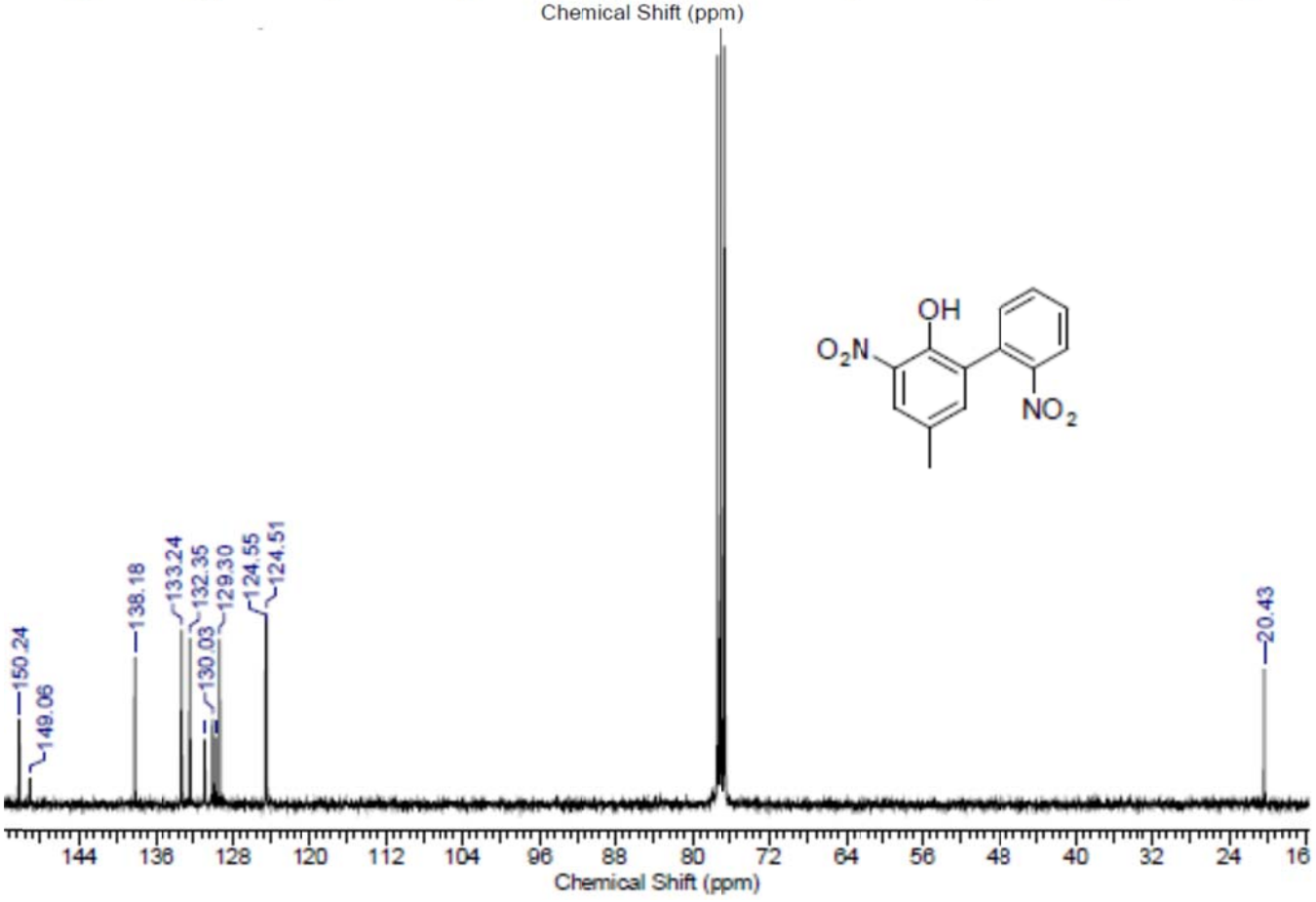
Compound 52:


NO2
O
HN
0.90
2.00
1.97
0.98
0.96
0.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5
Chemical Shift (ppm)

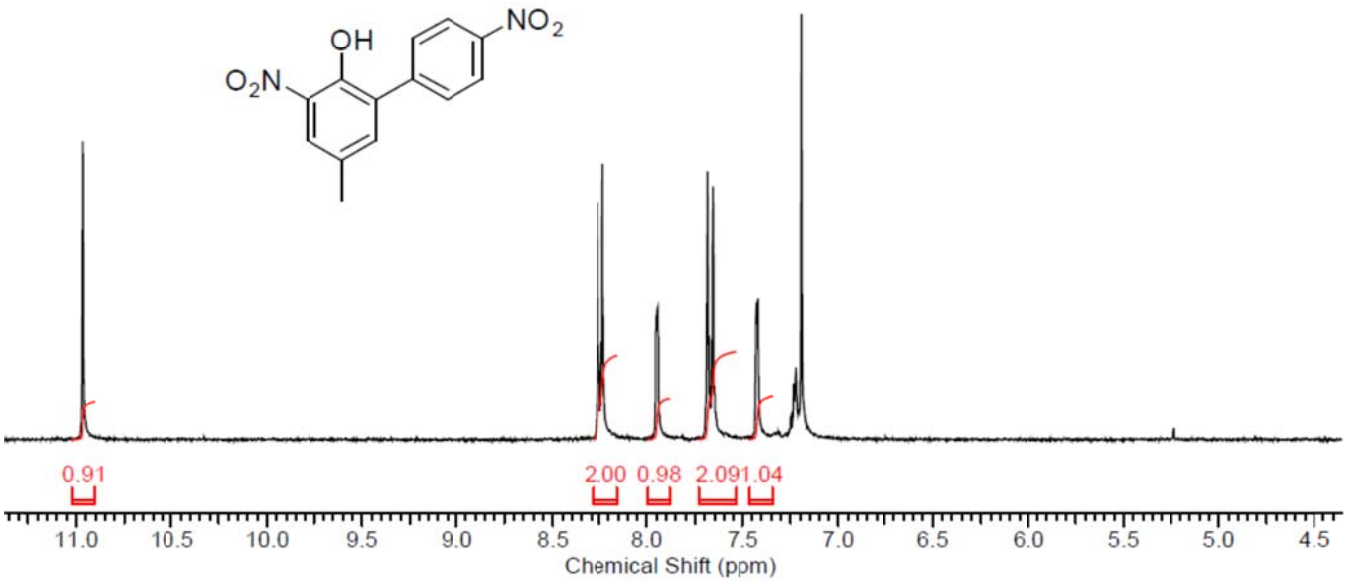

NO2
O
HN
161.05
146.31
143.80
140.80
136.92
129.18
127.38
123.30
105.82
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
Chemical Shift (ppm)

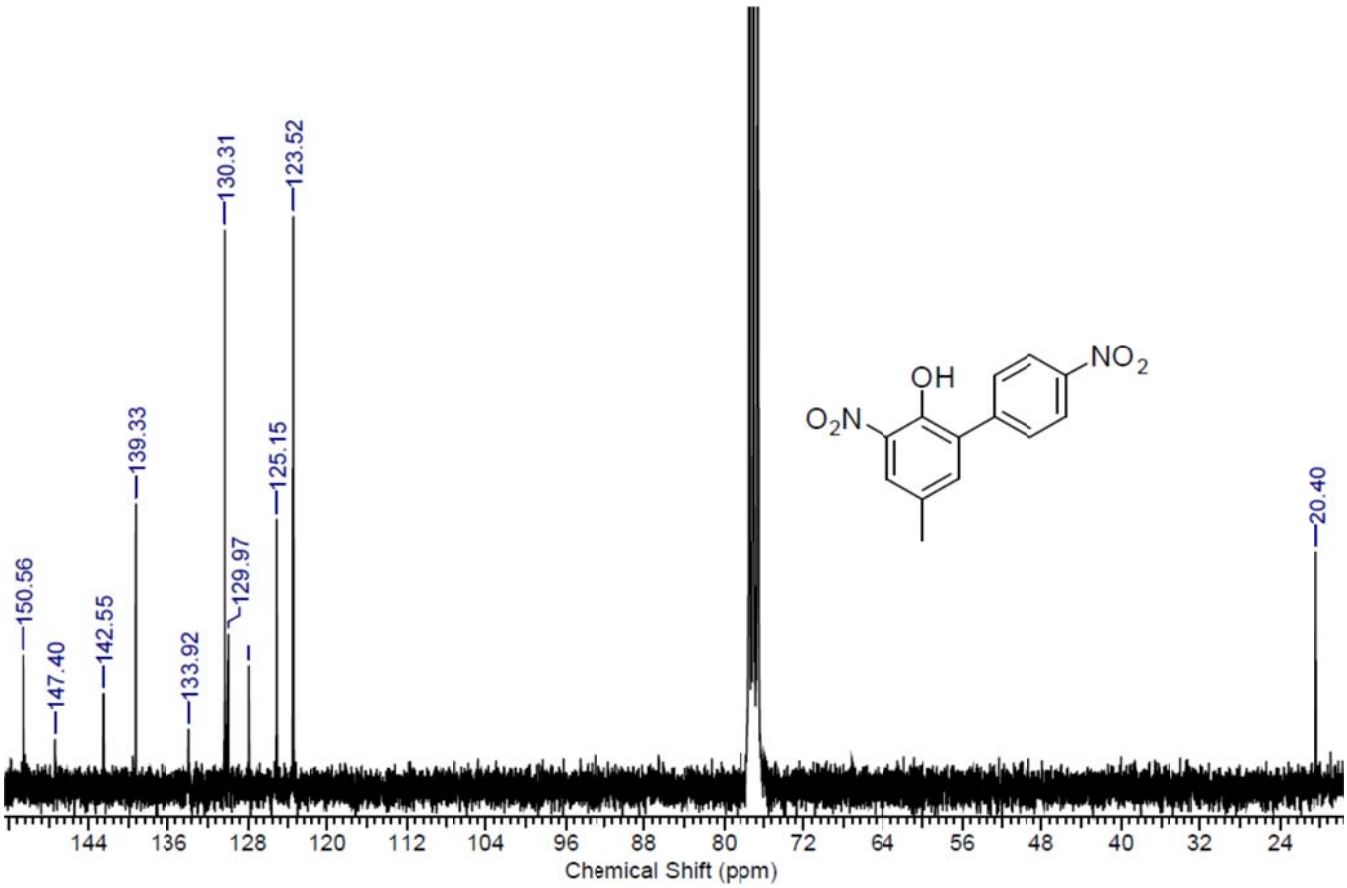
Compound 16:


OH
O_2N
NO_2
0.96
1.00 1.04 1.03 1.12 2.12
3.50
11 10 9 8 7 6 5 4 3 2
Chemical Shift (ppm)

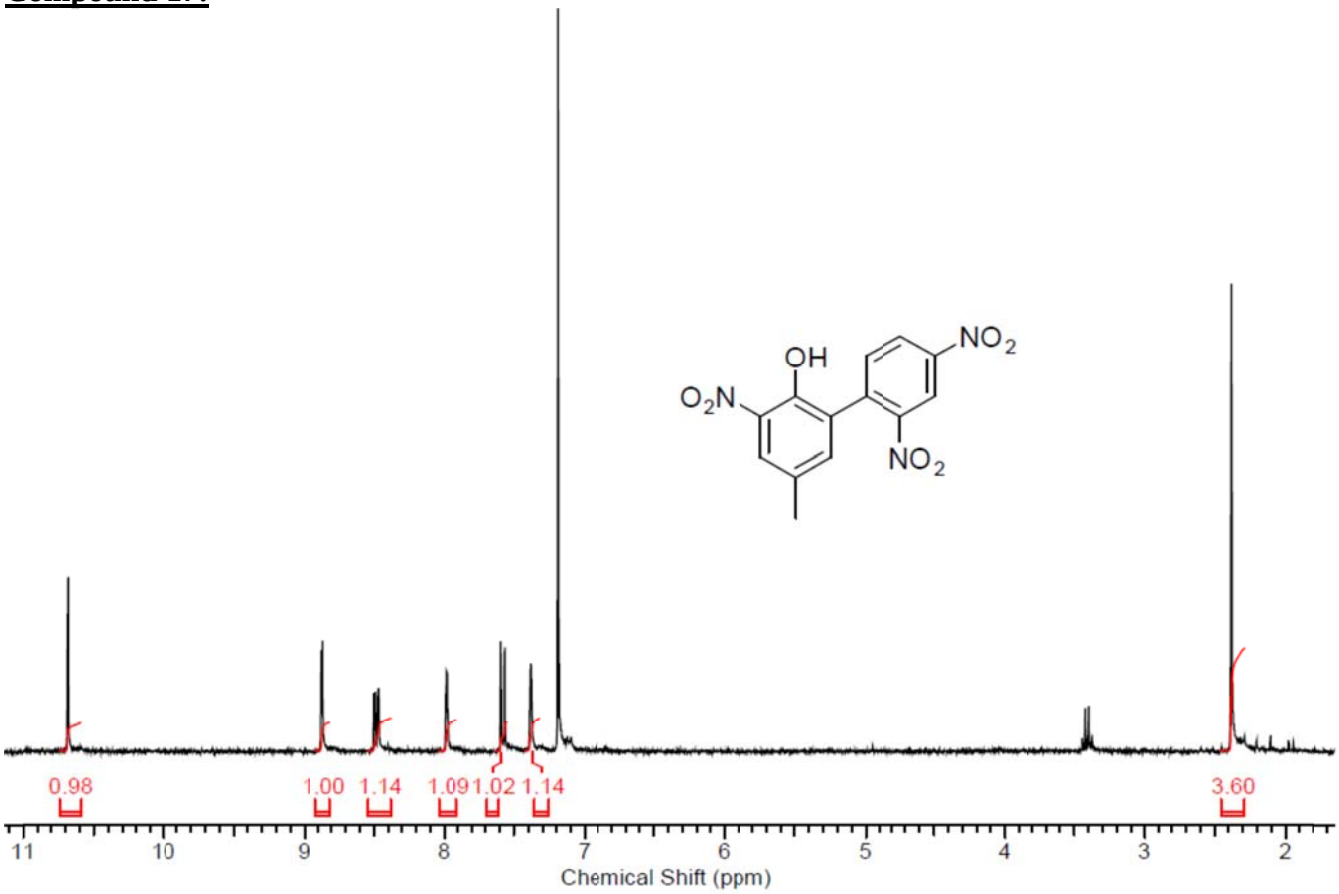

OH
O_2N
NO_2
150.24
149.06
138.18
133.24
132.35
130.03
129.30
124.55
124.51
20.43
144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16
Chemical Shift (ppm)

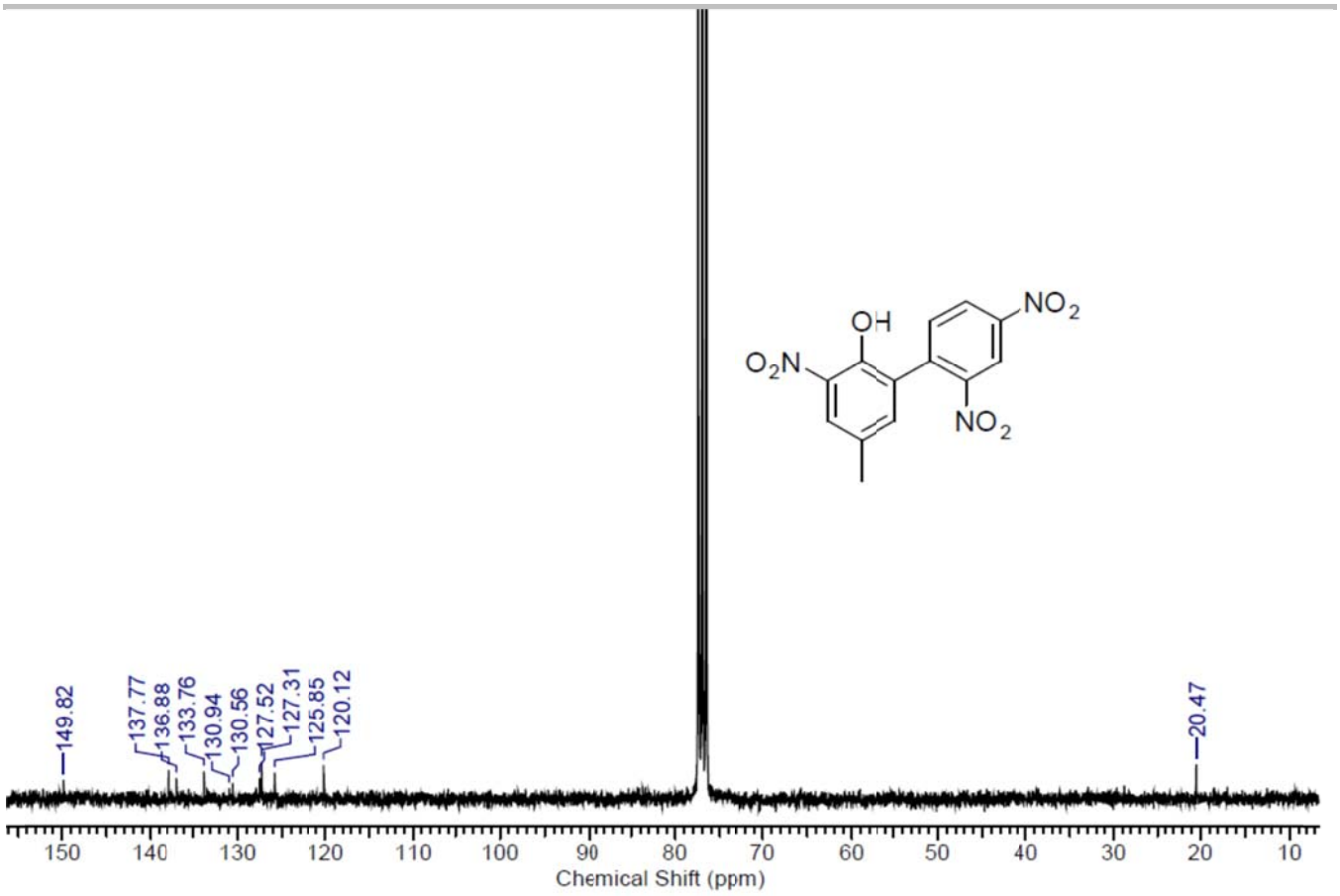
Compound 15:


OH
O_2N
NO_2
0.91
2.00
0.98
2.09
1.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
Chemical Shift (ppm)

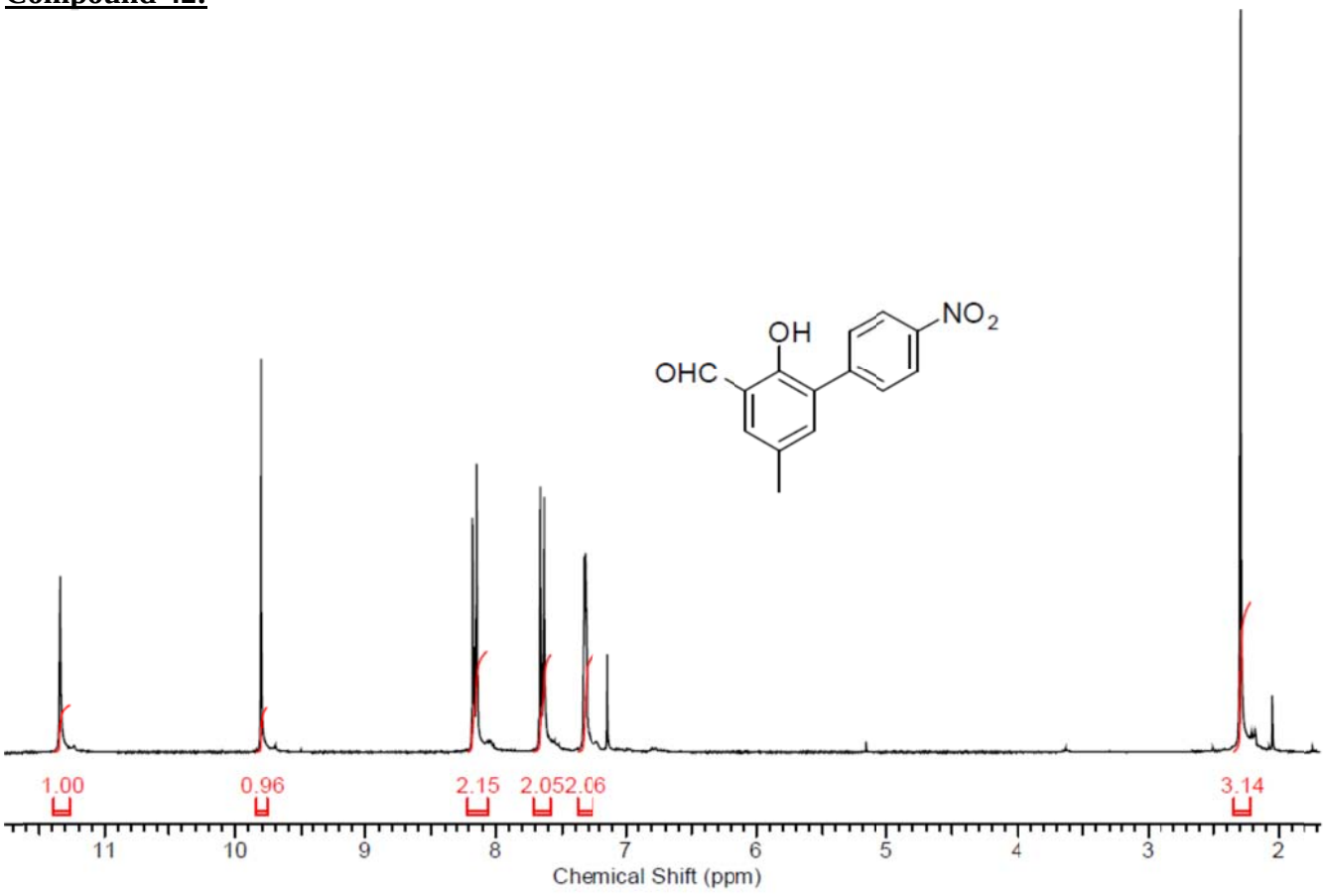

150.56
147.40
142.55
139.33
133.92
130.31
129.97
125.15
123.52
20.40
OH
O_2N
NO_2
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

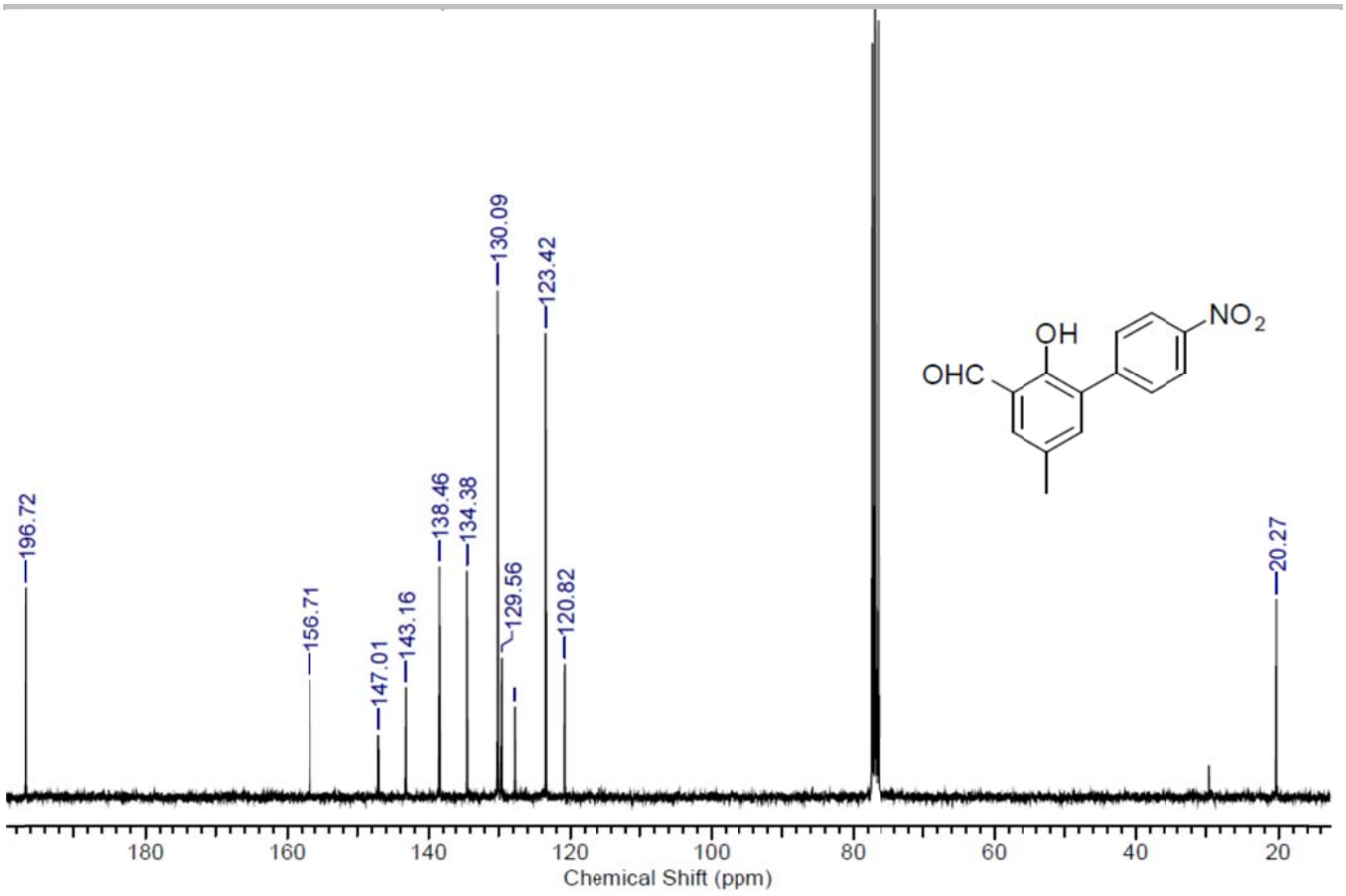
Compound 17:


OH
O_2N
NO_2
NO_2
0.98
1.00
1.14
1.09
1.02
1.14
3.60
11
10
9
8
7
6
5
4
3
2
Chemical Shift (ppm)

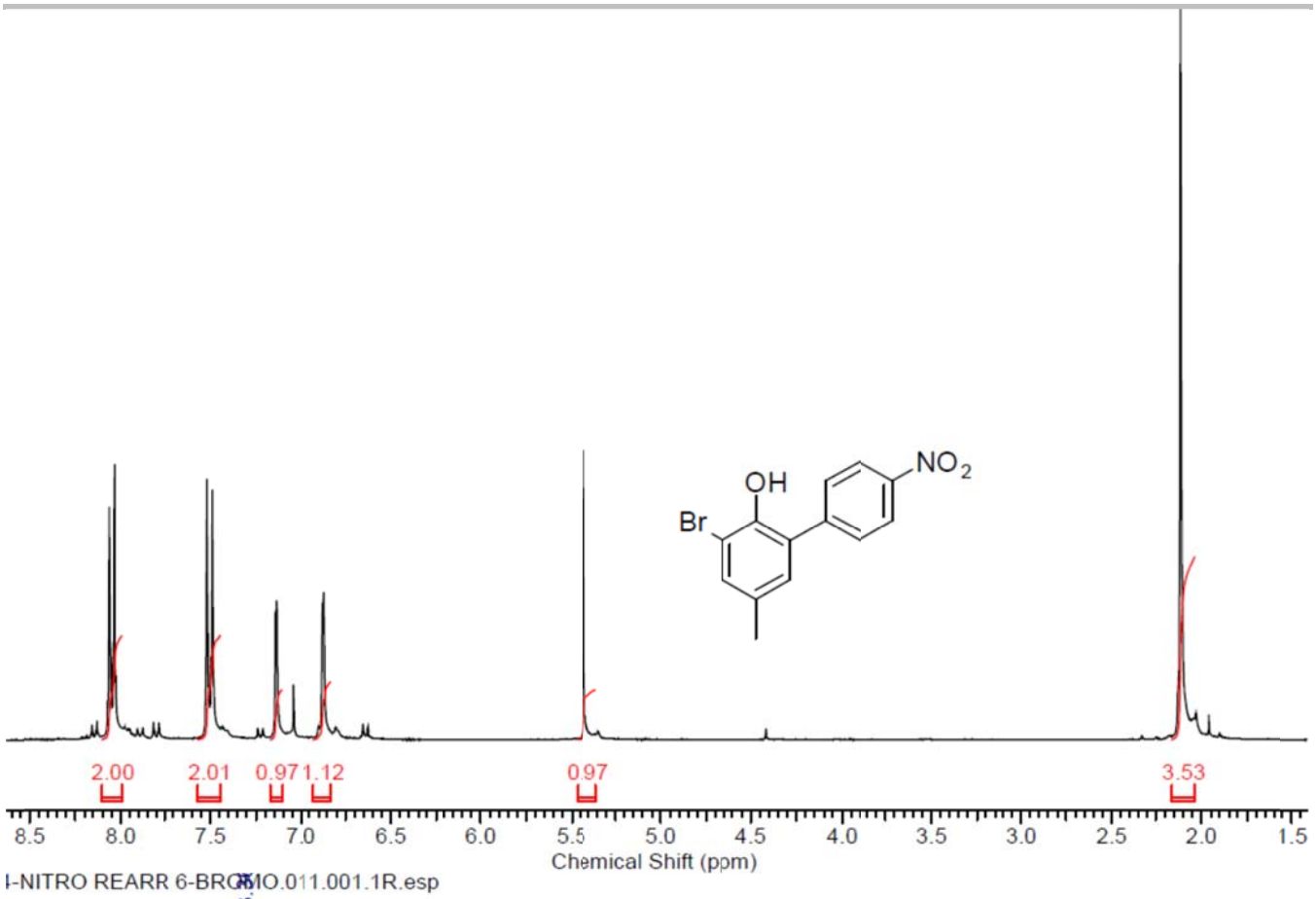

OH
O_2N
NO_2
NO_2
149.82
137.77
136.88
133.76
130.94
130.56
127.52
127.31
125.85
120.12
20.47
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)

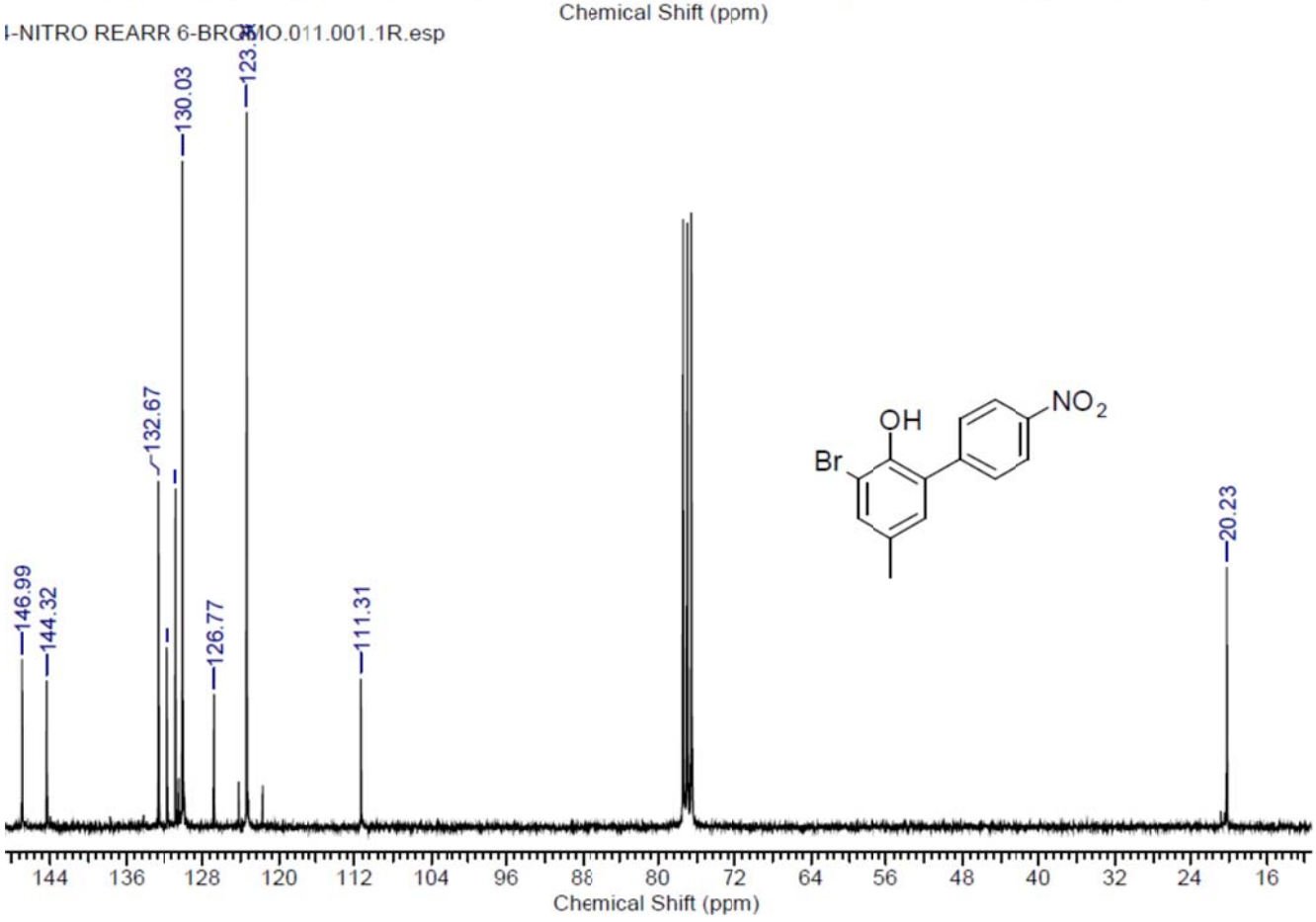
Compound 42:


OH
OHC
NO_2
1.00
0.96
2.15
2.05
2.06
3.14
11 10 9 8 7 6 5 4 3 2
Chemical Shift (ppm)

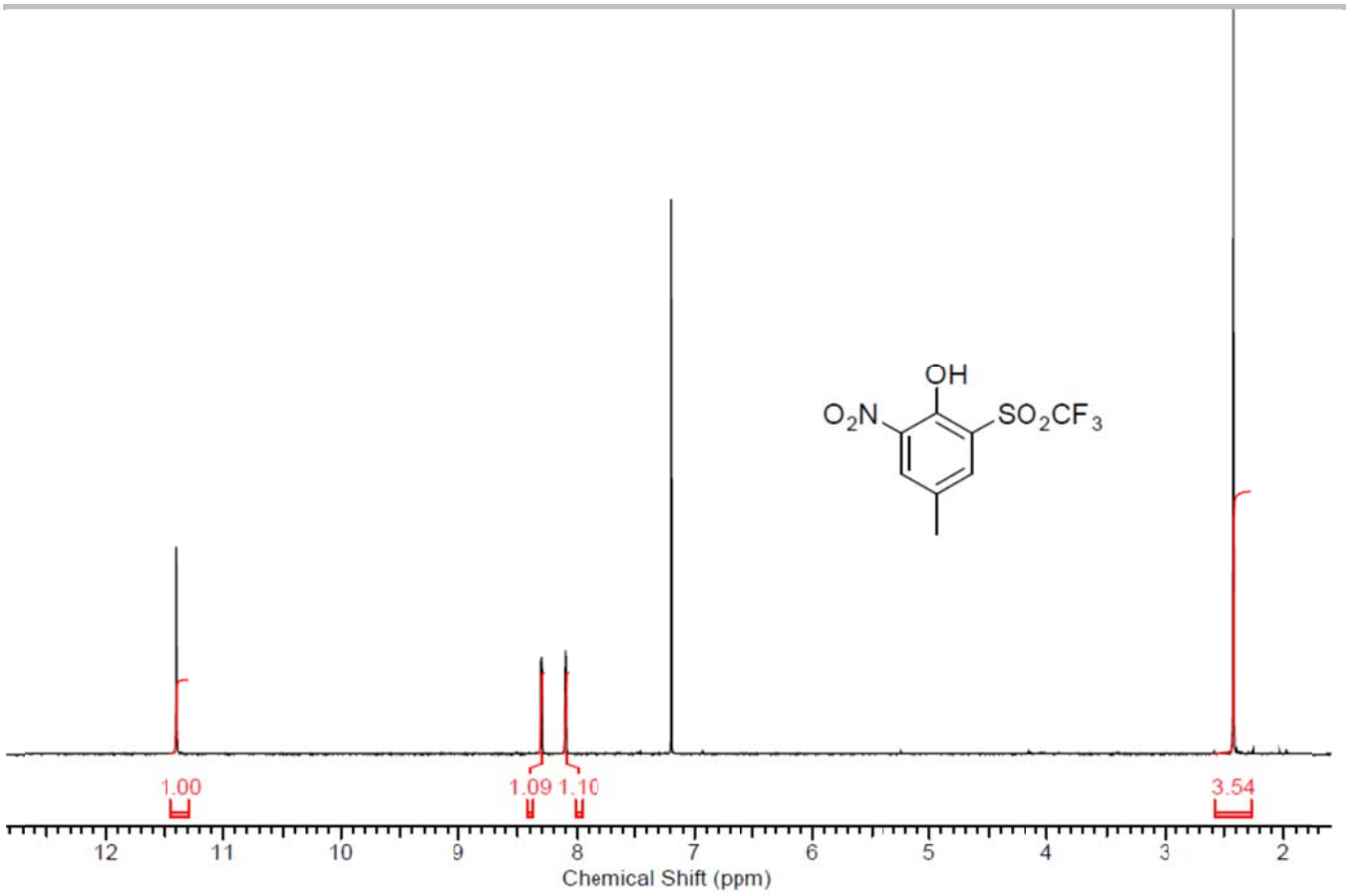

196.72
156.71
147.01
143.16
138.46
134.38
130.09
129.56
123.42
120.82
20.27
OH
OHC
NO2
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

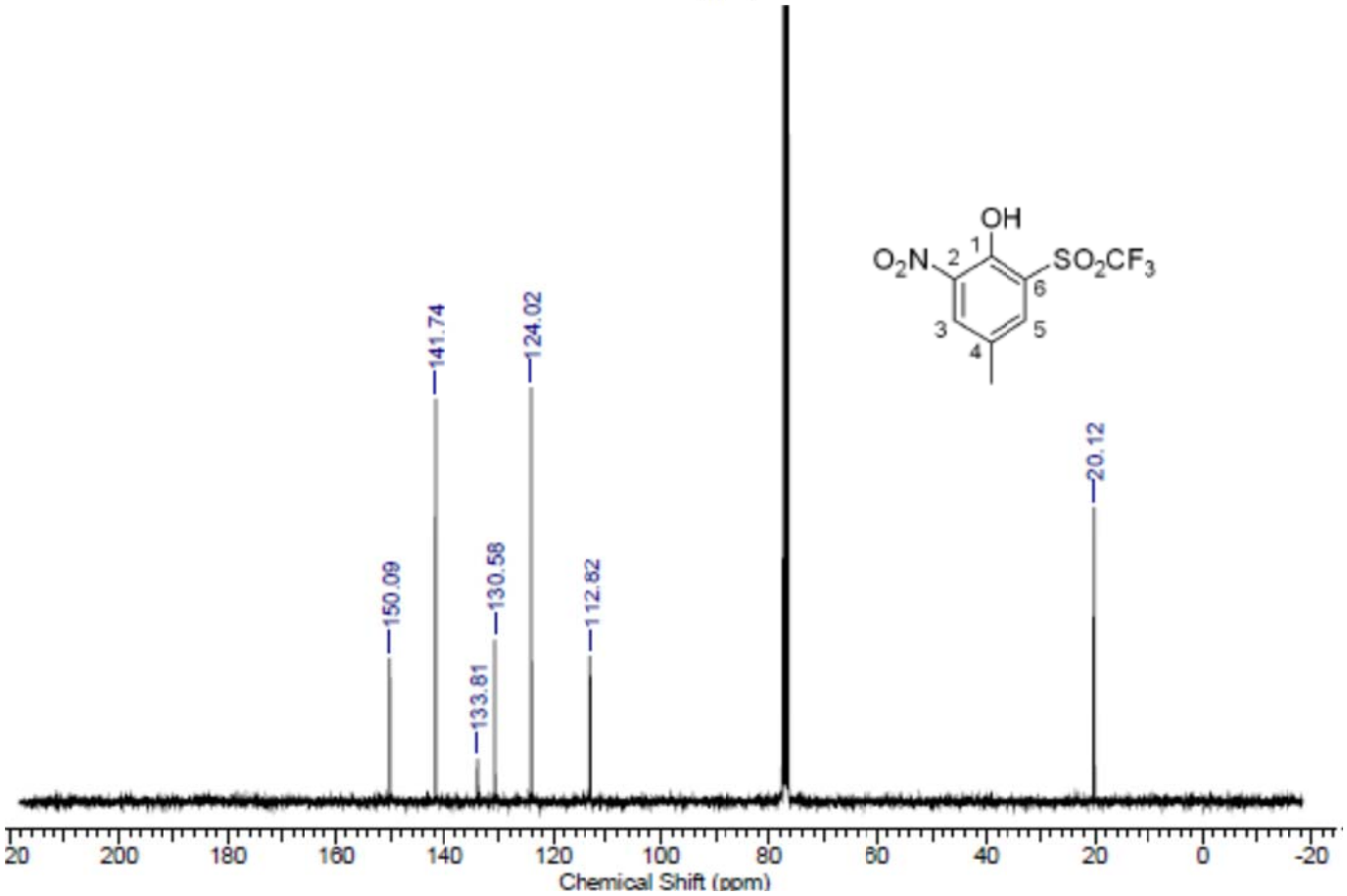
Compound 41:

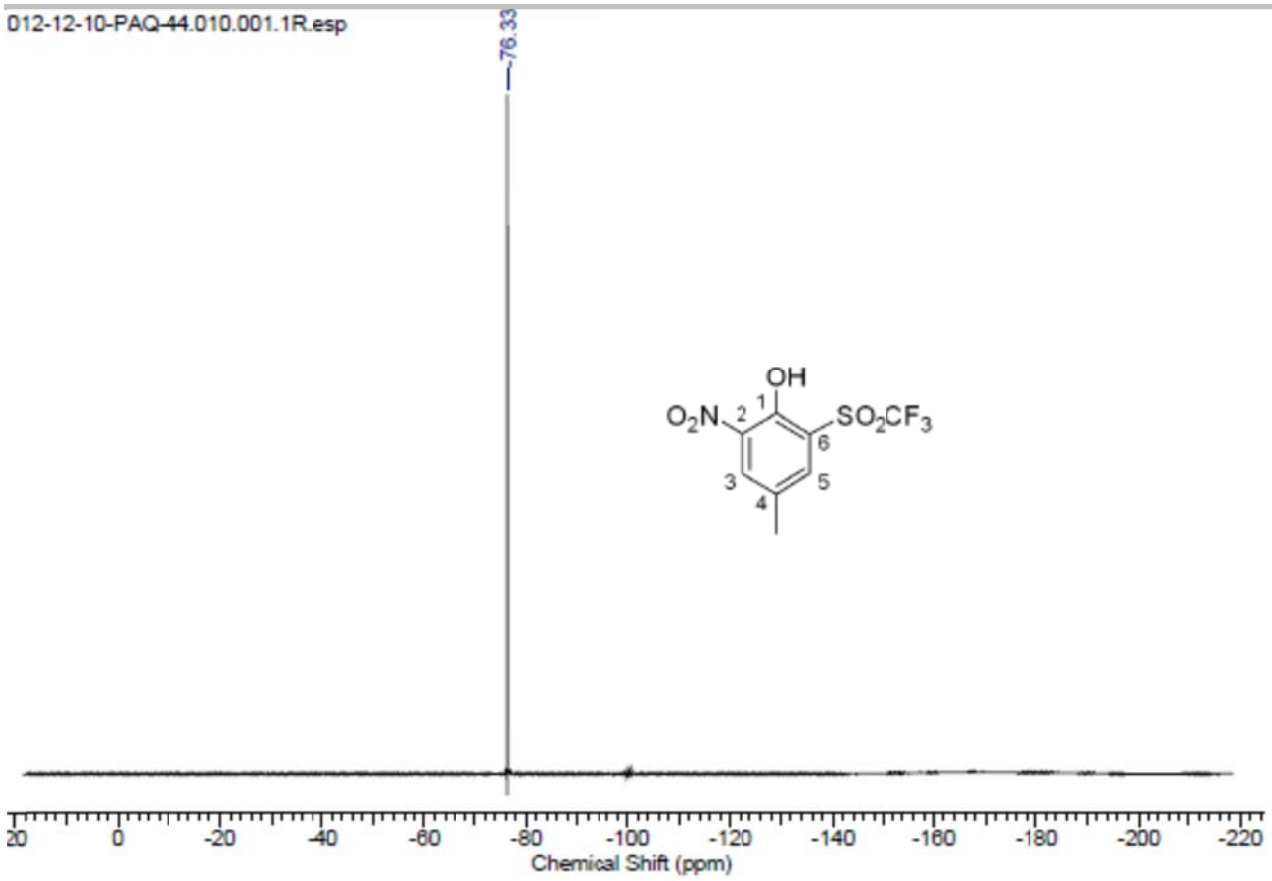

OH
Br
NO2
2.00
2.01
0.97
1.12
0.97
3.53
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Chemical Shift (ppm)


I-NITRO REARR 6-BRO MO.011.001.1R.esp
130.03
123.
132.67
146.99
144.32
126.77
111.31
20.23
OH
Br
NO2
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

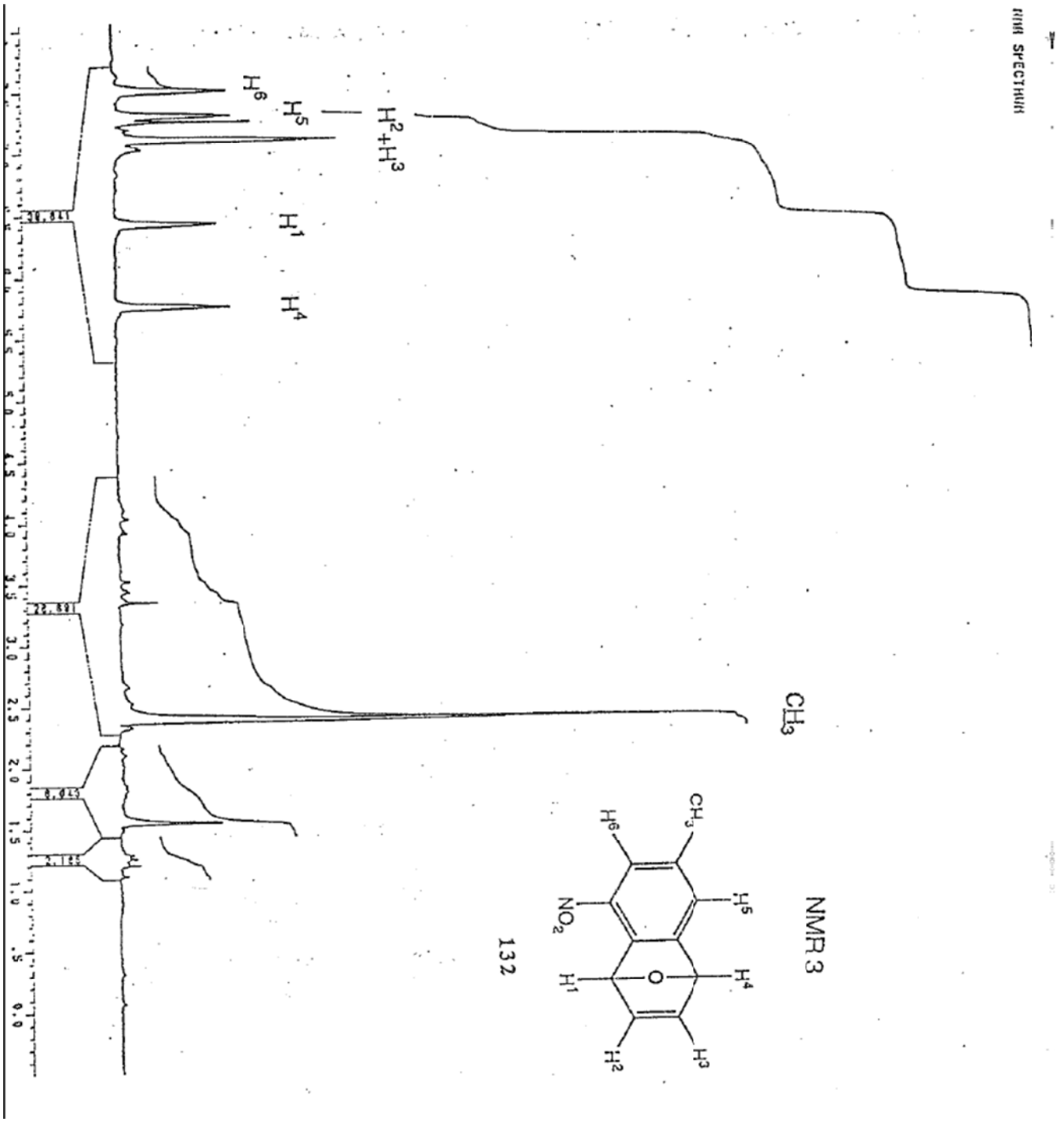
Compound 10:


OH
O2N
SO2CF3
1.00
1.09
1.10
3.54
12
11
10
9
8
7
6
5
4
3
2
Chemical Shift (ppm)

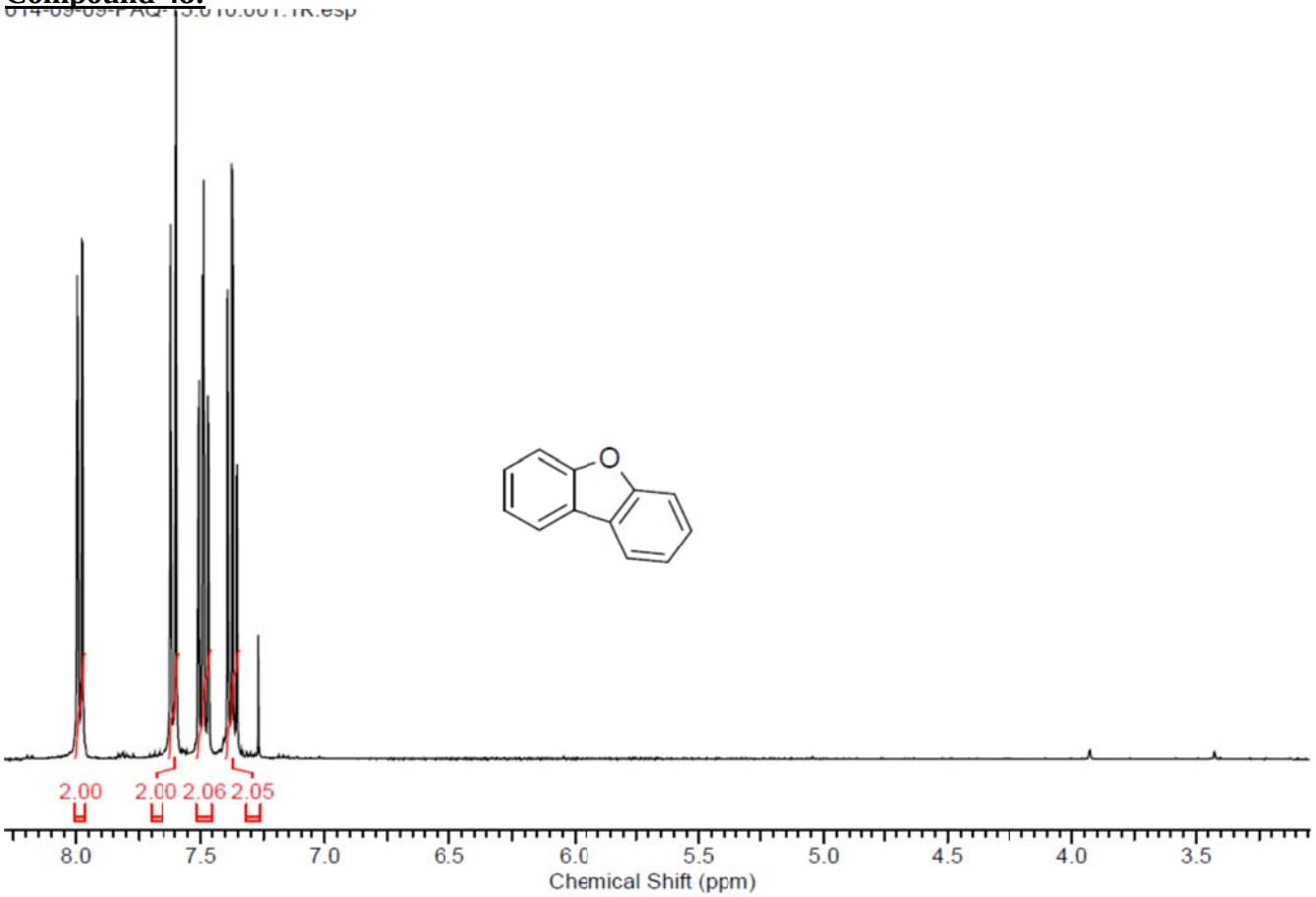

OH
O2N
SO2CF3
1
2
3
4
5
6
150.09
141.74
133.81
130.58
124.02
112.82
20.12
20
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

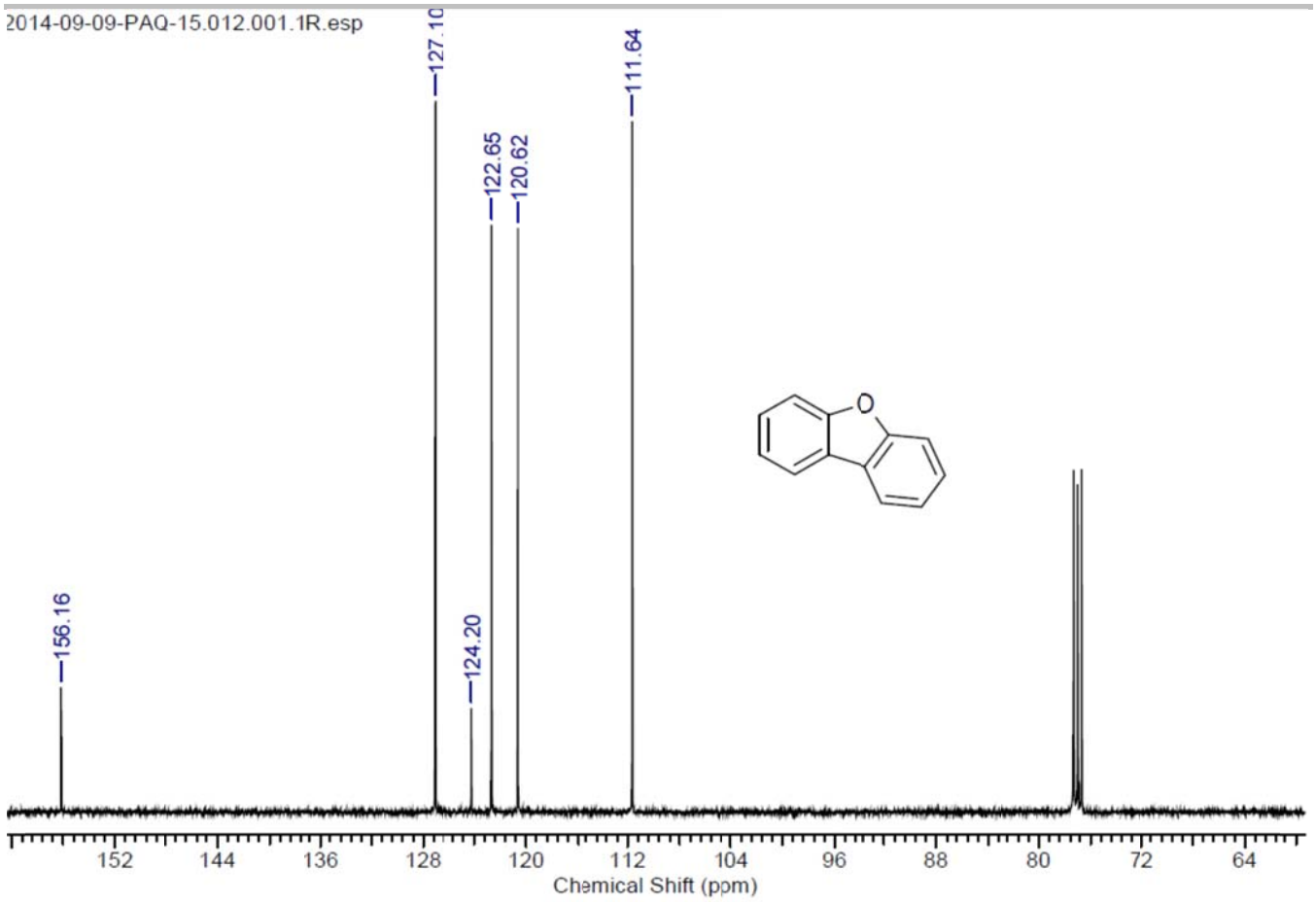

012-12-10-PAQ-44.010.001.1R.esp
-76.33
OH
O_2N
SO_2CF_3
1
2
3
4
5
6
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Chemical Shift (ppm)

Compound 9:

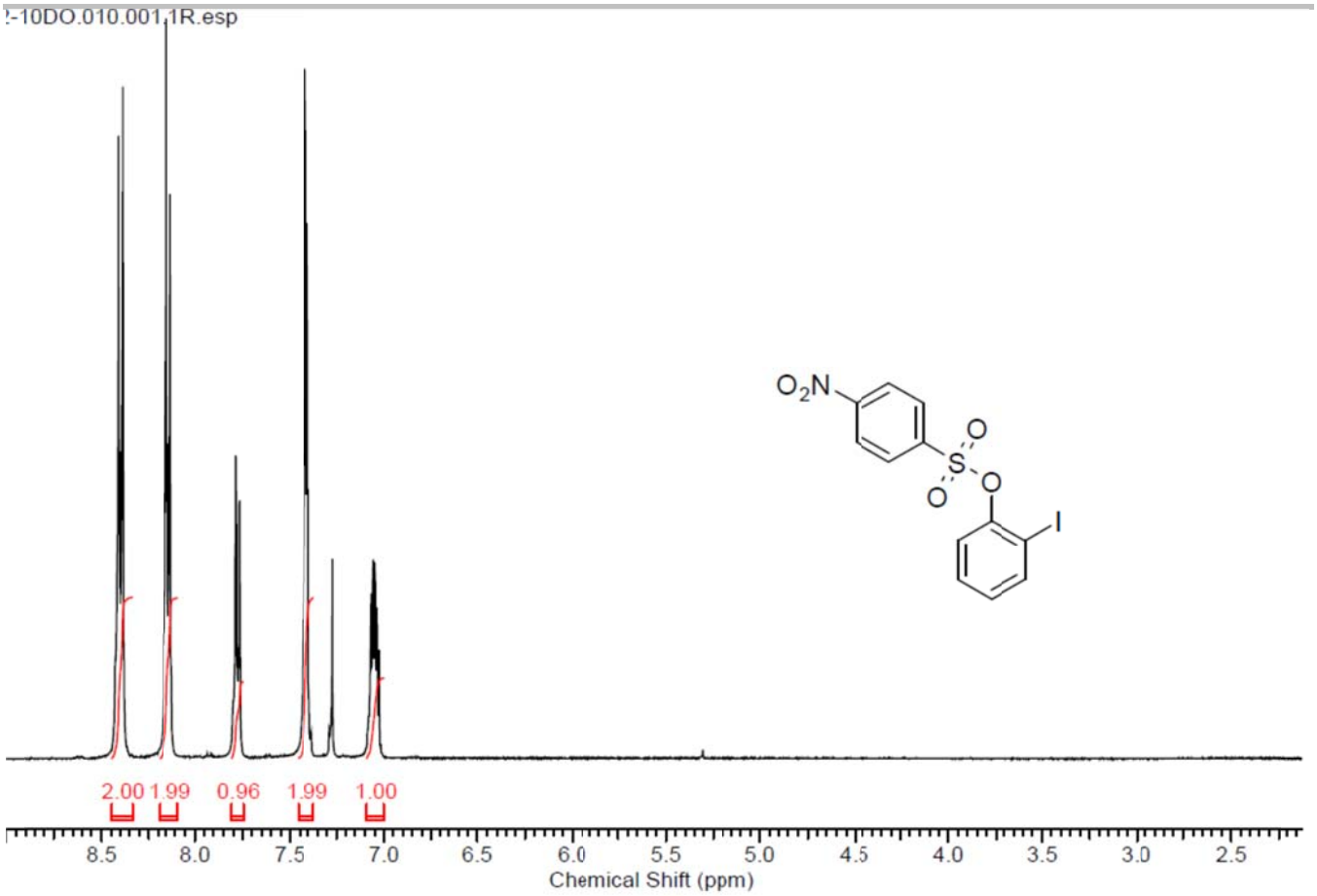


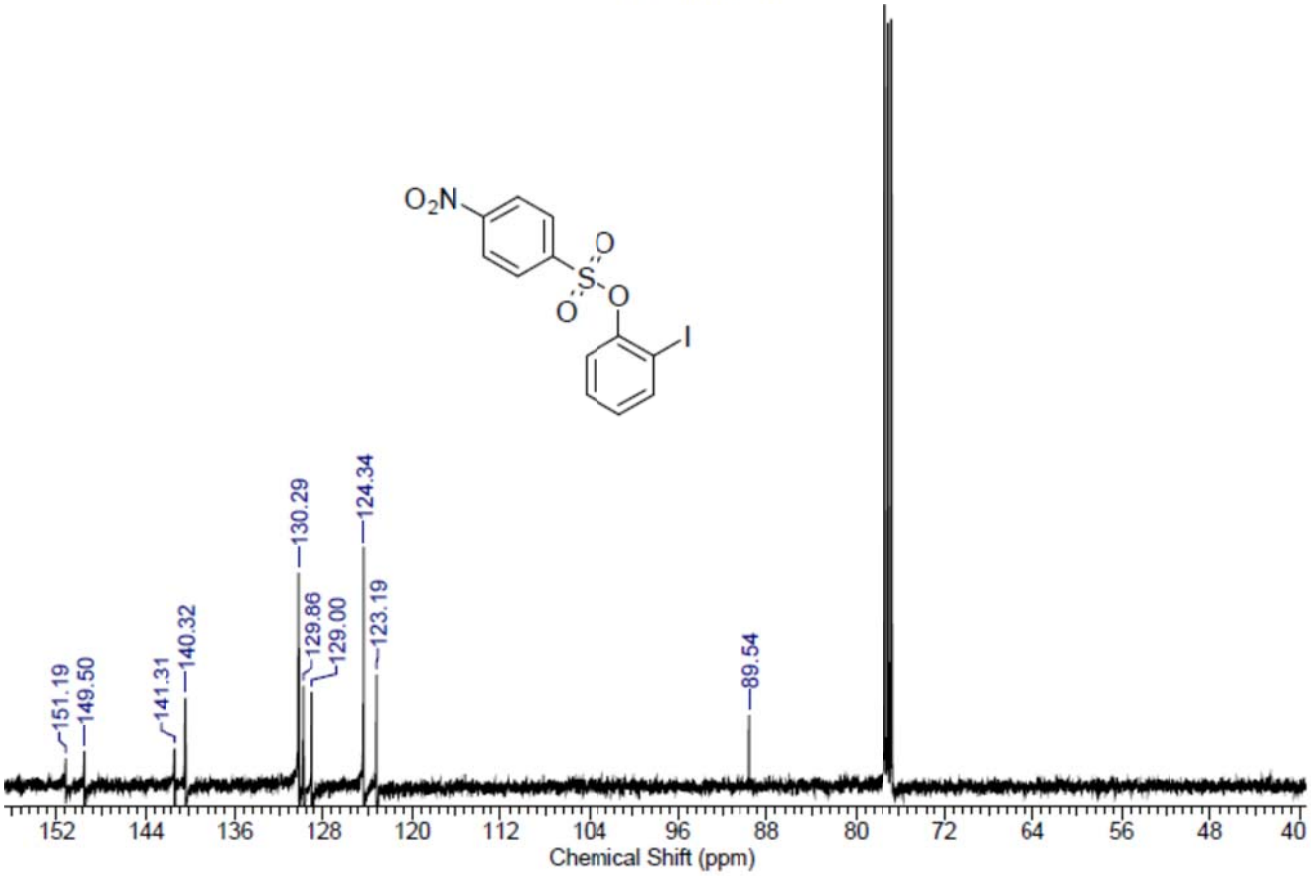
Compound 48:



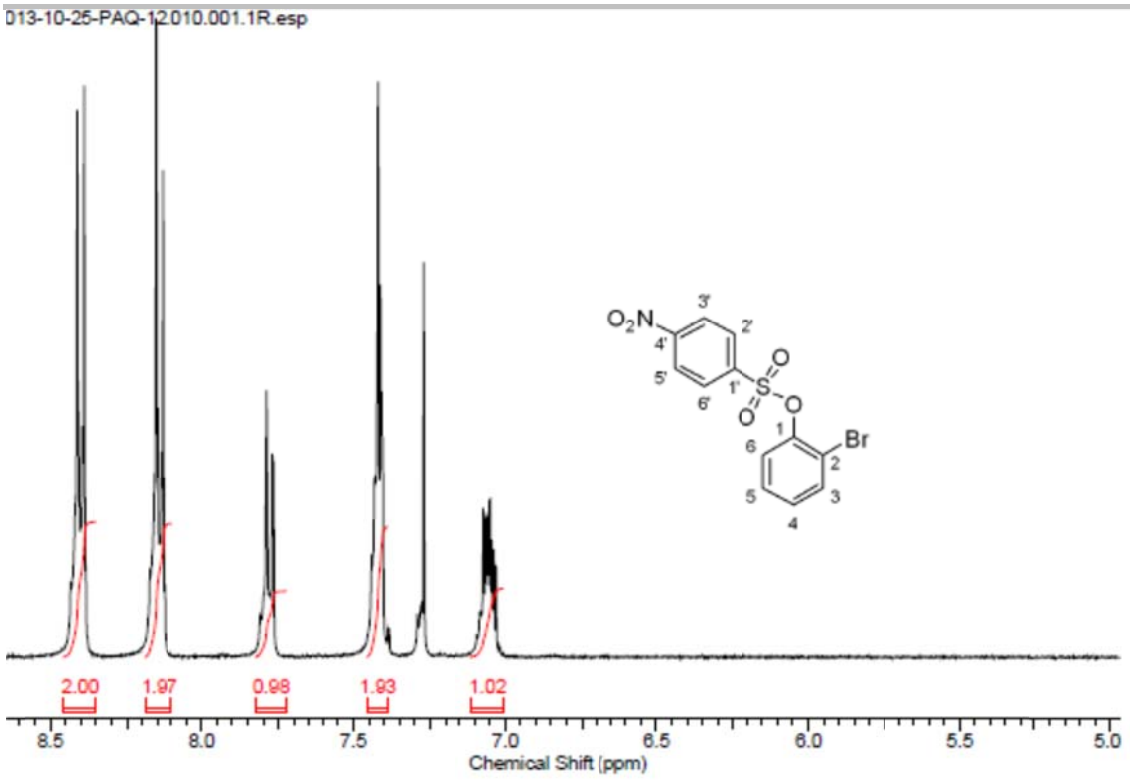

2014-09-09-PAQ-15.012.001.1R.esp
127.10
122.65
120.62
111.64
156.16
124.20
O
152
144
136
128
120
112
104
96
88
80
72
64
Chemical Shift (ppm)

Compound 54:

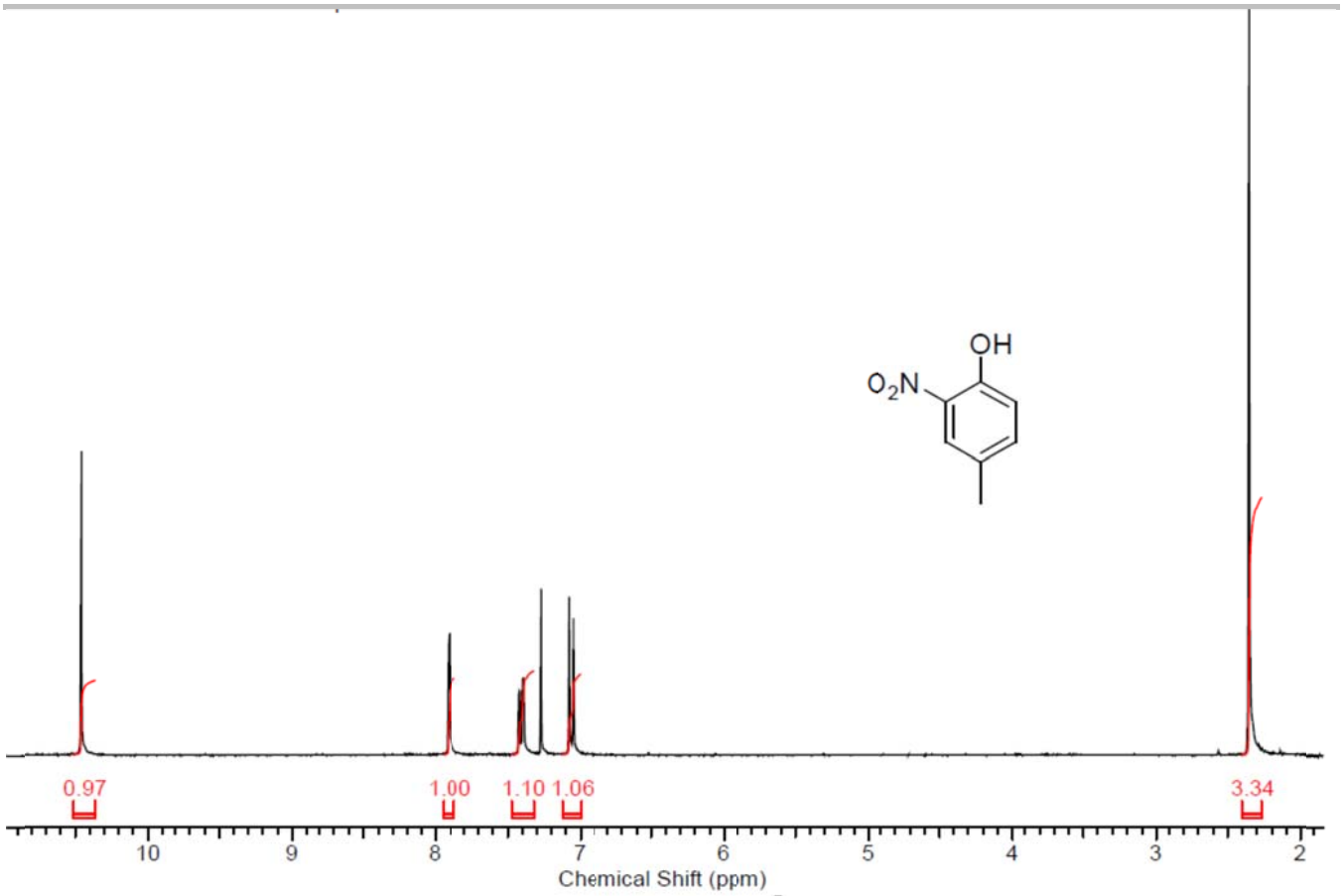

-10DO.010.001.1R.esp
O_2N
O
S
O
O
I
2.00 1.99 0.96 1.99 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
Chemical Shift (ppm)

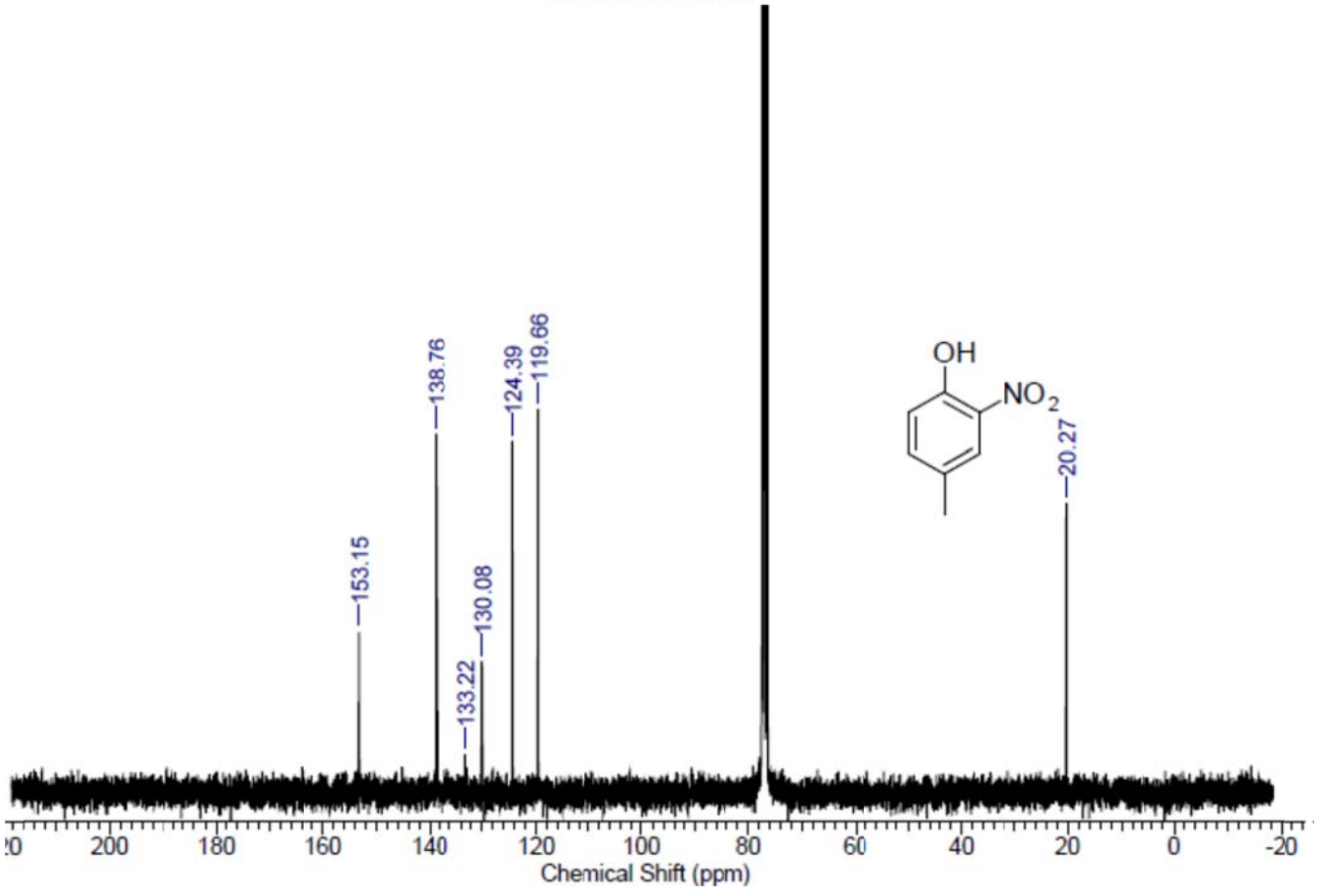

O_2N
O
S
O
O
I
151.19
149.50
141.31
140.32
130.29
129.86
129.00
124.34
123.19
89.54
152 144 136 128 120 112 104 96 88 80 72 64 56 48 40
Chemical Shift (ppm)

Compound 53:

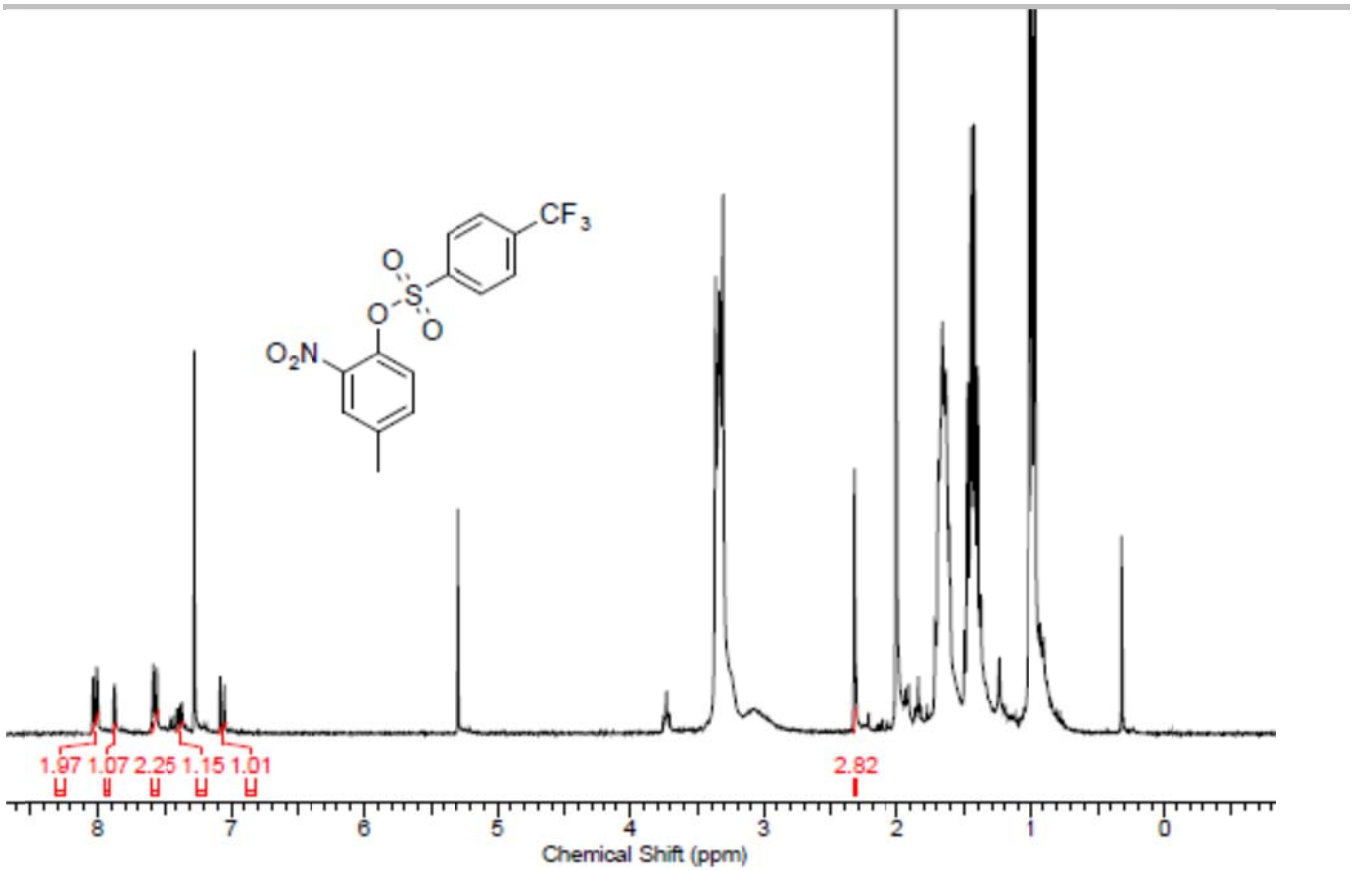

013-10-25-PAQ-12010.001.1R.esp
2.00
1.97
0.98
1.93
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
Chemical Shift (ppm)
O2N
Br

Compound 18:

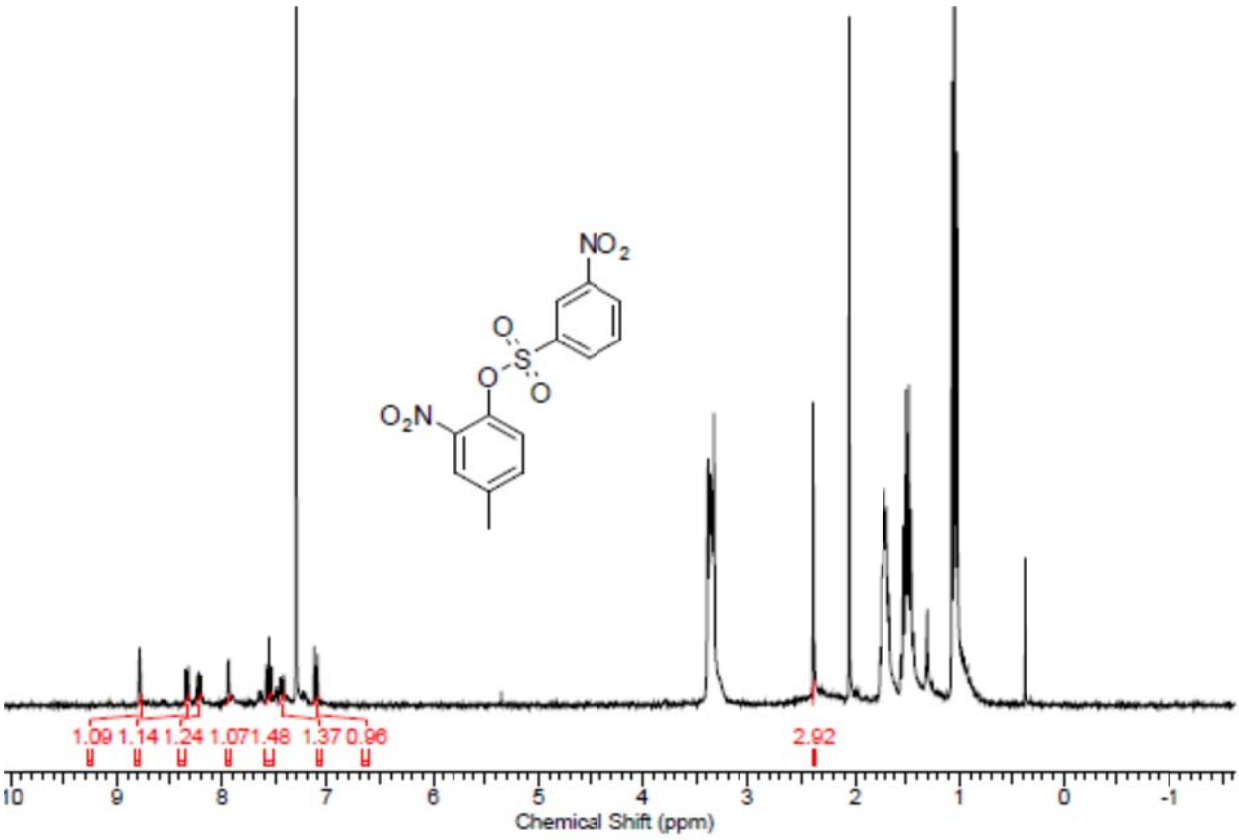

OH
O2N
0.97
1.00
1.10
1.06
3.34
10
9
8
7
6
5
4
3
2
Chemical Shift (ppm)


153.15
138.76
133.22
130.08
124.39
119.66
OH
NO2
20.27
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

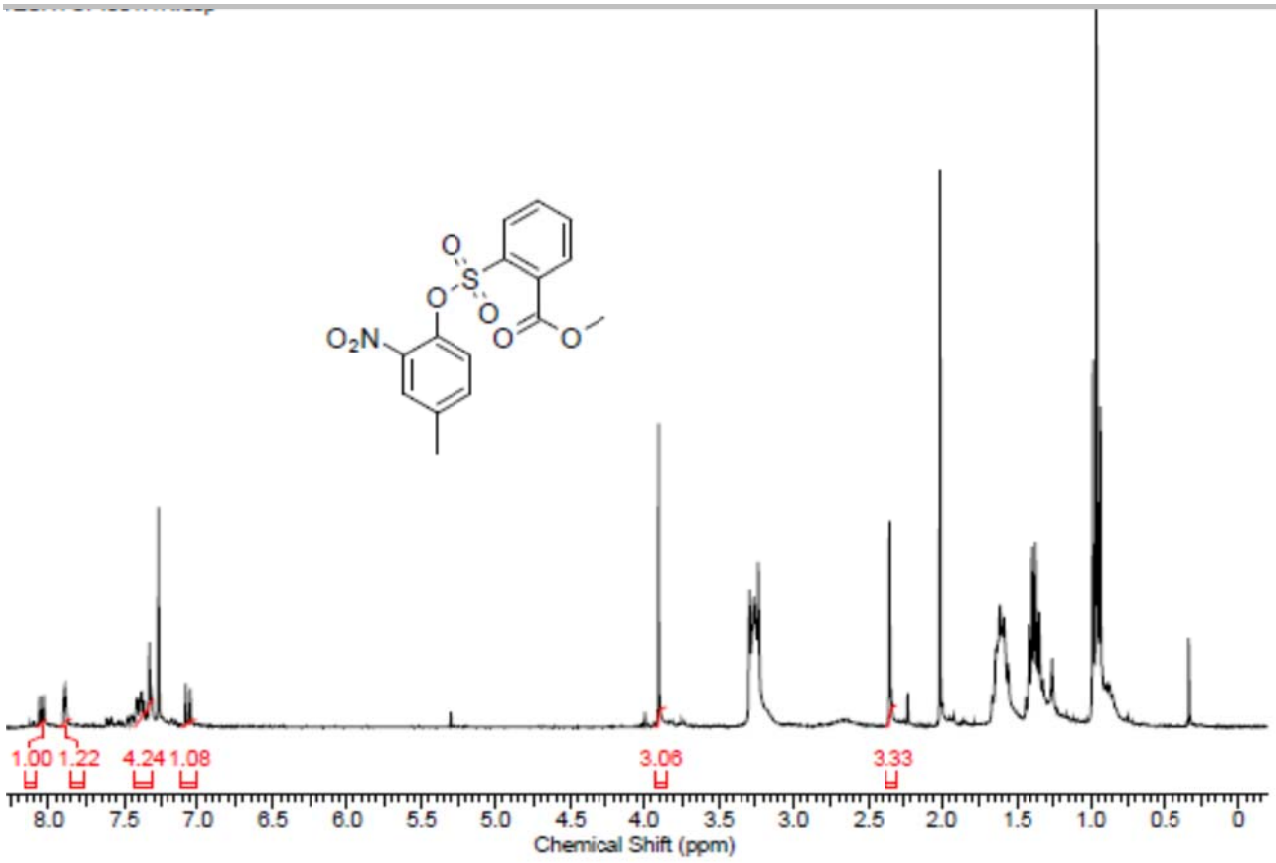
Compound 46:



Compound 45a:



Compound 47 (*ex* crude reaction mixture):


O
S
O
O
O
O
O
O2N
1.00
1.22
4.24
1.08
3.06
3.33
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
Chemical Shift (ppm)

Part C: X-ray crystal structure data

Cpd no.	UoM Identifier	CCDC no.
10	s3767	1056926
16	s3898	1056929
20	s3726	1056923
25	S3776	1056927
50	s3883	1056928
21	S3727	1056924

Cif files of these structures can be obtained, frre of charge, from the Cambridge Crystallographic Data Centre: http://www.ccdc.cam.ac.uk/

CCDC 1056923
Formula: C15 H17 N1 O5 S1 Si1
Unit Cell Parameters: a 9.8463(2) b 9.1987(2) c 18.7908(5) P21/c

Summary of Data CCDC 1056924
Formula: C15 H16 N2 O7 S1 Si1
Unit Cell Parameters: a 13.5825(3) b 10.5322(2) c 12.8580(3) P21/c

Summary of Data CCDC 1056926
Compound Name:
Formula: C8 H6 F3 N1 O5 S1
Unit Cell Parameters: a 5.3555(6) b 12.8070(14) c 16.0563(15) P21/n

Summary of Data CCDC 1056927
Formula: C12 H9 N1 O3
Unit Cell Parameters: a 20.5236(9) b 7.6948(3) c 18.8253(9) Cc

Summary of Data CCDC 1056928
Compound Name:
Formula: C14 H16 N2 O5 S1 Si1
Unit Cell Parameters: a 13.2148(2) b 10.9938(2) c 12.0527(2) P21/c

Summary of Data CCDC 1056929
Compound Name:
Formula: C13 H10 N2 O5
Unit Cell Parameters: a 15.6137(4) b 7.7484(2) c 21.2252(5) P21/n

Crystal data and structure refinement for s3727na.

Identification code	s3727na
Empirical formula	C15 H16 N2 O7 S Si
Formula weight	396.45
Temperature	150(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.5825(3) A alpha = 90 deg. b = 10.5322(2) A beta = 101.968(2) deg. c = 12.8580(3) A gamma = 90 deg.
Volume	1799.40(7) A^3
Z, Calculated density	4, 1.463 Mg/m^3
Absorption coefficient	2.617 mm^-1
F(000)	824
Crystal size	0.15 x 0.14 x 0.10 mm
Theta range for data collection	3.33 to 67.80 deg.
Limiting indices	-15<=h<=16, -12<=k<=12, -15<=l<=13
Reflections collected / unique	9327 / 3225 [R(int) = 0.0490]
Completeness to theta = 66.60	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7798 and 0.477511
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3225 / 0 / 238
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0961
R indices (all data)	R1 = 0.0437, wR2 = 0.1016
Largest diff. peak and hole	0.343 and -0.303 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3727na.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

C(1)	2698(1)	6361(2)	9570(1)	20(1)
C(2)	3421(1)	6000(2)	9009(1)	20(1)
C(3)	3497(2)	4682(2)	8863(2)	25(1)
C(4)	2893(2)	3820(2)	9265(2)	28(1)
C(5)	2206(2)	4249(2)	9848(2)	27(1)
C(6)	2103(1)	5542(2)	10009(2)	25(1)
C(7)	5268(2)	6290(2)	8032(2)	34(1)
C(8)	3513(2)	8144(2)	7427(2)	33(1)
C(9)	4877(2)	8224(2)	9664(2)	33(1)
C(10)	1119(1)	8742(2)	10422(1)	19(1)
C(11)	1452(1)	9652(2)	11205(1)	19(1)
C(12)	949(1)	9878(2)	12013(2)	21(1)
C(13)	107(1)	9156(2)	12030(1)	21(1)
C(14)	-260(1)	8258(2)	11271(2)	24(1)
C(15)	246(1)	8065(2)	10447(2)	24(1)
N(1)	2371(1)	10403(2)	11221(1)	24(1)
N(2)	-421(1)	9346(2)	12912(1)	27(1)
O(1)	2648(1)	7698(1)	9775(1)	22(1)
O(2)	1009(1)	7796(2)	8538(1)	30(1)
O(3)	2045(1)	9716(1)	9046(1)	29(1)
O(4)	3150(1)	9829(1)	11238(1)	30(1)
O(5)	2288(1)	11552(1)	11254(2)	44(1)
O(6)	-1078(1)	8589(2)	12999(1)	38(1)
O(7)	-158(1)	10243(2)	13510(1)	37(1)
S(1)	1692(1)	8513(1)	9310(1)	21(1)
Si(1)	4278(1)	7189(1)	8529(1)	22(1)

Table 3. Bond lengths [A] and angles [deg] for s3727na.

C(1)-C(6)	1.380(3)
C(1)-C(2)	1.387(3)
C(1)-O(1)	1.437(2)
C(2)-C(3)	1.407(3)
C(2)-Si(1)	1.8989(19)
C(3)-C(4)	1.393(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.389(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.388(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-Si(1)	1.862(2)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-Si(1)	1.868(2)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-Si(1)	1.867(2)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(15)	1.390(3)
C(10)-C(11)	1.395(3)
C(10)-S(1)	1.7796(18)
C(11)-C(12)	1.379(3)
C(11)-N(1)	1.474(2)
C(12)-C(13)	1.376(3)

C(12)-H(12)	0.9500
C(13)-C(14)	1.376(3)
C(13)-N(2)	1.476(2)
C(14)-C(15)	1.391(3)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
N(1)-O(5)	1.217(2)
N(1)-O(4)	1.215(2)
N(2)-O(6)	1.219(2)
N(2)-O(7)	1.224(2)
O(1)-S(1)	1.5685(13)
O(2)-S(1)	1.4256(15)
O(3)-S(1)	1.4203(16)

C(6)-C(1)-C(2)	125.35(18)
C(6)-C(1)-O(1)	118.97(17)
C(2)-C(1)-O(1)	115.45(16)
C(1)-C(2)-C(3)	114.81(17)
C(1)-C(2)-Si(1)	122.43(14)
C(3)-C(2)-Si(1)	122.71(14)
C(4)-C(3)-C(2)	121.89(18)
C(4)-C(3)-H(3)	119.1
C(2)-C(3)-H(3)	119.1
C(5)-C(4)-C(3)	120.10(19)
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	119.96(19)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(1)-C(6)-C(5)	117.82(18)
C(1)-C(6)-H(6)	121.1
C(5)-C(6)-H(6)	121.1
Si(1)-C(7)-H(7A)	109.5
Si(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
Si(1)-C(8)-H(8A)	109.5
Si(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
Si(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
Si(1)-C(9)-H(9A)	109.5
Si(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
Si(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(15)-C(10)-C(11)	119.07(17)
C(15)-C(10)-S(1)	117.81(14)
C(11)-C(10)-S(1)	122.83(14)
C(12)-C(11)-C(10)	121.67(17)
C(12)-C(11)-N(1)	116.56(17)
C(10)-C(11)-N(1)	121.76(16)
C(13)-C(12)-C(11)	117.40(18)
C(13)-C(12)-H(12)	121.3
C(11)-C(12)-H(12)	121.3
C(14)-C(13)-C(12)	123.22(17)
C(14)-C(13)-N(2)	118.43(17)
C(12)-C(13)-N(2)	118.35(17)

C(13)-C(14)-C(15)	118.50(18)
C(13)-C(14)-H(14)	120.7
C(15)-C(14)-H(14)	120.7
C(10)-C(15)-C(14)	120.07(18)
C(10)-C(15)-H(15)	120.0
C(14)-C(15)-H(15)	120.0
O(5)-N(1)-O(4)	125.50(18)
O(5)-N(1)-C(11)	116.81(16)
O(4)-N(1)-C(11)	117.65(16)
O(6)-N(2)-O(7)	124.82(17)
O(6)-N(2)-C(13)	117.64(17)
O(7)-N(2)-C(13)	117.53(17)
C(1)-O(1)-S(1)	122.24(12)
O(3)-S(1)-O(2)	120.62(9)
O(3)-S(1)-O(1)	106.57(8)
O(2)-S(1)-O(1)	110.05(8)
O(3)-S(1)-C(10)	107.23(9)
O(2)-S(1)-C(10)	107.57(9)
O(1)-S(1)-C(10)	103.49(8)
C(7)-Si(1)-C(9)	109.71(10)
C(7)-Si(1)-C(8)	109.96(11)
C(9)-Si(1)-C(8)	111.24(11)
C(7)-Si(1)-C(2)	108.12(10)
C(9)-Si(1)-C(2)	109.15(9)
C(8)-Si(1)-C(2)	108.60(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s3727na. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	20(1)	18(1)	19(1)	0(1)	0(1)	2(1)
C(2)	20(1)	20(1)	18(1)	0(1)	2(1)	2(1)
C(3)	26(1)	22(1)	26(1)	-1(1)	4(1)	5(1)
C(4)	30(1)	19(1)	31(1)	2(1)	-1(1)	0(1)
C(5)	27(1)	27(1)	25(1)	6(1)	0(1)	-6(1)
C(6)	23(1)	32(1)	21(1)	1(1)	5(1)	-1(1)
C(7)	28(1)	39(1)	40(1)	-8(1)	16(1)	0(1)
C(8)	44(1)	27(1)	30(1)	5(1)	11(1)	0(1)
C(9)	27(1)	32(1)	40(1)	-10(1)	8(1)	-5(1)
C(10)	18(1)	20(1)	18(1)	0(1)	4(1)	5(1)
C(11)	18(1)	18(1)	20(1)	2(1)	3(1)	3(1)
C(12)	23(1)	21(1)	20(1)	0(1)	4(1)	3(1)
C(13)	21(1)	24(1)	19(1)	4(1)	6(1)	6(1)
C(14)	19(1)	24(1)	29(1)	2(1)	7(1)	1(1)
C(15)	21(1)	24(1)	26(1)	-4(1)	3(1)	0(1)
N(1)	27(1)	22(1)	25(1)	-2(1)	8(1)	-2(1)
N(2)	26(1)	33(1)	23(1)	5(1)	9(1)	6(1)
O(1)	20(1)	21(1)	26(1)	-4(1)	5(1)	3(1)
O(2)	28(1)	38(1)	22(1)	-8(1)	0(1)	6(1)
O(3)	35(1)	27(1)	28(1)	5(1)	14(1)	6(1)
O(4)	20(1)	30(1)	41(1)	-2(1)	9(1)	0(1)
O(5)	44(1)	17(1)	76(1)	-4(1)	25(1)	-4(1)
O(6)	36(1)	46(1)	39(1)	5(1)	21(1)	-5(1)

O(7)	40(1)	46(1)	29(1)	-9(1)	15(1)	0(1)
S(1)	22(1)	24(1)	18(1)	-1(1)	5(1)	5(1)
Si(1)	22(1)	22(1)	25(1)	-2(1)	8(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s3727na.

	x	y	z	U(eq)
H(3)	3973	4372	8478	30
H(4)	2951	2937	9139	33
H(5)	1806	3659	10136	32
H(6)	1639	5852	10409	30
H(7A)	5753	6887	7837	52
H(7B)	4955	5791	7407	52
H(7C)	5616	5719	8591	52
H(8A)	3961	8571	7031	50
H(8B)	3123	8780	7725	50
H(8C)	3053	7582	6948	50
H(9A)	5113	7699	10296	49
H(9B)	4383	8840	9811	49
H(9C)	5448	8675	9481	49
H(12)	1173	10508	12537	26
H(14)	-845	7780	11308	29
H(15)	-6	7470	9902	29

Table 6. Torsion angles [deg] for s3727na.

C(6)-C(1)-C(2)-C(3)	2.6(3)
O(1)-C(1)-C(2)-C(3)	176.86(16)
C(6)-C(1)-C(2)-Si(1)	-174.91(15)
O(1)-C(1)-C(2)-Si(1)	-0.6(2)
C(1)-C(2)-C(3)-C(4)	-0.6(3)
Si(1)-C(2)-C(3)-C(4)	176.88(15)
C(2)-C(3)-C(4)-C(5)	-1.4(3)
C(3)-C(4)-C(5)-C(6)	1.5(3)
C(2)-C(1)-C(6)-C(5)	-2.5(3)
O(1)-C(1)-C(6)-C(5)	-176.55(16)
C(4)-C(5)-C(6)-C(1)	0.3(3)
C(15)-C(10)-C(11)-C(12)	1.2(3)
S(1)-C(10)-C(11)-C(12)	174.86(14)
C(15)-C(10)-C(11)-N(1)	-179.87(17)
S(1)-C(10)-C(11)-N(1)	-6.2(3)
C(10)-C(11)-C(12)-C(13)	1.0(3)
N(1)-C(11)-C(12)-C(13)	-177.95(16)
C(11)-C(12)-C(13)-C(14)	-1.8(3)
C(11)-C(12)-C(13)-N(2)	177.58(16)
C(12)-C(13)-C(14)-C(15)	0.3(3)
N(2)-C(13)-C(14)-C(15)	-179.09(17)
C(11)-C(10)-C(15)-C(14)	-2.8(3)
S(1)-C(10)-C(15)-C(14)	-176.73(15)
C(13)-C(14)-C(15)-C(10)	2.1(3)
C(12)-C(11)-N(1)-O(5)	-54.5(2)
C(10)-C(11)-N(1)-O(5)	126.5(2)
C(12)-C(11)-N(1)-O(4)	123.05(19)
C(10)-C(11)-N(1)-O(4)	-55.9(2)

C(14)-C(13)-N(2)-O(6)	9.1(3)
C(12)-C(13)-N(2)-O(6)	-170.27(18)
C(14)-C(13)-N(2)-O(7)	-171.78(18)
C(12)-C(13)-N(2)-O(7)	8.8(3)
C(6)-C(1)-O(1)-S(1)	-68.7(2)
C(2)-C(1)-O(1)-S(1)	116.63(16)
C(1)-O(1)-S(1)-O(3)	-142.98(14)
C(1)-O(1)-S(1)-O(2)	-10.59(16)
C(1)-O(1)-S(1)-C(10)	104.12(14)
C(15)-C(10)-S(1)-O(3)	141.06(15)
C(11)-C(10)-S(1)-O(3)	-32.66(18)
C(15)-C(10)-S(1)-O(2)	9.95(17)
C(11)-C(10)-S(1)-O(2)	-163.76(15)
C(15)-C(10)-S(1)-O(1)	-106.52(15)
C(11)-C(10)-S(1)-O(1)	79.76(16)
C(1)-C(2)-Si(1)-C(7)	170.23(16)
C(3)-C(2)-Si(1)-C(7)	-7.06(19)
C(1)-C(2)-Si(1)-C(9)	50.94(18)
C(3)-C(2)-Si(1)-C(9)	-126.35(17)
C(1)-C(2)-Si(1)-C(8)	-70.49(17)
C(3)-C(2)-Si(1)-C(8)	112.22(17)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for s3727na [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Crystal data and structure refinement for s3883ma.

Identification code	s3883ma
Empirical formula	C14 H16 N2 O5 S Si
Formula weight	352.44
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.2148(2) A alpha = 90 deg. b = 10.9938(2) A beta = 111.8790(10) deg. c = 12.0527(2) A gamma = 90 deg.
Volume	1624.90(5) A^3
Z, Calculated density	4, 1.441 Mg/m^3
Absorption coefficient	2.726 mm^-1
F(000)	736
Crystal size	0.29 x 0.19 x 0.16 mm
Theta range for data collection	3.60 to 72.15 deg.
Limiting indices	-16<=h<=16, -13<=k<=13, -14<=l<=14
Reflections collected / unique	15650 / 3176 [R(int) = 0.0266]
Completeness to theta = 66.60	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6695 and 0.553297
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3176 / 0 / 211
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0289, wR2 = 0.0791
R indices (all data)	R1 = 0.0313, wR2 = 0.0807
Largest diff. peak and hole	0.297 and -0.403 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3883ma.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

C(1)	10657(1)	2731(2)	13186(1)	33(1)
C(2)	9943(1)	1302(1)	10871(1)	27(1)
C(3)	11018(1)	3837(1)	11046(1)	28(1)
C(4)	8708(1)	3572(1)	11046(1)	20(1)
C(5)	8008(1)	3505(1)	9787(1)	18(1)
C(6)	6589(1)	4542(1)	10321(1)	28(1)
C(7)	7272(1)	4666(1)	11458(1)	30(1)
C(8)	8328(1)	4132(1)	11825(1)	25(1)
C(9)	6265(1)	4399(1)	7099(1)	20(1)
C(10)	5935(1)	5608(1)	6960(1)	26(1)
C(11)	6124(1)	6302(1)	6099(1)	28(1)
C(12)	6624(1)	5756(1)	5407(1)	23(1)
C(13)	6956(1)	4554(1)	5537(1)	27(1)
C(14)	6776(1)	3864(1)	6405(1)	26(1)
N(1)	6913(1)	3911(1)	9508(1)	21(1)
N(2)	6816(1)	6502(1)	4482(1)	29(1)
O(1)	8269(1)	3114(1)	8984(1)	23(1)
O(2)	6087(1)	2266(1)	7968(1)	30(1)
O(3)	4952(1)	3959(1)	8197(1)	33(1)
O(4)	7368(1)	6063(1)	3964(1)	38(1)
O(5)	6415(1)	7516(1)	4290(1)	45(1)
S(1)	5957(1)	3522(1)	8156(1)	23(1)
Si(1)	10103(1)	2857(1)	11520(1)	19(1)

Table 3. Bond lengths [A] and angles [deg] for s3883ma.

C(1)-Si(1)	1.8686(16)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-Si(1)	1.8595(15)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-Si(1)	1.8617(15)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-C(8)	1.3652(19)
C(4)-C(5)	1.4553(19)
C(4)-Si(1)	1.8867(14)
C(5)-O(1)	1.2198(16)
C(5)-N(1)	1.4293(17)
C(6)-C(7)	1.338(2)
C(6)-N(1)	1.3919(18)
C(6)-H(6)	0.9500
C(7)-C(8)	1.424(2)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-C(14)	1.387(2)
C(9)-C(10)	1.389(2)
C(9)-S(1)	1.7624(14)
C(10)-C(11)	1.384(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.380(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.383(2)
C(12)-N(2)	1.4793(19)

C(13)-C(14)	1.383(2)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
N(1)-S(1)	1.7027(12)
N(2)-O(5)	1.2194(19)
N(2)-O(4)	1.2221(18)
O(2)-S(1)	1.4203(11)
O(3)-S(1)	1.4304(11)

Si(1)-C(1)-H(1A)	109.5
Si(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
Si(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
Si(1)-C(2)-H(2A)	109.5
Si(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
Si(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
Si(1)-C(3)-H(3A)	109.5
Si(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
Si(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(8)-C(4)-C(5)	119.09(13)
C(8)-C(4)-Si(1)	123.24(11)
C(5)-C(4)-Si(1)	117.66(10)
O(1)-C(5)-N(1)	118.96(12)
O(1)-C(5)-C(4)	125.95(12)
N(1)-C(5)-C(4)	115.07(11)
C(7)-C(6)-N(1)	120.31(13)
C(7)-C(6)-H(6)	119.8
N(1)-C(6)-H(6)	119.8
C(6)-C(7)-C(8)	119.02(13)
C(6)-C(7)-H(7)	120.5
C(8)-C(7)-H(7)	120.5
C(4)-C(8)-C(7)	122.78(14)
C(4)-C(8)-H(8)	118.6
C(7)-C(8)-H(8)	118.6
C(14)-C(9)-C(10)	122.33(13)
C(14)-C(9)-S(1)	119.93(11)
C(10)-C(9)-S(1)	117.67(11)
C(11)-C(10)-C(9)	118.83(13)
C(11)-C(10)-H(10)	120.6
C(9)-C(10)-H(10)	120.6
C(12)-C(11)-C(10)	118.30(13)
C(12)-C(11)-H(11)	120.8
C(10)-C(11)-H(11)	120.8
C(11)-C(12)-C(13)	123.40(14)
C(11)-C(12)-N(2)	118.02(13)
C(13)-C(12)-N(2)	118.58(13)
C(14)-C(13)-C(12)	118.25(13)
C(14)-C(13)-H(13)	120.9
C(12)-C(13)-H(13)	120.9
C(13)-C(14)-C(9)	118.88(13)
C(13)-C(14)-H(14)	120.6
C(9)-C(14)-H(14)	120.6
C(6)-N(1)-C(5)	122.70(12)
C(6)-N(1)-S(1)	119.07(10)

C(5)-N(1)-S(1)	118.11(9)
O(5)-N(2)-O(4)	124.28(14)
O(5)-N(2)-C(12)	117.76(13)
O(4)-N(2)-C(12)	117.96(13)
O(2)-S(1)-O(3)	120.07(7)
O(2)-S(1)-N(1)	107.86(6)
O(3)-S(1)-N(1)	104.44(6)
O(2)-S(1)-C(9)	110.05(7)
O(3)-S(1)-C(9)	107.98(7)
N(1)-S(1)-C(9)	105.39(6)
C(2)-Si(1)-C(3)	112.84(7)
C(2)-Si(1)-C(1)	108.74(7)
C(3)-Si(1)-C(1)	109.50(8)
C(2)-Si(1)-C(4)	108.11(6)
C(3)-Si(1)-C(4)	109.85(6)
C(1)-Si(1)-C(4)	107.66(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s3883ma. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	32(1)	40(1)	22(1)	2(1)	3(1)	3(1)
C(2)	26(1)	20(1)	32(1)	0(1)	8(1)	1(1)
C(3)	23(1)	26(1)	34(1)	-1(1)	10(1)	-4(1)
C(4)	21(1)	17(1)	20(1)	0(1)	7(1)	-3(1)
C(5)	18(1)	16(1)	22(1)	1(1)	8(1)	-1(1)
C(6)	24(1)	29(1)	35(1)	-2(1)	16(1)	4(1)
C(7)	33(1)	32(1)	32(1)	-8(1)	18(1)	1(1)
C(8)	29(1)	25(1)	22(1)	-4(1)	10(1)	-3(1)
C(9)	15(1)	22(1)	20(1)	-1(1)	2(1)	0(1)
C(10)	26(1)	26(1)	27(1)	-2(1)	10(1)	6(1)
C(11)	30(1)	22(1)	29(1)	1(1)	9(1)	7(1)
C(12)	19(1)	28(1)	18(1)	0(1)	2(1)	-1(1)
C(13)	26(1)	30(1)	25(1)	-5(1)	10(1)	4(1)
C(14)	26(1)	22(1)	28(1)	-2(1)	8(1)	5(1)
N(1)	17(1)	23(1)	23(1)	0(1)	8(1)	1(1)
N(2)	27(1)	36(1)	20(1)	0(1)	2(1)	-5(1)
O(1)	21(1)	28(1)	20(1)	-1(1)	8(1)	4(1)
O(2)	28(1)	24(1)	33(1)	0(1)	5(1)	-7(1)
O(3)	16(1)	45(1)	37(1)	4(1)	9(1)	0(1)
O(4)	36(1)	53(1)	28(1)	-2(1)	15(1)	-4(1)
O(5)	60(1)	37(1)	37(1)	13(1)	17(1)	8(1)
S(1)	15(1)	25(1)	26(1)	1(1)	5(1)	-2(1)
Si(1)	18(1)	19(1)	18(1)	0(1)	4(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s3883ma.

	x	y	z	U(eq)

H(1A)	11347	2281	13452	50
H(1B)	10132	2298	13440	50
H(1C)	10782	3547	13538	50
H(2A)	9520	1343	10009	40
H(2B)	9562	785	11252	40
H(2C)	10664	957	11009	40
H(3A)	11720	3426	11228	41
H(3B)	11135	4613	11476	41
H(3C)	10682	3988	10183	41
H(6)	5879	4887	10067	33
H(7)	7056	5104	12012	37
H(8)	8787	4166	12646	30
H(10)	5586	5951	7447	31
H(11)	5914	7133	5987	33
H(13)	7298	4211	5042	32
H(14)	6999	3037	6524	31

Table 6. Torsion angles [deg] for s3883ma.

C(8)-C(4)-C(5)-O(1)	174.27(13)
Si(1)-C(4)-C(5)-O(1)	-6.33(18)
C(8)-C(4)-C(5)-N(1)	-7.57(18)
Si(1)-C(4)-C(5)-N(1)	171.84(9)
N(1)-C(6)-C(7)-C(8)	-0.7(2)
C(5)-C(4)-C(8)-C(7)	-0.5(2)
Si(1)-C(4)-C(8)-C(7)	-179.87(12)
C(6)-C(7)-C(8)-C(4)	5.0(2)
C(14)-C(9)-C(10)-C(11)	-0.1(2)
S(1)-C(9)-C(10)-C(11)	-177.17(11)
C(9)-C(10)-C(11)-C(12)	0.7(2)
C(10)-C(11)-C(12)-C(13)	-0.6(2)
C(10)-C(11)-C(12)-N(2)	179.54(13)
C(11)-C(12)-C(13)-C(14)	0.0(2)
N(2)-C(12)-C(13)-C(14)	179.86(13)
C(12)-C(13)-C(14)-C(9)	0.5(2)
C(10)-C(9)-C(14)-C(13)	-0.5(2)
S(1)-C(9)-C(14)-C(13)	176.50(11)
C(7)-C(6)-N(1)-C(5)	-8.2(2)
C(7)-C(6)-N(1)-S(1)	167.76(12)
O(1)-C(5)-N(1)-C(6)	-169.62(13)
C(4)-C(5)-N(1)-C(6)	12.07(18)
O(1)-C(5)-N(1)-S(1)	14.43(16)
C(4)-C(5)-N(1)-S(1)	-163.88(9)
C(11)-C(12)-N(2)-O(5)	-8.0(2)
C(13)-C(12)-N(2)-O(5)	172.20(14)
C(11)-C(12)-N(2)-O(4)	171.73(14)
C(13)-C(12)-N(2)-O(4)	-8.1(2)
C(6)-N(1)-S(1)-O(2)	-130.05(11)
C(5)-N(1)-S(1)-O(2)	46.05(11)
C(6)-N(1)-S(1)-O(3)	-1.25(12)
C(5)-N(1)-S(1)-O(3)	174.85(10)
C(6)-N(1)-S(1)-C(9)	112.42(11)
C(5)-N(1)-S(1)-C(9)	-71.48(11)
C(14)-C(9)-S(1)-O(2)	-12.37(13)
C(10)-C(9)-S(1)-O(2)	164.77(11)
C(14)-C(9)-S(1)-O(3)	-145.15(12)
C(10)-C(9)-S(1)-O(3)	31.99(13)
C(14)-C(9)-S(1)-N(1)	103.67(12)
C(10)-C(9)-S(1)-N(1)	-79.19(12)

C(8)-C(4)-Si(1)-C(2)	130.89(12)
C(5)-C(4)-Si(1)-C(2)	-48.48(12)
C(8)-C(4)-Si(1)-C(3)	-105.59(13)
C(5)-C(4)-Si(1)-C(3)	75.03(11)
C(8)-C(4)-Si(1)-C(1)	13.58(14)
C(5)-C(4)-Si(1)-C(1)	-165.80(10)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for s3883ma [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Crystal data and structure refinement for s3776na.

Identification code	s3776na
Empirical formula	C12 H9 N O3
Formula weight	215.20
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, Cc
Unit cell dimensions	a = 20.5236(9) A alpha = 90 deg. b = 7.6948(3) A beta = 96.529(2) deg. c = 18.8253(9) A gamma = 90 deg.
Volume	2953.7(2) A^3
Z, Calculated density	12, 1.452 Mg/m^3
Absorption coefficient	0.881 mm^-1
F(000)	1344
Crystal size	0.22 x 0.15 x 0.07 mm
Theta range for data collection	4.34 to 70.00 deg.
Limiting indices	-24<=h<=23, -8<=k<=9, -21<=l<=22
Reflections collected / unique	6146 / 3891 [R(int) = 0.0421]
Completeness to theta = 66.60	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9409 and 0.659741
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3891 / 2 / 437
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1187
R indices (all data)	R1 = 0.0465, wR2 = 0.1211
Absolute structure parameter	0.06(19)
Largest diff. peak and hole	0.379 and -0.342 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3776na.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	6902(1)	3541(3)	2177(2)	17(1)
C(2)	6826(1)	4116(3)	2875(2)	14(1)
C(3)	6756(1)	5900(3)	2983(2)	18(1)
C(4)	6758(1)	7091(4)	2428(2)	21(1)
C(5)	6824(1)	6491(4)	1749(2)	22(1)
C(6)	6897(1)	4728(4)	1622(2)	19(1)
C(7)	6837(1)	2882(4)	3479(2)	15(1)
C(8)	6499(1)	1302(3)	3404(1)	15(1)
C(9)	6527(1)	115(3)	3958(2)	16(1)
C(10)	6891(1)	540(3)	4600(2)	15(1)
C(11)	7213(1)	2119(3)	4710(2)	15(1)
C(12)	7186(1)	3279(3)	4145(2)	16(1)
C(13)	5231(1)	1455(3)	6174(2)	17(1)
C(14)	5292(1)	889(3)	5477(2)	17(1)
C(15)	5348(1)	-908(3)	5365(2)	18(1)
C(16)	5351(1)	-2089(4)	5922(2)	20(1)
C(17)	5293(1)	-1496(4)	6610(2)	21(1)
C(18)	5231(1)	275(4)	6733(2)	21(1)
C(19)	5276(1)	2117(3)	4871(2)	16(1)
C(20)	4902(1)	1743(3)	4217(2)	17(1)
C(21)	4859(1)	2922(3)	3658(2)	17(1)
C(22)	5199(1)	4479(4)	3756(2)	15(1)
C(23)	5590(1)	4870(3)	4386(2)	17(1)
C(24)	5629(1)	3683(3)	4936(2)	17(1)
C(25)	8302(1)	8650(4)	4125(2)	19(1)
C(26)	8591(1)	8907(4)	4831(2)	18(1)
C(27)	8932(1)	10459(3)	4977(2)	19(1)
C(28)	8969(1)	11722(3)	4464(2)	22(1)
C(29)	8655(1)	11484(4)	3777(2)	22(1)
C(30)	8326(1)	9937(4)	3609(2)	23(1)
C(31)	8554(1)	7610(3)	5413(2)	17(1)
C(32)	8578(1)	5818(3)	5292(2)	18(1)
C(33)	8568(1)	4634(4)	5840(2)	20(1)
C(34)	8528(1)	5254(3)	6530(2)	22(1)
C(35)	8509(2)	7014(3)	6675(2)	21(1)
C(36)	8522(1)	8191(3)	6114(2)	20(1)
N(1)	6939(1)	-729(3)	5178(1)	17(1)
N(2)	5124(1)	5777(3)	3190(1)	19(1)
N(3)	8512(1)	4008(3)	7107(1)	26(1)
O(1)	7003(1)	1813(2)	2087(1)	22(1)
O(2)	7130(1)	-212(3)	5786(1)	23(1)
O(3)	6782(1)	-2252(2)	5036(1)	24(1)
O(4)	5150(1)	3195(2)	6278(1)	20(1)
O(5)	4889(1)	5314(3)	2586(1)	27(1)
O(6)	5297(1)	7271(2)	3333(1)	24(1)
O(7)	8522(1)	2455(3)	6968(1)	38(1)
O(8)	8481(1)	4567(3)	7713(1)	36(1)
O(9)	7991(1)	7129(3)	3958(1)	31(1)

Table 3. Bond lengths [A] and angles [deg] for s3776na.

C(1)-O(1)	1.359(3)
C(1)-C(6)	1.387(4)
C(1)-C(2)	1.413(4)
C(2)-C(3)	1.398(4)
C(2)-C(7)	1.479(4)
C(3)-C(4)	1.390(4)

C(3)-H(3)	0.9500
C(4)-C(5)	1.380(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.389(4)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.399(4)
C(7)-C(12)	1.404(4)
C(8)-C(9)	1.384(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.386(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.386(4)
C(10)-N(1)	1.457(3)
C(11)-C(12)	1.386(4)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-O(4)	1.366(3)
C(13)-C(18)	1.390(4)
C(13)-C(14)	1.402(4)
C(14)-C(15)	1.406(4)
C(14)-C(19)	1.480(4)
C(15)-C(16)	1.387(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.389(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.391(4)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(20)	1.404(4)
C(19)-C(24)	1.404(4)
C(20)-C(21)	1.385(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.388(4)
C(21)-H(21)	0.9500
C(22)-C(23)	1.386(4)
C(22)-N(2)	1.456(3)
C(23)-C(24)	1.376(4)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(25)-O(9)	1.352(3)
C(25)-C(30)	1.392(4)
C(25)-C(26)	1.405(4)
C(26)-C(27)	1.395(4)
C(26)-C(31)	1.491(4)
C(27)-C(28)	1.378(4)
C(27)-H(27)	0.9500
C(28)-C(29)	1.389(4)
C(28)-H(28)	0.9500
C(29)-C(30)	1.387(4)
C(29)-H(29)	0.9500
C(30)-H(30)	0.9500
C(31)-C(32)	1.400(4)
C(31)-C(36)	1.401(4)
C(32)-C(33)	1.379(4)
C(32)-H(32)	0.9500
C(33)-C(34)	1.395(4)
C(33)-H(33)	0.9500
C(34)-C(35)	1.383(4)
C(34)-N(3)	1.452(4)
C(35)-C(36)	1.394(4)
C(35)-H(35)	0.9500

C(36)-H(36)	0.9500
N(1)-O(2)	1.231(3)
N(1)-O(3)	1.236(3)
N(2)-O(6)	1.224(3)
N(2)-O(5)	1.237(3)
N(3)-O(7)	1.224(3)
N(3)-O(8)	1.227(4)
O(1)-H(1)	0.8400
O(4)-H(4A)	0.8400
O(9)-H(9A)	0.8400

O(1)-C(1)-C(6)	122.6(3)
O(1)-C(1)-C(2)	117.2(2)
C(6)-C(1)-C(2)	120.2(2)
C(3)-C(2)-C(1)	117.8(2)
C(3)-C(2)-C(7)	120.8(3)
C(1)-C(2)-C(7)	121.4(2)
C(4)-C(3)-C(2)	122.0(3)
C(4)-C(3)-H(3)	119.0
C(2)-C(3)-H(3)	119.0
C(5)-C(4)-C(3)	119.0(3)
C(5)-C(4)-H(4)	120.5
C(3)-C(4)-H(4)	120.5
C(4)-C(5)-C(6)	120.7(3)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(1)-C(6)-C(5)	120.3(3)
C(1)-C(6)-H(6)	119.8
C(5)-C(6)-H(6)	119.8
C(8)-C(7)-C(12)	118.5(2)
C(8)-C(7)-C(2)	121.0(2)
C(12)-C(7)-C(2)	120.5(2)
C(9)-C(8)-C(7)	121.2(2)
C(9)-C(8)-H(8)	119.4
C(7)-C(8)-H(8)	119.4
C(8)-C(9)-C(10)	118.3(2)
C(8)-C(9)-H(9)	120.8
C(10)-C(9)-H(9)	120.8
C(9)-C(10)-C(11)	122.5(3)
C(9)-C(10)-N(1)	118.4(2)
C(11)-C(10)-N(1)	119.1(2)
C(12)-C(11)-C(10)	118.3(2)
C(12)-C(11)-H(11)	120.9
C(10)-C(11)-H(11)	120.9
C(11)-C(12)-C(7)	121.1(2)
C(11)-C(12)-H(12)	119.4
C(7)-C(12)-H(12)	119.4
O(4)-C(13)-C(18)	121.4(3)
O(4)-C(13)-C(14)	117.6(2)
C(18)-C(13)-C(14)	120.9(2)
C(13)-C(14)-C(15)	117.6(3)
C(13)-C(14)-C(19)	121.8(2)
C(15)-C(14)-C(19)	120.5(3)
C(16)-C(15)-C(14)	121.6(3)
C(16)-C(15)-H(15)	119.2
C(14)-C(15)-H(15)	119.2
C(15)-C(16)-C(17)	119.7(3)
C(15)-C(16)-H(16)	120.1
C(17)-C(16)-H(16)	120.1
C(16)-C(17)-C(18)	119.8(3)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1

C(13)-C(18)-C(17)	120.3(3)
C(13)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8
C(20)-C(19)-C(24)	118.6(3)
C(20)-C(19)-C(14)	120.5(2)
C(24)-C(19)-C(14)	121.0(2)
C(21)-C(20)-C(19)	120.9(3)
C(21)-C(20)-H(20)	119.6
C(19)-C(20)-H(20)	119.6
C(20)-C(21)-C(22)	118.5(3)
C(20)-C(21)-H(21)	120.8
C(22)-C(21)-H(21)	120.8
C(23)-C(22)-C(21)	122.3(3)
C(23)-C(22)-N(2)	118.6(2)
C(21)-C(22)-N(2)	119.0(2)
C(24)-C(23)-C(22)	118.5(2)
C(24)-C(23)-H(23)	120.7
C(22)-C(23)-H(23)	120.7
C(23)-C(24)-C(19)	121.2(3)
C(23)-C(24)-H(24)	119.4
C(19)-C(24)-H(24)	119.4
O(9)-C(25)-C(30)	120.4(3)
O(9)-C(25)-C(26)	118.6(2)
C(30)-C(25)-C(26)	120.9(3)
C(27)-C(26)-C(25)	117.1(3)
C(27)-C(26)-C(31)	119.6(2)
C(25)-C(26)-C(31)	123.3(2)
C(28)-C(27)-C(26)	122.1(3)
C(28)-C(27)-H(27)	118.9
C(26)-C(27)-H(27)	118.9
C(27)-C(28)-C(29)	120.2(3)
C(27)-C(28)-H(28)	119.9
C(29)-C(28)-H(28)	119.9
C(30)-C(29)-C(28)	119.2(3)
C(30)-C(29)-H(29)	120.4
C(28)-C(29)-H(29)	120.4
C(29)-C(30)-C(25)	120.4(3)
C(29)-C(30)-H(30)	119.8
C(25)-C(30)-H(30)	119.8
C(32)-C(31)-C(36)	118.3(2)
C(32)-C(31)-C(26)	122.3(2)
C(36)-C(31)-C(26)	119.4(2)
C(33)-C(32)-C(31)	121.7(2)
C(33)-C(32)-H(32)	119.2
C(31)-C(32)-H(32)	119.2
C(32)-C(33)-C(34)	118.6(2)
C(32)-C(33)-H(33)	120.7
C(34)-C(33)-H(33)	120.7
C(35)-C(34)-C(33)	121.7(3)
C(35)-C(34)-N(3)	119.7(3)
C(33)-C(34)-N(3)	118.6(2)
C(34)-C(35)-C(36)	118.9(3)
C(34)-C(35)-H(35)	120.5
C(36)-C(35)-H(35)	120.5
C(35)-C(36)-C(31)	120.9(2)
C(35)-C(36)-H(36)	119.6
C(31)-C(36)-H(36)	119.6
O(2)-N(1)-O(3)	123.7(2)
O(2)-N(1)-C(10)	117.6(2)
O(3)-N(1)-C(10)	118.7(2)
O(6)-N(2)-O(5)	123.1(2)
O(6)-N(2)-C(22)	118.7(2)

O(5)-N(2)-C(22)	118.2(2)
O(7)-N(3)-O(8)	123.0(3)
O(7)-N(3)-C(34)	118.9(2)
O(8)-N(3)-C(34)	118.1(2)
C(1)-O(1)-H(1)	109.5
C(13)-O(4)-H(4A)	109.5
C(25)-O(9)-H(9A)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s3776na. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	20(1)	16(1)	16(2)	-1(1)	1(1)	0(1)
C(2)	14(1)	20(1)	8(1)	1(1)	0(1)	0(1)
C(3)	19(1)	21(1)	14(1)	-5(1)	0(1)	0(1)
C(4)	25(1)	17(1)	20(2)	2(1)	1(1)	2(1)
C(5)	26(1)	23(2)	16(2)	4(1)	0(1)	-2(1)
C(6)	24(1)	24(2)	10(1)	-2(1)	1(1)	-3(1)
C(7)	14(1)	17(1)	13(1)	-1(1)	2(1)	3(1)
C(8)	17(1)	21(1)	8(1)	-1(1)	1(1)	1(1)
C(9)	18(1)	17(1)	16(1)	-3(1)	4(1)	-1(1)
C(10)	16(1)	16(1)	13(1)	1(1)	3(1)	4(1)
C(11)	16(1)	19(1)	10(1)	-4(1)	-1(1)	-1(1)
C(12)	19(1)	17(1)	12(1)	-2(1)	2(1)	-1(1)
C(13)	16(1)	19(1)	17(2)	-5(1)	0(1)	-2(1)
C(14)	15(1)	17(1)	18(1)	-1(1)	-1(1)	0(1)
C(15)	19(1)	20(1)	14(2)	-1(1)	0(1)	2(1)
C(16)	22(1)	17(1)	21(2)	1(1)	-2(1)	-1(1)
C(17)	24(1)	21(2)	17(2)	5(1)	-2(1)	2(1)
C(18)	23(1)	23(2)	17(2)	0(1)	2(1)	2(1)
C(19)	17(1)	17(1)	14(1)	-4(1)	4(1)	2(1)
C(20)	18(1)	17(1)	15(1)	-2(1)	3(1)	-1(1)
C(21)	17(1)	21(1)	14(1)	-3(1)	2(1)	1(1)
C(22)	18(1)	19(1)	9(1)	0(1)	4(1)	2(1)
C(23)	20(1)	16(1)	15(1)	-1(1)	4(1)	0(1)
C(24)	16(1)	20(1)	15(1)	-4(1)	1(1)	0(1)
C(25)	21(1)	20(1)	16(2)	0(1)	2(1)	1(1)
C(26)	18(1)	21(1)	14(1)	-2(1)	3(1)	3(1)
C(27)	18(1)	21(1)	17(1)	0(1)	2(1)	3(1)
C(28)	23(1)	20(1)	24(2)	0(1)	5(1)	2(1)
C(29)	26(1)	24(1)	18(2)	4(1)	8(1)	6(1)
C(30)	24(1)	32(2)	14(2)	-1(1)	2(1)	7(1)
C(31)	14(1)	22(1)	15(1)	-2(1)	-1(1)	0(1)
C(32)	22(1)	19(1)	13(1)	-2(1)	3(1)	-1(1)
C(33)	20(1)	17(1)	22(2)	0(1)	0(1)	-1(1)
C(34)	20(1)	25(1)	19(2)	3(1)	-1(1)	0(1)
C(35)	25(1)	27(1)	12(1)	-1(1)	3(1)	7(1)
C(36)	25(1)	21(1)	14(1)	-1(1)	4(1)	3(1)
N(1)	18(1)	20(1)	13(1)	1(1)	3(1)	2(1)
N(2)	22(1)	21(1)	16(1)	1(1)	6(1)	0(1)
N(3)	32(1)	26(1)	20(1)	6(1)	3(1)	3(1)
O(1)	38(1)	18(1)	9(1)	-3(1)	6(1)	2(1)
O(2)	35(1)	24(1)	11(1)	1(1)	1(1)	-1(1)

O(3)	32(1)	16(1)	24(1)	1(1)	3(1)	-2(1)
O(4)	31(1)	18(1)	12(1)	-2(1)	1(1)	1(1)
O(5)	42(1)	28(1)	10(1)	2(1)	-2(1)	-5(1)
O(6)	33(1)	19(1)	22(1)	4(1)	2(1)	-4(1)
O(7)	65(2)	21(1)	30(1)	6(1)	13(1)	6(1)
O(8)	59(2)	35(1)	15(1)	5(1)	4(1)	4(1)
O(9)	43(1)	34(1)	14(1)	-3(1)	0(1)	-13(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s3776na.

	x	y	z	U(eq)
H(3)	6706	6311	3449	22
H(4)	6715	8299	2515	25
H(5)	6819	7293	1365	26
H(6)	6944	4333	1152	23
H(8)	6244	1040	2963	18
H(9)	6302	-964	3901	20
H(11)	7445	2398	5161	18
H(12)	7407	4362	4209	19
H(15)	5384	-1325	4896	21
H(16)	5393	-3297	5835	24
H(17)	5297	-2297	6994	26
H(18)	5188	681	7202	25
H(20)	4676	666	4157	20
H(21)	4602	2673	3218	21
H(23)	5824	5935	4437	20
H(24)	5900	3926	5368	20
H(27)	9145	10652	5445	22
H(28)	9210	12757	4580	27
H(29)	8665	12370	3427	26
H(30)	8116	9754	3139	28
H(32)	8601	5407	4819	21
H(33)	8588	3421	5750	24
H(35)	8487	7415	7149	25
H(36)	8509	9403	6207	24
H(1)	7023	1605	1652	32
H(4A)	5108	3382	6710	24(8)
H(9A)	7994	6928	3520	46

Table 6. Torsion angles [deg] for s3776na.

O(1)-C(1)-C(2)-C(3)	176.7(2)
C(6)-C(1)-C(2)-C(3)	-0.9(4)
O(1)-C(1)-C(2)-C(7)	-1.6(4)
C(6)-C(1)-C(2)-C(7)	-179.2(2)
C(1)-C(2)-C(3)-C(4)	0.2(4)
C(7)-C(2)-C(3)-C(4)	178.5(2)
C(2)-C(3)-C(4)-C(5)	0.7(4)
C(3)-C(4)-C(5)-C(6)	-1.0(4)
O(1)-C(1)-C(6)-C(5)	-176.8(3)
C(2)-C(1)-C(6)-C(5)	0.6(4)
C(4)-C(5)-C(6)-C(1)	0.3(4)
C(3)-C(2)-C(7)-C(8)	137.9(3)
C(1)-C(2)-C(7)-C(8)	-43.8(3)

C(3)-C(2)-C(7)-C(12)	-41.6(3)
C(1)-C(2)-C(7)-C(12)	136.7(3)
C(12)-C(7)-C(8)-C(9)	-2.8(4)
C(2)-C(7)-C(8)-C(9)	177.6(2)
C(7)-C(8)-C(9)-C(10)	1.2(4)
C(8)-C(9)-C(10)-C(11)	1.6(4)
C(8)-C(9)-C(10)-N(1)	-178.1(2)
C(9)-C(10)-C(11)-C(12)	-2.5(4)
N(1)-C(10)-C(11)-C(12)	177.2(2)
C(10)-C(11)-C(12)-C(7)	0.7(4)
C(8)-C(7)-C(12)-C(11)	1.9(4)
C(2)-C(7)-C(12)-C(11)	-178.6(2)
O(4)-C(13)-C(14)-C(15)	-177.4(2)
C(18)-C(13)-C(14)-C(15)	0.4(4)
O(4)-C(13)-C(14)-C(19)	0.6(4)
C(18)-C(13)-C(14)-C(19)	178.4(2)
C(13)-C(14)-C(15)-C(16)	-0.7(4)
C(19)-C(14)-C(15)-C(16)	-178.8(2)
C(14)-C(15)-C(16)-C(17)	0.4(4)
C(15)-C(16)-C(17)-C(18)	0.2(4)
O(4)-C(13)-C(18)-C(17)	177.9(2)
C(14)-C(13)-C(18)-C(17)	0.2(4)
C(16)-C(17)-C(18)-C(13)	-0.5(4)
C(13)-C(14)-C(19)-C(20)	-135.2(3)
C(15)-C(14)-C(19)-C(20)	42.8(4)
C(13)-C(14)-C(19)-C(24)	44.4(4)
C(15)-C(14)-C(19)-C(24)	-137.6(3)
C(24)-C(19)-C(20)-C(21)	-2.8(4)
C(14)-C(19)-C(20)-C(21)	176.8(2)
C(19)-C(20)-C(21)-C(22)	0.7(4)
C(20)-C(21)-C(22)-C(23)	1.4(4)
C(20)-C(21)-C(22)-N(2)	-176.1(2)
C(21)-C(22)-C(23)-C(24)	-1.2(4)
N(2)-C(22)-C(23)-C(24)	176.3(2)
C(22)-C(23)-C(24)-C(19)	-1.0(4)
C(20)-C(19)-C(24)-C(23)	3.0(4)
C(14)-C(19)-C(24)-C(23)	-176.6(2)
O(9)-C(25)-C(26)-C(27)	177.3(2)
C(30)-C(25)-C(26)-C(27)	-3.5(4)
O(9)-C(25)-C(26)-C(31)	-2.1(4)
C(30)-C(25)-C(26)-C(31)	177.1(2)
C(25)-C(26)-C(27)-C(28)	2.1(4)
C(31)-C(26)-C(27)-C(28)	-178.4(2)
C(26)-C(27)-C(28)-C(29)	0.8(4)
C(27)-C(28)-C(29)-C(30)	-2.4(4)
C(28)-C(29)-C(30)-C(25)	1.0(4)
O(9)-C(25)-C(30)-C(29)	-178.9(3)
C(26)-C(25)-C(30)-C(29)	2.0(4)
C(27)-C(26)-C(31)-C(32)	-142.9(3)
C(25)-C(26)-C(31)-C(32)	36.6(4)
C(27)-C(26)-C(31)-C(36)	34.4(3)
C(25)-C(26)-C(31)-C(36)	-146.1(3)
C(36)-C(31)-C(32)-C(33)	0.2(4)
C(26)-C(31)-C(32)-C(33)	177.5(2)
C(31)-C(32)-C(33)-C(34)	0.6(4)
C(32)-C(33)-C(34)-C(35)	-1.1(4)
C(32)-C(33)-C(34)-N(3)	179.5(3)
C(33)-C(34)-C(35)-C(36)	0.9(4)
N(3)-C(34)-C(35)-C(36)	-179.8(3)
C(34)-C(35)-C(36)-C(31)	-0.1(4)
C(32)-C(31)-C(36)-C(35)	-0.5(4)
C(26)-C(31)-C(36)-C(35)	-177.9(3)

C(9)-C(10)-N(1)-O(2)	-163.8(2)
C(11)-C(10)-N(1)-O(2)	16.5(3)
C(9)-C(10)-N(1)-O(3)	15.8(3)
C(11)-C(10)-N(1)-O(3)	-163.9(2)
C(23)-C(22)-N(2)-O(6)	-14.0(3)
C(21)-C(22)-N(2)-O(6)	163.5(2)
C(23)-C(22)-N(2)-O(5)	165.8(2)
C(21)-C(22)-N(2)-O(5)	-16.6(4)
C(35)-C(34)-N(3)-O(7)	179.2(3)
C(33)-C(34)-N(3)-O(7)	-1.4(4)
C(35)-C(34)-N(3)-O(8)	0.2(4)
C(33)-C(34)-N(3)-O(8)	179.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for s3776na [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#1	0.84	1.98	2.780(3)	157.9
O(4)-H(4A)...O(5)#2	0.84	2.02	2.822(3)	158.5
O(9)-H(9A)...O(8)#3	0.84	2.23	2.958(3)	144.8

Symmetry transformations used to generate equivalent atoms:
#1 x,-y,z-1/2 #2 x,-y+1,z+1/2 #3 x,-y+1,z-1/2

Crystal data and structure refinement for s3726ma.

Identification code	s3726ma
Empirical formula	C15 H17 N O5 S Si
Formula weight	351.45
Temperature	150(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.8463(2) A alpha = 90 deg. b = 9.1987(2) A beta = 92.4730(10) deg. c = 18.7908(5) A gamma = 90 deg.
Volume	1700.36(7) A^3
Z, Calculated density	4, 1.373 Mg/m^3
Absorption coefficient	2.586 mm^-1
F(000)	736
Crystal size	0.22 x 0.18 x 0.15 mm
Theta range for data collection	4.49 to 72.28 deg.
Limiting indices	-12<=h<=12, -9<=k<=11, -22<=l<=23
Reflections collected / unique	8472 / 3227 [R(int) = 0.0333]
Completeness to theta = 72.28	96.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6977 and 0.476706
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3227 / 0 / 212
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0977
R indices (all data)	R1 = 0.0402, wR2 = 0.1011
Extinction coefficient	0.0005(2)
Largest diff. peak and hole	0.413 and -0.343 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3726ma.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2698(2)	1794(2)	878(1)	24(1)
C(2)	2822(2)	2830(2)	1415(1)	24(1)
C(3)	3210(2)	4218(2)	1193(1)	32(1)
C(4)	3465(2)	4513(2)	487(1)	40(1)
C(5)	3322(2)	3440(2)	-20(1)	39(1)
C(6)	2918(2)	2052(2)	171(1)	31(1)
C(7)	2590(2)	4160(2)	2882(1)	41(1)
C(8)	788(2)	1573(3)	2456(1)	45(1)
C(9)	3856(2)	1167(2)	2737(1)	42(1)
C(10)	2488(2)	-1715(2)	141(1)	25(1)
C(11)	1241(2)	-2410(2)	23(1)	28(1)
C(12)	916(2)	-3121(2)	-606(1)	38(1)
C(13)	1851(2)	-3127(2)	-1137(1)	41(1)
C(14)	3084(2)	-2426(2)	-1037(1)	39(1)
C(15)	3407(2)	-1731(2)	-398(1)	32(1)
N(1)	204(2)	-2410(2)	562(1)	38(1)
O(1)	2214(1)	408(1)	1092(1)	28(1)
O(2)	4453(1)	-687(1)	950(1)	38(1)
O(3)	2588(2)	-2004(1)	1512(1)	39(1)
O(4)	-156(1)	-1235(2)	790(1)	52(1)
O(5)	-266(2)	-3584(2)	727(1)	54(1)
S(1)	3046(1)	-1033(1)	984(1)	27(1)
Si(1)	2495(1)	2419(1)	2381(1)	27(1)

Table 3. Bond lengths [A] and angles [deg] for s3726ma.

C(1)-C(6)	1.377(2)
C(1)-C(2)	1.389(2)
C(1)-O(1)	1.4253(18)
C(2)-C(3)	1.402(2)
C(2)-Si(1)	1.8952(16)
C(3)-C(4)	1.388(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.374(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.389(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-Si(1)	1.858(2)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-Si(1)	1.8623(19)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-Si(1)	1.869(2)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(15)	1.386(2)
C(10)-C(11)	1.394(2)
C(10)-S(1)	1.7697(16)
C(11)-C(12)	1.376(2)
C(11)-N(1)	1.469(2)
C(12)-C(13)	1.387(3)
C(12)-H(12)	0.9500

C(13)-C(14)	1.381(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.385(3)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
N(1)-O(4)	1.220(2)
N(1)-O(5)	1.221(2)
O(1)-S(1)	1.5765(12)
O(2)-S(1)	1.4253(13)
O(3)-S(1)	1.4236(13)

C(6)-C(1)-C(2)	124.80(15)
C(6)-C(1)-O(1)	119.71(14)
C(2)-C(1)-O(1)	115.33(13)
C(1)-C(2)-C(3)	115.10(15)
C(1)-C(2)-Si(1)	123.08(12)
C(3)-C(2)-Si(1)	121.82(13)
C(4)-C(3)-C(2)	121.74(17)
C(4)-C(3)-H(3)	119.1
C(2)-C(3)-H(3)	119.1
C(5)-C(4)-C(3)	120.34(17)
C(5)-C(4)-H(4)	119.8
C(3)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	120.17(16)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(1)-C(6)-C(5)	117.83(17)
C(1)-C(6)-H(6)	121.1
C(5)-C(6)-H(6)	121.1
Si(1)-C(7)-H(7A)	109.5
Si(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
Si(1)-C(8)-H(8A)	109.5
Si(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
Si(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
Si(1)-C(9)-H(9A)	109.5
Si(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
Si(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(15)-C(10)-C(11)	118.56(15)
C(15)-C(10)-S(1)	118.04(13)
C(11)-C(10)-S(1)	122.81(12)
C(12)-C(11)-C(10)	121.61(16)
C(12)-C(11)-N(1)	116.76(16)
C(10)-C(11)-N(1)	121.63(15)
C(11)-C(12)-C(13)	118.93(18)
C(11)-C(12)-H(12)	120.5
C(13)-C(12)-H(12)	120.5
C(14)-C(13)-C(12)	120.47(17)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(13)-C(14)-C(15)	120.08(17)
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-H(14)	120.0

C(14)-C(15)-C(10)	120.34(17)
C(14)-C(15)-H(15)	119.8
C(10)-C(15)-H(15)	119.8
O(4)-N(1)-O(5)	125.13(16)
O(4)-N(1)-C(11)	117.62(15)
O(5)-N(1)-C(11)	117.19(16)
C(1)-O(1)-S(1)	122.23(9)
O(3)-S(1)-O(2)	120.62(9)
O(3)-S(1)-O(1)	104.80(7)
O(2)-S(1)-O(1)	109.27(7)
O(3)-S(1)-C(10)	107.83(8)
O(2)-S(1)-C(10)	107.67(8)
O(1)-S(1)-C(10)	105.73(7)
C(7)-Si(1)-C(8)	110.35(9)
C(7)-Si(1)-C(9)	109.28(10)
C(8)-Si(1)-C(9)	110.56(11)
C(7)-Si(1)-C(2)	107.85(9)
C(8)-Si(1)-C(2)	110.29(8)
C(9)-Si(1)-C(2)	108.45(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s3726ma. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	23(1)	20(1)	29(1)	2(1)	3(1)	-1(1)
C(2)	22(1)	20(1)	28(1)	0(1)	2(1)	1(1)
C(3)	35(1)	19(1)	43(1)	-1(1)	7(1)	1(1)
C(4)	48(1)	22(1)	52(1)	13(1)	14(1)	5(1)
C(5)	48(1)	34(1)	34(1)	14(1)	11(1)	8(1)
C(6)	38(1)	29(1)	27(1)	1(1)	3(1)	3(1)
C(7)	38(1)	46(1)	40(1)	-17(1)	6(1)	1(1)
C(8)	38(1)	62(1)	36(1)	-1(1)	10(1)	-15(1)
C(9)	49(1)	50(1)	28(1)	1(1)	-2(1)	12(1)
C(10)	29(1)	17(1)	28(1)	0(1)	3(1)	2(1)
C(11)	29(1)	23(1)	31(1)	-2(1)	4(1)	-1(1)
C(12)	41(1)	32(1)	41(1)	-9(1)	-5(1)	1(1)
C(13)	58(1)	35(1)	31(1)	-8(1)	-2(1)	13(1)
C(14)	56(1)	30(1)	32(1)	4(1)	16(1)	15(1)
C(15)	34(1)	22(1)	40(1)	5(1)	11(1)	3(1)
N(1)	32(1)	43(1)	42(1)	-10(1)	8(1)	-13(1)
O(1)	33(1)	21(1)	32(1)	-3(1)	8(1)	-6(1)
O(2)	30(1)	30(1)	53(1)	2(1)	-6(1)	-4(1)
O(3)	58(1)	27(1)	32(1)	7(1)	-1(1)	-10(1)
O(4)	39(1)	54(1)	65(1)	-28(1)	23(1)	-11(1)
O(5)	54(1)	52(1)	56(1)	-2(1)	15(1)	-26(1)
S(1)	31(1)	20(1)	30(1)	2(1)	-1(1)	-4(1)
Si(1)	25(1)	30(1)	25(1)	-4(1)	3(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s3726ma.

	x	y	z	U(eq)
H(3)	3300	4977	1534	39
H(4)	3740	5460	353	48
H(5)	3500	3649	-503	46
H(6)	2798	1305	-175	38
H(7A)	1981	4873	2649	62
H(7B)	3525	4527	2892	62
H(7C)	2315	3997	3371	62
H(8A)	656	1307	2953	68
H(8B)	726	700	2157	68
H(8C)	84	2267	2296	68
H(9A)	4747	1622	2687	64
H(9B)	3817	252	2469	64
H(9C)	3719	969	3241	64
H(12)	66	-3599	-675	46
H(13)	1642	-3618	-1573	50
H(14)	3712	-2419	-1407	47
H(15)	4263	-1263	-328	38

Table 6. Torsion angles [deg] for s3726ma.

C(6)-C(1)-C(2)-C(3)	-0.4(2)
O(1)-C(1)-C(2)-C(3)	-175.83(13)
C(6)-C(1)-C(2)-Si(1)	179.58(13)
O(1)-C(1)-C(2)-Si(1)	4.10(19)
C(1)-C(2)-C(3)-C(4)	-0.9(2)
Si(1)-C(2)-C(3)-C(4)	179.20(14)
C(2)-C(3)-C(4)-C(5)	1.0(3)
C(3)-C(4)-C(5)-C(6)	0.1(3)
C(2)-C(1)-C(6)-C(5)	1.4(3)
O(1)-C(1)-C(6)-C(5)	176.69(15)
C(4)-C(5)-C(6)-C(1)	-1.2(3)
C(15)-C(10)-C(11)-C(12)	0.9(3)
S(1)-C(10)-C(11)-C(12)	-170.13(14)
C(15)-C(10)-C(11)-N(1)	-178.53(16)
S(1)-C(10)-C(11)-N(1)	10.4(2)
C(10)-C(11)-C(12)-C(13)	-0.7(3)
N(1)-C(11)-C(12)-C(13)	178.75(17)
C(11)-C(12)-C(13)-C(14)	-0.3(3)
C(12)-C(13)-C(14)-C(15)	1.2(3)
C(13)-C(14)-C(15)-C(10)	-1.0(3)
C(11)-C(10)-C(15)-C(14)	0.0(2)
S(1)-C(10)-C(15)-C(14)	171.45(13)
C(12)-C(11)-N(1)-O(4)	-124.93(19)
C(10)-C(11)-N(1)-O(4)	54.6(3)
C(12)-C(11)-N(1)-O(5)	52.4(3)
C(10)-C(11)-N(1)-O(5)	-128.12(19)
C(6)-C(1)-O(1)-S(1)	61.65(19)
C(2)-C(1)-O(1)-S(1)	-122.63(13)
C(1)-O(1)-S(1)-O(3)	155.19(12)
C(1)-O(1)-S(1)-O(2)	24.61(14)
C(1)-O(1)-S(1)-C(10)	-91.02(13)
C(15)-C(10)-S(1)-O(3)	-135.10(14)
C(11)-C(10)-S(1)-O(3)	36.01(16)
C(15)-C(10)-S(1)-O(2)	-3.49(15)
C(11)-C(10)-S(1)-O(2)	167.62(13)
C(15)-C(10)-S(1)-O(1)	113.23(13)

C(11)-C(10)-S(1)-O(1)	-75.66(15)
C(1)-C(2)-Si(1)-C(7)	-173.63(14)
C(3)-C(2)-Si(1)-C(7)	6.30(16)
C(1)-C(2)-Si(1)-C(8)	-53.06(16)
C(3)-C(2)-Si(1)-C(8)	126.87(15)
C(1)-C(2)-Si(1)-C(9)	68.14(16)
C(3)-C(2)-Si(1)-C(9)	-111.93(15)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for s3726ma [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Crystal data and structure refinement for s3898ma.

Identification code	s3898ma
Empirical formula	C13 H10 N2 O5
Formula weight	274.23
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 15.6137(4) A alpha = 90 deg. b = 7.7484(2) A beta = 110.1920(10) deg. c = 21.2252(5) A gamma = 90 deg.
Volume	2410.03(10) A^3
Z, Calculated density	8, 1.512 Mg/m^3
Absorption coefficient	1.010 mm^-1
F(000)	1136
Crystal size	0.23 x 0.19 x 0.15 mm
Theta range for data collection	6.04 to 72.30 deg.
Limiting indices	-19<=h<=18, -9<=k<=9, -18<=l<=26
Reflections collected / unique	12895 / 4561 [R(int) = 0.0231]
Completeness to theta = 66.60	96.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8633 and 0.658587
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4561 / 0 / 365
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1116
R indices (all data)	R1 = 0.0475, wR2 = 0.1131
Largest diff. peak and hole	0.294 and -0.336 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3898ma.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

C(12)	5981(1)	10577(2)	971(1)	19(1)
C(1)	8758(1)	10754(2)	2871(1)	15(1)
C(2)	9168(1)	10929(2)	3570(1)	16(1)
C(3)	8745(1)	10361(2)	4016(1)	16(1)
C(4)	7889(1)	9622(2)	3773(1)	17(1)
C(5)	7474(1)	9462(2)	3076(1)	15(1)
C(6)	7888(1)	9985(2)	2626(1)	15(1)
C(7)	7405(1)	9003(3)	4236(1)	22(1)
C(8)	7379(1)	9843(2)	1891(1)	14(1)
C(9)	7686(1)	9094(2)	1405(1)	14(1)
C(10)	7165(1)	9060(2)	727(1)	16(1)
C(11)	6308(1)	9817(2)	507(1)	19(1)
C(13)	6504(1)	10573(2)	1648(1)	17(1)
C(14)	1556(1)	9176(2)	2795(1)	14(1)
C(15)	1814(1)	8991(2)	3494(1)	16(1)
C(16)	2664(1)	9545(2)	3930(1)	17(1)
C(17)	3287(1)	10260(2)	3680(1)	18(1)
C(18)	3038(1)	10432(2)	2982(1)	16(1)
C(19)	2190(1)	9934(2)	2541(1)	15(1)
C(20)	4215(1)	10866(3)	4134(1)	23(1)
C(21)	1981(1)	10083(2)	1803(1)	15(1)
C(22)	1189(1)	10817(2)	1343(1)	16(1)
C(23)	1010(1)	10801(2)	655(1)	19(1)
C(24)	1635(1)	10061(3)	405(1)	21(1)
C(25)	2438(1)	9369(2)	847(1)	21(1)
C(26)	2602(1)	9376(2)	1532(1)	18(1)
N(1)	10060(1)	11728(2)	3856(1)	18(1)
N(2)	8576(1)	8217(2)	1589(1)	15(1)
N(3)	1193(1)	8229(2)	3786(1)	19(1)
N(4)	508(1)	11705(2)	1565(1)	17(1)
O(1)	9117(1)	11293(2)	2414(1)	17(1)
O(2)	10462(1)	12205(2)	3472(1)	27(1)
O(3)	10399(1)	11906(2)	4466(1)	27(1)
O(4)	8922(1)	7652(2)	2161(1)	17(1)
O(5)	8921(1)	8054(2)	1154(1)	25(1)
O(6)	757(1)	8668(2)	2344(1)	16(1)
O(7)	1414(1)	8148(2)	4399(1)	28(1)
O(8)	444(1)	7680(2)	3408(1)	28(1)
O(9)	759(1)	12338(2)	2131(1)	19(1)
O(10)	-275(1)	11812(2)	1166(1)	28(1)

Table 3. Bond lengths [A] and angles [deg] for s3898ma.

C(12)-C(13)	1.387(3)
C(12)-C(11)	1.388(3)
C(12)-H(12)	0.9498
C(1)-O(1)	1.343(2)
C(1)-C(2)	1.406(3)
C(1)-C(6)	1.409(2)
C(2)-C(3)	1.397(3)
C(2)-N(1)	1.453(2)
C(3)-C(4)	1.381(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.401(3)
C(4)-C(7)	1.509(2)
C(5)-C(6)	1.387(2)
C(5)-H(5)	0.9500
C(6)-C(8)	1.489(3)
C(7)-H(7A)	0.9800

C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(13)	1.402(2)
C(8)-C(9)	1.405(2)
C(9)-C(10)	1.386(3)
C(9)-N(2)	1.474(2)
C(10)-C(11)	1.386(3)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(13)-H(13)	0.9500
C(14)-O(6)	1.343(2)
C(14)-C(15)	1.403(2)
C(14)-C(19)	1.409(2)
C(15)-C(16)	1.398(3)
C(15)-N(3)	1.445(2)
C(16)-C(17)	1.376(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.402(3)
C(17)-C(20)	1.511(3)
C(18)-C(19)	1.386(2)
C(18)-H(18)	0.9500
C(19)-C(21)	1.490(2)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(26)	1.399(2)
C(21)-C(22)	1.405(2)
C(22)-C(23)	1.388(3)
C(22)-N(4)	1.473(2)
C(23)-C(24)	1.385(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.389(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.386(3)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
N(1)-O(3)	1.226(2)
N(1)-O(2)	1.244(2)
N(2)-O(5)	1.225(2)
N(2)-O(4)	1.2276(19)
N(3)-O(7)	1.226(2)
N(3)-O(8)	1.243(2)
N(4)-O(10)	1.226(2)
N(4)-O(9)	1.230(2)
O(1)-H(1)	0.8400
O(6)-H(6)	0.8400

C(13)-C(12)-C(11)	120.36(17)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
O(1)-C(1)-C(2)	125.54(16)
O(1)-C(1)-C(6)	117.02(16)
C(2)-C(1)-C(6)	117.41(16)
C(3)-C(2)-C(1)	122.37(16)
C(3)-C(2)-N(1)	117.46(16)
C(1)-C(2)-N(1)	120.17(16)
C(4)-C(3)-C(2)	120.06(17)
C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0
C(3)-C(4)-C(5)	117.77(16)
C(3)-C(4)-C(7)	121.84(17)
C(5)-C(4)-C(7)	120.38(17)

C(6)-C(5)-C(4)	123.13(16)
C(6)-C(5)-H(5)	118.4
C(4)-C(5)-H(5)	118.4
C(5)-C(6)-C(1)	119.24(17)
C(5)-C(6)-C(8)	119.54(16)
C(1)-C(6)-C(8)	121.07(16)
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(13)-C(8)-C(9)	115.66(16)
C(13)-C(8)-C(6)	117.07(15)
C(9)-C(8)-C(6)	127.25(16)
C(10)-C(9)-C(8)	122.92(16)
C(10)-C(9)-N(2)	115.30(15)
C(8)-C(9)-N(2)	121.74(15)
C(11)-C(10)-C(9)	119.62(17)
C(11)-C(10)-H(10)	120.2
C(9)-C(10)-H(10)	120.2
C(10)-C(11)-C(12)	119.27(17)
C(10)-C(11)-H(11)	120.4
C(12)-C(11)-H(11)	120.4
C(12)-C(13)-C(8)	122.16(17)
C(12)-C(13)-H(13)	118.9
C(8)-C(13)-H(13)	118.9
O(6)-C(14)-C(15)	125.50(16)
O(6)-C(14)-C(19)	116.87(15)
C(15)-C(14)-C(19)	117.62(16)
C(16)-C(15)-C(14)	121.97(16)
C(16)-C(15)-N(3)	117.71(16)
C(14)-C(15)-N(3)	120.32(16)
C(17)-C(16)-C(15)	120.28(17)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(18)	118.05(17)
C(16)-C(17)-C(20)	121.95(17)
C(18)-C(17)-C(20)	120.00(17)
C(19)-C(18)-C(17)	122.66(16)
C(19)-C(18)-H(18)	118.7
C(17)-C(18)-H(18)	118.7
C(18)-C(19)-C(14)	119.39(16)
C(18)-C(19)-C(21)	120.02(15)
C(14)-C(19)-C(21)	120.44(15)
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(26)-C(21)-C(22)	116.17(16)
C(26)-C(21)-C(19)	118.06(16)
C(22)-C(21)-C(19)	125.72(16)
C(23)-C(22)-C(21)	122.54(17)
C(23)-C(22)-N(4)	115.73(15)
C(21)-C(22)-N(4)	121.70(16)
C(24)-C(23)-C(22)	119.53(17)
C(24)-C(23)-H(23)	120.2
C(22)-C(23)-H(23)	120.2
C(23)-C(24)-C(25)	119.54(17)
C(23)-C(24)-H(24)	120.2

C(25)-C(24)-H(24)	120.2
C(26)-C(25)-C(24)	120.20(17)
C(26)-C(25)-H(25)	119.9
C(24)-C(25)-H(25)	119.9
C(25)-C(26)-C(21)	121.98(17)
C(25)-C(26)-H(26)	119.0
C(21)-C(26)-H(26)	119.0
O(3)-N(1)-O(2)	121.82(15)
O(3)-N(1)-C(2)	119.33(15)
O(2)-N(1)-C(2)	118.85(15)
O(5)-N(2)-O(4)	123.44(15)
O(5)-N(2)-C(9)	117.91(15)
O(4)-N(2)-C(9)	118.63(14)
O(7)-N(3)-O(8)	121.69(16)
O(7)-N(3)-C(15)	119.40(16)
O(8)-N(3)-C(15)	118.91(15)
O(10)-N(4)-O(9)	123.52(16)
O(10)-N(4)-C(22)	117.99(15)
O(9)-N(4)-C(22)	118.47(14)
C(1)-O(1)-H(1)	109.5
C(14)-O(6)-H(6)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s3898ma. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(12)	12(1)	18(1)	24(1)	-2(1)	1(1)	1(1)
C(1)	14(1)	12(1)	18(1)	0(1)	5(1)	2(1)
C(2)	13(1)	13(1)	18(1)	-2(1)	1(1)	1(1)
C(3)	18(1)	13(1)	16(1)	-1(1)	2(1)	4(1)
C(4)	19(1)	12(1)	20(1)	0(1)	7(1)	3(1)
C(5)	14(1)	12(1)	20(1)	-2(1)	4(1)	0(1)
C(6)	14(1)	11(1)	17(1)	-2(1)	4(1)	2(1)
C(7)	24(1)	21(1)	21(1)	0(1)	10(1)	-1(1)
C(8)	13(1)	12(1)	16(1)	0(1)	3(1)	-3(1)
C(9)	11(1)	12(1)	16(1)	1(1)	3(1)	-1(1)
C(10)	18(1)	15(1)	17(1)	-1(1)	6(1)	-2(1)
C(11)	18(1)	18(1)	15(1)	0(1)	0(1)	-2(1)
C(13)	16(1)	16(1)	19(1)	-4(1)	5(1)	0(1)
C(14)	13(1)	12(1)	18(1)	0(1)	4(1)	2(1)
C(15)	18(1)	14(1)	19(1)	2(1)	8(1)	4(1)
C(16)	19(1)	16(1)	17(1)	1(1)	5(1)	5(1)
C(17)	16(1)	14(1)	20(1)	0(1)	2(1)	3(1)
C(18)	14(1)	12(1)	22(1)	1(1)	6(1)	2(1)
C(19)	14(1)	12(1)	18(1)	1(1)	5(1)	2(1)
C(20)	19(1)	22(1)	22(1)	-1(1)	0(1)	0(1)
C(21)	14(1)	13(1)	17(1)	2(1)	5(1)	-4(1)
C(22)	14(1)	14(1)	20(1)	2(1)	6(1)	-2(1)
C(23)	19(1)	18(1)	18(1)	4(1)	2(1)	-3(1)
C(24)	25(1)	23(1)	16(1)	1(1)	8(1)	-7(1)
C(25)	22(1)	20(1)	23(1)	-1(1)	12(1)	-2(1)
C(26)	16(1)	16(1)	21(1)	2(1)	7(1)	-1(1)
N(1)	15(1)	16(1)	20(1)	-3(1)	2(1)	1(1)

N(2)	14(1)	14(1)	18(1)	0(1)	5(1)	-1(1)
N(3)	19(1)	18(1)	20(1)	5(1)	9(1)	4(1)
N(4)	15(1)	15(1)	20(1)	4(1)	5(1)	0(1)
O(1)	13(1)	19(1)	19(1)	0(1)	5(1)	-4(1)
O(2)	18(1)	35(1)	28(1)	-7(1)	7(1)	-9(1)
O(3)	22(1)	32(1)	19(1)	-6(1)	-3(1)	-4(1)
O(4)	16(1)	18(1)	16(1)	4(1)	4(1)	1(1)
O(5)	20(1)	39(1)	20(1)	2(1)	11(1)	7(1)
O(6)	13(1)	18(1)	18(1)	2(1)	5(1)	-3(1)
O(7)	33(1)	37(1)	18(1)	6(1)	12(1)	1(1)
O(8)	18(1)	42(1)	25(1)	8(1)	7(1)	-6(1)
O(9)	19(1)	16(1)	20(1)	-2(1)	6(1)	-1(1)
O(10)	14(1)	40(1)	25(1)	2(1)	0(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s3898ma.

	x	y	z	U(eq)
H(3)	9048	10484	4486	20
H(5)	6880	8971	2904	18
H(7A)	7845	8900	4693	32
H(7B)	7127	7874	4083	32
H(7C)	6928	9832	4231	32
H(10)	7395	8521	416	20
H(11)	5949	9815	43	22
H(12)	5395	11103	824	22
H(13)	6261	11082	1958	21
H(16)	2812	9426	4402	21
H(18)	3467	10909	2804	19
H(20A)	4231	10882	4600	34
H(20B)	4329	12031	4002	34
H(20C)	4685	10078	4095	34
H(23)	462	11295	358	23
H(24)	1514	10028	-65	26
H(25)	2877	8888	680	25
H(26)	3153	8887	1826	21
H(1)	9643	11686	2611	25
H(6)	420	8279	2546	25

Table 6. Torsion angles [deg] for s3898ma.

O(1)-C(1)-C(2)-C(3)	178.92(16)
C(6)-C(1)-C(2)-C(3)	0.5(3)
O(1)-C(1)-C(2)-N(1)	-0.9(3)
C(6)-C(1)-C(2)-N(1)	-179.32(15)
C(1)-C(2)-C(3)-C(4)	-1.1(3)
N(1)-C(2)-C(3)-C(4)	178.73(15)
C(2)-C(3)-C(4)-C(5)	0.3(3)
C(2)-C(3)-C(4)-C(7)	-179.56(16)
C(3)-C(4)-C(5)-C(6)	1.0(3)
C(7)-C(4)-C(5)-C(6)	-179.14(16)
C(4)-C(5)-C(6)-C(1)	-1.5(3)
C(4)-C(5)-C(6)-C(8)	-177.10(16)
O(1)-C(1)-C(6)-C(5)	-177.79(15)
C(2)-C(1)-C(6)-C(5)	0.8(2)

O(1)-C(1)-C(6)-C(8)	-2.3(2)
C(2)-C(1)-C(6)-C(8)	176.28(15)
C(5)-C(6)-C(8)-C(13)	51.7(2)
C(1)-C(6)-C(8)-C(13)	-123.74(18)
C(5)-C(6)-C(8)-C(9)	-130.06(19)
C(1)-C(6)-C(8)-C(9)	54.5(2)
C(13)-C(8)-C(9)-C(10)	-0.3(2)
C(6)-C(8)-C(9)-C(10)	-178.50(16)
C(13)-C(8)-C(9)-N(2)	-177.51(15)
C(6)-C(8)-C(9)-N(2)	4.3(3)
C(8)-C(9)-C(10)-C(11)	1.1(3)
N(2)-C(9)-C(10)-C(11)	178.54(15)
C(9)-C(10)-C(11)-C(12)	-0.8(3)
C(13)-C(12)-C(11)-C(10)	-0.3(3)
C(11)-C(12)-C(13)-C(8)	1.2(3)
C(9)-C(8)-C(13)-C(12)	-0.9(3)
C(6)-C(8)-C(13)-C(12)	177.53(16)
O(6)-C(14)-C(15)-C(16)	179.54(16)
C(19)-C(14)-C(15)-C(16)	0.5(3)
O(6)-C(14)-C(15)-N(3)	-1.2(3)
C(19)-C(14)-C(15)-N(3)	179.76(15)
C(14)-C(15)-C(16)-C(17)	-1.5(3)
N(3)-C(15)-C(16)-C(17)	179.21(16)
C(15)-C(16)-C(17)-C(18)	0.8(3)
C(15)-C(16)-C(17)-C(20)	-179.68(17)
C(16)-C(17)-C(18)-C(19)	0.9(3)
C(20)-C(17)-C(18)-C(19)	-178.61(17)
C(17)-C(18)-C(19)-C(14)	-1.9(3)
C(17)-C(18)-C(19)-C(21)	-177.45(16)
O(6)-C(14)-C(19)-C(18)	-177.96(15)
C(15)-C(14)-C(19)-C(18)	1.1(2)
O(6)-C(14)-C(19)-C(21)	-2.4(2)
C(15)-C(14)-C(19)-C(21)	176.68(15)
C(18)-C(19)-C(21)-C(26)	50.6(2)
C(14)-C(19)-C(21)-C(26)	-124.87(18)
C(18)-C(19)-C(21)-C(22)	-132.04(19)
C(14)-C(19)-C(21)-C(22)	52.5(2)
C(26)-C(21)-C(22)-C(23)	2.1(3)
C(19)-C(21)-C(22)-C(23)	-175.28(17)
C(26)-C(21)-C(22)-N(4)	-175.95(15)
C(19)-C(21)-C(22)-N(4)	6.7(3)
C(21)-C(22)-C(23)-C(24)	-1.0(3)
N(4)-C(22)-C(23)-C(24)	177.15(16)
C(22)-C(23)-C(24)-C(25)	-1.0(3)
C(23)-C(24)-C(25)-C(26)	1.7(3)
C(24)-C(25)-C(26)-C(21)	-0.6(3)
C(22)-C(21)-C(26)-C(25)	-1.3(3)
C(19)-C(21)-C(26)-C(25)	176.29(16)
C(3)-C(2)-N(1)-O(3)	-1.4(2)
C(1)-C(2)-N(1)-O(3)	178.36(16)
C(3)-C(2)-N(1)-O(2)	178.17(16)
C(1)-C(2)-N(1)-O(2)	-2.0(2)
C(10)-C(9)-N(2)-O(5)	23.9(2)
C(8)-C(9)-N(2)-O(5)	-158.62(16)
C(10)-C(9)-N(2)-O(4)	-154.34(15)
C(8)-C(9)-N(2)-O(4)	23.1(2)
C(16)-C(15)-N(3)-O(7)	2.5(2)
C(14)-C(15)-N(3)-O(7)	-176.81(16)
C(16)-C(15)-N(3)-O(8)	-177.87(16)
C(14)-C(15)-N(3)-O(8)	2.9(2)
C(23)-C(22)-N(4)-O(10)	25.3(2)
C(21)-C(22)-N(4)-O(10)	-156.58(17)

C(23)-C(22)-N(4)-O(9)	-152.82(16)
C(21)-C(22)-N(4)-O(9)	25.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for s3898ma [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)	0.84	1.88	2.5880(18)	141.6
O(1)-H(1)...O(9)#1	0.84	2.36	2.9419(17)	127.2
O(1)-H(1)...N(1)	0.84	2.49	2.921(2)	112.7
O(6)-H(6)...O(8)	0.84	1.88	2.5853(18)	141.3
O(6)-H(6)...O(4)#2	0.84	2.25	2.8655(17)	130.4
O(6)-H(6)...N(3)	0.84	2.49	2.917(2)	112.6

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 x-1,y,z

Crystal data and structure refinement for s3767na.

Identification code	s3767na
Empirical formula	C8 H6 F3 N O5 S
Formula weight	285.20
Temperature	100(2) K
Wavelength	1.5418 A
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 5.3555(6) A alpha = 90 deg. b = 12.8070(14) A beta = 96.773(8) deg. c = 16.0563(15) A gamma = 90 deg.
Volume	1093.6(2) A^3
Z, Calculated density	4, 1.732 Mg/m^3
Absorption coefficient	3.248 mm^-1
F(000)	576
Crystal size	0.18 x 0.08 x 0.02 mm
Theta range for data collection	2.7728 to 73.9454 deg.
Limiting indices	-6<=h<=5, -15<=k<=9, -19<=l<=15
Reflections collected / unique	4685 / 2078 [R(int) = 0.0724]
Completeness to theta = 66.60	96.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.63119
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2078 / 0 / 165
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0703, wR2 = 0.1827
R indices (all data)	R1 = 0.0968, wR2 = 0.2202
Largest diff. peak and hole	0.473 and -0.475 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s3767na.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

C(1)	1562(7)	9565(3)	2932(2)	39(1)
C(2)	460(8)	10486(3)	3187(2)	40(1)
C(3)	-1218(8)	10349(3)	3793(3)	44(1)
C(4)	-1693(9)	9385(3)	4114(2)	48(1)
C(5)	-587(9)	8493(3)	3857(3)	53(1)
C(6)	1067(9)	8601(3)	3254(3)	49(1)
C(7)	1699(10)	9698(4)	1159(3)	56(1)
C(8)	-1135(12)	7429(4)	4203(3)	75(2)
F(1)	232(8)	8901(4)	1057(2)	118(2)
F(2)	3169(7)	9704(3)	570(2)	78(1)
F(3)	403(7)	10560(3)	1111(2)	95(1)
N(1)	-2600(8)	11241(3)	4065(2)	56(1)
O(1)	4926(7)	8618(2)	2171(2)	59(1)
O(2)	5177(5)	10544(2)	2245(2)	48(1)
O(3)	952(6)	11392(2)	2840(2)	49(1)
O(4)	-4253(7)	11092(3)	4510(2)	72(1)
O(5)	-2062(8)	12116(3)	3830(3)	77(1)
S(1)	3709(2)	9610(1)	2179(1)	42(1)

Table 3. Bond lengths [A] and angles [deg] for s3767na.

C(1)-C(6)	1.376(6)
C(1)-C(2)	1.401(5)
C(1)-S(1)	1.766(4)
C(2)-O(3)	1.327(4)
C(2)-C(3)	1.411(5)
C(3)-C(4)	1.373(6)
C(3)-N(1)	1.456(5)
C(4)-C(5)	1.372(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.394(5)
C(5)-C(8)	1.513(6)
C(6)-H(6)	0.9500
C(7)-F(1)	1.287(6)
C(7)-F(2)	1.301(5)
C(7)-F(3)	1.301(6)
C(7)-S(1)	1.853(5)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
N(1)-O(4)	1.217(4)
N(1)-O(5)	1.227(5)
O(1)-S(1)	1.429(3)
O(2)-S(1)	1.428(3)
O(3)-H(3)	0.8400
C(6)-C(1)-C(2)	122.6(3)
C(6)-C(1)-S(1)	117.2(3)
C(2)-C(1)-S(1)	120.2(3)
O(3)-C(2)-C(1)	120.1(3)
O(3)-C(2)-C(3)	125.0(3)
C(1)-C(2)-C(3)	114.9(3)
C(4)-C(3)-C(2)	122.1(4)
C(4)-C(3)-N(1)	118.0(4)
C(2)-C(3)-N(1)	119.8(4)
C(5)-C(4)-C(3)	122.0(4)
C(5)-C(4)-H(4)	119.0
C(3)-C(4)-H(4)	119.0
C(4)-C(5)-C(6)	117.3(4)

C(4)-C(5)-C(8)	122.0(4)
C(6)-C(5)-C(8)	120.7(4)
C(1)-C(6)-C(5)	121.1(4)
C(1)-C(6)-H(6)	119.5
C(5)-C(6)-H(6)	119.5
F(1)-C(7)-F(2)	109.0(4)
F(1)-C(7)-F(3)	110.6(5)
F(2)-C(7)-F(3)	108.4(4)
F(1)-C(7)-S(1)	110.3(4)
F(2)-C(7)-S(1)	107.7(4)
F(3)-C(7)-S(1)	110.8(3)
C(5)-C(8)-H(8A)	109.5
C(5)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(5)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(4)-N(1)-O(5)	122.4(4)
O(4)-N(1)-C(3)	119.0(4)
O(5)-N(1)-C(3)	118.6(3)
C(2)-O(3)-H(3)	109.5
O(2)-S(1)-O(1)	119.9(2)
O(2)-S(1)-C(1)	111.94(17)
O(1)-S(1)-C(1)	108.18(18)
O(2)-S(1)-C(7)	105.8(2)
O(1)-S(1)-C(7)	105.3(2)
C(1)-S(1)-C(7)	104.4(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s3767na. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	49(2)	30(2)	41(2)	0(1)	12(2)	-2(2)
C(2)	50(2)	33(2)	39(2)	1(1)	9(2)	-2(2)
C(3)	53(2)	36(2)	46(2)	-3(2)	13(2)	-1(2)
C(4)	68(3)	35(2)	42(2)	-1(2)	17(2)	-5(2)
C(5)	81(3)	31(2)	50(2)	4(2)	22(2)	-8(2)
C(6)	65(3)	35(2)	49(2)	-3(2)	16(2)	1(2)
C(7)	72(3)	52(3)	45(2)	-5(2)	12(2)	-13(2)
C(8)	125(5)	32(3)	77(3)	4(2)	48(3)	-10(3)
F(1)	145(4)	130(4)	75(2)	1(2)	-5(2)	-89(3)
F(2)	98(2)	88(3)	53(2)	-4(1)	29(2)	-4(2)
F(3)	105(3)	112(3)	63(2)	-11(2)	-12(2)	49(2)
N(1)	71(3)	40(2)	61(2)	1(2)	29(2)	6(2)
O(1)	72(2)	31(2)	81(2)	4(1)	36(2)	8(1)
O(2)	50(2)	36(2)	60(2)	5(1)	13(1)	-5(1)
O(3)	68(2)	24(2)	59(2)	3(1)	26(1)	2(1)
O(4)	88(2)	55(2)	81(2)	8(2)	50(2)	9(2)
O(5)	110(3)	32(2)	102(3)	2(2)	62(2)	6(2)
S(1)	50(1)	30(1)	49(1)	2(1)	15(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic

displacement parameters (A^2 x 10^3) for s3767na.

	x	y	z	U(eq)
H(4)	-2823	9334	4526	57
H(6)	1865	8000	3062	59
H(8A)	339	7183	4570	112
H(8B)	-1521	6937	3739	112
H(8C)	-2577	7479	4524	112
H(3)	75	11864	3024	74

Table 6. Torsion angles [deg] for s3767na.

C(6)-C(1)-C(2)-O(3)	-178.2(4)
S(1)-C(1)-C(2)-O(3)	2.5(6)
C(6)-C(1)-C(2)-C(3)	-0.6(6)
S(1)-C(1)-C(2)-C(3)	-179.9(3)
O(3)-C(2)-C(3)-C(4)	178.4(4)
C(1)-C(2)-C(3)-C(4)	0.9(6)
O(3)-C(2)-C(3)-N(1)	1.5(7)
C(1)-C(2)-C(3)-N(1)	-176.0(4)
C(2)-C(3)-C(4)-C(5)	-0.8(7)
N(1)-C(3)-C(4)-C(5)	176.2(4)
C(3)-C(4)-C(5)-C(6)	0.3(7)
C(3)-C(4)-C(5)-C(8)	-179.3(5)
C(2)-C(1)-C(6)-C(5)	0.2(7)
S(1)-C(1)-C(6)-C(5)	179.4(4)
C(4)-C(5)-C(6)-C(1)	0.0(7)
C(8)-C(5)-C(6)-C(1)	179.6(5)
C(4)-C(3)-N(1)-O(4)	-5.7(7)
C(2)-C(3)-N(1)-O(4)	171.4(4)
C(4)-C(3)-N(1)-O(5)	174.8(5)
C(2)-C(3)-N(1)-O(5)	-8.2(7)
C(6)-C(1)-S(1)-O(2)	-145.7(3)
C(2)-C(1)-S(1)-O(2)	33.6(4)
C(6)-C(1)-S(1)-O(1)	-11.5(4)
C(2)-C(1)-S(1)-O(1)	167.8(3)
C(6)-C(1)-S(1)-C(7)	100.3(4)
C(2)-C(1)-S(1)-C(7)	-80.4(4)
F(1)-C(7)-S(1)-O(2)	-177.7(4)
F(2)-C(7)-S(1)-O(2)	63.5(4)
F(3)-C(7)-S(1)-O(2)	-54.9(4)
F(1)-C(7)-S(1)-O(1)	54.4(4)
F(2)-C(7)-S(1)-O(1)	-64.3(4)
F(3)-C(7)-S(1)-O(1)	177.2(3)
F(1)-C(7)-S(1)-C(1)	-59.4(4)
F(2)-C(7)-S(1)-C(1)	-178.2(3)
F(3)-C(7)-S(1)-C(1)	63.4(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for s3767na [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

O(3)-H(3)...O(5)	0.84	1.85	2.569(4)	142.0
O(3)-H(3)...O(1)#1	0.84	2.27	2.889(4)	130.9
O(3)-H(3)...N(1)	0.84	2.46	2.900(4)	113.6

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2