Electronic Supplementary Information

Multisubstituted naphthalene synthesis from 4-hydroxy-2-pyrones and *o*-silylaryl triflates

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Contents

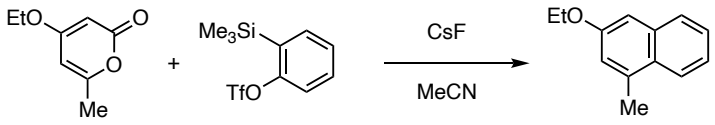
General Information

All reactions were performed with dry glassware under atmosphere of argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 1.05715). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, spherical neutral, particle size 40–50 μm, Cat. No. 37562-85 or particle size 63–210 μm, Cat. No. 37565-85). Preparative TLC (PTLC) was performed on silica gel (Wako Pure Chemical Industries Ltd., Wakogel B-5F, Cat. No. 230-00043). Melting points (Mp) were measured on an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 400 MHz. ^{13}C NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 101 MHz. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 25 ºC. $CDCl_3$ (Kanto Chemical Co. Inc., Cat. No. 07663-23) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from the solvent peak (δ 7.26 for ^{1}H NMR in $CDCl_3$, δ 77.0 for ^{13}C NMR in $CDCl_3$) as an internal reference with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, and m signify singlet, doublet, triplet, quartet, and multiplet, respectively. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-T100CS "AccuTOF CS" mass spectrometer under positive electrospray ionization (ESI^+) conditions or JMS-700 (JEOL, Tokyo, Japan) mass spectrometer under electron impact ionization (EI) conditions.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 3-Methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**9b**),[S1] 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**9c**),[S2] 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**9d**),[S2] 6-(trimethylsilyl)-2,3-dihydro-1*H*-inden-5-yl trifluoromethanesulfonate (**9f**),[S3] and 6-(trimethylsilyl)benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate (**9g**)[S3] were prepared according to the reported methods.

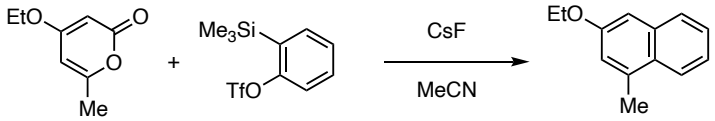
Experimental Procedures

*A typical procedure for the synthesis of naphthalenes **11***



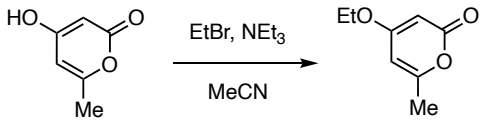
To a mixture of 2-(trimethylsilyl)phenyl triflate (**9a**) (44.8 mg, 0.150 mmol, 1.5 equiv) dissolved in acetonitrile (2.0 mL) were added 4-ethoxy-6-methyl-2-pryone (**2a**) (15.4 mg, 0.100 mmol, 1.0 equiv) and cesium fluoride (45.6 mg, 0.300 mmol, 3.0 equiv). The mixture was heated at 50 °C (oil bath) with stirring for 24 h. After cooling to room temperature, to the mixture was added water (10 mL). The mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with brine (15 mL), and then dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane) to give 2-ethoxy-4-methylnaphthalene (**11a**) (13.8 mg, 74.3 μmol, 74%) as a colorless solid.

*Synthesis of naphthalenes **11a** in a 1 mmol scale*



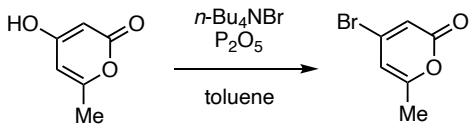
To a mixture of 4-ethoxy-6-methyl-2-pryone (**2a**) (154 mg, 1.00 mmol, 1.0 equiv) dissolved in acetonitrile (20 mL) were added 2-(trimethylsilyl)phenyl triflate (**9a**) (448 mg, 1.50 mmol, 1.5 equiv) and cesium fluoride (456 mg, 3.00 mmol, 3.0 equiv). The mixture was heated at 50 °C (oil bath) with stirring for 24 h. After cooling to room temperature, to the mixture was added water (20 mL). The mixture was extracted with EtOAc (30 mL × 3). The combined organic extract was washed with brine (20 mL), and then dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (n-hexane) to give 2-ethoxy-4-methylnaphthalene (**11a**) (130 mg, 0.700 mmol, 70%) as a colorless solid.

A typical procedure for O-alkylation[S4]



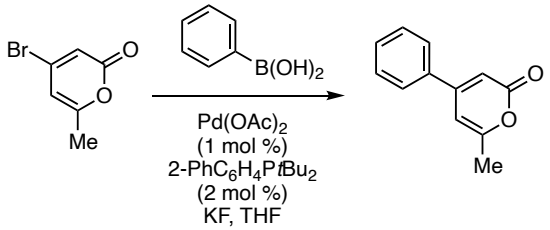
To a mixture of 4-hydroxy-6-methyl-2-pyrone (**1a**) (1.00 g, 7.93 mmol, 1.0 equiv) in acetonitrile (20 mL) at room temperature were added bromoethane (1.18 mL, 15.9 mmol, 2.0 equiv) and trierhylamine (2.21 mL, 15.9 mmol, 2.0 equiv) at 60 °C. After stirring for 16 h at the same temperature, the mixture was cooled to room temperature. To the resulting mixture was added water (10 mL). The mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/1) to give 4-ethoxy-6-methyl-2-pyrone (882 mg, 5.72 mmol, 72%) (**2a**) as a colorless solid.

A typical procedure for dehydrative bromination[S5]



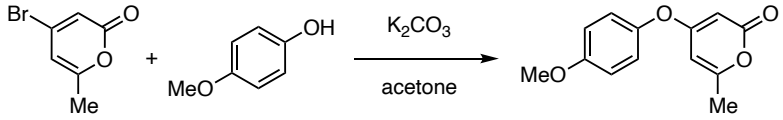
To a mixture of 4-hydroxy-6-methyl-2-pyrone (**1a**) (1.50 g, 11.9 mmol, 1.0 equiv) in toluene (31 mL) were added P_2O_5 (4.01 g, 28.3 mmol, 2.4 equiv) and *n*-Bu_4NBr (4.48 g, 13.8 mmol, 1.2 equiv) at room temperature. After stirring for 1.5 h at 100 °C, the mixture was cooled to room temperature. The resulting upper toluene layer was separated. The lower layer was extracted with EtOAc (50 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL) and dried (Na_2SO_4). Then, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/1) to give 4-bromo-6-methyl-2-pyrone (**2b**) (2.02 g, 10.7 mmol, 90%) as an orange solid.

A typical procedure for the synthesis of 4-aryl-2-pyrones[S6]



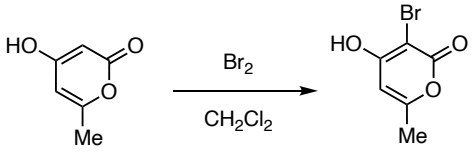
A mixture of $Pd(OAc)_2$ (2.3 mg, 10 μmol, 1.0 mol%), (2-biphenylyl)-di-*tert*-butyl-phosphine (6.0 mg, 20 μmol, 2.0 mol%), phenylboronic acid (183 mg, 1.50 mmol, 1.5 equiv), 4-bromo-6-methyl-2-pyrone (189 mg, 1.00 mmol, 1.0 equiv), and potassium fluoride (174 mg, 2.99 mmol, 3.00 equiv) in THF (5 mL) was stirred for 24 h at room temperature. To the mixture was added water (10 mL). The mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 4/1) to give 6-methyl-4-phenyl-2*H*-pyrone (**2c**) (186.2 mg, 1.00 mmol, quant.) as a colorless solid.

*Synthesis of **2f***[S7]



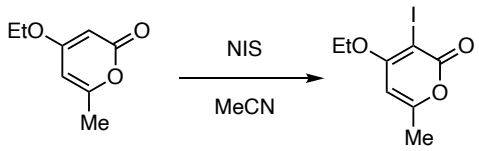
To a mixture of 4-bromo-6-methyl-2-pyrone (**2b**) (945 mg, 5.00 mmol, 1.0 equiv), 4-methoxyphenol (931 mg, 7.50 mmol, 1.5 equiv) and K_2CO_3 (1.24 g, 9.00 mmol, 1.8 equiv) was added acetone (20 mL) at room temperature. After stirring for 16 h at 65 °C, the mixture was cooled to room temperature. To the mixture was added water (10 mL). The mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with the with aqueous NaOH (1 M, 20 mL). The mixture was washed with brine (15 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from EtOH (10 mL) to give 4-(4-methoxyphenoxy)-6-methyl-2-pyrone (**2f**) (732 mg, 3.15 mmol, 63%) as an orange solid.

*A procedure for bromination of pyrone **1a** at 3-position*



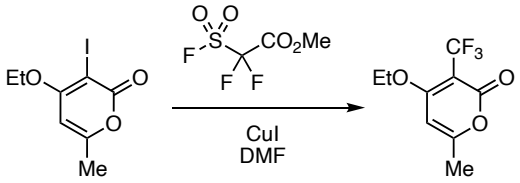
To a mixture of 4-hydroxy-6-methyl-2-pyrone (**1a**) (1.26 g, 10.0 mmol, 1.0 equiv) in dichloromethane (60 mL) was added bromine (0.600 mL, 11.0 mmol, 1.1 equiv) at room temperature in the dark. To the mixture was added an aqueous saturated sodium bicarbonate (10 mL) and an aqueous saturated sodium thiosulfate (30 mL) . The mixture was extracted with dichloromethane (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from EtOH (10 mL) to give 3-bromo-4-hydroxy-6-methyl-2-pyrone (1.93 g, 9.63 mmol, 96%) as a pale yellow solid.

Synthesis of ***2h***[S4]



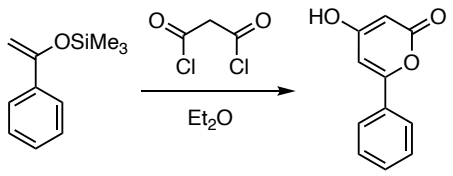
A mixture of 4-ethoxy-6-methyl-2-pyrone (**1a**) (233 mg, 1.51 mmol, 1.0 equiv) and *N*-iodosuccinimide (1.06 g, 4.71 mol, 3.1 equiv) in acetonitrile (45 mL) was stirred for 24 h at 60 °C. After cooling to room temperature, to the mixture was added an aqueous saturated sodium thiosulfate (30 mL). The mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/1) to give the 4-ethoxy-3-Iodo-6-methyl-2-pyrone (**2h**) (393.5 mg, 1.41 mmol, 93%) as a yellow solid.

Synthesis of ***2i***[S4]



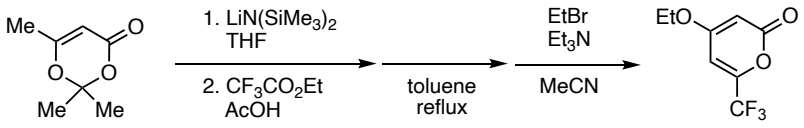
A mixture of 4-ethoxy-3-Iodo-6-methyl-2-pyrone (**2h**) (550 mg, 1.96 mmol, 1.0 equiv) and copper(I) iodide (571 mg, 3.00 mmol, 1.5 equiv) in DME (10 mL) was added methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (382 μL, 3.00 mmol, 1.5 equiv) at room temperature. After stirring for 18 h at 70 °C, the mixture was cooled to room temperature. To the mixture was added water (10 mL). The mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 4/1) to give the 4-ethoxy-6-methyl-3-(trifluomethyl)-2-pyrone (**2i**) (276 mg, 1.24 mmol, 62%) as a pale yellow solid.

A typical procedure for the synthesis of 6-aryl-4-hydroxy-2-pyrones[S8]



To a mixture of 1-phenyl-1-(trimethylsilyloxy)ethene (4.09 mL, 20.0 mmol, 2.0 equiv) in Et_2O (57 mL) at room temperature was added dropwise malonyl dichloride (973 μL, 10.0 mmol, 1.00 equiv) at –78 °C. The mixture was warmed up gradually to room temperature and stirred for 16 h at room temperature. The resulting solid was collected by filtration and washed with Et_2O (30 mL) to give 4-hydroxy-6-phenyl-2*H*-pyrone (**1b**) (1.47 g, 7.81 mmol, 78%) as a yellow solid.

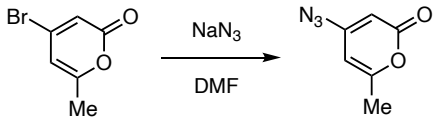
Synthesis of ***2m***[S9]



To a solution of hexamethyldisilazane (4.17 mL, 20.0 mmol, 2.0 equiv) in THF (5.0 mL) was cannulated *n*-BuLi (2.64 M) (2.64 mL, 20.0 mmol, 2.0 equiv) at 0 °C. After stirring for 30 min at 0 °C, then the resulting mixture was cannulated into a solution of 2,2,6-trimethyl-l,3-dioxin-4-one (**8**) (1.30 mL, 10.0 mmol, 1.0 equiv) in THF (10 mL) at –78 °C. After stirring for 1 h at –78 °C, to the resulting mixture was added a solution of ethyl

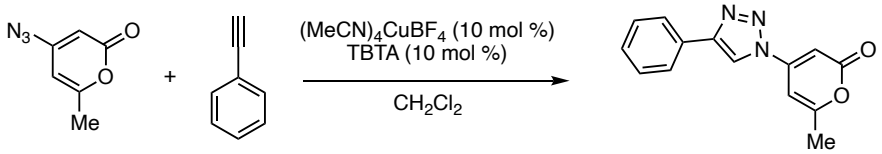
2,2,2-trifluoroacetate (1.30 mL, 10.9 mmol, 1.1 equiv) in THF (2.5 mL) quickly. The cooling bath was removed and stirring was continued at –78 to 0 °C for 2 h. After cooling to –45 °C, then AcOH (1.44 mL, 25.0 mmol, 2.5 equiv) was added to the mixture at the same temperature. After stirring for 10 min at the same temperature, the mixture was then warmed to –10 °C. The resulting mixture was poured into 1 M HCl (10 mL) at 0 °C. The mixture was extracted with *tert*-butyl methyl ether (20 mL). The mixture was washed with $NaHCO_3$ (20 mL), water (10 mL), and brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. To the residue was then added toluene (20 mL) at room temperature. After stirring for 10 min at the same temperature, the mixture was stirred for 1 h at reflux. The mixture was concentrated under reduced pressure. To a mixture of the resulting mixture in acetonitrile (20 mL) was added bromoethane (2.00 mL, 27.0 mmol, 2.7 equiv) and triethylamine (2.00 mL, 14.3 mmol, 1.4 equiv) at room temperature. After stirring for 16 h at 60 °C. the mixture was cooled to room temperature. To the mixture was added water (10 mL). The mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 4/1) to give 4-ethoxy-6-trifluoromethyl-2*H*-pyrone (**2m**) (348 mg, 1.67 mmol, 17% from **8**) as a yellow solid.

Synthesis of ***2n***[S10]



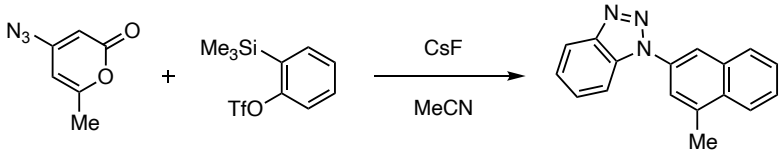
A mixture of 4-bromo-6-methyl-2-pyrone (945 mg, 5.00 mmol, 1.0 equiv) in DMF (20 mL) was added sodium azide (390 mg, 6.00 mmol, 1.5 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added an iced water (20 mL). The mixture was extracted with *n*-hexane/EtOAc = 1/1 (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/1) to give the 4-azide-6-methyl-2-pyrone (**2n**) (333 mg, 2.20 mmol, 44%) as an orange solid.

Synthesis of ***2o***



To a solution of 4-azide-6-methyl-2-pyrone (**2n**) (60.4 mg, 0.400 mmol, 1.0 equiv), tetrakis(acetonitrile)copper(I) tetrafluoroborate (12.6 mg, 40.1 μmol, 10 mol %) and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (21.2 mg, 40.0 μmol, 10 mol %) in CH_2Cl_2 (3.2 mL) was added phenylacetylene (65.9 μL, 0.600 mmol, 1.5 equiv) at room temperature. After stirring for 24 h at the same temperature, to the mixture was added water (10 mL). The mixture was extracted with EtOAc (10 mL × 3). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/1) to give the 6-methyl-4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)- 2-pyrone (**2o**) (184.7 mg, 0.29 mmol, 73%) as an off-white solid.

Synthesis of ***12***



To a mixture of 2-(trimethylsilyl)phenyl triflate (89.5 mg, 0.300 mmol, 3.0 equiv) dissolved in acetonitrile (2.0 mL) were added 4-azide-6-methyl-2-pryone (**2n**) (15.1 mg, 0.100 mmol, 1.0 equiv) and cesium fluoride (91.1 mg, 0.600 mmol, 6.0 equiv) at room temperature. The mixture was heated at 50 °C (oil bath) with stirring for 24 h. After cooling to room temperature, to the mixture was added water (10 mL). The mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with brine (15 mL), and then dried (Na_2SO_4).

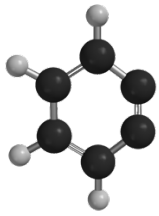
After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2/1) to give 1-(4-methylnaphthalen-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (**12**) (25.8 mg, 99.4 μmol, 99%) as a colorless solid.

Computational Methods

Geometry optimizations and frequency calculations were performed at B3LYP/6-311+G(d,p) level of theory with Spartan 18 program (Wavefunction,. Inc. Irvine, CA) in the gas phase unless otherwise noted. Cartesian coordinates obtained by the DFT calculation with B3LYP/6-311+G(d,p) were shown as calculated geometries described below. All the stationary geometries were confirmed to be energy minima by achieving vibrational frequency analyses. Transition structures were also confirmed to be true transition states on the potential energy surfaces by achieving vibrational frequency analyses and intrinsic reaction coordinate approaches. Gibbs free energies were corrected to a reference state of 1 mol/L at 298.15 K.

Calculated geometries

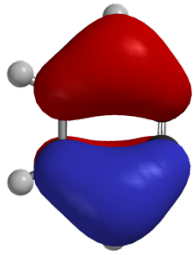
Optimized structure of benzyne (**III**)



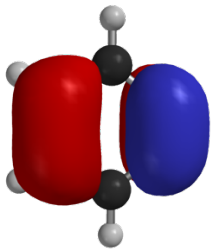
black: carbon, grey: hydrogen,
E = –230.972685 hartrees
G = –230.924507 hartrees

H	2.541116	0.000000	-0.447825
C	1.458962	0.000000	-0.445623
C	-1.458962	0.000000	-0.445623
C	0.622287	0.000000	-1.546299
C	0.702541	0.000000	0.745125
C	-0.702541	0.000000	0.745125
C	-0.622287	0.000000	-1.546300
H	1.228382	0.000000	1.694622
H	-1.228382	0.000000	1.694622
H	-2.541116	0.000000	-0.447825

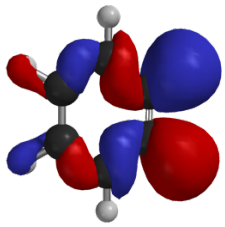
Representative molecular orbitals of benzyne (**III**)



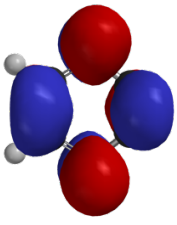
HOMO–1 –7.49 eV



HOMO –7.48 eV

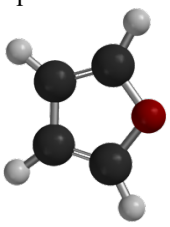


LUMO –2.35eV



LUMO+1 –1.07 eV

Optimized structure of furan (**15a**)

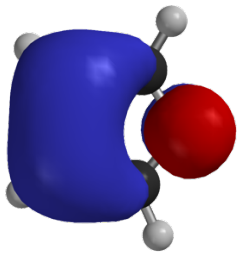


black: carbon, grey: hydrogen, red: oxygen

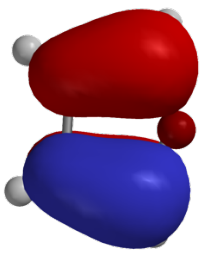
E = –230.087800 hartrees

C	-1.094804	0.000000	0.569071
H	-2.050138	0.000000	1.065832
C	-0.717413	0.000000	-0.735804
H	-1.376100	0.000000	-1.589743
C	0.717413	0.000000	-0.735804
H	1.376100	0.000000	-1.589743
C	1.094804	0.000000	0.569071
H	2.050138	0.000000	1.065832
O	0.000000	0.000000	1.381288

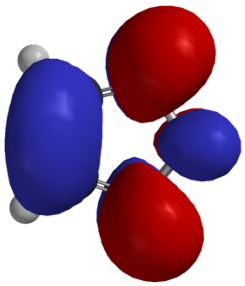
Representative molecular orbitals of furan (**15a**)



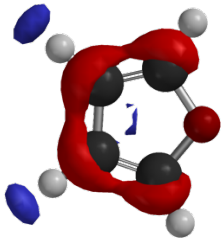
HOMO–1 –7.87 eV



HOMO –6.53 eV

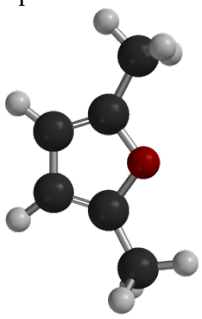


LUMO –0.17 eV



LUMO+1 +0.27 eV

Optimized structure of 2,5-dimethylfuran (**15b**)

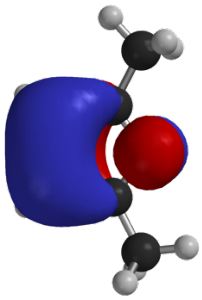


black: carbon, grey: hydrogen, red: oxygen

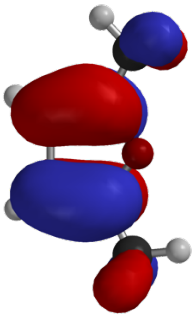
E = –308.751284 hartrees

C	-1.109742	0.000000	-0.032542
C	-0.714872	0.000000	-1.333894
H	-1.365926	0.000000	-2.194489
C	0.721085	0.000000	-1.331122
H	1.376114	0.000000	-2.188635
C	1.110468	0.000000	-0.028157
O	-0.000309	0.000000	0.776077
C	2.429829	0.000000	0.658671
H	3.232122	0.000000	-0.080640
H	2.549204	-0.883201	1.294450
H	2.549204	0.883201	1.294450
C	-2.435569	0.000000	0.652656
H	-2.291998	0.000000	1.734149
H	-3.024805	-0.883275	0.389513
H	-3.024805	0.883275	0.389513

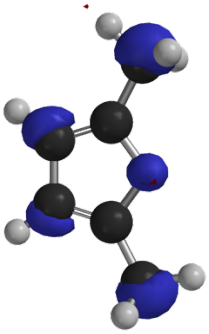
Representative molecular orbitals of 2,5-dimethylfuran (**15b**)



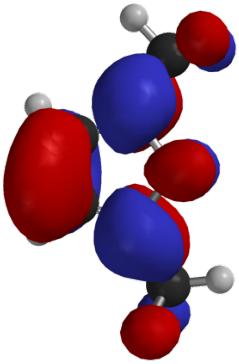
HOMO–1 –7.53 eV



HOMO –5.81 eV

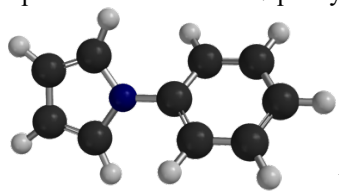


LUMO +0.13 eV



LUMO+1 +0.22 eV

Optimized structure of *N*-phenylpyrrole (**15c**)

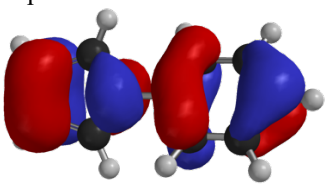


black: carbon, grey: hydrogen, blue: nitrogen

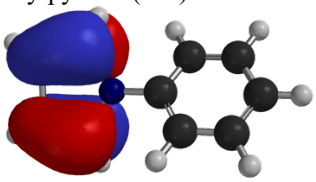
E = –441.33409 hartrees

C	1.217771	1.414496	1.097436
H	0.513210	1.630865	1.882686
C	2.467921	1.924923	0.845921
H	2.986363	2.650085	1.455759
C	2.932453	1.334403	-0.365391
H	3.884790	1.501747	-0.844448
C	1.948049	0.488539	-0.814361
H	1.921165	-0.168721	-1.666314
N	0.894144	0.533294	0.080512
C	-0.317638	-0.195237	-0.028404
C	-2.710897	-1.630358	-0.241470
C	-0.896169	-0.416069	-1.281849
C	-0.941397	-0.696288	1.118145
C	-2.137163	-1.400569	1.007707
C	-2.081768	-1.139143	-1.383782
H	-0.429325	-0.004337	-2.168137
H	-0.479297	-0.552288	2.086982
H	-2.612656	-1.784837	1.902991
H	-2.522128	-1.304143	-2.360590
H	-3.637428	-2.186363	-0.323393

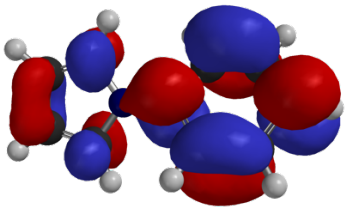
Representative molecular orbitals of *N*-phenylpyrrole (**15c**)



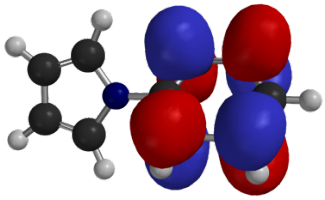
HOMO–1 –6.31 eV



HOMO –6.06 eV

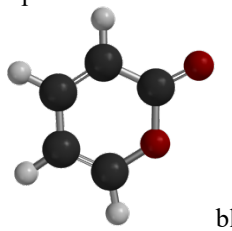


LUMO –0.87 eV



LUMO+1 –0.78 eV

Optimized structure of pyrone **2p**

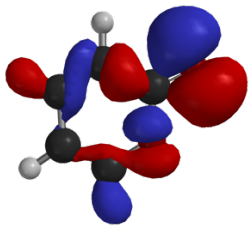


black: carbon, grey: hydrogen, red: oxygen

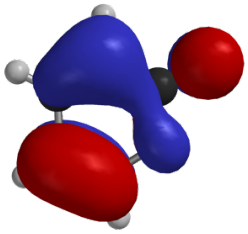
E = –343.466381 hartrees
G = –343.41539 hartrees

C	-1.397862	0.000000	0.471715
H	-2.429962	0.000000	0.798981
C	-0.325606	0.000000	1.291688
H	-0.461609	0.000000	2.363787
C	0.973252	0.000000	0.692142
H	1.853943	0.000000	1.325319
C	1.109914	0.000000	-0.657798
H	2.075199	0.000000	-1.145892
C	-0.043180	0.000000	-1.535678
O	-0.058701	0.000000	-2.736337
O	-1.295388	0.000000	-0.867927

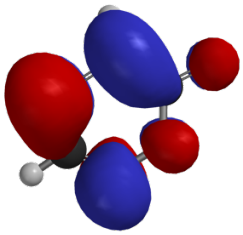
Representative molecular orbitals of pyrone **2p**



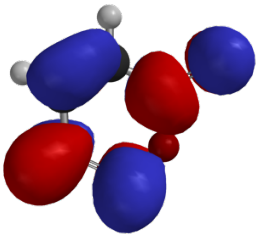
HOMO–1 –7.96 eV



HOMO –6.95 eV

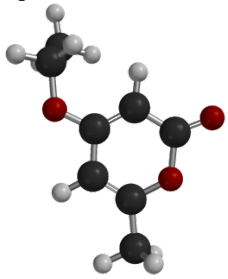


LUMO –2.17 eV



LUMO+1 –0.40 eV

Optimized structure of pyrone **2a**

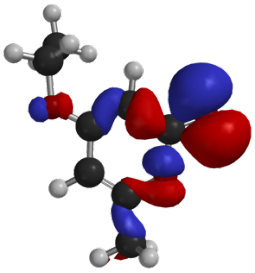


black: carbon, grey: hydrogen, red: oxygen

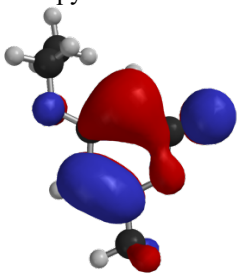
E = –536.693574 hartrees
G = –536.560297 hartrees

C	0.199667	-2.072265	0.788281
C	-0.054362	-0.799254	1.162882
H	-0.413750	-0.567329	2.154259
C	0.169172	0.260089	0.221423
C	0.628218	-0.025277	-1.036196
H	0.811190	0.722677	-1.791948
C	0.904627	-1.378085	-1.433355
O	1.314687	-1.767029	-2.496900
O	0.657898	-2.370755	-0.446086
O	-0.103684	1.484495	0.706663
C	0.078434	2.654338	-0.118414
H	0.193605	3.465677	0.600802
H	1.013951	2.563933	-0.676813
C	-1.111918	2.907086	-1.030932
H	-1.249600	2.099689	-1.751725
H	-0.953286	3.835125	-1.587794
H	-2.027541	3.011269	-0.444767
C	0.022533	-3.286169	1.638239
H	0.973160	-3.816020	1.741547
H	-0.685466	-3.975408	1.167787
H	-0.345191	-3.017442	2.628980

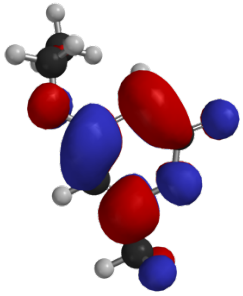
Representative molecular orbitals of pyrone **2a**



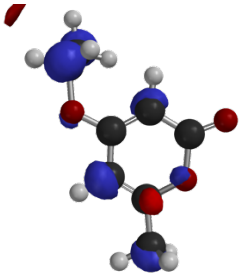
HOMO–1 –7.60 eV



HOMO –6.48 eV

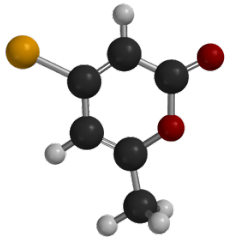


LUMO –1.40 eV



LUMO+1 –0.16 eV

Optimized structure of pyrone **2b**

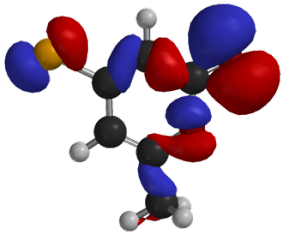


black: carbon, grey: hydrogen, red: oxygen, orange: bromine

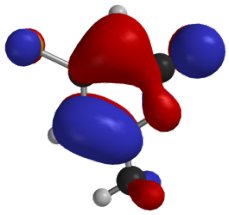
E = –2956.341452 hartrees

C	-0.744107	0.000000	0.216629
C	0.344084	0.000000	1.025960
H	0.231850	0.000000	2.099030
C	1.631613	0.000000	0.411213
C	1.785720	0.000000	-0.935399
H	2.750678	0.000000	-1.420422
C	0.625048	0.000000	-1.799157
O	0.602796	0.000000	-2.999269
O	-0.624736	0.000000	-1.126449
Br	3.159872	0.000000	1.551230
C	-2.166510	0.000000	0.666734
H	-2.228063	0.000000	1.754699
H	-2.684123	-0.881241	0.277600
H	-2.684123	0.881241	0.277600

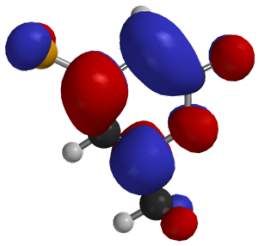
Representative molecular orbitals of pyrone **2b**



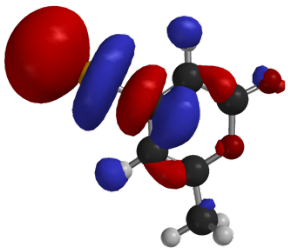
HOMO–1 –8.06 eV



HOMO –6.97 eV

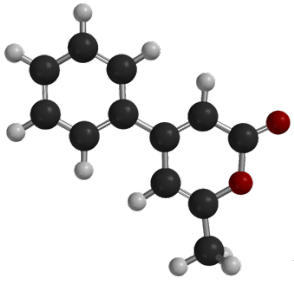


LUMO –2.24 eV



LUMO+1 –1.00 eV

Optimized structure of pyrone **2c**

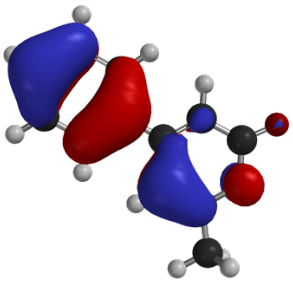


black: carbon, grey: hydrogen, red: oxygen

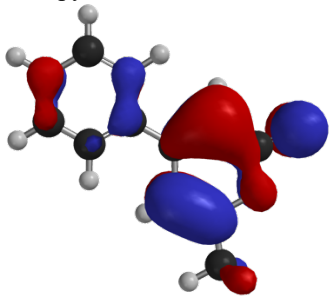
E = –613.911799 hartrees

C	-2.533536	0.000000	-0.787808
C	-1.447422	0.000000	0.018846
H	-1.612076	0.000000	1.084111
C	-0.120485	0.000000	-0.544714
C	-0.019061	0.000000	-1.909351
H	0.926870	0.000000	-2.429300
C	-1.165752	0.000000	-2.782488
O	-1.170709	0.000000	-3.986815
O	-2.420805	0.000000	-2.132896
C	-3.957925	0.000000	-0.340053
H	-4.022942	0.000000	0.747947
H	-4.476186	-0.880980	-0.729357
H	-4.476186	0.880980	-0.729357
C	1.078247	0.000000	0.339298
C	3.351907	0.000000	2.016798
C	2.379356	0.000000	-0.194145
C	0.953664	0.000000	1.738170
C	2.073402	0.000000	2.565986
C	3.497806	0.000000	0.629848
H	2.530206	0.000000	-1.265136
H	-0.023148	0.000000	2.201510
H	1.942439	0.000000	3.642089
H	4.487489	0.000000	0.187455
H	4.224845	0.000000	2.659364

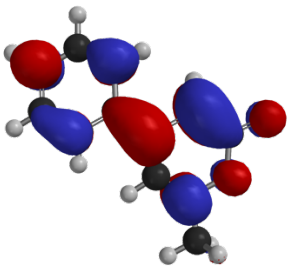
Representative molecular orbitals of pyrone **2c**



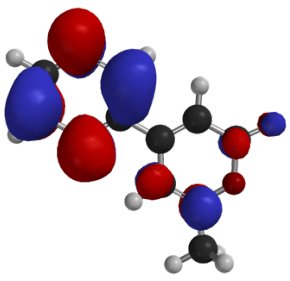
HOMO–1 –7.35 eV



HOMO –6.49 eV

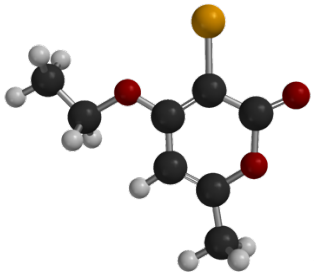


LUMO –2.35 eV



LUMO+1 –1.03 eV

Optimized structure of pyrone **2g**

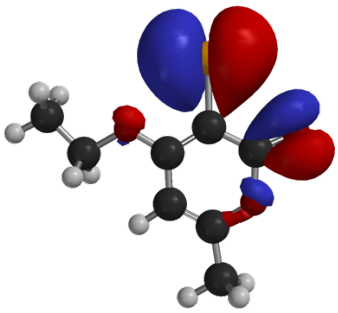


black: carbon, grey: hydrogen, red: oxygen, orange: bromine

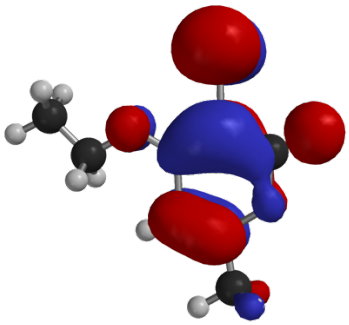
E = –3110.224302 hartrees

C	0.480282	-1.982743	-0.411666
C	0.169283	-0.808690	0.189306
H	0.067670	-0.773082	1.262294
C	-0.021482	0.360921	-0.618385
C	0.117871	0.265629	-1.984436
C	0.445617	-0.975614	-2.636473
O	0.585331	-1.207330	-3.804242
O	0.616849	-2.076433	-1.742659
O	-0.336835	1.554241	-0.096374
C	-0.478134	1.724334	1.328118
H	-1.251200	1.044490	1.700733
H	0.471548	1.482549	1.816693
C	-0.863563	3.170004	1.568653
H	-1.809618	3.404006	1.077245
H	-0.096037	3.843630	1.183057
H	-0.975231	3.347083	2.641562
C	0.705739	-3.285078	0.282391
H	1.706619	-3.662965	0.056224
H	-0.011939	-4.029885	-0.073340
H	0.600540	-3.175809	1.361706
Br	-0.123310	1.780741	-3.100407

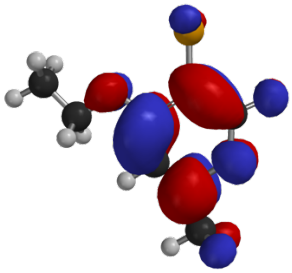
Representative molecular orbitals of pyrone **2g**



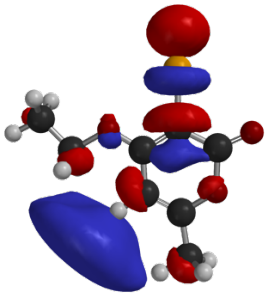
HOMO–1 –7.69 eV



HOMO –6.28 eV

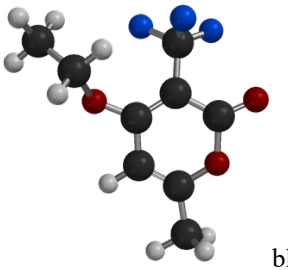


LUMO –1.76 eV



LUMO+1 –0.53 eV

Optimized structure of pyrone **2i**

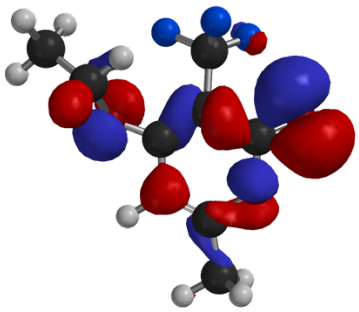


black: carbon, grey: hydrogen, red: oxygen, blue: fluorine

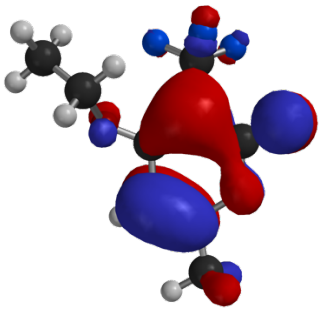
E = –873.823675 hartrees

C	2.347185	0.603480	0.646130
C	1.209897	0.020494	1.087050
H	1.089429	-0.263005	2.122174
C	0.130455	-0.220112	0.178330
C	0.282167	0.084806	-1.161776
C	1.453564	0.827202	-1.603956
O	1.657365	1.310220	-2.681554
O	2.474907	0.991261	-0.635303
O	-0.945740	-0.795544	0.745068
C	-2.262866	-0.177137	0.645556
H	-2.328665	0.538178	1.471616
H	-2.353461	0.368538	-0.292673
C	-3.312340	-1.259614	0.770887
H	-3.183203	-1.819974	1.699583
H	-3.257351	-1.952179	-0.069532
H	-4.305342	-0.803266	0.780856
C	3.554946	0.912033	1.463837
H	3.746486	1.989195	1.460709
H	4.433969	0.423749	1.032190
H	3.424610	0.573953	2.491359
C	-0.694932	-0.291257	-2.243236
F	-1.525225	0.731593	-2.586072
F	-1.499210	-1.316264	-1.865052
F	-0.081230	-0.692841	-3.366316

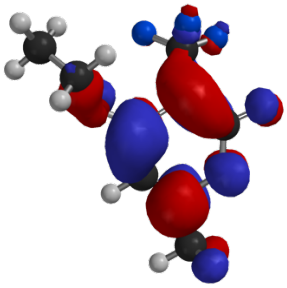
Representative molecular orbitals of pyrone **2i**



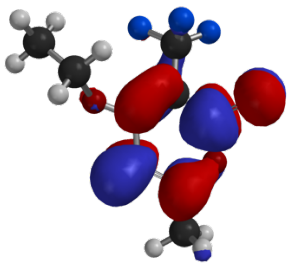
HOMO–1 –8.11 eV



HOMO –7.08 eV

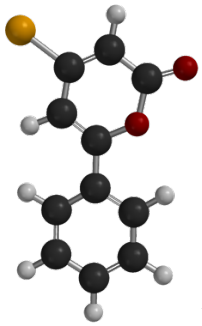


LUMO –2.24 eV



LUMO+1 –0.56 eV

Optimized structure of pyrone **2j**

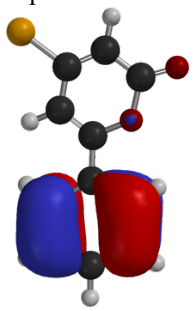


black: carbon, grey: hydrogen, red: oxygen, orange: bromine

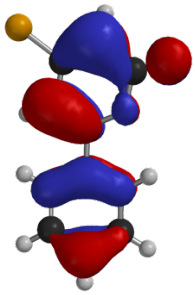
E = –3148.123749 hartrees

C	0.236884	0.000000	0.729832
C	-0.568283	0.000000	1.830448
H	-1.641477	0.000000	1.738521
C	0.046443	0.000000	3.111916
C	1.394295	0.000000	3.272786
H	1.876156	0.000000	4.239151
C	2.254880	0.000000	2.113123
O	3.455435	0.000000	2.084449
O	1.580283	0.000000	0.866440
Br	-1.097105	0.000000	4.638868
C	-0.207198	0.000000	-0.674100
C	-1.024289	0.000000	-3.359141
C	-1.571939	0.000000	-1.007829
C	0.740369	0.000000	-1.709830
C	0.331587	0.000000	-3.039560
C	-1.974197	0.000000	-2.336910
H	-2.329123	0.000000	-0.233501
H	1.793948	0.000000	-1.465030
H	1.076322	0.000000	-3.827260
H	-3.031370	0.000000	-2.576551
H	-1.341620	0.000000	-4.395823

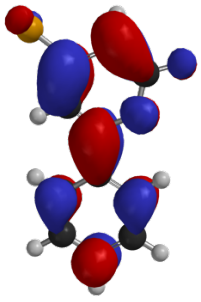
Representative molecular orbitals of pyrone **2j**



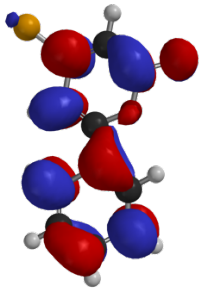
HOMO–1 –7.66 eV



HOMO –6.67 eV

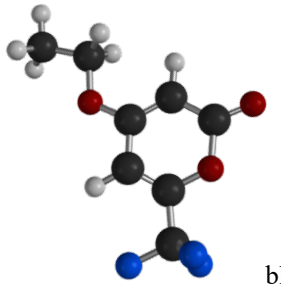


LUMO –2.63 eV



LUMO+1 –1.29 eV

Optimized structure of pyrone **2m**

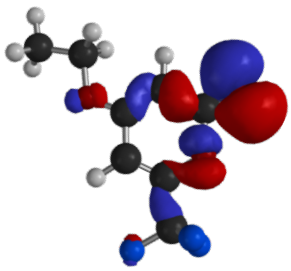


black: carbon, grey: hydrogen, red: oxygen, blue: fluorine

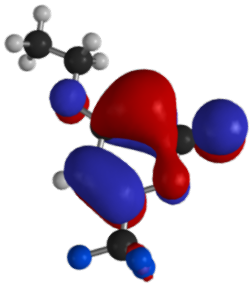
E = –834.504047 hartrees
G = –834.396158 hartrees

C	0.427051	-2.211226	0.230186
C	0.127993	-1.027101	0.789747
H	-0.003550	-0.916747	1.855186
C	-0.016799	0.106824	-0.086224
C	0.149508	-0.045337	-1.434111
H	0.051325	0.767827	-2.136700
C	0.471129	-1.323857	-2.015419
O	0.642267	-1.589429	-3.171117
O	0.599231	-2.402244	-1.082762
O	-0.313154	1.249796	0.545989
C	-0.490011	2.455301	-0.228717
H	0.425044	2.644340	-0.799560
H	-1.314910	2.301938	-0.932006
C	-0.783767	3.583654	0.737140
H	0.043091	3.720901	1.436705
H	-1.693471	3.382963	1.306704
H	-0.923252	4.514150	0.181120
C	0.607641	-3.494256	1.011568
F	1.843074	-3.999838	0.843886
F	0.425153	-3.285875	2.330198
F	-0.273592	-4.431783	0.618187

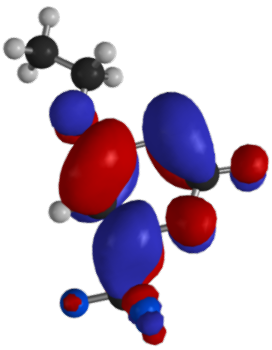
Representative molecular orbitals of pyrone **2m**



HOMO–1 –8.24 eV



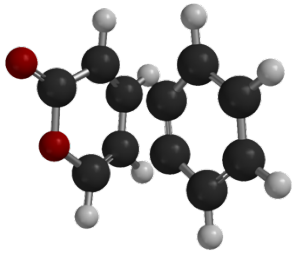
HOMO –7.24 eV



LUMO –2.25 eV

LUMO+1 –0.72 eV

Transition state structure **TS1A**

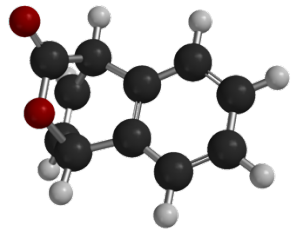


black: carbon, grey: hydrogen, red: oxygen

E = –574.433375 hartrees
G = –574.312383 hartrees
Imaginary frequency: *i* 193 cm^{-1}

H	-2.996472	1.031529	0.236446
C	-1.975622	1.253715	-0.052521
C	0.731690	1.848966	-0.867126
C	-0.902862	0.377938	0.029542
C	-1.614982	2.511564	-0.571025
C	-0.300348	2.801419	-0.966221
C	0.279295	0.657403	-0.333040
H	-2.377271	3.277952	-0.670552
H	-0.070231	3.785066	-1.363290
H	1.743718	2.063253	-1.188384
C	-0.731602	-2.150013	0.541988
H	-1.777808	-2.427009	0.558832
C	0.010083	-1.872128	1.662483
H	-0.472156	-1.857876	2.630187
C	1.339851	-1.466880	1.477684
H	1.943504	-1.156148	2.322482
C	1.813897	-1.310073	0.195250
H	2.809404	-0.939212	-0.009185
O	-0.173655	-2.360175	-0.662738
C	1.140641	-1.933940	-0.936199
O	1.580925	-2.135352	-2.034614

Optimized structure of cycloadduct **IV**



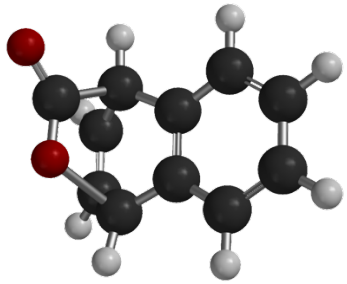
black: carbon, grey: hydrogen, red: oxygen

E = –574.562903 hartrees
G = –574.43372 hartrees

H	-1.852442	-0.251693	-2.275583
C	-1.683302	-0.152806	-1.208579
C	-1.245387	0.147523	1.554950
C	-0.398812	-0.031555	-0.702375
C	-2.762421	-0.137815	-0.317190
C	-2.544539	0.013230	1.049908
C	-0.177523	0.106901	0.671874
H	-3.773756	-0.234558	-0.695039
H	-3.387739	0.028814	1.731107
H	-1.079958	0.273139	2.619523
C	0.906203	0.004837	-1.470803
H	0.793240	0.015091	-2.550970
C	1.305771	0.221391	1.002760

H	1.515022	0.373356	2.057870
O	1.549219	1.294244	-1.136213
C	1.792067	1.441687	0.190716
C	1.805920	-1.093804	-0.931181
H	2.213741	-1.862894	-1.573415
C	2.029539	-0.968594	0.375161
H	2.673021	-1.605589	0.967856
O	2.322134	2.419095	0.639623

Transition state structure **TS2A**

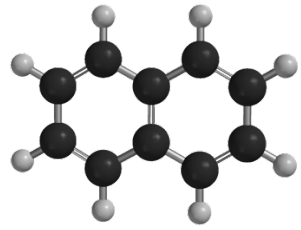


black: carbon, grey: hydrogen, red: oxygen

E = –574.536876 hartrees
G = –574.411400 hartrees
Imaginary frequency: *i* 544 cm^{-1}

H	-1.892428	-0.291147	-2.286026
C	-1.721935	-0.181768	-1.220547
C	-1.253308	0.166949	1.531285
C	-0.419803	-0.224528	-0.709239
C	-2.786339	-0.011139	-0.345511
C	-2.549612	0.160764	1.024710
C	-0.179676	-0.048347	0.666316
H	-3.801989	0.003491	-0.723272
H	-3.387786	0.300250	1.698244
H	-1.077082	0.330583	2.588511
C	0.785080	-0.360782	-1.505212
H	0.709621	-0.226909	-2.578630
C	1.255573	0.032277	1.026578
H	1.462532	0.197167	2.078522
O	1.522150	1.445781	-1.024256
C	1.720896	1.499384	0.217774
C	1.863706	-1.142268	-0.971840
H	2.529150	-1.689089	-1.627015
C	2.100377	-0.954629	0.351049
H	2.971422	-1.361568	0.851052
O	2.149452	2.355528	0.957508

Optimized structure of naphthalene



black: carbon, grey: hydrogen

E = –385.988787 hartrees
G = –385.871853 hartrees

H	3.372939	0.001267	-1.242475
C	2.430023	0.000251	-0.707618
H	1.243197	0.000646	-2.486396

C	1.243811	0.000398	-1.401298
C	1.243811	-0.000398	1.401298
C	0.000000	0.000000	-0.715503
C	2.430023	-0.000251	0.707618
C	0.000000	0.000000	0.715503
C	-1.243811	-0.000398	-1.401298
H	3.372939	-0.001267	1.242475
H	-1.243197	0.000646	2.486396
H	1.243197	-0.000646	2.486396
C	-2.430023	-0.000251	-0.707618
H	-1.243197	-0.000646	-2.486396
H	-3.372939	-0.001267	-1.242475
C	-2.430023	0.000251	0.707618
H	-3.372939	0.001267	1.242475
C	-1.243811	0.000398	1.401298

Optimized structure of carbon dioxide

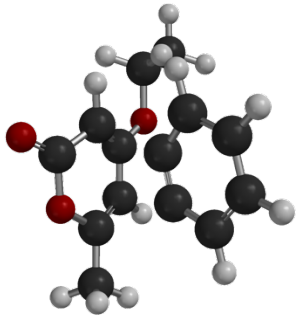
black: carbon, red: oxygen

E = –188.646921 hartrees

G = –188.655928 hartrees

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	-1.160871
O	0.000000	0.000000	1.160871

Transition state structure **TS1B**



black: carbon, grey: hydrogen, red: oxygen

E = –767.659787 hartrees

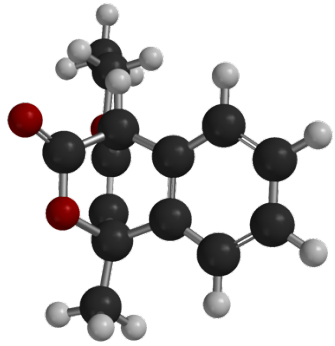
G = –767.455306 hartrees

Imaginary frequency: *i* 226 cm^{-1}

H	-3.645860	1.578664	-0.438038
C	-2.609895	1.719432	-0.729761
C	0.114087	2.111426	-1.551913
C	-1.621330	0.744316	-0.624028
C	-2.172639	2.944222	-1.261698
C	-0.842535	3.137282	-1.662622
C	-0.422251	0.964091	-1.002790
H	-2.881107	3.759986	-1.369203
H	-0.542531	4.095805	-2.073530
H	1.137466	2.246075	-1.882212
C	-1.413114	-1.890527	-0.069436
C	-0.559598	-1.569642	0.954790
H	-0.910807	-1.559205	1.977009
C	0.713339	-1.070990	0.632006
C	1.009933	-0.841714	-0.711923

H	1.965798	-0.455581	-1.032292
O	-0.966687	-2.057597	-1.335286
C	0.290428	-1.581657	-1.733871
O	0.644925	-1.800579	-2.860691
C	-2.821851	-2.357006	0.096971
H	-2.864500	-3.449114	0.026373
H	-3.444507	-1.946543	-0.699125
H	-3.218589	-2.047824	1.063860
O	1.497791	-0.698479	1.659057
C	2.820934	-0.205433	1.368600
H	2.739106	0.708703	0.772296
H	3.354801	-0.960431	0.781359
C	3.523697	0.066898	2.682361
H	4.536539	0.427037	2.481549
H	3.593805	-0.841371	3.284370
H	2.995153	0.829756	3.257817

Optimized structure of cycloadduct **V**



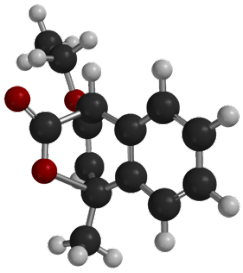
black: carbon, grey: hydrogen, red: oxygen

E = –767.776006 hartrees
G = –767.564118 hartrees

H	2.686160	2.683847	-0.030838
C	2.538591	1.624561	-0.206352
C	2.185783	-1.120106	-0.694201
C	1.267024	1.100852	-0.381527
C	3.642693	0.764226	-0.261602
C	3.469514	-0.594665	-0.506049
C	1.095025	-0.268633	-0.612094
H	4.640495	1.163835	-0.120024
H	4.331074	-1.250746	-0.552758
H	2.048941	-2.177633	-0.894110
C	-0.067317	1.840801	-0.377829
C	-0.369572	-0.642414	-0.783455
H	-0.528046	-1.687716	-1.025966
O	-0.656935	1.545217	-1.733771
C	-0.865986	0.234849	-1.957732
C	-0.966870	1.182774	0.647874
H	-1.436890	1.749694	1.439032
C	-1.142361	-0.126499	0.433725
O	-1.365458	-0.186155	-2.966377
C	-0.007913	3.349239	-0.282641
H	-1.014473	3.763088	-0.360631
H	0.602759	3.766618	-1.084773
H	0.417043	3.645963	0.679375
O	-1.969165	-0.893194	1.178602
C	-2.074747	-2.307334	0.934662
H	-1.089618	-2.774119	1.044526
H	-2.433319	-2.479030	-0.085795
C	-3.050334	-2.867857	1.950413

H	-4.029849	-2.397294	1.844548
H	-2.691322	-2.697819	2.967606
H	-3.164929	-3.944351	1.798161

Transition state structure **TS2B**

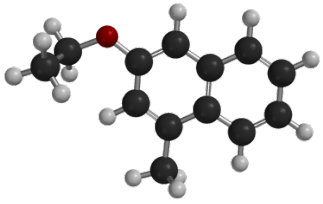


black: carbon, grey: hydrogen, red: oxygen

E = –767.763286 hartrees
G = –767.554593 hartrees
Imaginary frequency: *i* 345 cm^{-1}

H	-2.963313	-0.270547	-2.537619
C	-2.790936	-0.074438	-1.483542
C	-2.355639	0.465350	1.238847
C	-1.490337	0.009385	-0.980555
C	-3.872362	0.082696	-0.614860
C	-3.655544	0.349064	0.739886
C	-1.274605	0.278902	0.380835
H	-4.886289	0.003632	-0.996577
H	-4.501893	0.471956	1.409992
H	-2.186308	0.694204	2.287927
C	-0.249392	-0.144689	-1.767295
C	0.160335	0.476503	0.742155
H	0.319544	0.698152	1.792903
O	0.386134	1.723485	-1.364289
C	0.634655	1.819185	-0.119410
C	0.807204	-0.883355	-1.143929
H	1.537676	-1.425699	-1.734193
C	1.034603	-0.579945	0.172512
O	1.160868	2.707682	0.533198
C	-0.306743	-0.068071	-3.264258
H	0.698972	-0.047733	-3.690446
H	-0.842049	0.830657	-3.579815
H	-0.834376	-0.944584	-3.663475
O	2.117360	-1.058099	0.801789
C	2.539403	-0.431801	2.036648
H	1.768731	-0.585772	2.802121
H	2.648952	0.644881	1.862835
C	3.850666	-1.069378	2.451441
H	4.608473	-0.945226	1.671585
H	3.722593	-2.138567	2.649200
H	4.213616	-0.587829	3.366388

Optimized structure of naphthalene **11a**

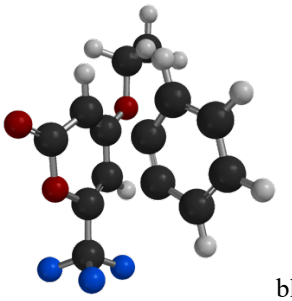


black: carbon, grey: hydrogen, red: oxygen

E = –579.197342 hartrees
G = –578.999027 hartrees

H	3.818800	-0.172519	3.316818
C	2.861335	-0.186847	2.807769
H	3.725084	-0.064775	0.856672
C	2.810186	-0.127162	1.436858
C	0.448528	-0.285302	2.924976
C	1.566716	-0.145812	0.746583
C	1.667542	-0.266190	3.561474
C	0.355470	-0.227833	1.508405
C	1.508644	-0.088400	-0.663529
H	1.716094	-0.312817	4.643573
H	-0.456998	-0.346736	3.516436
C	0.295535	-0.113985	-1.315700
H	2.420347	-0.030383	-1.246754
C	-0.904883	-0.191368	-0.565676
H	-1.860437	-0.204551	-1.073052
C	-0.892091	-0.249502	0.813353
C	-2.196480	-0.330692	1.568541
H	-2.319076	0.515933	2.251340
H	-2.256460	-1.242741	2.170835
H	-3.043967	-0.329615	0.880931
O	0.340492	-0.071698	-2.682253
C	-0.860858	-0.125613	-3.458483
H	-0.530426	-0.480751	-4.436420
H	-1.541981	-0.879965	-3.050880
C	-1.538138	1.232684	-3.595046
H	-0.850366	1.956766	-4.037725
H	-1.870382	1.623563	-2.631148
H	-2.412231	1.146309	-4.247898

Transition state structure **TS1C**



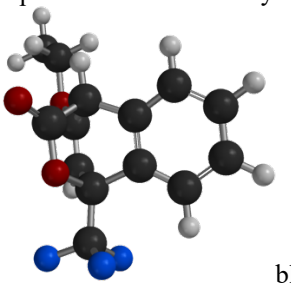
black: carbon, grey: hydrogen, red: oxygen, blue: fluorine

E = –1065.467318 hartrees
G = –1065.288001 hartrees
Imaginary frequency: *i* 235 cm^{-1}

H	-3.658584	1.562196	-0.520565
C	-2.619184	1.715428	-0.787420
C	0.128942	2.125558	-1.550242
C	-1.623596	0.749510	-0.682759
C	-2.166854	2.948451	-1.287772
C	-0.829048	3.149632	-1.659850
C	-0.419320	0.968809	-1.032436
H	-2.872632	3.766209	-1.395060
H	-0.522935	4.114902	-2.049680
H	1.157616	2.265834	-1.859866
C	-1.383361	-1.848445	-0.081162
C	-0.538229	-1.560351	0.948239
H	-0.887434	-1.544188	1.969859
C	0.741504	-1.074603	0.610876
C	1.023539	-0.855536	-0.734817

H	1.971861	-0.459906	-1.066732
O	-0.977322	-2.047428	-1.346814
C	0.285585	-1.581307	-1.758772
O	0.625116	-1.798483	-2.886433
C	-2.800848	-2.342149	0.135153
O	1.523728	-0.711456	1.636649
C	2.838851	-0.178830	1.371044
H	2.735882	0.762945	0.822535
H	3.389558	-0.891328	0.747749
C	3.523694	0.034056	2.705433
H	4.526297	0.437469	2.542004
H	3.614643	-0.908445	3.249310
H	2.963761	0.740743	3.321418
F	-3.253418	-1.973677	1.349685
F	-3.649698	-1.873498	-0.788599
F	-2.848111	-3.692114	0.079026

Optimized structure of cycloadduct **VI**



black: carbon, grey: hydrogen, red: oxygen, blue: fluorine

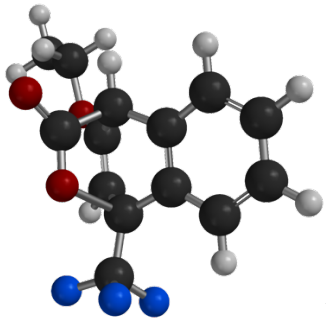
E = –1065.589122 hartrees

G = –1065.402904 hartrees

H	2.702856	2.677243	-0.034207
C	2.551278	1.620185	-0.208587
C	2.191702	-1.127905	-0.690615
C	1.280026	1.094531	-0.387212
C	3.650455	0.755333	-0.258955
C	3.475264	-0.603447	-0.500997
C	1.102451	-0.274906	-0.613521
H	4.647915	1.154132	-0.115542
H	4.335681	-1.261156	-0.543881
H	2.052664	-2.185493	-0.887170
C	-0.074008	1.803443	-0.398451
C	-0.362289	-0.654827	-0.782993
H	-0.515864	-1.701650	-1.021174
O	-0.654655	1.534490	-1.733942
C	-0.863679	0.212877	-1.957189
C	-0.967226	1.172065	0.647306
H	-1.425357	1.743592	1.440005
C	-1.133317	-0.139374	0.437260
O	-1.362569	-0.196986	-2.965760
C	-0.035863	3.329547	-0.297718
O	-1.929540	-0.908808	1.204125
C	-2.083595	-2.314965	0.927431
H	-1.109880	-2.811186	1.002030
H	-2.471958	-2.447735	-0.087546
C	-3.052219	-2.870544	1.951790
H	-4.020610	-2.371942	1.876982
H	-2.667131	-2.733473	2.964378
H	-3.198588	-3.939819	1.777882
F	0.715008	3.886499	-1.261654
F	-1.265627	3.861371	-0.376726

F	0.488677	3.698910	0.894650

Transition state structure **TS2C**

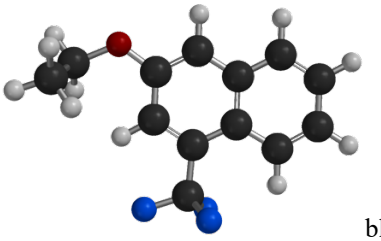


black: carbon, grey: hydrogen, red: oxygen, blue: fluorine

E = –1065.570167 hartrees
G = –1065.386433 hartrees
Imaginary frequency: *i* 382 cm^{-1}

H	-2.976471	-0.344272	-2.489343
C	-2.789900	-0.111581	-1.449261
C	-2.325125	0.517381	1.249936
C	-1.486742	0.026389	-0.967946
C	-3.856085	0.039375	-0.565717
C	-3.626363	0.353685	0.774505
C	-1.255026	0.332075	0.381132
H	-4.870747	-0.081723	-0.926800
H	-4.464410	0.475030	1.451479
H	-2.147557	0.781181	2.286793
C	-0.238109	-0.099074	-1.740838
C	0.181505	0.562290	0.719542
H	0.352483	0.823956	1.757121
O	0.352975	1.768469	-1.429997
C	0.594819	1.904413	-0.190008
C	0.839799	-0.810420	-1.148003
H	1.579635	-1.327540	-1.742316
C	1.065400	-0.490283	0.166714
O	1.057553	2.836315	0.436061
C	-0.300978	-0.090140	-3.261599
O	2.150857	-0.956707	0.779845
C	2.517638	-0.485555	2.102883
H	1.721116	-0.750024	2.805432
H	2.622545	0.602378	2.073055
C	3.823715	-1.157875	2.469623
H	4.606744	-0.896930	1.754621
H	3.713191	-2.244285	2.487515
H	4.139107	-0.825239	3.462285
F	-1.056134	0.902860	-3.742911
F	0.918559	0.006092	-3.810279
F	-0.843996	-1.260242	-3.693525

Optimized structure of naphthalene **11m**



black: carbon, grey: hydrogen, red: oxygen, blue: fluorine

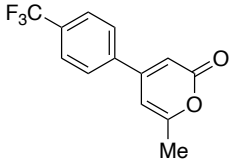
E = –877.01741 hartrees
G = –876.844247 hartrees

H	3.839217	-0.163801	3.301701
C	2.879247	-0.181386	2.798115
H	3.727649	-0.061218	0.840091
C	2.819036	-0.124612	1.429253
C	0.463714	-0.285741	2.938604
C	1.569134	-0.147709	0.750785
C	1.689373	-0.262573	3.558299
C	0.362147	-0.230155	1.520834
C	1.508683	-0.092959	-0.658662
H	1.745485	-0.307727	4.639789
H	-0.431522	-0.348786	3.541954
C	0.301357	-0.122250	-1.323161
H	2.423015	-0.032656	-1.237760
C	-0.898496	-0.200015	-0.578482
H	-1.853610	-0.217717	-1.079656
C	-0.868164	-0.251900	0.798737
C	-2.184139	-0.324896	1.532253
O	0.350559	-0.083858	-2.684899
C	-0.853615	-0.125712	-3.464959
H	-0.520011	-0.471250	-4.444599
H	-1.534174	-0.884628	-3.065319
C	-1.527673	1.234783	-3.586207
H	-0.838939	1.962954	-4.020245
H	-1.864700	1.616587	-2.620286
H	-2.400235	1.154902	-4.241381
F	-2.363115	0.723650	2.374385
F	-3.245932	-0.324843	0.693600
F	-2.294290	-1.446481	2.287216

Characterization Data of New Compounds

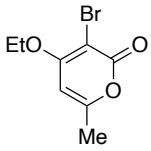
4-Hydroxy-6-phenyl-2*H*-pyrone (**1b**),[S11] 4-hydroxy-6-(4-methylphenyl)-2*H*-pyrone (**1c**),[S12] 6-(4-chlorophenyl)-4-hydroxy-2*H*-pyrone (**1d**),[S12] 4-ethoxy-6-methyl-2-pyrone (**2a**),[S4] 4-bromo-6-methyl-2-pyrone (**2a**), 6-methyl-4-ethoxy-2-pyrone (**2b**),[S5] 6-methyl-4-phenyl-2-pyrone (**2c**),[S6] 4-(4-chlorophenyl)-6-methyl-2-pyrone (**2d**),[S6] 4-(4-methoxyphenyloxy)-6-methyl-2-pyrone (**2f**),[S7] 3-iodo-4-ethoxy-6-methyl-2-pyrone (**2h**),[S4] 3-(trifluoromethyl)-4-ethoxy-6-methyl-2-pyrone (**2i**),[S4] 4-bromo-6-phenyl-2*H*-pyrone (**2j**),[S13] and 4-azido-6-methyl-2-pyrone (**2n**)[S10] were identical in spectra data with those reported in the literature.

6-Methyl-4-(4-(trifluoromethyl)phenyl)-2-pyrone (**2e**)



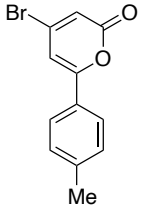
Colorless solid; Mp 138–140 °C; TLC R_f 0.35 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80–7.71 (AA'BB', 2H), 7.70–7.64 (AA'BB', 2H), 6.37 (d, 1H, J = 0.7 Hz), 6.28 (d, 1H, J = 0.7 Hz), 2.35 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 162.9, 162.8, 154.1, 139.4, 132.3 (q, $J_{C–F}$ = 32.8 Hz), 127.1, 126.1 (q, $J_{C–F}$ = 3.7 Hz), 123.7 (q, $J_{C–F}$ = 272 Hz), 109.4, 103.2, 20.2; ^{19}F{^{1}H} NMR ($CDCl_3$, 367 MHz): δ −62.9 (s); IR (NaCl, cm^{-1}) 1375, 1437, 1465, 1508, 1541, 1647, 1684, 1700, 1717; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_9FNaO_2^+$ 277.0453; Found 277.0452.

2-Bromo-3-ethoxy-6-methyl-2-pyrone (**2g**)



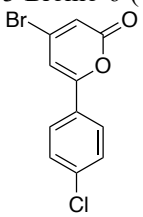
Off white solid; Mp 137–139 °C; TLC R_f 0.38 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.01 (q, 1H, J = 0.8 Hz), 4.21 (q, 2H, J = 7.0 Hz), 2.26 (d, 3H, J = 0.8 Hz), 1.46 (t, 3H, J = 7.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 166.3, 162.5, 161.0, 95.7, 88.4, 66.3, 20.2, 14.6; IR (NaCl, cm^{-1}) 816, 840, 993, 1007, 1059, 1226, 1319, 1455, 1531, 1721; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_8H_9{}^{79}BrNaO_3^+$ 254.9633; Found 254.9633.

3-Bromo-6-(4-methylphenyl)-2-pyrone (**2k**)



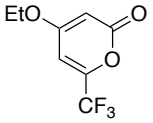
Orange solid; Mp 126–128 °C; TLC R_f 0.55 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74–7.68 (AA'BB', 2H), 7.31–7.23 (AA'BB', 2H), 6.79 (d, 1H, J = 1.6 Hz), 6.54 (d, 1H, J = 1.6 Hz), 2.41 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 160.3, 160.2, 142.4, 141.4, 129.8, 127.3, 125.9, 114.9, 105.3, 21.5; IR (NaCl, cm^{-1}) IR (NaCl, cm^{-1}) 844, 859, 1036, 1149, 1324, 1498, 1501, 1510, 1531, 1741, 1754; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_9{}^{79}BrO_2Na^+$ 286.9680; Found 286.9684.

3-Bromo-6-(4-chlorophenyl)-2-pyrone (**2l**)



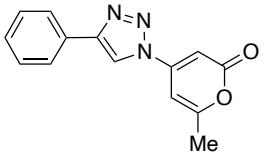
Colorless solid; Mp 150–152 °C; TLC R_f 0.53 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78–7.71 (AA'BB', 2H), 7.49–7.41 (AA'BB', 2H), 6.80 (d, 1H, J = 1.6 Hz), 6.59 (d, 1H, J = 1.6 Hz,); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 159.7, 158.9, 141.1, 140.0, 129.5, 128.6, 127.2, 115.8, 106.2; IR (NaCl, cm^{-1}) 823, 836, 1009, 1035, 1092, 1258, 1271, 1308, 1319, 1408, 1534, 1717; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_6{}^{79}Br{}^{35}ClO_2Na^+$ 306.9138; Found 306.9137.

3-Ethoxy-6-trifluoromethyl-2-pyrone (**2m**)



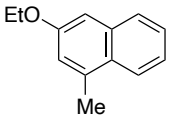
Yellow solid; Mp 46–48 °C; TLC R_f 0.50 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.43 (d, 1H, J = 2.2 Hz), 5.60 (d, 1H, J = 2.2 Hz), 4.07 (q, 2H, J = 7.0 Hz), 1.44 (t, 3H, J = 7.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 168.1, 161.1, 148.6 (q, $J_{C–F}$ = 39.7 Hz), 117.8 (q, $J_{C–F}$ = 273 Hz), 103.0 (q, $J_{C–F}$ = 3.6 Hz), 92.3, 65.6, 13.9; ^{19}F NMR ($CDCl_3$, 367 MHz): δ −71.7 (s); IR (NaCl, cm^{-1}) 1083, 1163, 1201, 1232, 1351, 1362, 1435, 1581, 1767, 1770; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_8H_7F_3O_3Na^+$ 231.0246; Found 231.0245.

6-Methyl-4-(4-phenyl-1*H*-1,2,3-triazol-lyl)-2-pyrone (**2o**)



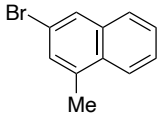
Colorless solid; Mp 206–208 °C;TLC R_f 0.50 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23–8.20 (m, 1H), 7.93–7.86 (AA'BB'C, 2H), 7.53–7.45 (AA'BB'C, 2H), 7.45–7.37 (AA'BB'C, 1H), 6.99–6.97 (m, 1H), 6.40 (s, 1H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 164.9, 162.4, 149.4, 148.4, 129.2, 129.1, 128.9, 126.1, 116.4, 97.7, 97.5, 20.5; IR (NaCl, cm^{-1}) 834, 1025, 1235, 1308, 1324, 1535, 1567, 1640, 1710, 1720; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{11}N_3O_2Na^+$ 276.0750; Found 276.0749.

2-Ethoxy-4-methylnaphthalene (**11a**)



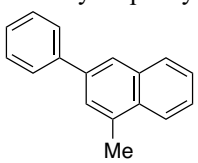
Colorless solid; Mp 59–61 °C; TLC R_f 0.43 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, 1H, J = 8.0 Hz), 7.72 (d, 1H, J = 8.0 Hz), 7.44 (ddd, 1H, J = 8.0, 8.0, 1.2 Hz), 7.37 (ddd, 1H, J = 8.0, 8.0, 1.4 Hz), 7.05–6.97 (m, 2H), 4.14 (q, 2H, J = 7.0 Hz), 2.65 (s, 3H), 1.48 (t, 3H, J = 7.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 156.4, 135.1, 134.9, 128.3, 127.3, 126.1, 124.0, 123.3, 119.6, 104.7, 63.2, 19.2, 14.8; IR (NaCl, cm^{-1}) 816, 1057, 1178, 1278, 1348, 1409, 1457, 1464, 1625, 2923; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{13}H_{14}O^{\cdot+}$ 186.1044; Found 186.1045.

2-Bromo-4-methylnaphthalene (**11b**)



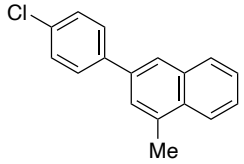
Colorless oil; TLC R_f 0.66 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (dd, 1H J = 7.7, 2.0 Hz), 7.87 (s, 1H), 7.75 (dd, 1H J = 7.7, 2.0 Hz), 7.57–7.46 (m, 2H), 7.42 (s, 1H), 2.67 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 136.6, 134.6, 131.1, 129.6, 128.2, 127.6, 126.6, 126.1, 124.2, 119.4, 19.1; IR (NaCl, cm^{-1}) 830, 880, 1095, 1143, 1203, 1262, 1372, 1412, 1585, 3057; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{10}H_9{}^{79}Br^{\cdot+}$ 219.9886; Found 219.9888.

4-Methyl-2-phenylnaphthalene (**11c**)



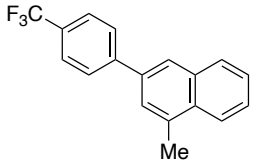
Colorless solid; Mp 65–67 °C; TLC R_f 0.50 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06–7.98 (m, 1H), 7.98–7.87 (AA'BB'C, 2H), 7.77–7.69 (AA'BB'C, 2H), 7.60–7.63 (m, 1H), 7.57–7.45 (m, 4H), 7.45–7.35 (AA'BB'C, 1H), 2.77 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 141.2, 138.2, 134.8, 133.8, 131.8, 128.81, 128.78, 127.4, 127.2, 126.3, 126.0, 125.8, 124.2, 124.0, 19.5; IR (NaCl, cm^{-1}) 847, 1076, 1179, 1303, 1491, 1598, 2726, 3054; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{17}H_{14}{}^{\cdot+}$ 218.1096; Found 218.1096.

2-(4-Chlorolphenyl)-4-methylnaphthalene (**11d**)



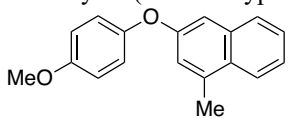
Colorless solid; Mp 58–60 °C; TLC R_f 0.48 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05–7.99 (m, 1H), 7.93–7.88 (m, 1H), 7.87 (s, 1H), 7.68–7.62 (AA'BB', 2H), 7.58–7.50 (m, 3H), 7.48–7.42 (AA'BB', 2H), 2.78 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 139.6, 136.9, 135.1, 133.7, 133.3, 131.9, 128.9, 128.8, 128.6, 126.1, 126.0, 125.9, 124.1, 124.0, 19.5; IR (NaCl, cm^{-1}) 877, 1092, 1378, 1457, 1497, 1517, 1558, 1684, 2952; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{17}H_{13}{}^{35}Cl^{\cdot+}$ 252.0705; Found 252.0706.

4-Methyl-2-(4-trifluoromethylphenyl)naphthalene (**11e**)



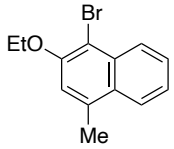
Colorless solid; Mp 59–61 °C; TLC R_f 0.50 (*n*-hexane) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08–8.00 (m, 1H), 8.06–7.88 (m, 2H), 7.87–7.70 (AA'BB', 4H), 7.62–7.56 (m, 3H), 2.78 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 144.7, 136.6, 135.3, 133.7, 132.2, 129.2 (q, $J_{C–F}$ = 33.2 Hz), 128.9, 127.6, 126.3, 126.3, 125.9, 125.7 (q, $J_{C–F}$ = 4.0 Hz), 124.8, 124.3 (q, $J_{C–F}$ = 272 Hz), 124.0, 19.5; ^{19}F{^{1}H} NMR ($CDCl_3$, 367 MHz): δ −62.3 (s); IR (NaCl, cm^{-1}) 836, 1075, 1130, 1168, 1325, 1376, 1458, 1508, 1560, 2925; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{18}H_{13}F_3O^{\cdot+}$ 286.0969; Found 286.0969.

4-Methyl-2-(4-methoxyphenyloxy)naphthalene (**11f**)



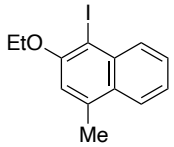
Colorless solid; Mp 62–64 °C; TLC R_f 0.55 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (dd, 1H, *J* = 7.3, 1.7 Hz), 7.67 (dd, 1H, *J* = 7.3, 1.7 Hz), 7.48–7.38 (m, 2H), 7.12 (s, 1H), 7.09–6.89 (m, 5H), 3.84 (s, 3H), 2.68 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 155.94, 155.91, 150.0, 136.7, 134.5, 129.0, 127.6, 126.2, 124.2, 124.0, 121.0, 119.9, 114.8, 110.4, 55.6, 19.4; IR (NaCl, cm^{-1}) 831, 973, 1126, 1216, 1398, 1441,1504, 1627, 2908, 2949; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{18}H_{16}O_2{}^{\cdot+}$ 264.1152; Found 264.1150.

1-Bromo-2-ethoxy-4-methylnaphthalene (**11g**)



Off white solid; Mp 60–62 °C; TLC R_f 0.35 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (dd, 1H, *J* = 8.1, 0.6 Hz), 7.92 (dd, 1H, *J* = 8.1, 0.6 Hz), 7.56 (ddd, 1H, *J* = 7.2, 7.2, 1.2 Hz), 7.42 (ddd, 1H, *J* = 7.2, 7.2, 1.2 Hz), 7.12 (q, 1H, *J* = 0.8 Hz), 4.25 (q, 2H, *J* = 7.0 Hz), 2.68 (d, 3H, *J* = 0.8 Hz), 1.51 (t, 3H, *J* = 7.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 152.7, 135.6, 133.1, 129.2, 127.3, 126.8, 124.3, 124.2, 116.5, 107.3, 65.9, 19.7, 15.1; IR (NaCl, cm^{-1}) 859, 933, 1032, 1073, 1146, 1219, 1271, 1344, 1455, 1505, 1615, 3069; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{13}H_{13}{}^{79}BrO^{\cdot+}$ 264.0150; Found 264.0150.

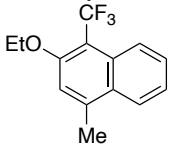
2-Ethoxy-1-iodo-4-methylnaphthalene (**11h**)



Yellow solid;Mp 78–80 °C; TLC R R_f 0.35 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): 8.19 (d, 1H, *J* = 8.4 Hz), 7.92 (d, 1H, *J* = 8.4 Hz), 7.56 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.41 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.06 (s, 1H), 4.24 (q, 2H, *J* = 7.0 Hz), 2.69 (s, 3H), 1.53 (t, 3H, *J* = 7.0 Hz);^{3}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 155.7, 137.6, 135.5, 131.9, 129.4, 127.8, 124.4, 124.3, 115.9, 86.3, 66.1, 19.7, 15.2; IR (NaCl, cm^{-1}) 821, 1032, 1057, 1070, 1142, 1212,

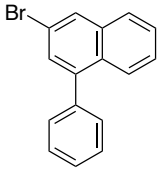
1235, 1268, 1341, 1455, 1504, 1595, 2727, 3062; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{13}H_{13}OI^{\cdot+}$ 312.0009; Found 312.0011.

2-Ethoxy-4-methyl-1-trifluoromethylnaphthalene (**11i**)



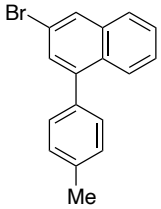
Colorless solid; Mp 86–88 °C; TLC R_f 0.35 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (d, 1H, J = 8.1 Hz), 7.96 (dd, 1H, J = 8.1, 1.1 Hz), 7.56 (ddd, 1H, J = 8.1, 8.1, 1.1 Hz), 7.45 (ddd, 1H, J = 8.1, 8.1, 1.1 Hz), 7.14 (s, 1H), 4.23 (q, 2H, J = 7.0 Hz), 2.71 (s, 3H), 1.47 (t, 3H J = 7.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 155.7 (q, $J_{C–F}$ = 1.7 Hz), 141.1, 131.2, 128.4, 127.6, 125.4 (q, $J_{C–F}$ = 276 Hz), 124.6 (q, $J_{C–F}$ = 5.0 Hz), 124.5, 124.1, 116.7, 109.9 (q, $J_{C–F}$ = 28.8 Hz), 66.2, 20.2, 15.0; ^{19}F{^{1}H} NMR ($CDCl_3$, 367 MHz): δ −51.9 (s); IR (NaCl, cm^{-1}) 1049, 1100, 1185, 1216, 1298, 1346, 1389, 1598, 1620; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{14}H_{13}F_3O^{\cdot+}$ 254.0917; Found 254.0918.

2-Bromo-4-phenylnaphthalene (**11j**)



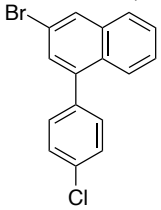
Colorless oil; TLC R_f 0.55 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, 1H, J = 1.8 Hz), 7.88–7.78 (m, 2H), 7.57–7.40 (m, 8H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 142.2, 139.2, 134.9, 130.2, 129.9, 129.4 (two signals overlapped), 128.4, 127.7, 127.4, 126.8, 126.3, 126.2, 119.2; IR (NaCl, cm^{-1}) 851, 964, 1030, 1126, 1283, 1369, 1445, 1571, 3056; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{16}H_{11}{}^{79}Br^{\cdot+}$ 282.0045; Found 282.0044.

2-Bromo-4-(4-methylphenyl)naphthalene (**11k**)



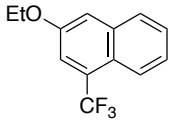
Colorless solid; Mp 46–48 °C; TLC R_f 0.55 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (s, 1H). 7.88 (d, 1H, J = 8.3 Hz) 7.81 (d, 1H, J = 8.3 Hz), 7.57–7.47 (m, 2H), 7.44 (dd, 1H, J = 7.0, 7.0 Hz), 7.40–7.27 (m, 4H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 142.3, 137.5, 136.3, 134.9, 130.3, 129.84, 129.76, 129.2, 129.1, 127.4, 126.7, 126.3, 126.2, 119.3, 21.2; IR (NaCl, cm^{-1}) 828, 1458, 1464, 1501, 1521, 1581, 2923, 2952; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{17}H_{13}{}^{79}Br^{\cdot+}$ 296.0199; Found 296.0201.

2-Bromo-4-(4-chlorophenyl)naphthalene (**11l**)



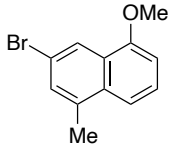
Colorless solid; Mp 111–113 °C; TLC R_f 0.50 (*n*-hexane);^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, 1H, J = 1.8 Hz), 7.85–7.75 (m, 2H), 7.56–7.37 (m, 7H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 140.9, 137.6, 134.9, 133.9, 131.2, 130.0, 129.9, 129.7, 128.6, 127.5, 127.0, 126.6, 125.8, 119.2; IR (NaCl, cm^{-1}) 833, 1395, 1457, 1507, 1540, 2726, 3055, 3546; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{16}H_{10}{}^{79}Br^{35}Cl^{\cdot+}$ 300.9146; Found 300.9147.

2-Bromo-4-(trifluoromethyl)naphthalene (**11m**)



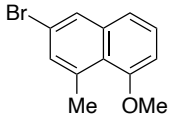
Colorless solid; Mp 73–75 °C; TLC R_f 0.40 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, 1H, J = 7.6 Hz), 7.78 (d, 1H, J = 7.6 Hz), 7.55 (d, 1H, J = 2.3 Hz), 7.52 (ddd, 1H, J = 7.6, 7.6, 1.2 Hz), 7.46 (ddd, 1H, J = 7.6, 7.6, 1.2 Hz), 7.27 (d, 1H, J = 2.3 Hz), 4.17 (q, 2H, J = 7.0 Hz), 1.50 (t, 3H, J = 7.0 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 155.1, 135.4, 127.5 (q, $J_{C–F}$ = 30.4 Hz), 127.5, 127.0, 125.6, 125.0, 124.2 (q, $J_{C–F}$ = 274 Hz), 124.2 (q, $J_{C–F}$ = 2.0 Hz), 124.1, 118.5 (q, $J_{C–F}$ = 6.0 Hz), 63.9, 14.7; IR (NaCl, cm^{-1}) 1130, 1160, 1259, 1364, 1464, 1521, 1560, 3648; ^{19}F{^{1}H} NMR ($CDCl_3$, 367 MHz): δ −60.1 (s); HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{13}H_{11}F_3O^{\cdot+}$ 240.0762; Found 240.0762.

2-Bromo-4-methyl-8-methoxynaphthalene (**11n**)



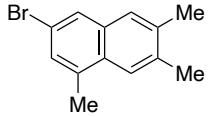
Colorless solid; Mp 78–80 °C; TLC R_f 0.38 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (d, 1H, J = 2.0 Hz), 7.52 (dd, 1H, J = 7.7, 7.7 Hz), 7.47–7.39 (m, 2H), 6.85 (d, 1H, J = 7.7 Hz), 3.99 (s, 3H), 2.64 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 154.9, 136.2, 132.1, 130.2, 126.7, 126.1, 122.7, 118.9, 116.4, 104.6, 55.6, 19.5; IR (NaCl, cm^{-1}) 1364, 1438, 1490, 1517, 1560, 2853, 2923, 2952; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{12}H_{11}{}^{79}BrO^{\cdot+}$ 249.9993; Found 249.9993.

2-Bromo-4-methyl-5-methoxynaphthalene (**11n'**)



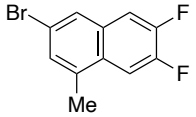
Colorless solid; Mp 59–61 °C; TLC R R_f 0.45 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, 1H, J = 2.0 Hz), 7.35 (dd, 1H, J = 7.7, 7.7 Hz), 7.31–7.29 (m, 2H), 6.80 (dd, 1H, J = 7.7, 0.8 Hz), 3.91 (s, 3H), 2.85 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 158.1, 137.9, 137.1, 130.9, 127.9, 126.7, 123.7, 120.3, 119.8, 105.4, 55.3, 25.0; IR (NaCl, cm^{-1}) 846, 1085, 1129, 1339, 1435, 1507, 1574, 2932, 2959; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{12}H_{11}{}^{79}BrO^{\cdot+}$ 249.9991; Found 249.9993.

2-Bromo-4,6,7-trimethylnaphthalene (**11o**)



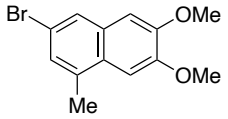
Colorless solid; Mp 74–76 °C; TLC R_f 0.55 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, 1H J = 1.0 Hz), 7.67 (s, 1H), 7.48 (s, 1H), 7.31 (d, 1H, J = 1.0 Hz), 2.62 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 136.4, 135.8, 135.7, 133.5, 129.9, 128.7, 127.2, 127.1, 123.8, 118.3, 20.5, 20.0, 19.1; IR (NaCl, cm^{-1}) 889, 1339, 1395, 1459, 1497, 1521, 1587, 2923; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{13}H_{13}{}^{79}Br^{\cdot+}$ 248.0201; Found 248.0201.

1-Bromo-6,7-difluoro-4-methylnaphthalene (**11p**)



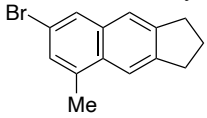
Colorless solid; Mp 68–70 °C; TLC R_f 0.55 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, 1H, J = 0.7 Hz), 7.65 (dd, 1H, J = 8.0, 3.4 Hz), 7.46 (dd, 1H, J = 8.0, 3.4 Hz), 7.41 (d, 1H, J = 0.7 Hz), 2.61 (s, 3H,); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 150.2 (dd, $J_{C–F}$ = 252, 15.2 Hz), 149.8 (dd, $J_{C–F}$ = 250, 15.0 Hz), 136.1 (d, $J_{C–F}$ = 7.3 Hz), 131.5 (d, $J_{C–F}$ = 7.3 Hz), 129.9, 128.2 (dd, $J_{C–F}$ = 1.3, 1.3 Hz), 127.4 (dd, $J_{C–F}$ = 1.3, 1.3 Hz), 119.9, 113.3 (d, $J_{C–F}$ = 17.1 Hz), 110.8 (d, $J_{C–F}$ = 17.1 Hz), 19.3; ^{19}F{^{1}H} NMR ($CDCl_3$, 367 MHz): δ −135.5 (d, J = 21.0 Hz), −136.2 (d, J = 21.0 Hz); IR (NaCl, cm^{-1}) 883, 1142, 1261, 1341, 1422, 1497, 1521, 1594, 2726, 2952; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{11}H_7{}^{79}BrF_2{}^{\cdot+}$ 255.9698; Found 255.9699.

2-Bromo-4-methyl-6,7-dimethoxynaphthalene (**11q**)



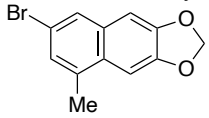
Colorless solid; Mp 89–91 °C; TLC R_f 0.45 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, 1H, J = 1.6 Hz), 7.29 (d, 1H, J = 1.6 Hz), 7.13 (s, 1H), 7.02 (s, 1H), 4.02 (s, 3H), 3.99 (s, 3H), 2.60 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 149.8, 149.4, 134.9, 130.5, 128.0, 126.7, 126.6, 117.4, 106.1, 102.9, 55.9, 55.8, 19.4; IR (NaCl, cm^{-1}) 857, 1065, 1155, 1245, 1362, 1458, 1508, 2923, 2950; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{13}H_{13}{}^{79}BrO_2{}^{\cdot+}$ 280.0099; Found 280.0098.

6-Bromo-2,3-dihydro-8-methyl-1*H*-benz[*f*]indene (**11r**)



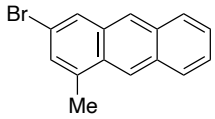
Off white solid; Mp 50–52 °C; TLC R_f 0.55 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (s, 1H+1H), 7.55 (s, 1H), 7.32 (s, 1H), 3.10–3.01 (m, 4H), 2.63 (s, 3H), 2.20–2.10 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 144.2, 143.9, 135.9, 134.0, 130.5, 128.6, 127.8, 121.9, 118.6, 118.2, 32.9, 32.5, 26.1, 19.3; IR (NaCl, cm^{-1}) 880, 1339, 1419, 1490, 1507, 1541, 2923, 2952; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{14}H_{13}{}^{79}Br^{\cdot+}$ 260.0202; Found 260.0201.

6-Bromo-8-methylnaphtho[2,3-*d*]-1,3-dioxol (**11s**)



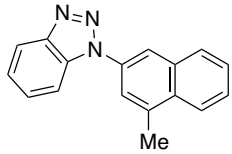
Colorless solid; Mp 104–106 °C; TLC R_f 0.25 (*n*-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, 1H, J = 1.1 Hz) 7.28 (d, 1H, J = 1.1 Hz), 7.20 (s, 1H), 7.01 (s, 1H), 6.05 (s, 2H), 2.55 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 147.90, 147.88, 135.4, 131.8, 128.2, 128,1, 127.2, 117.7, 103.6, 101.3, 100.8, 19.6; IR (NaCl, cm^{-1}) 867, 942, 1045, 1235, 1438, 1508, 2953; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{12}H_9{}^{79}BrO^{2\cdot+}$ 260.0202; Found 260.0201.

2-Bromo-4-methylanthracene (**11t**)



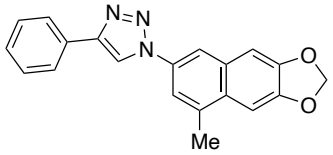
Colorless solid; Mp 66–68 °C; TLC R_f 0.53 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.49 (s, 1H), 8.31 (s, 1H), 8.06–7.96 (m, 3H), 7.53–7.46 (m, 2H), 7.38 (s, 1H), 2.79 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 136.6, 132.5, 131.9, 131.6, 129.6, 128.8, 128.5, 128.2, 127.9, 126.0, 125.9, 125.7, 123.2, 119.1, 19.5; IR (NaCl, cm^{-1}) 1364, 1424, 1508, 1534, 1684, 1740, 1772, 2727; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{15}H_{11}{}^{79}Br^{\cdot+}$ 270.0046; Found 270.0044.

2-(1*H*-Benzotriazol-1-yl)-4-methylnaphthalene (**12**)



Colorless solid; Mp 94–96 °C; TLC R_f 0.48 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19 (d, 1H, J = 8.4 Hz), 8.14–8.05 (m, 2H), 8.01–7.94 (m, 1H), 7.86 (d, 1H, J = 8.4 Hz), 7.81 (s, 1H), 7.68–7.56 (m, 3H), 7.51–7.44 (m, 1H), 2.84 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 146.5, 137.3, 134.0, 133.5, 132.5, 132.2, 128.9, 128.2, 127.1, 126.9, 124.4, 124.3, 121.8, 120.4, 119.1, 110.6, 19.6; IR (NaCl, cm^{-1}) 876, 1063, 1196, 1246, 1339, 1490, 1507, 2952; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{17}H_{13}N_3{}^{\cdot+}$ 259.1111; Found 259.1109.

9-Methyl-7-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-naphtho[2,3-*d*]-1,3-dioxol (**14**)



Colorless solid; Mp 184–186 °C; TLC R_f 0.38 (*n*-hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (s, 1H), 7.97–7.92 (AA'BB'C, 2H), 7.91 (d, 1H, J = 1.5 Hz), 7.65 (d, 1H, J = 1.5 Hz), 7.51–7.44 (AA'BB'C, 2H), 7.41–7.30 (AA'BB'C, 1H), 7.32 (s, 1H), 7.21 (s, 1H), 6.11 (s, 2H), 2.70 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 148.6, 148.5, 148.3, 135.7, 133.1, 130.6, 130.4, 129.4, 128.9, 128.4, 125.8, 118.2, 117.7, 116.2, 104.7, 101.5, 100.9, 20.0; IR (NaCl, cm^{-1}) 1375, 1457, 1472, 1517, 1541, 2855, 2923, 2953; HRMS (EI) *m/z*: $[M]^{\cdot+}$ Calcd for $C_{20}H_{15}N_3O_2^{\cdot+}$ 329.1162; Found 329.1164.

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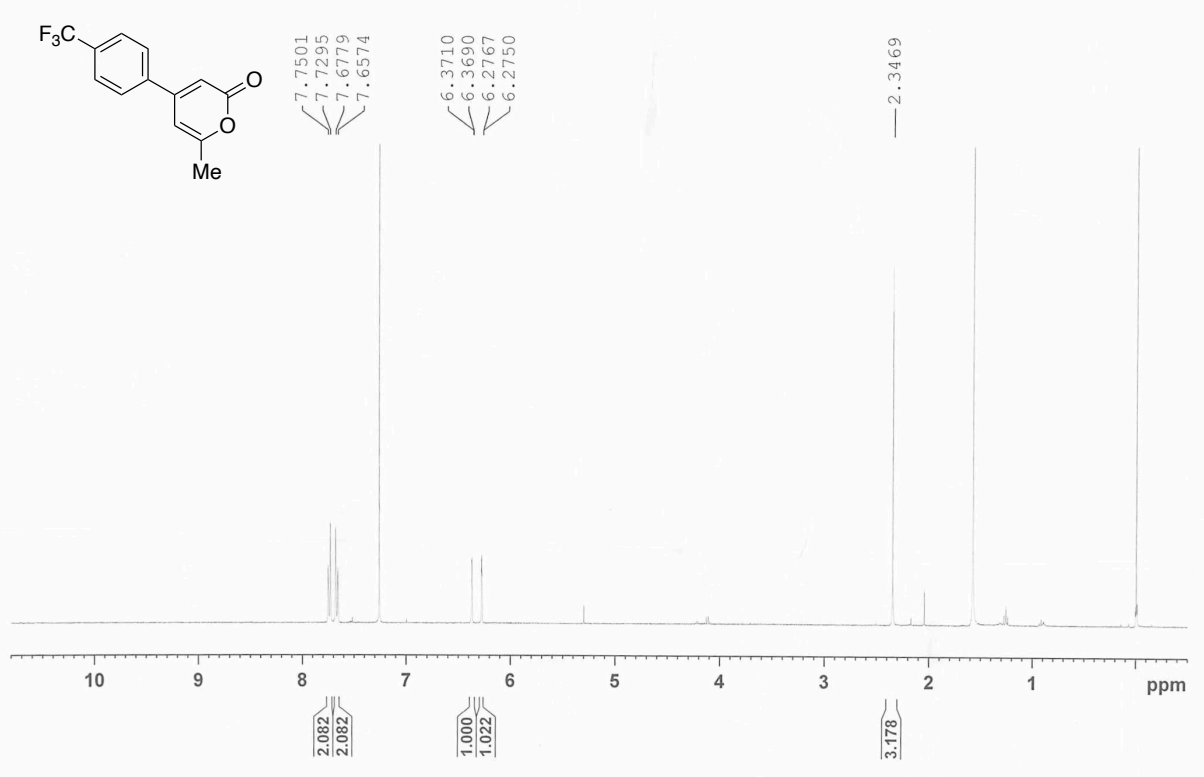
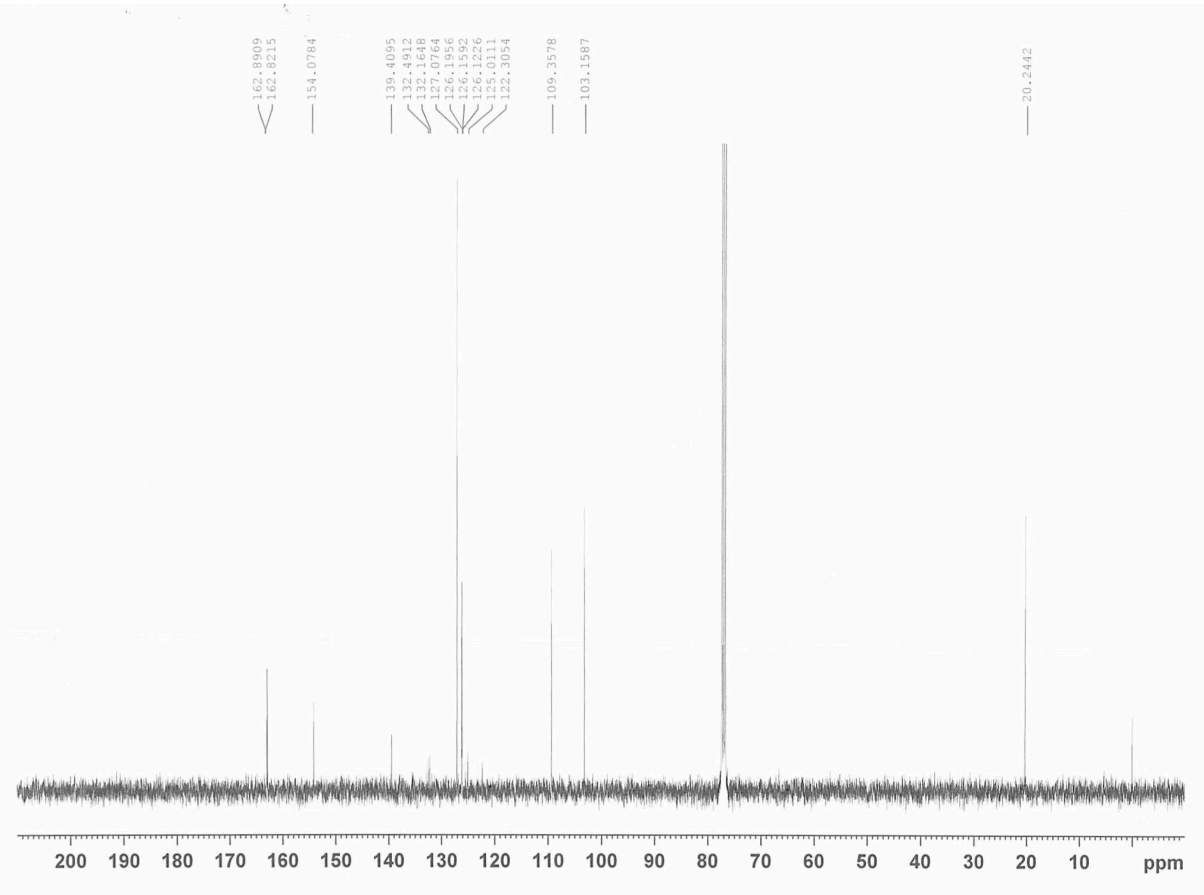
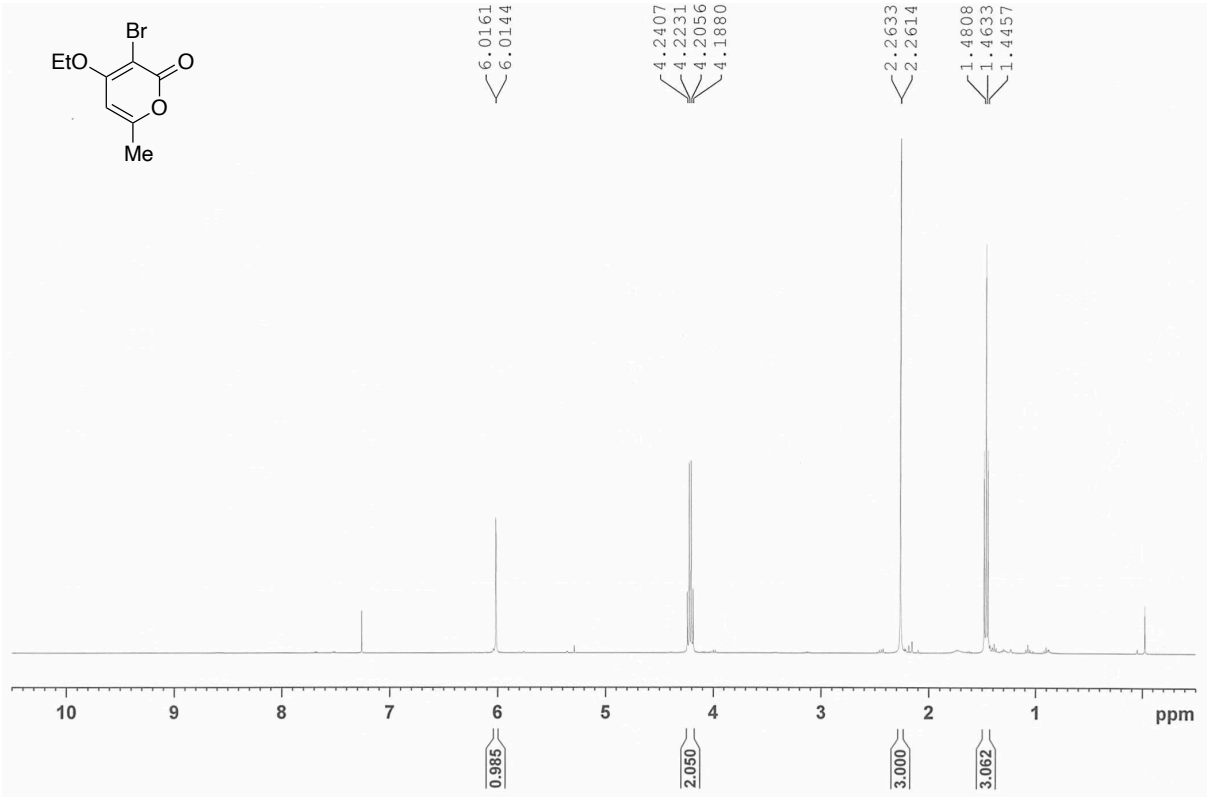
^{1}H and ^{13}C NMR Spectra of Compounds

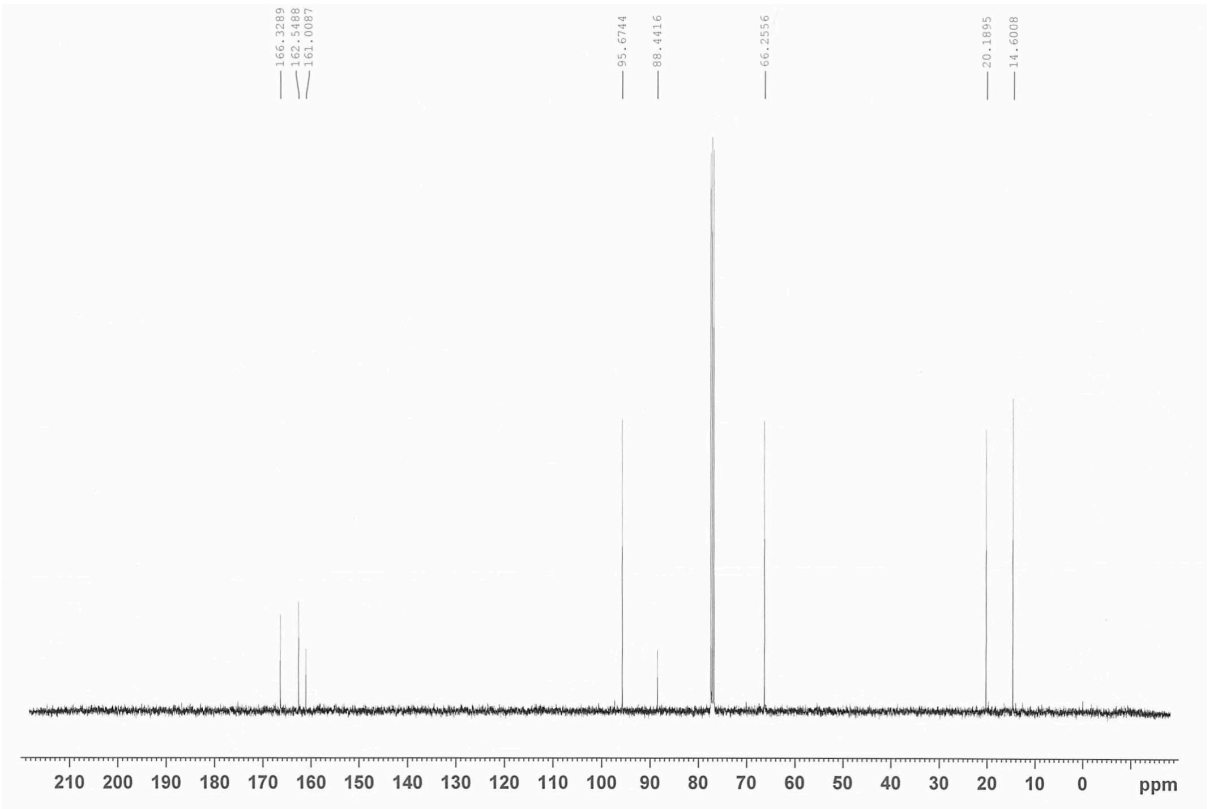
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 6-methyl-4-(4-(trifluoromethyl)phenyl)-2-pyrone (**2e**) ($CDCl_3$)



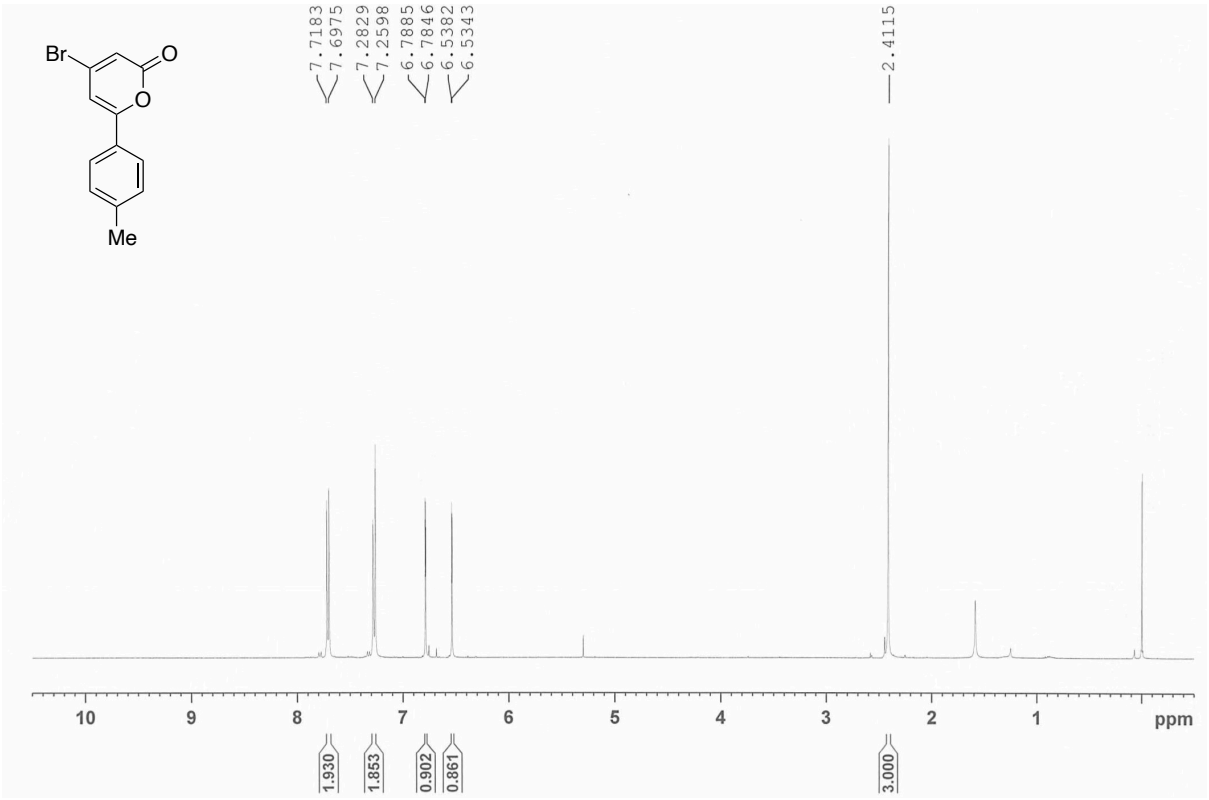


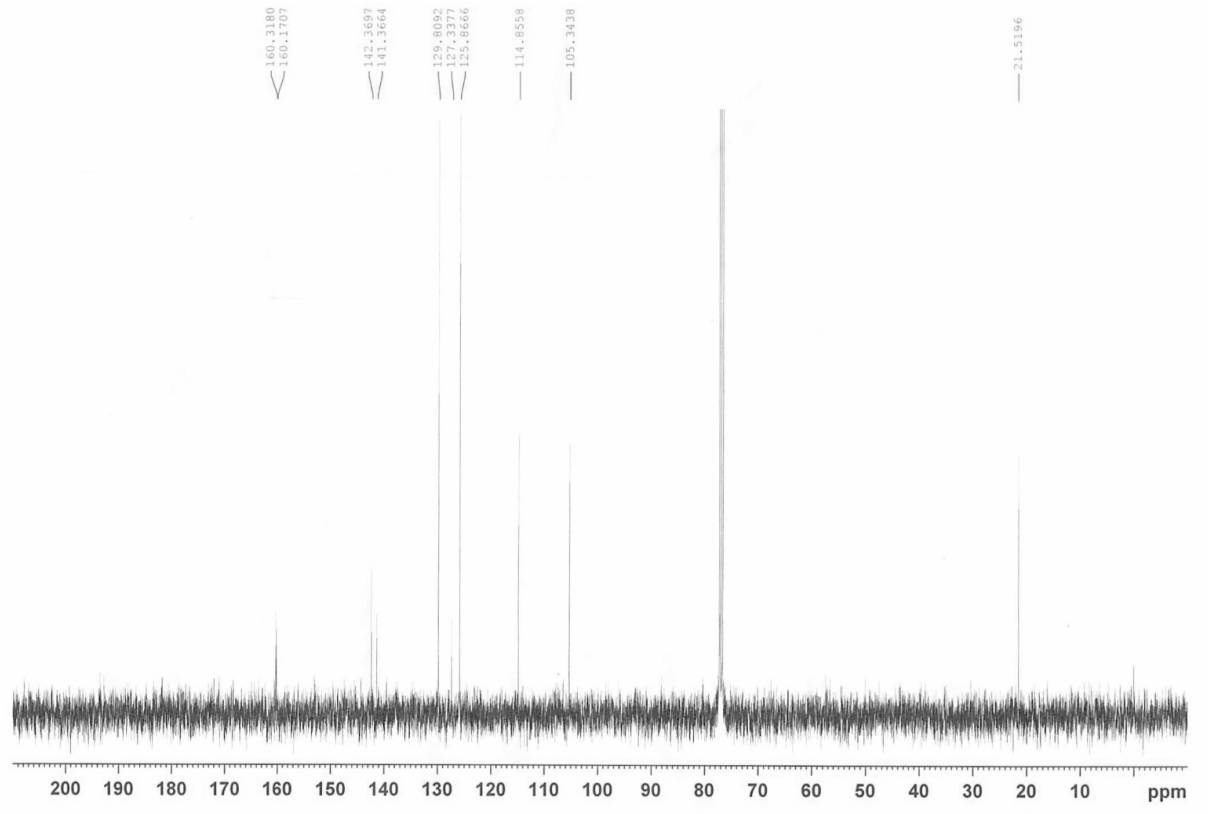
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-3-ethoxy-6-methyl-2-pyrone (**2g**) ($CDCl_3$)



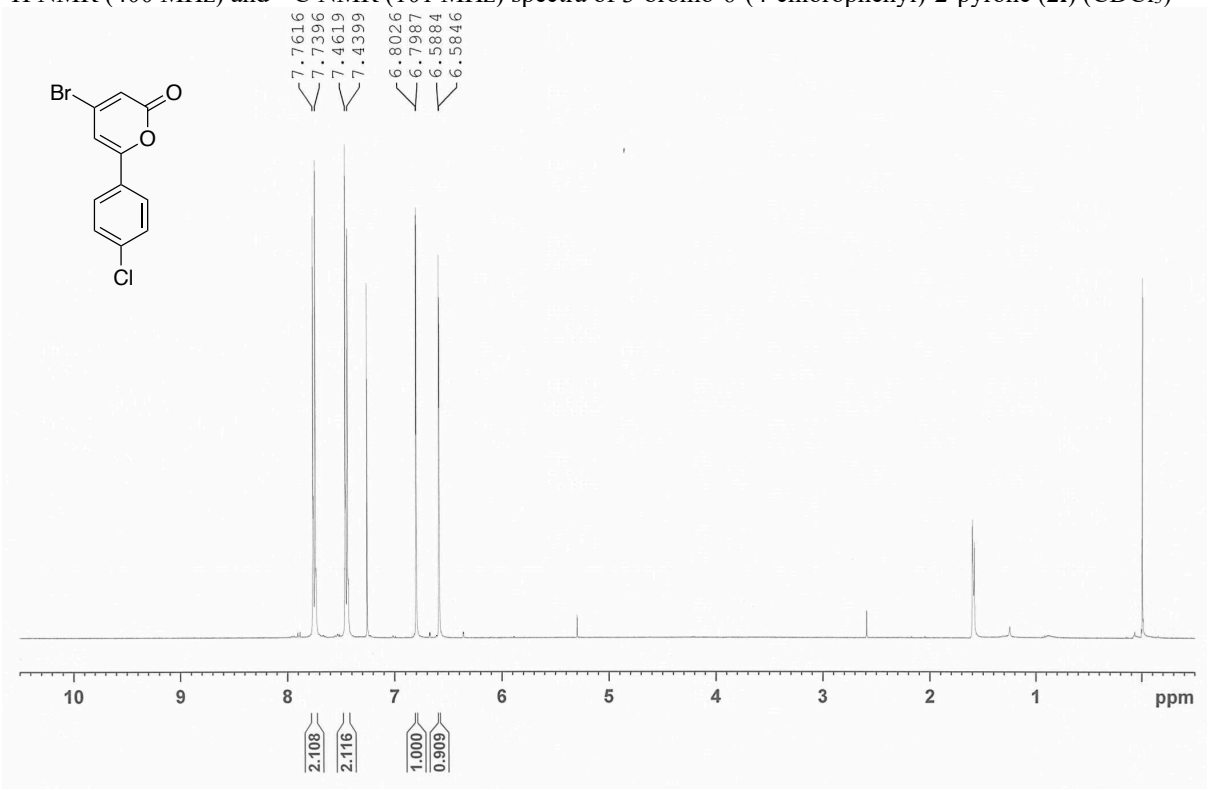


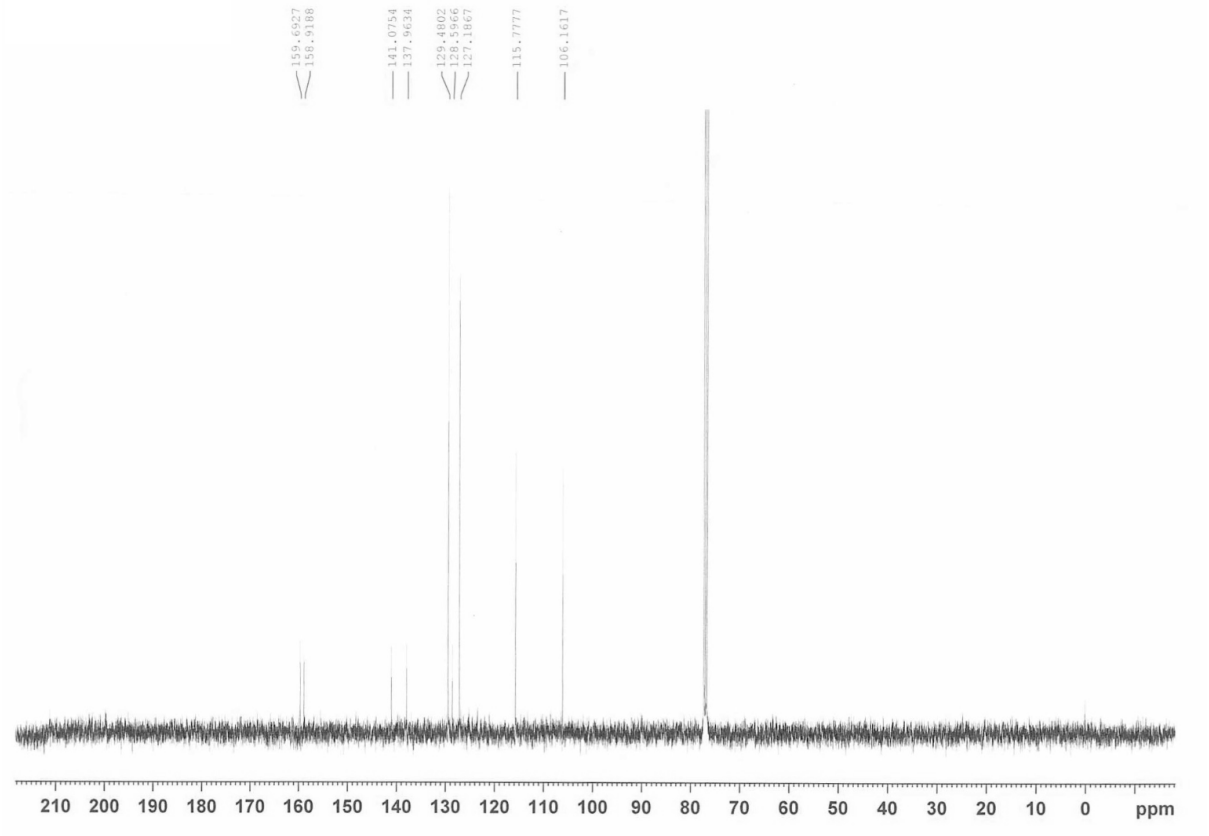
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3-bromo-6-(4-methylphenyl)-2-pyrone (**2k**) ($CDCl_3$)



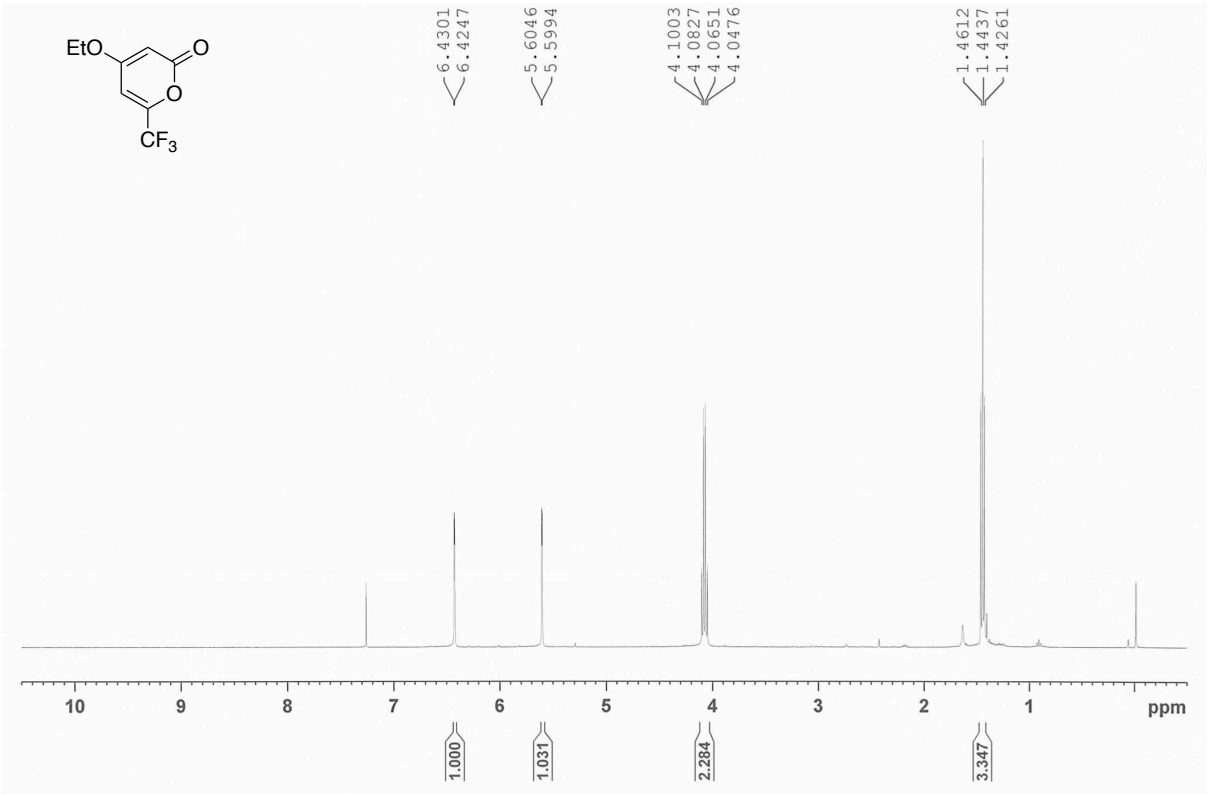


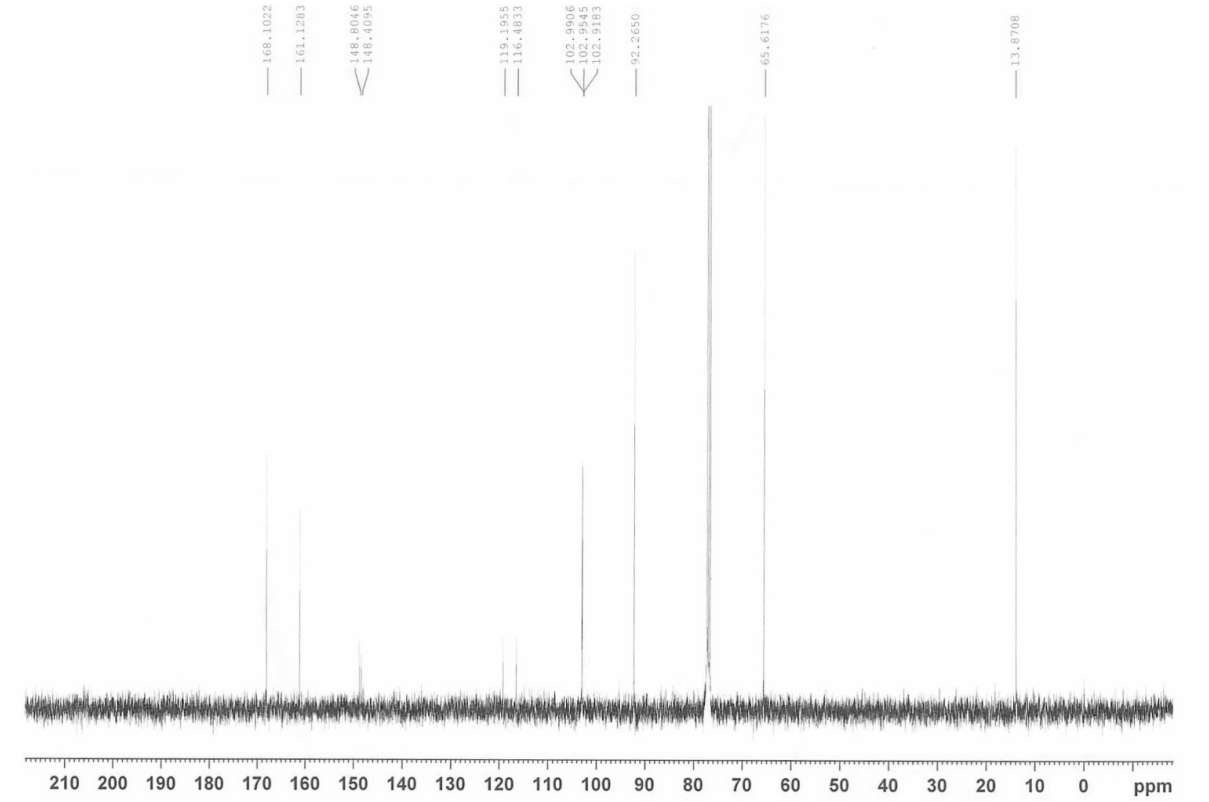
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3-bromo-6-(4-chlorophenyl)-2-pyrone (**2l**) ($CDCl_3$)



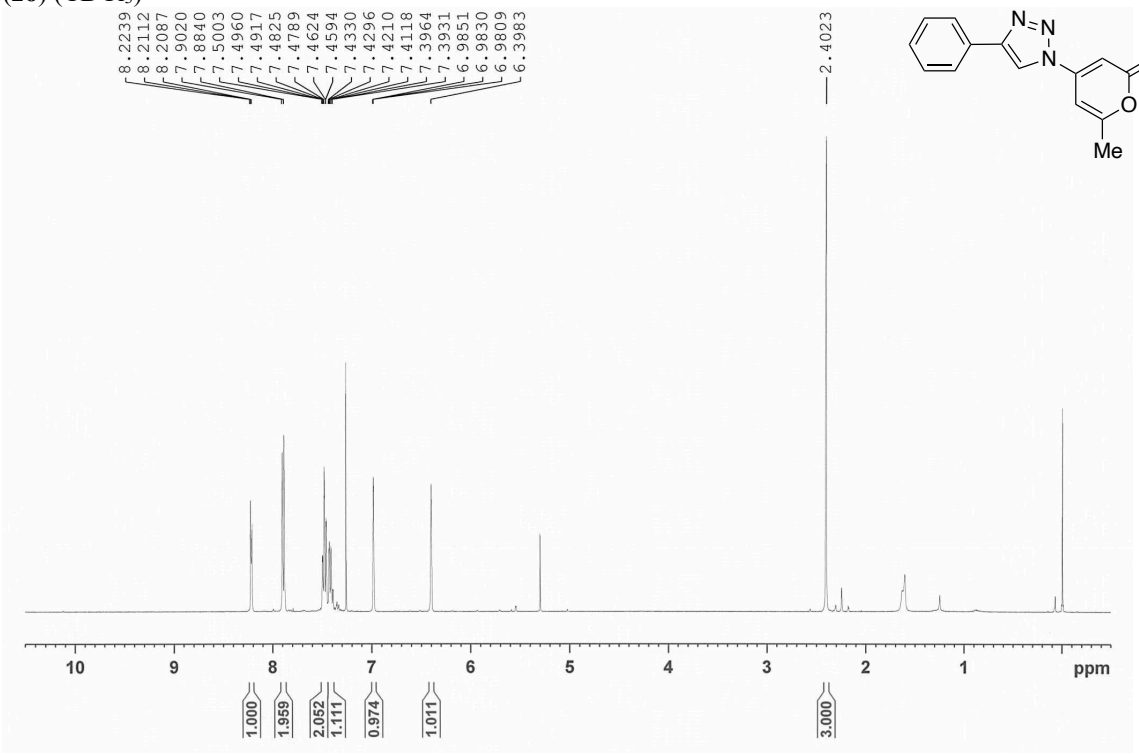


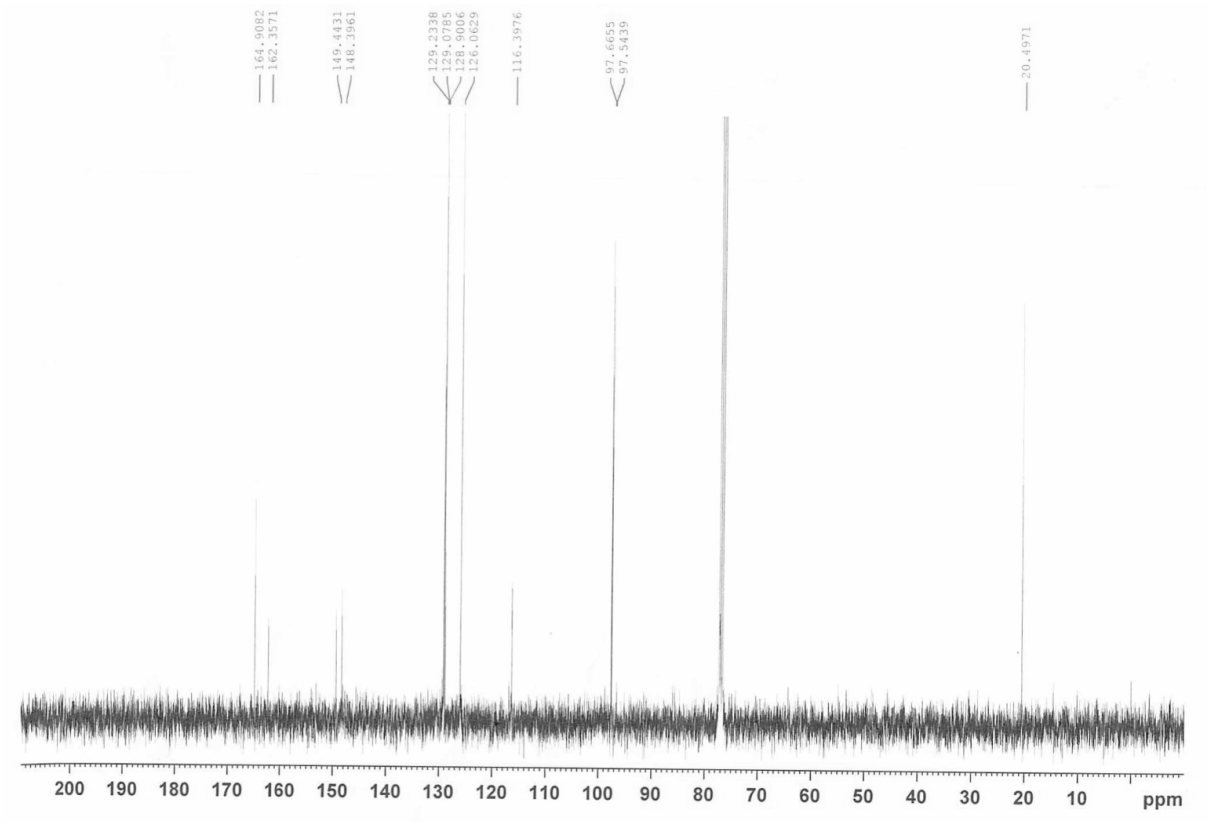
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3-ethoxy-6-trifluoromethyl-2-pyrone (**2m**) ($CDCl_3$)



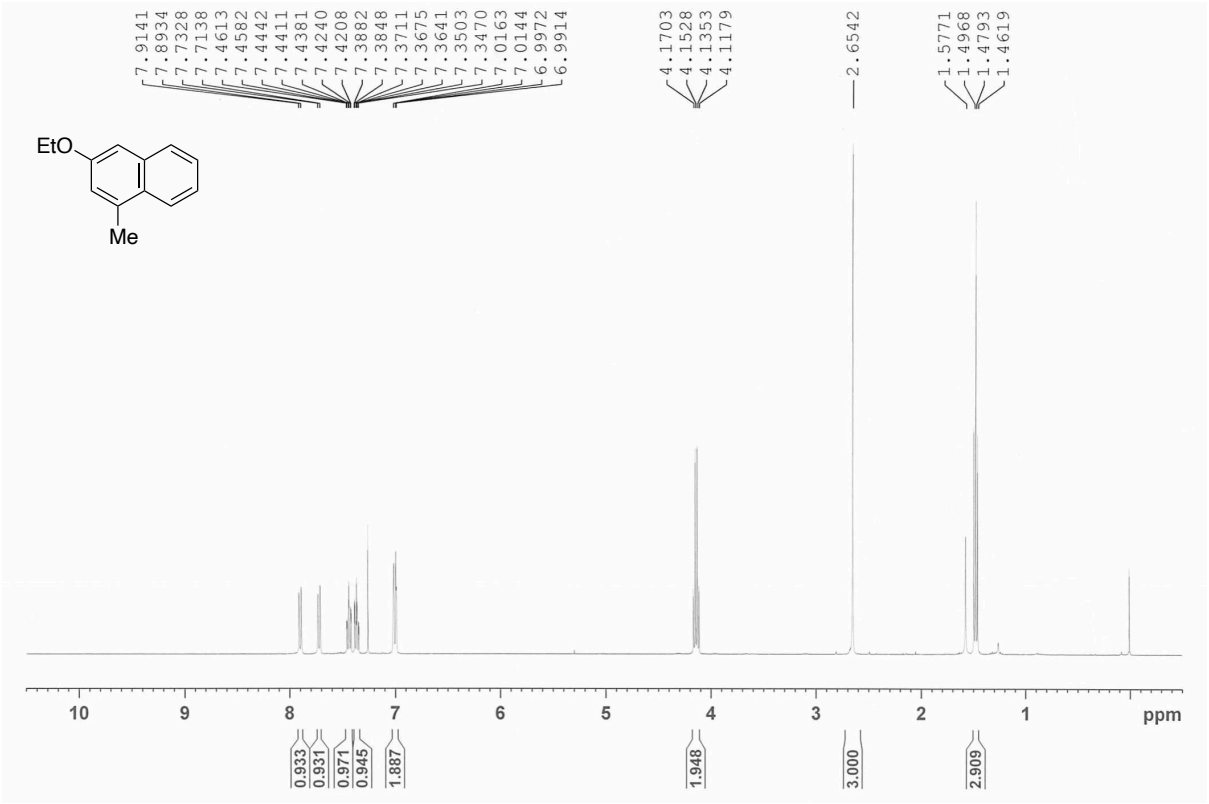


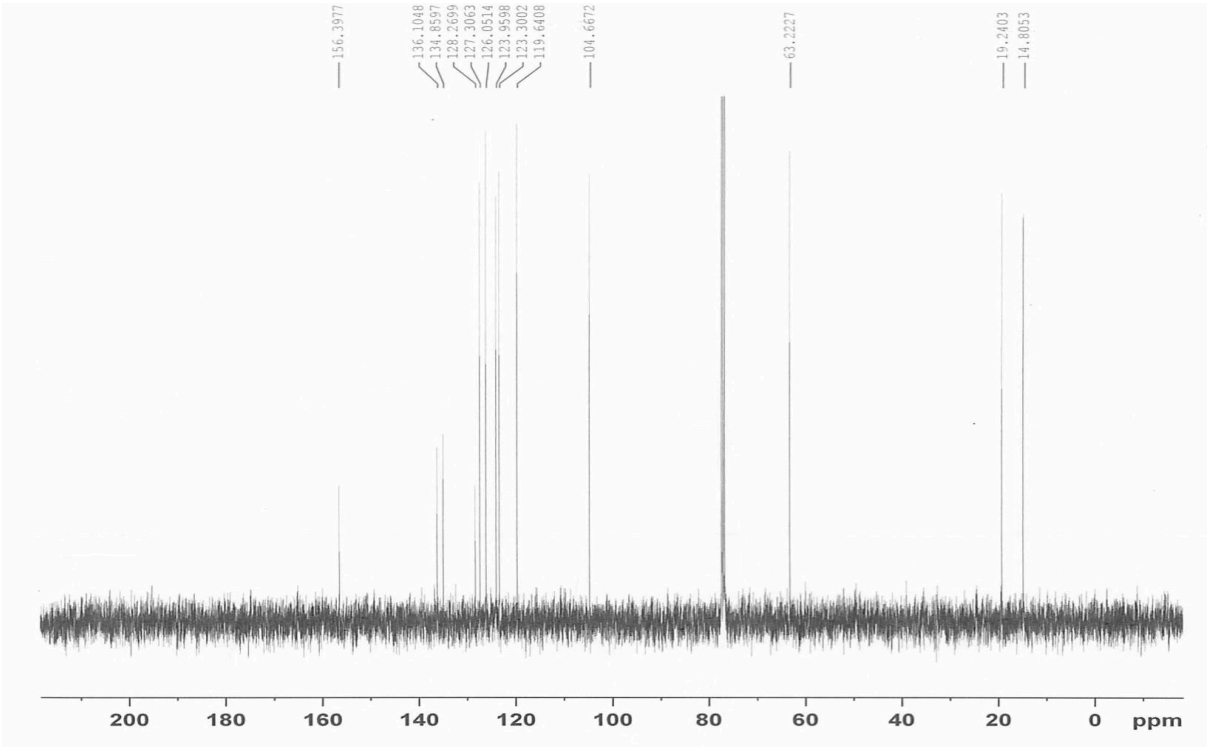
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 6-methyl-4-(4-phenyl-1*H*-1,2,3-triazol-lyl)-2-pyrone (**2o**) ($CDCl_3$)



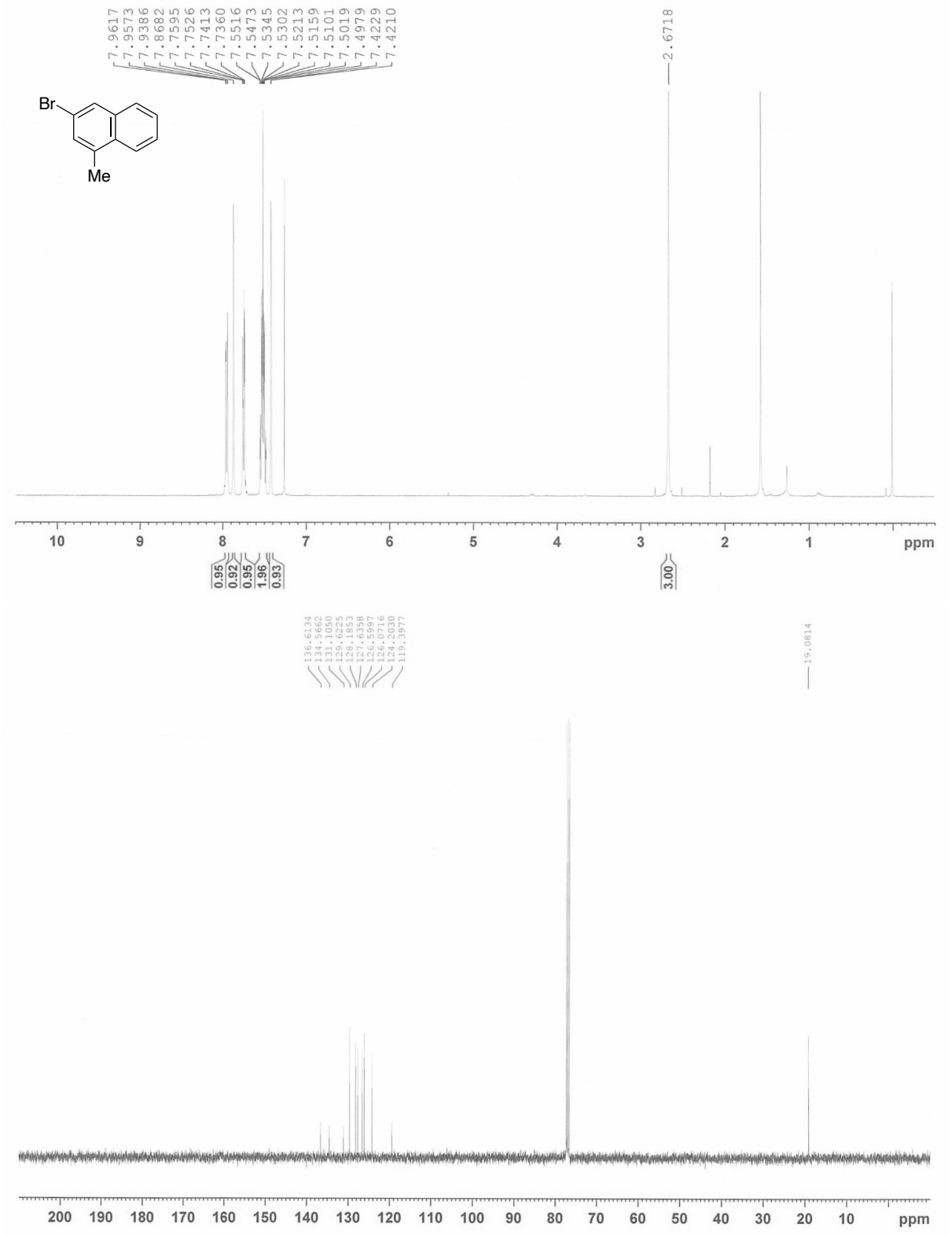


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-ethoxy-4-methylnaphthalene (**11a**) ($CDCl_3$)

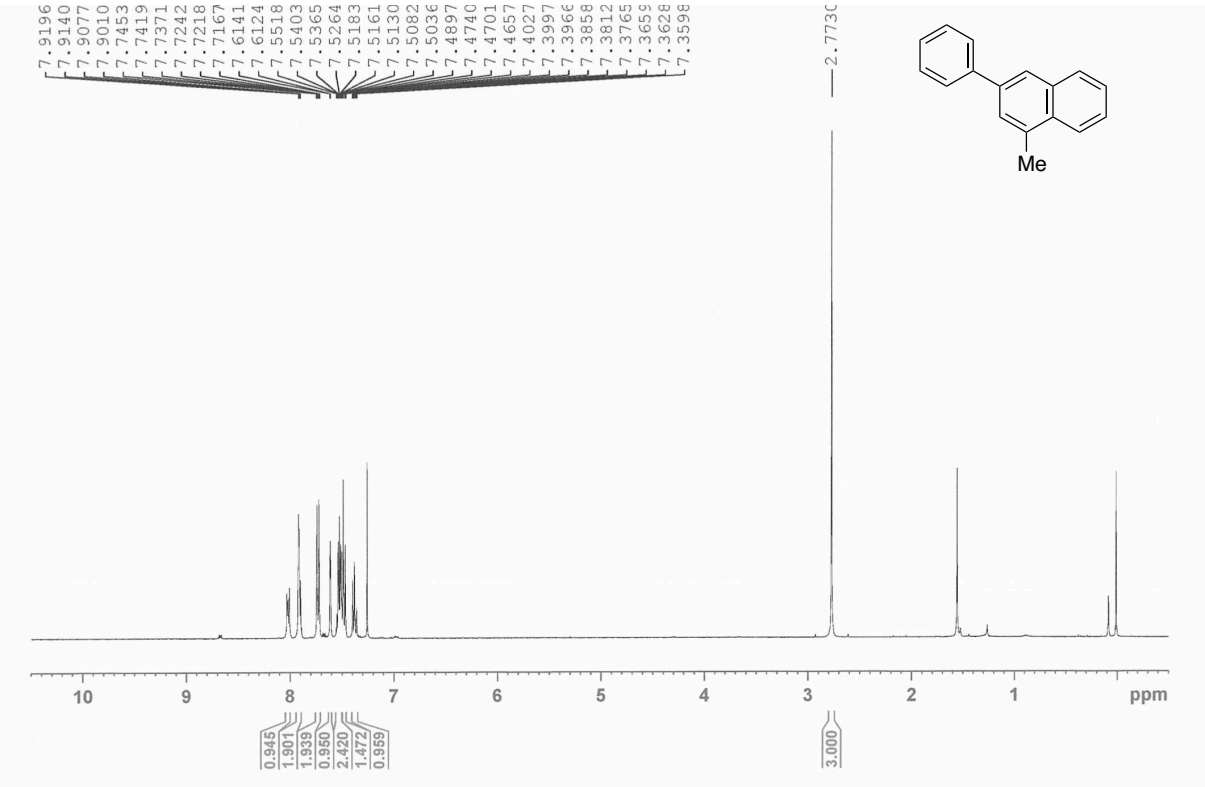


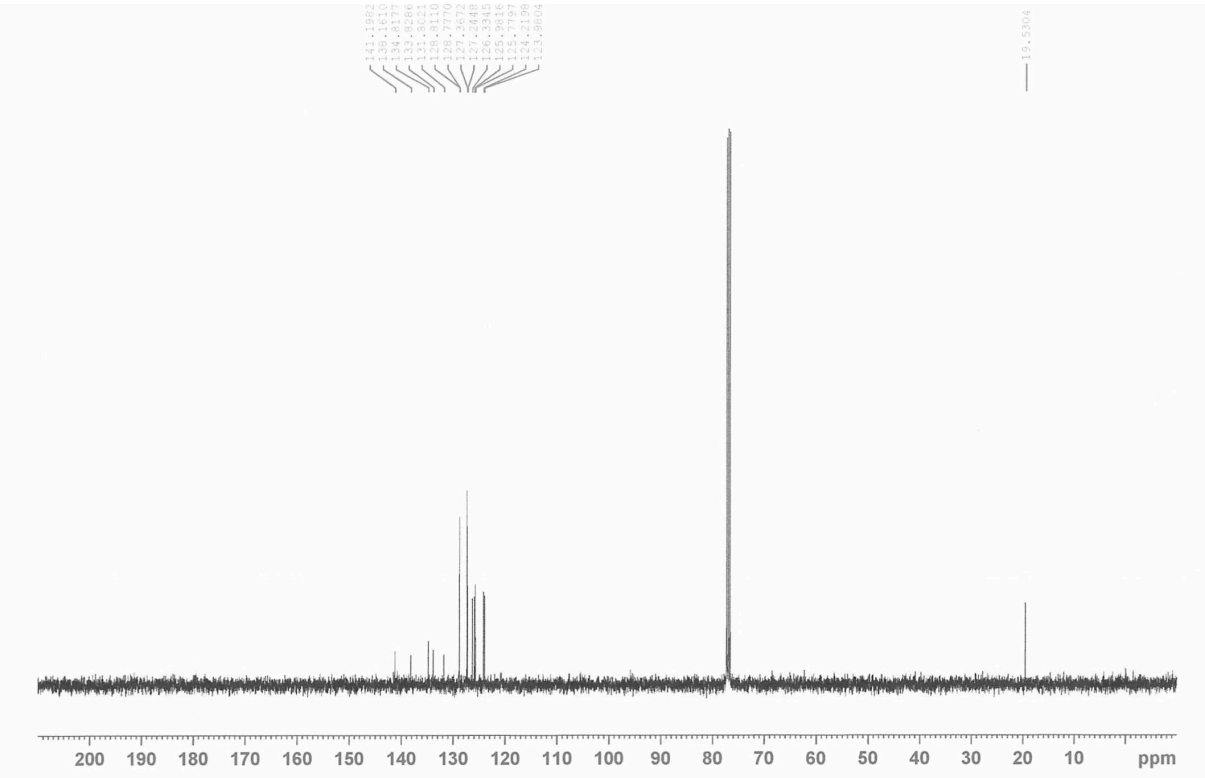


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4-methylnaphthalene (**11b**) ($CDCl_3$)

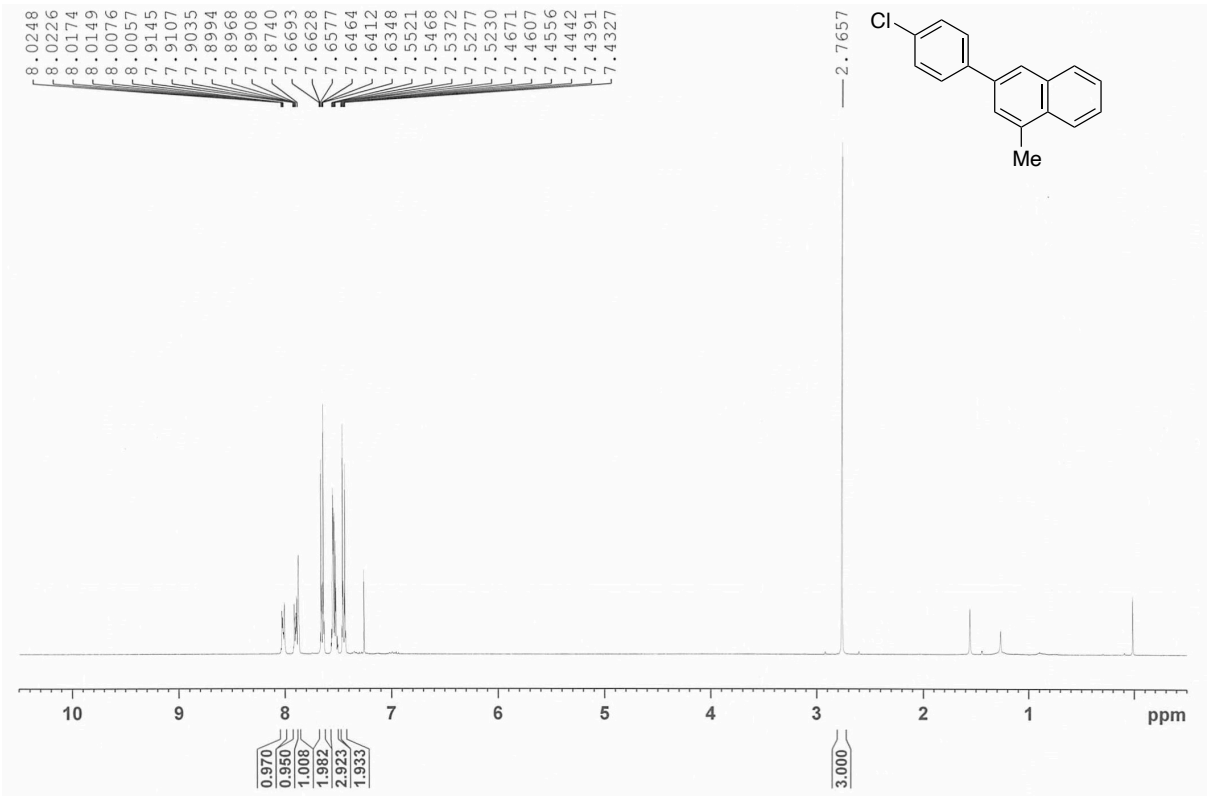


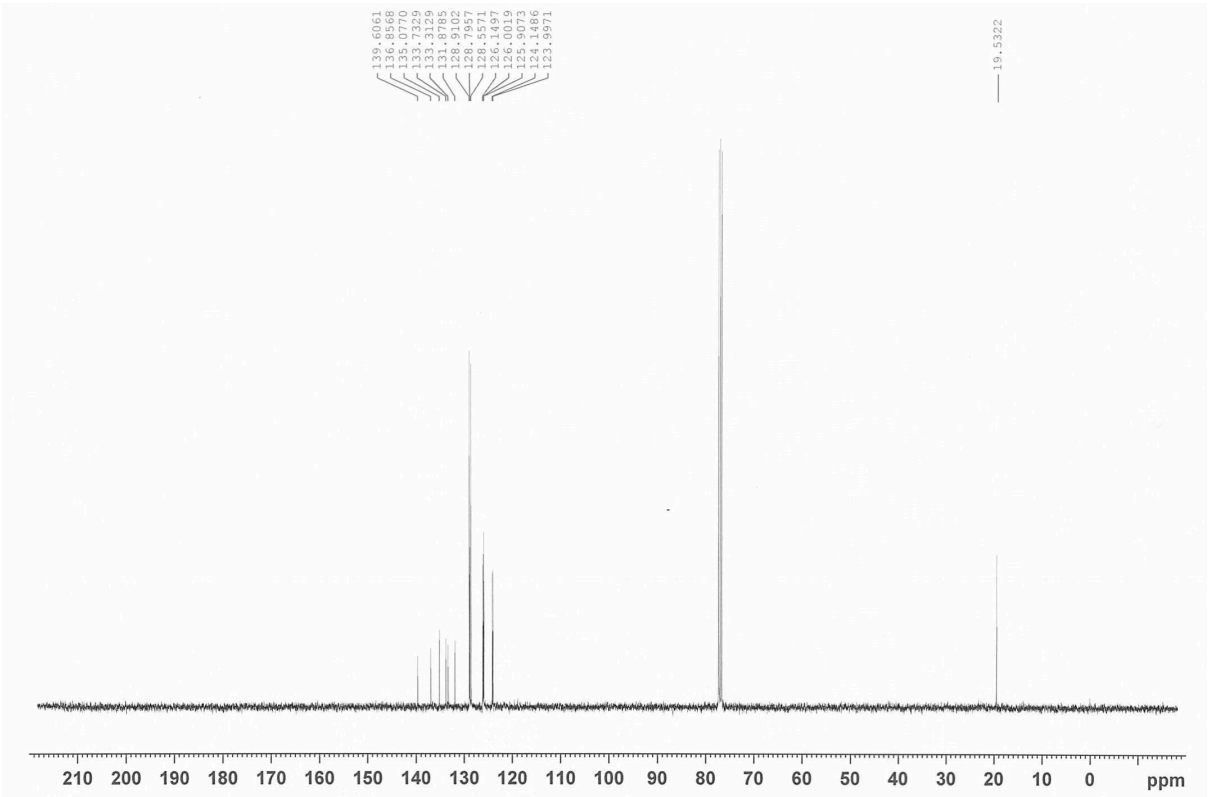
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4-methyl-2-phenylnaphthalene (**11c**) ($CDCl_3$)



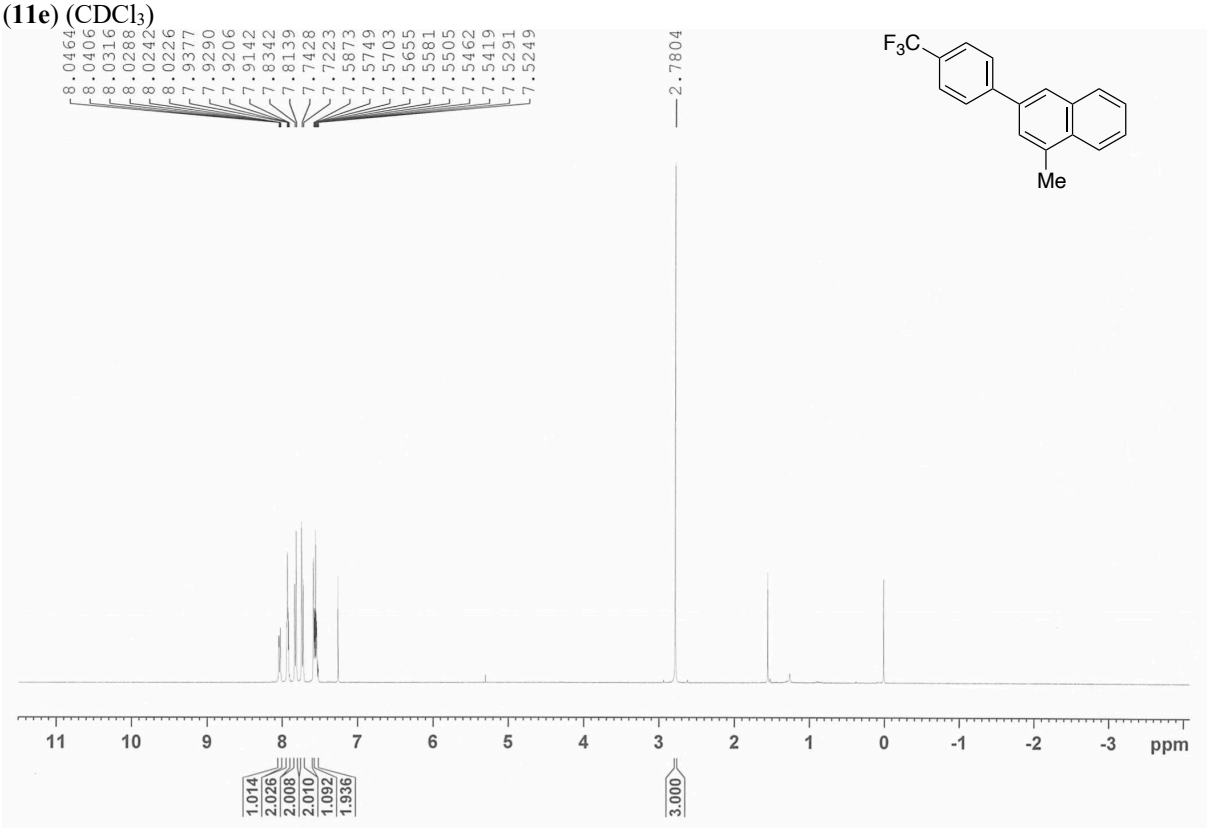


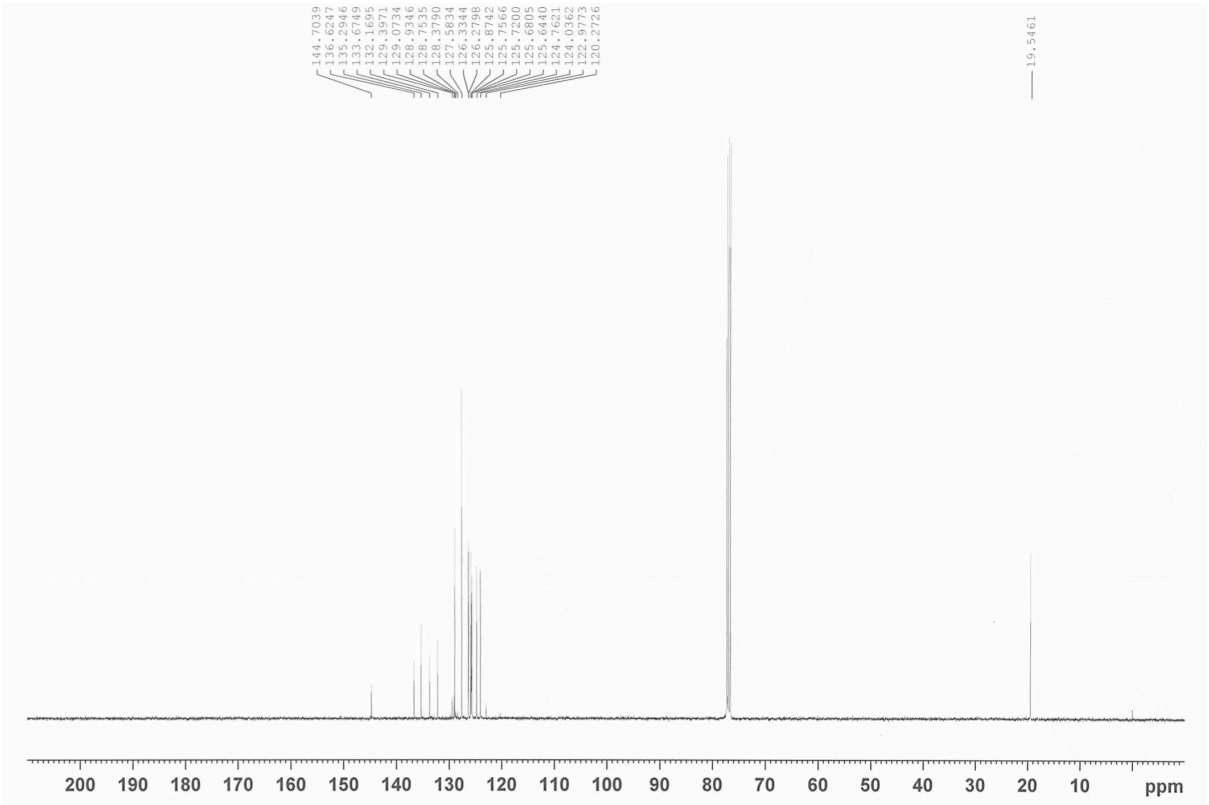
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-(4-chlorolphenyl)-4-methylnaphthalene (**11d**) ($CDCl_3$)



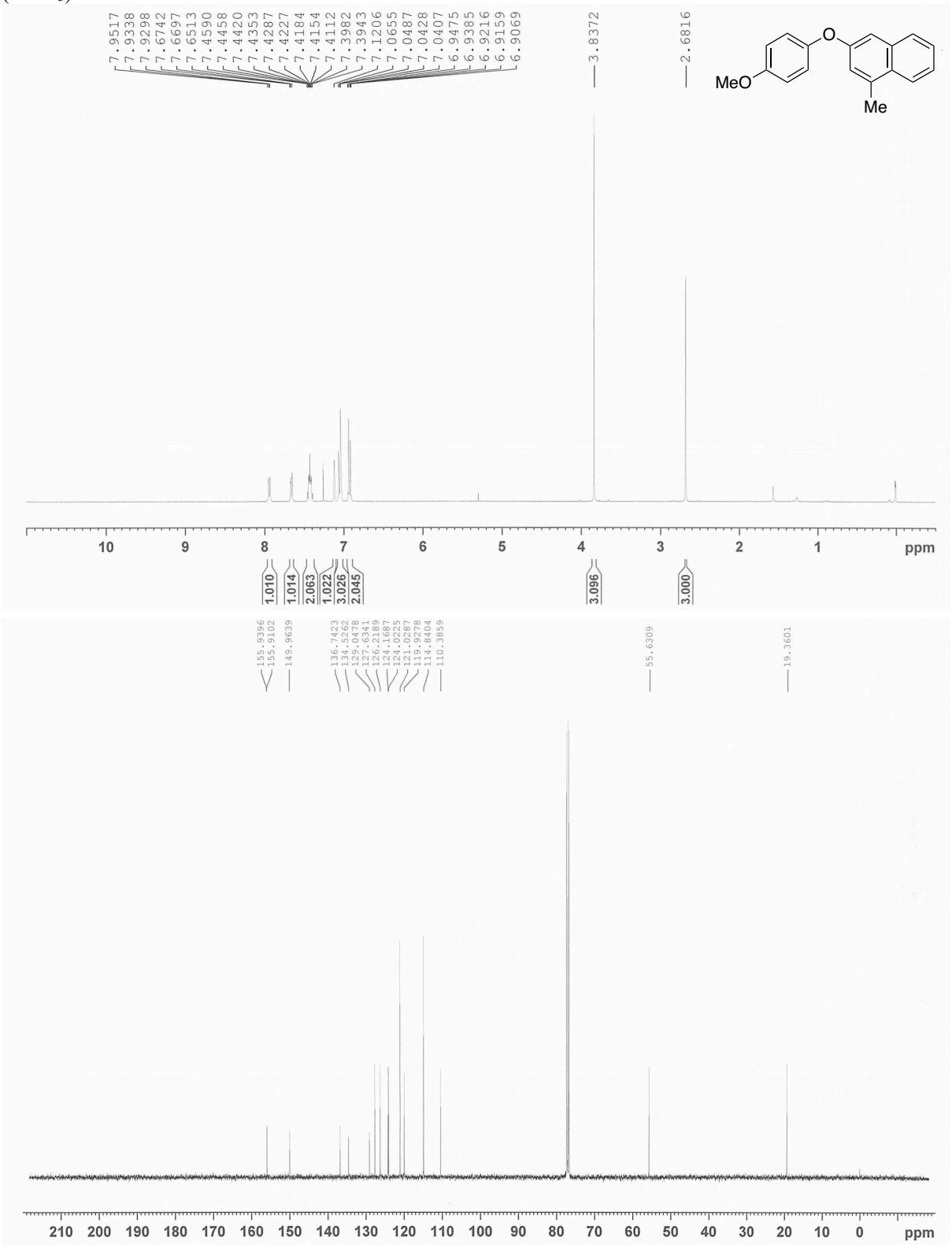


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4-methyl-2-(4-trifluoromethylphenyl)naphthalene (**11e**) ($CDCl_3$)

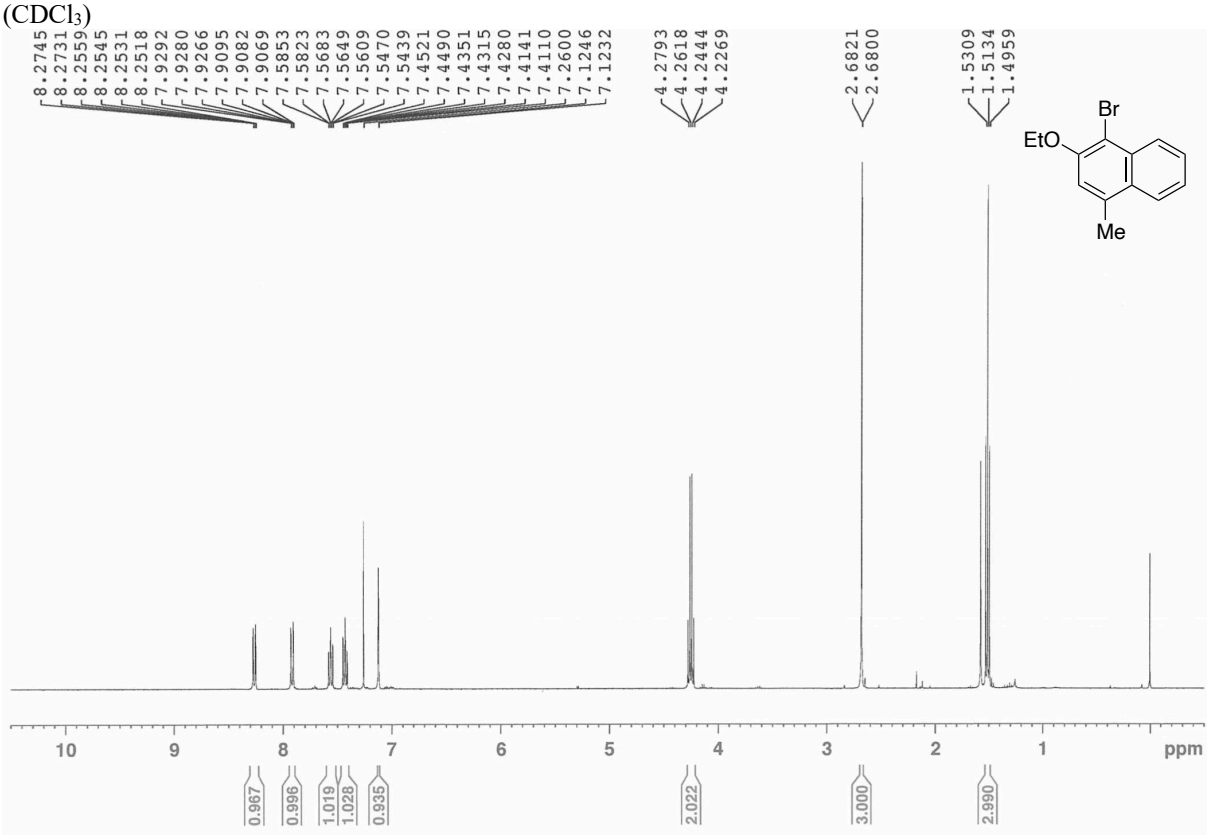


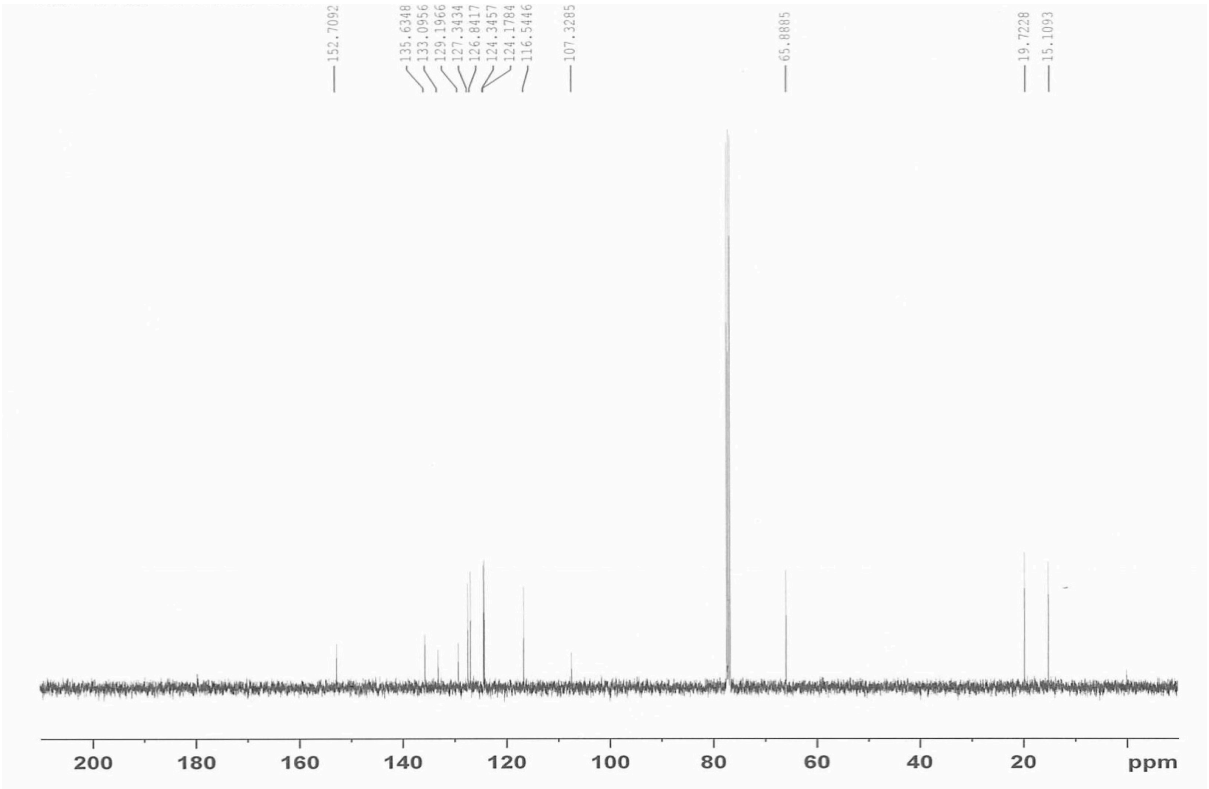


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4-methyl-2-(4-methoxyphenyloxy)naphthalene (**11f**) ($CDCl_3$)

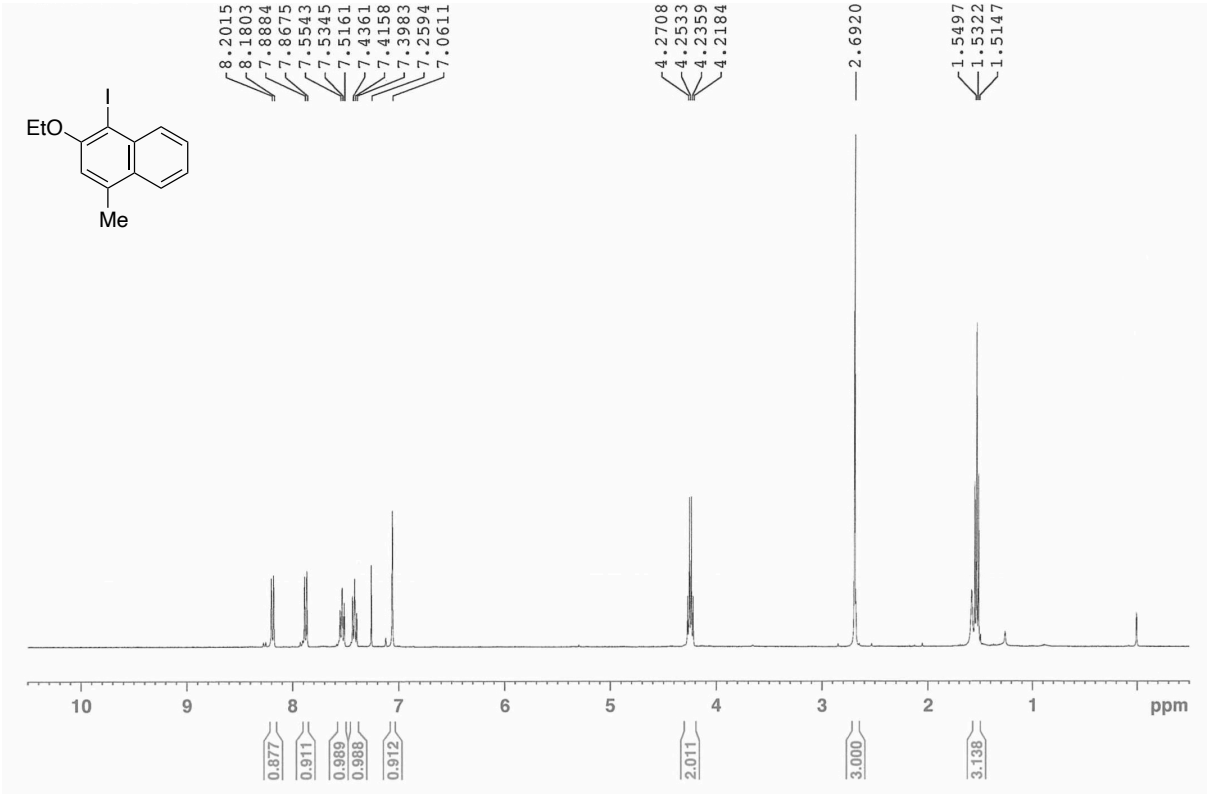


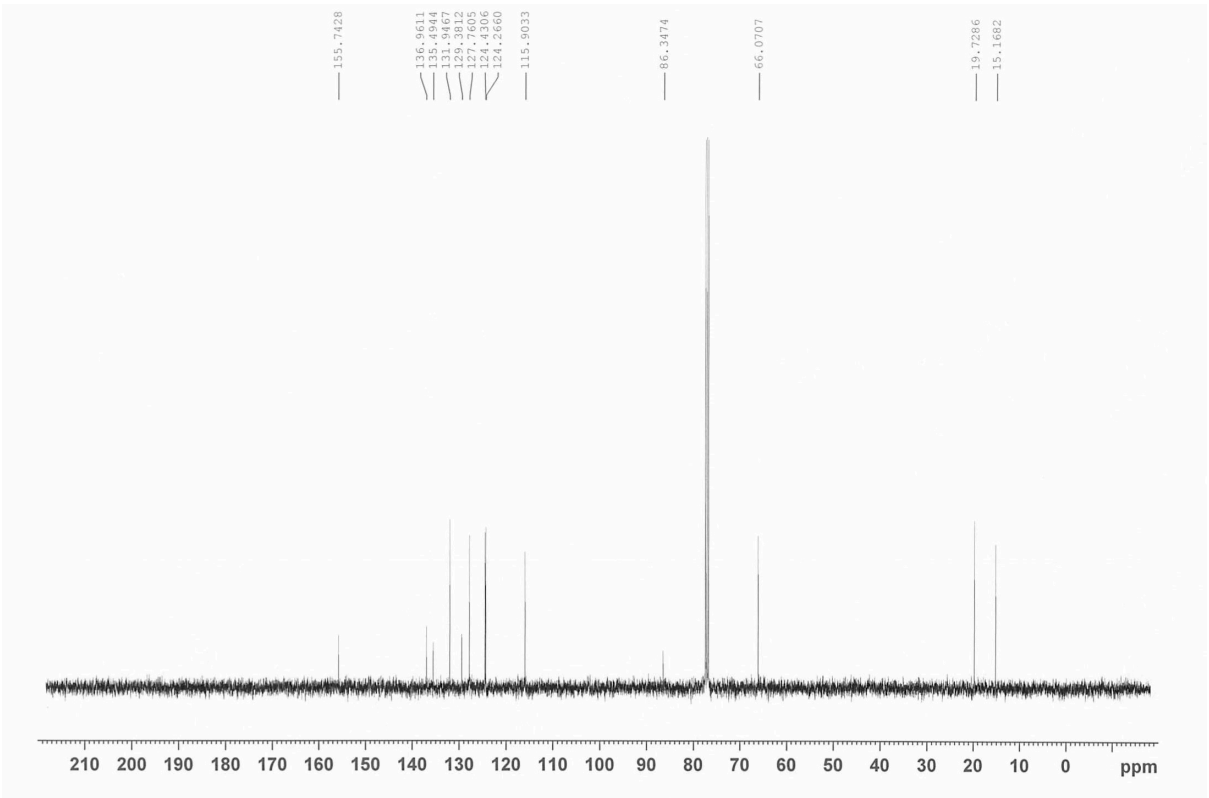
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 1-bromo-2-ethoxy-4-methylnaphthalene (**11g**) ($CDCl_3$)



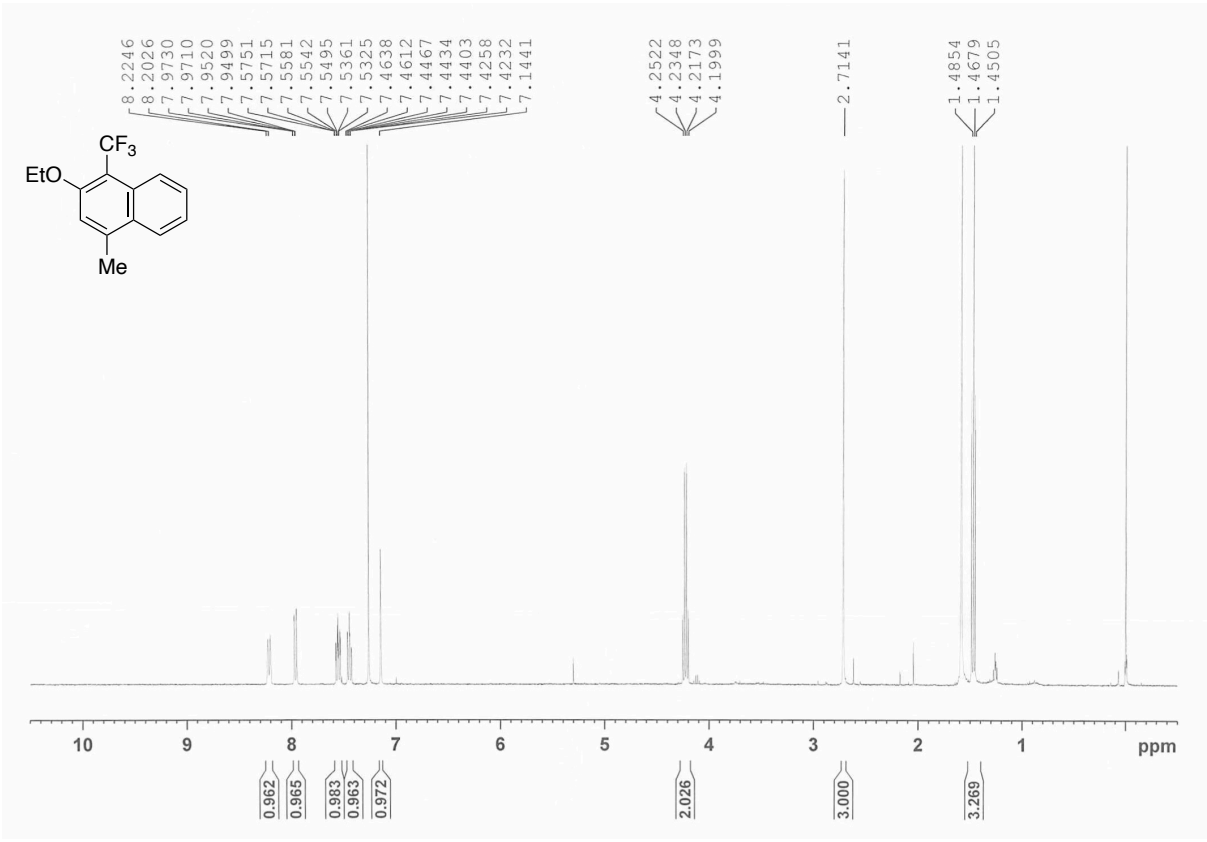


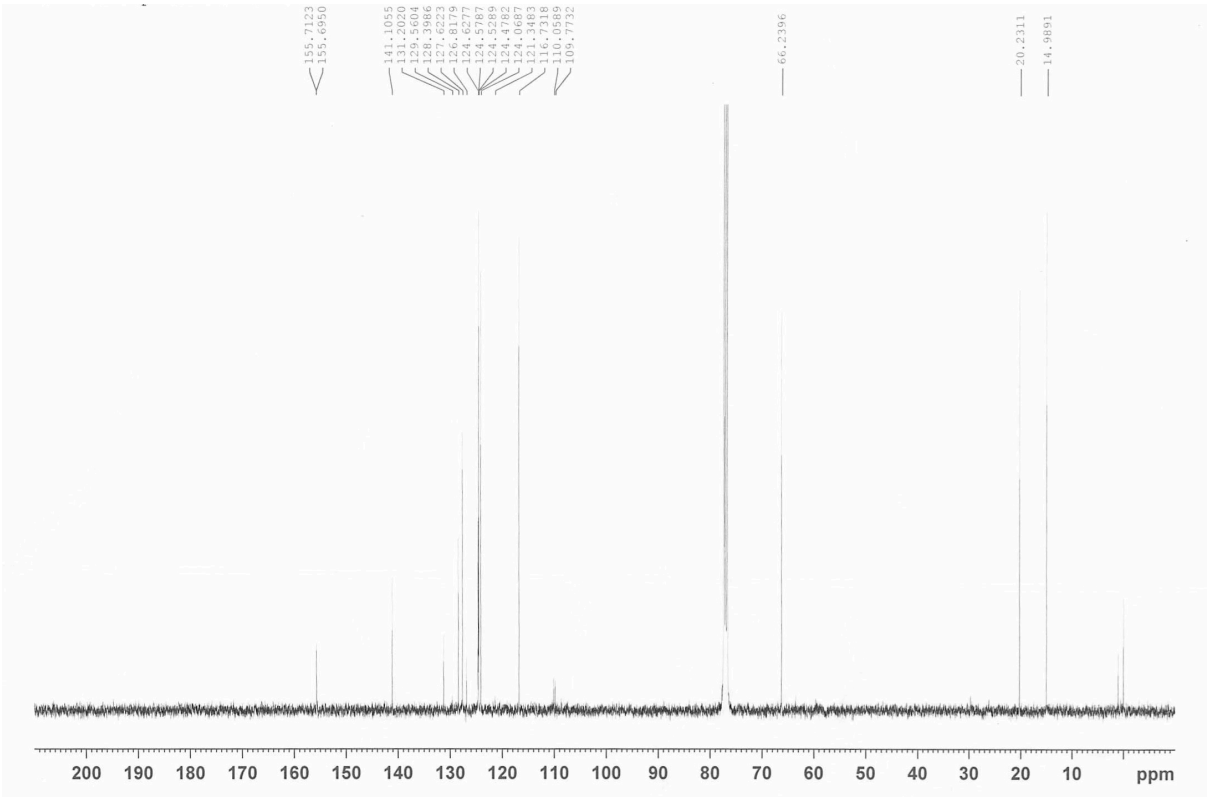
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-ethoxy-1-iodo-4-methylnaphthalene (**11h**) ($CDCl_3$)



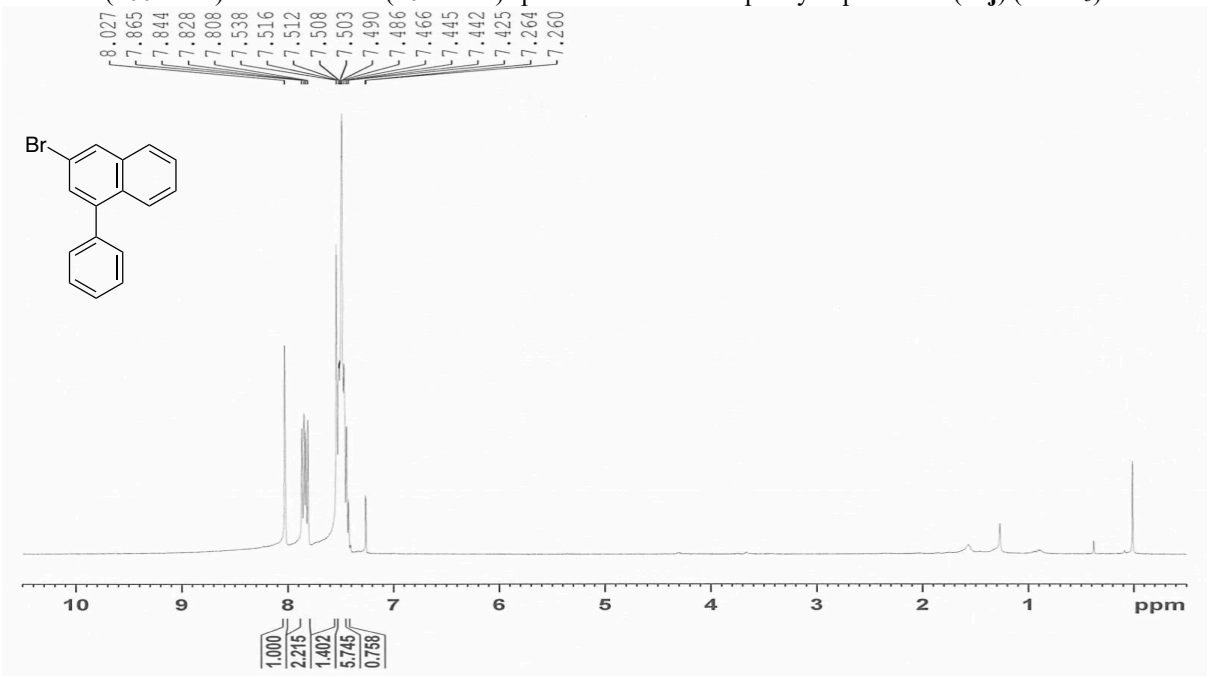


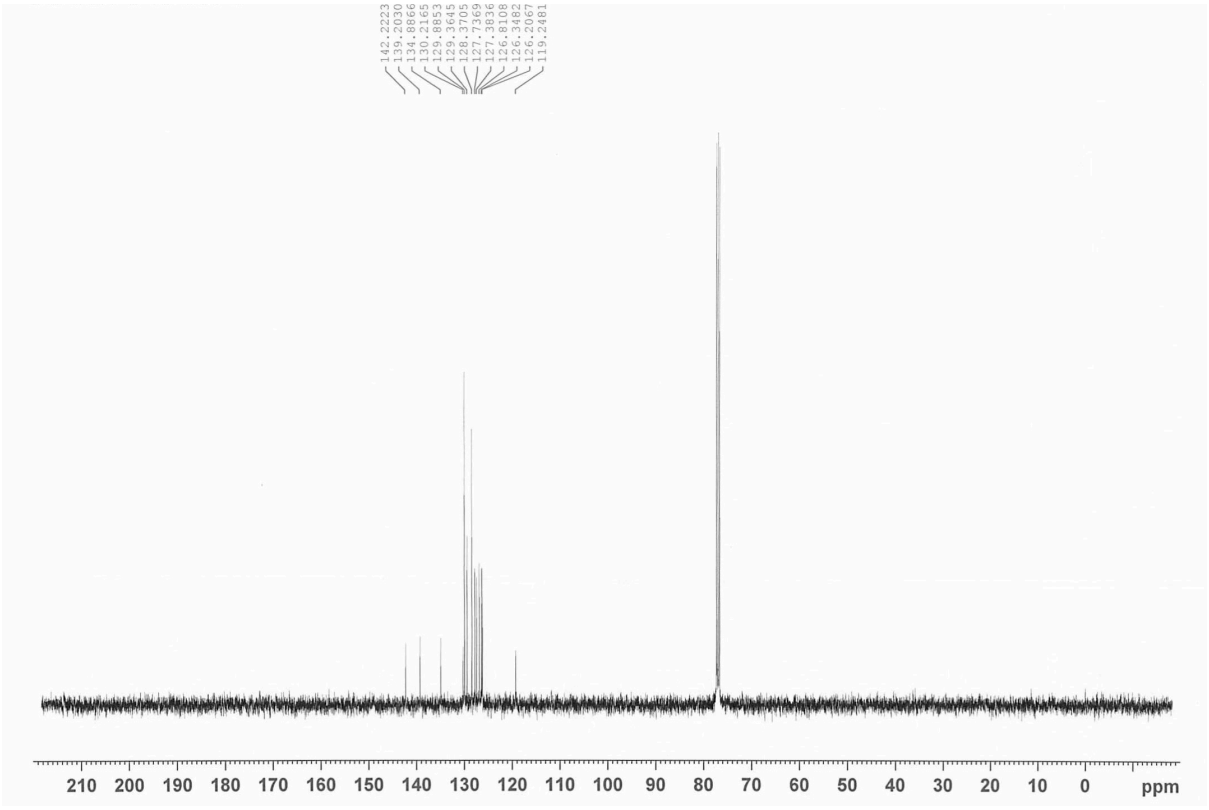
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-ethoxy-4-methyl-1-trifluoromethylnaphthalene (**11i**) ($CDCl_3$)



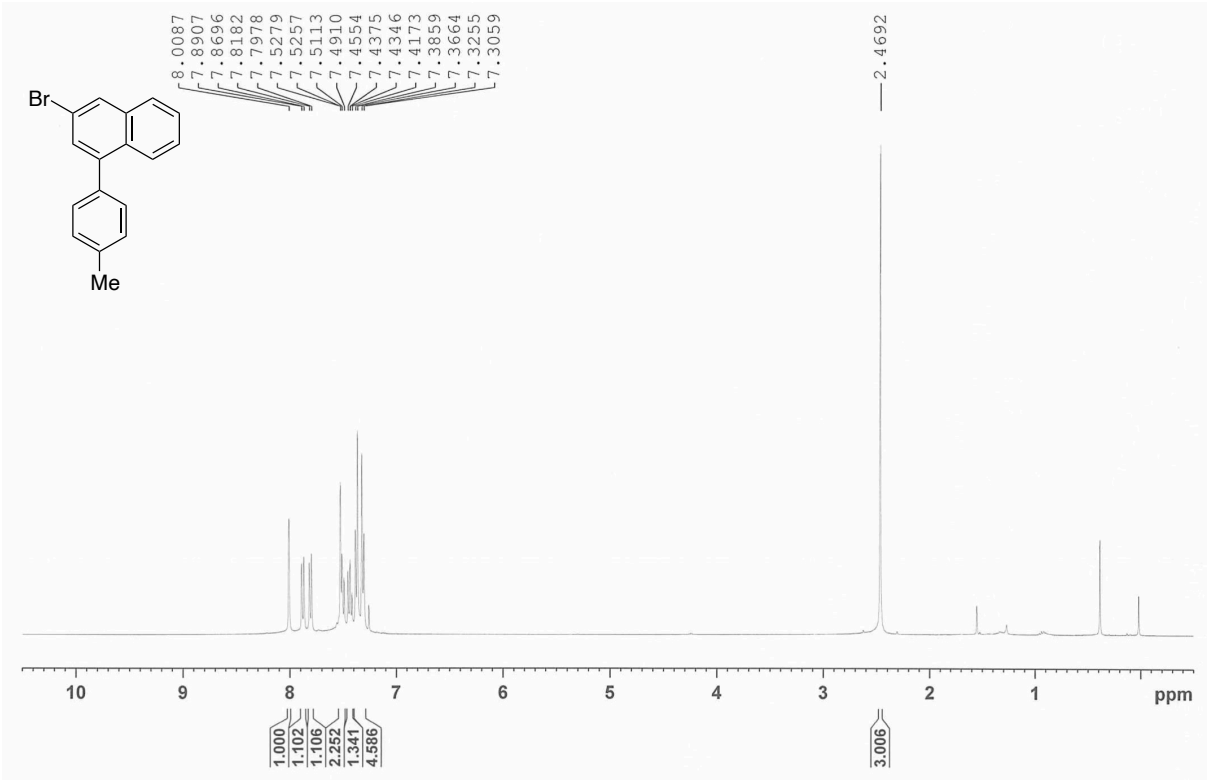


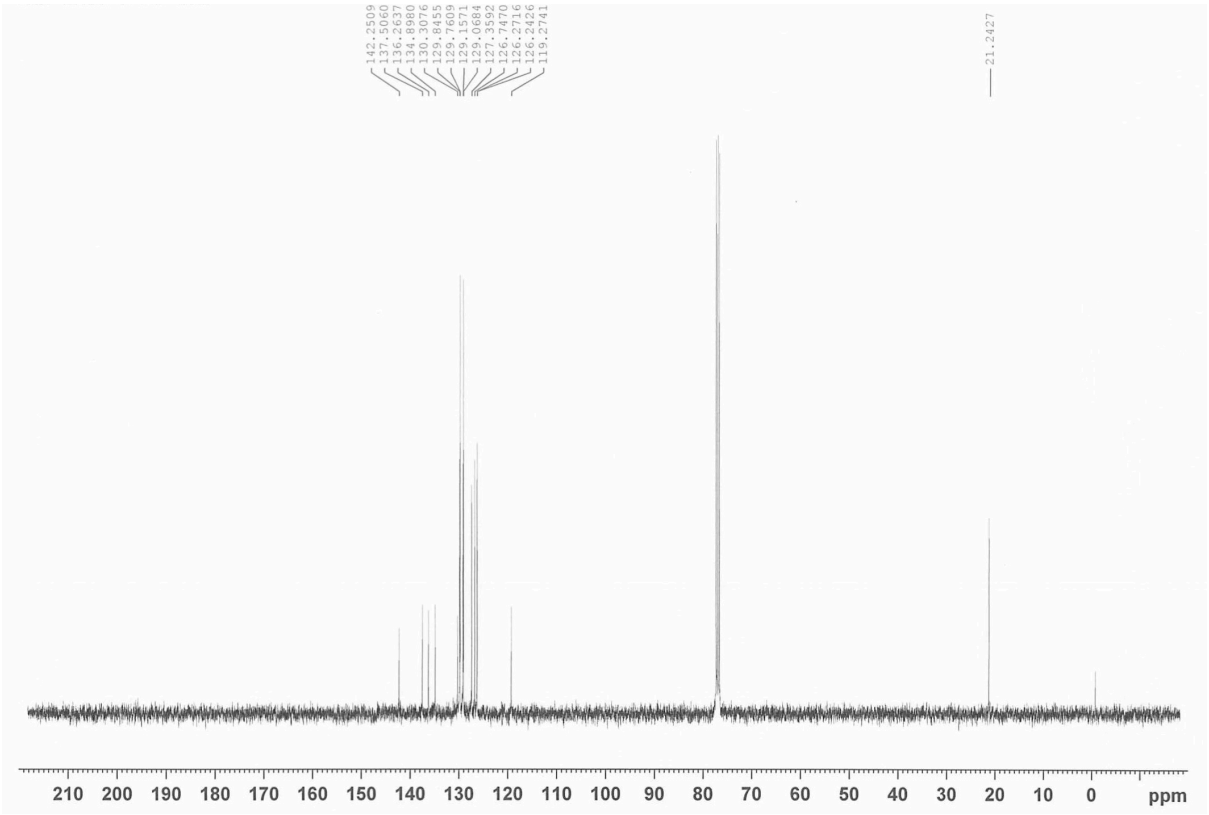
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4-phenylnaphthalene (**11j**) ($CDCl_3$)



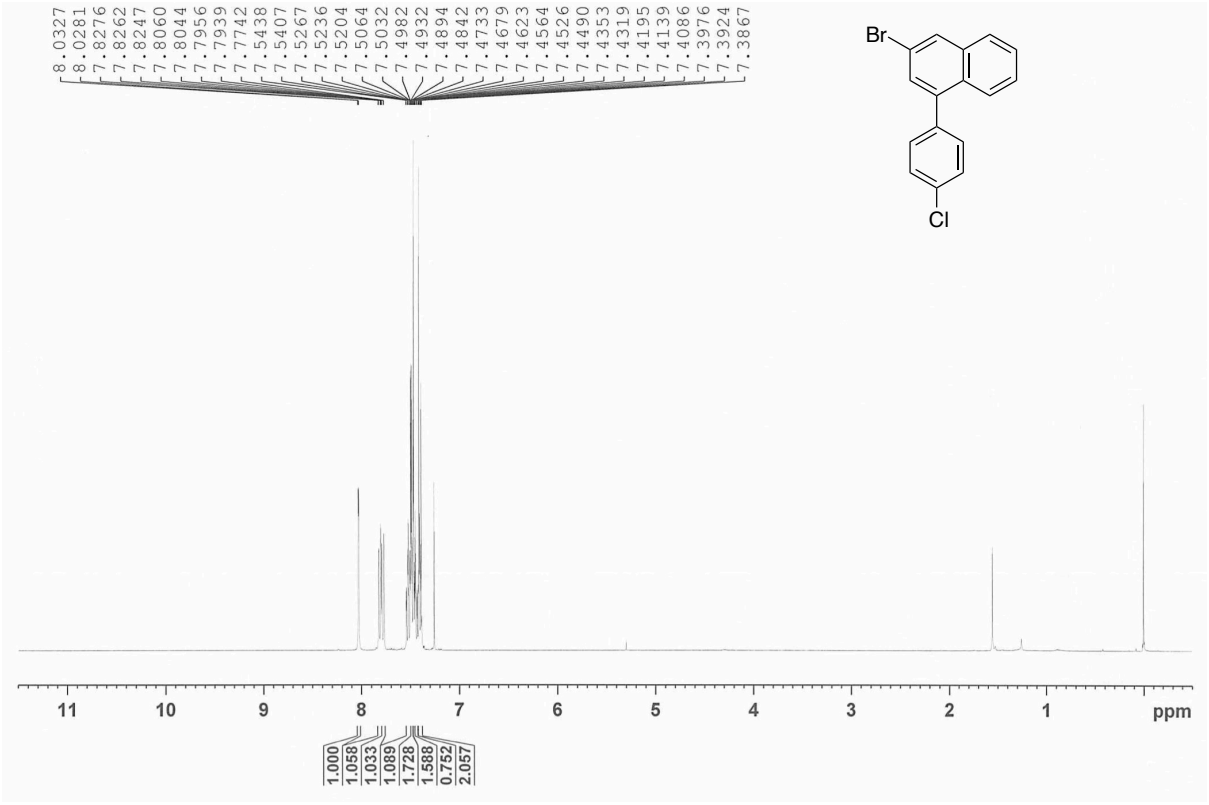


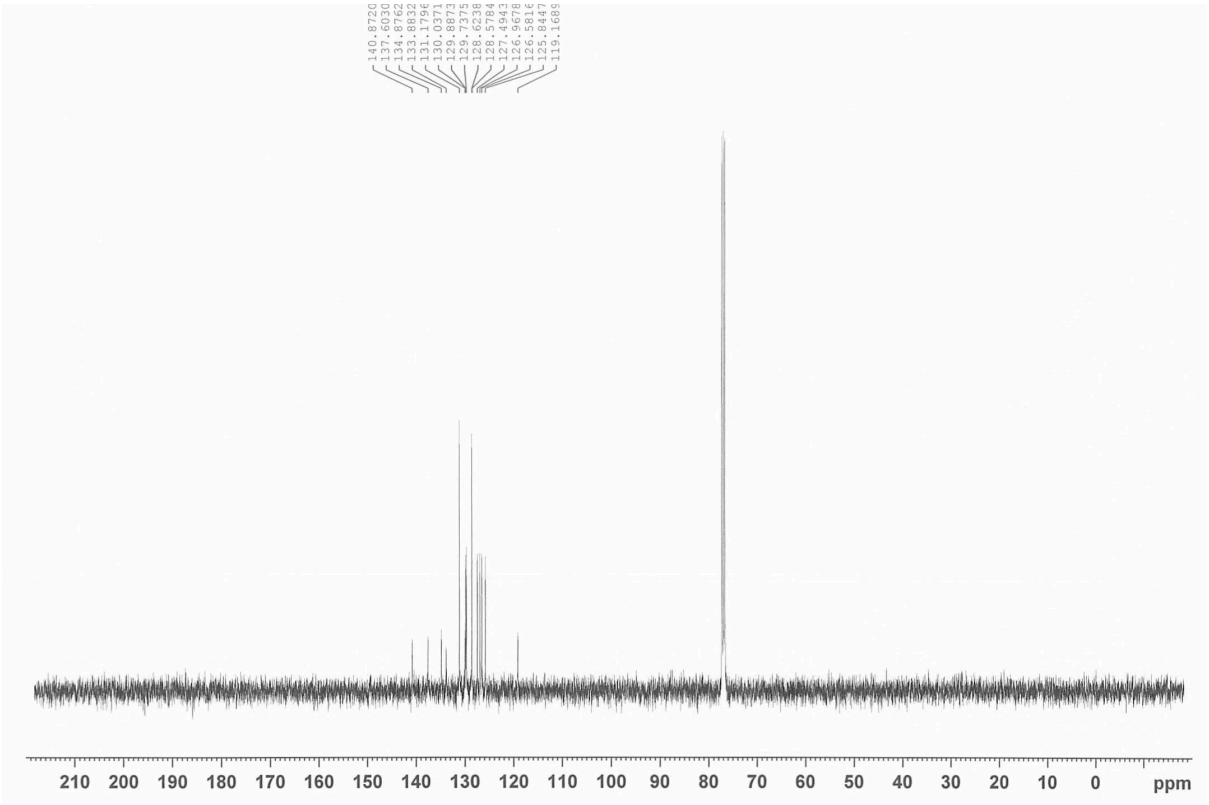
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4-(4-methylphenyl)naphthalene (**11k**) ($CDCl_3$)



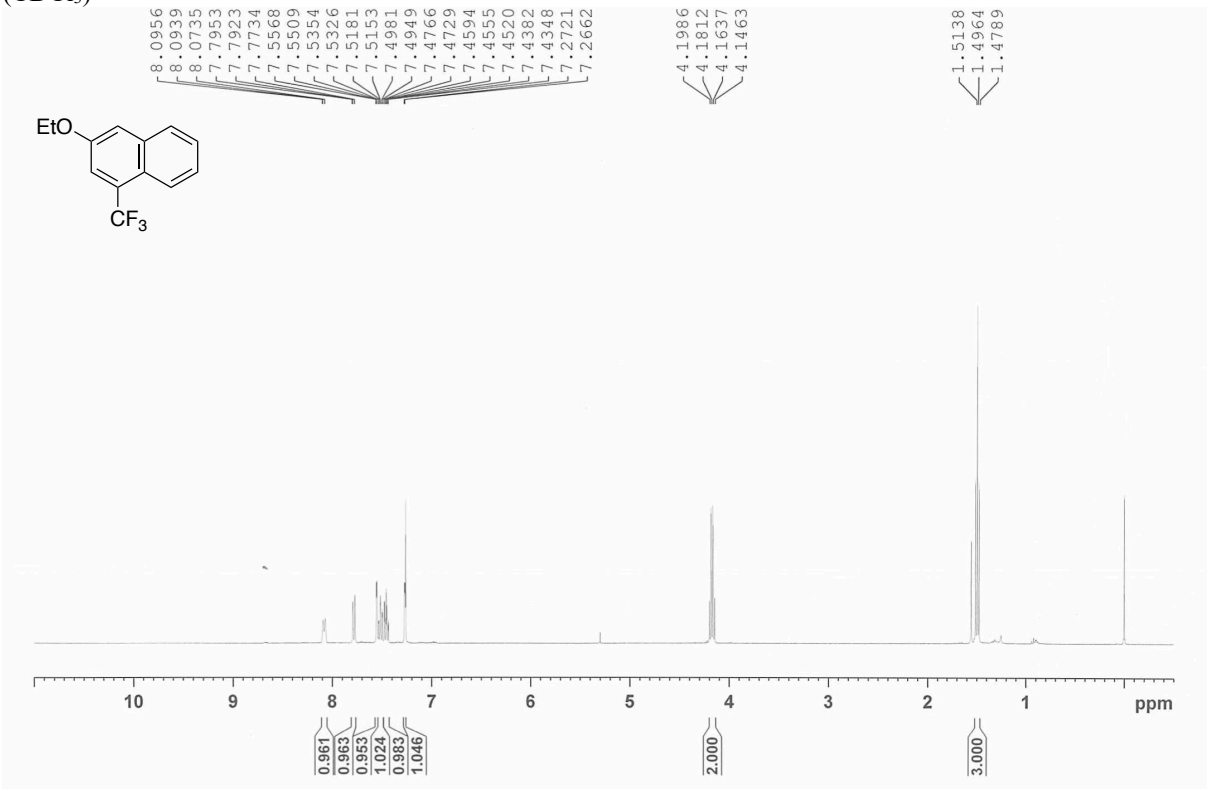


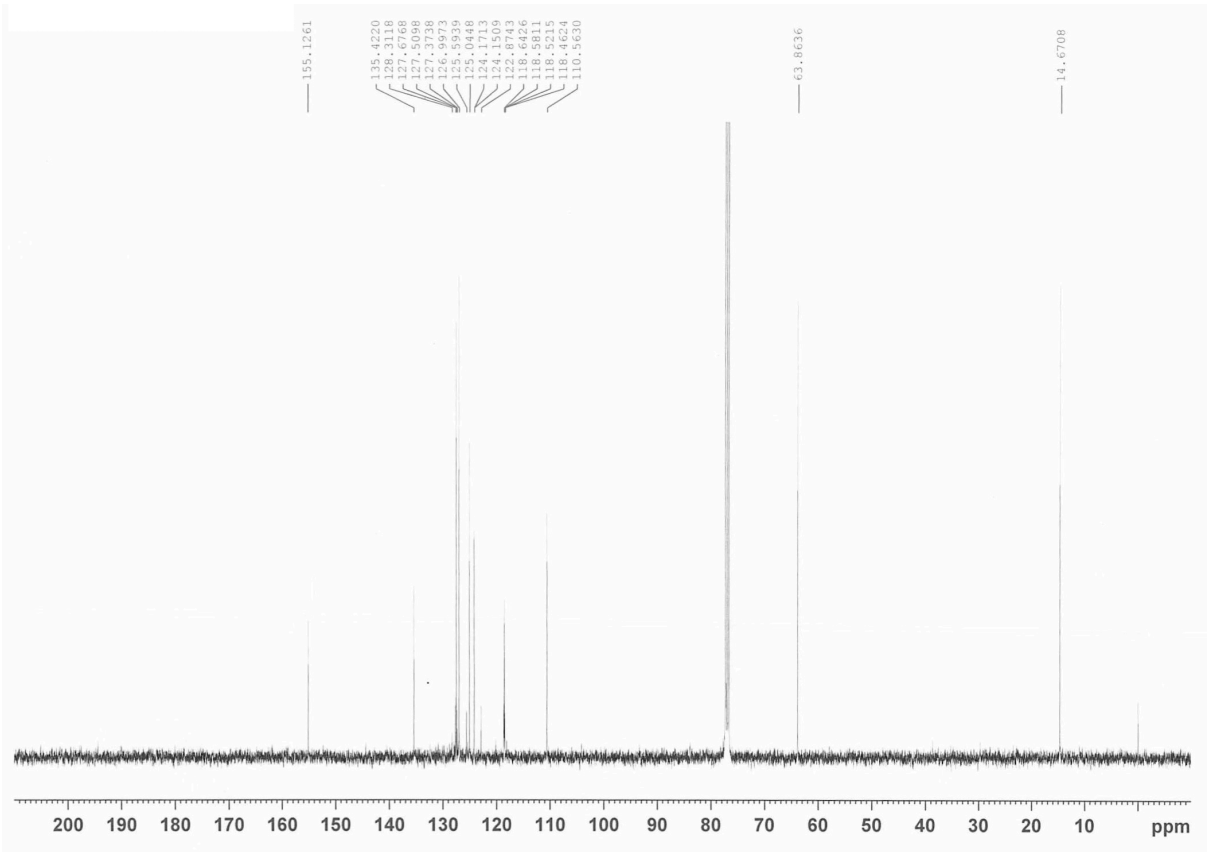
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4-(4-chlorophenyl)naphthalene (**11l**) ($CDCl_3$)



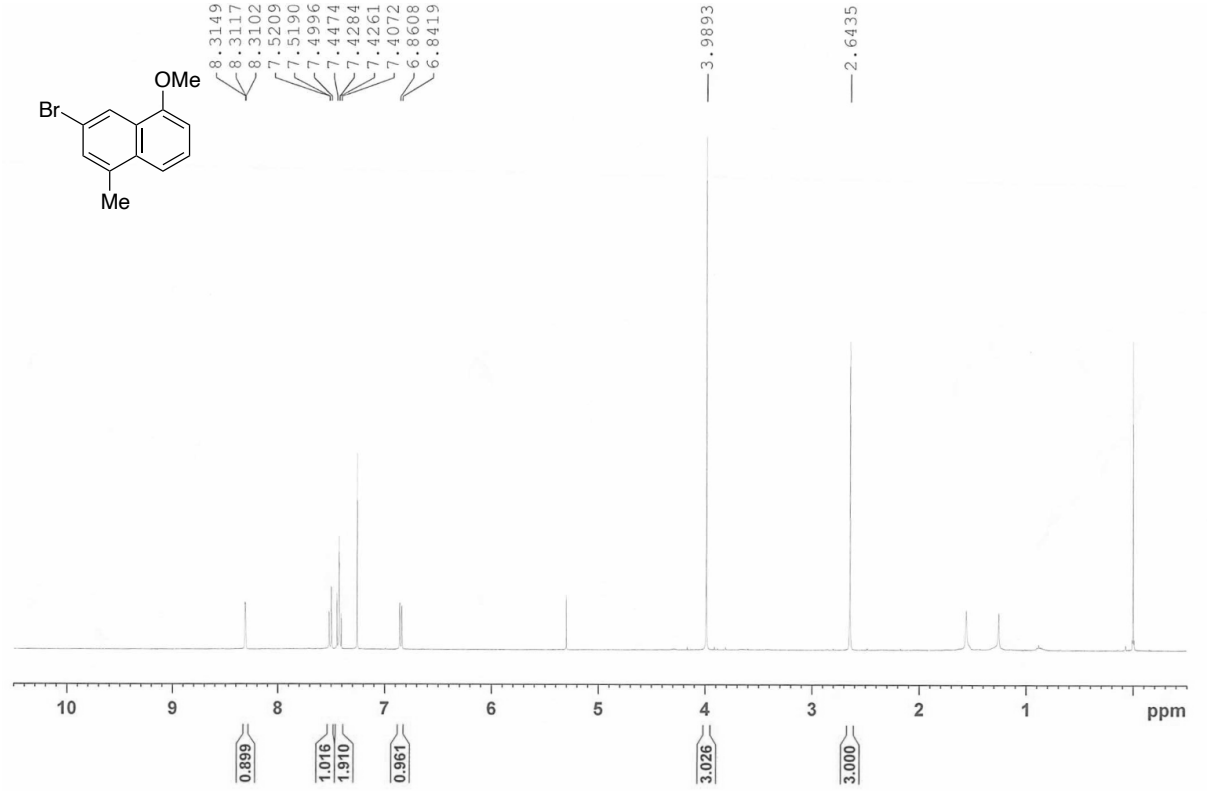


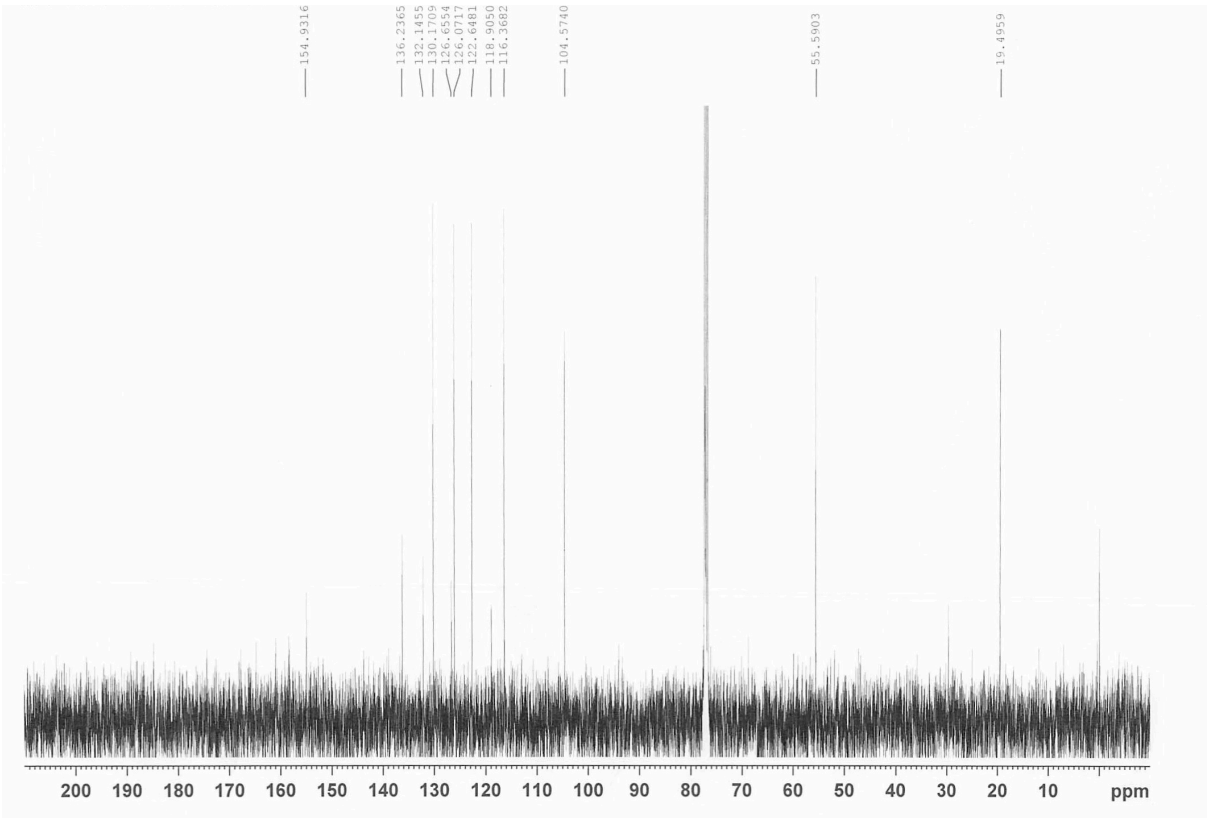
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4-(trifluoromethyl)naphthalene (**11m**) ($CDCl_3$)



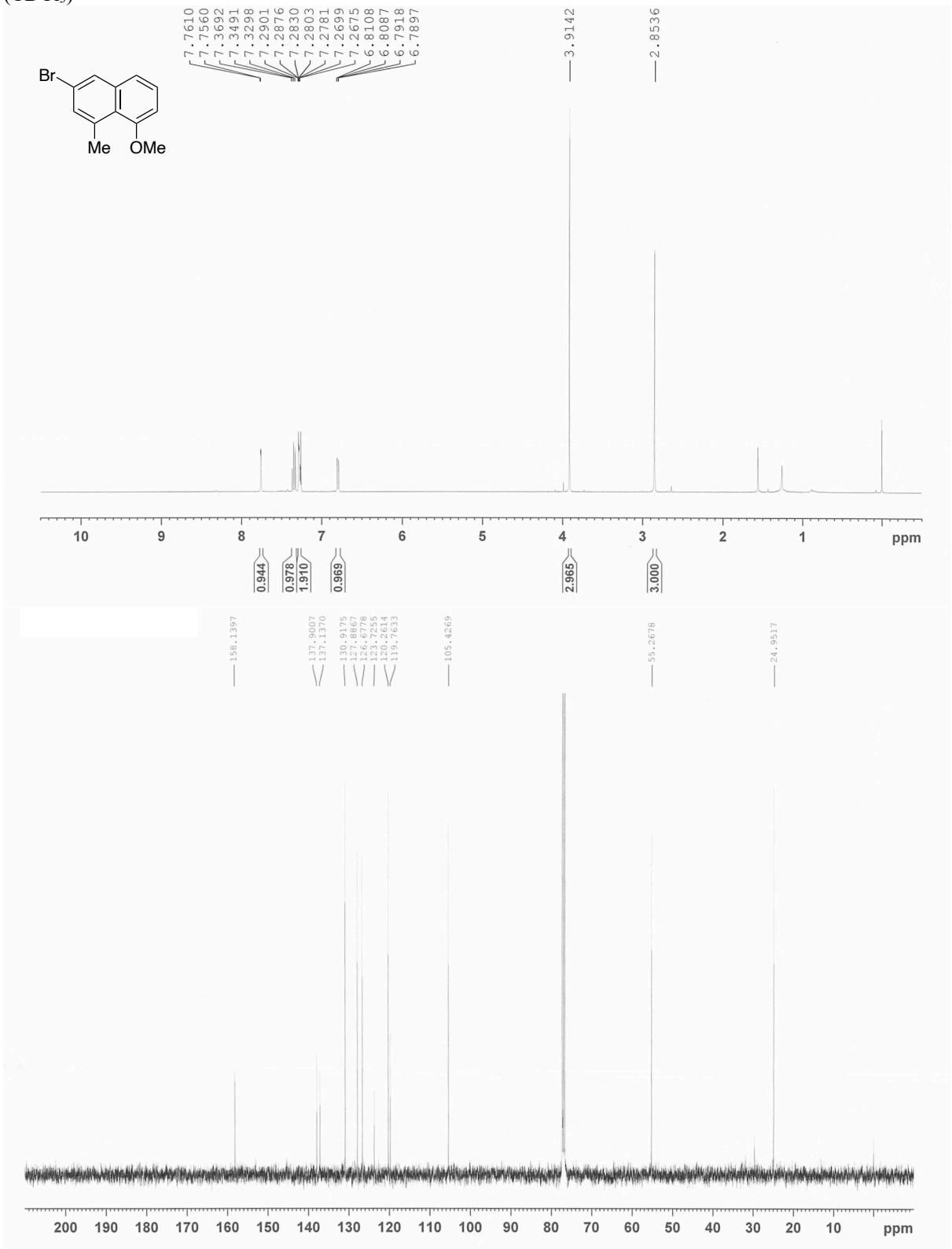


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4-methyl-8-methoxynaphthalene (**11n**) ($CDCl_3$)

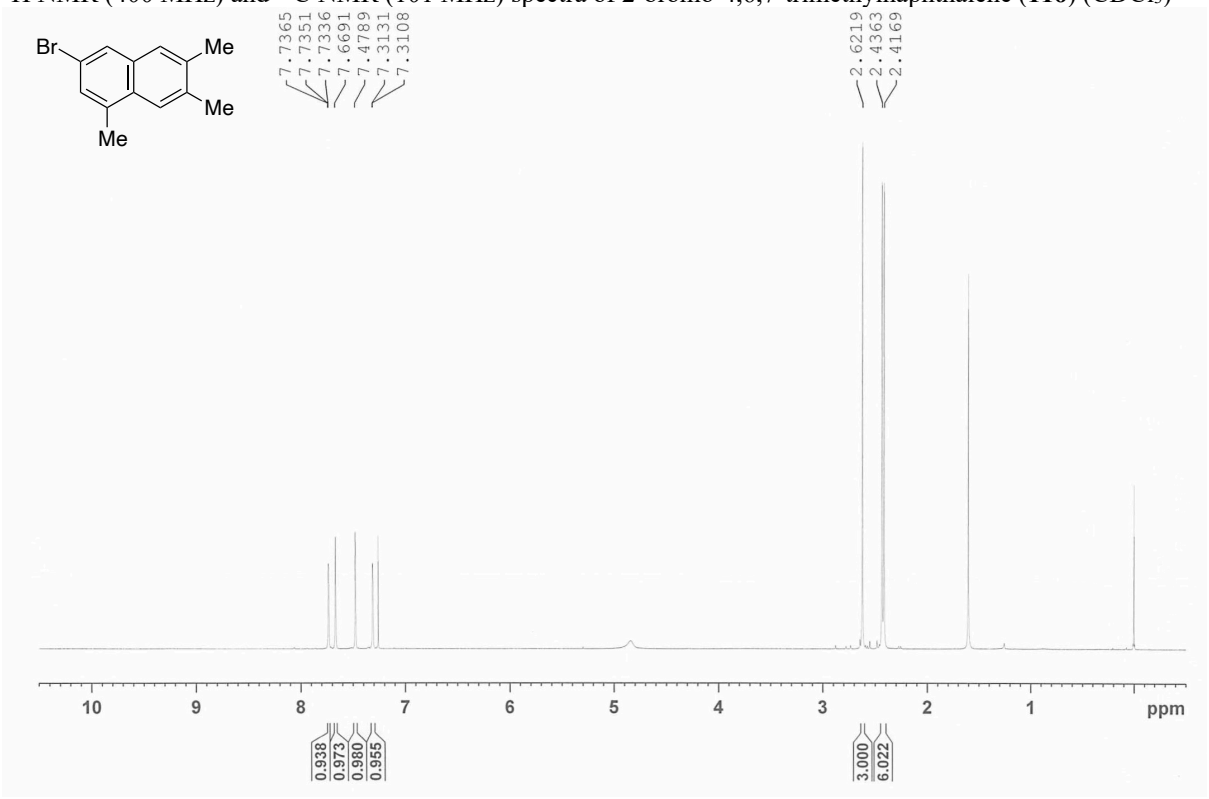


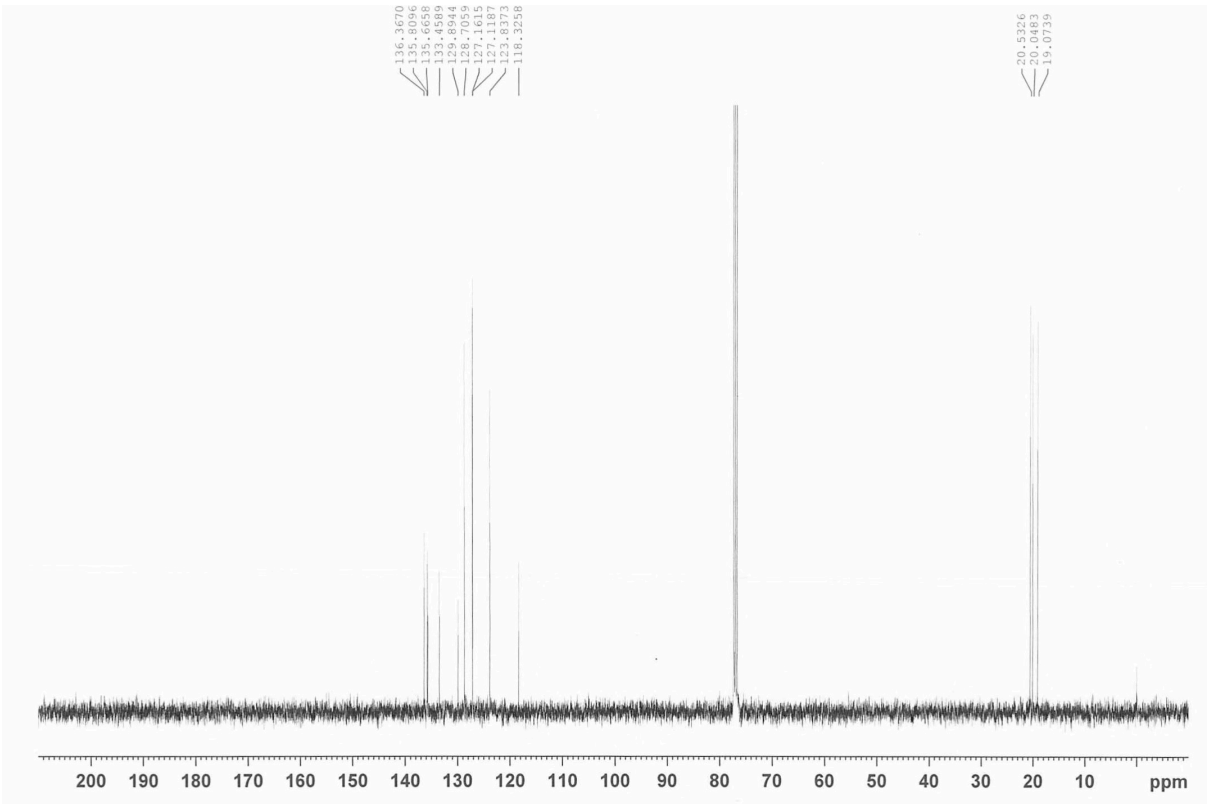


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4-methyl-5-methoxynaphthalene (**11n'**) ($CDCl_3$)

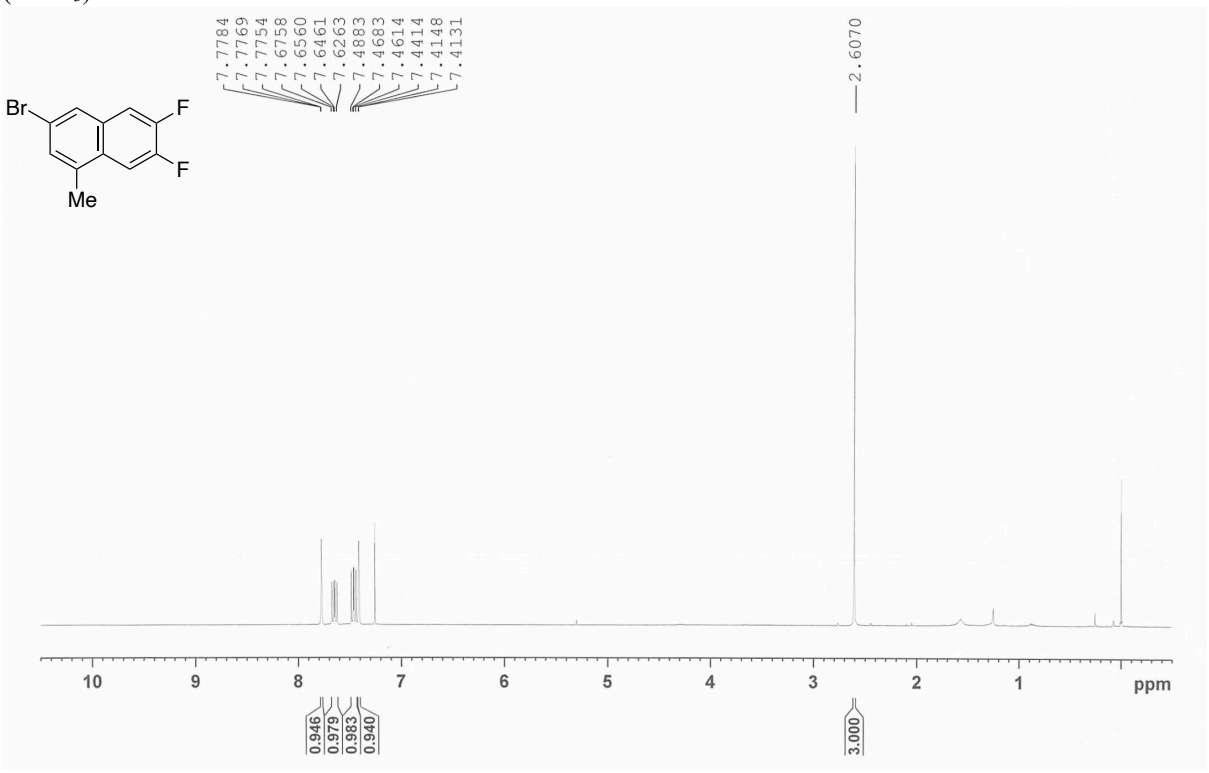


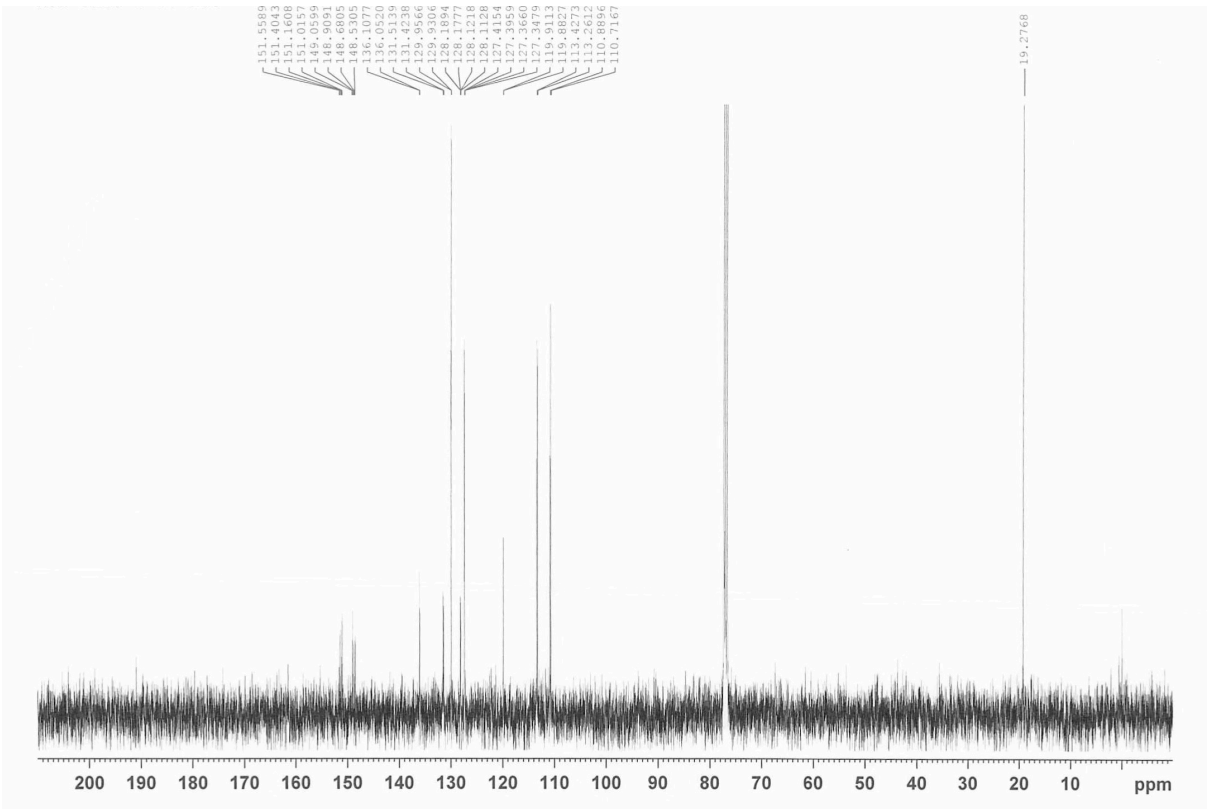
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4,6,7-trimethylnaphthalene (**11o**) ($CDCl_3$)



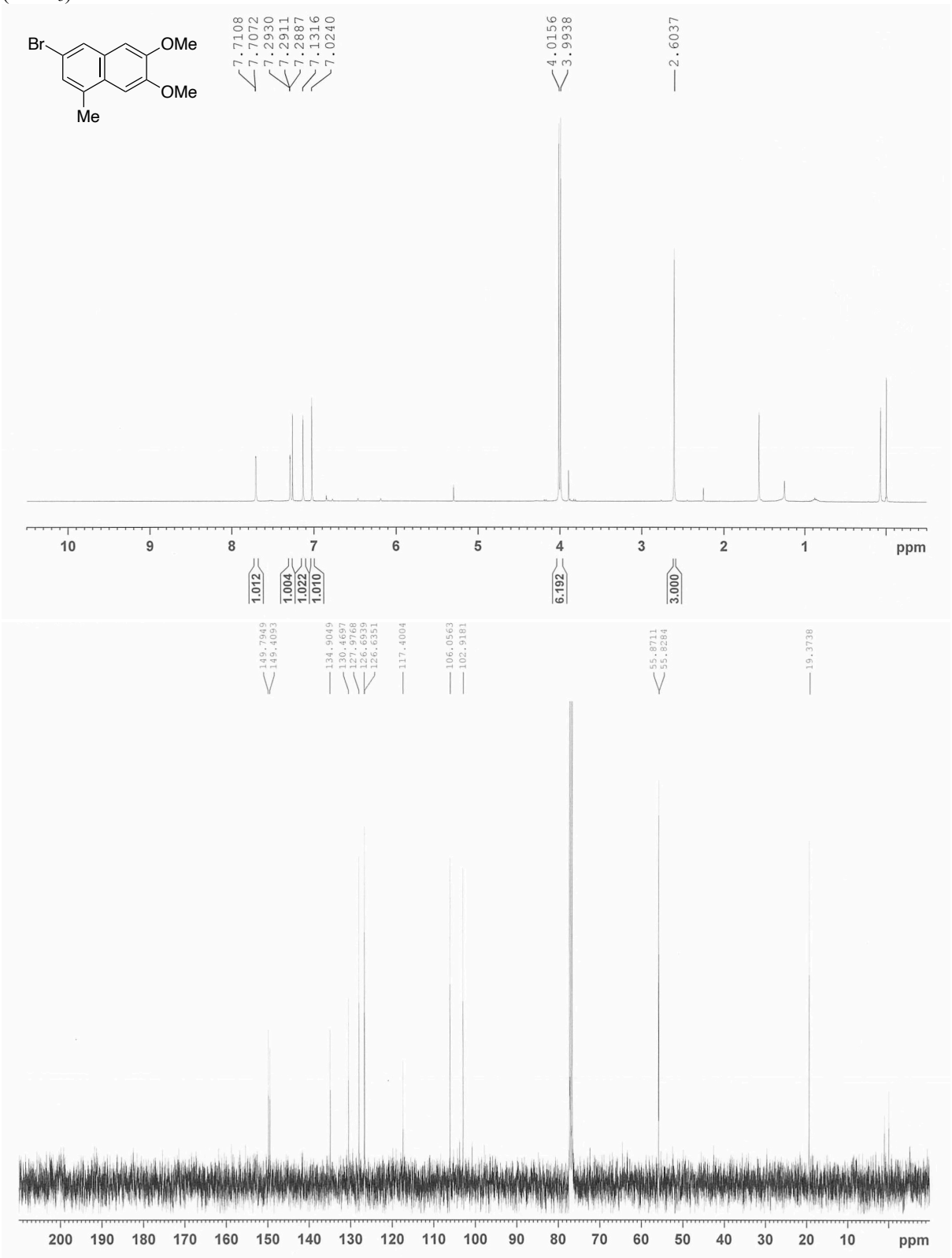


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 1-bromo-6,7-difluoro-4-methylnaphthalene (**11p**) ($CDCl_3$)

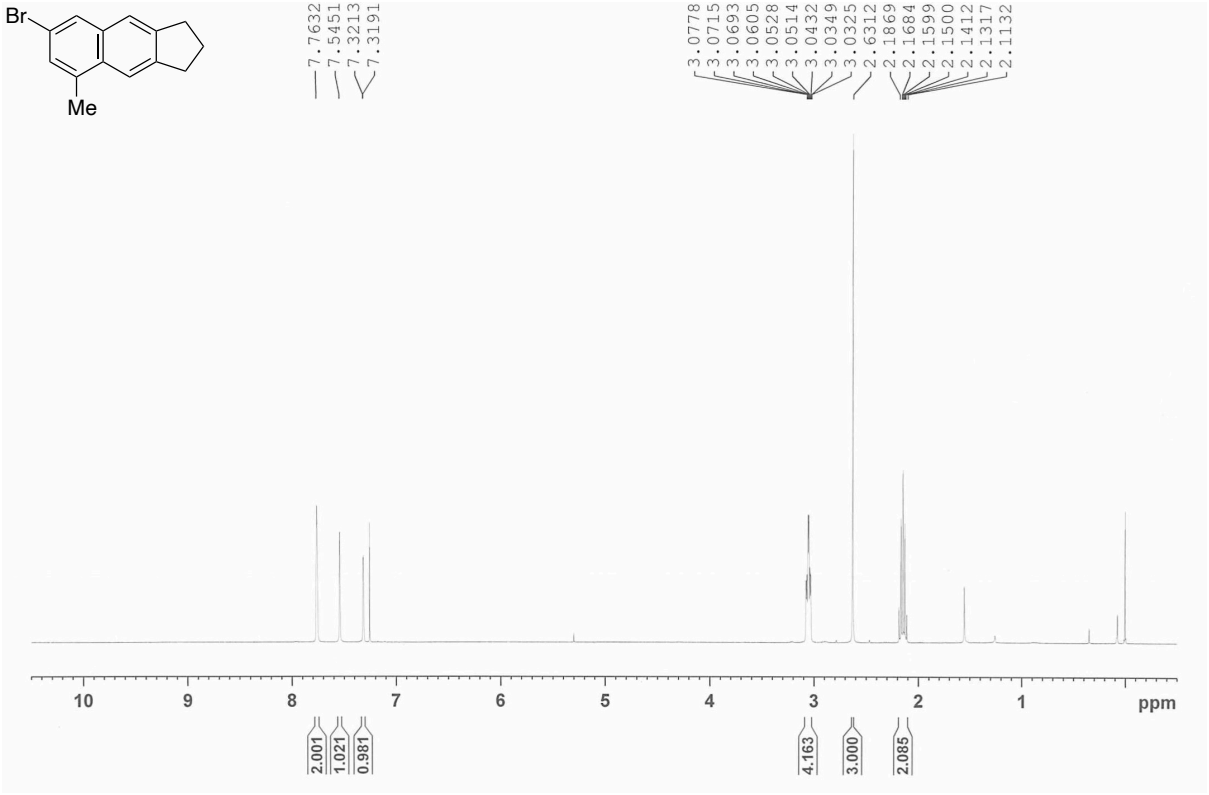


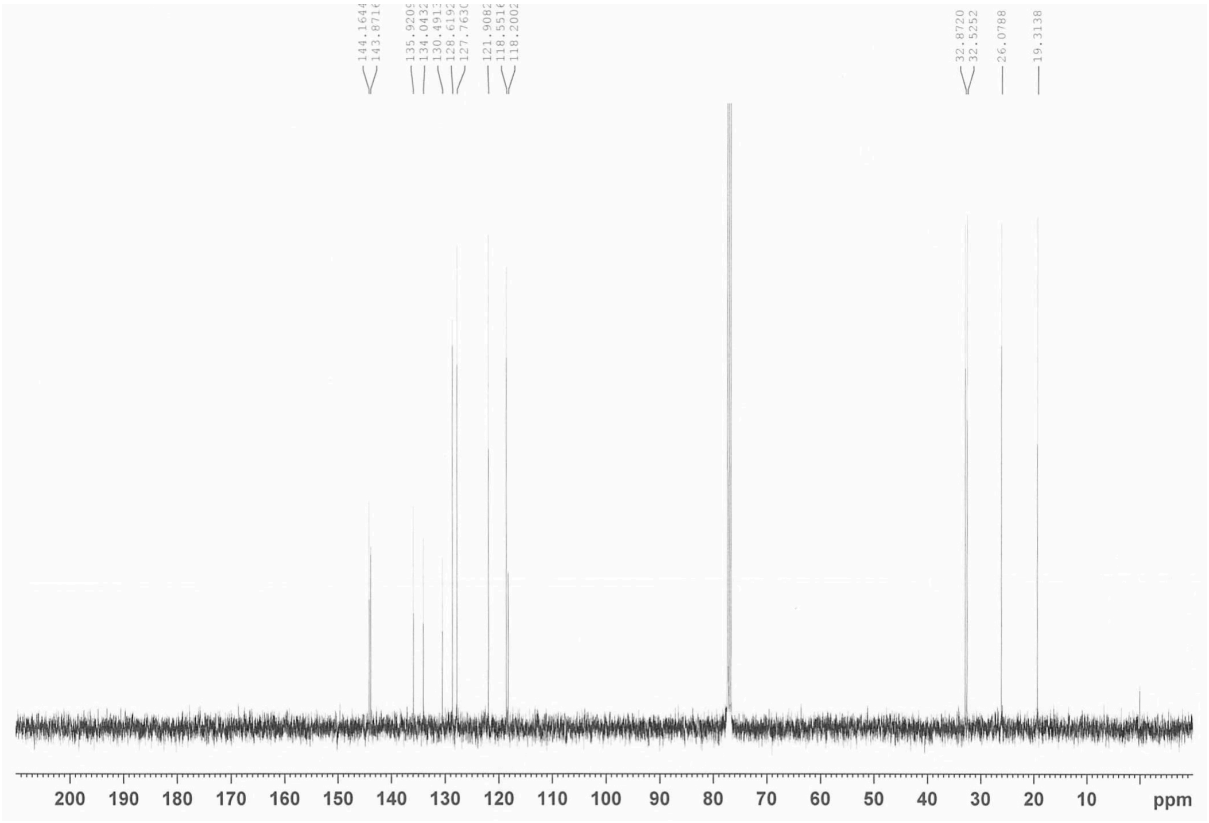


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4-methyl-6,7-dimethoxynaphthalene (**11q**) ($CDCl_3$)

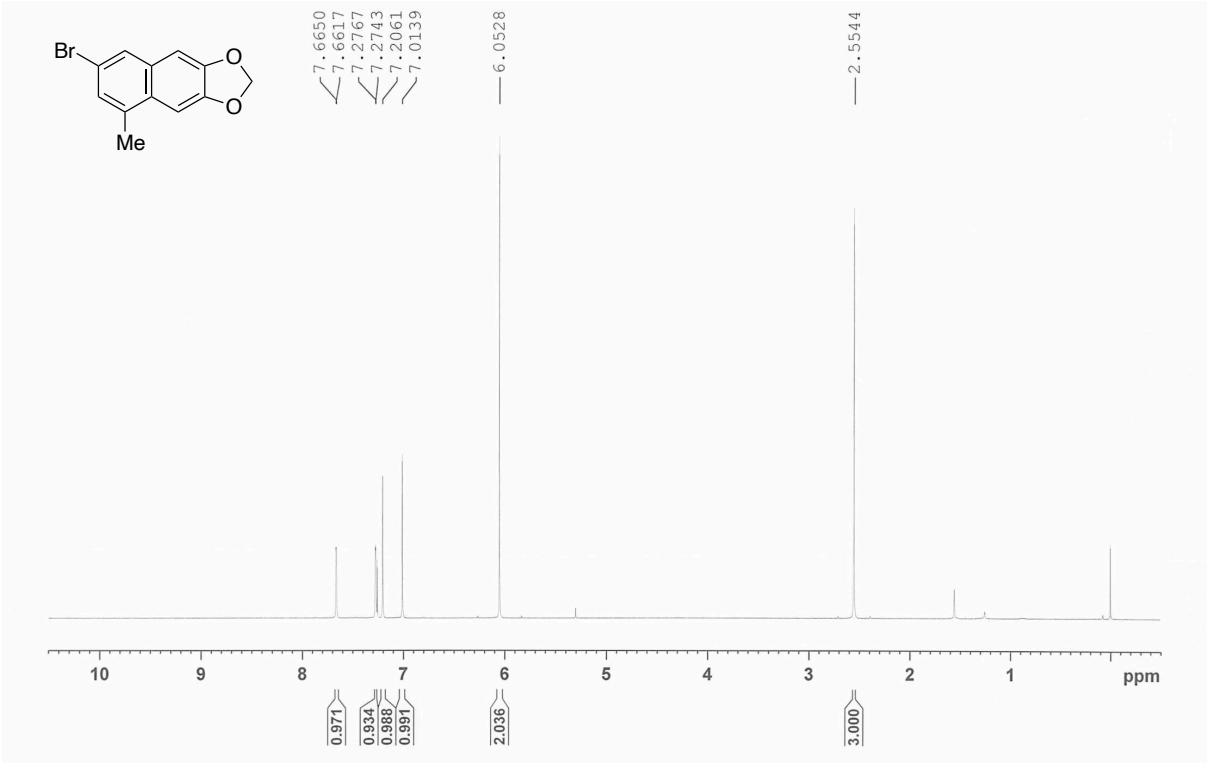


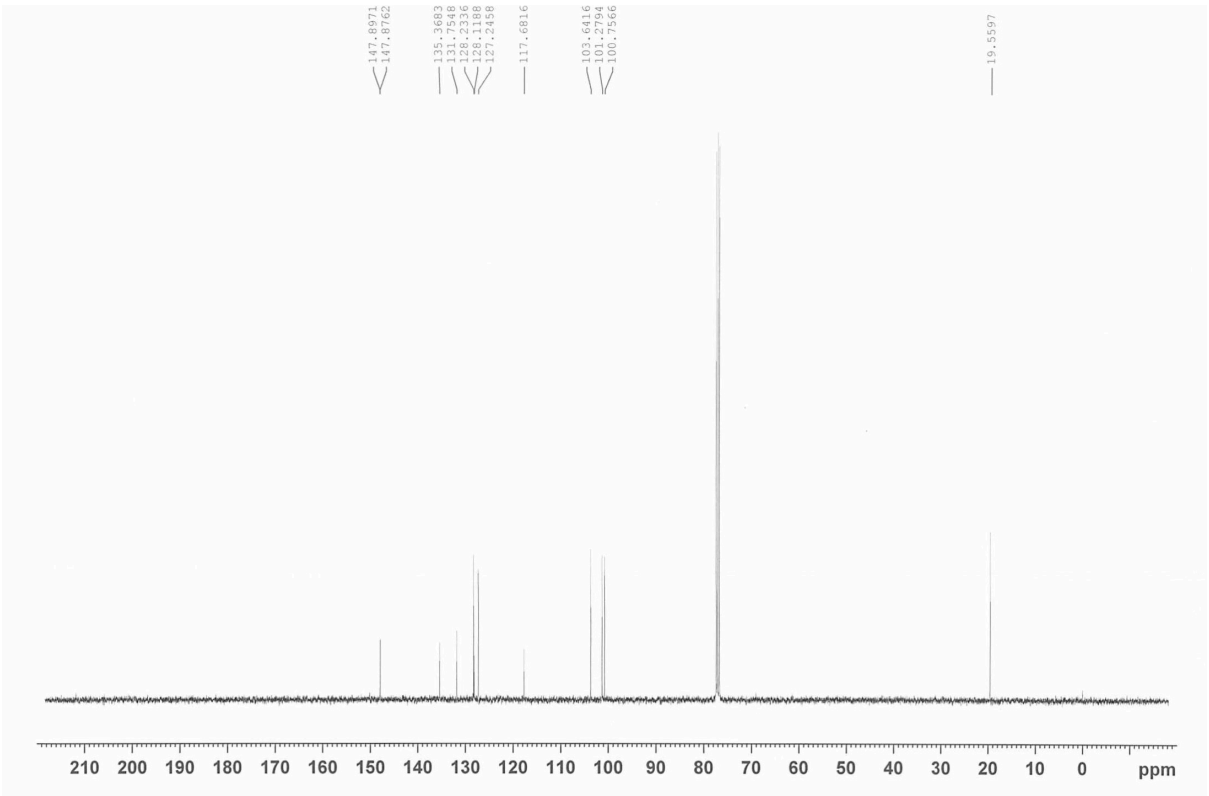
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 6-bromo-2,3-dihydro-8-methyl-1*H*-benz[*f*]indene (**11r**) ($CDCl_3$)



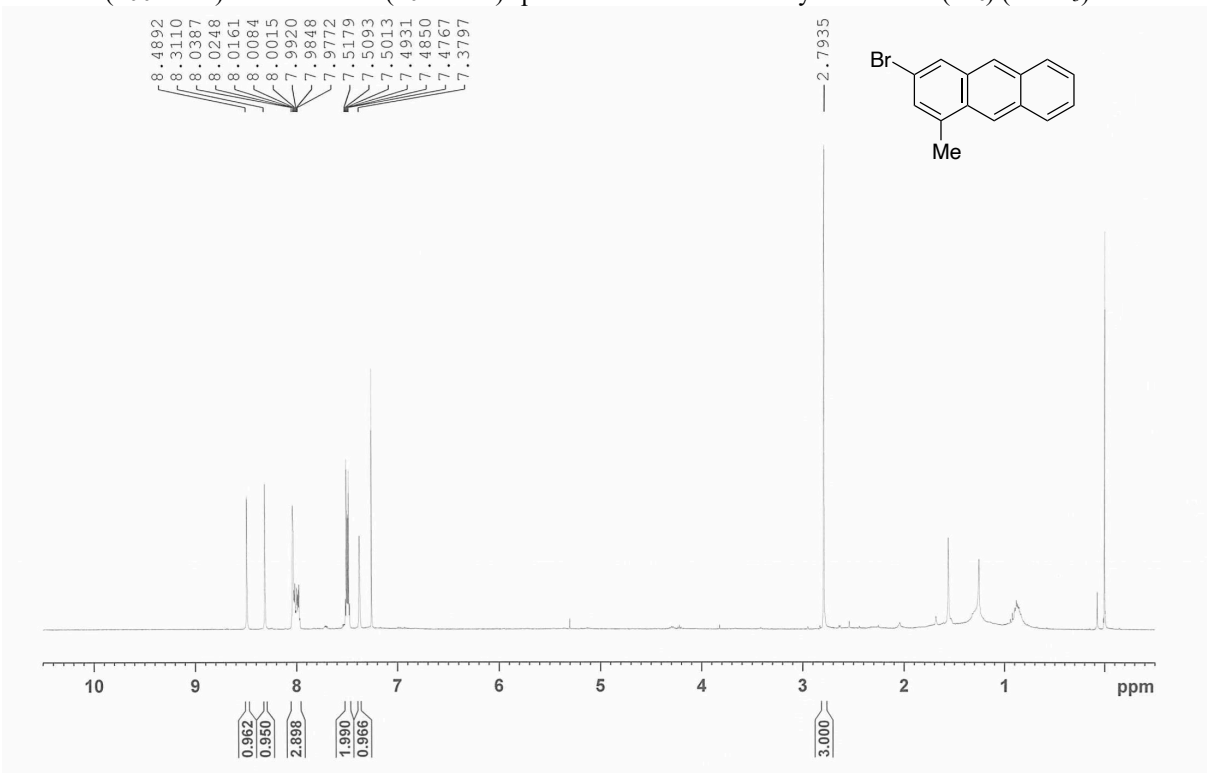


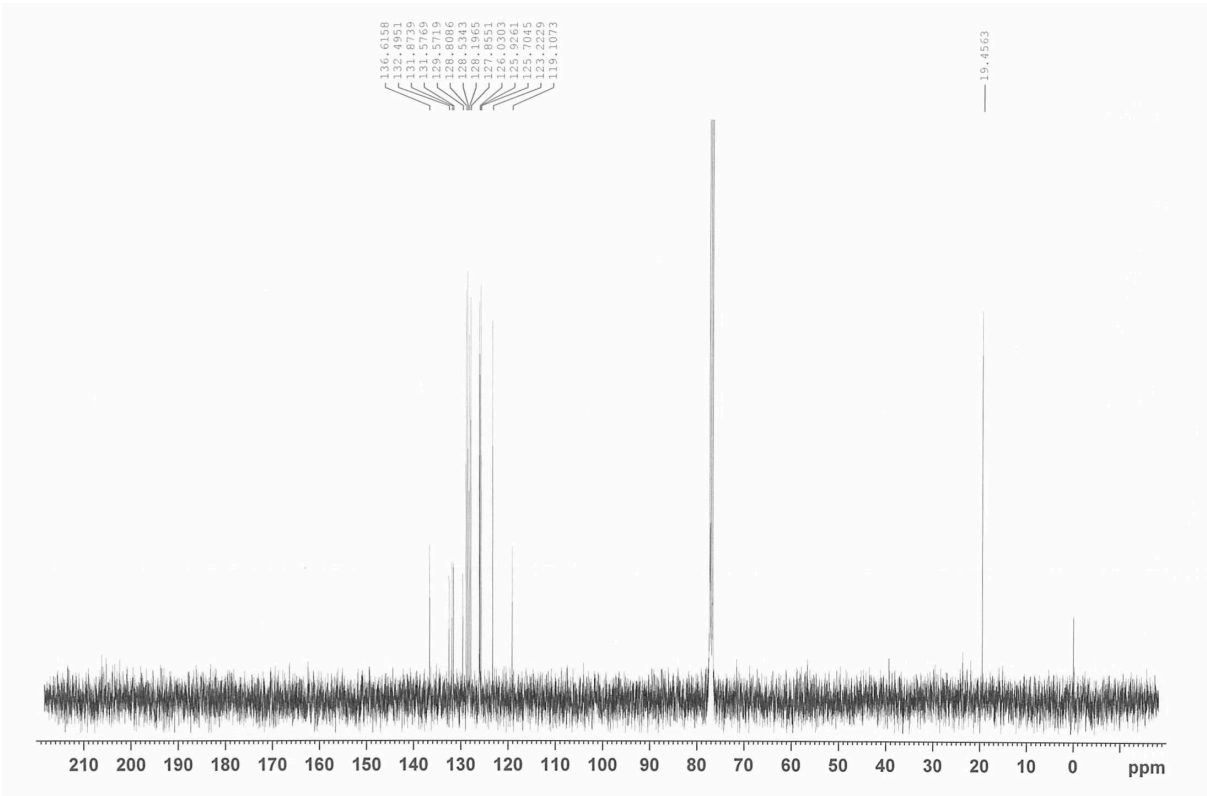
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 6-bromo-8-methylnaphtho[2,3-*d*]-1,3-dioxol (**11s**) ($CDCl_3$)



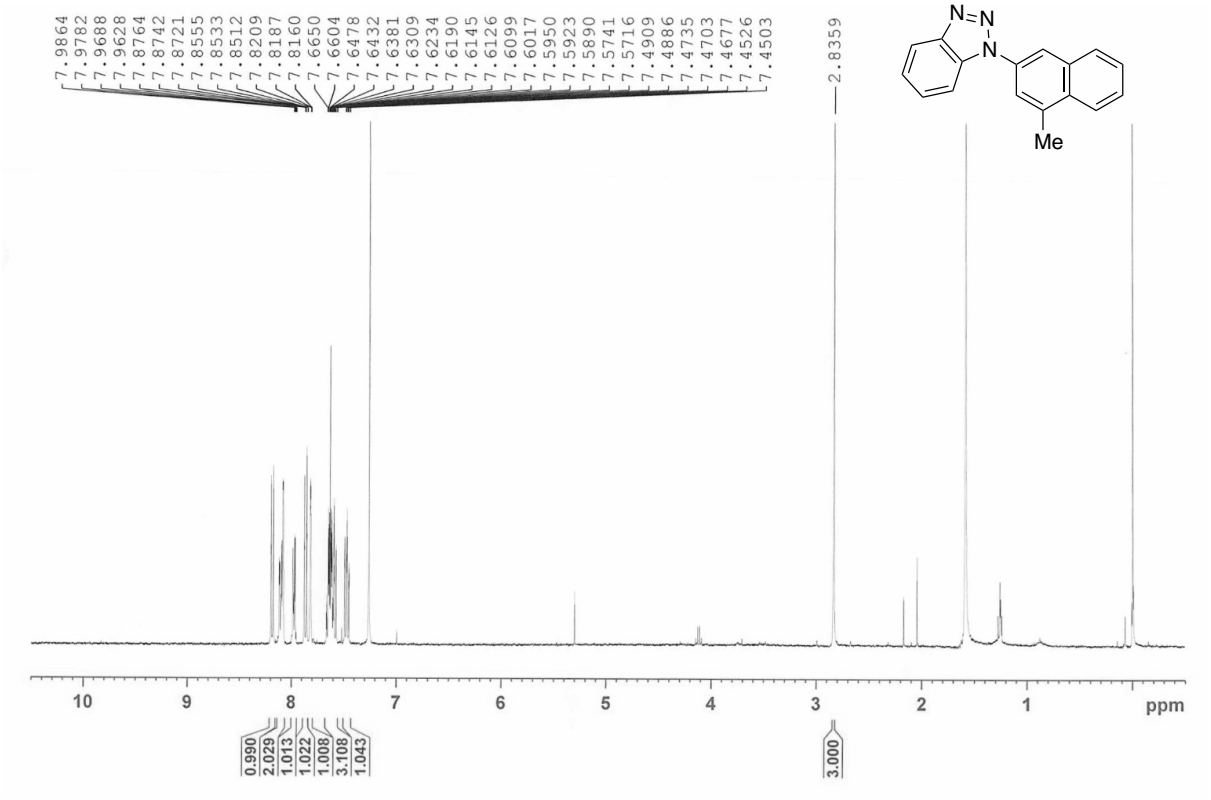


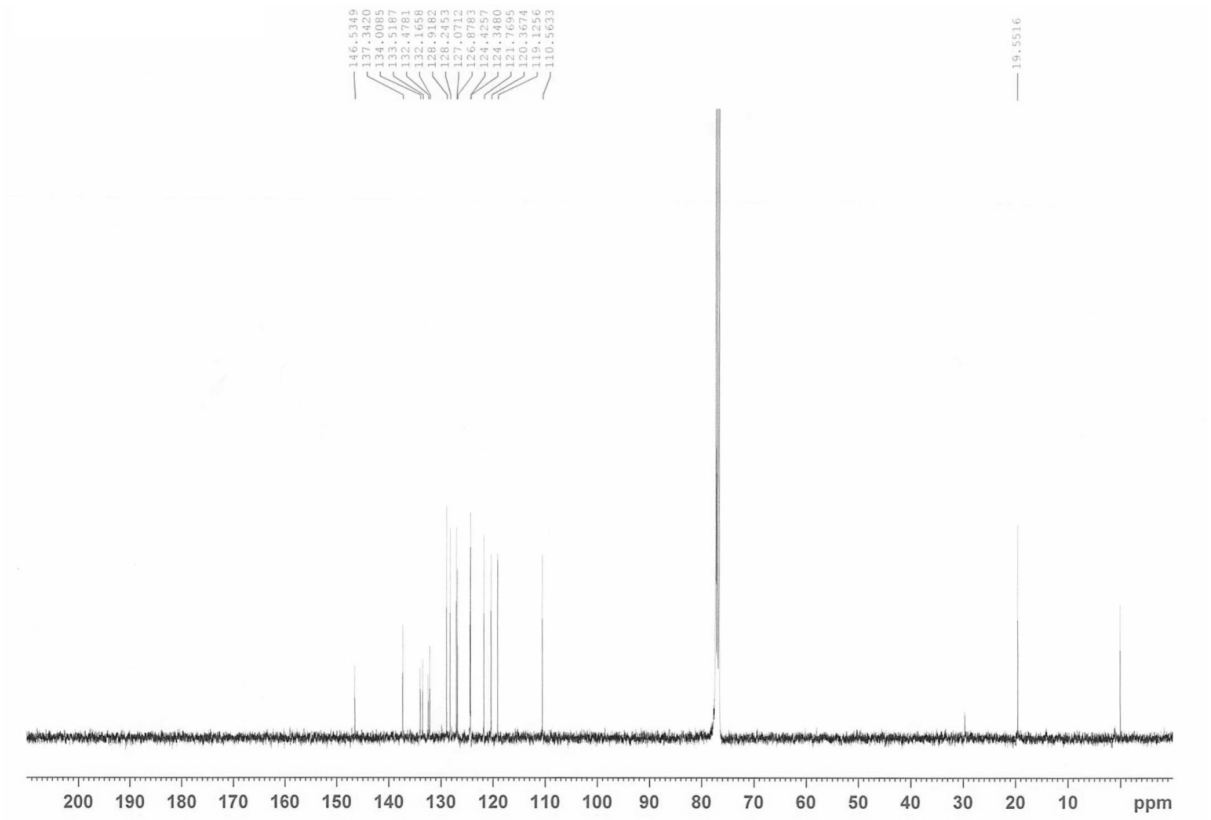
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-bromo-4-methylanthracene (**11t**) ($CDCl_3$)





^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2-(1*H*-benzotriazol-1-yl)-4-methylnaphthalene (**12**) ($CDCl_3$)





^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 9-methyl-7-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2-naphtho[2,3-*d*]-1,3-dioxol (**14**) ($CDCl_3$)