Supplementary Material (ESI)

Metal-free arylations via photochemical activation of the Ar-OSO_2R bond in aryl nonaflates.

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1. General section

NMR spectra were recorded on a 200, 300 and 400 MHz spectrometers. The attributions were made on the basis of ^{1}H and ^{13}C NMR, as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from TMS. UV and fluorescence spectra were recorded on UV Jasco V-550 spectrophotometer and PerkinElmer LS 55 fluorescence spectrometer, respectively. GC-MS analyses were carried out by using a Thermo Scientific DSQII single quadrupole GC/MS system. A Restek Rtx-5MS (30 m × 0.25 mm × 0.25 μm) capillary column was used for analytes separation with helium as carrier gas at 1 mL min^{-1}. The injection in the GC system was performed in split mode and the injector temperature was 250 °C. The GC oven temperature was held at 80 °C for 2 min, increased to 220 °C by a temperature ramp of 10 °C min^{-1} and held for ten min. The transfer line temperature was 250 °C and the ion source temperature 250 °C. Mass spectral analyses were carried out in full scan mode.

The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes in a multilamp reactor fitted with ten 15 W phosphor coated lamps (maximum of emission 310 nm) or 4 Hg lamps, 15W each (emission centered at 254 nm, see Table 1). The reaction course was followed by GC analyses and the products formed were identified and quantified by comparison with authenthic samples. Workup of the photolytes involved concentration in vacuo and chromatographic separation by using silica gel. Solvent of HPLC purity were employed in the photochemical reactions. 4-Methoxyphenol (**2b**), 4-*tert*-butylphenol (**2c**), sesamol (**2d**), 2-methoxyphenol (**2f**), 3-methoxyphenol (**2g**), anisole (**5b**), *tert*-butylbenzene (**5c**), 1,4-dimethoxybenzene (**6b**), 4-fluoro-*tert*-butylbenzene (**9c**) and all of the employed π-bond nucleophiles were commercially available and used as received. 4-*N*,*N*-dimethylaminophenol (**2a**) was synthesized from 4-aminophenol.[S1] 4-*tert*-butylphenyl methyl ether (**6c**)[S2] and *N*-(4-methoxyphenyl)acetamide (**8b**)[S3] were obtained by methylation of the corresponding phenols. *N*-(4-(*tert*-butyl)phenyl)acetamide (**8c**)[S4] was prepared by *N*-acetylation of the corresponding aniline.

Synthesis of Aryl Nonaflates 1a-d. Compounds **1a-d** were prepared from the corresponding phenols by treatment with nonafluorobutanesulfonyl fluoride in the presence of a base as previously reported.[S5] In the case of **1a**, the procedure was slightly modified as detailed below.

Synthesis of 4-(dimethylamino)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (1a). A solution of 4-*N*,*N*-dimethylaminophenol (0.5 g, 3.64 mmol) in THF (20 mL) was slowly added to a suspension of NaH (60% dispersion in Et_2O, 0.24 g, 6 mmol) in THF (15 mL) at 0°C. After 15 min stirring, $C_4F_9SO_2F$ (1.38 mL, 7.68 mmol) was added dropwise and the solution was refluxed for 3 hours. Water (50 mL) was carefully added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with Et_2O (3×50 mL) and the combined organic extracts were washed with NaOH 5% (50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by recrystallization (AcOEt-hexane) to afford 1.02 g of **1a** (white solid, 67% yield, mp = 47-48°C). **1a:** ^{1}H NMR (400 MHz, CD_3COCD_3) δ: 3.00 (s, 6H), 6.80-7.25 (AA'BB', 4H, *J* = 9 Hz); ^{13}C NMR (100 MHz, CD_3COCD_3) δ: 39.5 (CH_3), 109.5-118.7 (m, 4C), 112.4 (CH), 121.6 (CH), 140.3, 150.3; IR (KBr) ν/cm^{-1} 2924, 1518, 1424, 1205, 1144, 893; MS (m/z) 419 (M^+, 5), 136 (100). Anal. Calcd for $C_{12}H_{10}F_9NO_3S$: C, 34.38; H, 2.40; N, 3.34. Found: C, 34.4; H, 2.4; N, 3.3.

1b: MS (m/z) 406 (M^+, 8), 123 (100), 95 (20). Spectroscopic data of **1b** were in accordance with the literature.[S5] Anal. Calcd for $C_{11}H_7F_9O_4S$: C, 32.52; H, 1.74. Found: C, 32.5; H, 1.7.

1c: MS (m/z) 432 (M^+, 12), 417 (100), 325 (15), 134 (17), 91 (12). Spectroscopic data of **1c** were in accordance with the literature.[S5] Anal. Calcd for $C_{14}H_{13}F_9O_3S$: C, 38.90; H, 3.03. Found: C, 38.9; H, 3.0.

Synthesis of benzo[d][1,3]dioxol-5-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (1d). 1d: Obtained in 51% yield, after purification by column chromatography (eluant: neat cyclohexane). White solid, mp =41-42°C. **1d:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.40 (s, 2H), 7.10-7.20 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 102.3 (CH_2), 103.3 (CH), 108.1 (CH), 109.4-118.7 (m, 4C), 114.4

(CH), 143.6, 147.3, 148.4. IR (KBr) ν/cm^{-1} 2924, 1507, 1426, 1247, 1193, 942, 870; MS (m/z) 420 (M^+, 11), 137 (100), 107 (32). Anal. Calcd for $C_{11}H_5F_9O_5S$: C, 31.44; H, 1.20. Found: C, 31.4; H, 1.2.

Synthesis of (4-hydroxyphenyl) 1,1,2,2,3,3,4,4,4-nonakis(fluoranyl)butane-1-sulfonate (1e). The title compound was prepared by treating **1b** with BBr_3 following a procedure reported for the synthesis of 3-trimethylsilyl-4-chloro-phenol.[S6] BBr_3 (1M in CH_2Cl_2, 0.98 mL, 0.98 mmoli) was added dropwise to a solution of **1b** (400 mg, 0.98 mmol) in CH_2Cl_2 at -78 °C. After 10 minutes the cooling bath was removed and the solution was stirred overnight. The reaction mixture was poured in 20 mL of ice and water and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2×20 mL) and the combined organic extracts were washed with water (2×20 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography by using silica gel (from neat cyclohexane to cyclohexane:ethyl acetate 95:5 as the eluant) to afford 290 mg of **1e** (white solid, 75% yield, mp = 53-54°C). **1e:** ^{1}H NMR (200 MHz, CD_3COCD_3) δ: 6.95-7.30 (AA'BB' system, 4H, *J* = 9 Hz), 8.90 (s, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ: 108.2-120.1 (m, 4C), 117.8 (CH), 123.8 (CH), 143.8, 158.9; IR (KBr) ν/cm^{-1} 3272, 2924, 1506, 1459, 1199, 1142, 893. Anal. Calcd for $C_{10}H_5F_9O_4S$: C, 30.62; H, 1.28. Found: C, 30.6; H, 1.3.

2. Photophysical parameters measured for 1a-c.

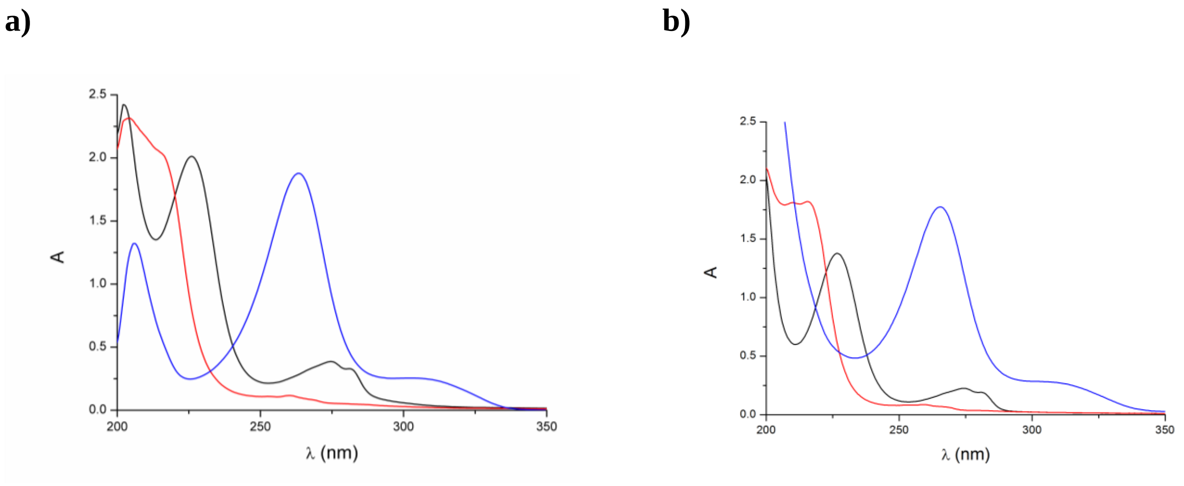


Figure S1. Absorption spectra of a 10^{-4} M solution **1a** (blue), **1b** (black) and **1c** (red) in a) MeOH and b) MeCN.

Table S1 Photophysical parameters measured for aryl nonaflates **1a-c** in MeOH.

ArONf	λ_{max} (nm), ε (M^{-1} cm^{-1})	λ_{em} (nm), $\Phi_F \times 10^3$
1a	308, 2494 264, 18786 206, 13181	377, 24 (343, 18)[a]
1b	274, 3852 226, 20124 203, 24100	302, 1.0 (302, 2.3)[a]
1c	261, 1148 215, 204604	306, 6.0 (309, 9.0)[a]

[a] Fluorescence quantum yield (Φ_F) measured in cyclohexane.

3. Photochemical irradiations on aryl nonaflates 1a-e.

General Procedure for the Photochemical Irradiations of 1a-c in neat solvent. A 0.05 M solution of aryl nonaflates **1a-c** was irradiated in the chosen solvent (MeCN, MeCN/W 5/1 $_{v/v}$, MeOH, TFE) and, when required, in the presence of a base (Cs_2CO_3 0.03M) and acetone 10%$_{v/v}$. Product distribution was analyzed by GC analysis. The amounts of **2a-c**, **5b-c** , **6b-c**, **7b-c**, **8b-c**, **9c** have been determined on the basis of calibration curves by comparison with either commercial standards or synthesized compounds. Products **3a-c** and **4a** were identified by GC-MS analyses (see Table S3). Preparative experiments were carried out only in TFE.

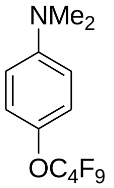
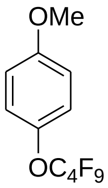
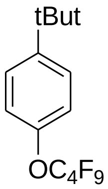
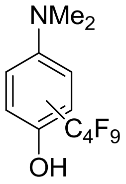
Quantum yields were measured at 254 nm (1 Hg lamp 15W) for **1b-1c** and at 310 nm (one phosphor coated lamp, 15W) for **1a**.

Table S2. Quantum yields of disappearance (Φ_R) for **1a-c**

ArONf	MeCN	MeOH
1a	0.63	0.78
1b	0.38	0.62
1c	0.39 (0.21)[a]	0.39

[a] In MeCN-H_2O 5-1 mixture.

Table S3. MS spectra of the observed photoproducts **3a-c** and **4a.**

Compound	Mass spectra (m/z)
 **3a**	355 (M^+, 33), 136 (100)
 **3b**	342 (M^+, 46), 123 (100), 95 (26), 69 (20)
 **3c**	368 (M^+, 11), 353 (100), 325 (44), 133 (18).
 **4a**	354 (M^+,100), 186 (78), 153 (15), 135 (13) .

Irradiation of 1b in neat TFE. A solution of **1b** (305 mg, 0.75 mmol), 147 mg (0.03 M, 0.45 mmol) of Cs_2CO_3, 1.5 mL of acetone ($10\%_{v/v}$) in 15 mL of TFE was irradiated for 24 h. (91 % consumption of **1b**). Purification by column chromatography (silica gel; eluant: neat hexane) gave 25 mg of **7b** (oil, 18% yield based on the consumption of **1b**). The amount of **5b** was determined on the basis of a calibration curve. Spectroscopic data of **7b** were in accordance with the literature.[S7] Anal. Calcd for $C_9H_9F_3O_2$: C, 52.43; H, 4.40. Found: C, 52.4; H, 4.3.

Irradiation of 1c in neat TFE. A solution of **1c** (324 mg, 0.75 mmol), 147 mg (0.03 M, 0.45 mmol) of Cs_2CO_3, 1.5 mL of acetone ($10\%_{v/v}$) in 15 mL of TFE was irradiated for 24 h. Purification by column chromatography (aluminium oxide neutral; eluant: neat hexane) gave 61 mg of **7c** (oil, 35% yield). The amounts of **5c** and **9c** were determined on the basis of calibration curves.

7c: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30 (s, 9H), 4.35-4.40 (q, 2H, *J* = 8 Hz), 6.90-7.40 (AA'BB' system, 4H, *J* = 9Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.3 (CH_3), 34.1, 66.1 (q, CH_2, *J* = 30 Hz), 114.4 (CH), 124.7 (q, CF_3, *J* = 280 Hz), 126.4 (CH), 145.3, 155.1; IR (KBr) ν/cm^{-1} 2964, 1514, 1239, 1164, 1078, 976, 829. Anal. Calcd for $C_{12}H_{15}F_3O$: C, 62.06; H, 6.51. Found: C, 62.1; H, 6.5.

General Procedure for the Photochemical Irradiations of 1b-e in the presence of π bond nucleophiles.

A solution of **1b-e** (1.5 mmol, 0.05M), the π nucleophile (0.5M except where otherwise indicated), acetone (10%$_{v/v}$), a base (Cs_2CO_3 0.03M or Et_3N 0.05M) in TFE (30 mL) was nitrogen purged in quartz tubes and irradiated in a multilamp reactor fitted with ten 15 W phosphor coated lamps (maximum of emission 310 nm). The reaction course was followed for GC analysis. The amounts of **2b-d**, **5b-c**, **7b-c, 9c** were determined on the basis of calibration curves. The photolyzed solutions were concentrated in vacuo and purified by silica gel column cromatography (eluant: cyclohexane:ethyl acetate mixture or hexane).

Synthesis of 4-methoxy-2',4',6'-trimethylbiphenyl (10b). From 609 mg (0.05 M, 1.5 mmol) of **1b**, 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 0.83 mL (0.2 M, 6 mmol) of mesitylene and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours. Purification by column chromatography (eluant: from neat cyclohexane to cyclohexane:ethyl acetate 95:5) gave 238 mg of **10b** (colorless solid**,** 70% yield, mp = 67-68 °C , lit.[S8] = 73-74°C). Spectroscopic data of **10b** were in accordance with literature data.[S9] Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.9; H, 8.0.

Synthesis of 4-methoxy-1-phenylbenzene (11b). From 609 mg (0.05 M, 1.5 mmol) of **1b,** 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3 , 1.34 mL (0.5 M, 15 mmol) of benzene and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours (91% consumption of **1b**). Purification by column chromatography (eluant: from neat cyclohexane to cyclohexane:ethyl acetate 95:5) gave 108 mg of **11b** (colorless solid**,** 43% yield based on the consumption of **1b**, mp =81-83 °C, lit.[S10] = 90-

90.5°C). Spectroscopic data of **11b** were in accordance with the literature.[S11] Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.8; H, 6.6.

Synthesis of 5-[(4-methoxyphenyl)methyl]-tetrahydrofuran-2-one (12b). From 609 mg (0.05 M, 1.5 mmol) of **1b**, 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 1.53 mL (0.5 M, 15 mmol) of 4-pentenoic acid and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours (91% consumption of **1b**). Purification by column chromatography (eluant: from cyclohexane:ethyl acetate 95:5 to cyclohexane:ethyl acetate 7:3) gave 174 mg of **12b** (oil**,** 62 % yield based on the consumption of **1b**). Spectroscopic data of **12b** were in accordance with the literature.[S12] Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.6; H, 6.6.

Synthesis of 1-methoxy-4-(2-propenyl)-benzene (13b). From 609 mg (0.05 M, 1.5 mmol) of **1b**, 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 2.38 mL (0.5 M, 15 mmol) of allyltrimethylsilane (ATMS) and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours. Purification by column chromatography (eluant: from neat cyclohexane to cyclohexane:ethyl acetate 98:2) gave 127 mg of **13b** (oil**,** 57 % yield). Spectroscopic data of **13b** were in accordance with the literature.[S13] Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.1; H, 8.3.

Synthesis of 1-butyl-2-(4-methoxyphenyl)acetylene (14b). From 609 mg (0.05 M, 1.5 mmol) of **1b**, 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 1.72 mL (0.5 M, 15 mmol) of 1-hexyne and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours (76% consumption of **1b**). Purification by column chromatography (eluant: neat hexane) gave 79 mg of **14b** (oil**,** 37 % yield based on the consumption of **1b**). Spectroscopic data of **14b** were in accordance with the literature.[S14] Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.9; H, 8.6.

Synthesis of 4'-tert-butyl-2,4,6-trimethylbiphenyl (10c). From 648 mg (0.05 M, 1.5 mmol) of **1c**, 0.293 g (0.03 M, 0.9 mmol) of $Cs_2CO_{3,}$ 2.09 mL (0.5M, 15 mmol) of mesitylene and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours. Purification by column chromatography (eluant: from neat hexane) gave 192 mg of **10c** (colorless solid**,** 51% yield, mp =106-107 °C, lit.[S15] = 108-110°C). Spectroscopic data of **10c** were in accordance with the literature.[S15] Anal. Calcd for $C_{19}H_{24}$:

C, 90.42; H, 9.58. Found: C, 90.4; H, 9.6.

Synthesis of 4-phenyl-1-tert-butylbenzene (11c). From 648 mg (0.05 M, 1.5 mmol) of **1c**, 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 1.34 mL (0.5 M, 15 mmol) of benzene and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours (83% consumption of **1c**). Purification by column chromatography (eluant: from neat hexane) gave 186 mg of **11c** (colourless solid**,** 71% yield based on the consumption of **1c**, mp =46-47 °C, lit.[S15] = 45-47° C). Spectroscopic data of **11c** were in accordance with the literature.[S15] Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.4; H, 8.6.

Synthesis of 5-(4-*tert*-butylbenzyl)-dihydrofuran-2(*3H*)-one (12c). From 648 mg (0.05 M, 1.5 mmol) of **1c**, 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 1.53 mL (0.5 M, 15 mmol) of 4-pentenoic acid and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours (87% consumption of **1c**). Purification by column chromatography (eluant: hexane:ethyl acetate 8:2) gave 84 mg of **12c** (oil**,** 28% yield based on the consumption of **1c**). Spectroscopic data of **12c** were in accordance with the literature.[S15] Anal. Calcd. $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found C, 77.6; H, 8.9.

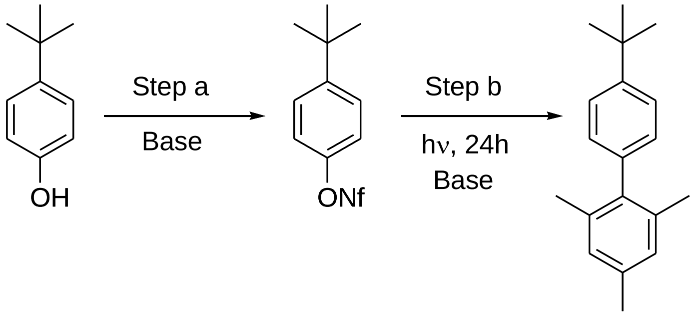
Synthesis of 5-mesitylbenzo[*d*][1,3]dioxole (10d). From 630 mg (0.05 M, 1.5 mmol) of **1d**, 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 2.09 mL (0.5 M, 15 mmol) of mesitylene and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours. Purification by column chromatography (eluant:neat cyclohexane to cyclohexane:ethyl acetate 95:5) gave 176 mg of **10d** (oil, 49% yield). Spectroscopic data of **10d** were in accordance with the literature.[S16] IR (neat) ν/cm^{-1} 2920, 1611, 1476, 1218, 1041, 939, 814. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.1; H, 6.7.

Synthesis of 2',4',6'-trimethylbiphenyl-4-ol (10e). From 588 mg (0.05 M, 1.5 mmol) of **1e**, 0.2 mL (0.05 M, 1.5 mmol) of Et_3N, 2.09 mL (0.5 M, 15 mmol) of mesitylene and 3 mL of acetone in 30 mL of TFE, irradiated for 24 hours. Purification by column chromatography (eluant: neat cyclohexane to cyclohexane:ethyl acetate 95:5) gave 197 mg of **10e** (white solid**,** 62% yield, mp= 139-140°C, lit.[S17] =148°C). IR (KBr) ν/cm^{-1} 3504, 2923, 1610, 1259, 1179, 836. Spectroscopic data of **10e** were in accordance with the literature.[S16] Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.9; H, 7.6.

4. Preparative irradiation with aryl nonaflates generated in situ.

Phenyl nonaflates were prepared in situ by adapting a procedure reported in the literature.[S18] We have chosen the one-pot photoarylation of mesitylene starting from nonaflate **1c** as a model reaction (Table S4).

Table S4. Protocol's development of the one-pot photoarylation.



2c **1c** **10c**

Entry	Step a (Conditions)	1c (% yield)	Step b (Conditions)	10c (% yield)[a]
1	**2c** 0.05M, TFE, Cs_2CO_3 0.03M	/	/	/
2	**2c** 0.05M, TFE, DBU 0.05M	/	/	/
3	**2c** 0.05M, MeCN Cs_2CO_3 0.05M	100%	Acetone 10%, Mesitylene 0.5M	32[b]
4	**2c** 0.05M, MeCN DBU 0.05M	100%	MeCN/TFE (1/9), DBU 0.03M, Acetone 10%, Mesitylene 0.5M	31
5	**2c** 0.05M, MeCN Cs_2CO_3 0.05M	100%	MeCN/TFE (2/8), Cs_2CO_3 0.03M, Acetone 10%, Mesitylene 0.5M	33
6	**2c** 0.05M, MeCN Cs_2CO_3 0.05M	100%	MeCN/TFE (1/9), Cs_2CO_3 0.03M, Acetone 10%, Mesitylene 0.5M	55[c]

[a] Yields determined by gas cromatography (GC) analysis. A complete consumption of **1c** was observed in each case except in entry 3 (93% consumption); [b] 20% of **2c** was also obtained. [c] Isolated yield.

The initial attempt was to perform steps *a* and *b* in TFE (where phenylation occurred efficiently) but unfortunately, no formation of ArONf occurred either by using DBU or Cs_2CO_3 as the base (entries 1,2). We decided to use MeCN as the solvent for the first step as reported in the literature.[S18] In the presence of Cs_2CO_3, **2c** was quantitatively converted to **1c** but the ensued irradiation gave **10c** in a low yield. The use of MeCN in the formation of ArONf, and the addition of TFE for the arylation step was found convenient albeit the ratio MeCN/TFE affected the arylation yields. Accordingly, the best results were obtained in MeCN/TFE 1/9 mixture, and a further increase of the amount of MeCN reduced considerably the yield of **10c**. The performance of the arylation also decreased when organic bases such as DBU were used instead of Cs_2CO_3. The conditions used in entry 6 (Table S4) were the best except for the reaction of **1b** with mesitylene where the arylation efficiency was maximum in neat MeCN. Thus, 270-350 μL (1.5-1.95 mmol see below) of $C_4F_9SO_2F$ were added to a solution of phenol (0.05 M, 1.5 mmol) and Cs_2CO_3 (1.5 mmol except where indicated) in MeCN (2.7 mL) placed in a quarz tube. After 15 min stirring, GC analysis revealed the complete formation of the corresponding nonaflates. TFE (24 mL), acetone (3 mL) and Cs_2CO_3 (0.03M, 0.9 mmol) were then added to the reaction mixture. After purging with nitrogen, π bond nucleophiles (0.5 M, 15 mmol) were injected into the quarz tube and the solution was irradiated at 310 nm. The reaction course was followed by GC analysis. The photolyzed solution was then evaporated and the resulting residue purified by column chromatography (silica gel; cyclohexane/ethyl acetate or hexane as eluant).

Synthesis of 4-methoxy-2',4',6'-trimethylbiphenyl (10b). From 186 mg (0.05 M, 1.5 mmol) of **2b**, 488 mg (1.5 mmol) of Cs_2CO_3, 270 μL (1.5 mmol) of $C_4F_9SO_2F$, TFE (24 mL), acetone (3 mL), 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 2.09 mL (0.5 M, 15 mmol) of mesitylene irradiated for 24 hours. Purification by column chromatography (eluant: from neat cyclohexane to cyclohexane:ethyl acetate 95:5) gave 173 mg of **10b** (51% yield).

Synthesis of 4-methoxy-1-phenylbenzene (11b). From 186 mg (0.05 M, 1.5 mmol) of **2b**, 488 mg (1.5 mmol) of Cs_2CO_3, 270 μL (1.5 mmol) of $C_4F_9SO_2F$, TFE (24 mL), acetone (3 mL), 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 1.34 mL (0.5 M, 15 mmol) of benzene irradiated for 24 hours (69% consumption of **1b**). Purification by column chromatography (eluant: from neat cyclohexane to cyclohexane:ethyl acetate 95:5) gave 38 mg of **11b** (20% yield based on the consumption of **1b**).

Synthesis of 5-[(4-methoxyphenyl)methyl]-tetrahydrofuran-2-one (12b). From 186 mg (0.05 M, 1.5 mmol) of **2b**, 488 mg (1.5 mmol) of Cs_2CO_3, 270 μL (1.5 mmol) of $C_4F_9SO_2F$, TFE (24 mL), acetone (3 mL), 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 1.53 mL (0.5 M, 15 mmol) of 4-pentenoic acid irradiated for 24 hours (75% consumption of **1b**). Purification by column chromatography (eluant: from cyclohexane:ethyl acetate 95:5 to cyclohexane:ethyl acetate 7:3) gave 97 mg of **12b** (oil**,** 42 % yield based on the consumption of **1b**).

Synthesis of 1-methoxy-4-(2-propenyl)-benzene (13b). From 186 mg (0.05 M, 1.5 mmol) of **2b**, 488 mg (1.5 mmol) of Cs_2CO_3, 270 μL (1.5 mmol) of $C_4F_9SO_2F$, TFE (24 mL), acetone (3 mL), 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3, 2.38 mL (0.5 M, 15 mmol) of allyltrimethylsilane irradiated for 24 hours (91% consumption of **1b**). Purification by column chromatography (eluant: from neat cyclohexane to cyclohexane:ethyl acetate 98:2) gave 125 mg of **13b** (62 % yield based on the consumption of **1b**).

Synthesis of 4'-*tert*-butyl-2,4,6-trimethylbiphenyl (10c). From 225 mg (0.05 M, 1.5 mmol) of **2c**, 488 mg (1.5 mmol) of Cs_2CO_3, 323 μL (1.8 mmol) of $C_4F_9SO_2F$, TFE (24 mL), acetone (3 mL), 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3 and 2.09 mL (0.5 M, 15 mmol) of mesitylene irradiated for 24 hours. Purification by column chromatography (eluant: from neat hexane) gave 208 mg of **10c** (55% yield).

Synthesis of 5-(4-*tert*-butylbenzyl)-dihydrofuran-2(*3H*)-one (12c). From 225 mg (0.05 M, 1.5 mmol) of **2c**, 488 mg (1.5 mmol) of Cs_2CO_3, 323 μL (1.8 mmol) of $C_4F_9SO_2F$, TFE (24 mL), acetone (3 mL), 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3 and 1.53 mL (0.5 M, 15 mmol) of 4-

pentenoic acid irradiated for 24 hours (82% consumption of **1c**). Purification by column chromatography (eluant: from neat hexane) gave 69 mg of **12c** (white solid**,** 24% yield based on the consumption of **1c**)

Synthesis of 5-mesitylbenzo[*d*][1,3]dioxole (10d). From 207 mg (0.05 M, 1.5 mmol) of **2d**, 635 mg (1.95 mmol) of Cs_2CO_3, 350 μL (1.95 mmol) of $C_4F_9SO_2F$, TFE (24 mL), acetone (3 mL), 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3 and 2.09 mL (0.5 M, 15 mmol) of mesitylene irradiated for 24 hours. Purification by column chromatography (eluant: neat cyclohexane to cyclohexane:ethyl acetate 95:5) gave 119 mg of **10d** (oil, 33% yield).

Synthesis of 2-methoxy-2',4',6'-trimethyl-biphenyl (10f). From 186 mg (0.5 M, 1.5 mmol) of 2-methoxyphenol, 635 mg (1.95 mmol) of Cs_2CO_3, 350 μL (1.95 mmol) of $C_4F_9SO_2F$, TFE (24 mL), acetone (3 mL), 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3 and 2.09 mL (0.5 M, 15 mmol) of mesitylene irradiated for 24 hours. Purification by column chromatography (eluant: neat cyclohexane to cyclohexane:ethyl acetate 95:5) gave 220 mg of **10f** (white solid**,** 65% yield, mp=55-56°C, lit.[S19] =59°C). Spectroscopic data of **10f** were in accordance with the literature.[S20] Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.9; H, 8.0.

Synthesis of 3-methoxy-2',4',6'-trimethyl-biphenyl (10g). From 186 mg (0.5 M, 1.5 mmol) of 3-methoxyphenol, 488 mg (1.5 mmol) of Cs_2CO_3, 270 μL (1.5 mmol) of $C_4F_9SO_2F$, TFE (24 mL), acetone (3 mL), 0.293 g (0.03 M, 0.9 mmol) of Cs_2CO_3 and 2.09 mL (0.5 M, 15 mmol) of mesitylene irradiated for 24 hours. Purification by column chromatography (eluant:neat cyclohexane to cyclohexane:ethyl acetate 95:5) gave 193 mg of **10g** (oil**,** 57% yield). Spectroscopic data of **10g** were in accordance with the literature.[S20] Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.9; H, 8.0.

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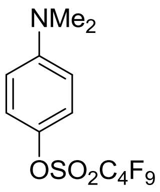
6. ^{1}H NMR and ^{13}C NMR for compounds 1a-e, 6c, 7c, 8b,c, 10b,d,e and 11b



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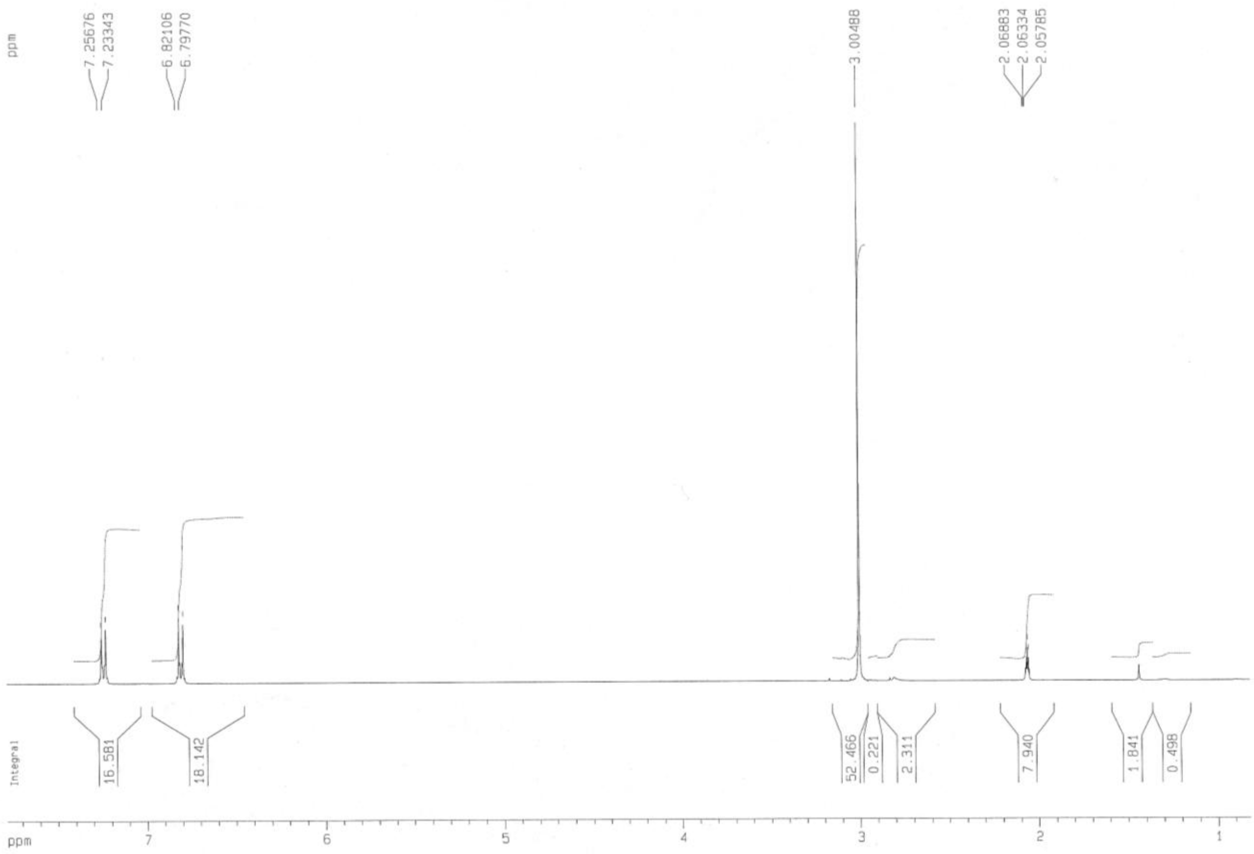

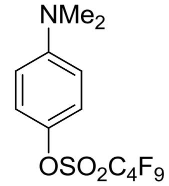

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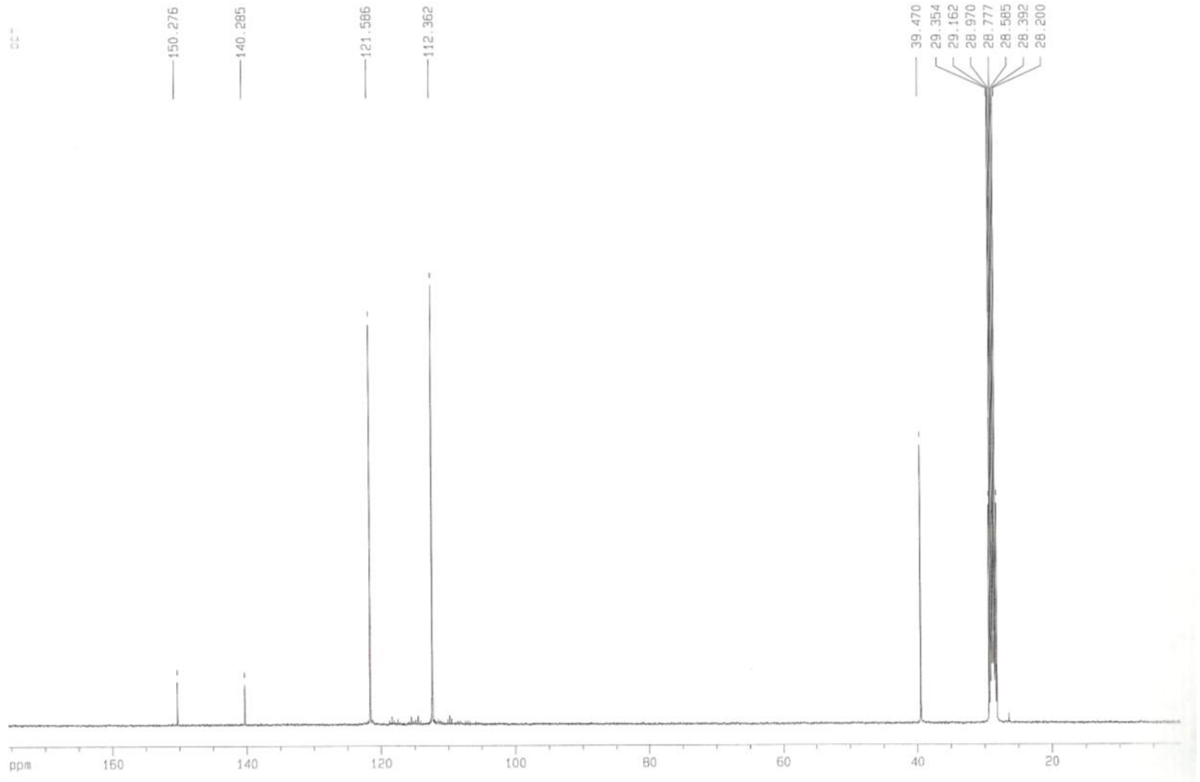
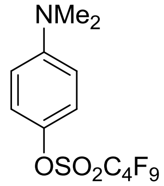
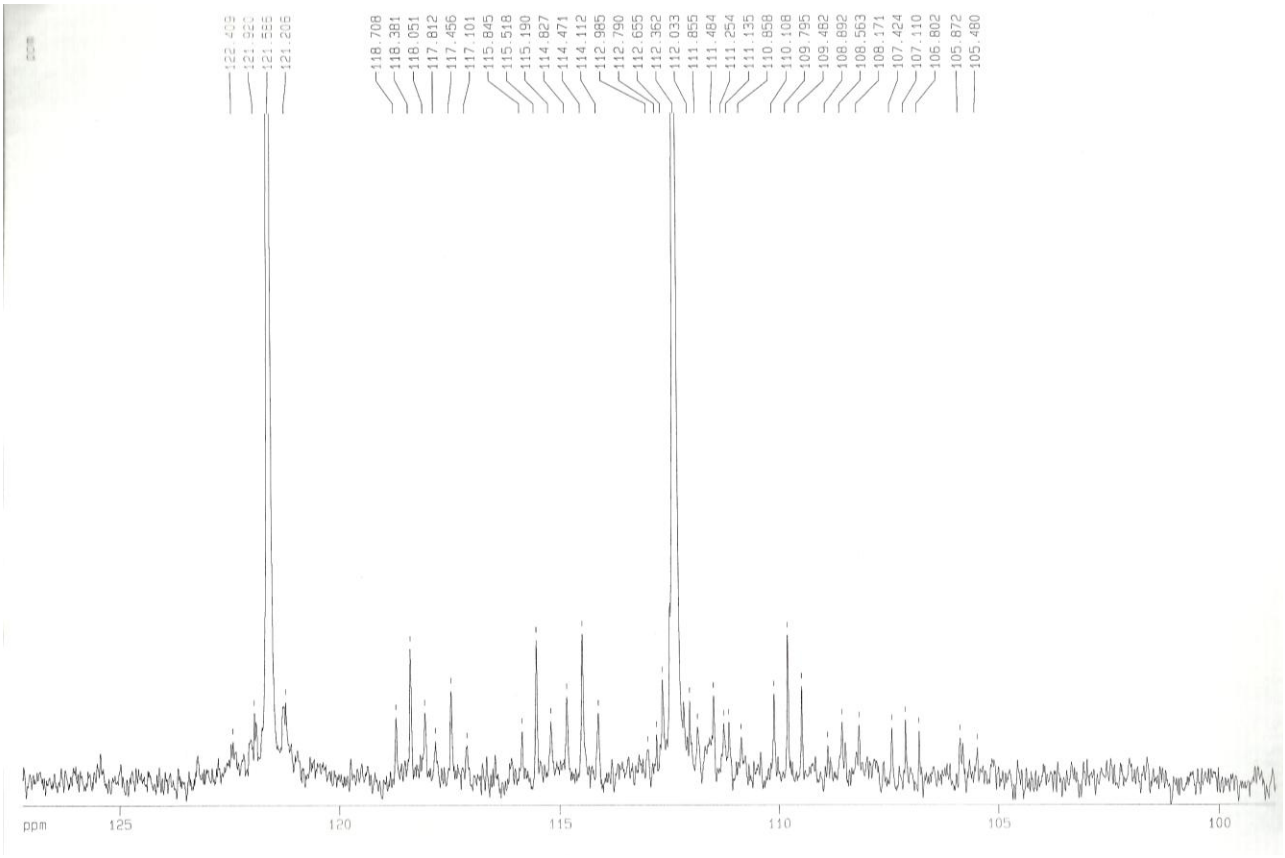
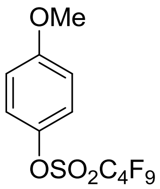




1a ^{13}C NMR, CD_3COCD_3 (enlargement 100-130 ppm)





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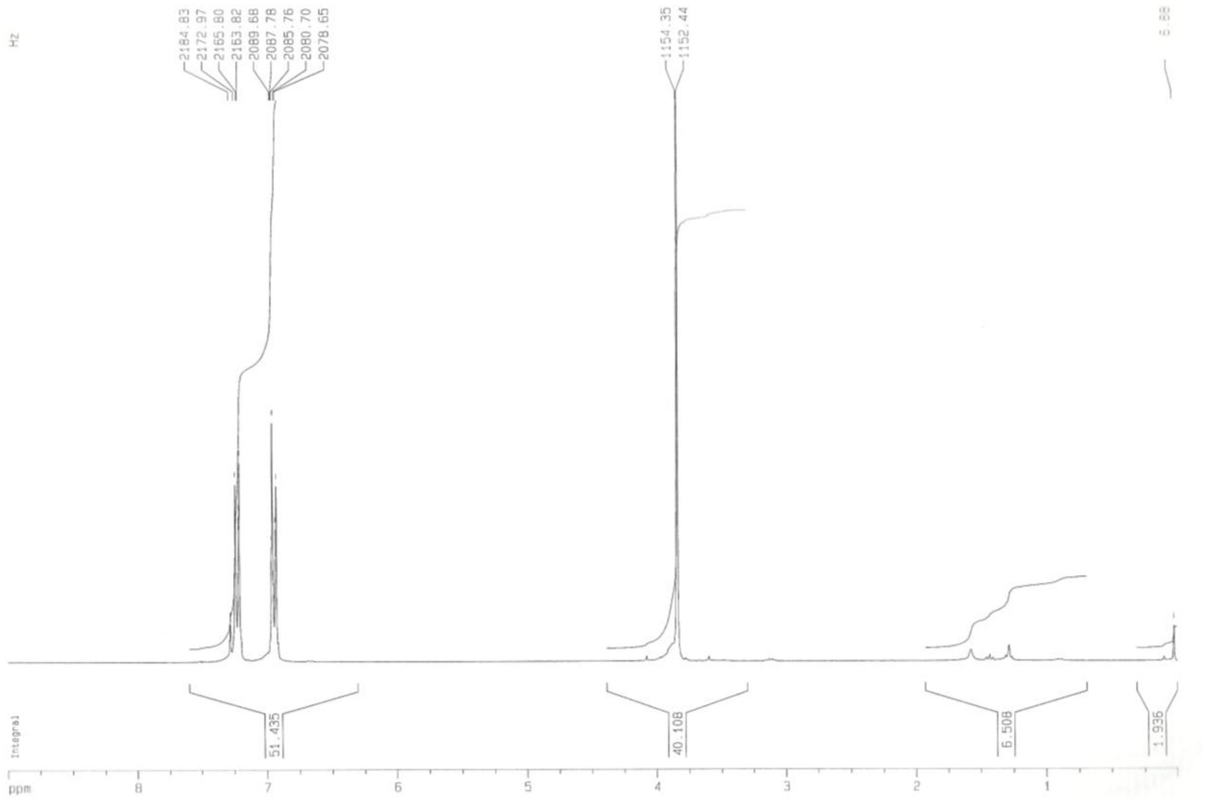

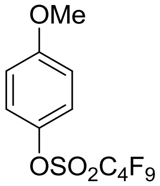

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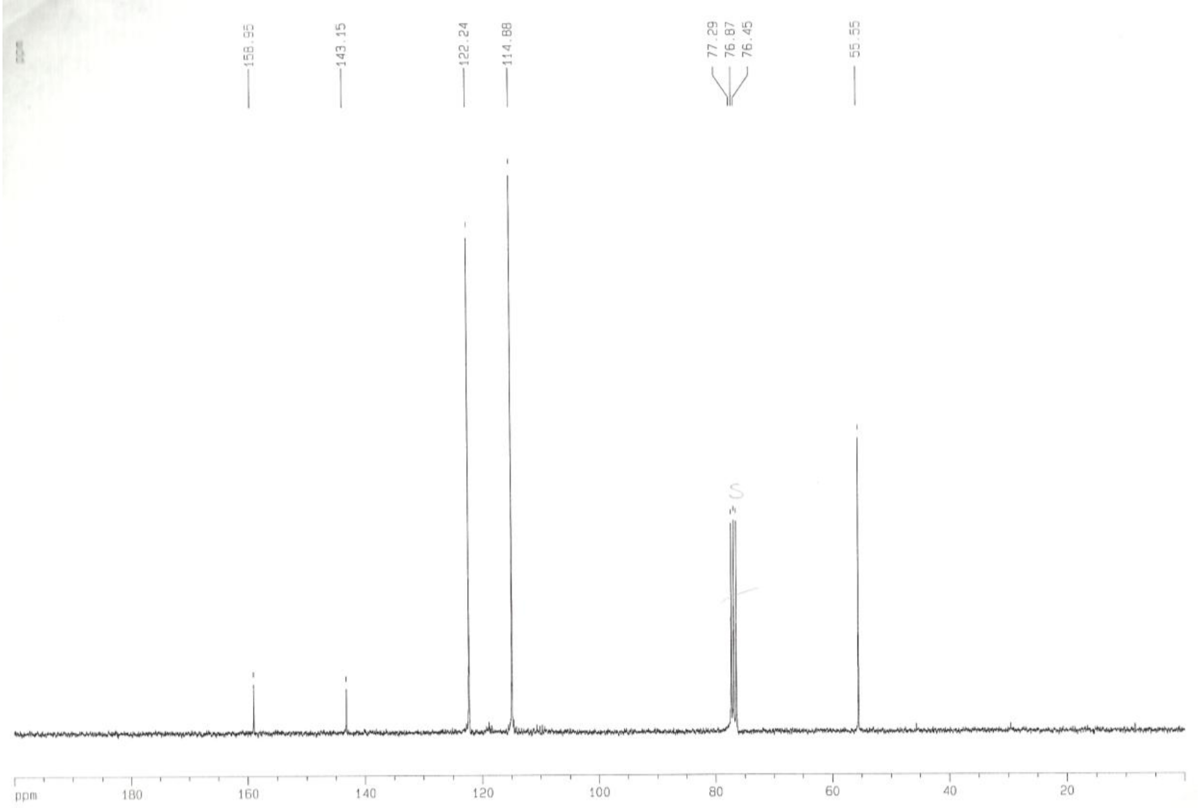

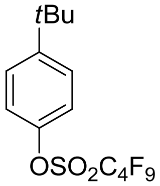

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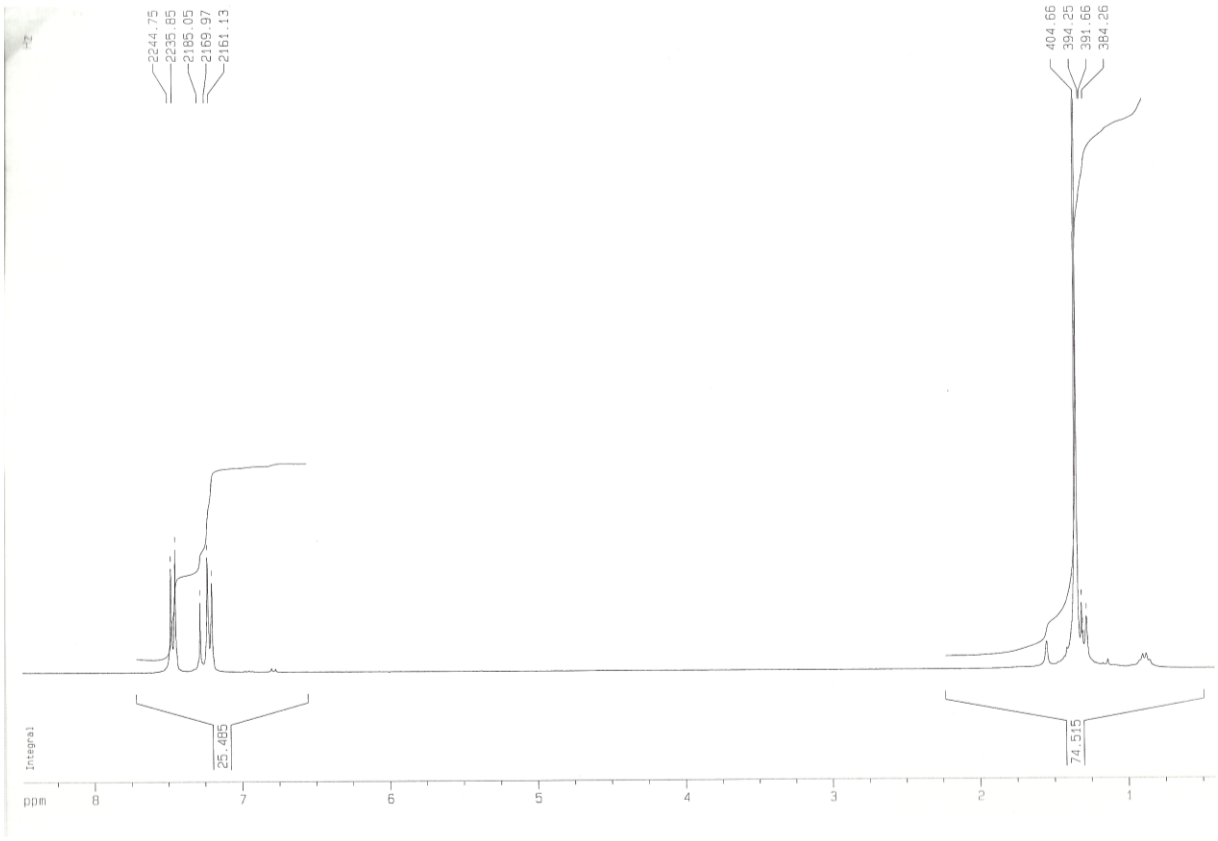

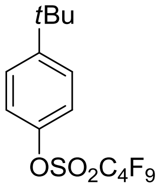

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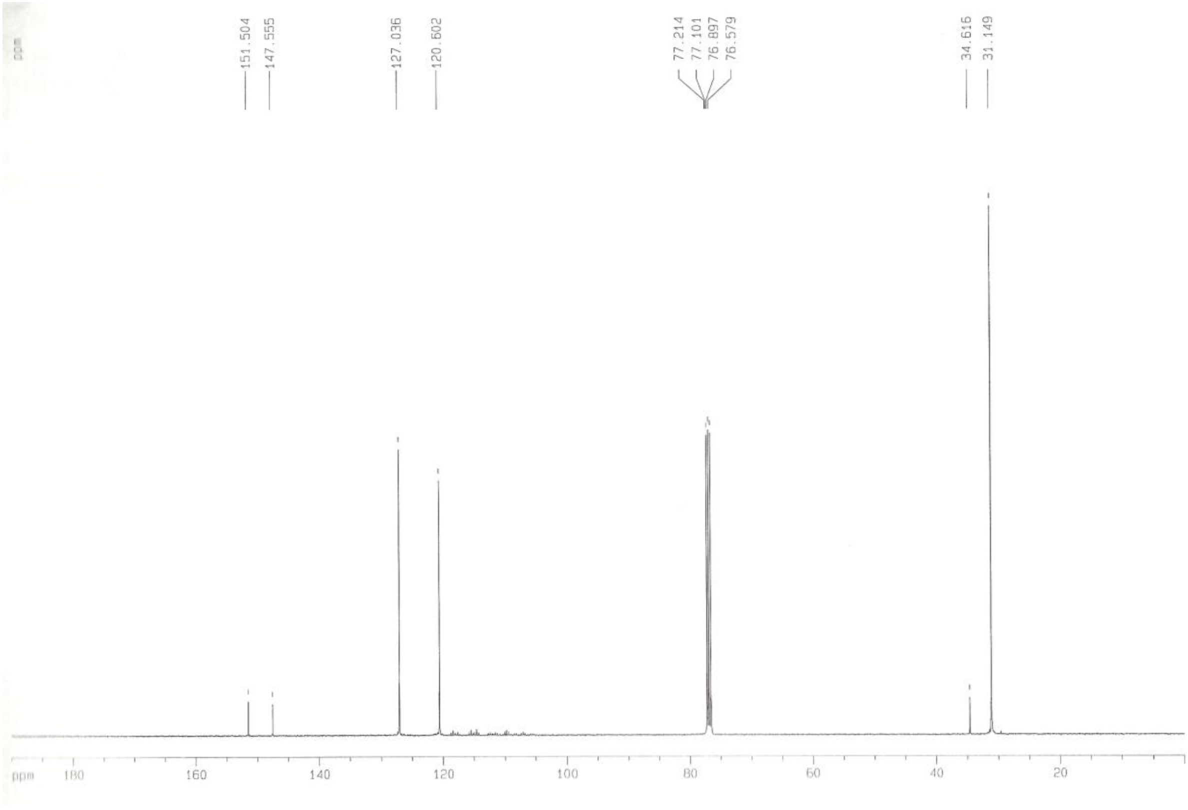
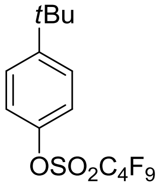
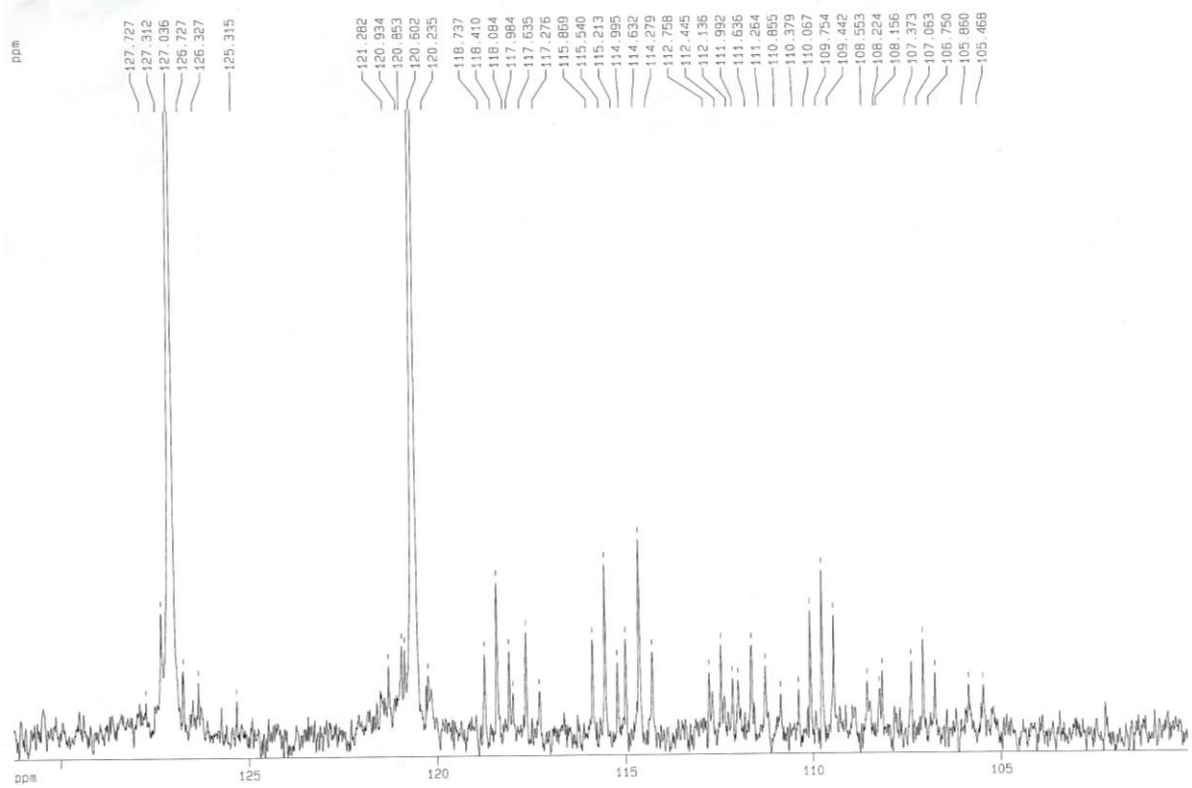
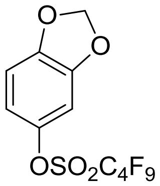




1c, ^{13}C NMR, $CDCl_3$ (enlargement 100-130 ppm)





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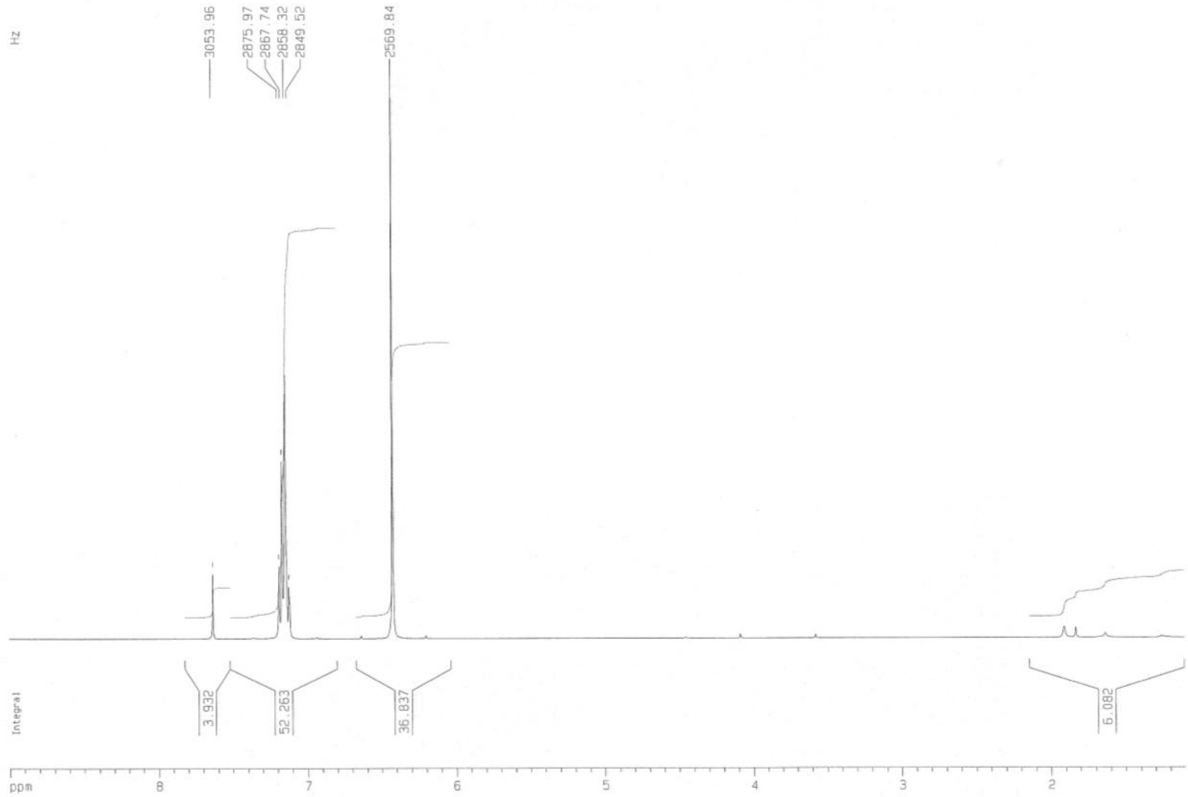

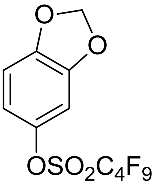

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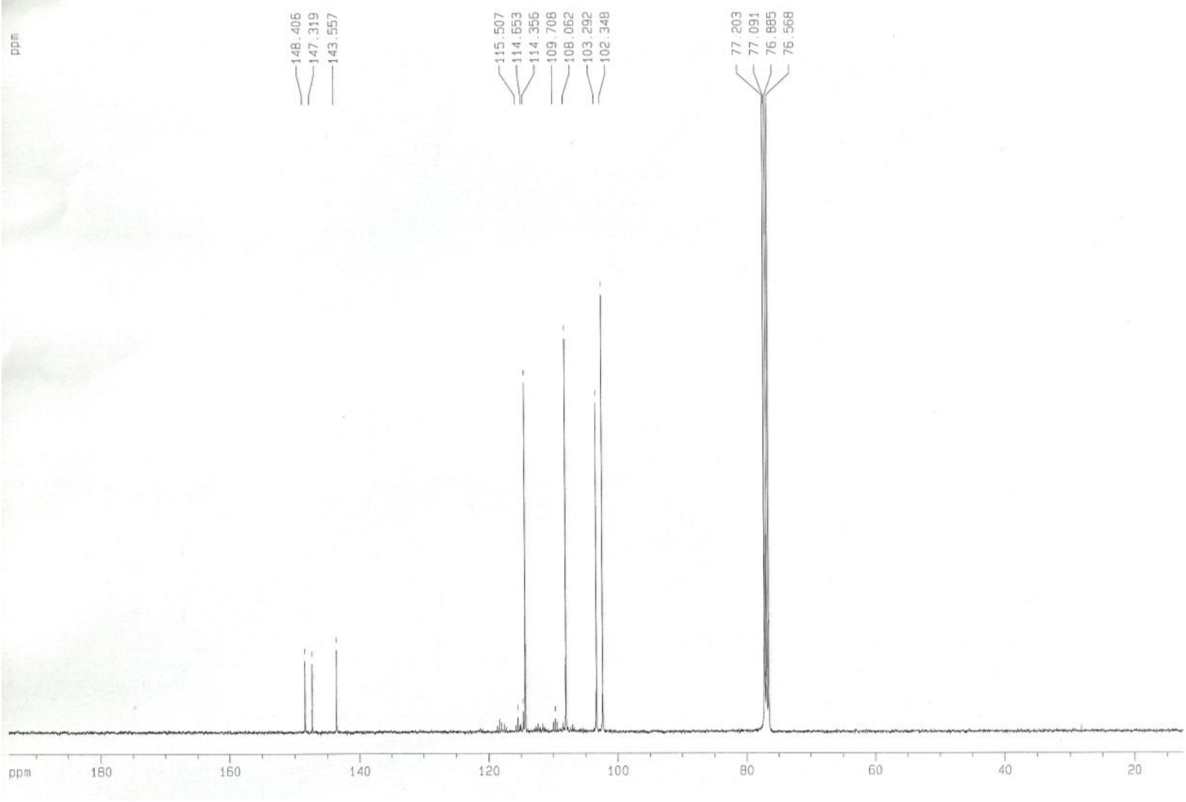
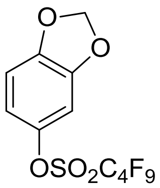
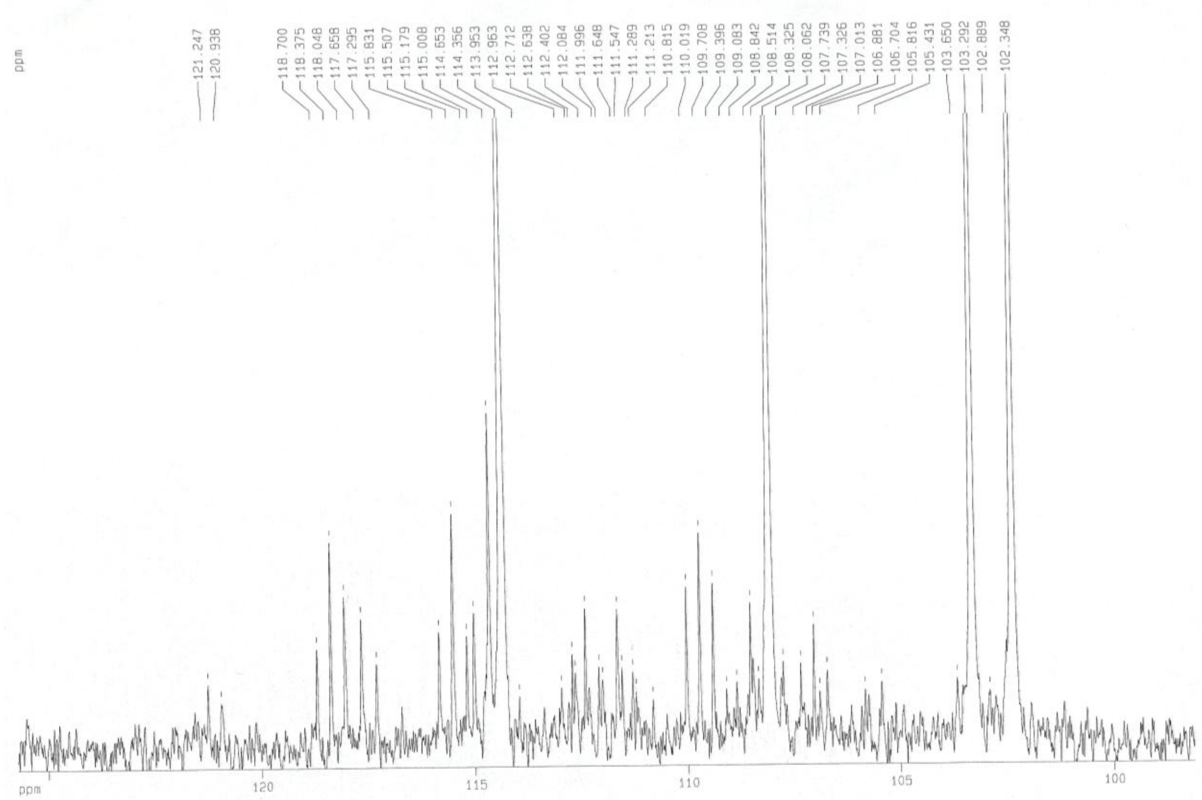
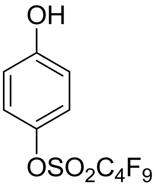




1d, ^{13}C NMR, $CDCl_3$ (enlargement 100-130 ppm)





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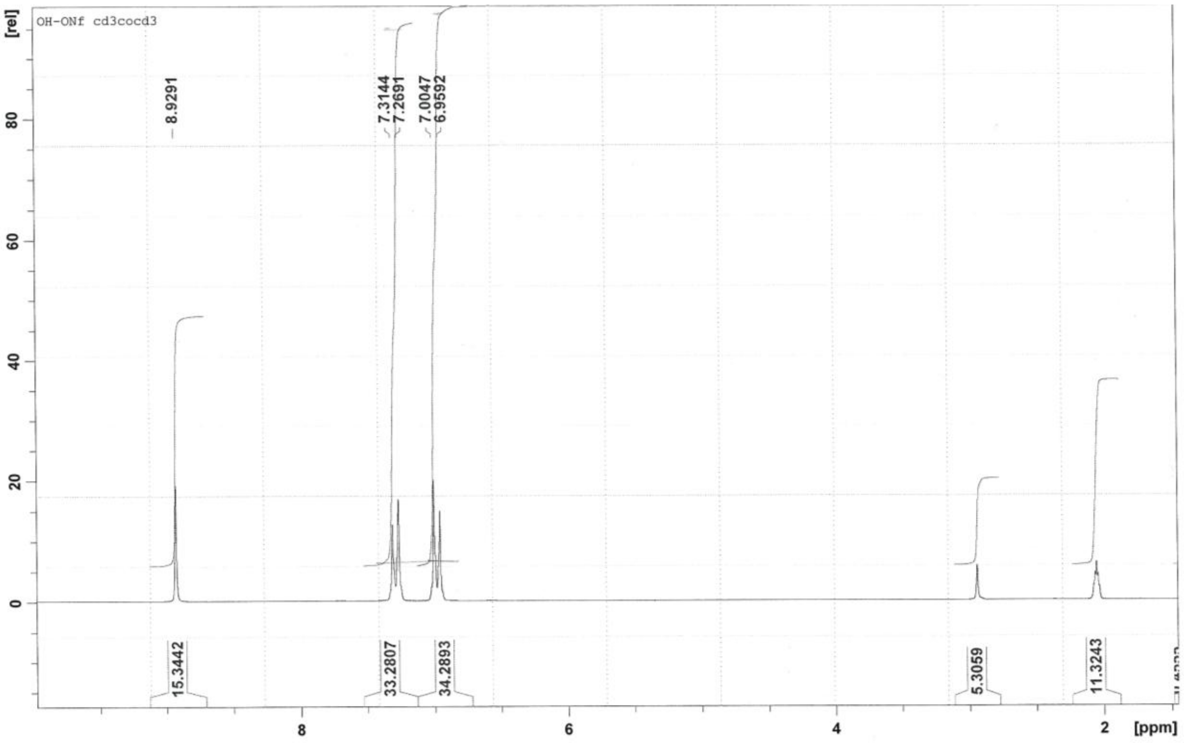

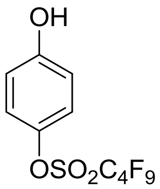

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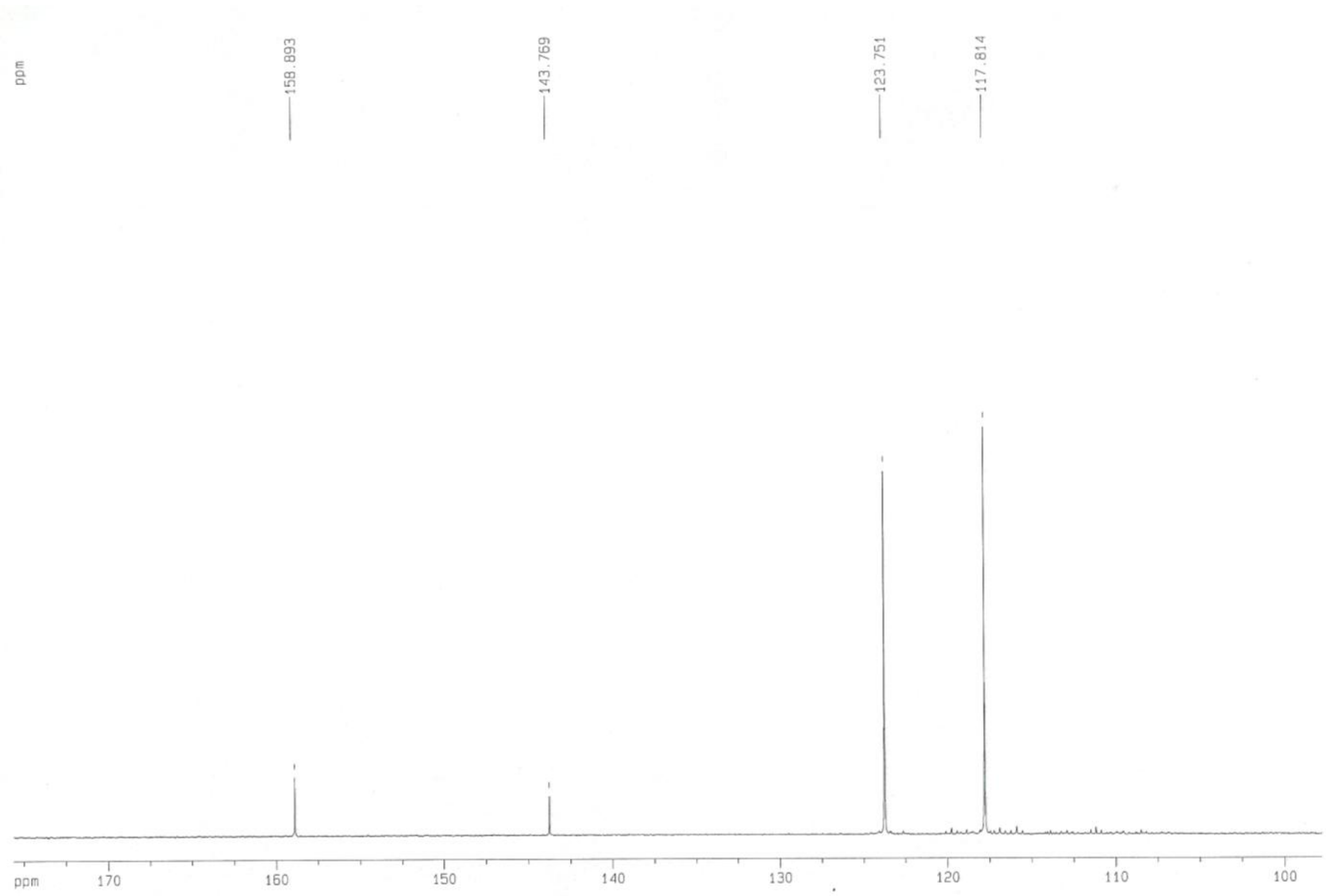
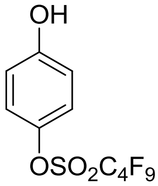
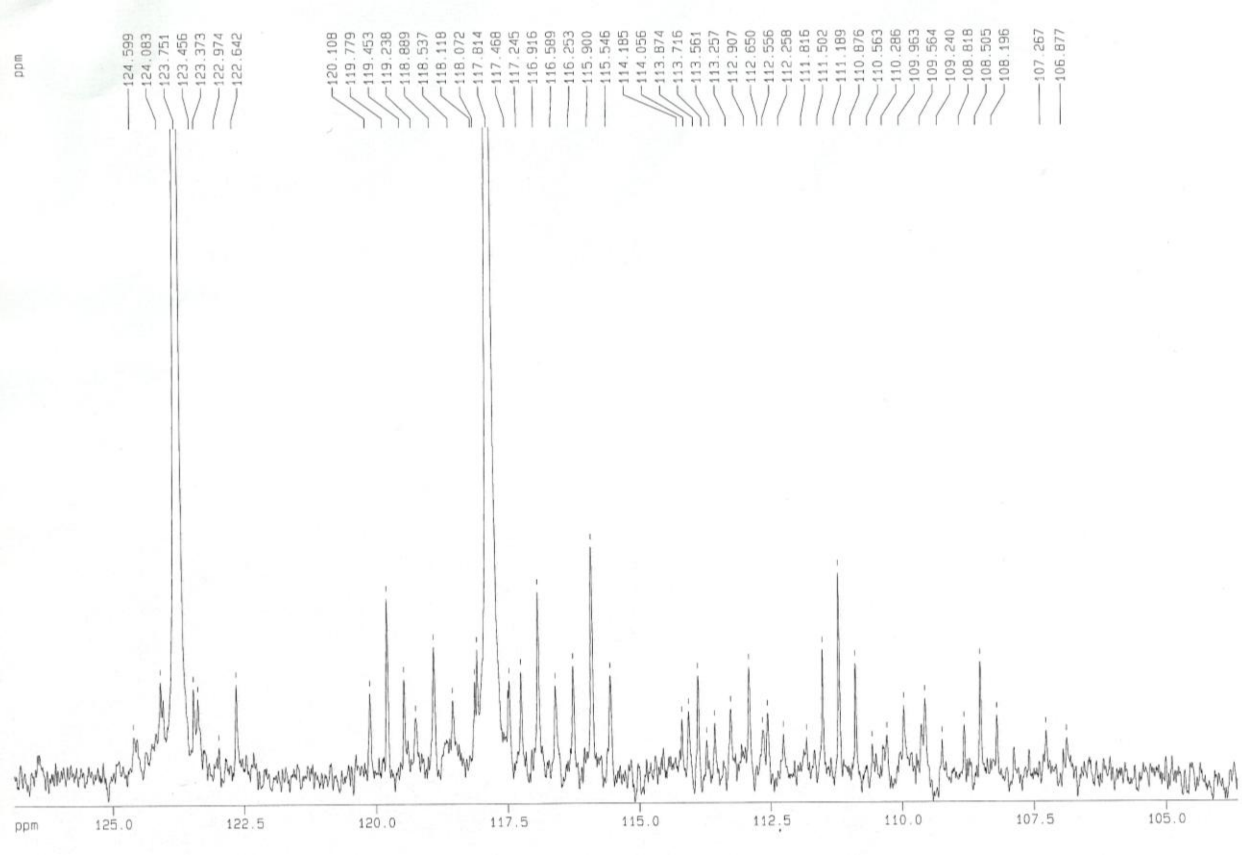
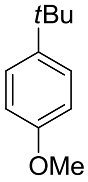


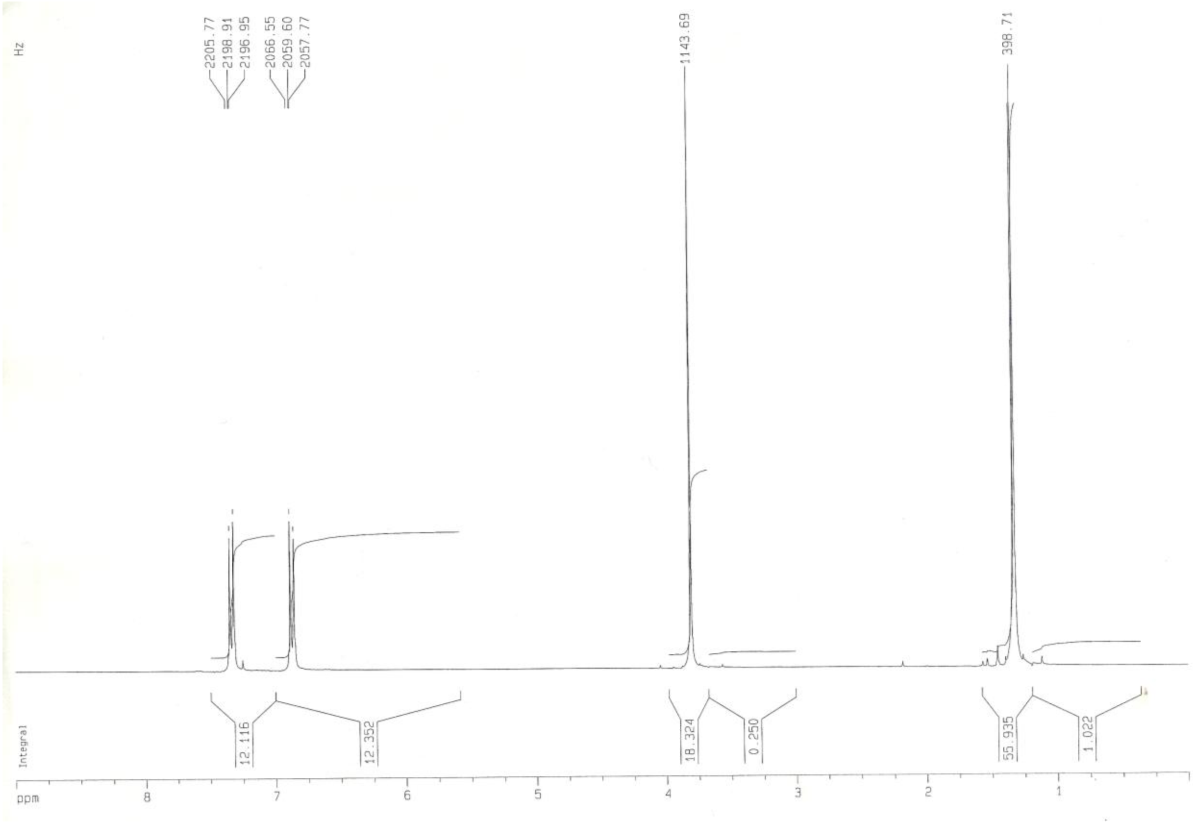


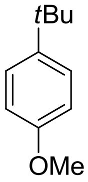
1e, ^{13}C NMR, CD_3COCD_3 (enlargement 100-130 ppm)





6c, ^{1}H NMR, CDCl$_3$





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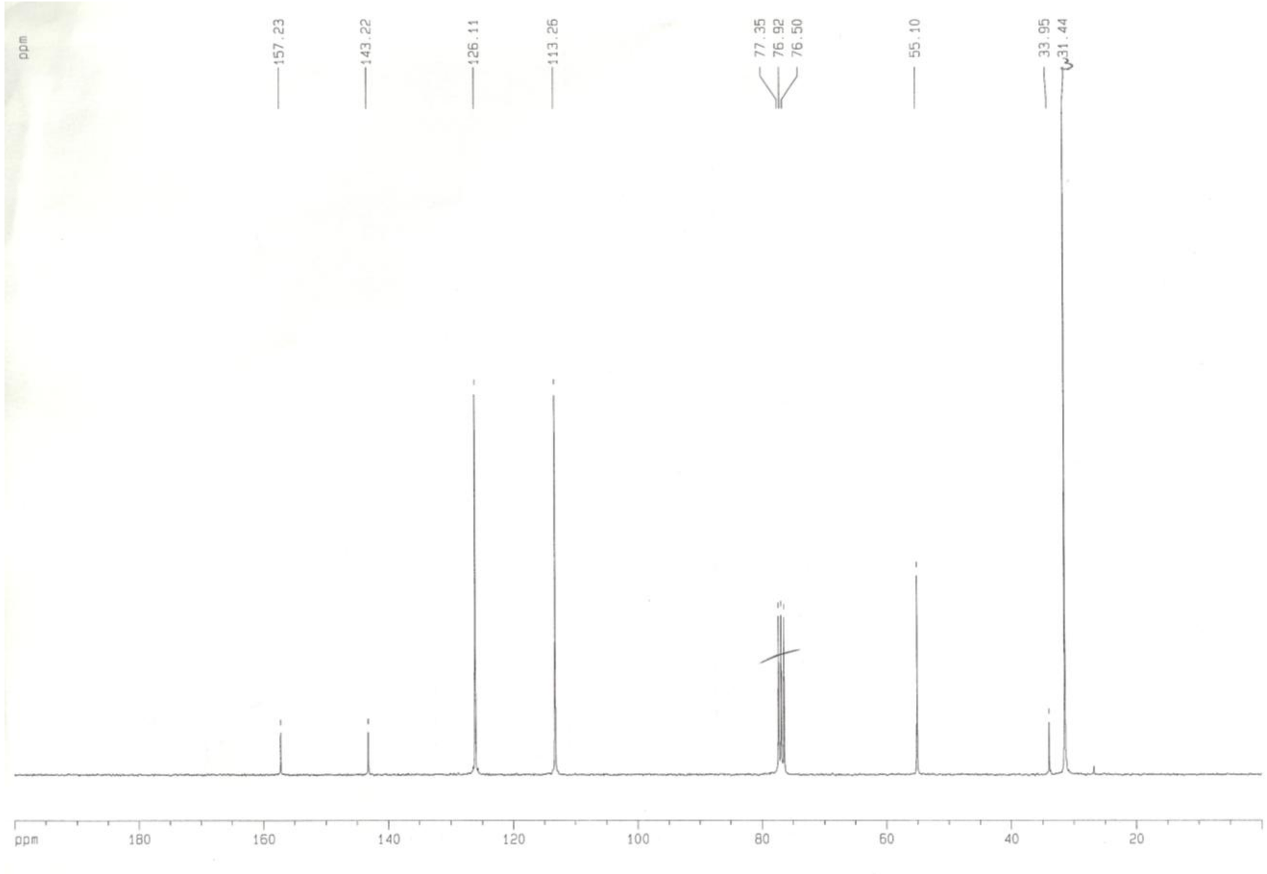

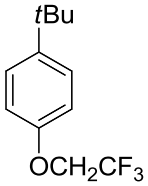

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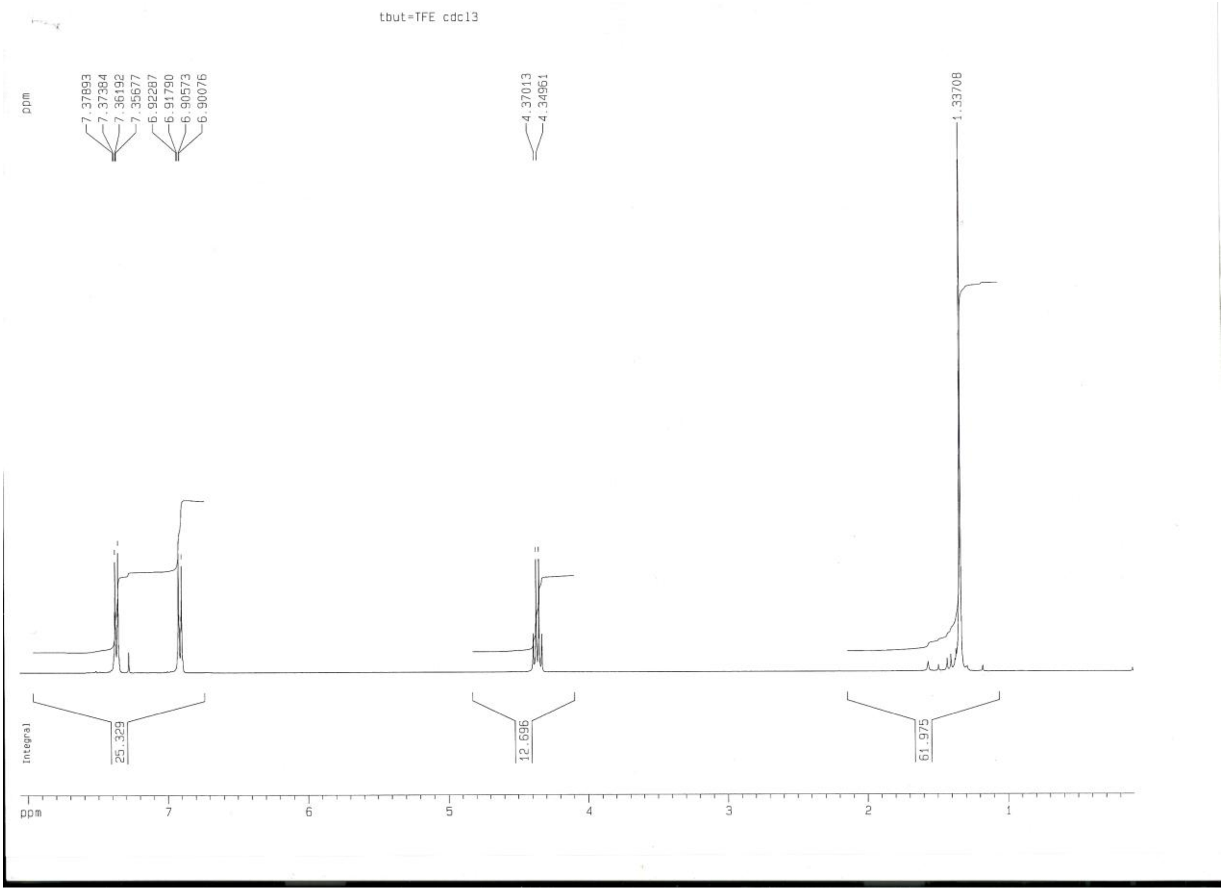

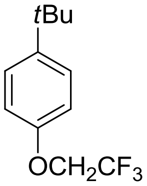

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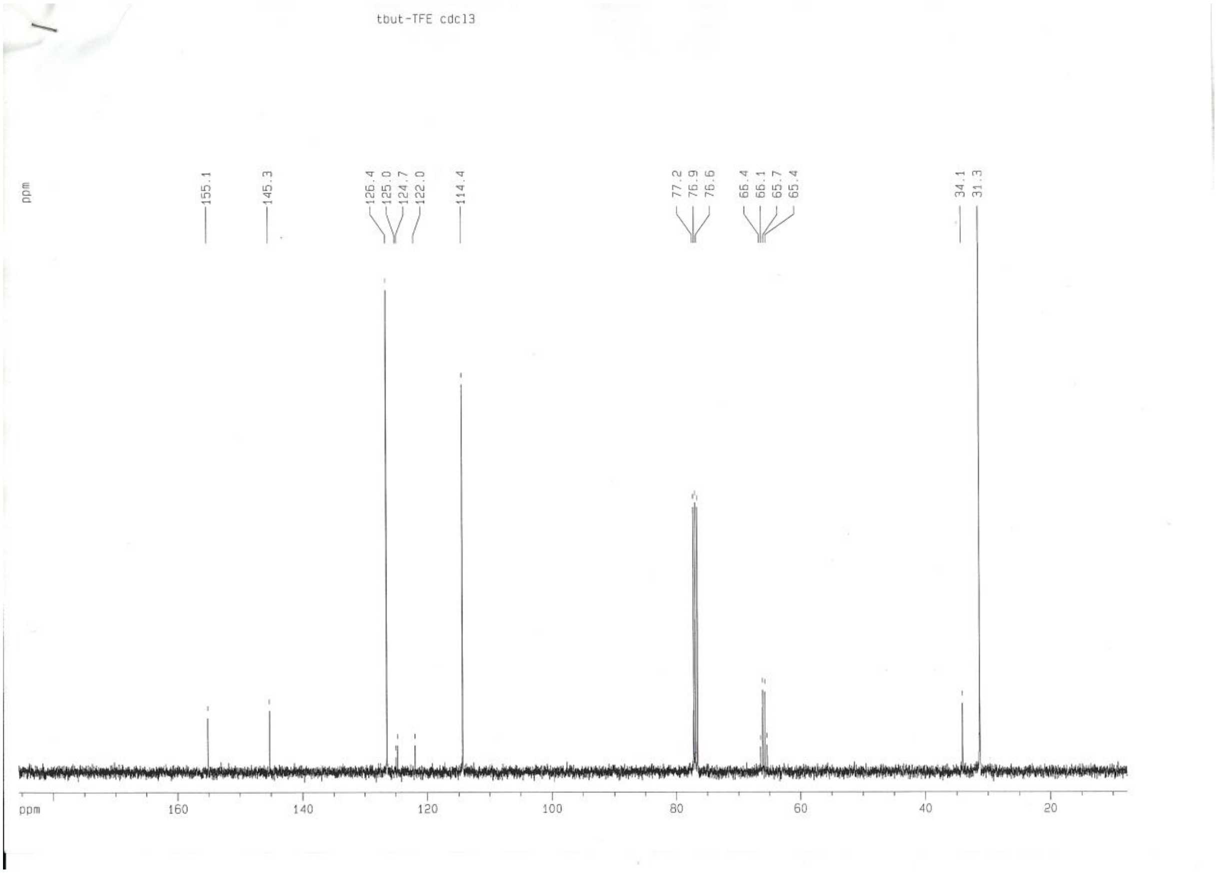

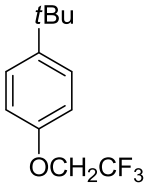

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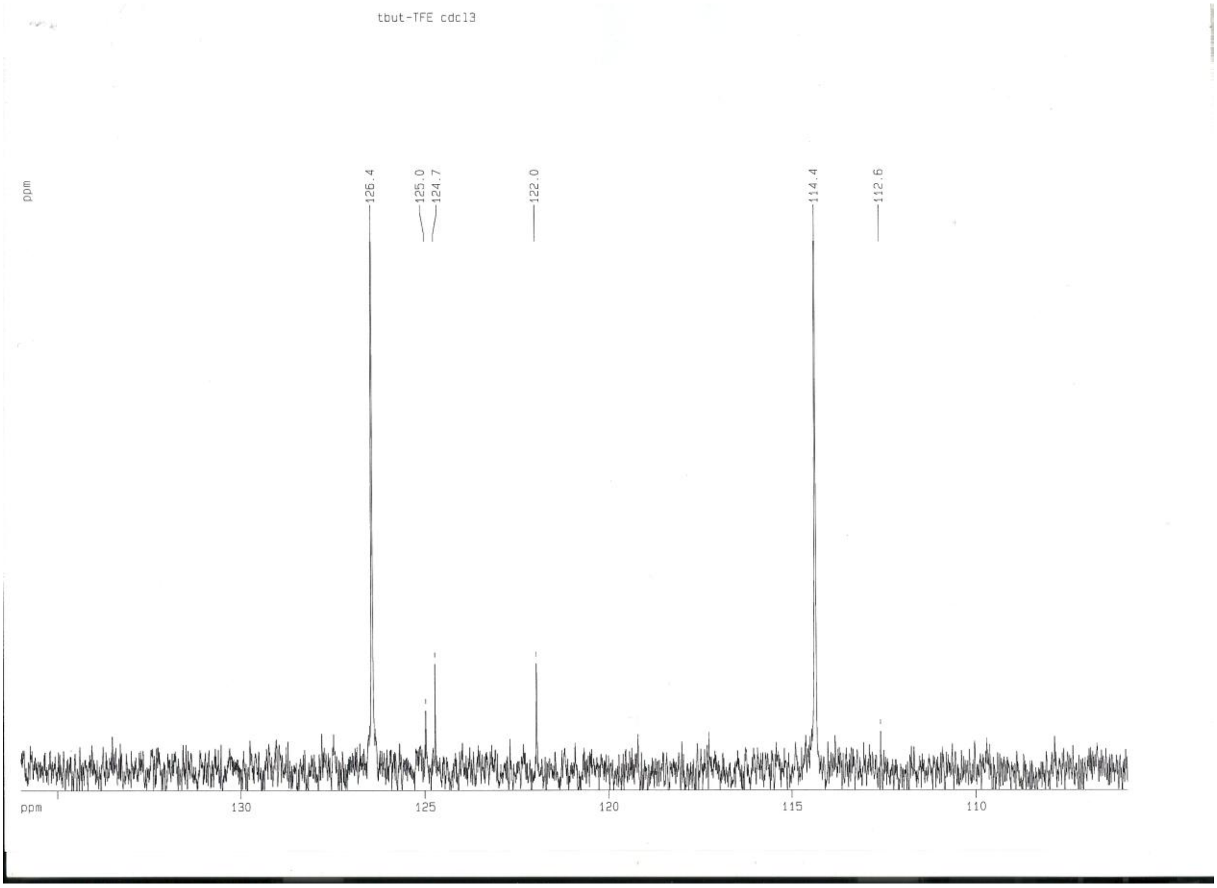

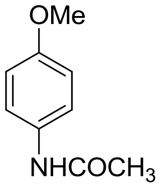

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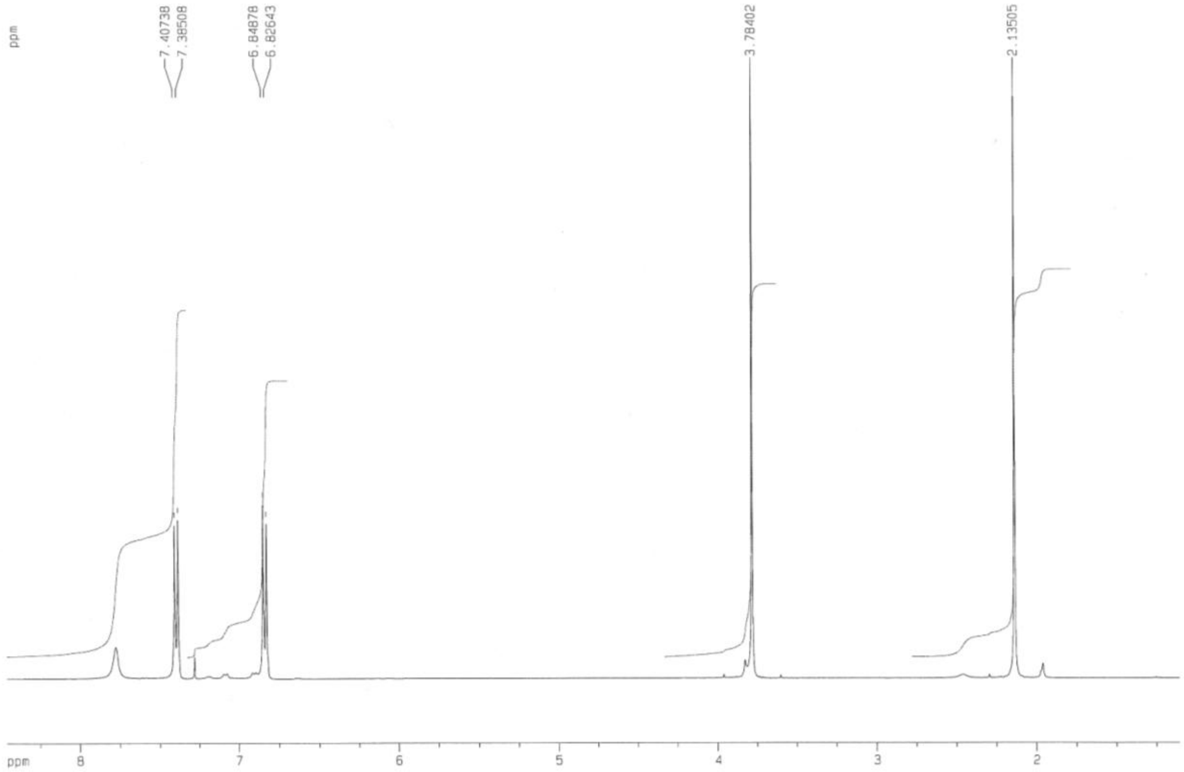

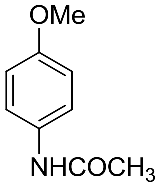

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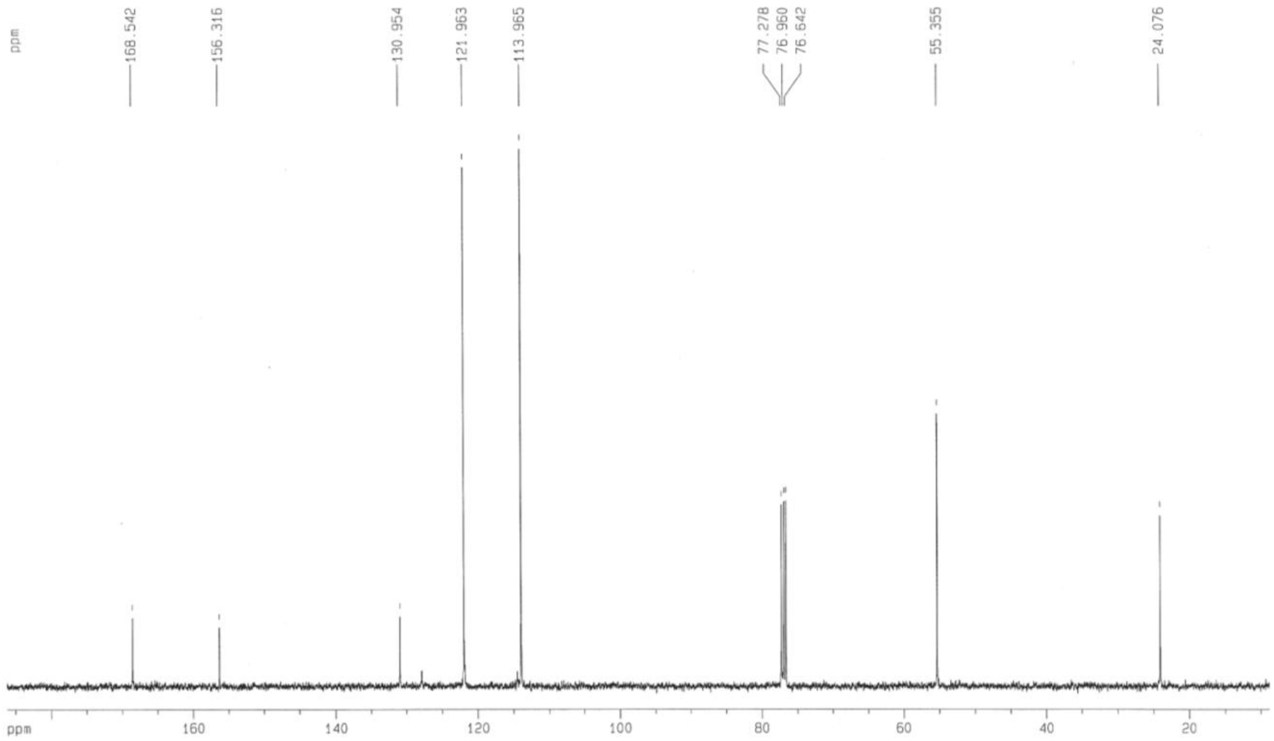

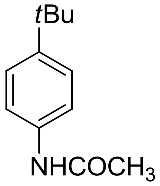

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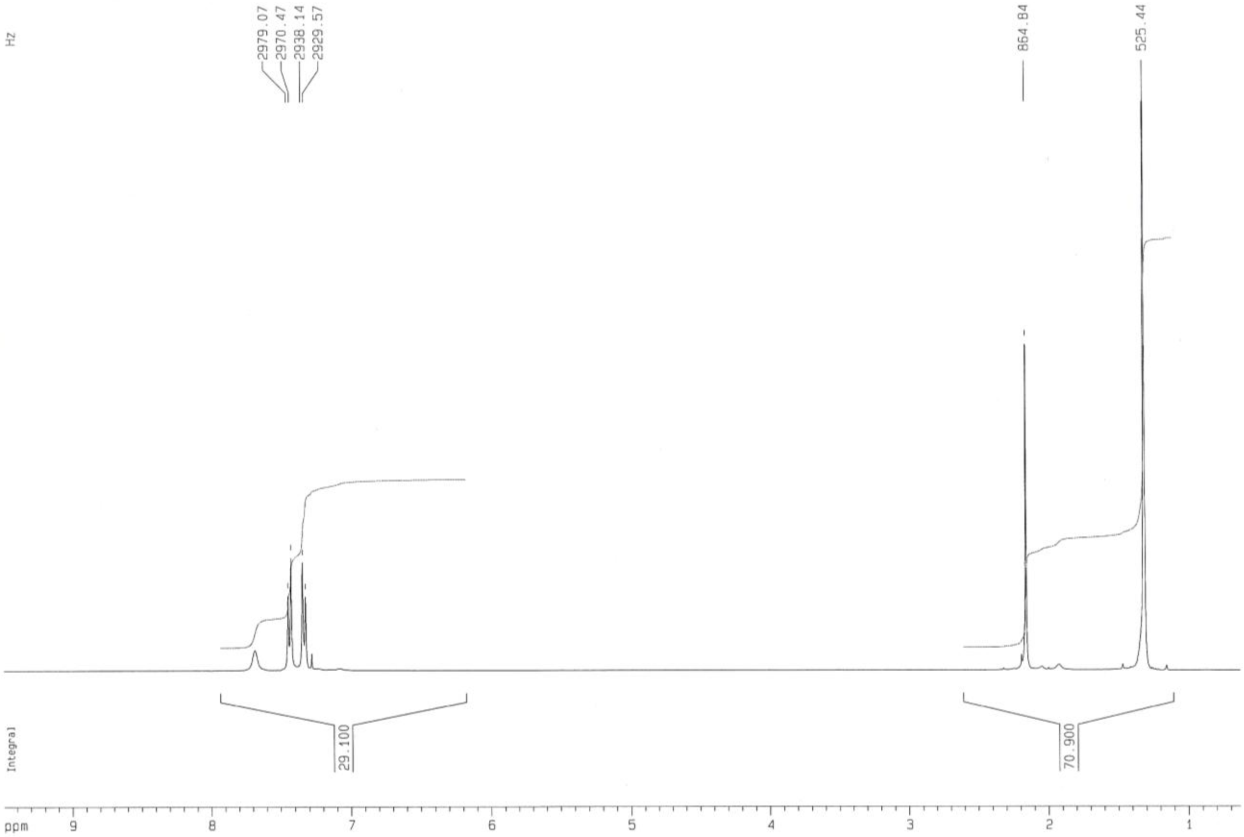

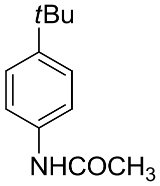

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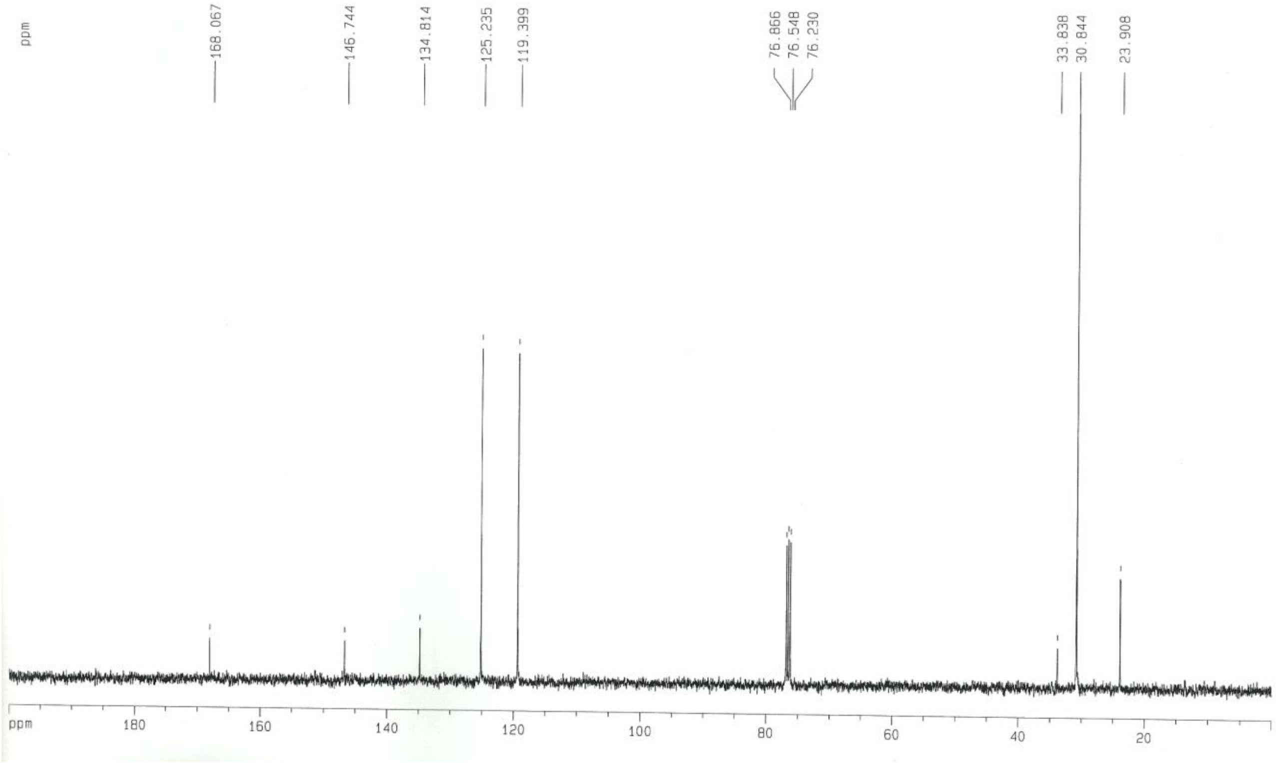

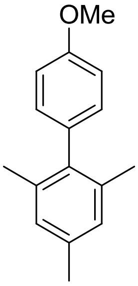

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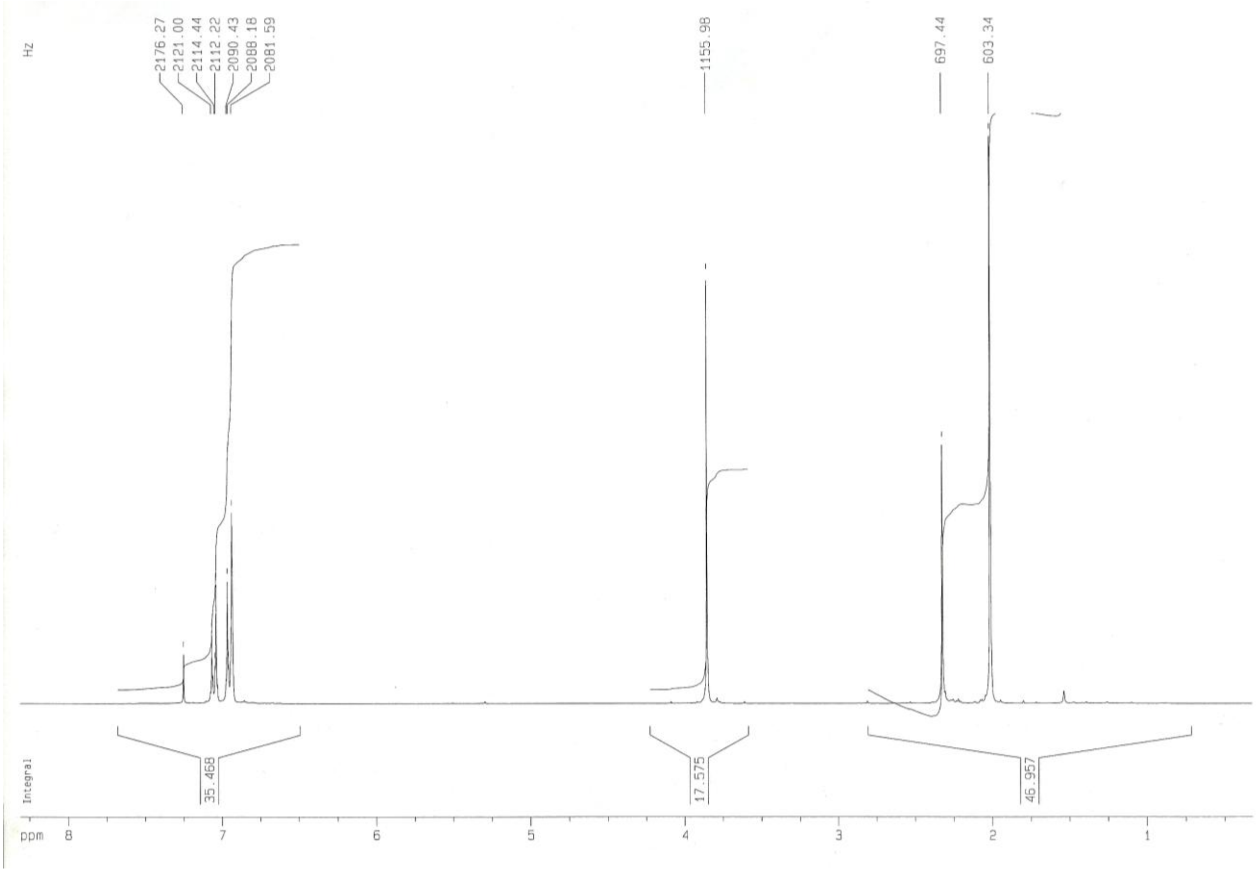
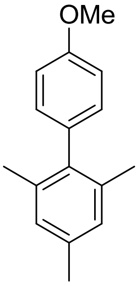
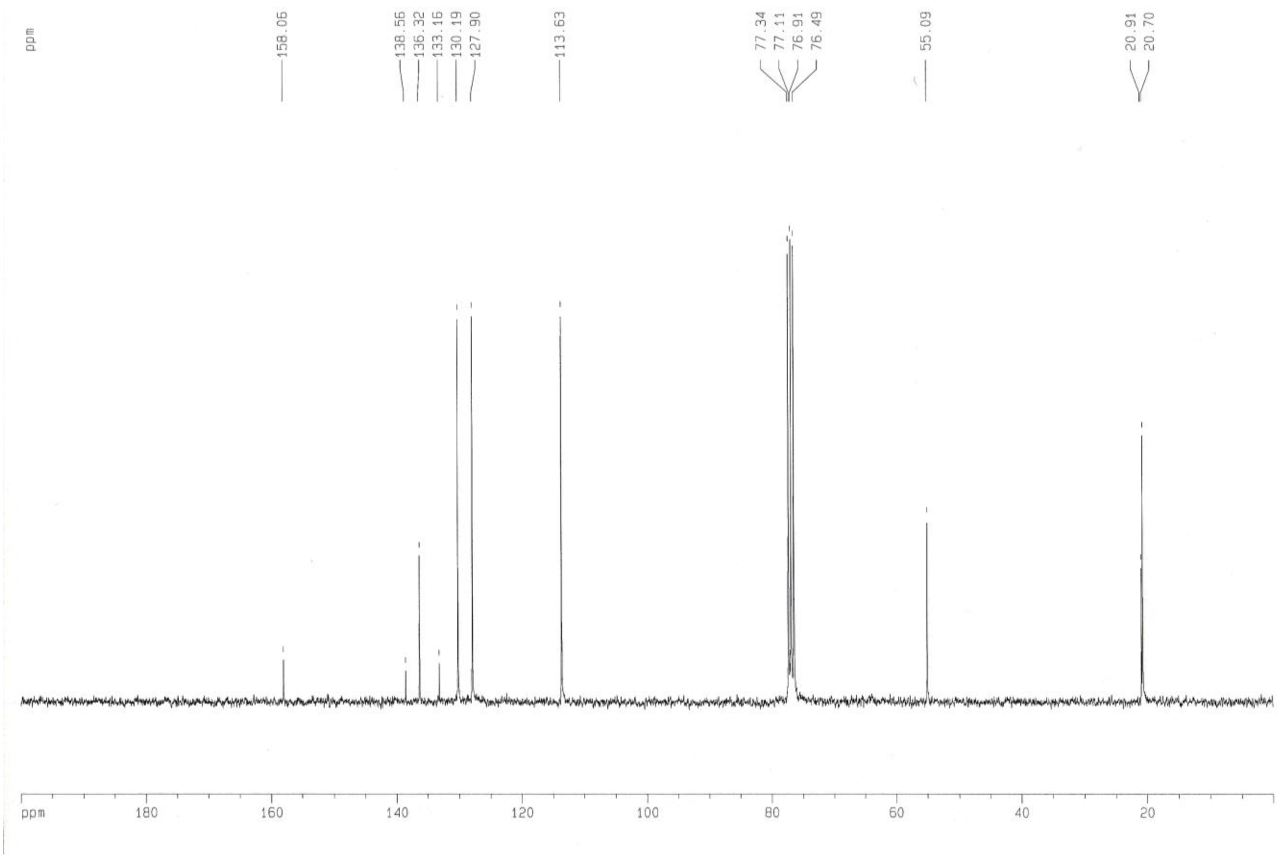
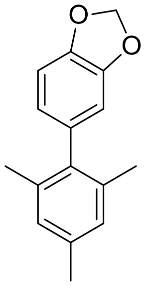


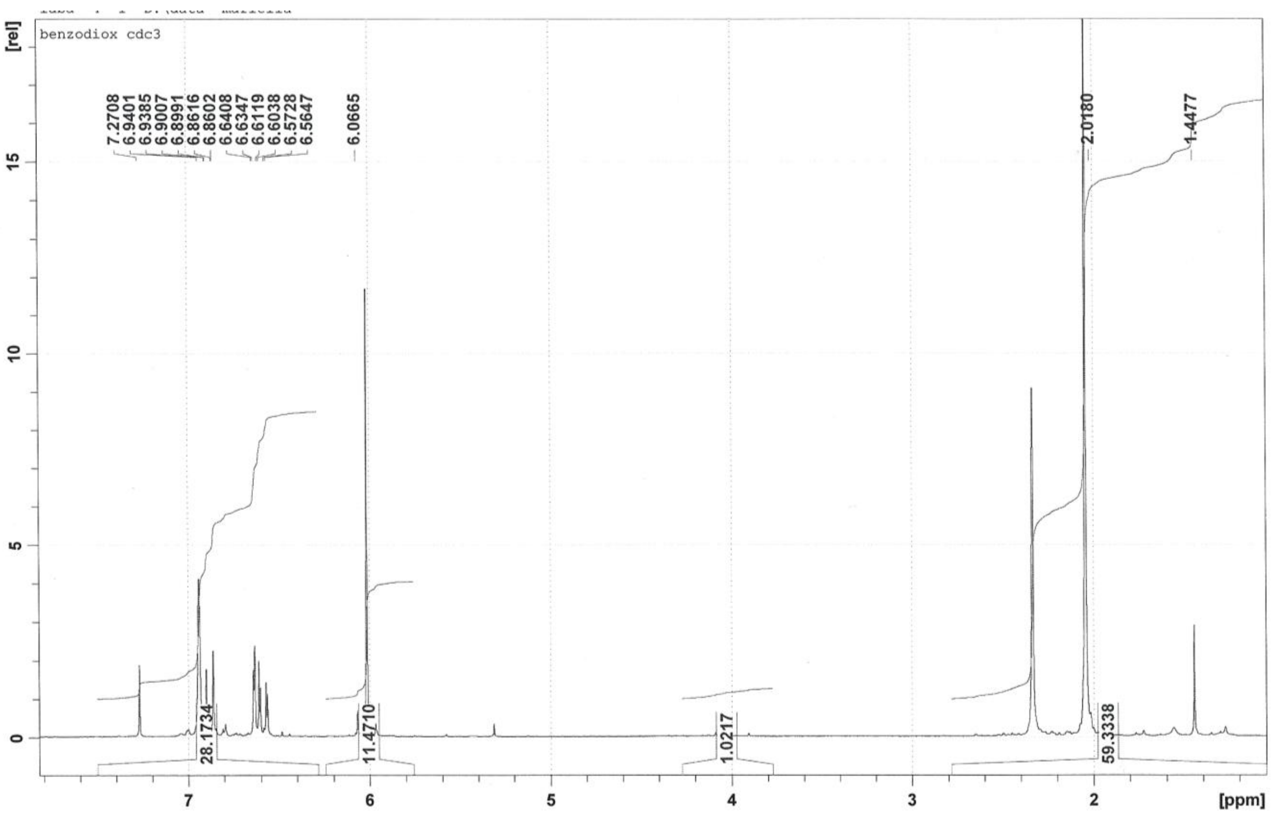


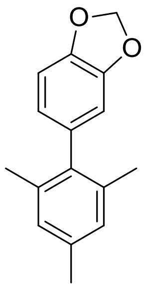
10b, ^{13}C NMR, $CDCl_3$





10d, ^{1}H NMR, $CDCl_3$





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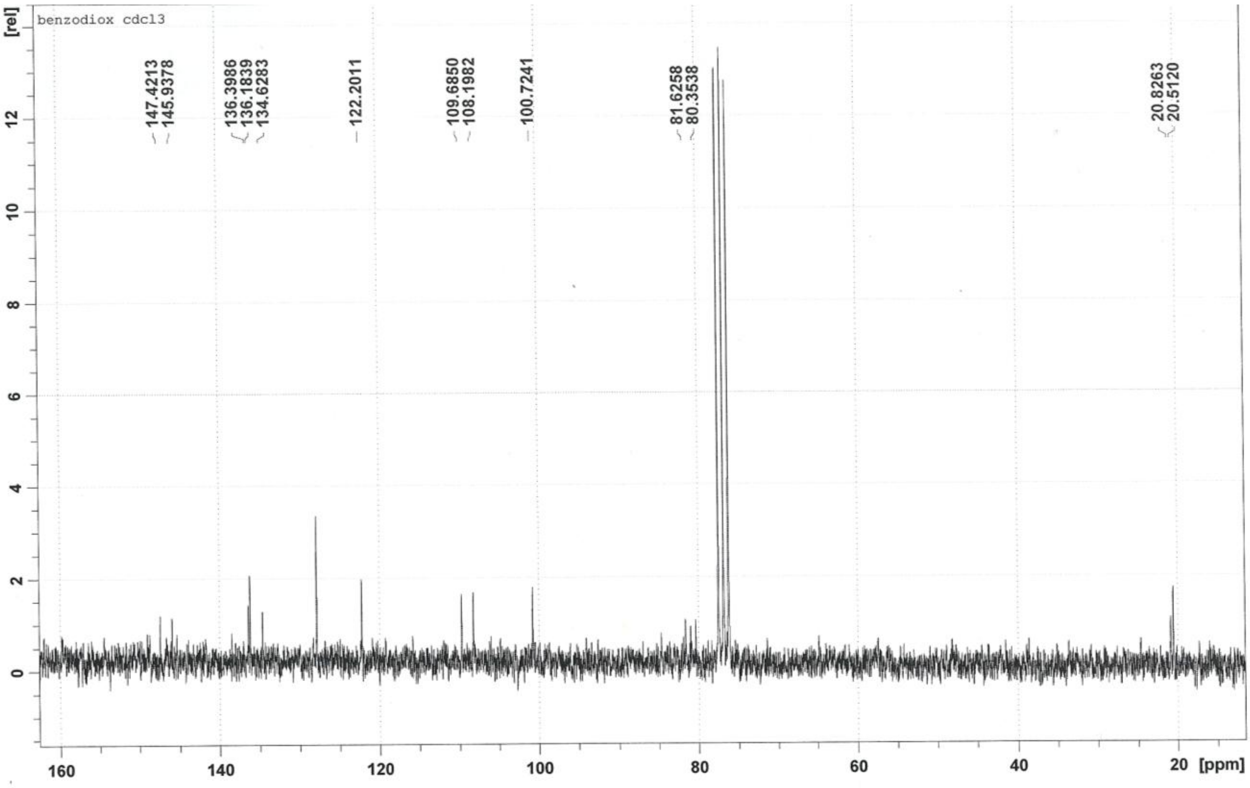
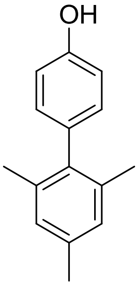
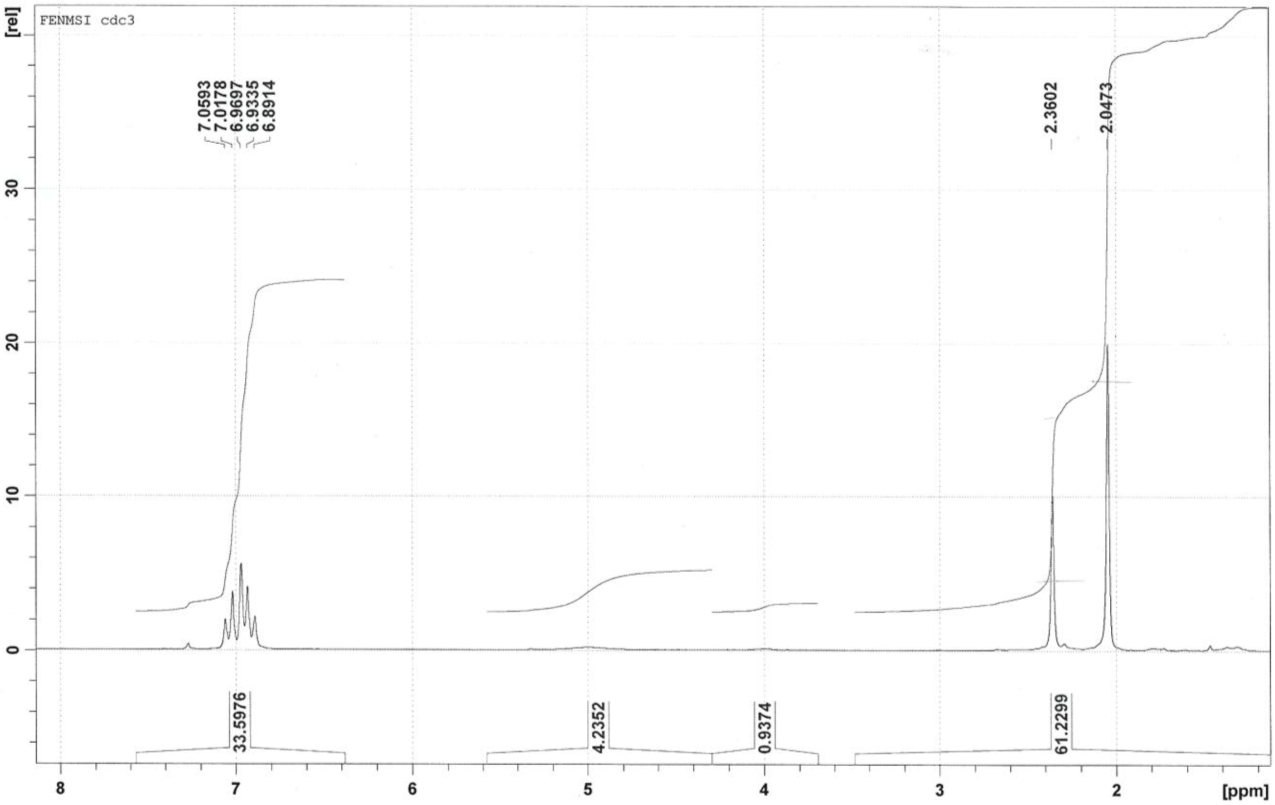
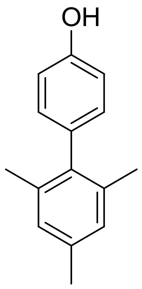


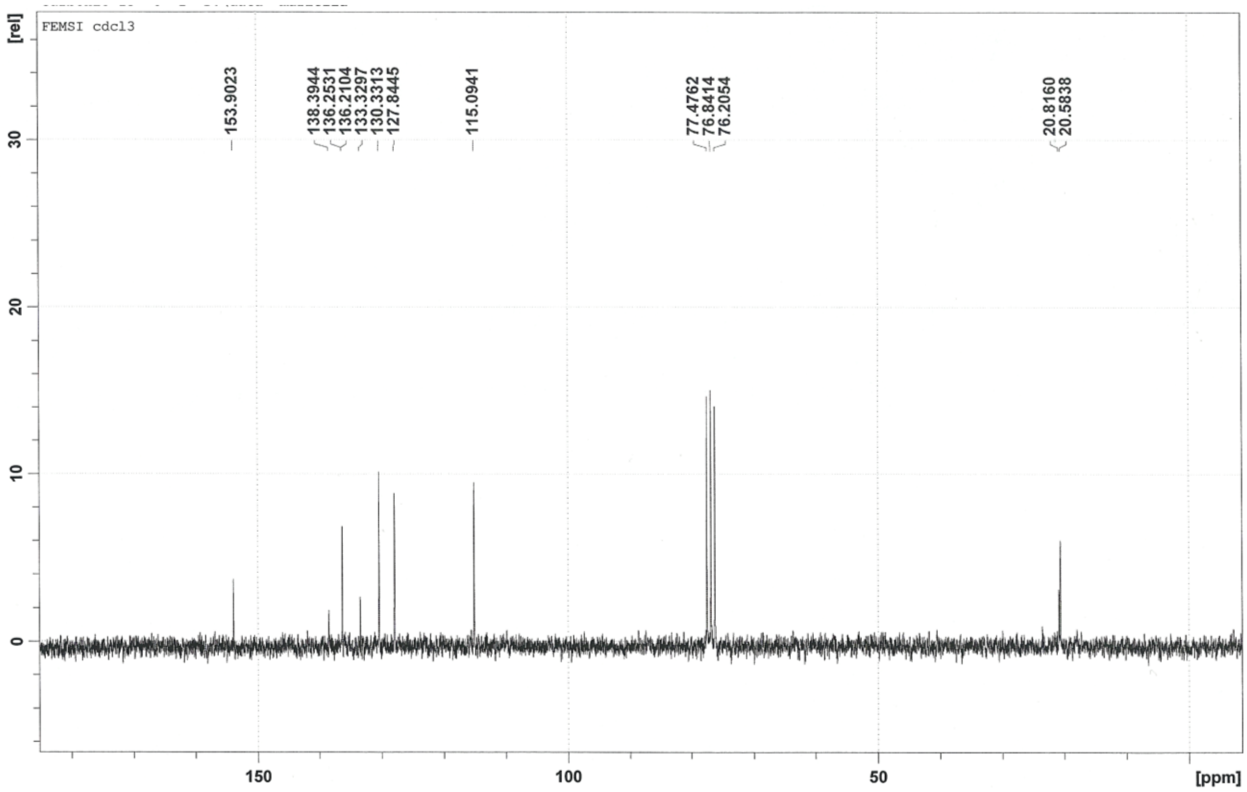


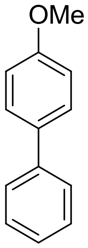
10e, ^{1}H NMR, $CDCl_3$



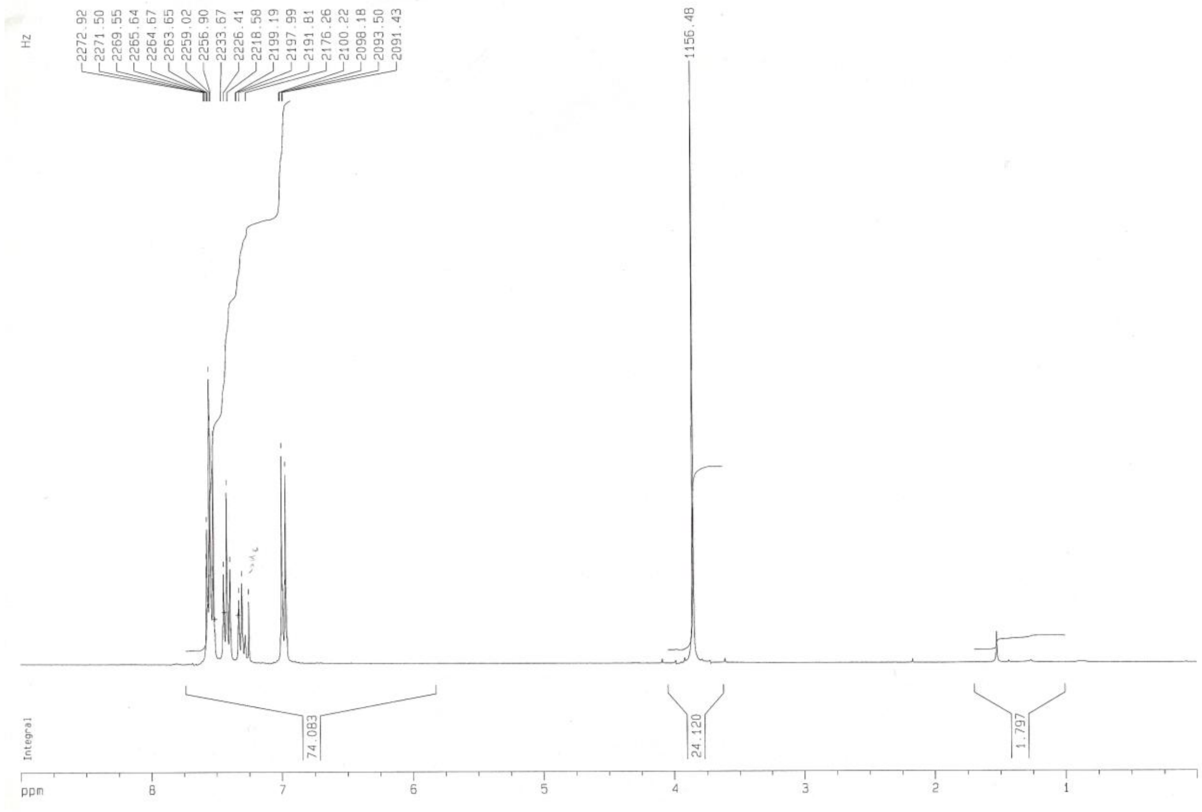


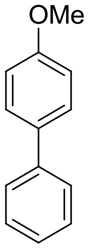
10e, ^{13}C NMR, $CDCl_3$





11b, ^{1}H NMR, CDCl$_3$





11b, ^{13}C NMR, $CDCl_3$