**SUPPLEMENTARY INFORMATION**

# Iron-catalyzed carbene and carbene radical cascade reactions: Mechanistic study and synthetic applications

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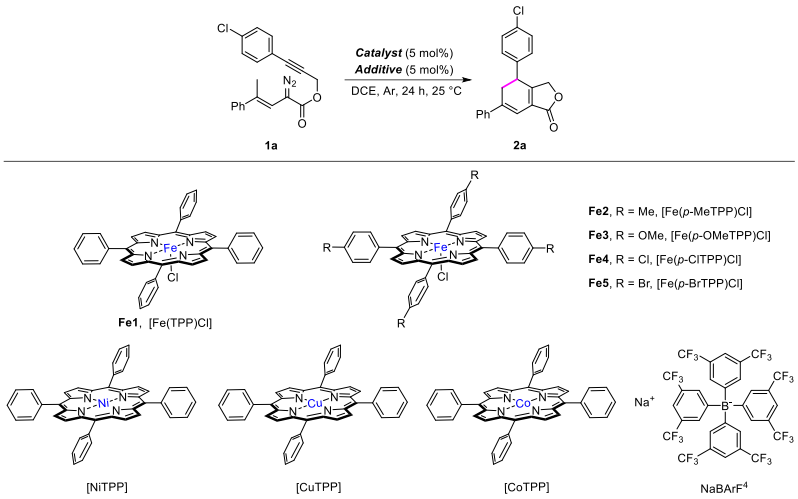
## General Information

All reactions were carried out in oven-dried glassware. Solvents were purified and distilled by following the standard methods. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). The $^{1}H$ NMR, $^{13}C$ NMR, and $^{19}F$ NMR spectra were recorded in $CDCl_3$ on 400 MHz and 500 MHz spectrometer; chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI Source). All substrates were obtained from commercial suppliers or prepared using the referenced literature procedures. Unless stated otherwise, all commercially available compounds were used as received.

## Condition Optimization

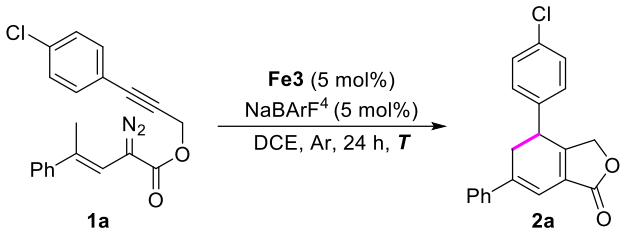
**Supplementary Table 1**. Initial screening of the catalyst and additive of allylic $Csp^3$-H bond insertion reaction.[a]




| Entry | Catalyst | Additive | Yield (%)[b] |
|---|---|---|---|
| 1 | **Fe1** | -- | < 5 |
| 2 | **Fe1** | $NaBArF^4$ | 54 |
| 3 | -- | $NaBArF^4$ | < 5 |
| 4 | **Fe2** | $NaBArF^4$ | 75 |
| 5 | **Fe3** | $NaBArF^4$ | **80** |
| 6 | **Fe4** | $NaBArF^4$ | 48 |
| 7 | **Fe5** | $NaBArF^4$ | 45 |
| 8 | $FeCl_3$ | -- | < 5 |
| 9 | $FeCl_2$ | -- | < 5 |
| 10 | $FeCl_2$ | $NaBArF^4$ | < 5[c] |
| 11 | $FeCl_3$ | $NaBArF^4$ | < 5[d] |
| 12 | [NiTPP] | $NaBArF^4$ | 10/11[e] |
| 13 | [CuTPP] | $NaBArF^4$ | <5/15[e] |
| 14 | [CoTPP] | $NaBArF^4$ | 17/25[e] |
| 15 | $CuPF_6(MeCN)_4$ | $NaBArF^4$ | 31/34[e] |
| 16 | $AgSbF_6$ | $NaBArF^4$ | 34/30[e] |
| 17 | $Rh_2(OAc)_4$ | $NaBArF^4$ | 41/44[e] |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **1a** (35.1 mg, 0.1 mmol), catalyst (5 mol%), and additive (5 mol%) in DCE (1.0 mL) under argon atmosphere at 25 °C for 24 h. [b]Isolated yield of **2a**. [c]10 mol% $NaBArF^4$ was used. [d]15 mol% $NaBArF^4$ was used. [e]In the absence of $NaBArF^4$.

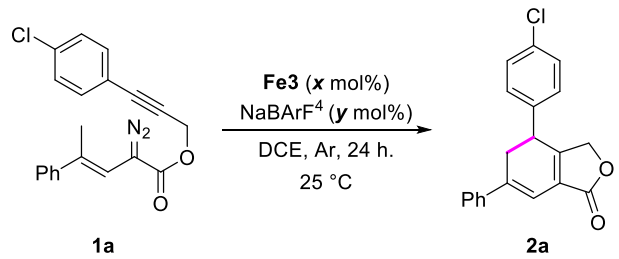
**Supplementary Table 2**. Screening of the reaction temperature of allylic $Csp^3$-H bond insertion reaction.[a]




| Entry | *T* (°C) | Yield (%)[b] |
|---|---|---|
| 1 | 10 | 40 |
| 2 | 25 | **80** |
| 3 | 40 | 71 |
| 4 | 50 | 52/< 5[c] |
| 5 | 70 | 23/< 5[c] |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **1a** (35.1 mg, 0.1 mmol), catalyst **Fe3** (4.1 mg, 5 mol%), and $NaBArF^4$ (4.4 mg, 5 mol%) in DCE (1.0 mL) under argon atmosphere at 25 °C for 24 h. [b]Isolated yield of **2a**. [c]Without $NaBArF^4$.

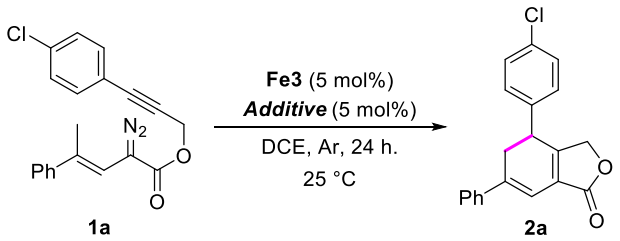
**Supplementary Table 3**. Screening of the catalyst and additive loading of allylic $Csp^3$-H bond insertion reaction.[a]




| Entry | x | y | Yield (%)[b] |
|---|---|---|---|
| 1 | 2.5 | 2.5 | 53 |
| 2 | 5 | 5 | **80** |
| 3 | 10 | 10 | 80 |
| 4 | 15 | 15 | 79 |
| 5 | 20 | 20 | 78 |
| 6 | 5 | 7.5 | 76 |
| 7 | 5 | 10 | 77 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **1a** (35.1 mg, 0.1 mmol), catalyst **Fe3** (x mol%) and $NaBArF^4$ (y mol%) in DCE (1.0 mL) under argon atmosphere at 25 °C for 24 h. [b]Isolated yield of **2a**.

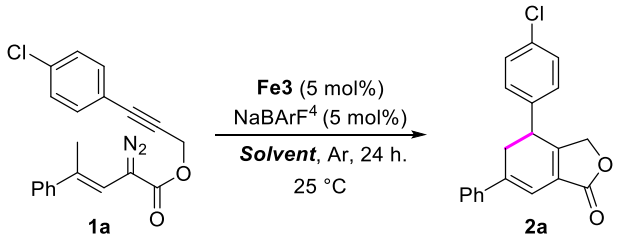
**Supplementary Table 4**. Screening of the additive of allylic $Csp^3$-H bond insertion reaction.[a]




| Entry | Additive | Yield (%)[b] |
|---|---|---|
| 1 | TsNa | < 5 |
| 2 | $CF_3CO_2Na$ | < 5 |
| 3 | $CF_3SO_2Na$ | < 5 |
| 4 | $CF_3CO_2Ag$ | 67 |
| 5 | AgOTf | 50 |
| 6 | $AgNTf_2$ | 51 |
| 7 | $NaNTf_2$ | < 5 |
| 8 | $NaBArF^4$ | **80** |
| 9 | $NaB(C_6F_5)_4$ | 75 |
| 10 | $KB(C_6F_5)_4$ | 72 |
| 11 | -- | < 5 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **1a** (35.1mg, 0.1 mmol), catalyst **Fe3** (4.1 mg, 5 mol%), and indicated additive (5 mol%) in DCE (1.0 mL) under argon atmosphere at 25 ℃ for 24 h. [b]Isolated yield of **2a**.

**Supplementary Table 5**. Screening of the solvent of allylic $Csp^3$-H bond insertion reaction.[a]

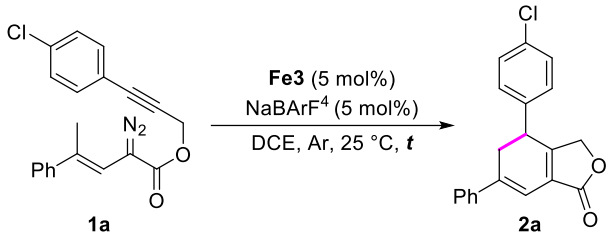



| Entry | Solvent | Yield (%)[b] |
|---|---|---|
| 1 | DCE | **80** |
| 2 | DCM | 79 |
| 3 | 1,4-Dioxane | < 5 |
| 4 | MeCN | < 5 |
| 5 | Toluene | 47 |
| 6 | Xylenes | 51 |
| 7 | Chlorobenzene | 38 |
| 8 | THF | < 5 |
| 9 | NMP | < 5 |

| | | |
|---|---|---|
| 10 | DMF | < 5 |
| 11 | hexane | < 5 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **1a** (35.1 mg, 0.1 mmol), catalyst **Fe3** (4.1 mg, 5 mol%), and $NaBArF^4$ (4.4 mg, 5 mol%) in indicated solvent (1.0 mL) under argon atmosphere at 25 ℃ for 24 h. [b]Isolated yield of **2a**.

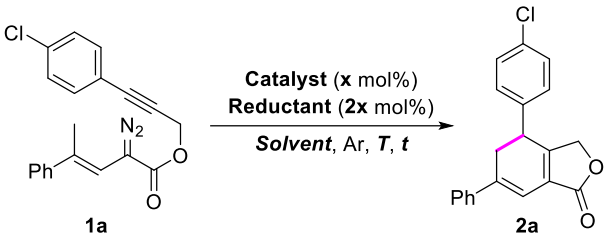
**Supplementary Table 6**. Screening of the reaction time of allylic $Csp^3$-H bond insertion reaction.[a]




| Entry | *t* (h) | Yield (%)[b] |
|---|---|---|
| 1 | 6 | 25 |
| 2 | 8 | 36 |
| 3 | 12 | 42 |
| 4 | 16 | 57 |
| 5 | 20 | 71 |
| 6 | 24 | **80** |
| 7 | 30 | 78 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **1a** (35.1 mg, 0.1 mmol), catalyst **Fe3** (4.1 mg, 5 mol%), and $NaBArF^4$ (4.4 mg, 5 mol%) in DCE (1.0 mL) under nitrogen atmosphere at 25 ℃ for indicated time. [b]Isolated yield of **2a**.

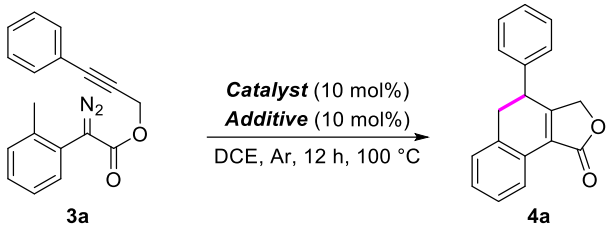
**Supplementary Table 7.** Optimization of the *in situ* reduction conditions.[a]




| Entry | Catalyst | Reductant | Solvent | x | *T* (°C) | *t* (h) | Yield (%)[b] |
|---|---|---|---|---|---|---|---|
| 2 | **Fe1** | Fe powder | DCM/MeOH = 9:1 | 5 | 60 | 6 | 31 |
| 3 | **Fe2** | Fe powder | DCM/MeOH = 9:1 | 5 | 60 | 6 | 32 |
| 4 | **Fe3** | Fe powder | DCM/MeOH = 9:1 | 5 | 60 | 6 | 35 |
| 5 | **Fe4** | Fe powder | DCM/MeOH = 9:1 | 5 | 60 | 6 | 32 |
| 6 | **Fe5** | Fe powder | DCM/MeOH = 9:1 | 5 | 60 | 6 | 35 |
| 7 | **Fe3** | Fe powder | DCM | 5 | 60 | 6 | < 5 |
| 8 | **Fe3** | Fe powder | MeOH | 5 | 60 | 6 | < 5 |
| 9 | **Fe3** | Fe powder | DCE | 5 | 60 | 6 | < 5/< 5[c] |
| 10 | **Fe3** | Fe powder | DMF | 5 | 60 | 6 | < 5/< 5[d] |
| 11 | **Fe3** | Fe powder | MeCN | 5 | 60 | 6 | < 5/< 5[e] |
| 12 | **Fe3** | Fe powder | DCM/MeOH = 9:1 | 5 | 25 | 6 | < 5 |
| 13 | **Fe3** | Fe powder | DCM/MeOH = 9:1 | 5 | 40 | 6 | < 5 |
| 14 | **Fe3** | Fe powder | DCM/MeOH = 9:1 | 5 | 50 | 6 | 14 |
| 15 | **Fe3** | Fe powder | DCM/MeOH = 9:1 | 5 | 70 | 6 | 51 |
| 16 | **Fe3** | Fe powder | DCM/MeOH = 9:1 | 5 | 80 | 6 | 41 |
| 17 | **Fe1** | Fe powder | DCM/MeOH = 9:1 | 5 | 70 | 6 | 49 |
| 18 | **Fe2** | Fe powder | DCM/MeOH = 9:1 | 5 | 70 | 6 | 47 |
| 19 | **Fe4** | Fe powder | DCM/MeOH = 9:1 | 5 | 70 | 6 | 51 |
| 20 | **Fe5** | Fe powder | DCM/MeOH = 9:1 | 5 | 70 | 6 | 53 |
| 21 | **Fe5** | Fe powder | DCM/MeOH = 9:1 | 2.5 | 70 | 6 | 17 |
| 22 | **Fe5** | Fe powder | DCM/MeOH = 9:1 | 7.5 | 70 | 6 | 54 |
| 23 | **Fe5** | Fe powder | DCM/MeOH = 9:1 | 10 | 70 | 6 | **57** |
| 24 | **Fe5** | Fe powder | DCM/MeOH = 9:1 | 10 | 70 | 4 | 31 |
| 25 | **Fe5** | Fe powder | DCM/MeOH = 9:1 | 10 | 70 | 5 | 45 |
| 26 | **Fe5** | Fe powder | DCM/MeOH = 9:1 | 10 | 70 | 7 | 55 |
| 27 | **Fe5** | Zn powder | DCM/MeOH = 9:1 | 10 | 70 | 6 | < 5 |
| 28 | **--** | Fe powder | DCM/MeOH = 9:1 | 10 | 70 | 6 | < 5 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **1a** (35.1 mg, 0.1 mmol), catalyst and reductant in indicated solvent (1.0 mL) under nitrogen atmosphere at indicated temperature for indicated time. [b]Isolated yield of **2a**. [c]DCE/MeOH = 9:1 as solvent. [d]DMF/MeOH = 9:1 as solvent. [e]MeCN/MeOH = 9:1 as solvent.

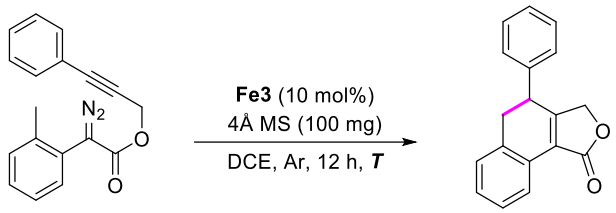
**Supplementary Table 8**. Initial screening of the catalyst and additive of benzyl $Csp^3$-H bond insertion reaction.[a]




| Entry | Catalyst | Additive | Yield (%)[b] |
|---|---|---|---|
| 1 | **Fe1** | -- | 44/< 5[c] |
| 2 | **Fe2** | -- | 54/< 5[c] |
| 3 | **Fe3** | -- | 64/< 5[c] |
| 4 | **Fe4** | -- | 37/< 5[c] |
| 5 | **Fe5** | -- | 32/< 5[c] |
| 6 | **--** | -- | < 5 |
| 7 | **Fe3** | $NaBArF^4$ | 59/< 5[c] |
| 8[d] | **Fe3** | $NaBArF^4$ | 62/< 5[c] |
| 9[d] | **Fe3** | -- | **71** |
| 10[d] | $FeCl_3$ | -- | < 5 |
| 11[d] | $FeCl_2$ | -- | < 5 |
| 12[d] | [NiTPP] | -- | 11 |
| 13[d] | [CuTPP] | -- | 10 |
| 14[d] | [CoTPP] | -- | 47 |
| 15[d] | $CuPF_6(MeCN)_4$ | -- | 22 |
| 16[d] | $AgSbF_6$ | -- | 13 |
| 17[d] | $Rh_2(OAc)_4$ | -- | 10 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **3a** (29.0 mg, 0.1 mmol), catalyst (10 mol%), and additive (10 mol%) in DCE (1.0 mL) under argon atmosphere at 100 °C for 12 h. [b]Isolated yield of **4a**. [c]At 25 °C. [d]The reaction was conducted in the presence of 4Å MS (100 mg).

**Supplementary Table 9**. Screening of the reaction temperature of benzyl $Csp^3$-H bond insertion reaction.[a]

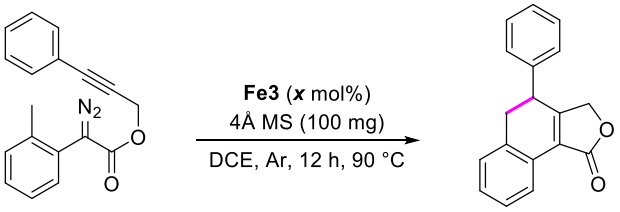



**3a** **4a**

| Entry | *T* (°C) | Yield (%)[b] |
|---|---|---|
| 1 | 25 | < 5 |
| 2 | 50 | < 5 |
| 3 | 70 | 14 |
| 4 | 80 | 57 |
| 5 | 85 | 66 |
| 6 | 90 | **82** |
| 7 | 95 | 76 |
| 8 | 100 | 71 |
| 9 | 105 | 69 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **3a** (29.0 mg, 0.1 mmol), catalyst **Fe3** (8.2 mg, 10 mol%) and 4Å MS (100 mg) in DCE (1.0 mL) under argon atmosphere at indicated temperature for 12 h. [b]Isolated yield of **4a**.

**Supplementary Table 10**. Screening of the catalyst loading of benzyl $Csp^3$-H bond insertion reaction.[a]

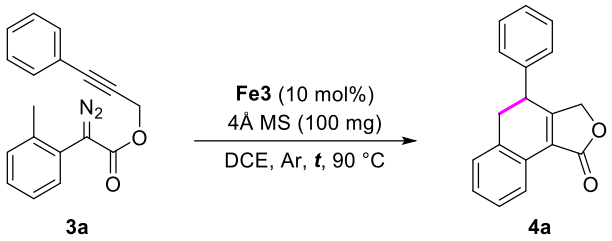



**3a** **4a**

| Entry | x | Yield (%)[b] |
|---|---|---|
| 1 | 5 | 44 |
| 2 | 7.5 | 65 |
| 3 | 10 | **82** |
| 4 | 12.5 | 77 |
| 5 | 15 | 77 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **3a** (29.0 mg, 0.1 mmol), catalyst **Fe3** (*x* mol%), and 4Å MS (100 mg) in DCE (1.0 mL) under argon atmosphere at 90 °C for 12 h. [b]Isolated yield of **4a**.

**Supplementary Table 11**. Screening of the reaction time of benzyl $Csp^3$-H bond insertion reaction.[a]

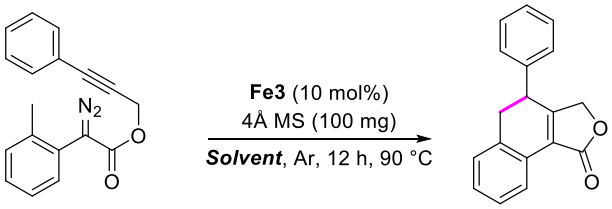



**3a** **4a**

| Entry | Time (h) | Yield (%)[b] |
|---|---|---|
| 1 | 2 | 45 |
| 2 | 4 | 59 |
| 3 | 6 | 75 |
| 4 | 8 | 78 |
| 5 | 12 | **82** |
| 6 | 16 | 81 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **3a** (29.0 mg, 0.1 mmol), catalyst **Fe3** (8.2 mg, 10 mol%), and 4Å MS (100 mg) in DCE (1.0 mL) under argon atmosphere at 90 °C for indicated time. [b]Isolated yield of **4a**.

**Supplementary Table 12**. Screening of the solvent of benzyl $Csp^3$-H bond insertion reaction.[a]

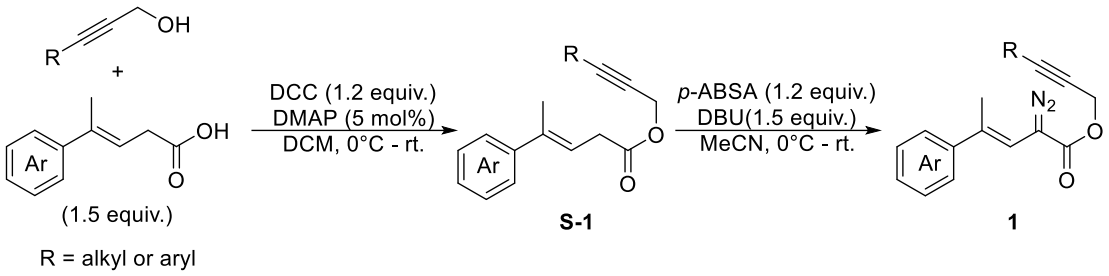



**3a** **4a**

| Entry | Additive | Yield (%)[b] |
|---|---|---|
| 1 | DCE | **82** |
| 2 | 1,4-Dioxane | 80 |
| 3 | MeCN | 43 |
| 4 | Toluene | 20 |
| 5 | Xylenes | 31 |
| 6 | Chlorobenzene | 21 |
| 7 | NMP | < 5 |

[a]Unless otherwise noted, the reactions were carried out with diazo compound **3a** (29.0 mg, 0.1 mmol), catalyst **Fe3** (8.2 mg, 10 mol%), and 4Å MS (100 mg) in different solvents (1.0 mL) under argon atmosphere at 90 °C for 12 h. [b]Isolated yield of **4a**.

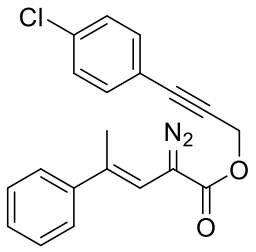
## General Procedure for the Preparation of Diazoacetates 1[1,2].



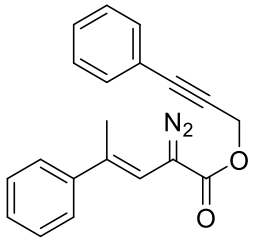

*Synthesis of **S-1***: To a 50-mL oven-dried flask containing a magnetic stirring bar, alcohol (3.0 mmol), acid (4.5 mmol) and DMAP (4-dimethylaminopyridine, 18.3 mg, 0.15 mmol) in DCM (10 mL), was added DCC (dicyclohexylcarbodiimide, 0.74 g, 3.6 mmol) in batches at 0 ℃, and the reaction mixture was stirred at room temperature overnight. After that, the reaction mixture was filtered through Celtie and rinsed with EtOAc (10 mL), and the filtrates were combined. After evaporating the solvents, the residue was purified by column chromatography on silica gel (Hexanes: EtOAc = 20:1) to provide the corresponding esters **S-1**.

*Synthesis of **1***: To a 50-mL oven-dried flask containing a magnetic stirring bar, **S-1** (3.0 mmol) and *p*-ABSA (4-Acetamidobenzenesulfonyl azide, 864 mg, 3.6 mmol, 1.2 eq.) in MeCN (10 mL) was added DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 684 mg,4.5 mmol, 1.5 eq.) in MeCN (2.0 mL) slowly at 0 ℃, and the resulting reaction mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with ether (10 mL), and washed with saturated aqueous $NH_4Cl$ (20 mL), $NaHCO_3$ (20 mL) and NaCl (20 mL) in sequence, and the organic phase was separated and dried with anhydrous $Na_2SO_4$. After evaporating the solvents, the residue was purified by column chromatography on silica gel (Hexanes: EtOAc = 20:1) to provide diazo compound **1**.

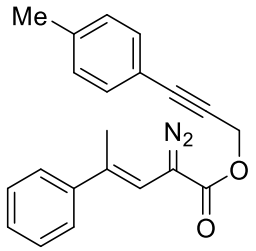
**NOTE**: Compounds **1** are prone to decomposition, and freshly prepared compounds **1** need to be used in the next step immediately after preparation.



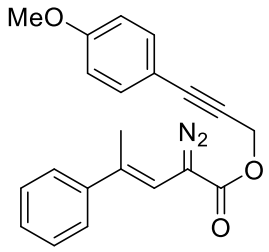

**3-(4-Chlorophenyl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1a**). Red oil; 866 mg, 82% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.44 – 7.40 (m, 2H), 7.40 – 7.37 (m, 2H), 7.31 – 7.35 (m, 2H), 7.29 – 7.27 (m, 3H), 6.00 (d, *J* = 1.3 Hz, 1H), 5.04 (s, 2H), 2.10 (d, *J* = 1.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.9, 142.6, 135.5, 135.1, 133.3, 128.8, 128.5, 127.6, 126.0, 120.7, 108.8, 85.7, 84.1, 53.4, 17.2.



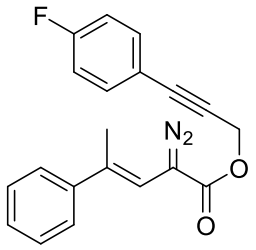

**(*E*)-3-Phenylprop-2-ynyl-2-diazo-4-phenylpent-3-enoate** (**1b**). Red oil; 864 mg, 91% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.55 – 7.47 (comp, 4H), 7.42 – 7.35 (comp, 5H), 7.35 – 7.31 (m, 1H), 6.07 (d, *J* = 1.2 Hz, 1H), 5.13 (s, 2H), 2.17 (d, *J* = 1.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 142.0, 134.7, 131.5, 128.4, 127.9, 127.8, 127.0, 125.4, 121.6, 108.3, 86.2, 82.4, 53.0, 16.6.



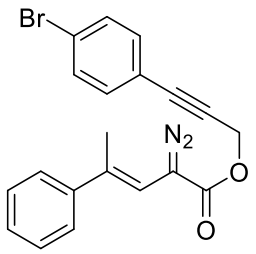

**3-(*p*-Tolyl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1c**). Red oil; 915 mg, 92% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.44 – 7.40 (m, 2H), 7.32 – 7.34 (m, 4H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.01 (d, *J* = 1.4 Hz, 1H), 5.06 (s, 2H), 2.34 (s, 3H), 2.10 (d, *J* = 1.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 166.0, 142.6, 139.1, 135.3, 132.0, 129.2, 128.5, 127.5, 126.0, 119.1, 109.0, 87.0, 82.3, 53.7, 21.6, 17.2.




**3-(4-Methoxyphenyl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1d**). Red oil; 917 mg, 88% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.39 – 7.43 (m, 4H), 7.32 – 7.35 (m, 2H), 7.28 – 7.24 (m, 1H), 6.85 – 6.82 (m, 2H), 6.00 (d, *J* = 1.4 Hz, 1H), 5.05 (s, 2H), 3.80 (s, 3H), 2.10 (d, *J* = 1.3 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 160.1, 142.6, 135.2, 133.6, 128.5, 127.5, 126.0, 114.2, 114.1, 109.0, 86.9, 81.7, 55.4, 53.7, 17.2.

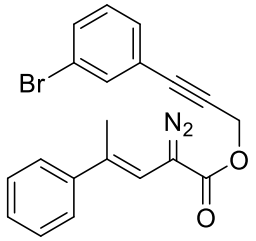



**3-(4-Fluorophenyl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1e**). Red oil; 851 mg, 85% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.47 – 7.40 (m, 4H), 7.32 – 7.36 (m, 2H), 7.28 – 7.25 (m, 1H), 6.99 – 7.03 (m, 2H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.05 (s, 2H), 2.11 (d, *J* = 1.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 163.9, 161.9, 142.5, 135.4, 134.1 (d, *J* = 7.5 Hz), 128.5, 127.6, 126.0, 118.3 (d, *J* = 3.8 Hz), 115.8(d, *J* = 22.5 Hz), 108.9, 85.8, 82.8, 67.2, 53.4, 17.2; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -109.98.

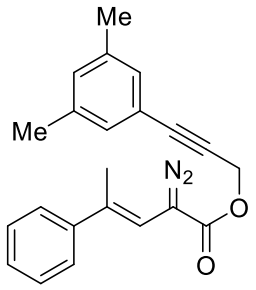



**3-(4-Bromophenyl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1f**). Red oil; 1020 mg, 88% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.44 – 7.42 (m, 2H), 7.42 – 7.40 (m, 2H), 7.33 – 7.29 (m, 4H), 7.28 – 7.25 (m, 1H), 5.99 (d, *J* = 1.5 Hz, 1H), 5.03

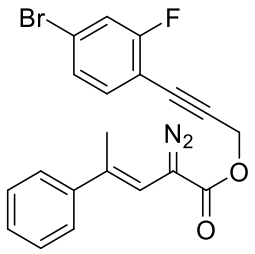
(s, 2H), 2.09 (d, $J$ = 1.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 168.3, 142.4, 135.4, 134.7, 132.1, 130.5, 129.8, 128.5, 127.5, 125.9, 124.1, 122.2, 108.8, 85.2, 84.4, 53.2, 17.1.



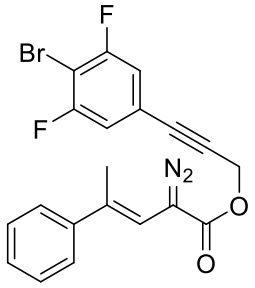

**3-(3-Bromophenyl) prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1g**). Red oil; 960 mg, 81% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61 (s, 1H), 7.45 (dt, $J$ = 8.2, 1.6 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.38 (d, $J$ = 7.8 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.27 (d, $J$ = 7.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16 (t, $J$ = 7.9 Hz, 1H), 6.00 (d, $J$ = 1.4 Hz, 1H), 5.04 (s, 2H), 2.10 (d, $J$ = 1.3 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 168.4, 142.5, 135.3, 133.8, 132.5, 130.0, 128.4, 127.5, 127.1, 125.9, 125.7, 124.3, 108.8, 87.6, 85.2, 53.4, 17.1.



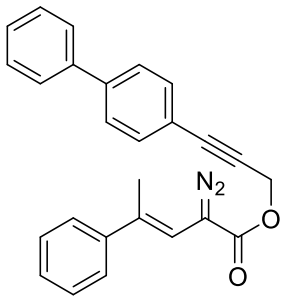

**3-(3,5-Dimethylphenyl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1h**). Red oil; 951 mg, 92% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.44 – 7.40 (m, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.26 (m, 1H), 7.10 (d, $J$ = 1.6 Hz, 2H), 6.96 (s, 1H), 6.01 (d, $J$ = 1.3 Hz, 1H), 5.05 (s, 2H), 2.27 (s, 6H), 2.09 (d, $J$ = 1.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 165.9, 142.5, 138.0, 135.1, 130.8, 129.7, 128.5, 127.5, 125.9, 121.7, 108.9, 87.2, 82.2, 53.6, 21.1, 17.1.



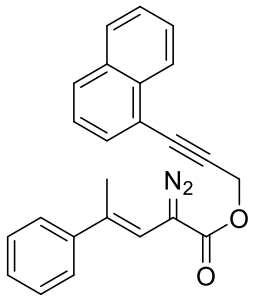

**3-(4-Bromo-2-fluorophenyl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1i**). Red oil; 1079 mg, 87% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.33 (d, *J* = 7.6 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.19 – 7.16 (m, 3H), 5.91 (d, *J* = 1.5 Hz, 2H), 4.98 (s, 2H), 2.01 (d, *J* = 1.3 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 163.7, 161.7, 142.4, 135.4, 134.6 (d, *J* = 2.5 Hz), 128.5, 127.6, 125.9, 123.5 (d, *J* = 8.8 Hz), 119.5 (d, *J* = 2.5 Hz), 110.0 (d, *J* = 15.0 Hz), 108.7, 89.3 (d, *J* = 3.8 Hz), 79.3, 53.3, 17.1; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -106.92.



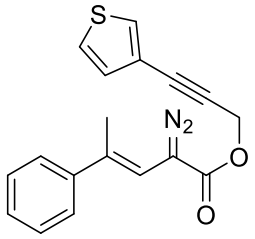

**3-(4-Bromo-3,5-difluorophenyl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1j**). Red oil; 1035 mg, 80% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.35 – 7.32 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 – 7.17 (m, 1H), 6.96 (d, *J* = 6.7 Hz, 2H), 5.91 (d, *J* = 1.4 Hz, 1H), 4.95 (s, 2H), 2.03 (d, *J* = 1.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.9, 161.0 (d, *J* = 5.0 Hz), 158.5 (d, *J* = 5.0 Hz), 142.5, 135.6, 128.5, 127.6, 126.0, 123.2 (t, *J* = 11.0 Hz), 115.5 (d, *J* = 28.0 Hz), 108.7, 99.6 (t, *J* = 24.0 Hz), 86.0, 83.9 (t, *J* = 4.0 Hz), 53.0, 17.2; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -104.60, -104.62.




**3-([1,1'-Biphenyl]-4-yl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1k**). Red oil; 1071 mg, 91% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.47 – 7.45 (m, 2H), 7.44 – 7.40 (m, 4H), 7.33 – 7.30 (m, 4H), 7.25 – 7.20 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 1H), 5.91 (d, *J* = 1.6 Hz, 1H), 4.97 (s, 2H), 1.98 (d, *J* = 1.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 165.9, 142.5, 141.6, 140.2, 135.2, 132.5, 128.9, 128.4, 127.8, 127.5, 127.1, 127.0, 125.9, 121.0, 108.8, 86.7, 83.7, 53.5, 17.1.

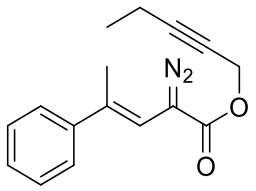



**3-(Naphthalen-1-yl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1l**). Red oil; 989 mg, 90% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 8.32 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.70 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.57 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.33 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.28 – 7.23 (m, 1H), 6.03 (d, *J* = 1.2 Hz, 1H), 5.21 (s, 2H), 2.10 (d, *J* = 1.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 166.1, 142.5, 135.3, 133.5, 133.2, 131.2, 129.5, 128.5, 128.4, 127.6, 127.1, 126.6, 126.2, 126.0, 125.2, 119.8, 108.9, 87.8, 85.0, 53.7, 17.2.

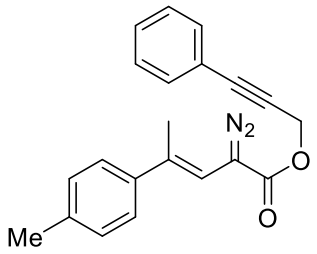



**3-(Thiophen-3-yl)prop-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1m**). Red oil;

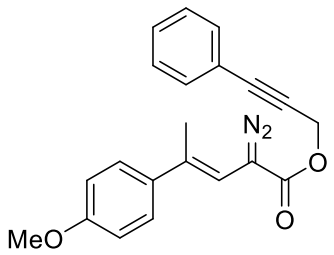
629 mg, 65% yield; $^1$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.48 (d, *J* = 1.8 Hz, 1H), 7.41 – 7.39 (m, 2H), 7.33 – 7.30 (m, 2H), 7.24 (dd, *J* = 5.1, 3.0 Hz, 2H), 7.11 (dd, *J* = 5.0, 1.2 Hz, 1H), 5.99 (d, *J* = 1.4 Hz, 1H), 5.03 (s, 2H), 2.08 (d, *J* = 1.3 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 170.4, 142.5, 135.3, 130.0, 128.5, 127.5, 125.9, 125.5, 121.2, 108.9, 82.7, 82.0, 53.5, 17.2.




**Pent-2-yn-1-yl (*E*)-2-diazo-4-phenylpent-3-enoate** (**1n**). Red oil; 692 mg, 86% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.41 (dd, *J* = 7.1, 1.6 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.25 (tt, *J* = 6.4, 1.3 Hz, 1H), 5.99 (d, *J* = 1.2 Hz, 1H), 4.82 (t, *J* = 2.2 Hz, 2H), 2.24 (qt, *J* = 7.5, 2.2 Hz, 2H), 2.09 (d, *J* = 1.3 Hz, 3H), 1.15 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 166.1, 142.6, 135.1, 128.5, 127.5, 125.9, 109.0, 89.3, 73.4, 53.6, 17.1, 13.6, 12.6.

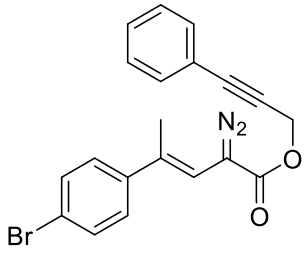



**3-Phenylprop-2-yn-1-yl (*E*)-2-diazo-4-(*p*-tolyl)pent-3-enoate** (**1o**). Red oil; 892 mg, 90% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 – 7.44 (m, 2H), 7.32 – 7.27 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.97 (d, *J* = 1.4 Hz, 1H), 5.04 (s, 2H), 2.33 (s, 3H), 2.06 (d, *J* = 1.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.0, 139.6, 137.3, 135.3, 132.0, 129.2, 129.1, 128.9, 128.4, 125.8z, 122.2, 107.9, 86.8, 83.1, 53.4, 21.0, 17.0.



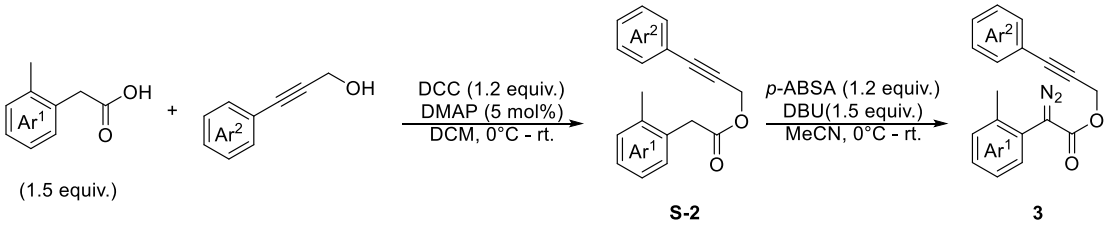

**3-Phenylprop-2-yn-1-yl (*E*)-2-diazo-4-(4-methoxyphenyl)pent-3-enoate** (**1p**). Red

oil; 987 mg, 95% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 – 7.43 (m, 2H), 7.36 – 7.33 (m, 2H), 7.31 – 7.28 (m, 3H), 6.87 – 6.83 (m, 2H), 5.91 (d, *J* = 1.2 Hz, 1H), 5.04 (s, 2H), 3.78 (s, 3H), 2.05 (d, *J* = 1.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.1, 159.3, 135.2, 134.9, 132.0, 128.9, 128.4, 127.1, 127.0, 122.2, 113.9, 113.8, 107.1, 107.0, 86.8, 83.1, 55.3, 53.4, 17.2.



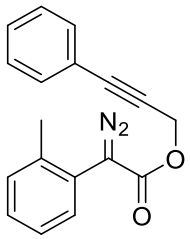

**3-Phenylprop-2-yn-1-yl (*E*)-2-diazo-4-(4-methoxyphenyl)pent-3-enoate** (**1q**). Red oil; 1032 mg, 87% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.48 – 7.43 (m, 4H), 7.34 – 7.30 (m, 3H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.07 (s, 2H), 2.07 (d, *J* = 1.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.7, 141.4, 133.7, 132.0, 131.5, 128.9, 128.4, 127.5, 122.1, 121.5, 109.6, 86.9, 82.9, 53.6, 16.9.

## General Procedure for the Preparation of Diazoacetates 3[3].

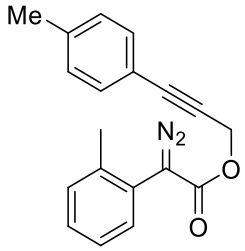



*Synthesis of* ***S-2***: To a 50-mL oven-dried flask containing a magnetic stirring bar, alcohol (3.0 mmol), acid (4.5 mmol) and DMAP (4-dimethylaminopyridine, 18.3 mg, 0.15 mmol) in DCM (10 mL), was added DCC (dicyclohexylcarbodiimide, 0.74 g, 3.6 mmol) in batches at 0 °C, and the reaction mixture was stirred at room temperature overnight. After that, the reaction mixture was filtered through Celtie and rinsed with EtOAc (10 mL), and the filtrates were combined. After evaporating the solvents, the residue was purified by column chromatography on silica gel (Hexanes: EtOAc = 30:1) to provide the corresponding esters **S-2**.

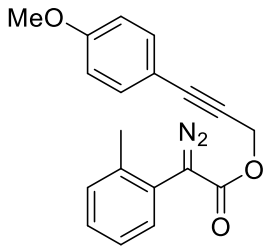
*Synthesis of **3***: To a 50-mL oven-dried flask containing a magnetic stirring bar, **S-2** (3.0 mmol) and *p*-ABSA (4-Acetamidobenzenesulfonyl azide, 864 mg, 3.6 mmol, 1.2 eq.) in MeCN (10 mL) was added DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 684 mg,4.5 mmol, 1.5 eq.) in MeCN (2.0 mL) slowly at 0 ℃, and the resulting reaction mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with ether (10 mL), and washed with saturated aqueous $NH_4Cl$ (20 mL), $NaHCO_3$ (20 mL) and NaCl (20 mL) in sequence, and the organic phase was separated and dried with anhydrous $Na_2SO_4$. After evaporating the solvents, the residue was purified by column chromatography on silica gel (Hexanes: EtOAc = 30:1) to provide diazo compound **3**.



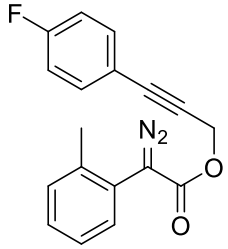

**3-Phenylprop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3a**). Red oil; 793 mg, 91% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.42 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.37 (dd, *J* = 7.4, 2.6 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.24 – 7.18 (m, 3H),, 5.02 (s, 2H), 2.28 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 138.0, 132.0, 131.03, 130.96, 129.2, 128.9, 128.4, 126.6, 124.0, 122.3, 86.7, 83.2, 53.3, 20.0.



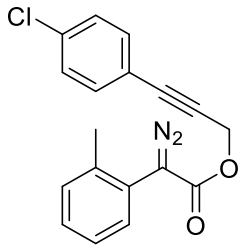

**3-(*p*-Tolyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3b**). Red oil; 803 mg, 88% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.40 – 7.36 (m, 1H), 7.35 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 2H), 5.03 (s, 2H), 2.30 (d, *J* = 6.3 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 139.1, 137.9, 132.0, 131.9, 131.0, 130.9, 129.2, 129.1, 126.6, 124.0, 119.2, 86.9, 82.5, 53.4, 21.5, 20.0.



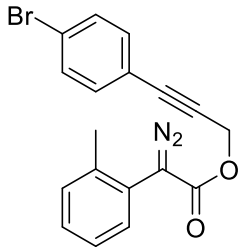

**3-(4-Methoxyphenyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3c**). Red oil; 826 mg, 86% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.45 – 7.40 (m, 3H), 7.30 – 7.27 (m, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.08 (s, 2H), 3.83 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.5, 160.1, 138.0, 133.64, 133.60, 131.1, 131.0, 129.2, 126.6, 124.1, 114.4, 114.1, 114.0, 86.7, 81.9, 55.5, 53.5, 20.0.



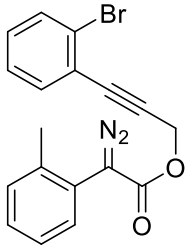

**3-(4-Fluorophenyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3d**). Red oil; 823 mg, 89% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 – 7.38 (m, 3H), 7.30 – 7.22 (m, 3H), 7.03 – 6.97 (m, 2H), 5.04 (s, 2H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 164.2, 161.7, 138.0, 134.0 (d, *J* = 9.0 Hz), 131.04, 130.98, 129.2, 126.6, 124.0, 118.4 (d, *J* = 3.0 Hz), 115.8 (q, *J* = 7.0 Hz), 85.7, 83.0, 53.2, 20.0; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -110.06.



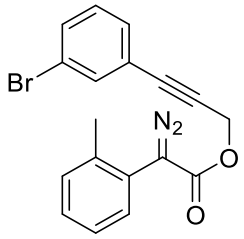

**3-(4-Chlorophenyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3e**). Red oil; 877 mg, 90% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.45 – 7.39 (m, 3H), 7.34 – 7.26 (m, 5H), 5.08 (s, 2H), 2.35 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 165.4, 137.9, 135.0, 133.3, 131.01, 130.99, 129.2, 128.8, 126.6, 123.9, 120.8, 85.6, 84.2, 53.2, 20.1.



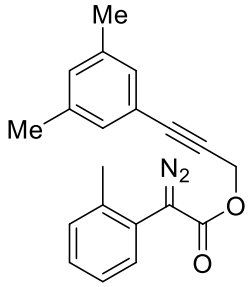

**3-(4-Bromophenyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3f**). Red oil; 997 mg, 90% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 – 7.45 (m, 2H), 7.45 – 7.42 (m, 1H), 7.35 – 7.32 (m, 2H), 7.31 – 7.27 (m, 3H), 5.07 (s, 2H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 138.0, 133.5, 131.7, 131.03, 130.98, 129.2, 126.6, 123.9, 123.3, 121.2, 85.6, 84.4, 53.2, 20.0.



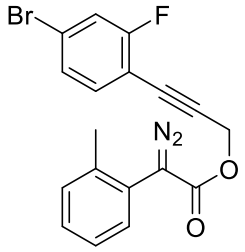

**3-(2-Bromophenyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3g**). Red oil; 919 mg, 83% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.40 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.20 – 7.15 (m, 4H), 7.09 (td, *J* = 7.7, 1.8 Hz, 1H), 5.03 (s, 2H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 138.0, 133.8, 132.6, 131.1, 131.0, 130.04, 129.99, 129.2, 127.1, 126.6, 125.8, 124.5, 124.0, 87.8, 85.2, 53.2, 20.1.



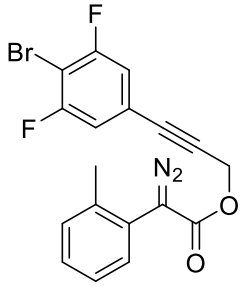

**3-(3-Bromophenyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3h**). Red oil; 942 mg, 85% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.57 (t, *J* = 1.8 Hz, 1H), 7.42 (dt, *J* = 8.0, 1.4 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.34 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.13 (t, *J* = 7.9 Hz, 1H), 5.01 (s, 2H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.3, 138.0, 134.8, 132.1, 131.02, 130.97, 130.6, 129.9, 129.2, 126.6, 124.3, 123.9, 122.2, 85.1, 84.6, 53.1, 20.0.




**3-(3,5-Dimethylphenyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3i**). Red oil; 841 mg, 88% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.47 – 7.43 (m, 1H), 7.32 – 7.28 (m, 3H), 7.13 (d, *J* = 1.7 Hz, 2H), 7.00 (s, 1H), 5.09 (s, 2H), 2.36 (s, 3H), 2.32 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 138.0, 131.0, 130.9, 130.8, 129.7, 129.1, 126.5, 124.0, 121.8, 87.0, 82.4, 53.4, 21.1, 20.1.

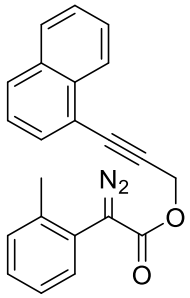



**3-(4-Bromo-2-fluorophenyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3j**). Red oil; 1011 mg, 87% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.44 – 7.40 (m, 1H), 7.36 – 7.27 (m, 6H), 5.09 (s, 2H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.1, 161.5, 138.0, 134.7, 131.1, 129.3, 127.6, 126.6, 123.9, 123.5, 123.4, 119.5 (d, *J* = 30.0 Hz), 110.2 (d, *J* = 16.0 Hz), 89.6, 79.2, 53.1, 20.0; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -107.93.

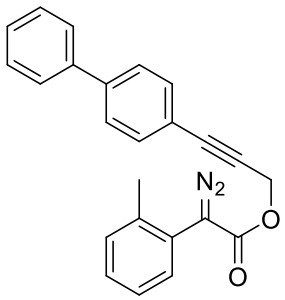



**3-(4-Bromo-3,5-difluorophenyl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3k**). Red oil; 997 mg, 82% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.43 – 7.39 (m, 1H), 7.30 – 7.26 (m, 3H), 7.07 – 7.01 (m, 2H), 5.04 (s, 2H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz,

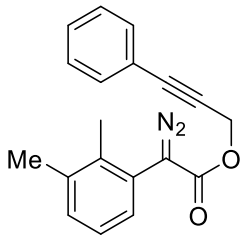
$CDCl_3$) (δ, ppm) 165.3, 161.0 (d, $J$ = 5.1 Hz), 158.6 (d, $J$ = 4.9 Hz), 138.0, 131.1, 129.3, 126.7, 123.8, 123.3 (t, $J$ = 11.1 Hz), 115.5 (q, $J$ = 9.2 Hz), 115.3, 99.6, 86.2, 83.8, 52.8, 20.0; $^{19}$F NMR (376 MHz, CDCl3) (δ, ppm) -104.66, -104.68.



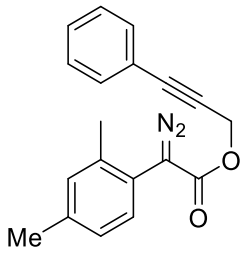

**3-(Naphthalen-1-yl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3l**). Red oil; 939 mg, 92% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.37 (dd, $J$ = 8.4, 1.2 Hz, 1H), 7.87 (d, $J$ = 9.1 Hz, 2H), 7.74 (dd, $J$ = 7.1, 1.2 Hz, 1H), 7.61 (ddd, $J$ = 8.4, 6.8, 1.4 Hz, 1H), 7.55 (ddd, $J$ = 8.2, 6.8, 1.4 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.33 – 7.28 (m, 3H), 5.26 (s, 2H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.5, 138.0, 133.5, 133.2, 131.04, 130.97, 129.4, 129.2, 128.4, 127.1, 126.6, 126.2, 126.1, 125.2, 124.0, 119.9, 88.1, 84.9, 53.5, 20.0.



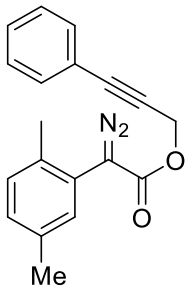

**3-([1,1'-Biphenyl]-4-yl)prop-2-yn-1-yl 2-diazo-2-(*o*-tolyl)acetate** (**3m**). Red oil; 989 mg, 90% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 – 7.58 (m, 6H), 7.50 – 7.46 (m, 6H), 7.42 – 7.38 (m, 1H), 7.35 – 7.29 (m, 3H), 5.14 (s, 2H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 141.6, 140.3, 137.9, 132.4, 131.0, 130.9, 129.1, 128.9, 127.8, 127.11, 127.06, 126.6, 124.0, 121.1, 86.6, 83.9, 53.3, 20.0.



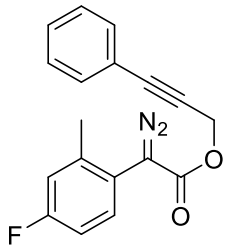

**3-Phenylprop-2-yn-1-yl 2-diazo-2-(2,3-dimethylphenyl)acetate** (**3n**). Red oil; 831 mg, 91% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 – 7.42 (m, 2H), 7.32 – 7.27 (m, 3H), 7.24 (dd, *J* = 6.7, 2.7 Hz, 1H), 7.17 – 7.11 (m, 2H), 5.04 (s, 2H), 2.28 (s, 3H), 2.21 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.1, 138.0, 136.9, 132.03, 131.97, 130.9, 128.9, 128.4, 126.2, 124.3, 122.3, 86.6, 83.3, 53.3, 39.7, 20.7.




**3-Phenylprop-2-yn-1-yl 2-diazo-2-(2,4-dimethylphenyl)acetate** (**3o**). Red oil; 822 mg, 90% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 (dd, *J* = 7.1, 2.4 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.09 (s, 2H), 2.36 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 165.6, 137.9, 136.8, 132.0,130.8, 128.9, 128.8, 128.4, 126.1, 124.2, 122.2, 86.6, 83.3, 53.2, 38.7, 20.7, 16.7.

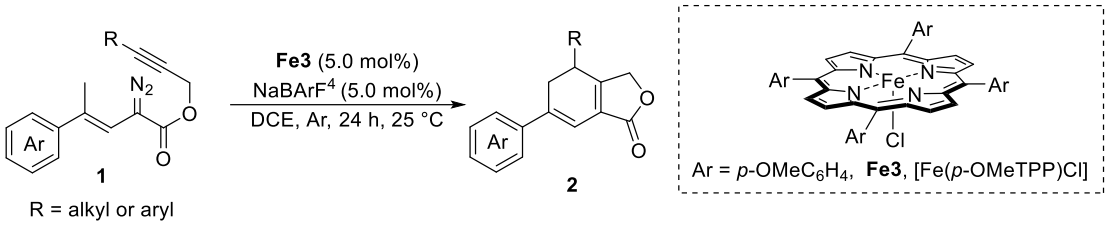



**3-Phenylprop-2-yn-1-yl 2-diazo-2-(2,5-dimethylphenyl)acetate** (**3p**). Red oil; 803 mg, 88% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 – 7.43 (m, 2H), 7.31 – 7.27 (m, 3H), 7.21 (d, *J* = 1.9 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 7.9, 1.9 Hz, 1H), 5.05 (s, 2H), 2.31 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.5, 136.1, 134.8, 132.0, 131.5, 131.4, 130.8, 130.0, 128.8, 128.4, 123.7, 122.3, 86.7, 83.3, 53.2, 20.9, 19.5.

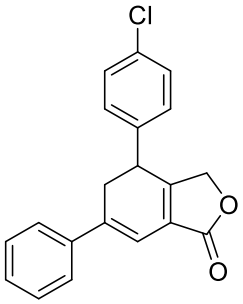


**3-Phenylprop-2-yn-1-yl 2-diazo-2-(4-fluoro-2-methylphenyl)acetate** (**3q**). Red oil; 869 mg, 94% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.50 – 7.46 (m, 2H), 7.39 (dd, *J* = 8.3, 5.7 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.00 – 6.95 (m, 2H), 5.08 (s, 2H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.4, 161.9, 140.9 (d, *J* = 8.5 Hz), 133.0, 132.0, 128.9, 128.4, 122.3, 120.0, 117.6 (d, *J* = 31.3 Hz), 113.7 (d, *J* = 21.2 Hz), 86.8, 83.1, 53.4, 20.1; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -111.30.

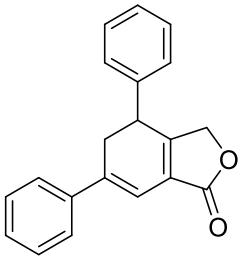
## General Procedure for the Allylic Csp$^3$-H Bond Insertion Reaction:



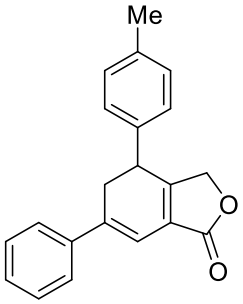

To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe3**, 5 mol%, 4.1 mg) and NaBArF$^4$ (5 mol%, 4.4 mg) in glovebox. Then, the vial was capped and took out from the glovebox, and DCE (0.5 mL) was injected into vial under argon atmosphere. The resulting reaction mixture was stirred at 25 °C for 0.5 h. A solution of diazo compound **1** (0.1 mmol) in DCE (1.0 mL) was added into the reaction vessel through syringe in 3.5 h, then the new mixture was stirred under these conditions for 20 h. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 10:1 to 6:1) to give pure products **2** in good to high yields.



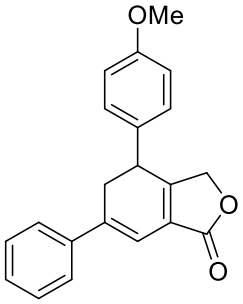

**4-(4-Chlorophenyl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2a**). Colourless oil; 25.8 mg, 80% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.50 – 7.45 (m, 4H), 7.38 – 7.31 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.69 (s, 1H), 4.77 – 4.65 (m, 2H), 4.07 (t, *J* = 9.9 Hz, 1H), 3.26 (dd, *J* = 17.6, 9.6 Hz, 1H), 3.04 (dd, *J* = 17.6, 11.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.6, 158.1, 139.4, 139.3, 139.2, 133.9, 129.6, 128.9, 128.8, 128.6, 126.6, 125.6, 112.5, 70.5, 40.1, 35.3; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}ClO_2$ $[M+H]^+$: 323.0834, found 323.0839.



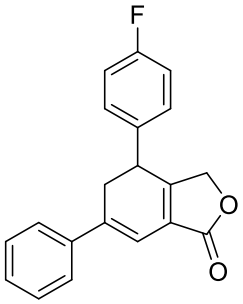

**4,6-Diphenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2b**). Colourless oil; 20.8 mg, 72% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.51 – 7.46 (m, 2H), 7.40 – 7.32 (m, 5H), 7.30 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.28 – 7.25 (m, 1H), 6.70 (s, 1H), 4.71 (s, 2H), 4.14 – 4.09 (m, 1H), 3.26 (ddd, *J* = 17.4, 9.7, 1.4 Hz, 1H), 3.09 (ddd, *J* = 17.4, 10.9, 1.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.9, 158.9, 141.0, 139.5, 139.4, 129.4, 128.8, 128.5, 128.0, 127.6, 126.4, 125.6, 112.5, 70.7, 40.9, 35.5; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{17}O_2$ $[M+H]^+$: 289.1223, found 289.1226.



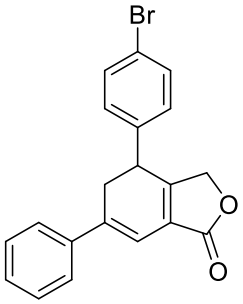

**6-Phenyl-4-(*p*-tolyl)-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2c**). Colourless oil; 23.9 mg, 79% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.51 – 7.45 (m, 2H), 7.38 – 7.30 (m, 3H), 7.16 (s, 4H), 6.69 (s, 1H), 4.71 (s, 2H), 4.08 (t, *J* = 10.4 Hz, 1H), 3.24 (dd, *J* = 17.1, 10.0 Hz, 1H), 3.06 (dd, *J* = 18.3, 11.8 Hz, 1H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.9, 159.3, 139.5, 139.3, 137.9, 137.7, 130.0, 128.7, 128.4, 127.4, 126.1, 125.6, 112.4, 70.7, 40.4, 35.5, 21.1; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1380, found 303.1380.



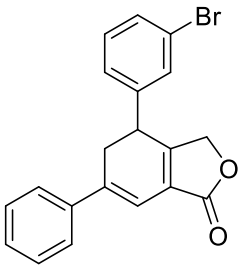

**4-(4-Methoxyphenyl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2d**). Colourless oil; 19.9 mg, 52% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 – 7.47 (m, 2H), 7.36 – 7.34 (m, 2H), 7.32 – 7.30 (m, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.89 – 6.87 (m, 2H), 6.69 (s, 1H), 4.71 (s, 2H), 4.06 (t, *J* = 10.2 Hz, 1H), 3.80 (s, 3H), 3.23 (dd, *J* = 17.4, 9.7 Hz, 1H), 3.05 (dd, *J* = 17.8, 10.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.0, 159.5, 159.3, 139.5, 139.3, 132.9, 128.8, 128.6, 128.4, 126.1, 125.6, 114.7, 112.4, 70.7, 55.4, 40.0, 35.6; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{19}O_3$ $[M+H]^+$: 319.1329, found 319.1324.



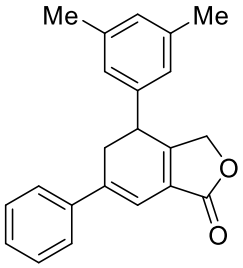

**4-(4-Fluorophenyl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2e**). Colourless oil; 26 mg, 85% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.43 – 7.41 (m, 2H), 7.33 – 7.27 (m, 3H), 7.21 – 7.18 (m, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.64 (s, 1H), 4.72 – 4.60 (m, 2H), 4.06 (t, *J* = 10.0 Hz, 1H), 3.21 (dd, *J* = 19.0, 9.7 Hz, 1H), 2.99 (dd, *J* = 17.4, 10.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.7, 163.6, 161.2, 158.5, 139.3, 139.2, 136.7 (d, *J* = 3.2 Hz), 129.1 (d, *J* = 8.2 Hz), 128.8, 128.6, 126.4, 125.6, 116.5, 116.2, 112.5 (d, *J* = 8.2 Hz), 70.6, 40.0, 35.5; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -114.15. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}FO_2$ $[M+H]^+$: 307.1229, found 307.1226.



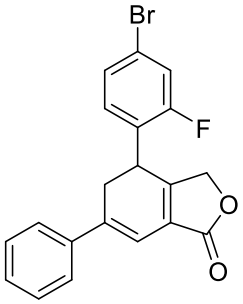

**4-(4-Bromophenyl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2f**). Colourless oil; 29.7 mg, 81% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.50 – 7.45 (m, 4H), 7.38 – 7.30 (m, 3H), 7.16 – 7.14 (m, 2H), 6.69 (s, 1H), 4.77 – 4.65 (m, 2H), 4.08 (t, *J* = 10.0 Hz, 1H), 3.26 (dd, *J* = 18.2, 8.9 Hz, 1H), 3.03 (dd, *J* = 19.1, 10.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.7, 158.0, 139.9, 139.2, 132.6, 129.2, 128.8, 128.6, 126.6, 125.6, 121.9, 112.5, 70.5, 40.2, 35.3; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}BrO_2$ $[M+H]^+$: 367.0329, found 367.0323.



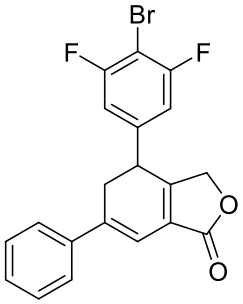

**4-(3-Bromophenyl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2g**). white solid; m.p. 152.5-153.6 ℃; 26.8 mg, 73% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.48 – 7.42 (m, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.29 (m, 1H), 7.26 – 7.19 (m, 2H), 6.70 (s, 1H), 4.72 (d, *J* = 4.0 Hz, 2H), 4.08 (t, *J* = 10.1 Hz, 1H), 3.26 (dd, *J* = 18.2, 10.5 Hz, 1H), 3.05 (dd, *J* = 18.3, 11.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.6, 157.7, 143.1, 139.2, 131.2, 131.0, 130.7, 128.8, 128.6, 126.8, 126.2, 125.6, 123.4, 112.5, 70.6, 40.4, 35.4; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}BrO_2$ $[M+H]^+$: 367.0329, found 367.0324.



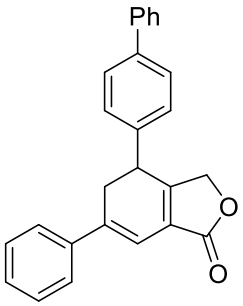

**4-(3,5-Dimethylphenyl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2h**). Colourless oil; 22.5 mg, 71% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.50 – 7.48 (m, 2H), 7.38 – 7.29 (m, 3H), 6.95 (s, 1H), 6.89 (s, 2H), 6.70 (s, 1H), 4.72 (s, 2H), 4.05 (t, *J* = 10.6 Hz, 1H), 3.23 (dd, *J* = 16.7, 10.4 Hz, 1H), 3.07 (dd, *J* = 16.5, 10.4 Hz, 1H), 2.32 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.0, 159.3, 140.9, 139.5, 139.3, 139.0, 129.6, 129.5, 128.7, 128.3, 126.1, 125.5, 125.4, 125.3, 112.3, 70.8, 40.7, 35.5, 21.4; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{21}O_2$ $[M+H]^+$: 316.1463, found 316.1462.



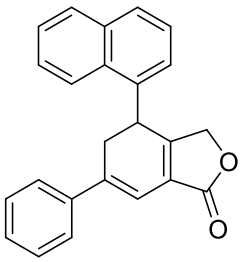

**4-(4-Bromo-2-fluorophenyl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2i**). Yellow oil; 16.5 mg, 43% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 – 7.47 (m, 2H), 7.39 – 7.32 (m, 4H), 7.29 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 4.76 (q, *J* = 18.4 Hz, 2H), 4.41 (t, *J* = 9.5 Hz, 1H), 3.25 (dd, *J* = 17.4, 9.7 Hz, 1H), 3.07 (dd, *J* = 17.4, 9.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.5, 161.1, 156.8, 139.1, 130.0, 128.9, 128.7, 128.5, 127.0, 126.8, 126.7, 125.7, 122.1 (d, *J* = 10.6 Hz), 120.0, 112.5 (d, *J* = 8.5 Hz), 70.5, 33.6, 29.8; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -114.52; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{15}BrFO_2$ $[M+H]^+$: 385.0234, found 385.0235.



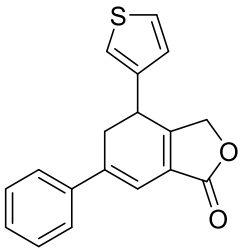

**4-(4-Bromo-3,5-difluorophenyl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2j**). Yellow oil; 27.0 mg, 67% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.47 – 7.44 (m, 2H), 7.39 – 7.36 (m, 3H), 6.89 (d, *J* = 7.1 Hz, 2H), 6.71 (s, 1H), 4.75 (q, *J* = 18.5 Hz, 2H), 4.07 (t, *J* = 9.4 Hz, 1H), 3.30 (dd, *J* = 17.4, 9.7 Hz, 1H), 3.04 (dd, *J* = 17.4, 9.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.2, 161.8 (d, *J* = 4.6 Hz), 159.3, 156.0, 142.8, 139.0 (d, *J* = 16.4 Hz), 128.9, 127.3, 125.7, 112.5 (d, *J* = 8.2 Hz), 111.0, 70.3, 40.0, 35.1; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -103.00, -103.03; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{14}BrF_2O_2$ $[M+H]^+$: 403.0140, found 403.0146.



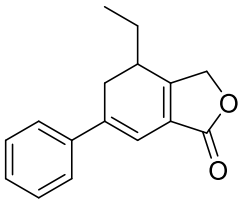

**4-([1,1'-Biphenyl]-4-yl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2k**). Colourless oil; 31.0 mg, 85% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.54 – 7.52 (m, 3H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.42 (m, 2H), 7.33 – 7.27 (m, 5H), 7.23 – 7.19 (m, 1H), 7.12 (dd, *J* = 12.8, 7.2 Hz, 1H), 6.68 (s, 1H), 4.69 (s, 2H), 4.09 (t, *J* = 10.1 Hz, 1H), 3.23 (dd, *J* = 17.4, 9.5 Hz, 1H), 3.06 (dd, *J* = 17.3, 10.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.9, 158.9, 140.9, 140.4, 139.9, 139.3, 139.2, 129.1, 128.9, 128.7, 128.4, 128.3, 128.00, 127.95, 127.6, 127.1, 126.3, 125.6, 125.4, 112.4, 70.7, 40.4, 35.3; HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{21}O_2$ $[M+H]^+$: 365.1537, found 365.1536.



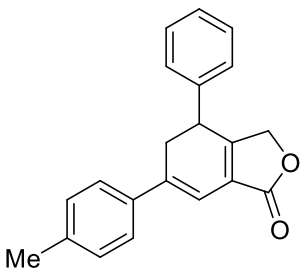

**4-(Naphthalen-1-yl)-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2l**). Colourless oil; 18.6 mg, 55% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.09 (d, *J* = 8.2 Hz, 1H), 7.93 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.46 (dd, *J* = 7.1, 2.2 Hz, 2H), 7.42 (d, *J* = 6.3 Hz, 1H), 7.38 (d, *J* = 4.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.31 – 7.29 (m, 1H), 6.77 (s, 1H), 4.94 (s, 1H), 4.73 (s, 2H), 3.38 (s, 1H), 3.29 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.9, 159.2, 139.4, 136.4, 134.6, 130.8, 129.7, 129.0, 128.8, 128.5, 126.9, 126.2, 125.8, 125.6, 124.9, 119.5, 112.4, 71.0, 34.8, 26.5; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{19}O_2$ $[M+H]^+$: 339.1380, found 339.1379.




**6-Phenyl-4-(thiophen-3-yl)-4,5-dihydroisobenzofuran-1(3H)-one** (**2m**). Yellow oil; 20.6 mg, 70% yield; $^{1}$H NMR (500 MHz, $CDCl_3$) (δ, ppm) 7.48 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.36 (m, 4H), 7.12 (d, *J* = 3.4 Hz, 1H), 7.02 (d, *J* = 6.2 Hz, 1H), 6.68 (s, 1H), 4.76 (q, *J* = 18.4 Hz, 2H), 4.25 (t, *J* = 9.7 Hz, 1H), 3.22 (dd, *J* = 17.2, 7.8 Hz, 1H), 3.08 (dd, *J* = 17.9, 9.3 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) (δ, ppm) 171.8, 158.9, 140.6, 139.4, 139.3, 128.8, 128.5, 127.3, 126.5, 125.7, 125.6, 121.7, 112.5, 70.7, 35.7, 34.5; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{15}O_2S$ $[M+H]^+$: 295.0787, found 295.0787.

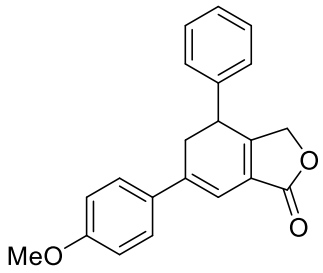



**4-Ethyl-6-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2n**). Colourless oil; 14.7 mg, 61% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.50 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.33 – 7.29 (m, 1H), 6.58 (s, 1H), 4.98 – 4.86 (m, 2H), 2.98 (dd, *J* = 16.5, 8.6 Hz, 1H), 2.83 (p, *J* = 7.9, 7.5 Hz, 1H), 2.70 (dd, *J* = 16.5, 9.8 Hz, 1H), 1.74 – 1.67 (m, 1H), 1.63 – 1.59 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 161.0, 140.0, 139.3, 128.8, 128.3, 125.6, 112.6, 70.8, 35.7, 31.6, 25.6, 11.7; HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1224, found 241.1225.

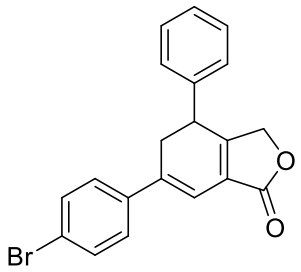



**4-Phenyl-6-(*p*-tolyl)-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2o**). Colourless oil; 23.0 mg, 76% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.31 – 7.22 (m, 5H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.59 (s, 1H), 4.62 (s, 2H), 4.02 (t, *J* = 10.3 Hz,

1H), 3.16 (dd, *J* = 17.4, 9.7 Hz, 1H), 2.98 (dd, *J* = 17.4, 10.9 Hz, 1H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.0, 158.5, 141.1, 139.2, 138.5, 136.5, 129.5, 129.4, 127.9, 127.6, 126.4, 125.5, 111.5, 70.7, 40.9, 35.4, 21.2; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{19}O_2$ $[M+H]^+$: 303.1380, found 303.1384.

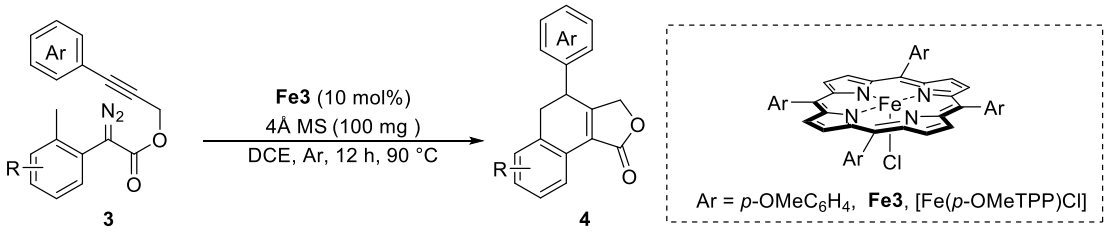



**6-(4-Methoxyphenyl)-4-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2p**). Colourless oil; 22.9 mg, 72% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.45 – 7.41 (m, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.30 (m, 1H), 7.28 – 7.26 (m, 2H), 6.93 – 6.85 (m, 2H), 6.62 (s, 1H), 4.70 (s, 2H), 4.09 (t, *J* = 10.2 Hz, 1H), 3.82 (s, 3H), 3.23 (dd, *J* = 17.3, 9.7 Hz, 1H), 3.04 (dd, *J* = 17.6, 11.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.0, 159.9, 157.9, 141.2, 138.8, 131.9, 129.4, 128.4, 127.9, 127.6, 126.9, 126.4, 114.1, 110.6, 70.7, 55.4, 40.8, 35.4; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{19}O_3$ $[M+H]^+$: 319.1329, found 319.1323.

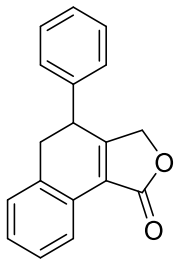



**6-(4-Bromophenyl)-4-phenyl-4,5-dihydroisobenzofuran-1(3*H*)-one** (**2q**). Colourless oil; 30.1 mg, 82% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.48 – 7.46 (m, 2H), 7.39 – 7.31 (m, 5H), 7.27 – 7.25 (m, 2H), 6.68 (s, 1H), 4.71 (s, 2H), 4.16 – 4.07 (m, 1H), 3.21 (dd, *J* = 18.0, 9.7 Hz, 1H), 3.04 (dd, *J* = 17.4, 11.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.7, 159.3, 140.7, 138.3, 138.1, 131.9, 129.5, 128.1, 127.5, 127.1, 126.2, 122.4, 112.9, 70.7, 40.8, 35.3; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}BrO_2$ $[M+H]^+$: 367,0329, found 367,0327.

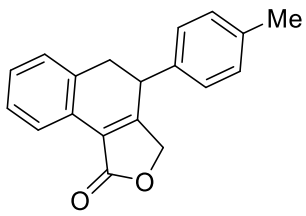
## General Procedure for the Benzyl $Csp^3$-H Bond Insertion Reaction:




To a 10-mL vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe3**, 10 mol%, 8.2 mg) and 4Å MS (100 mg). Then, the capped vial was evacuated and back-filled with argon (3 times). A solution of diazo compound **3** (0.1 mmol) in DCE (2.0 mL) was added into the reaction vessel in one-time and the reaction mixture was stirred at 90 ℃ for 12 h. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 10:1 to 5:1) to give the products **4** in good to high yields.

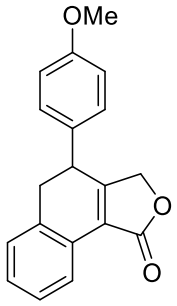



**4-Phenyl-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4a**). Colourless oil; 21.5 mg, 82% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.20 (d, *J* = 7.3 Hz, 1H), 7.32 – 7.30 (m, 3H), 7.26 – 7.24 (m, 2H), 7.20 – 7.16 (m, 3H), 4.67 (s, 2H), 4.05 (t, *J* = 8.7 Hz, 1H), 3.34 (dd, *J* = 16.0, 7.6 Hz, 1H), 3.23 (dd, *J* = 16.0, 9.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.4, 162.3, 140.2, 134.0, 129.3, 129.2, 128.0, 127.6, 127.4, 126.9, 124.5, 123.8, 70.0, 40.9, 36.8; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{15}O_2$ $[M+H]^+$: 263.1067, found 263.1068.

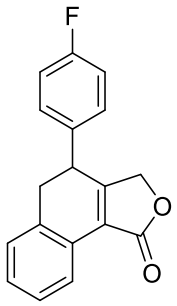



**4-(*p*-Tolyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4b**). Colourless oil; 21.3 mg,

77% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.28 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.24 – 7.21 (m, 2H), 7.17 – 7.15 (m, 2H), 4.76 (s, 2H), 4.14 – 4.06 (m, 1H), 3.40 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.29 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.5, 162.7, 137.7, 137.1, 134.1, 130.0, 129.1, 128.0, 127.4, 126.9, 124.3, 123.8, 70.1, 40.5, 36.9, 21.1; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.1223, found 277.1227.

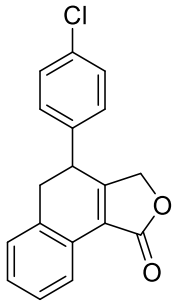



**4-(4-Methoxyphenyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4c**). Colourless oil; 19.0 mg, 65% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.19 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.33 – 7.24 (m, 2H), 7.18 – 7.14 (m, 1H), 7.12 – 7.09 (m, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.67 (s, 2H), 4.05 – 3.95 (m, 1H), 3.79 (s, 3H), 3.32 (dd, *J* = 16.1, 7.7 Hz, 1H), 3.20 (dd, *J* = 16.1, 9.7 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.5, 162.9, 159.3, 134.1, 132.1, 129.1, 128.7, 128.6, 128.1, 127.4, 126.9, 124.2, 123.8, 114.6, 70.1, 55.4, 40.1, 36.9; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{17}O_3$ $[M+H]^+$: 293.1172, found 293.1172.

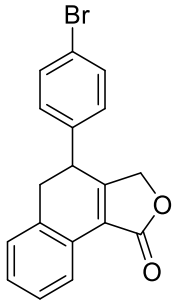



**4-(4-Fluorophenyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4d**). Yellow oil; 22.7 mg, 81% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.17 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.15 – 7.12 (m, 3H), 7.01 – 6.97 (m, 2H), 4.74 – 4.57 (m, 2H), 4.07 – 3.98 (m, 1H), 3.32 (dd, *J* = 16.1, 7.7 Hz, 1H), 3.16 (dd, *J* = 16.0, 9.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3, 162.4 (d, *J* = 45.3 Hz), 161.9, 135.9 (d, *J* = 3.2 Hz), 133.7, 129.3, 129.2, 129.1, 128.1, 127.5, 126.7, 124.6, 123.8, 116.2 (d,

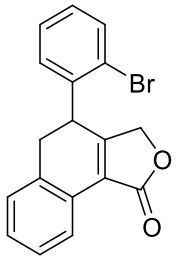
$J$ = 21.3 Hz), 69.9, 40.0, 36.9; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -114.21; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}FO_2$ $[M+H]^+$: 281.0972, found 281.0978.



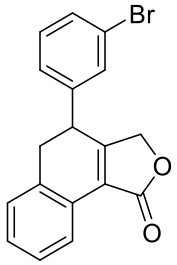

**4-(4-Chlorophenyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4e**). Colourless oil; 25.8 mg, 87% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.20 (dd, $J$ = 7.3, 1.7 Hz, 1H), 7.32 – 7.26 (m, 4H), 7.17 (d, $J$ = 6.7 Hz, 1H), 7.15 – 7.12 (m, 2H), 4.76 – 4.61 (m, 2H), 4.09 – 4.00 (m, 1H), 3.36 (dd, $J$ = 16.0, 7.7 Hz, 1H), 3.18 (dd, $J$ = 16.1, 9.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.2, 161.4, 138.6, 133.8, 133.6, 129.51, 129.48, 129.3, 128.9, 128.9, 128.1, 127.5, 126.7, 124.7, 123.8, 69.9, 40.0, 36.7; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}ClO_2$ $[M+H]^+$: 297.0677, found 297.0672.



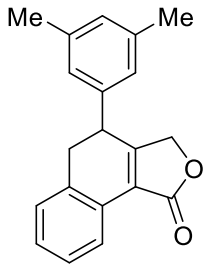

**4-(4-Bromophenyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4f**). Yellow solid; m.p. 162.4-163.2 ℃; 30.4 mg, 89% yield; $^1$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.18 (dd, $J$ = 7.4, 1.7 Hz, 1H), 7.44 (d, $J$ = 8.4 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.15 (d, $J$ = 6.6 Hz, 1H), 7.06 (d, $J$ = 8.4 Hz, 2H), 4.73 – 4.60 (m, 2H), 4.03 – 3.99 (m, 1H), 3.34 (dd, $J$ = 16.0, 7.7 Hz, 1H), 3.16 (dd, $J$ = 16.0, 9.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.2, 161.3, 139.2, 133.6, 132.5, 129.3, 128.1, 127.6, 126.7, 124.8, 123.9, 121.9, 69.9, 40.2, 36.7; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}BrO_2$ $[M+H]^+$: 341.0172, found 341.0168.



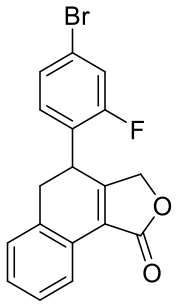

**4-(2-Bromophenyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4g**). Yellow solid; m.p. 178.2-179.2 ℃; 21.8 mg, 64% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.22 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.62 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.34 – 7.11 (m, 7H), 4.75 (q, *J* = 18.3 Hz, 2H), 4.65 (t, *J* = 8.2 Hz, 1H), 3.39 (dd, *J* = 16.2, 8.1 Hz, 1H), 3.23 (dd, *J* = 16.2, 8.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3, 161.1, 139.3, 133.7, 133.6, 129.5, 129.3, 128.7, 128.5, 128.2, 127.5, 126.7, 125.0, 124.0, 123.9, 70.1, 39.4, 35.3; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}BrO_2$ $[M+H]^+$: 341.0172, found 341.0167.



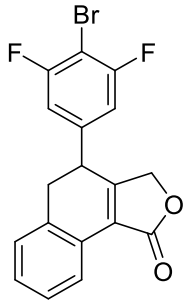

**4-(3-Bromophenyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4h**). Yellow solid; m.p. 166.3-166.3 ℃; 22.9 mg, 73% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.19 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.42 (dt, *J* = 8.0, 1.4 Hz, 1H), 7.36 – 7.35 (m, 1H), 7.31 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26 (dd, *J* = 6.9, 5.4 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.10 (dt, *J* = 7.7, 1.4 Hz, 1H), 4.74 – 4.62 (m, 2H), 4.05 – 3.97 (m, 1H), 3.33 (dd, *J* = 16.1, 7.7 Hz, 1H), 3.18 (dd, *J* = 16.1, 9.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.2, 161.0, 142.5, 133.5, 131.2, 130.9, 130.8, 129.4, 128.1, 127.6, 126.7, 126.2, 125.0, 123.9, 123.3, 69.9, 40.5, 36.7; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}BrO_2$ $[M+H]^+$: 341.0172, found 341.0166.



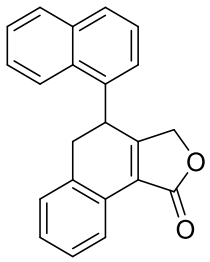

**4-(3,5-Dimethylphenyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4i**). Colourless oil; 21.0 mg, 72% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.18 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.26 – 7.22 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 6.79 (s, 2H), 4.66 (d, *J* = 1.9 Hz, 2H), 4.01 – 3.93 (m, 1H), 3.32 – 3.16 (m, 2H), 2.27 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.6, 162.8, 140.2, 138.9, 134.3, 129.6, 129.5, 129.0, 128.0, 127.3, 126.9, 125.5, 125.4, 124.3, 123.7, 70.2, 40.9, 36.9, 21.4; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{19}O_2$ $[M+H]^+$: 291.1380, found 291.1384.



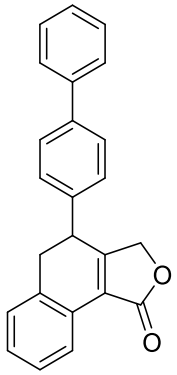

**4-(4-Bromo-2-fluorophenyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4j**). Yellow oil; 23.3 mg, 65% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.19 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.22 – 7.17 (m, 2H), 6.98 (t, *J* = 8.1 Hz, 1H), 4.80 – 4.67 (m, 2H), 4.36 (t, *J* = 8.1 Hz, 1H), 3.34 (dd, *J* = 16.1, 7.7 Hz, 1H), 3.22 (dd, *J* = 16.1, 8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.0, 160.1, 160.0 (d, *J* = 249.1 Hz), 133.4, 129.9, 129.4, 128.4, 128.1, 127.7, 126.6, 126.2, 126.0, 125.2, 124.0, 122.0 (d, *J* = 9.6 Hz), 119.9 (d, *J* = 5.6 Hz), 119.7 (d, *J* = 6.2 Hz), 69.9, 35.0, 32.9; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -114.47; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}BrFO_2$ $[M+H]^+$: 359.0077, found 359.0083.



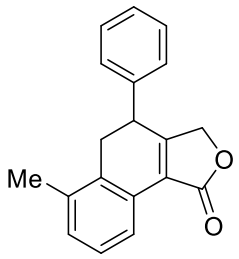

**4-(4-Bromo-3,5-difluorophenyl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4k**). Yellow oil; 29.8 mg, 79% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.19 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.17 (d, *J* = 6.5 Hz, 1H), 6.80 (d, *J* = 7.0 Hz, 2H), 4.79 – 4.66 (m, 2H), 4.02 (t, *J* = 7.8 Hz, 1H), 3.40 (dd, *J* = 16.1, 7.6 Hz, 1H), 3.15 (dd, *J* = 16.1, 8.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 170.8, 161.6 (d, *J* = 4.6 Hz), 159.4, 159.2 (d, *J* = 4.5 Hz), 142.2 (t, *J* = 7.9 Hz), 132.8, 129.7, 128.2, 127.8, 126.4, 125.4, 124.1, 111.2 (q, *J* = 10.2 Hz), 97.5 (t, *J* = 24.4 Hz), 69.7, 40.0, 36.3; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -103.19, -103.20; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{12}BrF_2O_2$ $[M+H]^+$: 376.9983, found 376.9982.



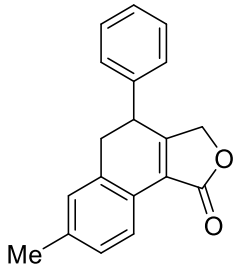

**4-(Naphthalen-1-yl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4l**). Colourless oil; 24.1 mg, 77% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.26 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 4.87 (t, *J* = 8.8 Hz, 1H), 4.74 – 4.63 (m, 2H), 3.44 (d, *J* = 8.5 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.4, 162.5, 135.4, 134.5, 134.1, 130.9, 129.6, 129.2, 128.6, 128.2, 127.5, 126.8, 126.1, 125.8, 123.9, 122.9, 70.2, 36.0; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{17}O_2$ $[M+H]^+$: 313.1223, found 313.1230.



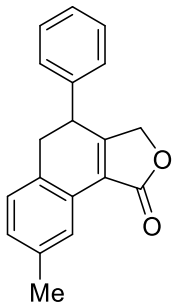
**4-([1,1'-Biphenyl]-4-yl)-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4m**). Colourless oil; 27.0 mg, 80% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.21 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.55 – 7.52 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.26 – 7.23 (m, 3H), 7.17 (d, *J* = 7.2 Hz, 1H), 4.71 (s, 2H), 4.08 (t, *J* = 8.7 Hz, 1H), 3.36 (dd, *J* = 16.0, 7.7 Hz, 1H), 3.25 (dd, *J* = 16.0, 9.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.4, 162.2, 140.9, 140.5, 139.2, 134.0, 129.2, 129.0, 128.0, 127.7, 127.5, 127.1, 126.9, 124.5, 123.8, 70.1, 40.5, 36.8; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{19}O_2$ $[M+H]^+$: 339.1380, found 339.1374.



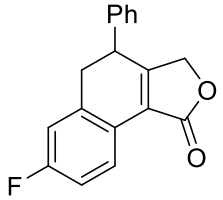

**6-Methyl-4-phenyl-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4n**). Colourless oil; 20.7 mg, 75% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.18 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.44 – 7.35 (m, 4H), 7.32 – 7.28 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 4.73 (d, *J* = 1.4 Hz, 2H), 4.12 (dd, *J* = 10.1, 8.1 Hz, 1H), 3.39 (dd, *J* = 16.5, 8.0 Hz, 1H), 3.18 (dd, *J* = 16.5, 10.2 Hz, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.6, 161.7, 140.8, 135.6, 132.3, 131.2, 129.3, 127.9, 127.6, 126.8, 126.7, 124.5, 121.7, 69.8, 40.7, 33.2, 20.0; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.1223, found 277.1232.




**7-Methyl-4-phenyl-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4o**). Colourless oil; 20.7 mg, 75% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.08 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.21 – 7.19 (m, 2H), 7.12 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.99 (d, *J* = 1.8 Hz, 1H), 4.73 – 4.62 (m, 2H), 4.03 (dd, *J* = 9.4, 7.6 Hz, 1H), 3.31 (dd, *J* = 16.0, 7.7 Hz, 1H), 3.19 (dd, *J* = 16.0, 9.5 Hz, 1H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.6, 161.2, 140.4, 139.2, 134.0, 129.3, 128.9, 127.93, 127.87, 127.6, 124.4, 124.1, 123.6, 70.1, 40.8, 36.8, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.1223, found 277.1232.



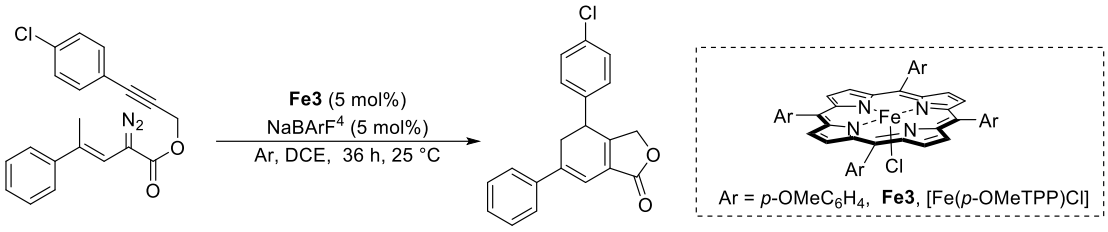

**8-Methyl-4-phenyl-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4p**). Colourless oil; 21.6 mg, 78% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.03 (s, 1H), 7.35 – 7.27 (m, 3H), 7.19 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.10 – 7.05 (m, 2H), 4.73 – 4.63 (m, 2H), 4.03 (ddt, *J* = 9.2, 7.6, 1.4 Hz, 1H), 3.31 (dd, *J* = 16.0, 7.7 Hz, 1H), 3.19 (dd, *J* = 16.0, 9.6 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.6, 162.4, 140.3, 137.2, 130.9, 129.7, 129.3, 127.9, 127.6, 126.7, 124.5, 124.4, 70.1, 41.0, 36.4, 21.4; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.1223, found 277.1229.




**7-Fluoro-4-phenyl-4,5-dihydronaphtho[1,2-*c*]furan-1(3*H*)-one** (**4q**). Yellow oil; 23.3 mg, 83% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.19 (dd, *J* = 8.5, 5.9 Hz,

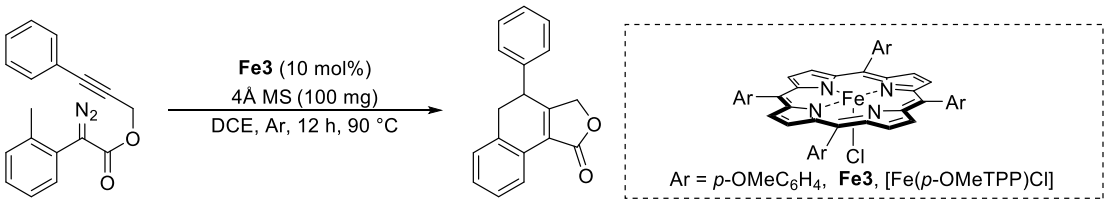
1H), 7.36 – 7.30 (m, 3H), 7.20 – 7.17 (m, 2H), 6.99 (td, *J* = 8.6, 2.7 Hz, 1H), 6.90 (dd, *J* = 9.1, 2.6 Hz, 1H), 4.75 – 4.64 (m, 2H), 4.06 (t, *J* = 8.5 Hz, 1H), 3.35 (dd, *J* = 16.2, 7.7 Hz, 1H), 3.22 (dd, *J* = 16.2, 9.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.4, 164.3, 161.8, 161.3 (d, *J* = 2.5 Hz), 139.9, 136.7 (d, *J* = 7.8 Hz), 129.4, 128.1, 127.5, 125.6 (d, *J* = 8.5 Hz), 123.9, 123.1 (d, *J* = 3.0 Hz), 115.5 (d, *J* = 21.6 Hz), 114.0 (d, *J* = 21.3 Hz), 70.1, 40.5, 36.9; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -111.28; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}FO_2$ $[M+H]^+$: 281.0972, found 281.0972.

## Synthetic Transformations




**1a** **2a**

*General Procedure for the 'Scale-up' Synthesis of **2a***: To a 50-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe3**, 5 mol%, 82.4 mg) and $NaBArF^4$ (5 mol%, 88.6 mg) in glovebox. Then, the vial was capped and taken out from the glovebox, and DCE (5.0 mL) was injected into vial under argon atmosphere. The resulting reaction mixture was stirred at 25 ℃ for 2 h. A solution of diazo compound **1a** (2.0 mmol, 701.6 mg) in DCE (5.0 mL) was added into the reaction vessel through syringe in 4 h, then the new mixture stirred under these conditions for 30 h. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 10:1 to 6:1) to give pure products **2a** (colourless oil, 464.8 mg, 72% yield).

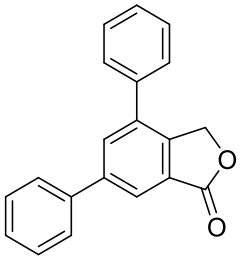



**3a** **4a**

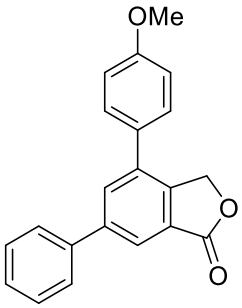
*General Procedure for the 'Scale-up' Synthesis of **4a***: To a 20-mL vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe3**, 10 mol%, 177.2 mg) and 4Å MS (500 mg). Then, the capped vial was evacuated and back-filled with argon (3 times). A solution of diazo compound **3a** (2.0 mmol, 580.6 mg) in DCE (10.0 mL) was added into the reaction vessel in one-time and the reaction mixture was stirred at 90 ℃ for 12 h. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 10:1 to 5:1) to give the products **4a** (colourless oil, 404.0 mg, 77% yield).


**2** **5** or **6**

*Synthesis of **5**:* To a 10-mL vial equipped with a magnetic stir bar, was charged with DDQ (2,3-dicyano-5,6-dichlorobenzoquinone, 0.3 mmol, 68.1 mg). A solution of **2** (0.1 mmol) in DCE (2.0 mL) was added to the reaction vessel. Then the reaction mixture was stirred at room temperature overnight. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 30:1 to 20:1) to give the pure products **5** in generally high yields.

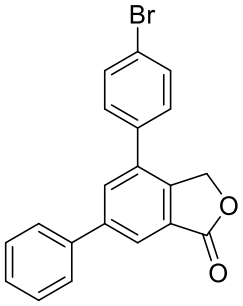



**4,6-Diphenylisobenzofuran-1(3*H*)-one** (**5b**). white solid; m.p. 177.3-178.5 °C; 25.8 mg, 90% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.13 (d, *J* = 1.6 Hz, 1H), 7.95 (d, *J* = 1.6 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.55 – 7.48 (m, 6H), 7.46 – 7.40 (m, 2H), 5.44 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.2, 143.6, 143.0, 139.5, 137.8, 137.5, 133.1, 129.4, 129.2, 128.7, 128.4, 127.9, 127.4, 127.3, 123.0, 69.8; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}O_2$ $[M+H]^+$: 287.1067, found 287.1069.

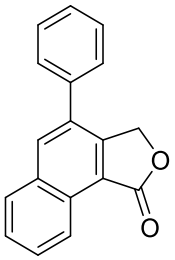



**4-(4-Methoxyphenyl)-6-phenylisobenzofuran-1(3*H*)-one** (**5d**). white solid; m.p.

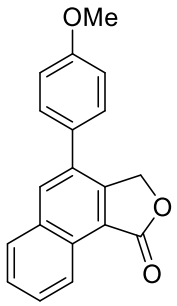
159.7-160.5 ℃; 27.2 mg, 86% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.09 (s, 1H), 7.91 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.40 (m, 3H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.44 (s, 2H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3, 160.1, 160.0, 143.6, 142.9, 139.6, 137.2, 132.8, 130.1, 129.3, 129.1, 128.4, 127.5, 127.3, 122.5, 114.8, 114.8, 69.9, 55.6; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{19}O_3$ $[M+H]^+$: 317.1172, found 317.1178.



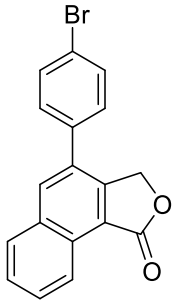

**4-(4-Bromophenyl)-6-phenylisobenzofuran-1(3*H*)-one** (**5f**). white solid; m.p. 186.2-187.1 ℃; 27.2 mg, 93% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.15 (d, *J* = 1.6 Hz, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.67 – 7.65 (m, 4H), 7.52 – 7.48 (m, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 5.42 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.0, 143.9, 142.9, 139.3, 136.7, 136.4, 132.9, 132.6, 129.5, 129.3, 128.6, 127.54, 127.46, 123.4, 123.1, 69.6; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{14}BrO_2$ $[M+H]^+$: 365.0172, found 365.0167.



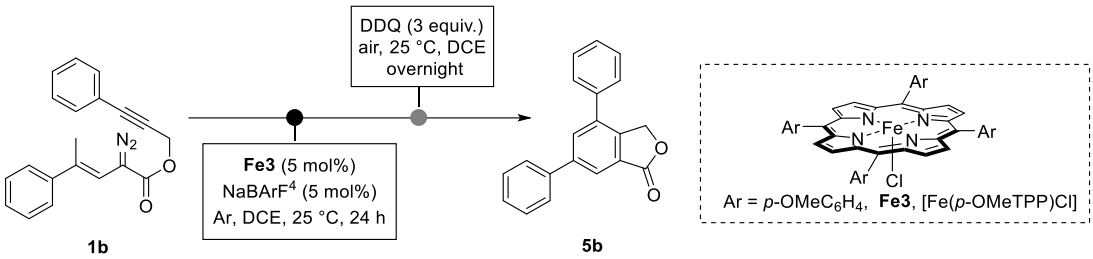

**4-Phenylnaphtho[1,2-*c*]furan-1(3*H*)-one** (**6a**). white solid; m.p. 181.7-182.6 ℃; 22.9 mg, 88% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.07 (d, *J* = 8.4 Hz, 1H), 8.14 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.68 – 7.65 (m, 1H), 7.54 – 7.52 (m, 4H), 7.49 – 7.46 (m, 1H), 5.45 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.6, 147.2, 137.9, 134.4, 134.05, 133.96, 129.4, 129.1, 128.7, 128.6, 128.1, 127.8, 123.5, 120.8, 69.4; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}O_2$ $[M+H]^+$: 261.0910, found 261.09106.



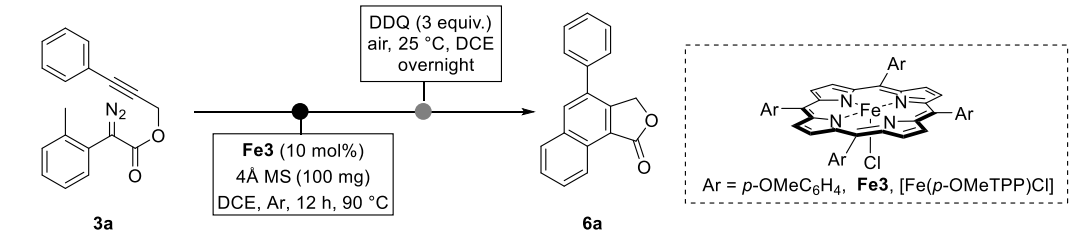

**4-(4-Methoxyphenyl)naphtho[1,2-*c*]furan-1(3*H*)-one** (**6c**). white solid; m.p. 173.5-174.2 ℃; 26.1 mg, 90% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.04 (d, *J* = 8.3 Hz, 1H), 8.08 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.66 – 7.62 (m, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 5.43 (s, 2H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.7, 159.9, 147.2, 134.1, 133.9, 133.6, 130.1, 129.3, 128.8, 128.5, 128.4, 127.7, 123.4, 120.7, 114.8, 69.4, 55.6; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{15}O_3$ $[M+H]^+$: 291.1016, found 291.1021.




**4-(4-Bromophenyl)naphtho[1,2-*c*]furan-1(3*H*)-one** (**6f**). white solid; m.p. 181.1-182.1 ℃; 32.2 mg, 95% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.06 (d, *J* = 8.3 Hz, 1H), 8.11 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.69 – 7.65 (m, 3H), 7.40 (d, *J* = 8.5 Hz, 2H), 5.41 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3, 146.7, 136.8, 134.31, 134.26, 134.0, 132.7, 132.6, 129.7, 129.3, 128.8, 128.7, 127.9, 123.5, 123.0, 121.1, 69.1; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{12Br}O_2$ $[M+H]^+$: 339.0015, found 339.0021.

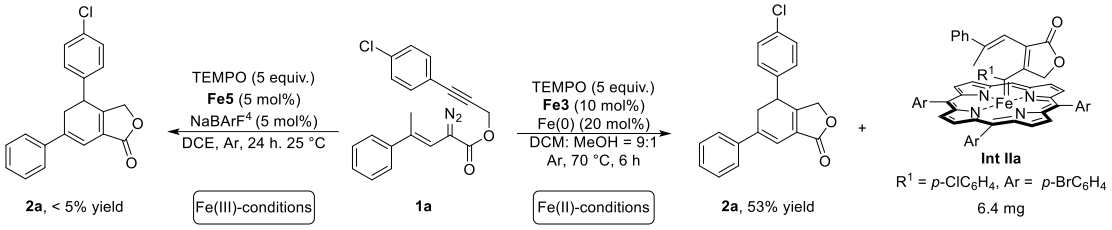



*'One-pot' Reaction for the Synthesis of **5b**:* To a 10-mL vial equipped with a magnetic stir bar, [Fe(*p*-OMeTPP)Cl] (**Fe3**, 5 mol%, 4.1 mg) and $NaBArF^4$ (5 mol%, 4.4 mg) were added successively in glovebox. After the vial was capped and taken out from the glovebox, DCE (0.5 mL) was injected into vial under argon atmosphere, and the mixture was stirred at 25 ℃ for 0.5 h. Then, a solution of diazo compound **1b** (0.1 mmol, 31.6 mg) in DCE (1.0 mL) was injected into the reaction vessel through syringe pump in 3.5 h. The new mixture was stirred under these conditions for 20 h. After the reaction was completed, DDQ (3.0 equiv., 68.1 mg) was added to the reaction mixture. Then, the reaction mixture was stirred under these conditions overnight. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 30:1 to 20:1) to give 18.0 mg pure product **5b** in 63% yield.



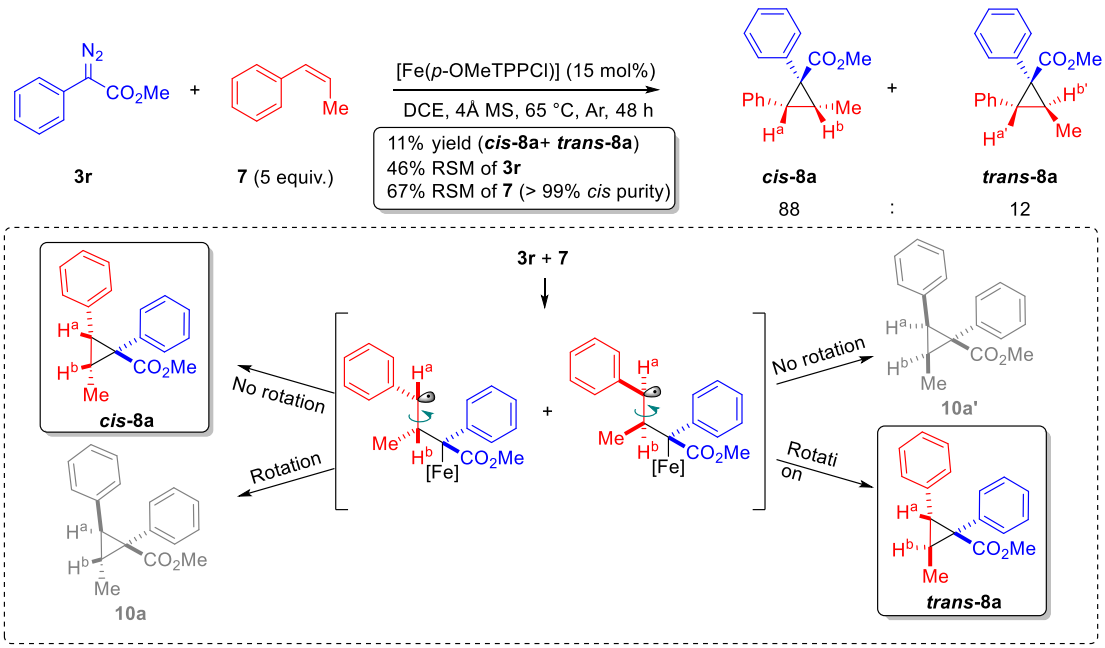

*"One-pot" Reaction for the Synthesis of **6a**:* To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe5**, 10 mol%, 8.2 mg) and 4Å MS (100 mg). The vial was evacuated and back-filled with argon (3 times) after being capped. Then, a solution of diazo compound **3a** (0.1 mmol, 29.0 mg) in DCE (2.0 mL) was injected into the reaction vessel and the reaction mixture was stirred at 90 ℃ for 12 h. After the reaction was completed and the reaction system was cooled to room temperature. Then, DDQ (3.0 equiv., 68.1 mg) was added to the reaction mixture. The reaction mixture was stirred under these conditions overnight. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 30:1 to 20:1) to give 17.4 mg pure product **6a** in 67% yield.

## Control Experiments:

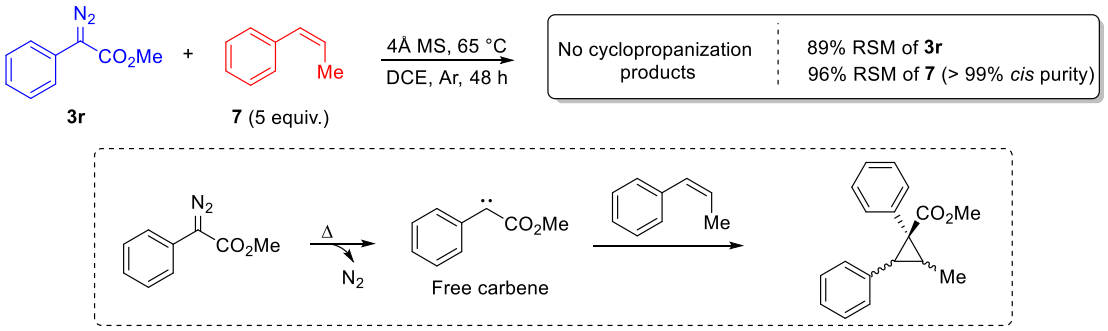



*Procedure for the Radical Inhibition Experiment of 'Fe(III)-conditions'*: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe3**, 5 mol%, 4.1 mg), $NaBArF^4$ (5 mol%, 4.4 mg) and TEMPO (2,2,6,6-tetramethylpiperidinooxy, 0.5 mmol, 78.1 mg) in glovebox. Then, the vial was capped and taken out from the glovebox, and DCE (0.5 mL) was injected into vial under argon atmosphere. The resulting reaction mixture was stirred at 25 °C for 0.5 h. A solution of diazo compound **1a** (0.1 mmol, 35.1 mg) in DCE (1.0 mL) was added into the reaction vessel through syringe in 3.5 h, then the new mixture stirred under these conditions for 20 h. After the reaction was completed, we could not effectively detect the generation of **2a**.

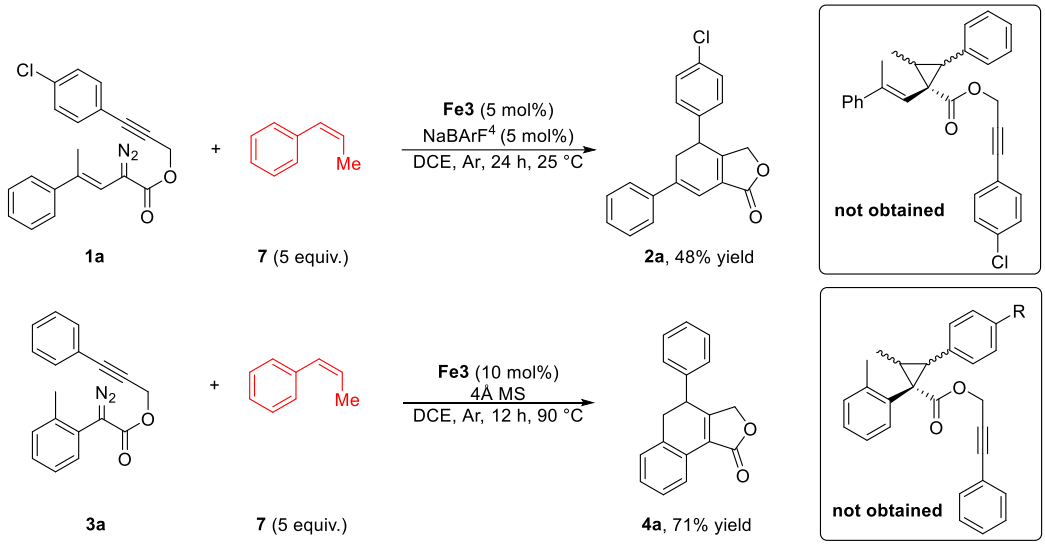
*Procedure for the Radical Inhibition Experiment of 'Fe(II)-conditions'*: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-BrTPP)Cl] (**Fe5**, 10 mol%, 10.2 mg), Fe powder (20 mol%, 1.1 mg) and TEMPO (2,2,6,6-tetramethylpiperidinooxy, 0.5 mmol, 78.1 mg). The capped vial was evacuated and back-filled with argon (3 times). Then 1.0 mL DCM: MeOH = 9:1 (v/v) was injected into vial under argon atmosphere and allowed the mixture to stir at 25 °C for 0.5 h. A solution of diazo compound **1a** (0.1 mmol, 35.1 mg) in 1.0 mL DCM: MeOH = 9:1 (v/v) was added into the reaction vessel through syringe in 0.5 h, then the new mixture stirred under 70 °C for 5.5 h. After the reaction was completed, the reaction mixture was directly purified by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 40:1 to 6:1) to give the compound **Int IIa** (6.4 mg) as red solid and **2a** (17.1 mg, 53% yield) as colourless oil.



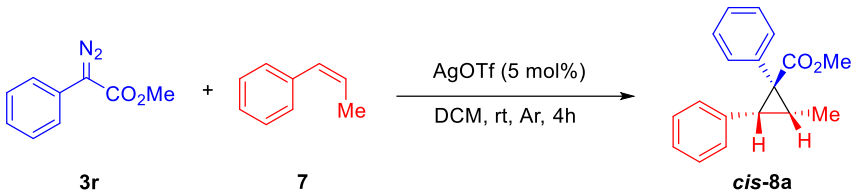

*Procedure for the synthesis of* ***cis-8a*** *and* ***trans-8a***: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe3**, 15 mol%, 24.7 mg) and 4Å MS (100 mg). Then, the capped vial was evacuated and back-filled with argon (3 times). A solution of diazo compound **3r** (0.2 mmol, 35.2 mg) and (*Z*)-prop-1-en-1-ylbenzene **7** (1.0 mmol, 118.2 mg) in DCE (2.0 mL) was added into the reaction vessel in one-time and the reaction mixture was stirred at 65 °C for 48 h. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 100:1 to 20:1) to give the products ***cis*-8a** and ***trans*-8a** (mixture, 5.8 mg, 11% yield) as colourless oil (**Supplementary Figure 1 and 2**).



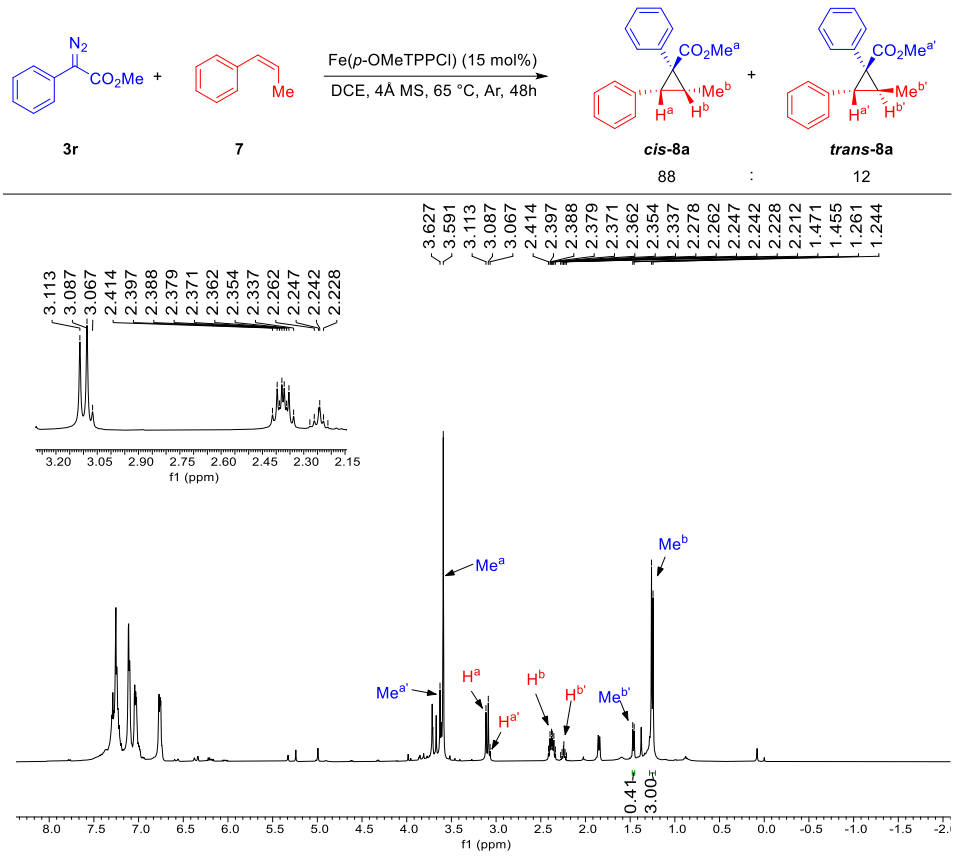

**NOTE**: To verify if the reaction could occur *via* a free carbene pathway under 65 °C. We conducted the reaction of **3r** with **7** in the absence of iron catalyst, and no reaction occurred.



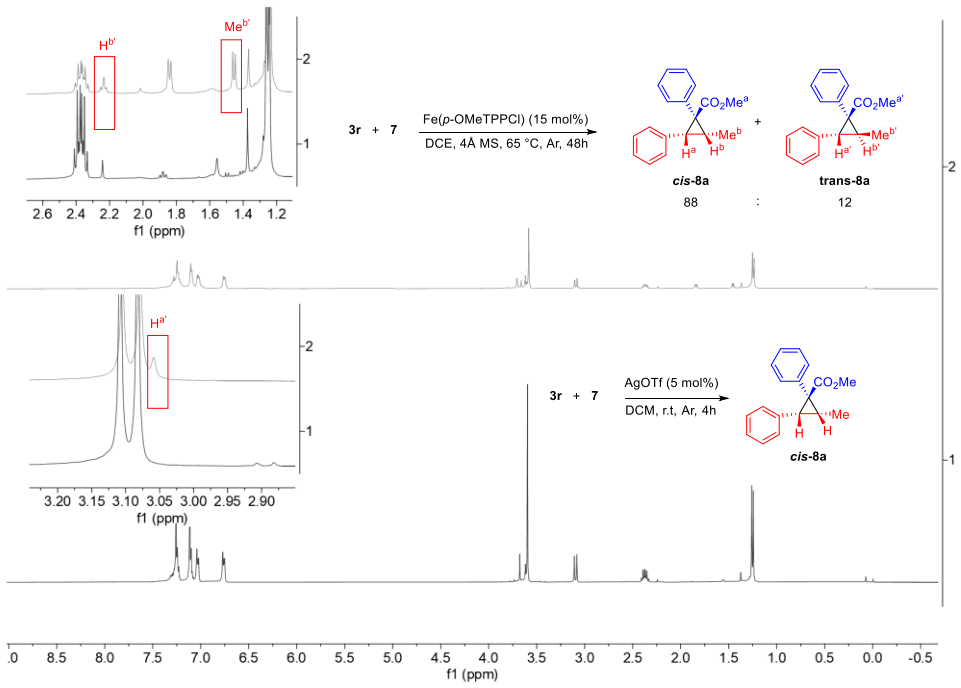

**NOTE**: The above two experimental results showed that the reaction with **1a** or **3a** preferentially underwent intramolecular transformation, rather than intermolecular cyclopropanization. For this reason, we chose substrate **3r** to react with **7** under current conditions.



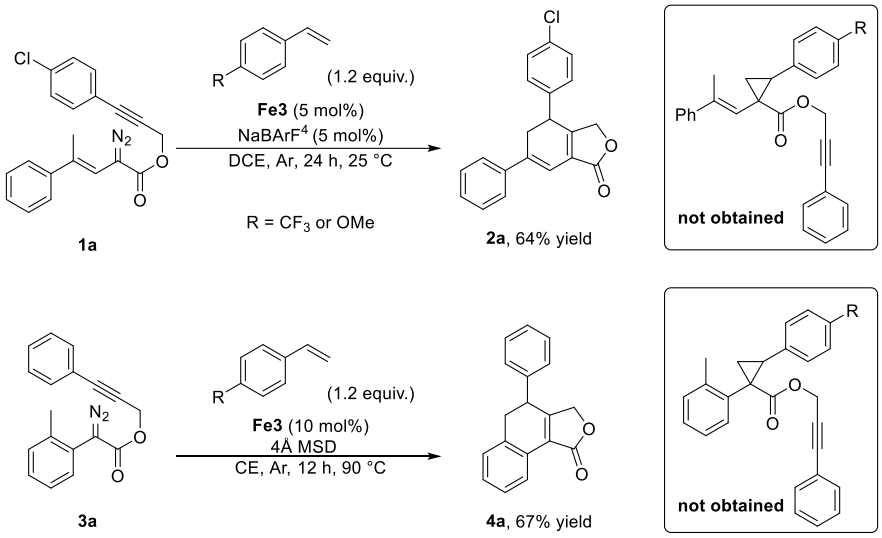

*Procedure for the synthesis of **cis-8a** under AgOTf-catalyzed* [4]: To a 25-mL oven-dried round bottom flask (covered with aluminium foil to exclude light) equipped with a magnetic stir bar, was charged with AgOTf (5 mol%, 6.4 mg) and (*Z*)-prop-1-en-1-ylbenzene **7** (2.5 mmol, 295.4 mg). Then, the capped flask was evacuated and back-filled with argon (3 times). The mixture was dissolved in dichloromethane (2 ml) and stirred at room temperature. A solution of diazo compound **3r** (0.5 mmol, 88.1 mg) in DCM (8.0 mL) was added into the flask through syringe in 3 h. After addition, the mixture was stirred for an additional 1 h and then concentrated *in vacuo*. The reaction mixture was purified by column chromatography on silica gel (eluent: PE: EA = 20:1 to 15:1) to give the products ***cis*-8a** (62.6 mg, 47% yield) as white solid[5,6].




**Supplementary Figure 1.** $^{1}$H NMR observation of compound ***cis*-8a** and ***trans*-8a**.




**Supplementary Figure 2.** $^{1}$H NMR comparison between Fe-catalyzed and Ag-catalyzed reaction.

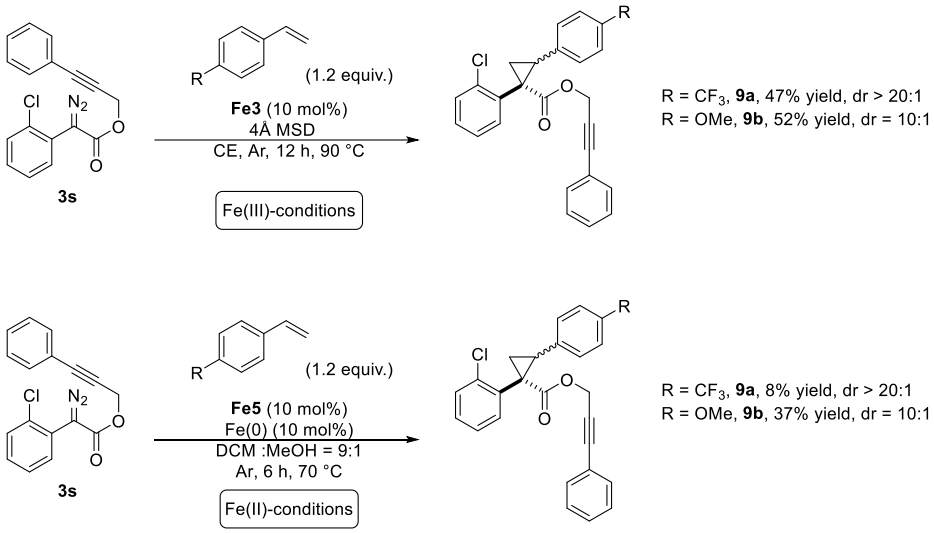



*Procedure for Cyclopropanation with Substrate **1a***: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe3**, 5 mol%, 4.1 mg) and $NaBArF^4$ (5 mol%, 4.4 mg) in glovebox. Then, the vial was capped and taken out from the glovebox, and DCE (0.5 mL) was injected into vial under argon atmosphere. The resulting reaction mixture was stirred at 25 ℃ for 0.5 h. A solution of diazo compound **1a** (0.1 mmol, 35.1 mg) and styrenes (0.12 mmol) in DCE (1.0 mL) was added into the reaction vessel through syringe in 3.5 h, then the new mixture stirred under these conditions for 20 h. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 10:1 to 6:1) to give the compound **2a** (20.7 mg, 64% yield) as colourless oil and cyclopropanation product could not be obtained.

*Procedure for Cyclopropanation with Substrate **3a***: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe3**, 10 mol%, 8.2 mg) and 4Å MS (100 mg). The capped vial was evacuated and back-filled with argon (3 times). A solution of diazo compound **3a** (0.1 mmol, 29.0 mg) and styrenes (0.12 mmol) in DCE (2.0 mL) was added into the reaction vessel in one-time and the reaction mixture was stirred at 90 ℃ for 12 h. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 10:1 to 5:1) to give the product **4a** (17.6 mg, 67% yield) as colourless oil and cyclopropanation product could not be obtained.

**NOTE**: The above two experimental results show that the reaction with substrates **1a** or **3a** underwent intramolecular transformation, rather than intermolecular cyclopropanation. For this reason, substrate **3s** was used to test the for the

cyclopropanation reaction under two different catalytic conditions. **3-Phenylprop-2-yn-1-yl 2-(2-chlorophenyl)-2-diazoacetate** (**3s**). Red oil; 848 mg, 91% yield; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.48 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.44 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.36 – 7.29 (m, 5H), 5.09 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.0, 134.0, 132.5, 132.1, 130.3, 129.9, 129.0, 128.5, 127.3, 123.8, 122.3, 86.9, 83.1, 53.5.



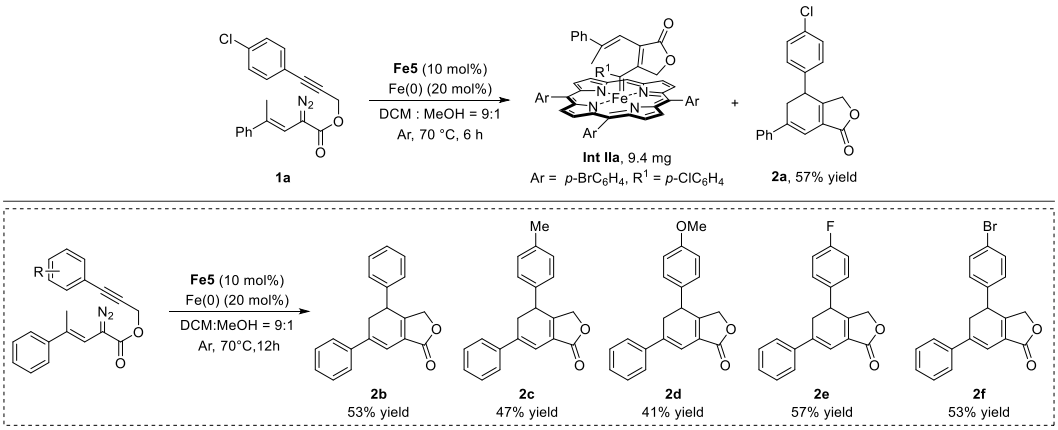

*Procedure for Cyclopropanation of Substrate **3s** under 'Fe(III)-conditions'*: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-OMeTPP)Cl] (**Fe3**, 10 mol%, 8.2 mg) and 4Å MS (100 mg). The capped vial was evacuated and back-filled with argon (3 times). A solution of diazo compound **3s** (0.1 mmol, 31.1 mg) and styrenes (0.12 mmol) in DCE (2.0 mL) was added into the reaction vessel in one-time and the reaction mixture was stirred at 90 °C for 12 h. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 30:1 to 20:1) to give the product **9a** (21.4 mg, 47% yield) as yellow oil or **9b** (21.7 mg, 52% yield) as yellow oil.

*Procedure for Cyclopropanation of Substrate **3s** under 'Fe(II)-conditions'*: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-BrTPP)Cl] (**Fe5**, 10 mol%, 10.2 mg) and Fe powder (20 mol%, 1.1 mg). The capped vial was evacuated and back-filled with argon (3 times). Then 1.0 mL DCM: MeOH = 9:1 (v/v) was injected into vial under argon atmosphere and allowed the mixture to stir at 25 °C

for 0.5 h. A solution of diazo compound **3s** (0.1 mmol, 31.1 mg) and styrenes (0.12 mmol) in 1.0 mL DCM: MeOH = 9:1 (v/v) was added into the reaction vessel through syringe in 0.5 h, then the new mixture stirred under 70 ℃ for 5.5 h. After the reaction was completed, the reaction mixture was purified directly by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 30:1 to 20:1) to give the product **9a** (3.6 mg, 8% yield) as yellow oil or **9b** (15.4 mg, 37% yield) as yellow oil.

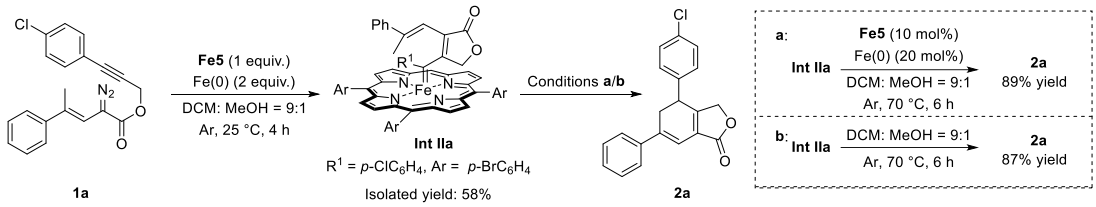
**3-Phenylprop-2-yn-1-yl 1-(2-chlorophenyl)-2-(4-(trifluoromethyl)phenyl) cyclopropane-1-carboxylate** (**9a**). yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.42 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.33 – 7.28 (m, 6H), 7.16 (s, 3H), 6.91 (d, *J* = 8.1 Hz, 2H), 4.97 – 4.88 (m, 2H), 3.43 (t, *J* = 8.3 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.99 (dd, *J* = 7.4, 5.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.9, 140.1, 137.3, 132.5, 132.0, 129.7, 129.3, 128.8, 128.4, 128.3, 126.6, 125.7, 124.5, 122.9, 122.4, 86.6, 83.0, 53.9, 37.3, 32.8, 22.1; $^{19}$F NMR (376 MHz, $CDCl_3$) (δ, ppm) -62.43; HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{19}ClF_3O_2$ $[M+H]^+$: 455.1021, found 455.1028.

**3-Phenylprop-2-yn-1-yl 1-(2-chlorophenyl)-2-(4-methoxyphenyl)cyclopropane-1-carboxylate** (**9b**). yellow oil; $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.40 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.10 (d, *J* = 6.4 Hz, 2H), 6.98 – 6.92 (m, 1H), 6.67 – 6.50 (m, 4H), 4.99 (d, *J* = 15.6 Hz, 1H), 4.78 (d, *J* = 15.5 Hz, 1H), 3.68 (s, 3H), 3.28 – 3.14 (m, 1H), 2.15 (q, *J* = 5.9, 5.2 Hz, 1H), 1.79 (t, *J* = 6.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) 173.2, 158.3, 140.2, 133.1, 132.0, 130.4, 130.2, 128.8, 128.4, 127.6, 125.5, 122.5, 113.1, 86.3, 83.4, 55.2, 53.4, 33.1, 22.7, 19.5. HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{19}ClF_3O_2$ $[M+H]^+$: 417.1252, found 417.1249.




*Procedure for the Synthesis of **2a** under 'Fe(II)-conditions'*: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-BrTPP)Cl] (**Fe5**, 10 mol%, 10.2 mg) and Fe powder (20 mol%, 1.1 mg). The capped vial was evacuated and back-filled with argon (3 times). Then 1.0 mL DCM: MeOH = 9:1 (v/v) was injected into vial under argon atmosphere and allowed the mixture to stir at 25 ℃ for 0.5 h. A solution of diazo compound **1a** (0.1 mmol, 35.1 mg) in 1.0 mL DCM: MeOH = 9:1 (v/v) was added into the reaction vessel through syringe in 0.5 h, then the new mixture stirred under 70 ℃ for 5.5 h. After the reaction was completed, the reaction mixture was directly purified by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 40:1 to 6:1) to give the compound **Int IIa** (9.4 mg) as red solid and **2a** (18.4 mg, 57% yield) as colourless oil.

*$^{1}$H and $^{13}$C NMR Spectra Date of **Int IIa***: $^{1}$H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.47 (s, 8H), 7.78 (d, *J* = 7.9 Hz, 8H), 7.62 (s, 8H), 7.47 – 7.42 (m, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 3H), 6.76 (d, *J* = 7.6 Hz, 2H), 6.12 (d, *J* = 8.4 Hz, 2H), 2.94 (d, *J* = 8.5 Hz, 2H), 0.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) (δ, ppm) **319.6**, 179.5, 171.3, 162.8, 146.3, 142.0, 141.8, 139.7, 134.7, 133.1, 131.2, 130.4, 128.3, 127.9, 126.2, 125.7, 122.8, 121.1, 114.3, 110.6, 106.6, 59.1, 18.1.




*Procedure for the Synthesis of **Int IIa***: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-BrTPP)Cl] (**Fe5**, 0.1 mmol, 102 mg) and Fe powder (0.1 mmol, 11.2 mg). The capped vial was evacuated and back-filled with argon (3 times). Then 3.0 mL DCM: MeOH = 9:1 (v/v) was injected into vial under argon atmosphere and allowed the mixture to stir at 25 ℃ for 0.5 h. A solution of diazo compound **1a** (0.1 mmol, 35.1 mg) in 2.0 mL DCM: MeOH = 9:1 (v/v) was added into the reaction vessel through syringe in 3.5 h. After the reaction was completed, the reaction mixture was directly purified by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 40:1 to 20:1) to give the compound **Int IIa** (75.8 mg, 58% yield) as red solid.

*Procedure for the Synthesis of **2a** under Condition **a***: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with [Fe(*p*-BrTPP)Cl] (**Fe5**, 10 mol%, 5.1 mg) Fe powder (20 mol%, 0.6 mg) and **Int IIa** (0.05 mmol, 65.3 mg). The capped vial was evacuated and back-filled with argon (3 times). Then 2.0 mL DCM: MeOH = 9:1 (v/v) was injected into vial under argon atmosphere and allowed the mixture to stir at 25 ℃ for 0.5 h. The new mixture was stirred under 70 ℃ for 5.5 h After the reaction was completed, the reaction mixture was directly purified by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 15:1 to 6:1) to give the compound **2a** (14.4 mg, 89% yield) as colourless oil.

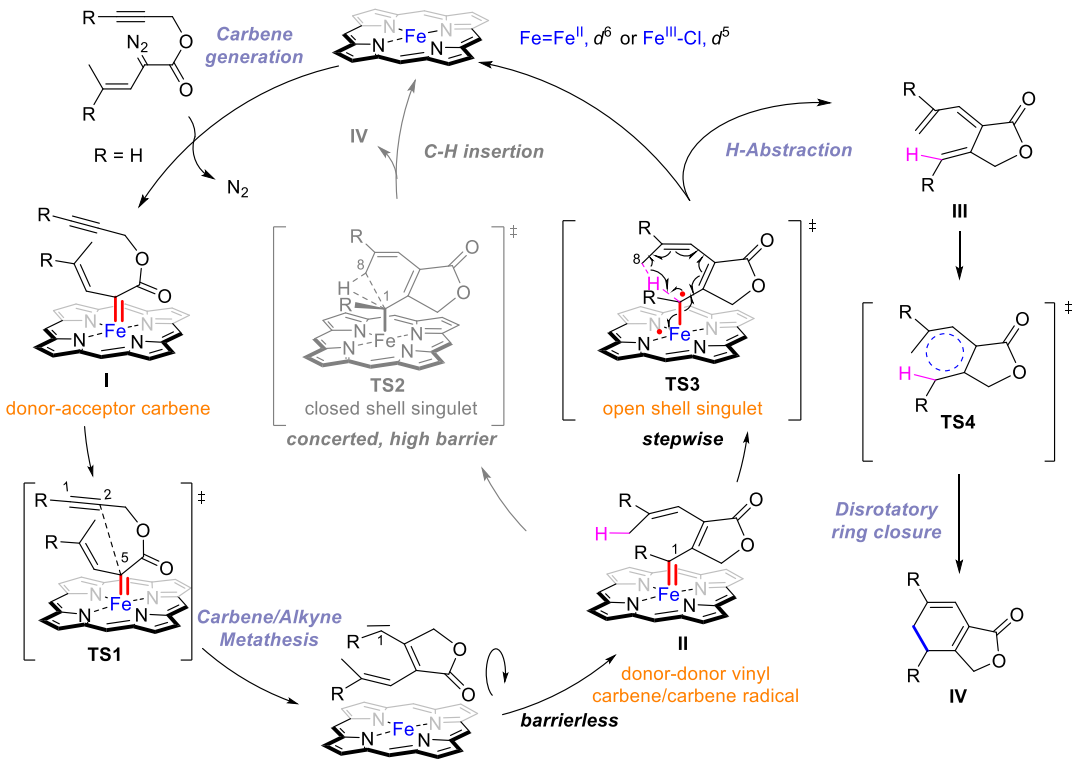
*Procedure for the Synthesis of **2a** under Condition **b***: To a 10-mL oven-dried vial equipped with a magnetic stir bar, was charged with **Int IIa** (0.05 mmol, 65.3 mg). The capped vial was evacuated and back-filled with argon (3 times). Then 2.0 mL DCM: MeOH = 9:1 (v/v) was injected into vial under argon atmosphere and allowed the mixture to stir at 25 ℃ for 0.5 h. The new mixture was stirred under 70 ℃ for 5.5 h After the reaction was completed, the reaction mixture was directly purified by column chromatography on silica gel without any additional treatment (eluent: PE: EA = 15:1 to 6:1) to give the compound **2a** (14.0 mg, 87% yield) as colourless oil.

## Computational Studies

*Methods*

All computations were performed using the Gaussian16 (Rev. B.01) suite of quantum chemical program[7]. Geometry optimizations on unsubstituted model systems (R=H) of the stationary points (reactants, intermediates, transition states, and products) were carried out in the gas phase. Depending on whether the species concerned bears a paired or unpaired electron, restricted or unrestricted (U)B3LYP hybrid density functional theory[8] is respectively used in conjunction with the D95 basis set[9] for all elements except Fe, which has been described by the SDD 16 basis set with an effective core potential (ECP) for the 10 core electrons and explicit basis set for the 16 valence electrons[10-12]. All stationary points were characterized by using frequency calculations in order to verify that the transition states (TSs) have one and only one imaginary frequency for the desired reaction coordinate.

Various different spin states were considered, as applicable. For instance, Fe(III) in the doublet, triplet and sextet state and Fe(II) in singlet, triplet, and quintet state, respectively. However, only the Fe(III)-doublet and Fe(II) singlet reaction path as lowest in energy are reported here unless stated otherwise[13]. The *guess=mix* keyword was employed as the broken symmetry (BS) correction in the case of the open-shell singlet state calculations[14-15]. All stationary points were characterized by using frequency calculations in order to verify that the transition states have only a single imaginary frequency for the desired reaction coordinate. The Gibbs free energies were evaluated using the OPBE functional[16], which combines Handy's optimized exchange (OPTX)[17] with the PBE correlation[18], and the def2TZVP basis set[19] adopting the /B3-LYP/SDD/ thermal corrections at 333.15 K. The NEVPT2[20-21] corrected CASSCF[22] calculations have been performed using the ORCA 5.0 version[23]. In analogy to Xantheas[24] *et al* we defined the amount of multireference character as $\beta = \frac{2(1-c1)^2}{(c1)^2(1-c1)^2}$ where c1 1s the coefficient of the main wavefunction contribution.

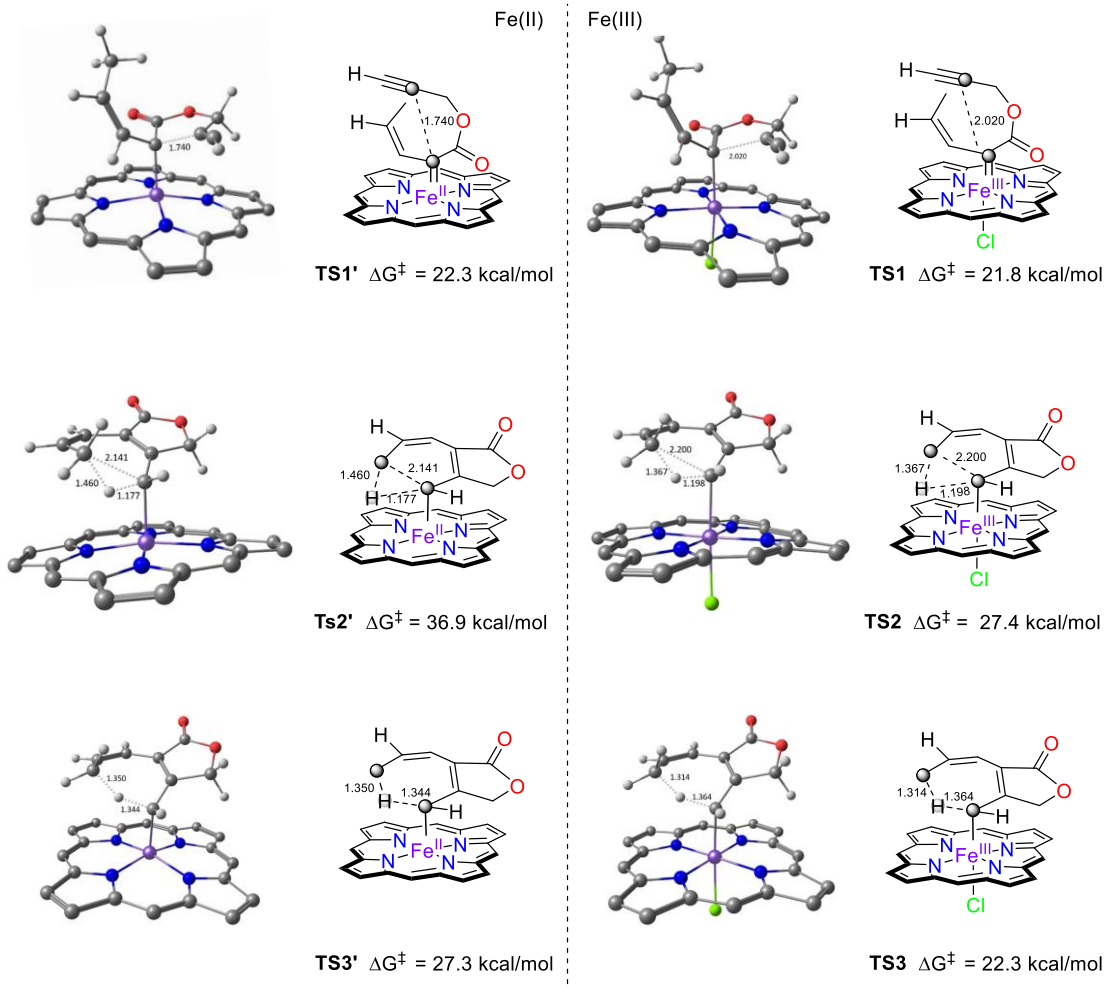



**Supplementary Figure 3.** General reaction scheme of the model reaction.

**Supplementary Table 12**. OPBE/def2TZVP Total Energies, B3-LYP/SDD thermal corrections and Fee Energies (a.u.) as well as imaginary frequencies ($cm^{-1}$) and <S**2> values of the stationary points.

| | imag/$cm^{-1}$ | <S**2> | E(tot) | Thermal | Free Energy | E(rel) |
|---|---|---|---|---|---|---|
| **I'** | | | -2712.26977 | 0.35686 | -2711.91291 | |
| **TS1'** | -184 | | -2712.23697 | 0.35955 | -2711.87742 | 22.3 |
| **II'** | | | -2712.36865 | 0.36132 | -2712.00733 | -59.2 |
| **TS2'** | -920 | | -2712.31044 | 0.36195 | -2711.94849 | 36.9 |
| **TS3'** | -1595 | 0.9324 | -2712.32262 | 0.35874 | -2711.96388 | 27.3 |
| **III'** | | | -2712.34645 | 0.35671 | -2711.98974 | 11.0 |
| **I** | | 1.1421 | -3172.44929 | 0.35473 | -3172.09457 | |
| **TS1** | -364 | 1.2005 | -3172.41770 | 0.35789 | -3172.05981 | 21.8 |
| **II** | | 1.3133 | -3172.54889 | 0.35790 | -3172.19099 | -60.5 |
| **TS2** | 506 | 0.8851 | -3172.50759 | 0.36018 | -3172.14740 | 27.4 |
| **TS3** | -1494 | 1.2991 | -3172.51190 | 0.35637 | -3172.15553 | 22.3 |

| | | | | | |
|---|---|---|---|---|---|
| **1a** + **Fe(Por)** | 1.1945 | -3172.61661 | 0.36243 | -3172.25418 | -39.7 |
| **III** | 1.1751 | -3172.56456 | 0.35335 | -3172.21121 | -12.7 |




**Supplementary Figure 4.** Graphical representation[25] of the transition states for the model reaction, bond distances in Å. Porphyrin-hydrogens are omitted for clarity.

**Supplementary Table 13**. Orbital occupations and energies, contributions and graphical representation of the active space orbitals as result of theNEVPT2-CASCF calculations.

| Fe(II) | | | |
|---|---|---|---|
| **I'** 8,8 | | | |
| 124 | 2.0000 | -0.332931 | -9.0595 |
| 125 | 1.8877 | -0.466052 | -12.6819 |
| 126 | 1.9710 | -0.372249 | -10.1294 |
| 127 | 1.7399 | -0.315346 | -8.5810 |
| 128 | 1.9415 | -0.222513 | -6.0549 |

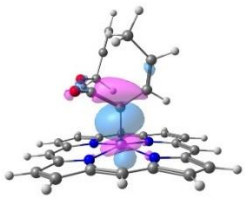
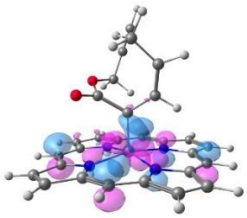
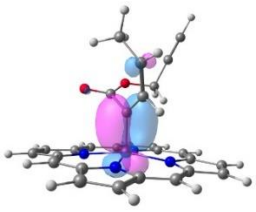
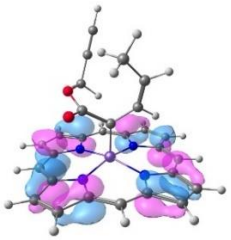
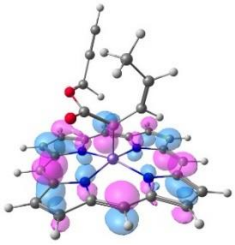
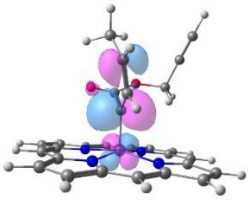
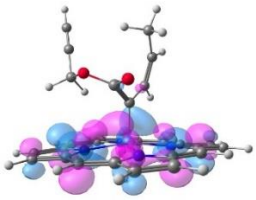
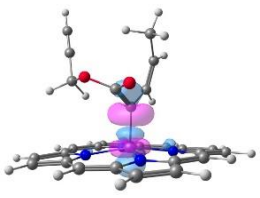
| | | | |
|---|---|---|---|
| 129 | 0.0566 | 0.017898 | 0.4870 |
| 130 | 0.2576 | 0.060543 | 1.6475 |
| 131 | 0.0245 | 0.148861 | 4.0507 |
| 132 | 0.1214 | 0.246082 | 6.6962 |

| | | | |
|---|---|---|---|
| 0.78397 [ | 0]: | 22220000 | Beta = 0.14% |
| 0.07991 [ | 49]: | 22020200 | |
| 0.04473 [ | 393]: | 12120101 | |
| 0.01769 [ | 5]: | 22202000 | |
| 0.01299 [ | 759]: | 02220002 | |
| 0.00708 [ | 861]: | 02020202 | |
| 0.00634 [ | 96]: | 21211010 | |
| 0.00510 [ | 360]: | 12220001 | |
| 0.00466 [ | 16]: | 22120100 | |
| 0.00383 [ | 126]: | 21120101 | |
| 0.00278 [ | 125]: | 21120110 | |
| 0.00254 [ | 442]: | 12020201 | |

Total Energy Correction: dE = -6.13356222372113

Reference Energy: E0 = -2702.25071906979383

Total Energy (E0+dE): E = -2708.38428129351496

| | | | |
|---|---|---|---|
|  |  |  |  |
| 125 | 126 | 127 | 128 |
|  |  |  |  |
| 129 | 130 | 131 | 132 |

**II'** 8,8

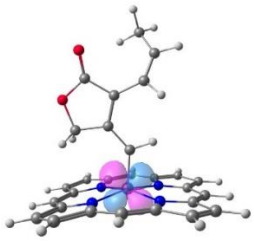
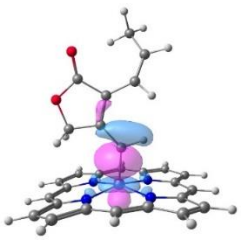
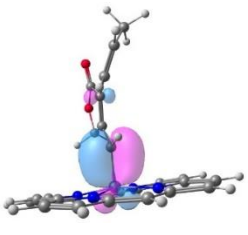
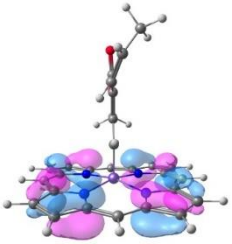
| | | | |
|---|---|---|---|
| 125 | 1.9764 | -0.508926 | -13.8486 |
| 126 | 1.8866 | -0.465623 | -12.6702 |
| 127 | 1.7592 | -0.322048 | -8.7634 |
| 128 | 1.9447 | -0.230497 | -6.2721 |
| 129 | 0.0617 | 0.007549 | 0.2054 |
| 130 | 0.2352 | 0.062198 | 1.6925 |
| 131 | 0.1157 | 0.255135 | 6.9426 |
| 132 | 0.0204 | 0.933982 | 25.4149 |
| 133 | 0.0000 | 0.042940 | 1.1685 |

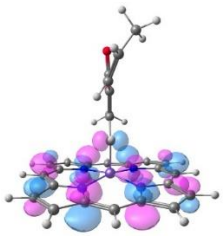
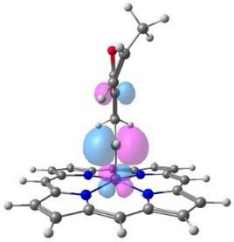
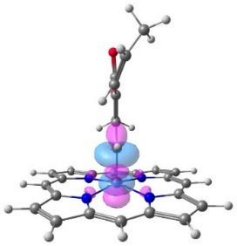
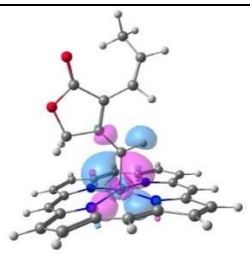
| | | | |
|---|---|---|---|
| 0.79702 [ | 0]: | 22220000 | Beta = 12% |
| 0.07486 [ | 49]: | 22020200 | |
| 0.04042 [ | 125]: | 21120110 | |
| 0.02151 [ | 5]: | 22202000 | |
| 0.01559 [ | 223]: | 20220020 | |
| 0.00660 [ | 325]: | 20020220 | |
| 0.00587 [ | 92]: | 21220010 | |
| 0.00566 [ | 491]: | 11220011 | |
| 0.00409 [ | 393]: | 12120101 | |
| 0.00285 [ | 46]: | 22021100 | |
| 0.00262 [ | 593]: | 11020211 | |

Total Energy Correction: dE = -6.10076205183395

Reference Energy: E0 = -2702.34511058280850

Total Energy (E0+dE): E = -2708.44587263464246

| | | | |
|---|---|---|---|
|  |  |  |  |
| 125 | 126 | 127 | 128 |

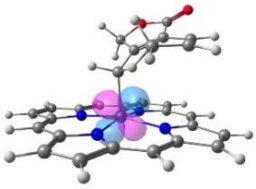
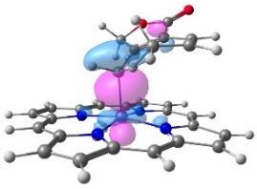
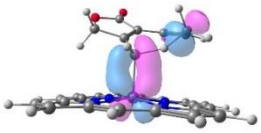
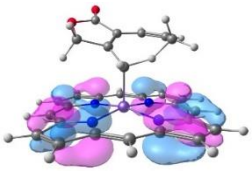
|  |  |  |  |
|---|---|---|---|
| 129 | 130 | 131 | 132 |
| **III'** 8,10 | | | |
| 125 | 1.9756 | -0.503209 | -13.6930 |
| 126 | 1.8398 | -0.396167 | -10.7803 |
| 127 | 1.5667 | -0.246682 | -6.7126 |
| 128 | 1.9123 | -0.223858 | -6.0915 |
| 129 | 0.3715 | -0.023483 | -0.6390 |
| 130 | 0.0488 | 0.006824 | 0.1857 |
| 131 | 0.1049 | 0.023306 | 0.6342 |
| 132 | 0.0136 | 0.160581 | 4.3696 |
| 133 | 0.1512 | 0.182100 | 4.9552 |
| 134 | 0.0157 | 1.114867 | 30.3371 |
| 135 | 0.0000 | 0.109743 | 2.9863 |

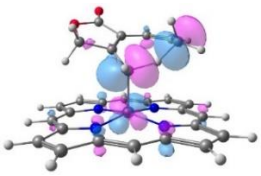
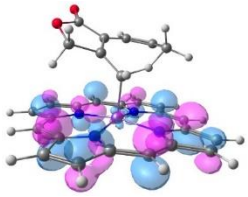
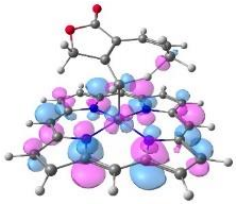
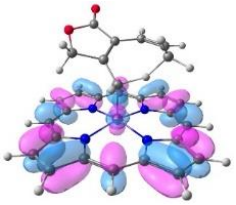
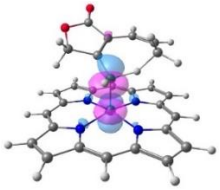
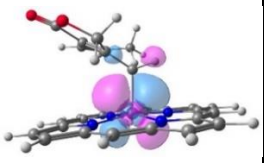
| | | | |
|---|---|---|---|
| 0.66830 [ | 0]: | 2222000000 | Beta = 40% |
| 0.09644 [ | 105]: | 2202200000 | |
| 0.04213 [ | 107]: | 2202101000 | |
| 0.03205 [ | 347]: | 2112100010 | |
| 0.02510 [ | 28]: | 2212100000 | |
| 0.02050 [ | 788]: | 2022000020 | |
| 0.01498 [ | 13]: | 2220020000 | |
| 0.00899 [ | 18]: | 2220002000 | |
| 0.00795 [ | 1209]: | 2002200020 | |
| 0.00565 [ | 270]: | 2122000010 | |
| 0.00544 [ | 356]: | 2112001010 | |

Total Energy Correction: dE = -6.14800038083467

Reference Energy: E0 = -2702.27466297203227

Total Energy (E0+dE): E = -2708.42266335286695

| | | | |
|---|---|---|---|
|  |  |  |  |
| 125 | 126 | 127 | 128 |

| | | | |
|---|---|---|---|
|  |  |  |  |
| 129 | 130 | 131 | 132 |
|  |  | | |
| 133 | 134 | | |

| Fe(III) | | | |
|---|---|---|---|
| **I** 5,10 | | | |
| 135 | 1.9626 | -0.596170 | -16.2226 |
| 136 | 1.9564 | -0.517058 | -14.0699 |
| 137 | 0.9848 | -0.217363 | -5.9147 |
| 138 | 0.0459 | 0.205835 | 5.6011 |
| 139 | 0.0189 | 0.259975 | 7.0743 |
| 140 | 0.0126 | 0.278138 | 7.5685 |
| 141 | 0.0063 | 0.791506 | 21.5380 |
| 142 | 0.0050 | 1.934591 | 52.6429 |
| 143 | 0.0032 | 2.339923 | 63.6725 |
| 144 | 0.0043 | 2.803195 | 76.2788 |

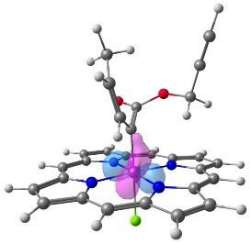
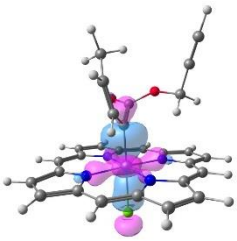
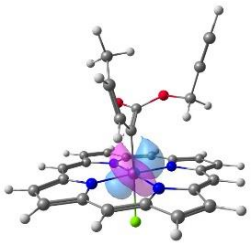
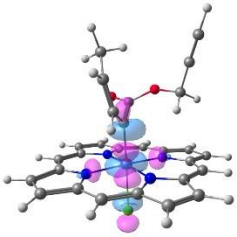
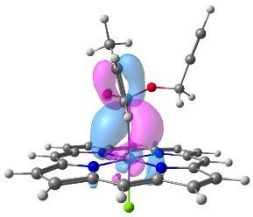
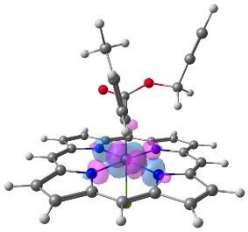
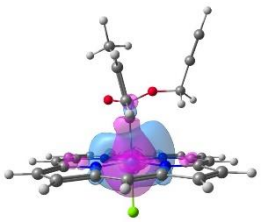
| | | | |
|---|---|---|---|
| 0.94321 [ | 0]: | 2210000000 | Beta=1% |
| 0.00947 [ | 51]: | 2012000000 | |
| 0.00605 [ | 2]: | 2200100000 | |
| 0.00537 [ | 9]: | 2111000000 | |

| | | |
|---|---|---|
| 0.00486 [ | 590]: | 0210020000 |
| 0.00484 [ | 200]: | 1111100000 |
| 0.00339 [ | 577]: | 0212000000 |

Total Energy Correction: dE = -6.27870309307491

Reference Energy: E0 = -3161.71350167773471

Total Energy (E0+dE): E = -3167.99220477080962

| | | | |
|---|---|---|---|
| |  |  |  |
| 134 | 135 | 136 | 137 |
|  |  |  |  |
| 138 | 139 | 140 | 141 |

| **II** 7,8 | | | |
|---|---|---|---|
| 134 | 1.9766 | -0.696683 | -18.9577 |
| 135 | 1.1232 | -0.301316 | -8.1992 |
| 136 | 1.0175 | -0.288609 | -7.8535 |
| 137 | 1.9225 | -0.263587 | -7.1726 |
| 138 | 0.8740 | -0.131148 | -3.5687 |
| 139 | 0.0289 | 0.006769 | 0.1842 |
| 140 | 0.0338 | 0.011146 | 0.3033 |
| 141 | 0.0234 | 0.188504 | 5.1295 |

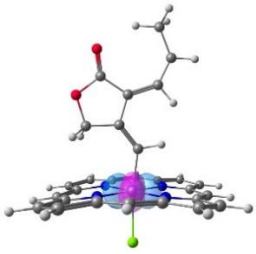
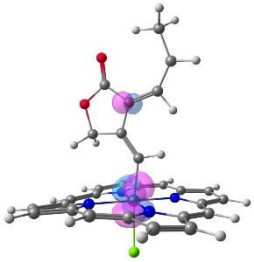
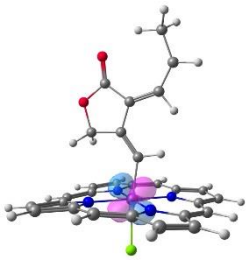
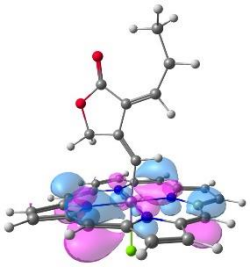
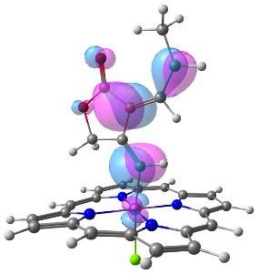
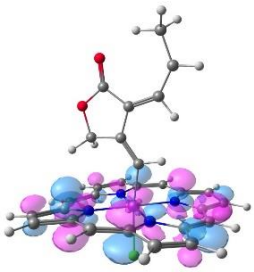
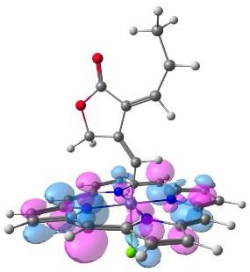
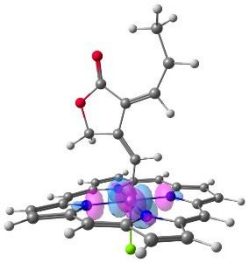
| | | | |
|---|---|---|---|
| 0.66355 [ | 65]: | 21121000 | Beta = 41% |
| 0.19336 [ | 5]: | 22120000 | |
| 0.07541 [ | 170]: | 20122000 | |
| 0.01291 [ | 51]: | 21211000 | |
| 0.01108 [ | 85]: | 21101020 | |

| | | |
|---|---|---|
| 0.00917 [ | 82]: | 21101200 |
| 0.00496 [ | 485]: | 10221001 |
| 0.00415 [ | 802]: | 01121002 |
| 0.00404 [ | 314]: | 12021001 |
| 0.00370 [ | 0]: | 22210000 |
| 0.00328 [ | 17]: | 22100020 |
| 0.00269 [ | 14]: | 22100200 |

Total Energy Correction: dE = -6.48225258340744

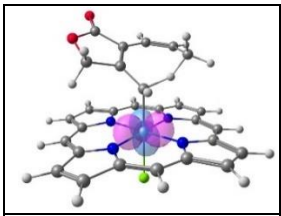
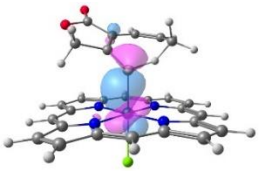
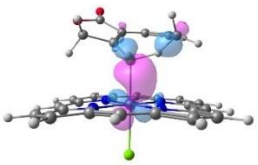
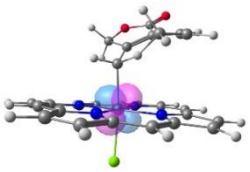
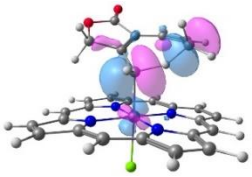
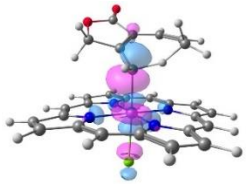
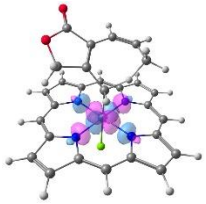
Reference Energy: E0 = -3161.70356859235562

Total Energy (E0+dE): E = -3168.18582117576307

| | | | |
|---|---|---|---|
|  |  |  |  |
| 134 x2-y2 | 135 xz | 136 yz | 137 pi |
|  |  |  |  |
| 138 | 139 | 140 | 141 |

| **TS3** 7,7 | | | |
|---|---|---|---|
| 134 | 1.9651 | -0.643789 | -17.5184 |
| 135 | 1.7412 | -0.457675 | -12.4540 |
| 136 | 1.6932 | -0.415344 | -11.3021 |
| 137 | 1.0119 | -0.250042 | -6.8040 |
| 138 | 0.3338 | -0.032428 | -0.8824 |
| 139 | 0.2259 | 0.067269 | 1.8305 |
| 140 | 0.0288 | 0.232446 | 6.3252 |

| | | | |
|---|---|---|---|
| 0.66297 [ | 0]: | 2221000 | Beta = 41% |
| 0.06173 [ | 5]: | 2211100 | |
| 0.04462 [ | 31]: | 2121100 | |
| 0.04259 [ | 44]: | 2111110 | |
| 0.03199 [ | 18]: | 2201110 | |
| 0.02961 [ | 17]: | 2201200 | |
| 0.01742 [ | 81]: | 2021020 | |
| 0.01165 [ | 64]: | 2101120 | |
| 0.00808 [ | 99]: | 2011120 | |
| 0.00720 [ | 32]: | 2121010 | |
| 0.00704 [ | 43]: | 2111200 | |
| 0.00547 [ | 117]: | 2001220 | |
| 0.00476 [ | 97]: | 2011210 | |
| 0.00381 [ | 275]: | 0221002 | |
| 0.00332 [ | 46]: | 2111020 | |
| 0.00315 [ | 173]: | 1122001 | |
| 0.00308 [ | 6]: | 2211010 | |
| 0.00304 [ | 138]: | 1212001 | |
| Total Energy Correction: dE = -6.40126555995175 | | | |
| Reference Energy: E0 = -3161.73332778288022 | | | |
| Total Energy (E0+dE): E = -3168.13459334283198 | | | |

| | | | |
|---|---|---|---|
|  |  |  |  |
| 134 | 135 | 136 | 137 |
|  |  |  | |
| 138 | 139 | 140 | |

**Supplementary Table 14**. Cartesian Coordinates (Å) of the stationary points of the

model reaction.

| I’ | | | | I | | | |
|---|---|---|---|---|---|---|---|
| Fe | 0.44798300 | 0.02897500 | -0.65649200 | Fe | 0.52024900 | 0.03504500 | -0.56125400 |
| C | -1.58432400 | -2.01856000 | -1.73373500 | C | -1.42310800 | -1.99352800 | -1.77541900 |
| C | -2.91753200 | -2.11229400 | -2.29725700 | C | -2.65562600 | -2.07686800 | -2.53221000 |
| C | -3.37964500 | -0.82594700 | -2.44901800 | C | -3.09393200 | -0.78805200 | -2.73391600 |
| C | -2.32953600 | 0.05760000 | -1.97730800 | C | -2.13041000 | 0.09067100 | -2.10205400 |
| H | -3.41253800 | -3.04056400 | -2.54978200 | H | -3.10448600 | -3.00180400 | -2.86843000 |
| H | -4.32551000 | -0.49354700 | -2.85607600 | H | -3.96857400 | -0.45065300 | -3.27377700 |
| C | -0.77230600 | -3.11520100 | -1.45786000 | C | -0.65813800 | -3.09413700 | -1.40096500 |
| H | -1.17506900 | -4.10510100 | -1.64833700 | H | -1.02211700 | -4.07955600 | -1.67174800 |
| C | 0.52221600 | -3.02538700 | -0.95901600 | C | 0.54073000 | -3.01439700 | -0.70115500 |
| C | 1.36359400 | -4.17378000 | -0.67306000 | C | 1.31961100 | -4.16764300 | -0.29131700 |
| C | 2.54665300 | -3.68645300 | -0.17863600 | C | 2.41080700 | -3.69214500 | 0.39235800 |
| H | 1.06911500 | -5.20300800 | -0.82898000 | H | 1.04818400 | -5.19335900 | -0.50137900 |
| C | 2.43465300 | -2.23831900 | -0.16871900 | C | 2.31047200 | -2.24507800 | 0.39421900 |
| H | 3.41952600 | -4.23577600 | 0.14804900 | H | 3.21639300 | -4.24947700 | 0.85081900 |
| C | 3.45837000 | -1.38464600 | 0.22880700 | C | 3.26297100 | -1.40067800 | 0.95483900 |
| H | 4.37998800 | -1.83313300 | 0.58741300 | H | 4.11671500 | -1.85518300 | 1.44681300 |
| C | 3.40044100 | 0.00393100 | 0.15051700 | C | 3.21883700 | -0.01184800 | 0.87922800 |
| C | 4.51473600 | 0.88313600 | 0.45865200 | C | 4.26728600 | 0.86432300 | 1.36585500 |
| C | 4.09195200 | 2.16612100 | 0.20906700 | C | 3.89101300 | 2.14996400 | 1.05694100 |
| H | 5.48395900 | 0.54728800 | 0.80287200 | H | 5.16898100 | 0.52483400 | 1.85752000 |
| C | 2.71440300 | 2.07477300 | -0.24293600 | C | 2.60393400 | 2.06721700 | 0.39173700 |
| H | 4.64534600 | 3.09055600 | 0.30871000 | H | 4.42261200 | 3.07273700 | 1.24730600 |
| C | 1.92621300 | 3.17210100 | -0.57792700 | C | 1.88021800 | 3.17035200 | -0.05376400 |
| H | 2.37414200 | 4.15884400 | -0.50817200 | H | 2.32032400 | 4.15307200 | 0.08083700 |
| C | 0.60365400 | 3.08756700 | -1.00822400 | C | 0.63112400 | 3.09600900 | -0.66608300 |
| C | -0.20718500 | 4.23413000 | -1.37638700 | C | -0.11841000 | 4.24804100 | -1.12902100 |
| C | -1.43427500 | 3.74894100 | -1.75982800 | C | -1.27973300 | 3.77349000 | -1.69183000 |
| H | 0.13446300 | 5.26049600 | -1.35203600 | H | 0.21836200 | 5.27226900 | -1.04037300 |
| C | -1.37508400 | 2.30393700 | -1.63258600 | C | -1.24244000 | 2.32797500 | -1.58417200 |
| H | -2.29664500 | 4.29930100 | -2.11219200 | H | -2.08128000 | 4.33211100 | -2.15617400 |
| C | -2.41032400 | 1.44758600 | -1.99863600 | C | -2.21032400 | 1.48060700 | -2.11715100 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -3.32776400 | 1.89511900 | -2.36965100 | H | -3.05823500 | 1.93451200 | -2.62009800 |
| N | 2.29733100 | 0.74226900 | -0.28068400 | N | 2.20397200 | 0.73823600 | 0.29338700 |
| N | -0.12139000 | 1.90255100 | -1.16060100 | N | -0.07664000 | 1.92669700 | -0.93502700 |
| N | -1.22932600 | -0.68218100 | -1.53023800 | N | -1.12066300 | -0.66095600 | -1.50295700 |
| N | 1.18935200 | -1.83784300 | -0.65414600 | N | 1.16051900 | -1.84477500 | -0.27662500 |
| C | -0.09004200 | 0.03707900 | 1.05998900 | C | -0.35614100 | 0.01520500 | 1.17631300 |
| C | 0.18467800 | 1.14503900 | 1.95845500 | Cl | 1.63894400 | 0.04487300 | -2.62859100 |
| H | 0.54951900 | 2.04691300 | 1.47592100 | C | -0.20318200 | 1.09556000 | 2.09824400 |
| C | 0.08330800 | 1.20067000 | 3.32874800 | H | 0.25039100 | 1.99800000 | 1.70229400 |
| H | 0.36544100 | 2.15776200 | 3.77195300 | C | -0.52679200 | 1.14259000 | 3.44828600 |
| C | -0.75580000 | -1.18249200 | 1.64119100 | H | -0.31408600 | 2.09564600 | 3.93547600 |
| C | -0.30821200 | 0.12475000 | 4.31360200 | C | -1.10705900 | -1.20815500 | 1.61326500 |
| H | 0.39604000 | -0.71706900 | 4.28288000 | C | -1.06757600 | 0.05715900 | 4.34431900 |
| H | -0.32262500 | 0.52597600 | 5.33184900 | H | -0.38041600 | -0.79847100 | 4.39110600 |
| H | -1.29974000 | -0.29357400 | 4.10134200 | H | -1.21543000 | 0.43778200 | 5.35954600 |
| O | -2.15211600 | -1.23170700 | 1.70024700 | H | -2.02767900 | -0.33820100 | 3.98916200 |
| O | -0.13010600 | -2.16106500 | 2.06845200 | O | -2.49603200 | -1.23520900 | 1.47670100 |
| C | -2.99480400 | -0.08179600 | 1.29634300 | O | -0.55907800 | -2.20468200 | 2.10130400 |
| H | -2.39347800 | 0.67870300 | 0.78956700 | C | -3.27543900 | -0.06533600 | 1.00661000 |
| H | -3.71625900 | -0.48939600 | 0.58221500 | H | -2.61100500 | 0.70990400 | 0.61410900 |
| C | -3.68440600 | 0.49067700 | 2.45820600 | H | -3.89488900 | -0.44372000 | 0.18858100 |
| C | -4.28228900 | 0.97805400 | 3.40525100 | C | -4.11300800 | 0.46802400 | 2.08655200 |
| H | -4.80409300 | 1.39815600 | 4.23514700 | C | -4.83227700 | 0.92579200 | 2.96111200 |
| | | | | H | -5.46214900 | 1.31959900 | 3.72662800 |

| **TS1'** | | | | **TS1** | | | |
|---|---|---|---|---|---|---|---|
| Fe | -0.04581600 | 0.11912500 | -0.59105000 | Fe | -0.09839500 | 0.15189300 | -0.58482900 |
| C | -2.70873300 | -1.41699900 | -0.88127100 | C | -2.14525900 | -2.11903600 | -0.70853400 |
| C | -4.14609200 | -1.21883000 | -0.85893100 | C | -3.57281400 | -2.37919100 | -0.66358700 |
| C | -4.36110900 | 0.13276200 | -0.71948100 | C | -4.19440100 | -1.16729400 | -0.46365600 |
| C | -3.05489600 | 0.76357000 | -0.65637800 | C | -3.14787600 | -0.16618800 | -0.37621500 |
| H | -4.87681000 | -2.01043700 | -0.95981200 | H | -4.02382500 | -3.35311400 | -0.80017000 |
| H | -5.30286600 | 0.66451900 | -0.68367500 | H | -5.25370100 | -0.95617300 | -0.40143900 |
| C | -2.09481000 | -2.65565600 | -1.04611000 | C | -1.18192600 | -3.09383200 | -0.96779700 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -2.73254300 | -3.53036400 | -1.13102500 | H | -1.52401900 | -4.11606900 | -1.09666100 |
| C | -0.71995100 | -2.84393000 | -1.13984500 | C | 0.17923500 | -2.84659900 | -1.12473000 |
| C | -0.08993000 | -4.13176500 | -1.36644400 | C | 1.15625900 | -3.86528600 | -1.47179200 |
| C | 1.26302400 | -3.90657100 | -1.42380000 | C | 2.36999800 | -3.23342700 | -1.57611700 |
| H | -0.62374800 | -5.06746300 | -1.46597500 | H | 0.92533600 | -4.91236000 | -1.61505500 |
| C | 1.46146700 | -2.48095200 | -1.23546900 | C | 2.13902700 | -1.82859300 | -1.29007000 |
| H | 2.06012900 | -4.62141400 | -1.57863000 | H | 3.33380300 | -3.65879600 | -1.82114400 |
| C | 2.70591400 | -1.86121600 | -1.27268600 | C | 3.13300600 | -0.85368000 | -1.31809000 |
| H | 3.57981900 | -2.49148400 | -1.40723100 | H | 4.14433500 | -1.16976800 | -1.55412600 |
| C | 2.90555000 | -0.48579000 | -1.19466200 | C | 2.91282000 | 0.50233100 | -1.09324900 |
| C | 4.19884200 | 0.15637900 | -1.35097600 | C | 3.94032200 | 1.52526000 | -1.18719000 |
| C | 3.98248800 | 1.51171900 | -1.27982300 | C | 3.32686000 | 2.73031400 | -0.94278000 |
| H | 5.13102700 | -0.37040200 | -1.50664400 | H | 4.97816400 | 1.33237900 | -1.42384500 |
| C | 2.55800000 | 1.69785600 | -1.07047200 | C | 1.92236600 | 2.44628000 | -0.69591700 |
| H | 4.70214400 | 2.31518700 | -1.36525200 | H | 3.76226100 | 3.72082000 | -0.94137400 |
| C | 1.94125500 | 2.94097000 | -0.93667500 | C | 0.96265700 | 3.42082800 | -0.41864200 |
| H | 2.56734900 | 3.82601700 | -1.00192700 | H | 1.29168600 | 4.45534200 | -0.39344200 |
| C | 0.57278900 | 3.12725400 | -0.75849400 | C | -0.39727800 | 3.17393300 | -0.22882200 |
| C | -0.07124900 | 4.42691800 | -0.70962100 | C | -1.39723300 | 4.21396300 | -0.06546300 |
| C | -1.42383500 | 4.19968800 | -0.61215400 | C | -2.62407600 | 3.59034800 | -0.03307200 |
| H | 0.45045600 | 5.37297900 | -0.77018300 | H | -1.17955400 | 5.27299000 | -0.02238800 |
| C | -1.61072800 | 2.75955000 | -0.59685500 | C | -2.37860600 | 2.16617100 | -0.16423300 |
| H | -2.22759500 | 4.92370500 | -0.57959700 | H | -3.60539800 | 4.04019600 | 0.04134400 |
| C | -2.85701500 | 2.13882700 | -0.57069900 | C | -3.37966400 | 1.19885600 | -0.21222800 |
| H | -3.73711500 | 2.77409300 | -0.52852500 | H | -4.41089800 | 1.53327700 | -0.15210100 |
| N | 1.90204300 | 0.46648600 | -1.01831200 | N | 1.68795700 | 1.07987700 | -0.78067400 |
| N | -0.37855000 | 2.10093400 | -0.66519100 | N | -1.00825600 | 1.91987100 | -0.24526700 |
| N | -2.04008900 | -0.19564700 | -0.73789300 | N | -1.89738500 | -0.76493900 | -0.50204500 |
| N | 0.23968600 | -1.83156800 | -1.05507500 | N | 0.79781300 | -1.60768100 | -1.00665300 |
| C | 0.23741400 | -0.00559200 | 1.35885400 | C | 0.38798600 | -0.12737900 | 1.49411600 |
| C | 1.36180800 | 0.83258600 | 1.88625700 | Cl | -0.42567100 | 0.47051300 | -2.87467800 |
| H | 1.55787000 | 1.73339600 | 1.31429000 | C | 1.21548400 | 0.91455200 | 2.11736200 |
| C | 2.12928800 | 0.64778800 | 2.99138200 | H | 1.09339900 | 1.90203200 | 1.68452100 |
| H | 2.91348300 | 1.39217300 | 3.14716200 | C | 2.09406100 | 0.83276400 | 3.16450500 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.24427900 | -1.46402400 | 1.79473800 | H | 2.62139400 | 1.76285600 | 3.38968200 |
| C | 2.06700700 | -0.43295300 | 4.04647400 | C | 0.68596400 | -1.55486000 | 1.89635600 |
| H | 2.69949600 | -1.28761900 | 3.77021300 | C | 2.46671400 | -0.32545100 | 4.05412600 |
| H | 2.42638500 | -0.04083800 | 5.00633000 | H | 3.28596900 | -0.90531200 | 3.60615500 |
| H | 1.05565100 | -0.82609500 | 4.19757400 | H | 2.81035900 | 0.04744800 | 5.02632600 |
| O | -1.01734000 | -1.91925600 | 2.21256100 | H | 1.64543700 | -1.02866800 | 4.22242100 |
| O | 1.20417700 | -2.23620400 | 1.77287800 | O | -0.38367700 | -2.27571000 | 2.42512400 |
| C | -1.96979600 | -0.83092700 | 2.38850700 | O | 1.77697000 | -2.11120400 | 1.73413500 |
| H | -2.80226600 | -0.97869800 | 1.69845900 | C | -1.61727800 | -1.51437400 | 2.63505400 |
| H | -2.32479600 | -0.85769400 | 3.42216800 | H | -2.36492200 | -1.88421300 | 1.92934500 |
| C | -1.25330700 | 0.48457900 | 2.11027800 | H | -1.94051000 | -1.71455500 | 3.66067900 |
| C | -1.49967800 | 1.69472000 | 2.40907400 | C | -1.39491900 | -0.05086900 | 2.43981100 |
| H | -1.48916800 | 2.76569400 | 2.41304200 | C | -1.79660400 | 1.11431300 | 2.63064900 |
| | | | | H | -1.99084100 | 2.16603100 | 2.62598300 |

| **II'** | | | | **II** | | | |
|---|---|---|---|---|---|---|---|
| C | -3.01041000 | -0.63965600 | -0.60735200 | C | 3.31933600 | 0.23217600 | 0.00629200 |
| C | -4.15734400 | 0.33019700 | -0.56651000 | C | 4.27436000 | -0.91903800 | 0.00812700 |
| O | -5.35149600 | 0.16870500 | -0.83807300 | O | 5.51158900 | -0.95206700 | 0.01191800 |
| O | -3.64957700 | 1.58126100 | -0.18237400 | O | 3.53183000 | -2.10843500 | 0.00462900 |
| C | -3.10983500 | -2.03267200 | -1.03343600 | C | 3.62126300 | 1.64320000 | 0.00793900 |
| H | -2.21212000 | -2.41551500 | -1.51894800 | H | 2.72346500 | 2.26128100 | 0.00623000 |
| C | -4.14146800 | -2.91434500 | -0.90096700 | C | 4.78725900 | 2.37543800 | 0.01081600 |
| H | -3.97127900 | -3.90054200 | -1.34005600 | H | 4.62688300 | 3.45744000 | 0.01113900 |
| C | -2.19096200 | 1.49493200 | 0.00390900 | C | 2.09055400 | -1.81798800 | -0.00004200 |
| H | -1.72111300 | 2.19699200 | -0.68995000 | H | 1.65950200 | -2.27255400 | -0.89487200 |
| H | -1.96046500 | 1.79160200 | 1.03018500 | H | 1.65271300 | -2.27631500 | 0.88954800 |
| C | -1.84288200 | 0.05046100 | -0.28753600 | C | 1.98793000 | -0.30379300 | 0.00266800 |
| C | -0.52302800 | -0.51132500 | -0.21928800 | C | 0.80947000 | 0.43364000 | 0.00298200 |
| H | -0.50124400 | -1.58829300 | -0.43458600 | H | 0.89211100 | 1.52000500 | 0.00571400 |
| C | 1.23500600 | -1.50944400 | 2.70091700 | C | -1.15362600 | 1.24158600 | 2.79336300 |
| C | 1.59011300 | -2.82920100 | 3.19434300 | C | -1.35263700 | 2.51050500 | 3.46811800 |
| C | 2.13597300 | -3.51668000 | 2.13758800 | C | -1.59413200 | 3.44961000 | 2.49293300 |
| C | 2.09895900 | -2.62589200 | 0.99004200 | C | -1.52491700 | 2.76394600 | 1.21572000 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 1.44964300 | -3.16145600 | 4.21437900 | H | -1.32491200 | 2.64468600 | 4.54104100 |
| H | 2.52779500 | -4.52506300 | 2.11958400 | H | -1.79942600 | 4.50520400 | 2.61032800 |
| C | 0.70993500 | -0.49277800 | 3.49440700 | C | -0.93660300 | 0.02895300 | 3.44345900 |
| H | 0.51149900 | -0.71689500 | 4.53831500 | H | -0.87958200 | 0.03686200 | 4.52711000 |
| C | 0.50322300 | 0.81466700 | 3.06086200 | C | -0.86771800 | -1.20181300 | 2.79802300 |
| C | 0.14445400 | 1.91411400 | 3.93862300 | C | -0.82021800 | -2.47601600 | 3.48752700 |
| C | 0.15462600 | 3.05656100 | 3.17420100 | C | -0.88710900 | -3.45771200 | 2.52669700 |
| H | -0.05856600 | 1.81399300 | 4.99660100 | H | -0.76985600 | -2.58825800 | 4.56212800 |
| C | 0.49357300 | 2.65642300 | 1.82076800 | C | -0.94712000 | -2.79145500 | 1.24095400 |
| H | -0.04481500 | 4.07463600 | 3.48139400 | H | -0.89426700 | -4.53116700 | 2.65963400 |
| C | 0.56598000 | 3.53022800 | 0.73928300 | C | -0.98106700 | -3.45067500 | 0.01581000 |
| H | 0.38939600 | 4.58522100 | 0.92499500 | H | -1.01046700 | -4.53505700 | 0.02106900 |
| C | 0.81825000 | 3.13182900 | -0.57079600 | C | -0.93962900 | -2.80357800 | -1.21550600 |
| C | 0.81826200 | 4.02802700 | -1.71259400 | C | -0.87130900 | -3.48251400 | -2.49409300 |
| C | 1.06309200 | 3.25877300 | -2.82511600 | C | -0.79649900 | -2.51043200 | -3.46414400 |
| H | 0.65225400 | 5.09559400 | -1.65477500 | H | -0.87850800 | -4.55722300 | -2.61646300 |
| C | 1.24018800 | 1.89328900 | -2.36466800 | C | -0.84780100 | -1.22944500 | -2.78774300 |
| H | 1.14328600 | 3.57401100 | -3.85697700 | H | -0.73854900 | -2.63340900 | -4.53718600 |
| C | 1.61659900 | 0.83595800 | -3.18953600 | C | -0.91048800 | -0.00505800 | -3.44590800 |
| H | 1.70399700 | 1.03144400 | -4.25419700 | H | -0.84515800 | -0.00799900 | -4.52911400 |
| C | 1.97108700 | -0.43027700 | -2.73100200 | C | -1.13138800 | 1.21410300 | -2.80956000 |
| C | 2.50716600 | -1.48421800 | -3.57542800 | C | -1.32418800 | 2.47650200 | -3.49826300 |
| C | 2.79793900 | -2.54556800 | -2.75270400 | C | -1.57304000 | 3.42517500 | -2.53429400 |
| H | 2.65063600 | -1.40102300 | -4.64459600 | H | -1.28773600 | 2.60018100 | -4.57218600 |
| C | 2.42330600 | -2.15050400 | -1.40541800 | C | -1.51463100 | 2.75196900 | -1.24989700 |
| H | 3.22341700 | -3.50512600 | -3.01526200 | H | -1.77681700 | 4.47966500 | -2.66364000 |
| C | 2.51721000 | -2.98003400 | -0.29040400 | C | -1.66156800 | 3.39102300 | -0.02077800 |
| H | 2.92317500 | -3.97708500 | -0.43323500 | H | -1.87223400 | 4.45569300 | -0.02683200 |
| N | 1.07244900 | 1.81750600 | -0.97854800 | N | -0.91190200 | -1.42231900 | -1.40698400 |
| N | 1.92621000 | -0.84655200 | -1.39885100 | N | -1.25036200 | 1.39882500 | -1.43750200 |
| N | 1.55437600 | -1.39148300 | 1.34676100 | N | -1.26170800 | 1.41281800 | 1.41867100 |
| N | 0.70070100 | 1.27401400 | 1.75510500 | N | -0.92172300 | -1.40842900 | 1.41887400 |
| Fe | 1.08516900 | 0.14927800 | 0.13769300 | Cl | -3.41998500 | -0.24839000 | -0.00910300 |
| C | -5.46616200 | -2.76593900 | -0.19887600 | Fe | -1.08045500 | -0.01099900 | -0.00180600 |

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|---|---|---|---|---|---|---|---|
| H | -5.52559400 | -1.87670700 | 0.42858600 | C | 6.23885600 | 1.98213800 | 0.01288500 |
| H | -6.28149800 | -2.69422600 | -0.93304400 | H | 6.39395500 | 0.90535300 | 0.01567900 |
| H | -5.65745600 | -3.65846900 | 0.41401600 | H | 6.73702400 | 2.41732500 | -0.86785100 |
| | | | | H | 6.73588500 | 2.42196200 | 0.89191300 |

| **TS2'** | | | | **TS2** | | | |
|---|---|---|---|---|---|---|---|
| C | -2.41761500 | -0.76159300 | -1.83566700 | C | -2.74531800 | -0.79301100 | -1.72400500 |
| C | -3.74180100 | -0.12369000 | -2.02246400 | C | -4.06910900 | -0.13126900 | -1.82306200 |
| O | -4.84837200 | -0.63501800 | -2.21487900 | O | -5.19265200 | -0.62806400 | -1.93081100 |
| O | -3.55091600 | 1.27877700 | -1.95461600 | O | -3.84902500 | 1.26612200 | -1.78004100 |
| C | -2.19714000 | -2.20812800 | -1.84683000 | C | -2.56950100 | -2.24637200 | -1.72711000 |
| H | -3.05146800 | -2.85320200 | -1.65925900 | H | -3.43163200 | -2.85501200 | -1.46687700 |
| C | -0.95669700 | -2.72128500 | -2.05472300 | C | -1.37088500 | -2.81689600 | -2.01131700 |
| H | -0.77159800 | -3.79022900 | -1.98155600 | H | -1.22631800 | -3.89106600 | -1.92872400 |
| C | -2.13070900 | 1.56132800 | -1.68410700 | C | -2.41004700 | 1.52664900 | -1.61486400 |
| H | -1.74188500 | 2.18110000 | -2.50180500 | H | -2.06790000 | 2.12822300 | -2.46616000 |
| H | -2.06182200 | 2.11591400 | -0.74591200 | H | -2.26414600 | 2.09065300 | -0.69174300 |
| C | -1.46903000 | 0.20043500 | -1.61895400 | C | -1.76696300 | 0.15389600 | -1.58353500 |
| C | -0.03101600 | 0.02749800 | -1.32590500 | C | -0.31563200 | -0.04065000 | -1.39831500 |
| H | 0.65590600 | 0.57402500 | -1.97379200 | H | 0.32206000 | 0.46717500 | -2.12534900 |
| C | 3.39168500 | -1.06454000 | -0.31395500 | C | 3.13625800 | -1.34695600 | -0.72205400 |
| C | 4.65384300 | -0.72125400 | -0.94942300 | C | 4.33539100 | -1.12680800 | -1.51119600 |
| C | 4.62080800 | 0.63040500 | -1.19774800 | C | 4.33160200 | 0.19720100 | -1.88432600 |
| C | 3.34305100 | 1.11963400 | -0.70533900 | C | 3.13807500 | 0.79628300 | -1.31127700 |
| H | 5.44853700 | -1.42488800 | -1.16009500 | H | 5.07354900 | -1.88609600 | -1.73288500 |
| H | 5.38438500 | 1.25020400 | -1.64919900 | H | 5.06858500 | 0.73361600 | -2.46720800 |
| C | 3.03933700 | -2.35159300 | 0.09576200 | C | 2.76515300 | -2.57531200 | -0.17150100 |
| H | 3.76498100 | -3.14525000 | -0.05858500 | H | 3.43659500 | -3.41687200 | -0.31215400 |
| C | 1.83224600 | -2.69023800 | 0.70762300 | C | 1.59554700 | -2.78957400 | 0.55811700 |
| C | 1.48070500 | -4.02976600 | 1.14601300 | C | 1.19182700 | -4.06917800 | 1.11322500 |
| C | 0.21650600 | -3.95666300 | 1.68283800 | C | -0.01952300 | -3.87137300 | 1.73491300 |
| H | 2.12662500 | -4.89387800 | 1.06125800 | H | 1.77089900 | -4.98036500 | 1.04205700 |
| C | -0.20833200 | -2.57189100 | 1.58252400 | C | -0.35431700 | -2.46703900 | 1.57539700 |
| H | -0.37336300 | -4.74989800 | 2.12306100 | H | -0.62389400 | -4.58939300 | 2.27324700 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.42442800 | -2.08654100 | 2.06116000 | C | -1.48135100 | -1.86133700 | 2.13240700 |
| H | -2.11271800 | -2.80155500 | 2.50264500 | H | -2.17040200 | -2.49547300 | 2.68210400 |
| C | -1.79319200 | -0.74256400 | 2.07468800 | C | -1.74606700 | -0.49208500 | 2.11265300 |
| C | -3.00505700 | -0.23586400 | 2.70032900 | C | -2.84043600 | 0.13326700 | 2.83785200 |
| C | -2.96600600 | 1.13249700 | 2.59508200 | C | -2.70989300 | 1.49050600 | 2.66822500 |
| H | -3.76214400 | -0.85328600 | 3.16533100 | H | -3.58495600 | -0.40447100 | 3.40951900 |
| C | -1.73697100 | 1.46677800 | 1.89206100 | C | -1.54839500 | 1.70011500 | 1.82122000 |
| H | -3.68665000 | 1.85599400 | 2.95240100 | H | -3.32943600 | 2.28178500 | 3.06826000 |
| C | -1.32865500 | 2.76742200 | 1.59933200 | C | -1.09352200 | 2.95011000 | 1.40148100 |
| H | -1.97019300 | 3.58164600 | 1.92363200 | H | -1.62297400 | 3.82787000 | 1.75867900 |
| C | -0.15267400 | 3.09932100 | 0.92461800 | C | -0.00734700 | 3.14620200 | 0.54838800 |
| C | 0.25797700 | 4.45827300 | 0.61150000 | C | 0.44347200 | 4.44076400 | 0.06771000 |
| C | 1.45033400 | 4.36959700 | -0.06674300 | C | 1.52140300 | 4.20964600 | -0.75417200 |
| H | -0.29652700 | 5.34637100 | 0.88478000 | H | -0.00726900 | 5.38676400 | 0.33648500 |
| C | 1.78126100 | 2.95671700 | -0.15727900 | C | 1.74780700 | 2.77336200 | -0.76403100 |
| H | 2.06528400 | 5.17161800 | -0.45344000 | H | 2.12923400 | 4.93078300 | -1.28435800 |
| C | 2.95444800 | 2.45972100 | -0.72393300 | C | 2.81637300 | 2.15156200 | -1.41121300 |
| H | 3.64136700 | 3.17581600 | -1.16623000 | H | 3.48838800 | 2.78275600 | -1.98506700 |
| N | -1.02851100 | 0.30782000 | 1.56454600 | N | -0.97921000 | 0.47726700 | 1.47588100 |
| N | 0.78675000 | 2.18269300 | 0.44697400 | N | 0.78958300 | 2.13519400 | 0.01850000 |
| N | 2.59191500 | 0.07171000 | -0.16934600 | N | 2.40957100 | -0.16425600 | -0.61566100 |
| N | 0.78671400 | -1.79809600 | 0.97822900 | N | 0.63222600 | -1.82136700 | 0.83823200 |
| Fe | 0.70335700 | 0.17193600 | 0.54217700 | Cl | 1.96218200 | 0.52404600 | 2.37038600 |
| C | 0.20489400 | -1.83348700 | -2.35829300 | Fe | 0.72306500 | 0.16546800 | 0.44931000 |
| H | 0.34073000 | -1.06984300 | -1.12132400 | C | -0.18909400 | -1.99350800 | -2.40405600 |
| H | 1.20002600 | -2.25686100 | -2.19857500 | H | 0.02057100 | -1.18782000 | -1.32043500 |
| H | 0.14282400 | -1.28628100 | -3.29979500 | H | 0.79463000 | -2.45523500 | -2.28185600 |
| | | | | H | -0.27718900 | -1.46028600 | -3.35135400 |

| **IV** + Por | | | | **IV** + Por | | | |
|---|---|---|---|---|---|---|---|
| C | -3.01677300 | -1.07928500 | -1.92106100 | C | -4.28780600 | -0.92050100 | -0.98187800 |
| C | -4.41108800 | -0.58649200 | -1.78827200 | C | -5.32793400 | 0.04800700 | -0.55886700 |
| O | -5.48523900 | -1.15956400 | -1.98451500 | O | -6.53590600 | -0.10441700 | -0.36140200 |
| O | -4.33592300 | 0.76417400 | -1.35792000 | O | -4.68307500 | 1.30340500 | -0.38560100 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.58192400 | -2.41965300 | -2.31363300 | C | -4.45618100 | -2.34965700 | -1.25106400 |
| H | -3.32102000 | -3.21037600 | -2.40382200 | H | -5.40406300 | -2.82451800 | -1.01480400 |
| C | -1.26237100 | -2.61989600 | -2.56341800 | C | -3.41654600 | -3.02836300 | -1.80027900 |
| H | -0.89916000 | -3.59786800 | -2.87338800 | H | -3.50960900 | -4.08745100 | -2.03369400 |
| C | -2.91723000 | 1.14738700 | -1.18873100 | C | -3.24056800 | 1.15421800 | -0.67328900 |
| H | -2.71958200 | 2.01144500 | -1.83500300 | H | -2.98130600 | 1.84804100 | -1.48262200 |
| H | -2.76247100 | 1.43942100 | -0.14379000 | H | -2.68039200 | 1.43234100 | 0.22715500 |
| C | -2.14886900 | -0.08870700 | -1.58355000 | C | -3.08182300 | -0.29699800 | -1.05332900 |
| C | -0.66204300 | -0.32155400 | -1.55133000 | C | -1.81491300 | -1.04942000 | -1.36393300 |
| H | -0.10046700 | 0.58600200 | -1.79061800 | H | -1.08767000 | -0.41823300 | -1.89059500 |
| C | 3.24323500 | -1.31542400 | -0.66318100 | C | 2.08948300 | -2.72269700 | 0.47232700 |
| C | 4.31757400 | -1.17850600 | -1.63170000 | C | 2.86433700 | -3.71938500 | -0.23776900 |
| C | 4.28951300 | 0.12064500 | -2.08001500 | C | 3.34369700 | -3.11773500 | -1.37715200 |
| C | 3.20039800 | 0.78486700 | -1.38465500 | C | 2.85850800 | -1.75264700 | -1.37125000 |
| H | 4.99473600 | -1.97354800 | -1.91477900 | H | 3.01714300 | -4.73424200 | 0.10399500 |
| H | 4.93958800 | 0.59768000 | -2.80152700 | H | 3.96526100 | -3.54347400 | -2.15344500 |
| C | 2.94418400 | -2.49520800 | 0.01787600 | C | 1.45743600 | -2.94878200 | 1.69049400 |
| H | 3.55761500 | -3.36685300 | -0.19086400 | H | 1.54661900 | -3.93478700 | 2.13536300 |
| C | 1.92064100 | -2.63390500 | 0.95418400 | C | 0.73335000 | -1.98414000 | 2.38257500 |
| C | 1.62003500 | -3.86607600 | 1.66338700 | C | 0.09603500 | -2.21066400 | 3.66319700 |
| C | 0.55199400 | -3.60355200 | 2.48718800 | C | -0.49367500 | -1.02554300 | 4.03299800 |
| H | 2.16209200 | -4.79425800 | 1.53954900 | H | 0.10901600 | -3.15185700 | 4.19607500 |
| C | 0.19693500 | -2.20878600 | 2.28890200 | C | -0.22406400 | -0.07109800 | 2.97728400 |
| H | 0.04754600 | -4.27453700 | 3.16976300 | H | -1.06096800 | -0.80535400 | 4.92726700 |
| C | -0.83461600 | -1.55732800 | 2.96325800 | C | -0.67749400 | 1.24274400 | 2.98205600 |
| H | -1.41842700 | -2.13722500 | 3.67194000 | H | -1.24857600 | 1.57997900 | 3.84130200 |
| C | -1.15620800 | -0.20938200 | 2.81106900 | C | -0.46356800 | 2.14807800 | 1.94770700 |
| C | -2.19943900 | 0.47190700 | 3.55803700 | C | -0.97601200 | 3.50351000 | 1.93920900 |
| C | -2.19189100 | 1.78453000 | 3.15123100 | C | -0.57648700 | 4.07583200 | 0.75508700 |
| H | -2.83792400 | -0.00069500 | 4.29247600 | H | -1.56229200 | 3.94216200 | 2.73531200 |
| C | -1.14746600 | 1.91108100 | 2.14892200 | C | 0.18705000 | 3.07445400 | 0.03915500 |
| H | -2.82306700 | 2.59645000 | 3.48733500 | H | -0.76840600 | 5.07664800 | 0.39253800 |
| C | -0.83143500 | 3.09757600 | 1.48801900 | C | 0.78267400 | 3.28686300 | -1.19928300 |
| H | -1.40236700 | 3.98499400 | 1.74520300 | H | 0.66650400 | 4.26333600 | -1.65903300 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.17167600 | 3.22870900 | 0.52806800 | C | 1.53666500 | 2.33375200 | -1.87429900 |
| C | 0.49777000 | 4.47059600 | -0.15173800 | C | 2.18106800 | 2.56464200 | -3.15135200 |
| C | 1.53308200 | 4.19591000 | -1.01347700 | C | 2.84976800 | 1.40882000 | -3.47621500 |
| H | -0.00115000 | 5.41502800 | 0.02109700 | H | 2.12625600 | 3.49112200 | -3.70694400 |
| C | 1.84763400 | 2.78578200 | -0.86161900 | C | 2.61015000 | 0.46554400 | -2.40211300 |
| H | 2.04801000 | 4.87184800 | -1.68332400 | H | 3.45028300 | 1.20069800 | -4.35156900 |
| C | 2.86167200 | 2.12682700 | -1.55596600 | C | 3.11663300 | -0.83000600 | -2.37869700 |
| H | 3.44425300 | 2.70632200 | -2.26618900 | H | 3.74341100 | -1.14491700 | -3.20714000 |
| N | -0.51740800 | 0.68044600 | 1.94358200 | N | 0.24277400 | 1.88291600 | 0.77030500 |
| N | 1.00456100 | 2.19788100 | 0.08551800 | N | 1.79199400 | 1.03496300 | -1.42269900 |
| N | 2.56156300 | -0.10489800 | -0.51763700 | N | 2.08021300 | -1.51497800 | -0.23368300 |
| N | 1.04243000 | -1.62050700 | 1.34560700 | N | 0.52493900 | -0.66763700 | 1.95679500 |
| Fe | 0.97567300 | 0.26945000 | 0.66099700 | Cl | 3.24004400 | 1.01184900 | 1.41681300 |
| C | -0.25469100 | -1.47695700 | -2.50936700 | Fe | 1.36174400 | 0.25195000 | 0.38337400 |
| H | -0.41251100 | -0.63608900 | -0.50577500 | C | -2.12255600 | -2.32488700 | -2.20160100 |
| H | 0.73477700 | -1.85056000 | -2.22467200 | H | -1.33706400 | -1.33500000 | -0.41218400 |
| H | -0.14849100 | -1.07085100 | -3.53011700 | H | -1.27567300 | -3.01852900 | -2.13042400 |
| | | | | H | -2.20553100 | -2.05048500 | -3.26740300 |

| **TS3'** | | | | **TS3** | | | |
|---|---|---|---|---|---|---|---|
| C | 2.41583000 | -0.59108400 | 1.69216200 | C | -2.66715200 | -0.60817200 | -1.62627800 |
| C | 3.66925700 | 0.17083100 | 1.93921700 | C | -3.93689500 | 0.15578600 | -1.79256600 |
| O | 4.83748500 | -0.22585500 | 2.00272200 | O | -5.10195100 | -0.25059700 | -1.80310600 |
| O | 3.32757500 | 1.53396300 | 2.10929200 | O | -3.60789700 | 1.51991600 | -1.95033300 |
| C | 2.43928700 | -2.03831400 | 1.52308700 | C | -2.68588300 | -2.05804000 | -1.49141700 |
| H | 3.37987300 | -2.46558700 | 1.17969200 | H | -3.61543400 | -2.48923100 | -1.12421000 |
| C | 1.36769500 | -2.85381200 | 1.76742300 | C | -1.63333400 | -2.87299900 | -1.80304800 |
| H | 1.44024600 | -3.90656400 | 1.49618900 | H | -1.70729400 | -3.93430300 | -1.56878000 |
| C | 1.87265000 | 1.68677900 | 1.93783600 | C | -2.14712200 | 1.67996400 | -1.85348800 |
| H | 1.45808400 | 2.09108200 | 2.87038200 | H | -1.78544000 | 2.10527200 | -2.79813400 |
| H | 1.69951000 | 2.39786100 | 1.12623900 | H | -1.93647900 | 2.37431600 | -1.03768900 |
| C | 1.35448100 | 0.28917900 | 1.63446600 | C | -1.60829700 | 0.27763800 | -1.60841500 |
| C | -0.05226800 | 0.02371300 | 1.31572700 | C | -0.19183500 | -0.00219200 | -1.39939900 |
| H | -0.77470400 | 0.54084100 | 1.96238700 | H | 0.50238500 | 0.52648700 | -2.06024000 |

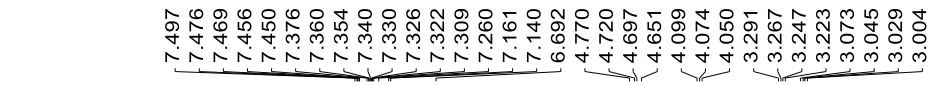
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.79405900 | -2.05290700 | -0.02963100 | C | 3.00558000 | -1.59608900 | -0.63201700 |
| C | -4.11426600 | -2.27467900 | 0.53256100 | C | 4.24166200 | -1.50429900 | -1.38390600 |
| C | -4.60007700 | -1.04564500 | 0.91009700 | C | 4.39568600 | -0.18589700 | -1.74555800 |
| C | -3.58135100 | -0.06859600 | 0.57238600 | C | 3.26219100 | 0.53829900 | -1.20392600 |
| H | -4.59260600 | -3.24177300 | 0.61384200 | H | 4.89522200 | -2.34053600 | -1.59291400 |
| H | -5.55474000 | -0.80738500 | 1.35982700 | H | 5.20219000 | 0.26906600 | -2.30478200 |
| C | -1.98009400 | -3.06282900 | -0.53762100 | C | 2.49863400 | -2.77622400 | -0.09228300 |
| H | -2.36148500 | -4.07929900 | -0.51156300 | H | 3.08006800 | -3.68354400 | -0.22120100 |
| C | -0.72129700 | -2.85831600 | -1.09522600 | C | 1.29695700 | -2.86670500 | 0.60331300 |
| C | 0.09626000 | -3.91415800 | -1.66243700 | C | 0.76440600 | -4.09956700 | 1.15056000 |
| C | 1.24843800 | -3.32487600 | -2.12424700 | C | -0.43808100 | -3.79110800 | 1.74160300 |
| H | -0.18939800 | -4.95696500 | -1.70213300 | H | 1.25939600 | -5.05959800 | 1.09074500 |
| C | 1.13778900 | -1.90667700 | -1.84550200 | C | -0.64339600 | -2.36685900 | 1.56840100 |
| H | 2.09358300 | -3.78961100 | -2.61417200 | H | -1.12211900 | -4.44906800 | 2.26046000 |
| C | 2.10481400 | -0.96727400 | -2.18874500 | C | -1.73882000 | -1.66930300 | 2.06629900 |
| H | 3.01274900 | -1.32361000 | -2.66539700 | H | -2.50443900 | -2.23194200 | 2.59028400 |
| C | 1.96678100 | 0.40350100 | -1.99492400 | C | -1.88725800 | -0.28755100 | 1.98786600 |
| C | 2.93863500 | 1.38879600 | -2.43119700 | C | -2.96635700 | 0.44873800 | 2.61606300 |
| C | 2.42421000 | 2.62280200 | -2.11700400 | C | -2.71131100 | 1.78465600 | 2.41680400 |
| H | 3.87691200 | 1.15347900 | -2.91512000 | H | -3.79048500 | -0.00721000 | 3.14770300 |
| C | 1.14038400 | 2.39512900 | -1.47826100 | C | -1.48406500 | 1.87317200 | 1.65087800 |
| H | 2.85875900 | 3.59785200 | -2.29197200 | H | -3.28851300 | 2.63712500 | 2.74812100 |
| C | 0.30669400 | 3.41080300 | -1.01892400 | C | -0.89729000 | 3.07204100 | 1.25569700 |
| H | 0.64351400 | 4.43568800 | -1.14246200 | H | -1.37935900 | 3.99551400 | 1.55956700 |
| C | -0.93754500 | 3.20476000 | -0.42615000 | C | 0.26307300 | 3.16372100 | 0.49009800 |
| C | -1.80389800 | 4.27304000 | 0.03614800 | C | 0.85312300 | 4.40981700 | 0.03834000 |
| C | -2.93430500 | 3.67990400 | 0.54651100 | C | 1.96066100 | 4.08230700 | -0.70807700 |
| H | -1.56830700 | 5.32680000 | -0.03173800 | H | 0.46366200 | 5.39164500 | 0.27136800 |
| C | -2.76562500 | 2.24775200 | 0.39088600 | C | 2.06341900 | 2.63463100 | -0.70246600 |
| H | -3.80739900 | 4.15247900 | 0.97636500 | H | 2.65943900 | 4.74406000 | -1.20194800 |
| C | -3.71453900 | 1.30270400 | 0.77226600 | C | 3.09568100 | 1.91825200 | -1.30399400 |
| H | -4.63029600 | 1.66145400 | 1.23246700 | H | 3.85017200 | 2.47889900 | -1.84658200 |
| N | 0.86593600 | 1.02629500 | -1.40094300 | N | -0.99822100 | 0.59345000 | 1.37804700 |
| N | -1.53527700 | 1.96066300 | -0.20864800 | N | 1.01004700 | 2.08654700 | 0.02389300 |

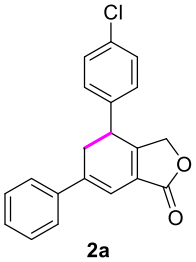
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N | -2.47336300 | -0.69506300 | -0.00449400 | N | 2.41332600 | -0.34093000 | -0.53457200 |
| N | -0.07663700 | -1.62276500 | -1.21428100 | N | 0.42198400 | -1.81270100 | 0.86355300 |
| Fe | -0.71155600 | 0.14035700 | -0.50596400 | Cl | 1.91696300 | 0.41982000 | 2.44275300 |
| C | 0.10249800 | -2.37134100 | 2.35215900 | Fe | 0.70543000 | 0.12280700 | 0.42723800 |
| H | -0.22730400 | -1.26571000 | 1.65153400 | C | -0.38110200 | -2.38628900 | -2.42164700 |
| H | -0.75400400 | -3.04546100 | 2.29290900 | H | -0.03321700 | -1.31037100 | -1.75158000 |
| H | 0.19410700 | -1.88871800 | 3.33185800 | H | 0.47482900 | -3.06219200 | -2.37741500 |
| | | | | H | -0.50257300 | -1.92977100 | -3.41129400 |

| **III**' + Por | | | | **III**+ Por | | | |
|---|---|---|---|---|---|---|---|
| C | -2.70785300 | 0.39197400 | 1.64758800 | C | 3.09644400 | 0.33852400 | -1.48049600 |
| C | -3.76573700 | -0.61593300 | 1.29130400 | C | 4.01405300 | -0.69921100 | -0.89494100 |
| O | -4.89287800 | -0.42384300 | 0.82359100 | O | 5.01312700 | -0.53991400 | -0.18572200 |
| O | -3.29259000 | -1.89767300 | 1.58440300 | O | 3.57454300 | -1.96842000 | -1.28091800 |
| C | -3.01184200 | 1.71126000 | 1.45559900 | C | 3.40013100 | 1.64909000 | -1.23440600 |
| H | -3.98406200 | 1.87307800 | 0.98273800 | H | 4.25355800 | 1.78250000 | -0.56457200 |
| C | -2.27384900 | 2.94008400 | 1.76364100 | C | 2.79362800 | 2.90026700 | -1.69861000 |
| H | -2.48348200 | 3.77126200 | 1.08789300 | H | 2.90958300 | 3.73726400 | -1.00750300 |
| C | -1.91111900 | -1.83399700 | 2.10823200 | C | 2.34716600 | -1.86604500 | -2.09932100 |
| H | -1.92732300 | -2.24769100 | 3.12222600 | H | 2.57561400 | -2.28722200 | -3.08422600 |
| H | -1.28388500 | -2.45343900 | 1.46280800 | H | 1.57349800 | -2.46237100 | -1.60929100 |
| C | -1.51413200 | -0.35687200 | 2.07967100 | C | 1.99959800 | -0.37706400 | -2.15755900 |
| C | -0.25137600 | 0.05508000 | 2.34330800 | C | 0.83402900 | 0.06997400 | -2.67825900 |
| H | 0.52873300 | -0.66579300 | 2.57814500 | H | 0.09393500 | -0.62927800 | -3.06188200 |
| C | 1.15389500 | 2.93052800 | -0.92832500 | C | -1.09640900 | 2.97128200 | 0.61646000 |
| C | 2.03474700 | 4.04664300 | -0.61978200 | C | -1.93171300 | 4.08836400 | 0.22256800 |
| C | 3.14119100 | 3.52281400 | 0.00175100 | C | -2.98504400 | 3.56760100 | -0.48995200 |
| C | 2.94498900 | 2.08284200 | 0.07221300 | C | -2.79578200 | 2.13071600 | -0.53422100 |
| H | 1.82170700 | 5.08071700 | -0.85696800 | H | -1.72961000 | 5.12199600 | 0.46960300 |
| H | 4.01420800 | 4.04233200 | 0.37437100 | H | -3.81707500 | 4.08992400 | -0.94301900 |
| C | -0.08064300 | 3.05921100 | -1.55949300 | C | 0.06839500 | 3.09600600 | 1.36512800 |
| H | -0.40157200 | 4.05724200 | -1.84347900 | H | 0.36753500 | 4.09111700 | 1.67944200 |
| C | -0.93574700 | 1.99616700 | -1.85164200 | C | 0.86866300 | 2.02422900 | 1.74377400 |
| C | -2.23227700 | 2.13931400 | -2.48379400 | C | 2.09071700 | 2.15499500 | 2.51265400 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.77143900 | 0.87649400 | -2.58642500 | C | 2.58996800 | 0.88725300 | 2.68852000 |
| H | -2.66220700 | 3.08012300 | -2.80170200 | H | 2.49660300 | 3.09388900 | 2.86490900 |
| C | -1.80241500 | -0.04280800 | -2.02580000 | C | 1.67219200 | -0.02213400 | 2.03160900 |
| H | -3.73008000 | 0.58477800 | -2.99395300 | H | 3.49127300 | 0.58019600 | 3.20124300 |
| C | -1.97675700 | -1.42539100 | -1.96365600 | C | 1.83973300 | -1.40220500 | 2.00151400 |
| H | -2.90804900 | -1.83320300 | -2.34439300 | H | 2.71231100 | -1.81757500 | 2.49484500 |
| C | -1.04019000 | -2.31877200 | -1.44991300 | C | 0.97350600 | -2.28198800 | 1.36233400 |
| C | -1.21918400 | -3.76146500 | -1.41635800 | C | 1.16573200 | -3.71649600 | 1.31266900 |
| C | -0.08697600 | -4.29197300 | -0.84838100 | C | 0.12221600 | -4.23665700 | 0.58383900 |
| H | -2.09793600 | -4.27823500 | -1.77805600 | H | 1.99541100 | -4.23788700 | 1.77013200 |
| C | 0.78825000 | -3.17543000 | -0.52530900 | C | -0.71079600 | -3.12124500 | 0.18266800 |
| H | 0.14755100 | -5.33111900 | -0.65896600 | H | -0.07611300 | -5.27058800 | 0.33522000 |
| C | 2.03457600 | -3.30610300 | 0.08310200 | C | -1.86867700 | -3.24427900 | -0.57802500 |
| H | 2.37841700 | -4.30869000 | 0.32011900 | H | -2.17575900 | -4.24066900 | -0.88015800 |
| C | 2.87276100 | -2.23970100 | 0.41086100 | C | -2.66249700 | -2.17084300 | -0.96785900 |
| C | 4.16380500 | -2.38194700 | 1.05245100 | C | -3.87150900 | -2.29928300 | -1.75520200 |
| C | 4.67635600 | -1.11307700 | 1.21086300 | C | -4.38022300 | -1.03237300 | -1.91809400 |
| H | 4.60923800 | -3.32642300 | 1.33607400 | H | -4.26778200 | -3.23705700 | -2.12101000 |
| C | 3.70205500 | -0.19151300 | 0.66296100 | C | -3.48363900 | -0.12484700 | -1.23140400 |
| H | 5.62179700 | -0.82060700 | 1.64846200 | H | -5.27496400 | -0.72796800 | -2.44451900 |
| C | 3.86506200 | 1.19396200 | 0.62213500 | C | -3.66471400 | 1.25273000 | -1.17342800 |
| H | 4.78128500 | 1.60578800 | 1.03502300 | H | -4.54071500 | 1.67016400 | -1.66010100 |
| N | 0.19462600 | -1.96615800 | -0.89779500 | N | -0.17869600 | -1.91787800 | 0.65807800 |
| N | 2.59323500 | -0.88959100 | 0.17503700 | N | -2.42092100 | -0.82860400 | -0.65709000 |
| N | 1.71982400 | 1.72816000 | -0.49821800 | N | -1.62637900 | 1.77002300 | 0.13912800 |
| N | -0.67690400 | 0.65189500 | -1.57293900 | N | 0.62108400 | 0.68325800 | 1.44064500 |
| Fe | 0.94442900 | -0.11638600 | -0.67478900 | Cl | -2.23267800 | -0.25474300 | 2.50720400 |
| C | -1.47145700 | 3.17815200 | 2.83093300 | Fe | -1.02126300 | -0.09947200 | 0.58362400 |
| H | 0.03833900 | 1.09843600 | 2.32983700 | C | 2.22174400 | 3.15051300 | -2.90318900 |
| H | -1.02926600 | 4.15906100 | 2.98629000 | H | 0.57388200 | 1.12073100 | -2.71389600 |
| H | -1.26846000 | 2.42315100 | 3.58511500 | H | 1.86762100 | 4.14750300 | -3.15335100 |
| | | | | H | 2.13110100 | 2.39009300 | -3.67339600 |

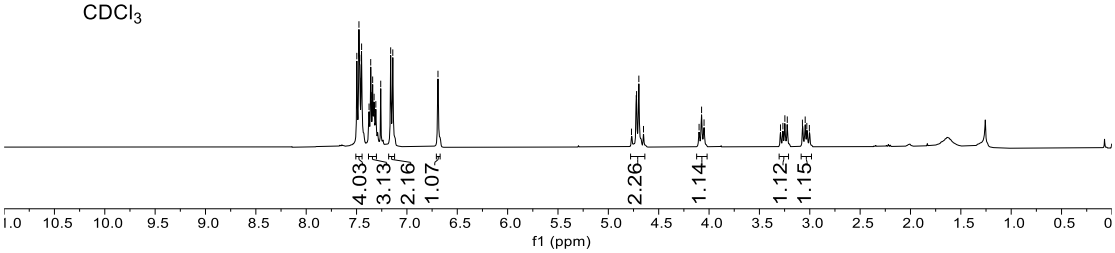
# NMR Spectra of New Compounds



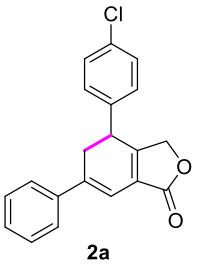




**2a**

$^{1}$H NMR, 400 MHz
$CDCl_3$

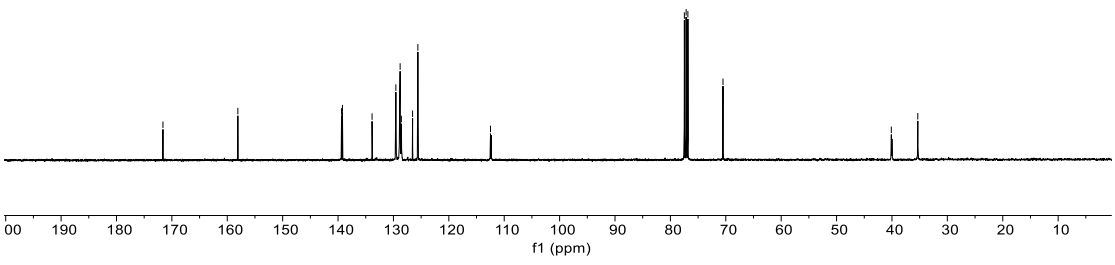


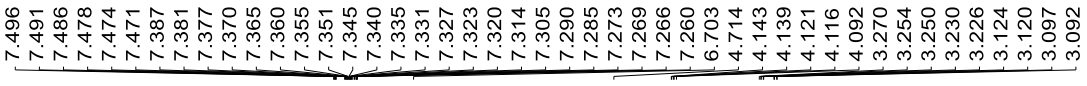


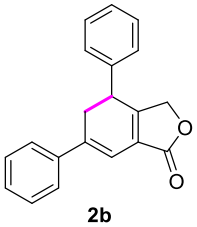



**2a**

$^{13}$C NMR, 100 MHz
$CDCl_3$

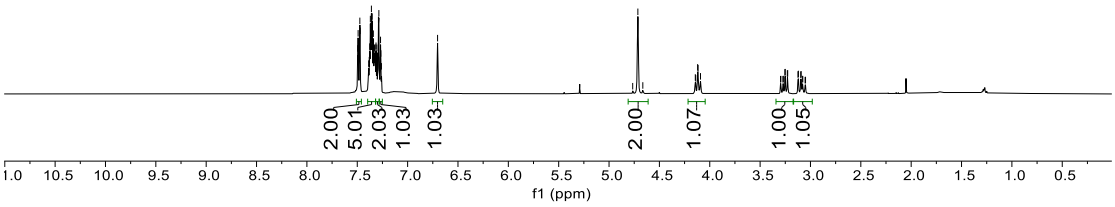


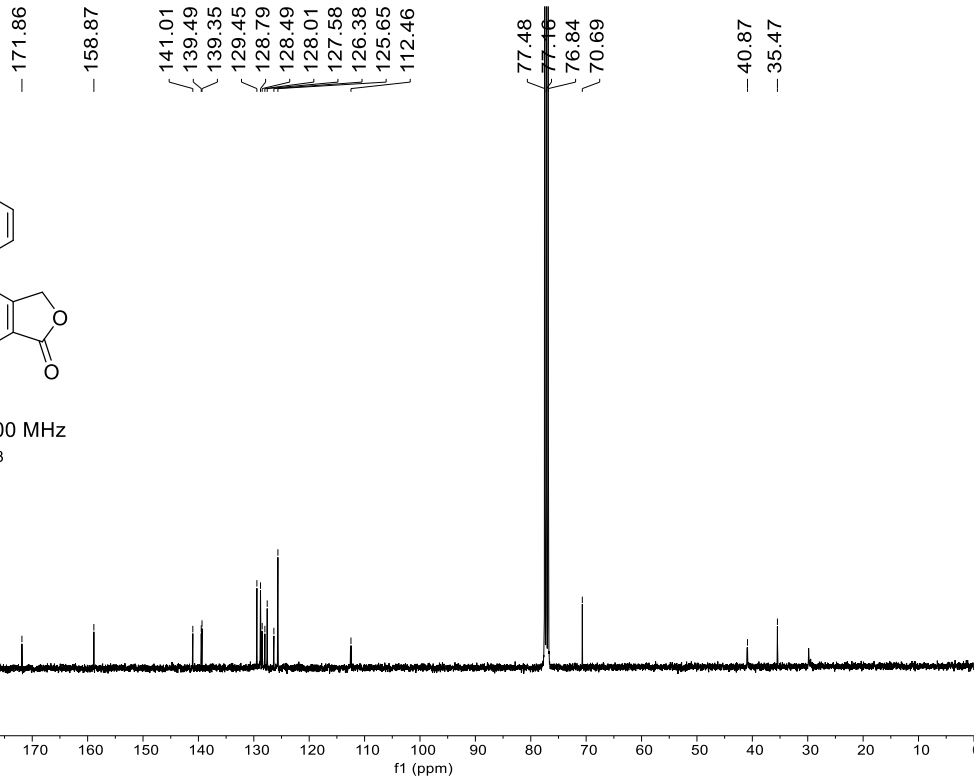


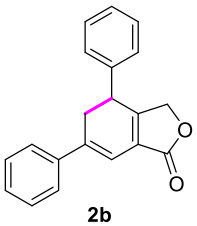



**2b**

$^{1}$H NMR, 400 MHz
$CDCl_3$

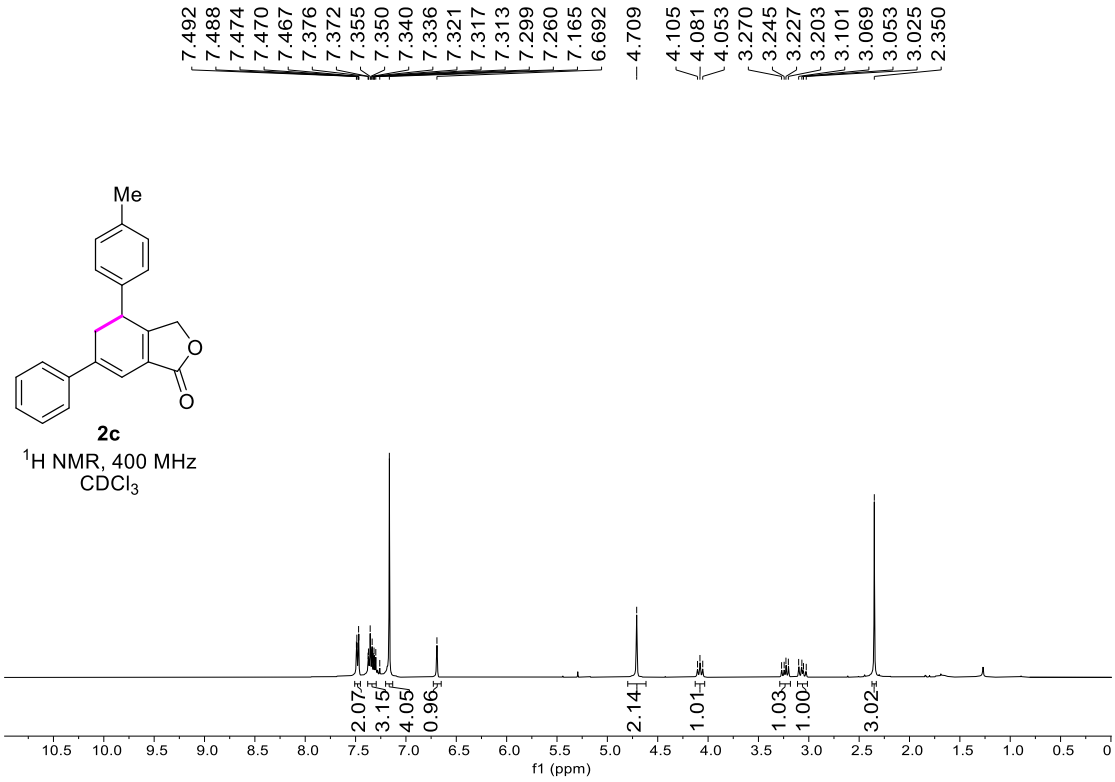


**2b**

$^{13}$C NMR, 100 MHz
$CDCl_3$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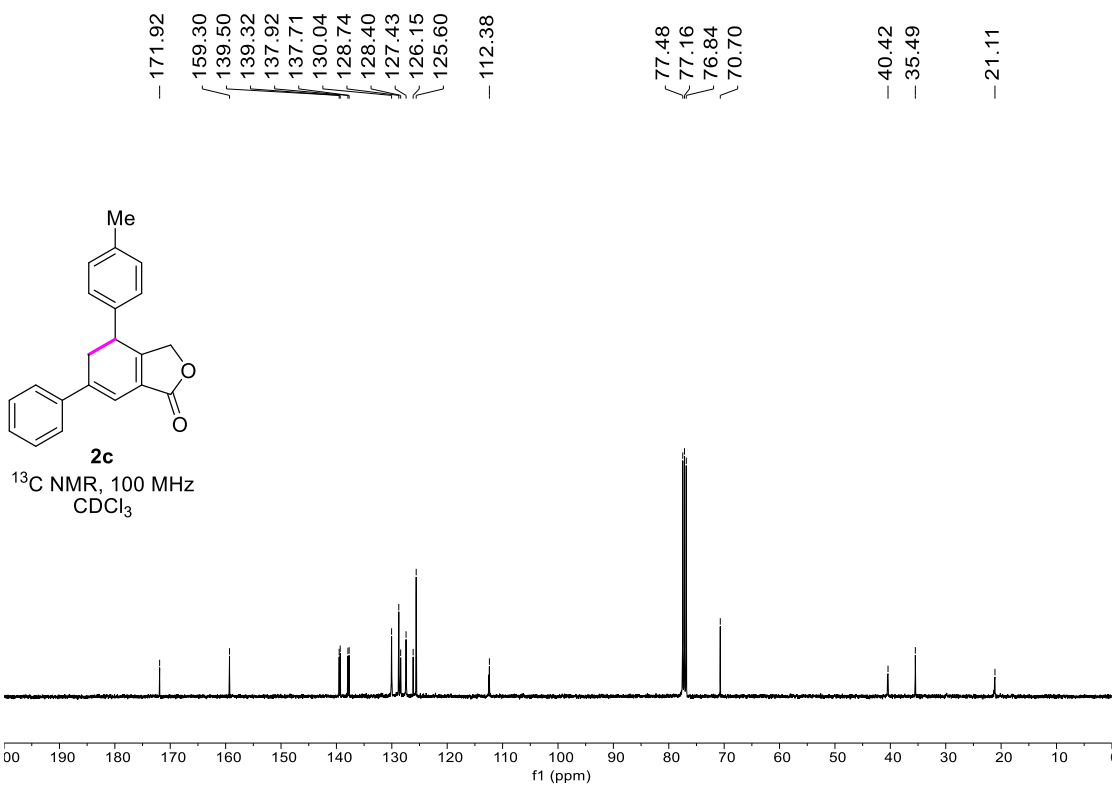
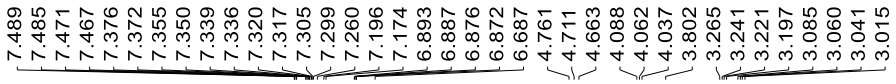
7.488
7.474
7.470
7.467
7.376
7.372
7.355
7.350
7.340
7.336
7.321
7.317
7.313
7.299
7.260
7.165
6.692
4.709
4.105
4.081
4.053
3.270
3.245
3.227
3.203
3.101
3.069
3.053
3.025
2.350
Me
O
O
2c
1H NMR, 400 MHz
CDCl3
2.07
3.15
4.05
0.96
2.14
1.01
1.03
1.00
3.02
f1 (ppm)


171.92
159.30
139.50
139.32
137.92
137.71
130.04
128.74
128.40
127.43
126.15
125.60
112.38
77.48
77.16
76.84
70.70
40.42
35.49
21.11
Me
O
O
2c
13C NMR, 100 MHz
CDCl3
f1 (ppm)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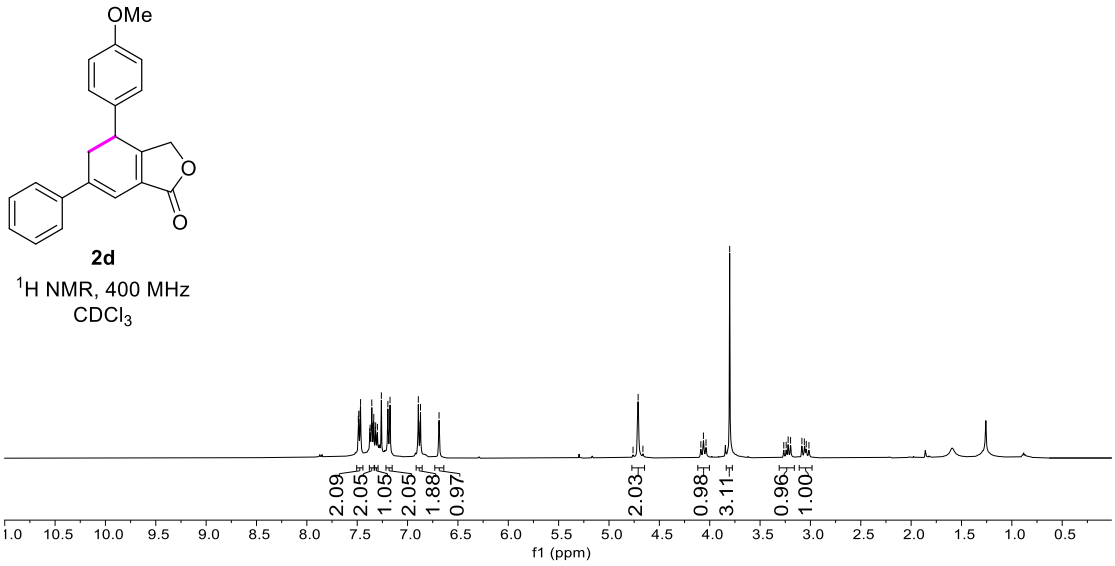
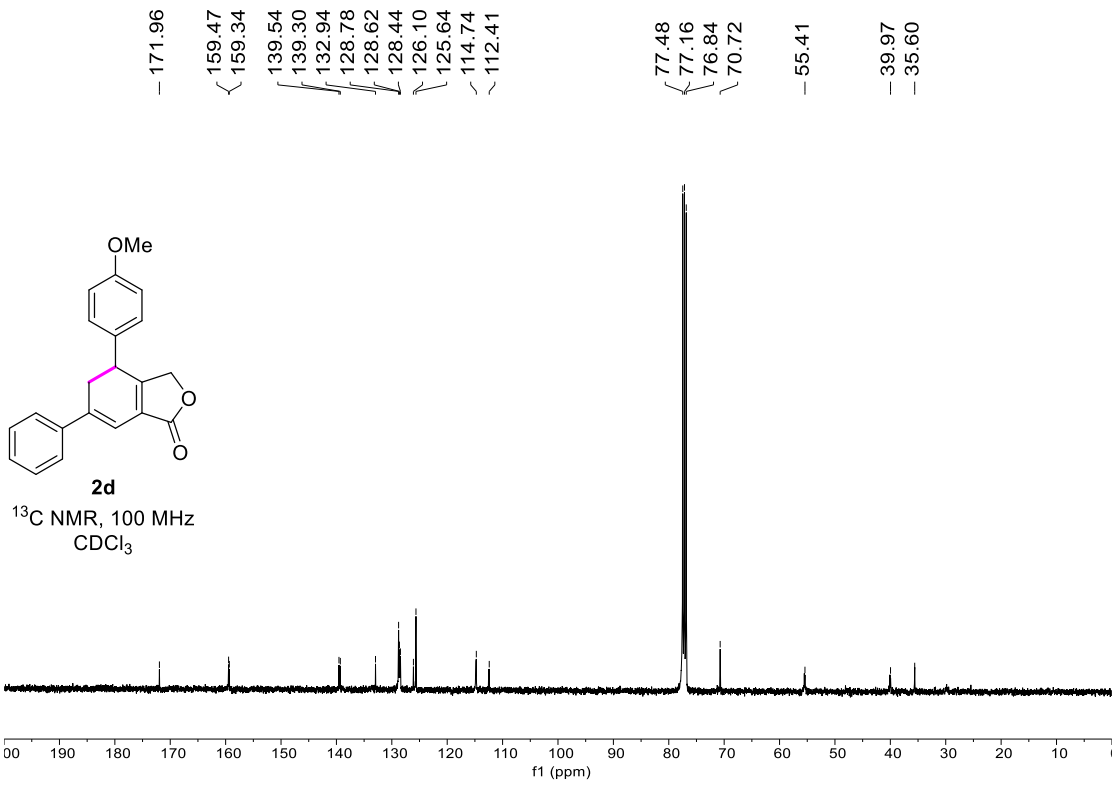
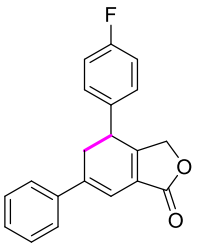
7.485
7.471
7.467
7.376
7.372
7.355
7.350
7.339
7.336
7.320
7.317
7.305
7.299
7.260
7.196
7.174
6.893
6.887
6.876
6.872
6.687
4.761
4.711
4.663
4.088
4.062
4.037
3.802
3.265
3.241
3.221
3.197
3.085
3.060
3.041
3.015

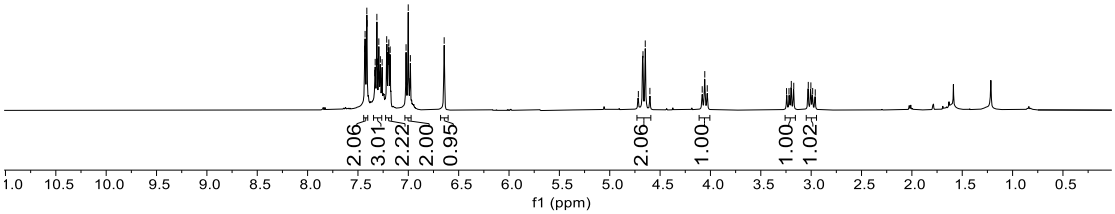

OMe
O
O
2d
1H NMR, 400 MHz
CDCl3
2.09
2.05
1.05
2.05
1.88
0.97
2.03
0.98
3.11
0.96
1.00
f1 (ppm)


171.96
159.47
159.34
139.54
139.30
132.94
128.78
128.62
128.44
126.10
125.64
114.74
112.41
77.48
77.16
76.84
70.72
55.41
39.97
35.60
OMe
O
O
2d
13C NMR, 100 MHz
CDCl3
f1 (ppm)

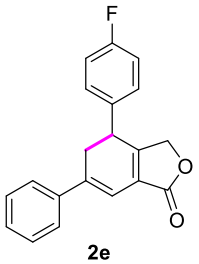




**2e**

$^{1}$H NMR, 400 MHz
$CDCl_3$

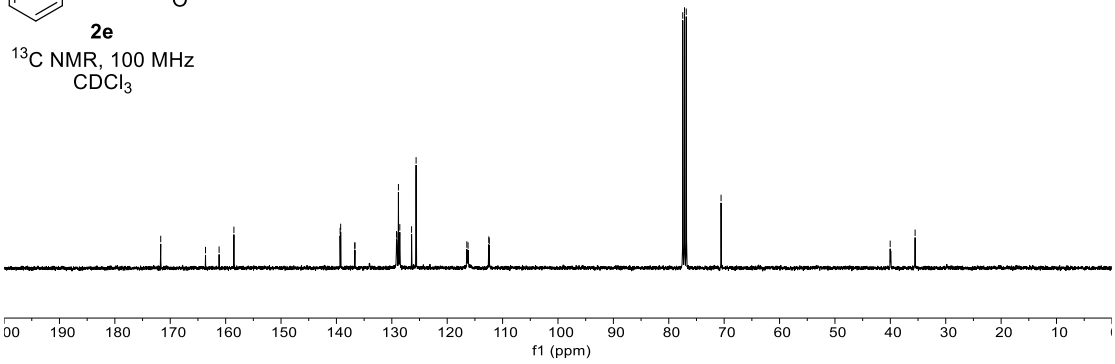


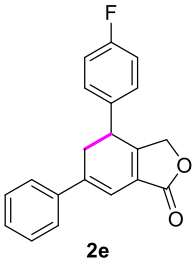





**2e**

$^{13}$C NMR, 100 MHz
$CDCl_3$



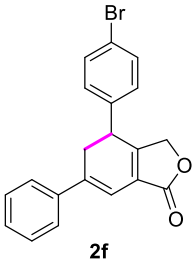



**2e**

$^{19}$F NMR, 376 MHz
$CDCl_3$

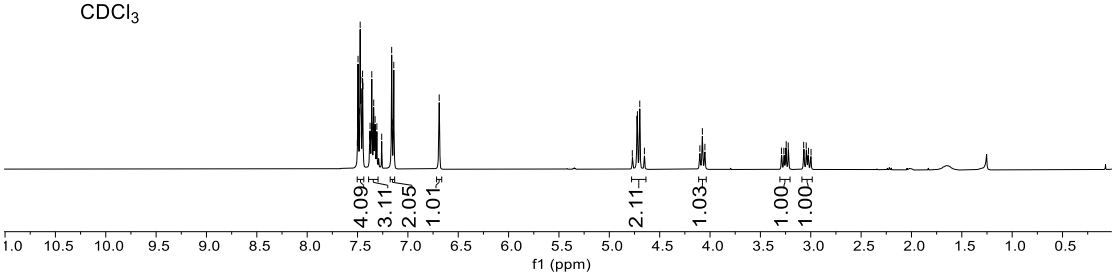


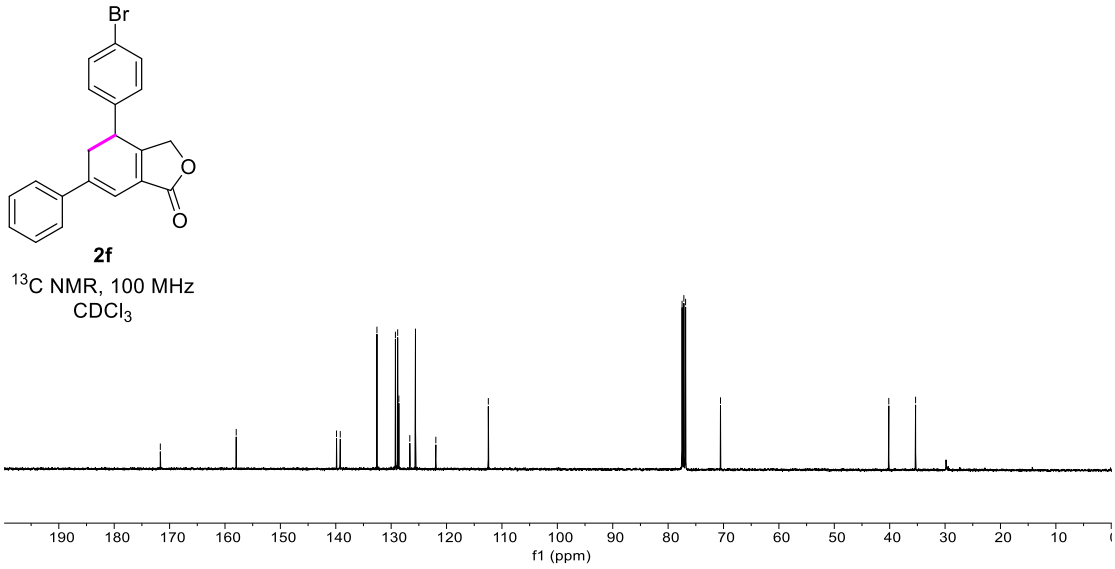





**2f**

$^{1}$H NMR, 400 MHz
$CDCl_3$

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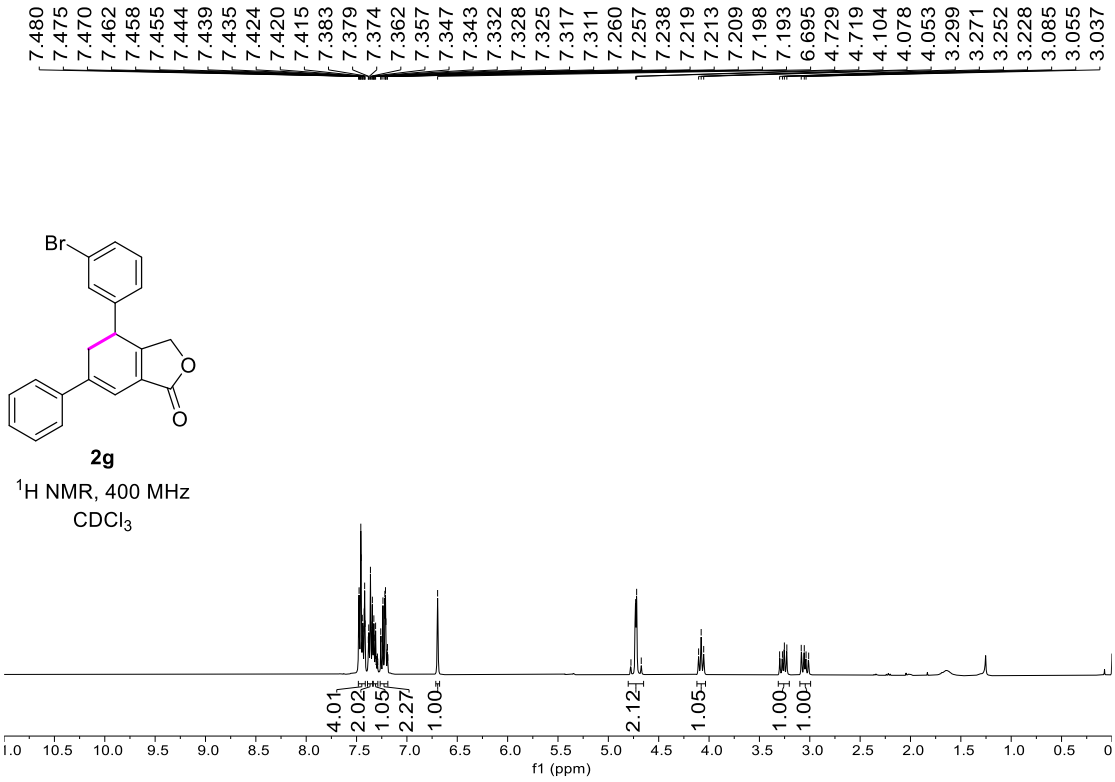
139.19
132.57
129.23
128.83
128.62
126.64
125.61
121.94
112.46
77.48
77.16
76.84
70.55
40.16
35.33
Br
O
O
2f
13C NMR, 100 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.455
7.444
7.439
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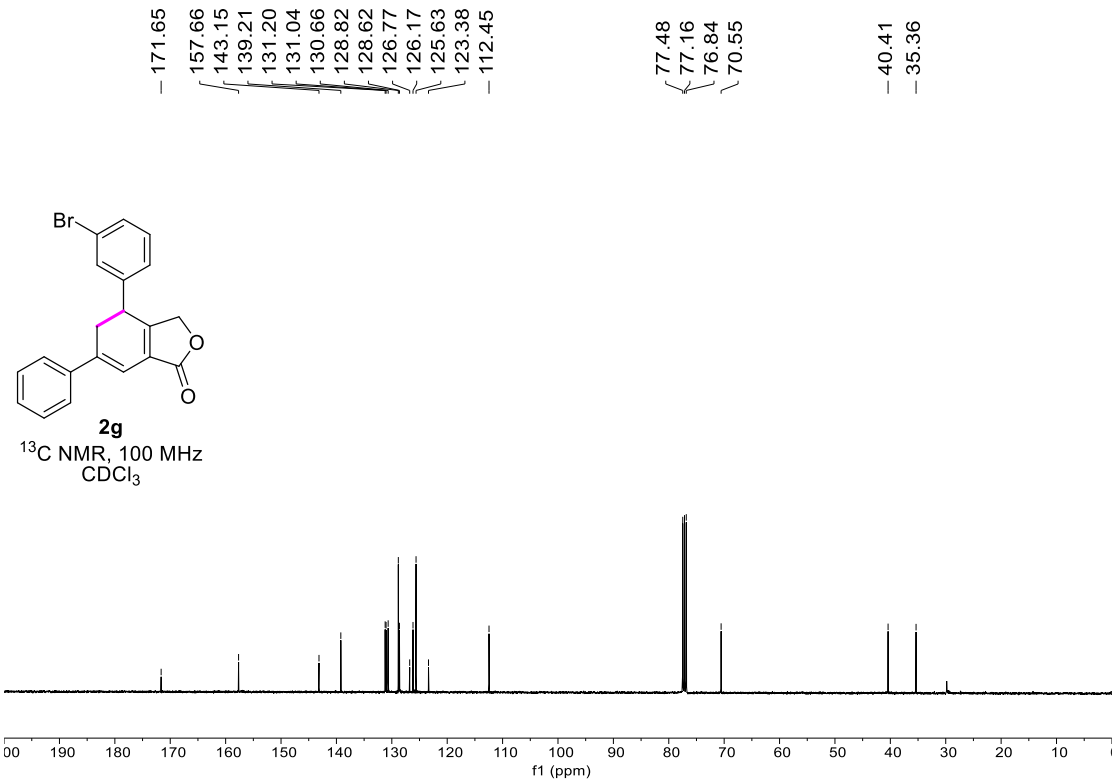
7.424
7.420
7.415
7.383
7.379
7.374
7.362
7.357
7.347
7.343
7.332
7.328
7.325
7.317
7.311
7.260
7.257
7.238
7.219
7.213
7.209
7.198
7.193
6.695
4.729
4.719
4.104
4.078
4.053
3.299
3.271
3.252
3.228
3.085
3.055
3.037
Br
O
O
2g
1H NMR, 400 MHz
CDCl3
4.01
2.02
1.05
2.27
1.00
2.12
1.05
1.00
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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157.66
143.15
139.21
131.20
131.04
130.66
128.82
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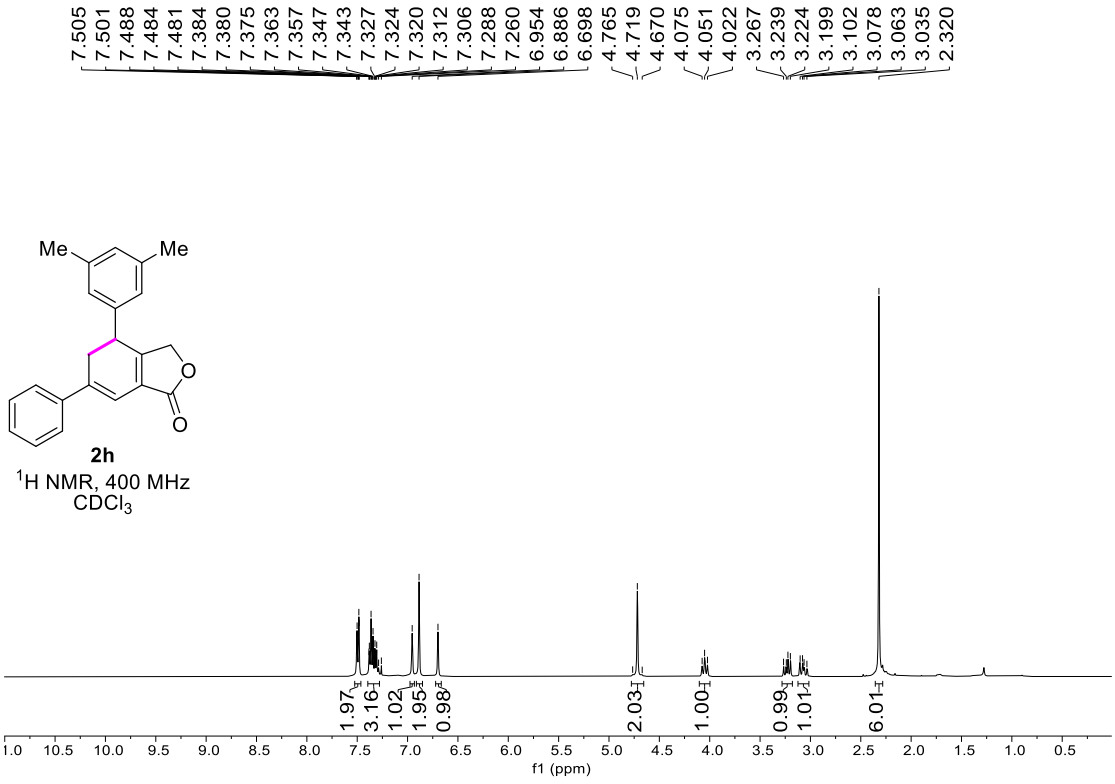
126.77
126.17
125.63
123.38
112.45
77.48
77.16
76.84
70.55
40.41
35.36
Br
O
O
2g
13C NMR, 100 MHz
CDCl3
f1 (ppm)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7.324
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4.075
4.051
4.022
3.267
3.239
3.224
3.199
3.102
3.078
3.063
3.035
2.320
Me
Me
O
O
2h
1H NMR, 400 MHz
CDCl3
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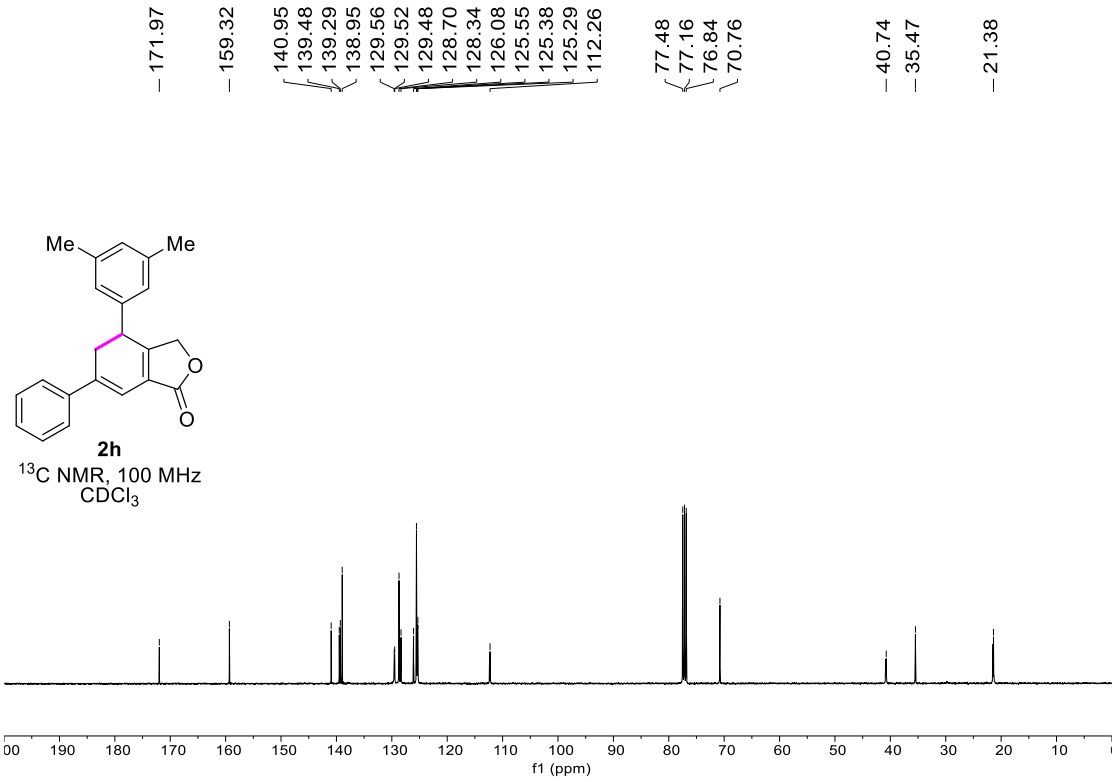
3.16
1.02
1.95
0.98
2.03
1.00
0.99
1.01
6.01
f1 (ppm)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159.32
140.95
139.48
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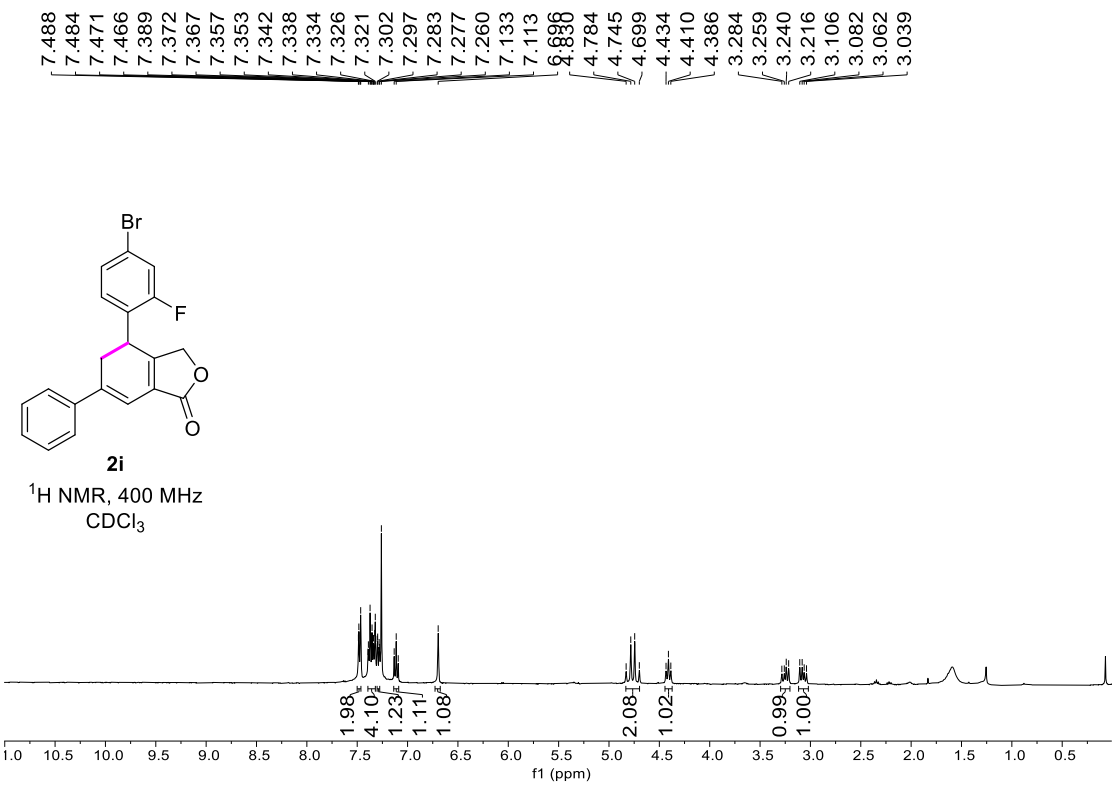
128.70
128.34
126.08
125.55
125.38
125.29
112.26
77.48
77.16
76.84
70.76
40.74
35.47
21.38
Me
Me
O
O
2h
13C NMR, 100 MHz
CDCl3
f1 (ppm)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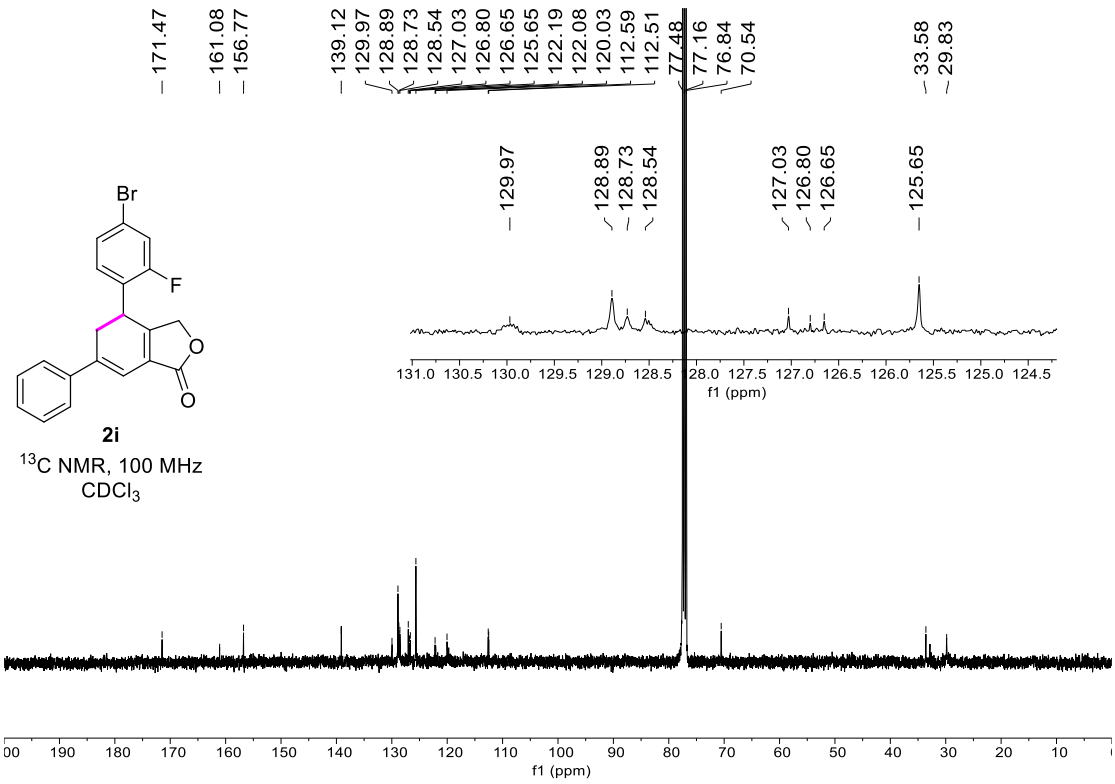
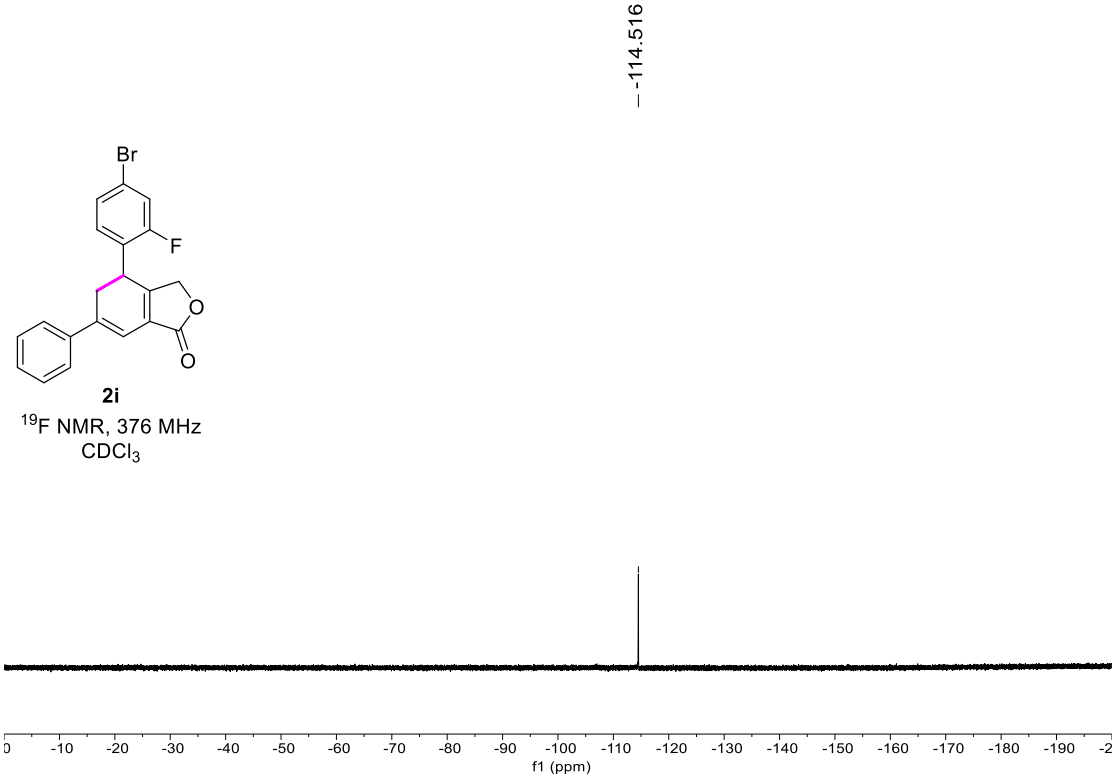
7.484
7.471
7.466
7.389
7.372
7.367
7.357
7.353
7.342
7.338
7.334
7.326
7.321
7.302
7.297
7.283
7.277
7.260
7.133
7.113
4.784
4.745
4.699
4.434
4.410
4.386
3.284
3.259
3.240
3.216
3.106
3.082
3.062
3.039
Br
F
O
O
2i
1H NMR, 400 MHz
CDCl3
1.98
4.10
1.23
1.11
1.08
2.08
1.02
0.99
1.00
f1 (ppm)




**2i**

$^{13}C$ NMR, 100 MHz

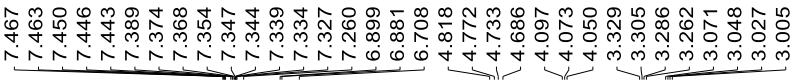
$CDCl_3$

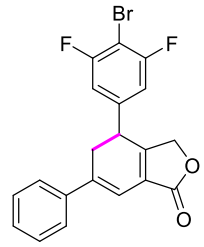



**2i**

$^{19}F$ NMR, 376 MHz

$CDCl_3$

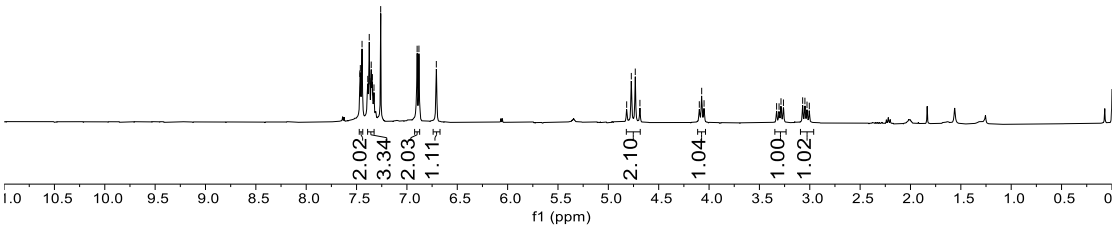


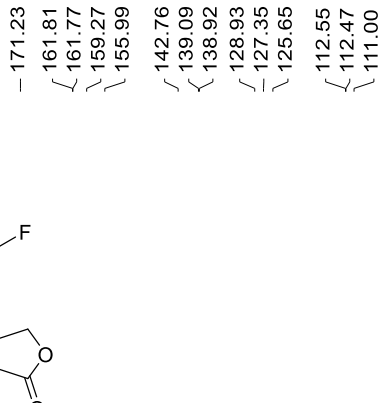



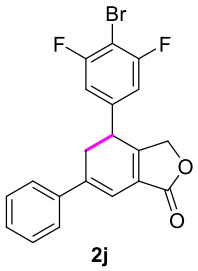

**2j**

$^{1}$H NMR, 400 MHz

$CDCl_3$



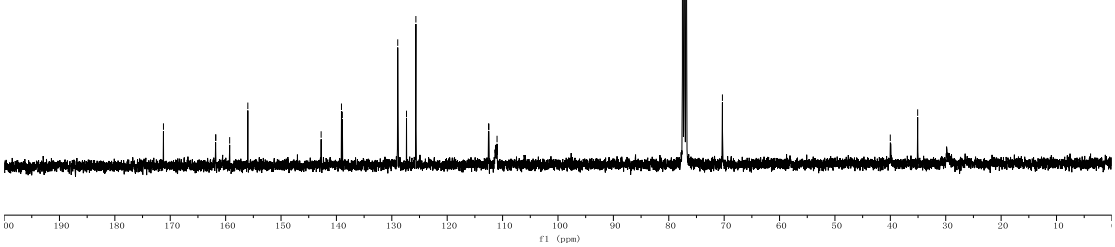



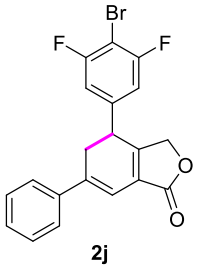




**2j**

$^{13}$C NMR, 100 MHz

$CDCl_3$





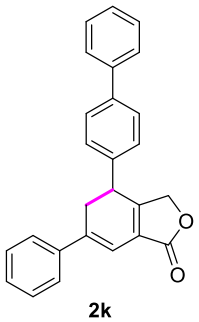

**2j**

$^{19}$F NMR, 376 MHz

$CDCl_3$



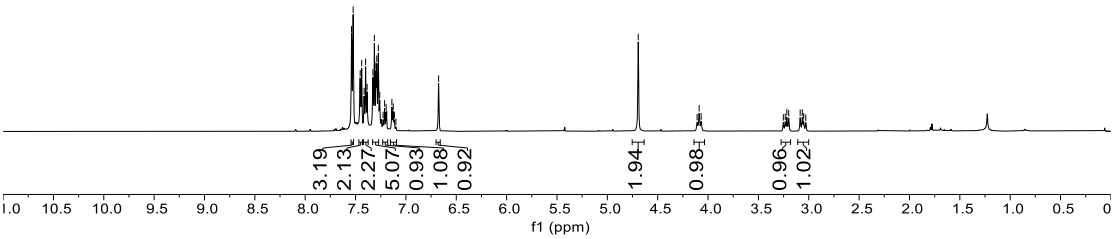


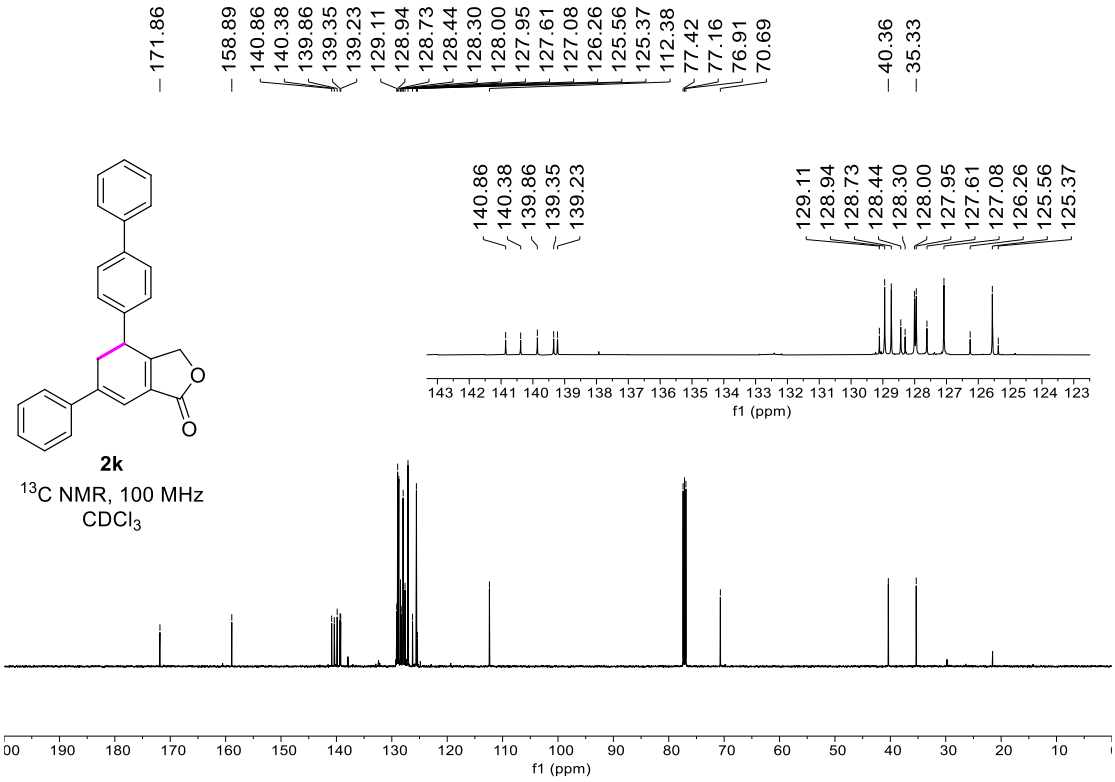


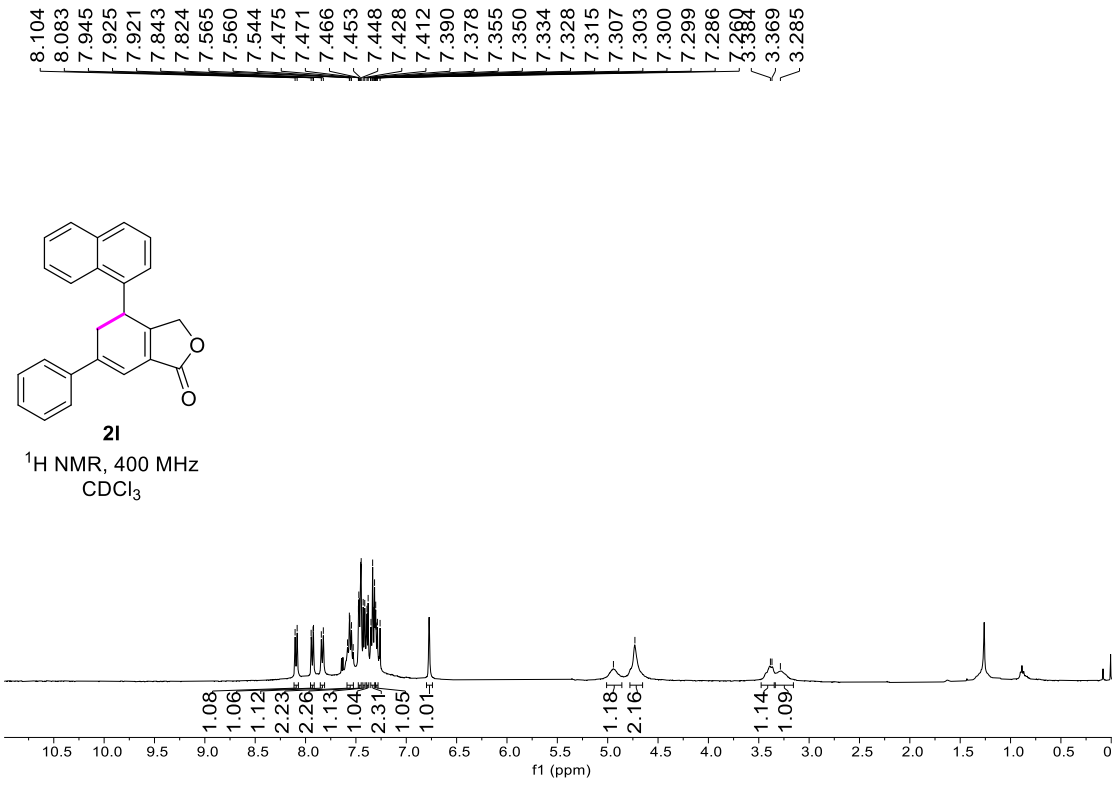

**2k**

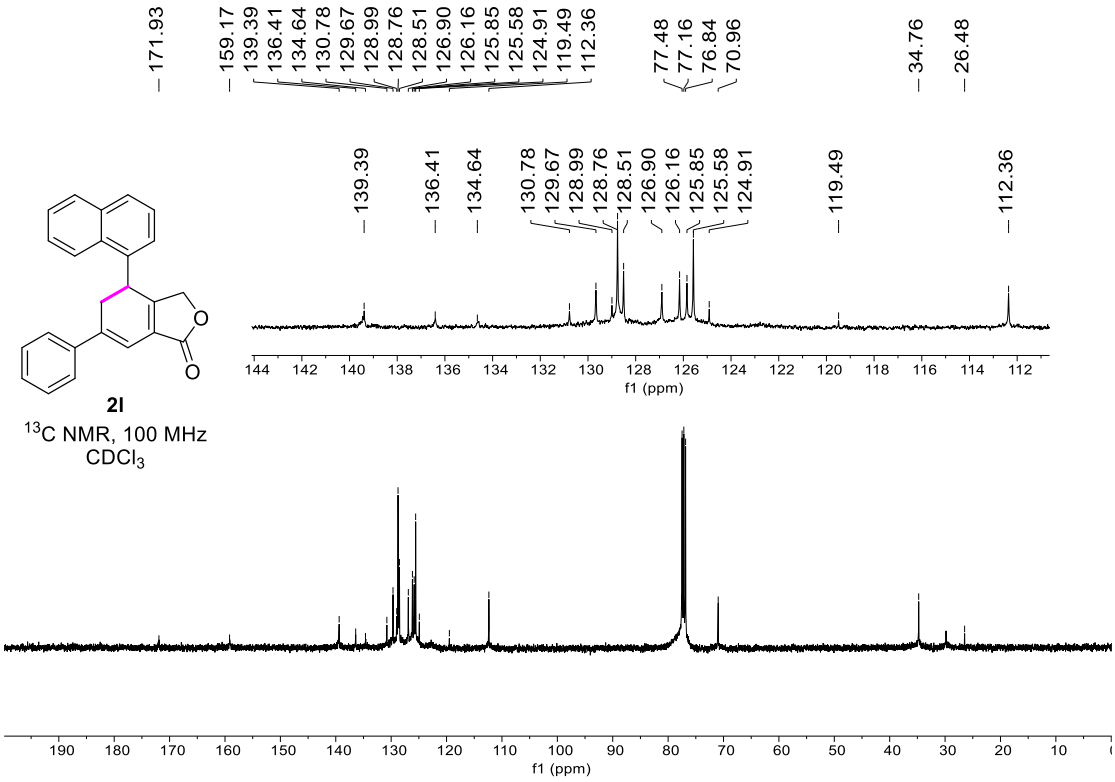
$^{1}$H NMR, 500 MHz

$CDCl_3$




171.86
158.89
140.86
140.38
139.86
139.35
139.23
129.11
128.94
128.73
128.44
128.30
128.00
127.95
127.61
127.08
126.26
125.56
125.37
112.38
77.42
77.16
76.91
70.69
40.36
35.33
O
O
2k
13C NMR, 100 MHz
CDCl3
f1 (ppm)

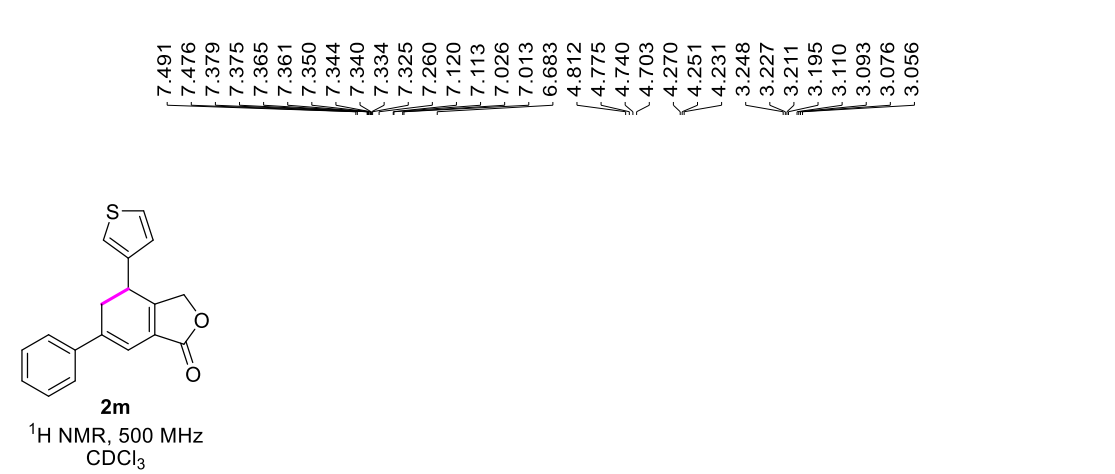

8.104
8.083
7.945
7.925
7.921
7.843
7.824
7.565
7.560
7.544
7.475
7.471
7.466
7.453
7.448
7.428
7.412
7.390
7.378
7.355
7.350
7.334
7.328
7.315
7.307
7.303
7.300
7.299
7.286
3.369
3.285
O
O
2l
1H NMR, 400 MHz
CDCl3
1.08
1.06
1.12
2.23
2.26
1.13
1.04
2.31
1.05
1.01
1.18
2.16
1.14
1.09
f1 (ppm)




**2l**

$^{13}C$ NMR, 100 MHz

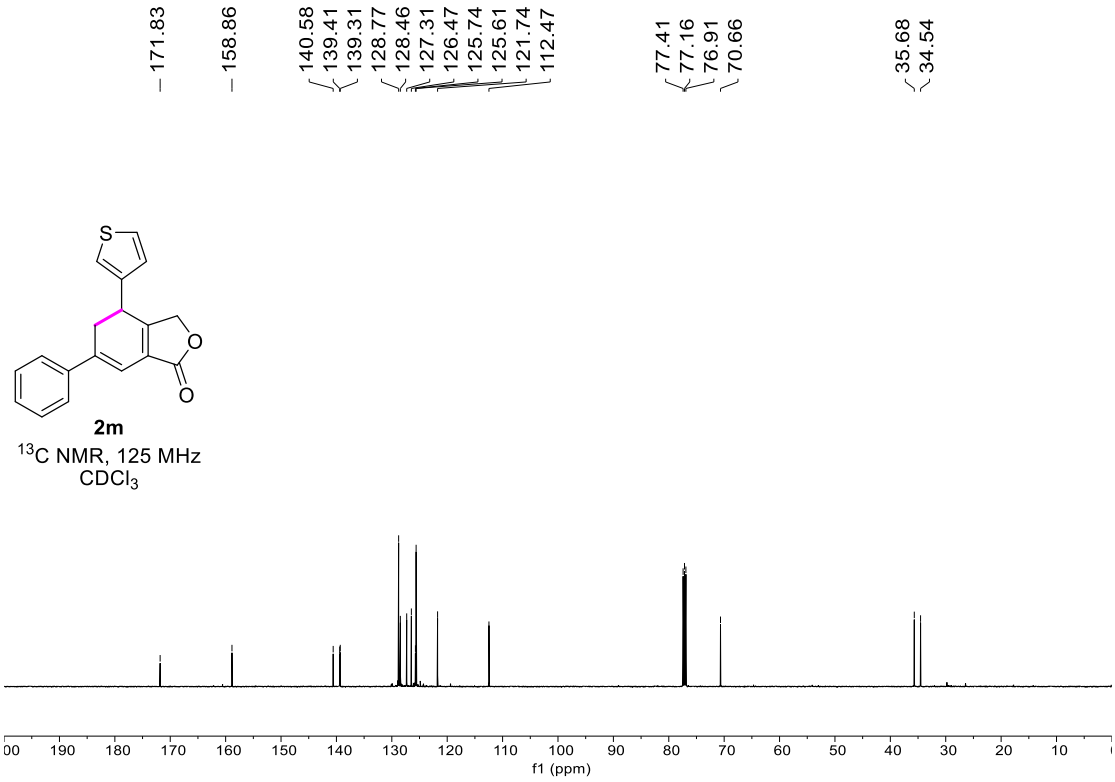
$CDCl_3$

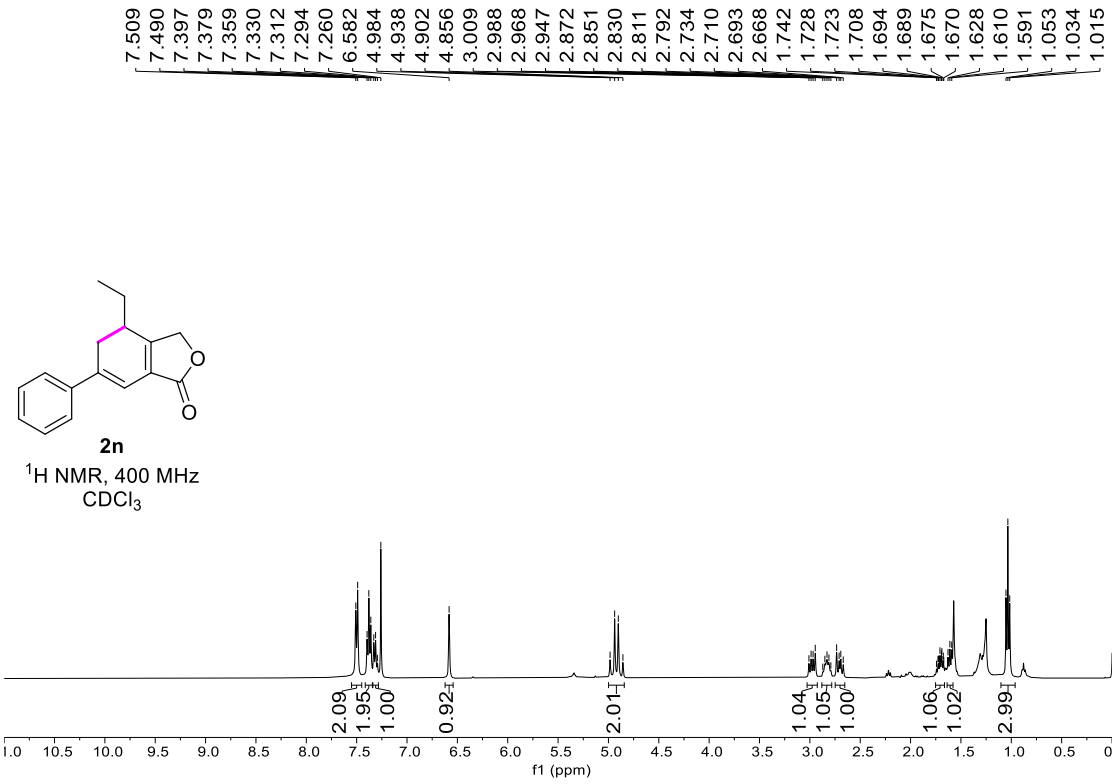


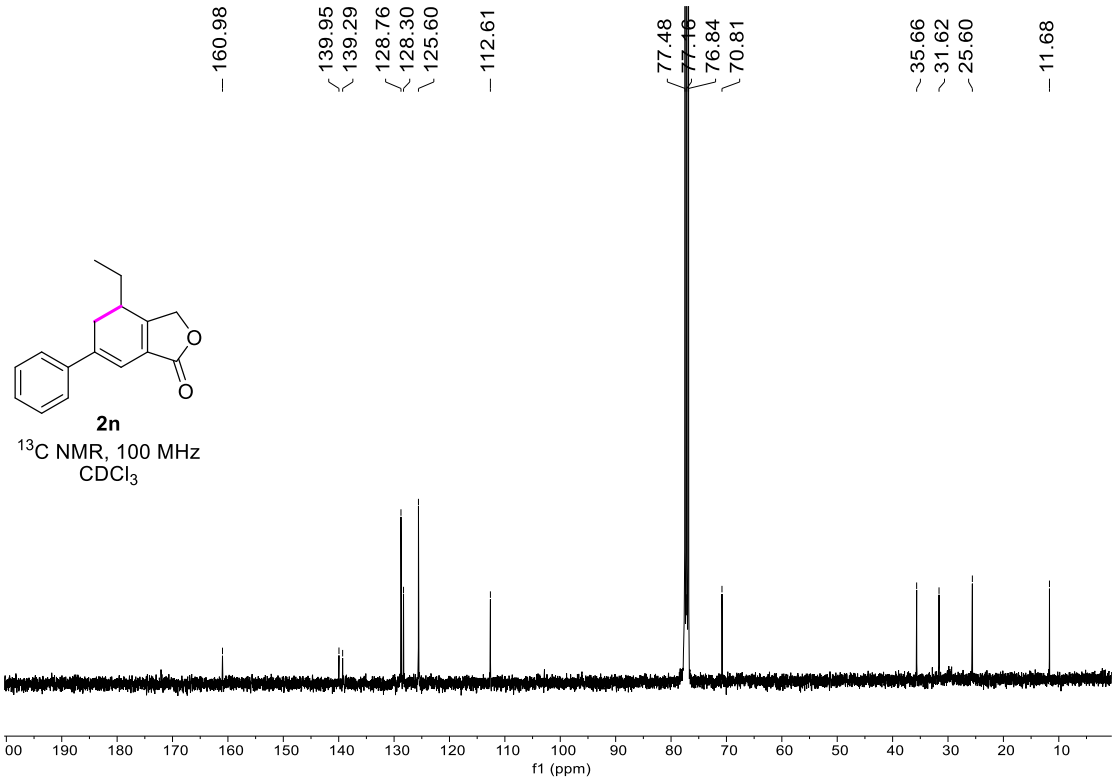

**2m**

$^{1}H$ NMR, 500 MHz

$CDCl_3$


171.83
158.86
140.58
139.41
139.31
128.77
128.46
127.31
126.47
125.74
125.61
121.74
112.47
77.41
77.16
76.91
70.66
35.68
34.54
S
O
O
2m
13C NMR, 125 MHz
CDCl3
f1 (ppm)

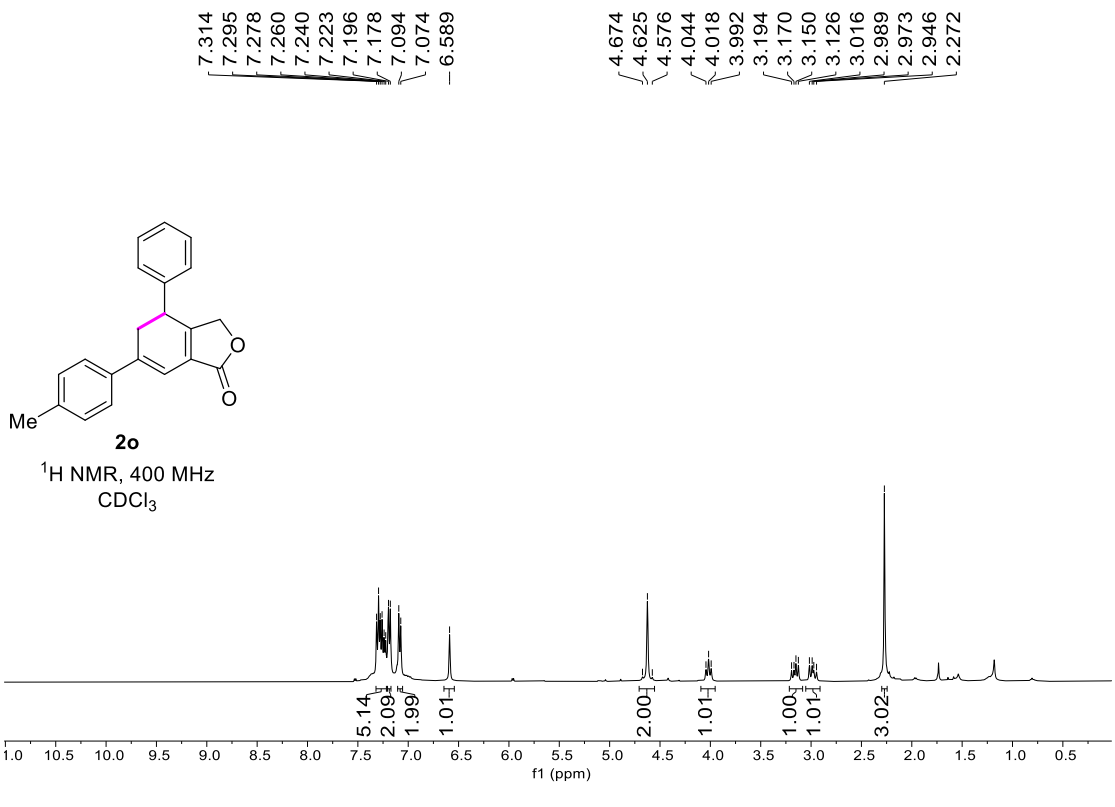

7.509
7.490
7.397
7.379
7.359
7.330
7.312
7.294
7.260
6.582
4.984
4.938
4.902
4.856
3.009
2.988
2.968
2.947
2.872
2.851
2.830
2.811
2.792
2.734
2.710
2.693
2.668
1.742
1.728
1.723
1.708
1.694
1.689
1.675
1.670
1.628
1.610
1.591
1.053
1.034
1.015
O
O
2n
1H NMR, 400 MHz
CDCl3
2.09
1.95
1.00
0.92
2.01
1.04
1.05
1.00
1.06
1.02
2.99
f1 (ppm)




**2n**

$^{13}C$ NMR, 100 MHz

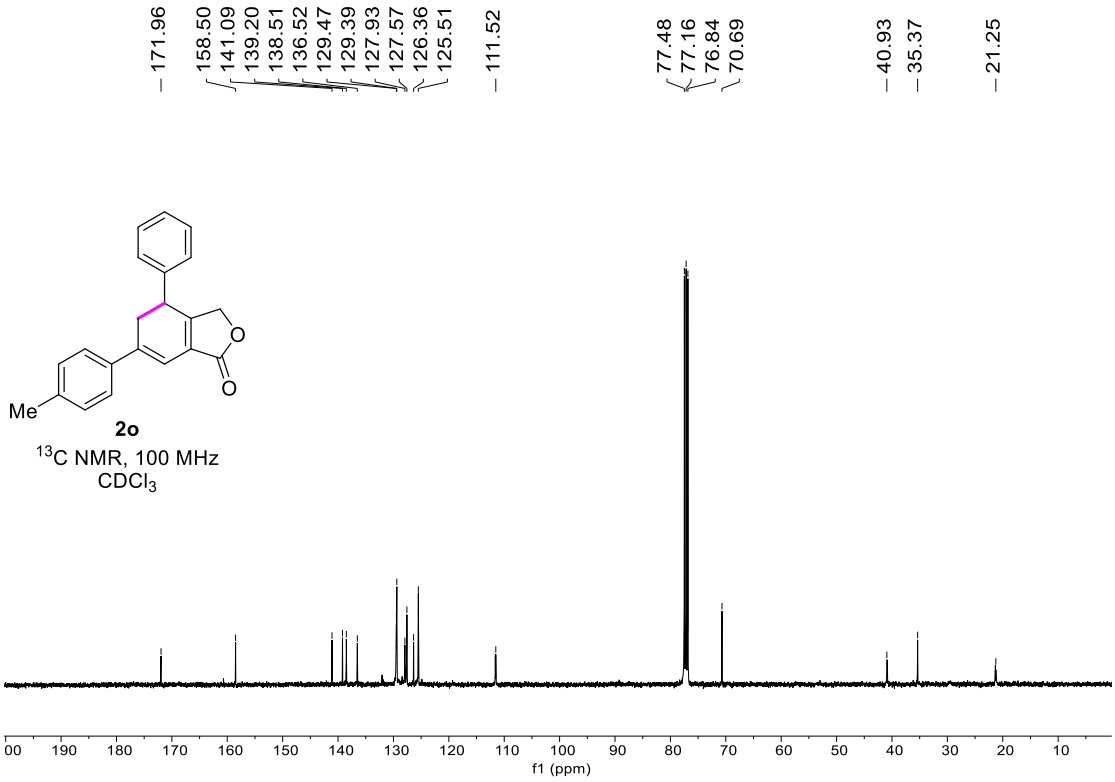
$CDCl_3$




**2o**

$^{1}H$ NMR, 400 MHz

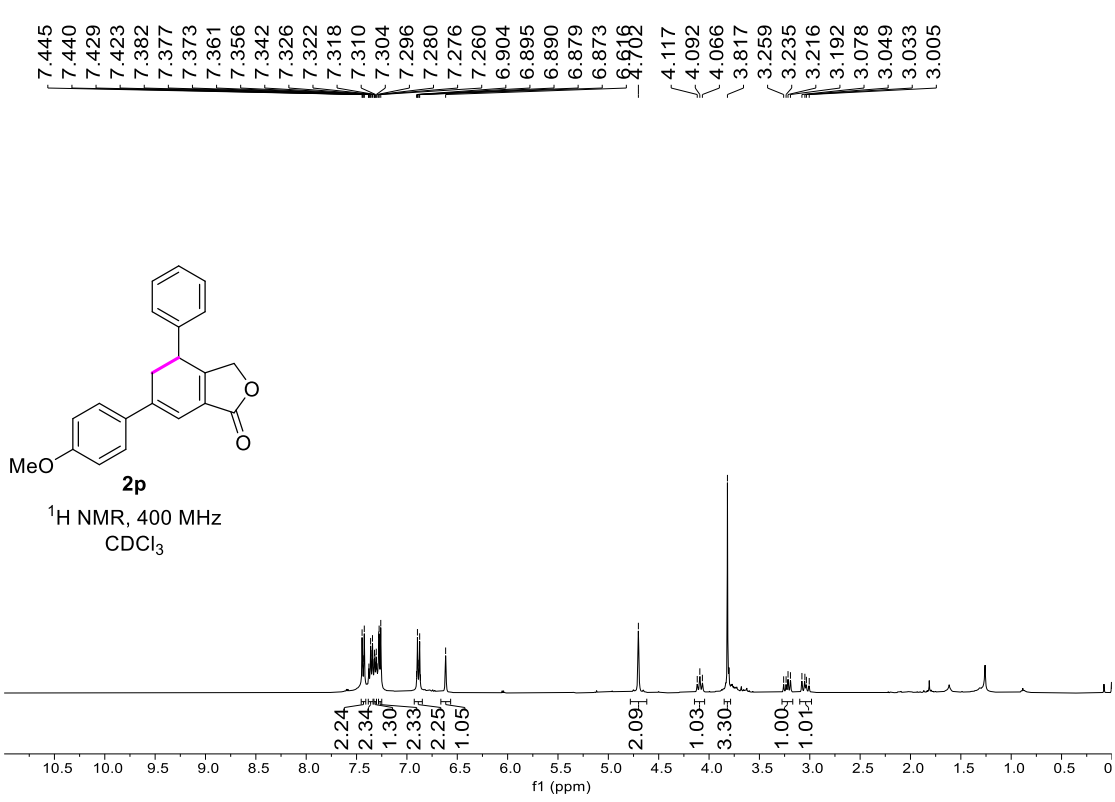
$CDCl_3$




**2o**

$^{13}$C NMR, 100 MHz

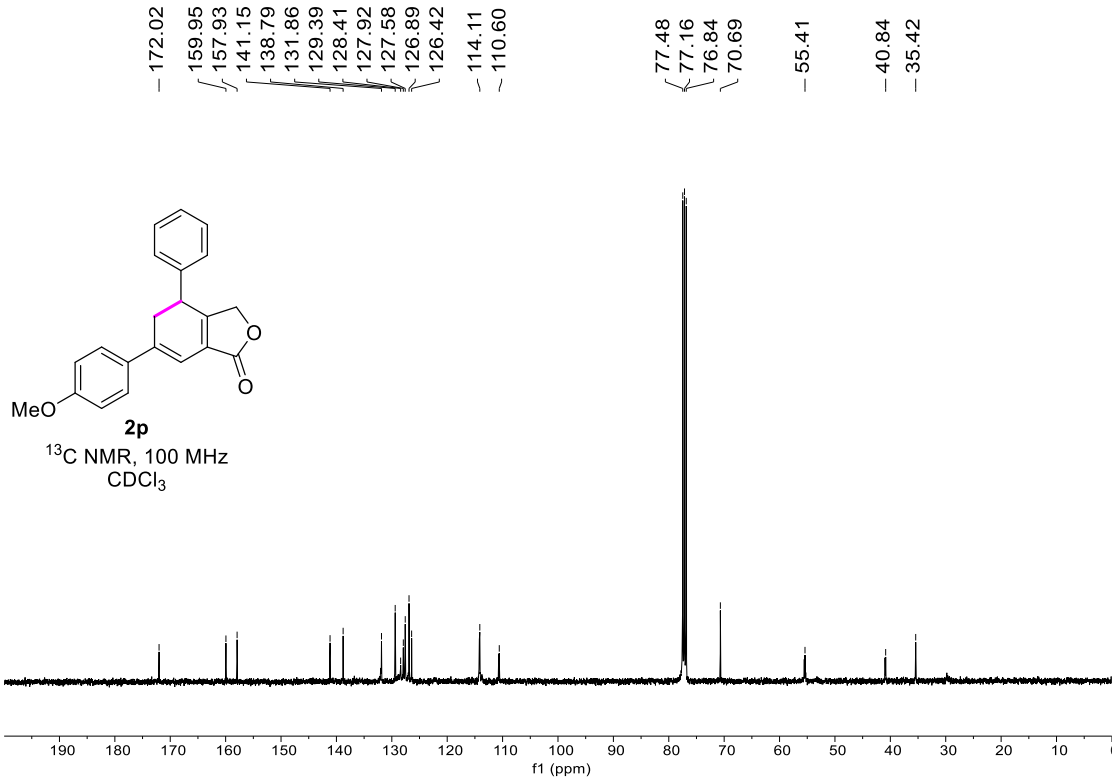
$CDCl_3$

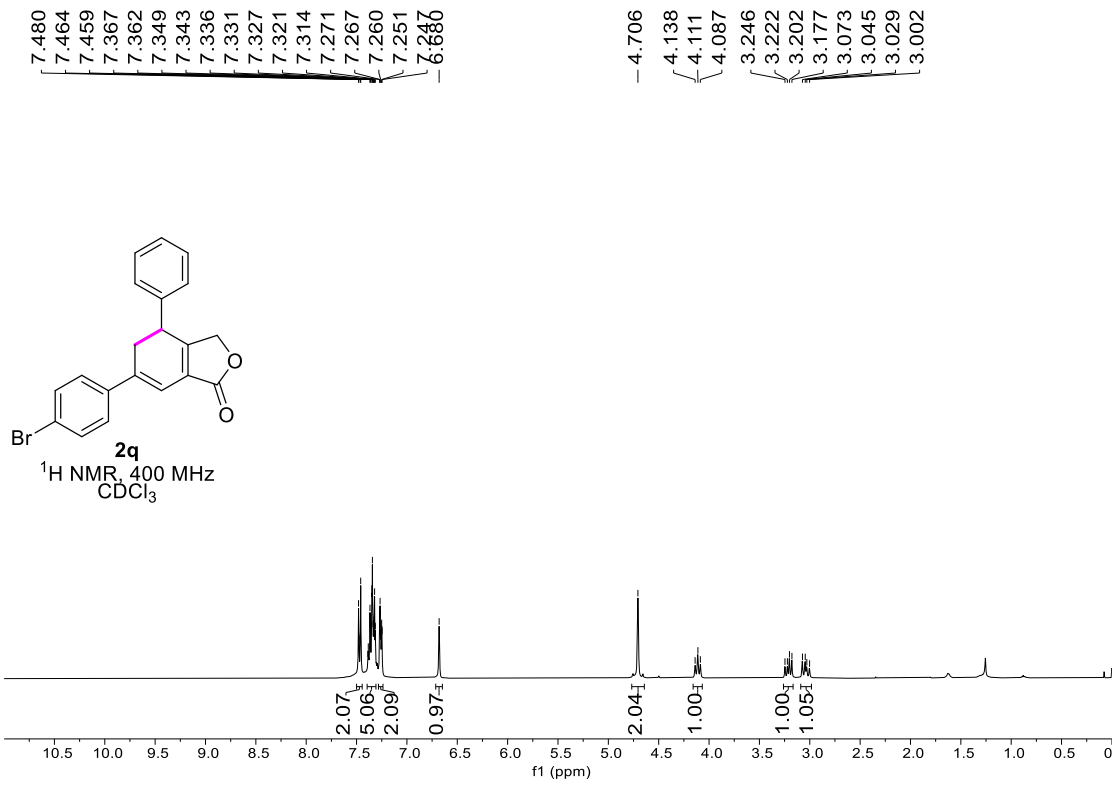


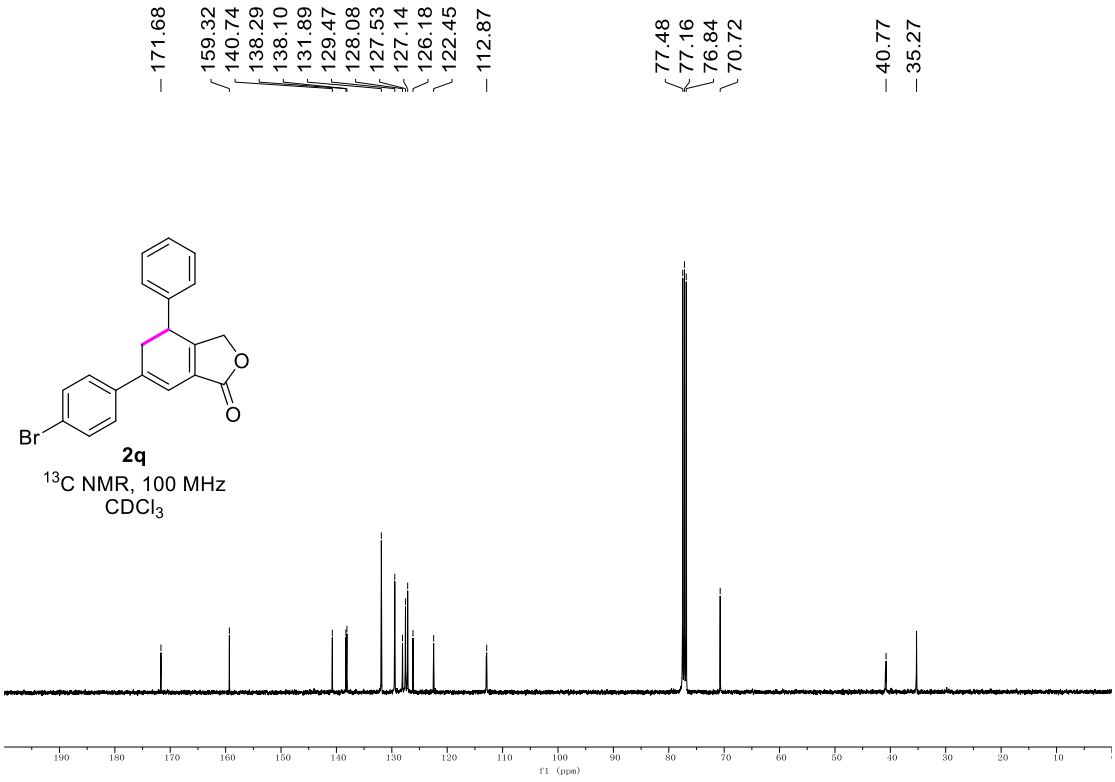

**2p**

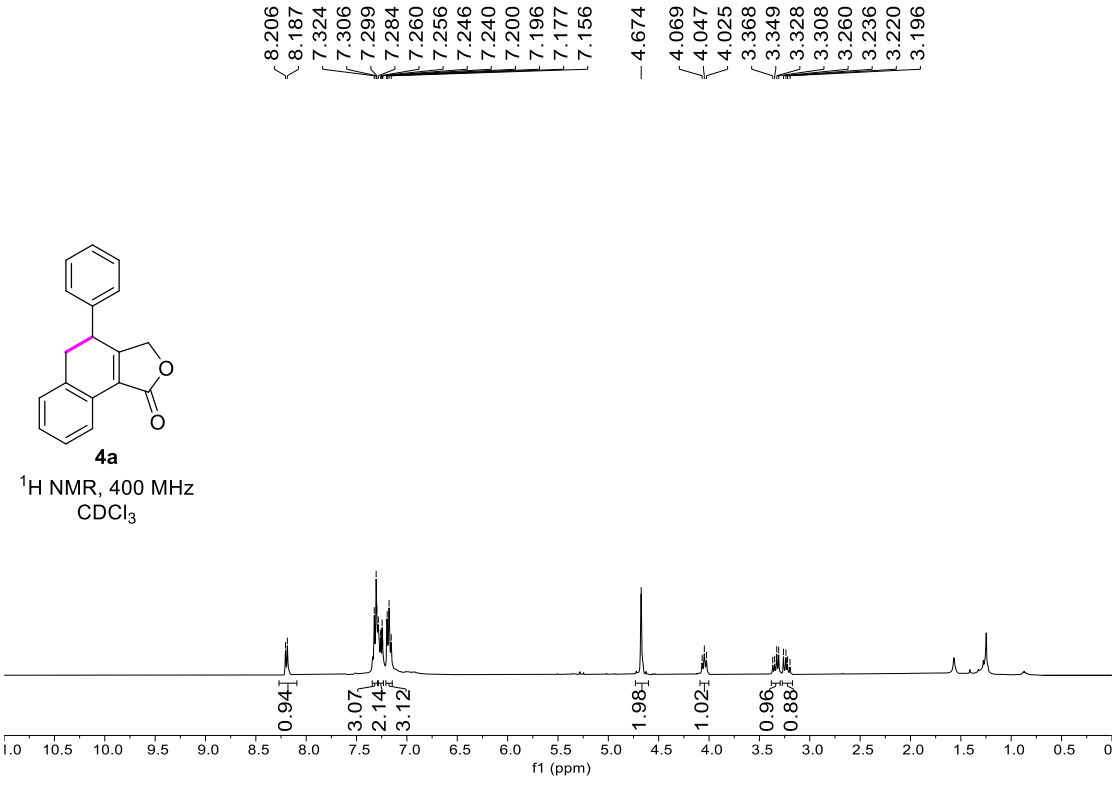
$^{1}$H NMR, 400 MHz

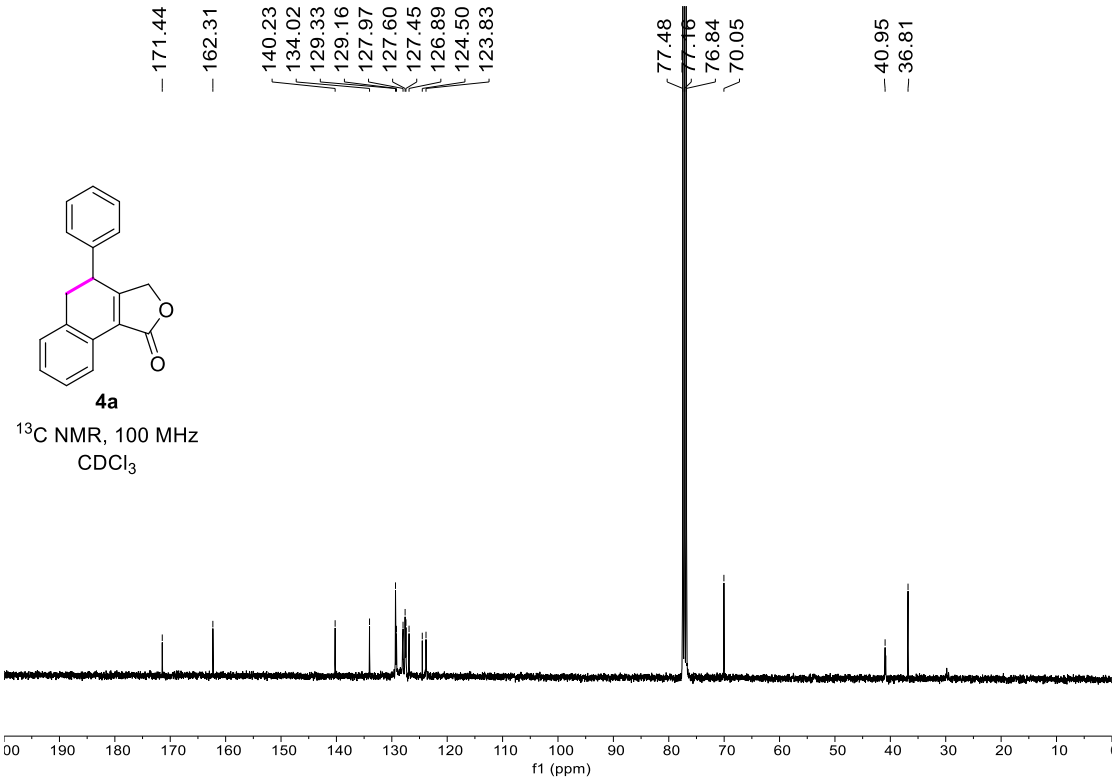
$CDCl_3$


172.02
159.95
157.93
141.15
138.79
131.86
129.39
128.41
127.92
127.58
126.89
126.42
114.11
110.60
77.48
77.16
76.84
70.69
55.41
40.84
35.42
MeO
O
O
2p
13C NMR, 100 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.480
7.464
7.459
7.367
7.362
7.349
7.343
7.336
7.331
7.327
7.321
7.314
7.271
7.267
7.260
7.251
7.247
6.680
4.706
4.138
4.111
4.087
3.246
3.222
3.202
3.177
3.073
3.045
3.029
3.002
Br
O
O
2q
1H NMR, 400 MHz
CDCl3
2.07
5.06
2.09
0.97
2.04
1.00
1.00
1.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


171.68
159.32
140.74
138.29
138.10
131.89
129.47
128.08
127.53
127.14
126.18
122.45
112.87
77.48
77.16
76.84
70.72
40.77
35.27
Br
O
O
2q
13C NMR, 100 MHz
CDCl3
f1 (ppm)

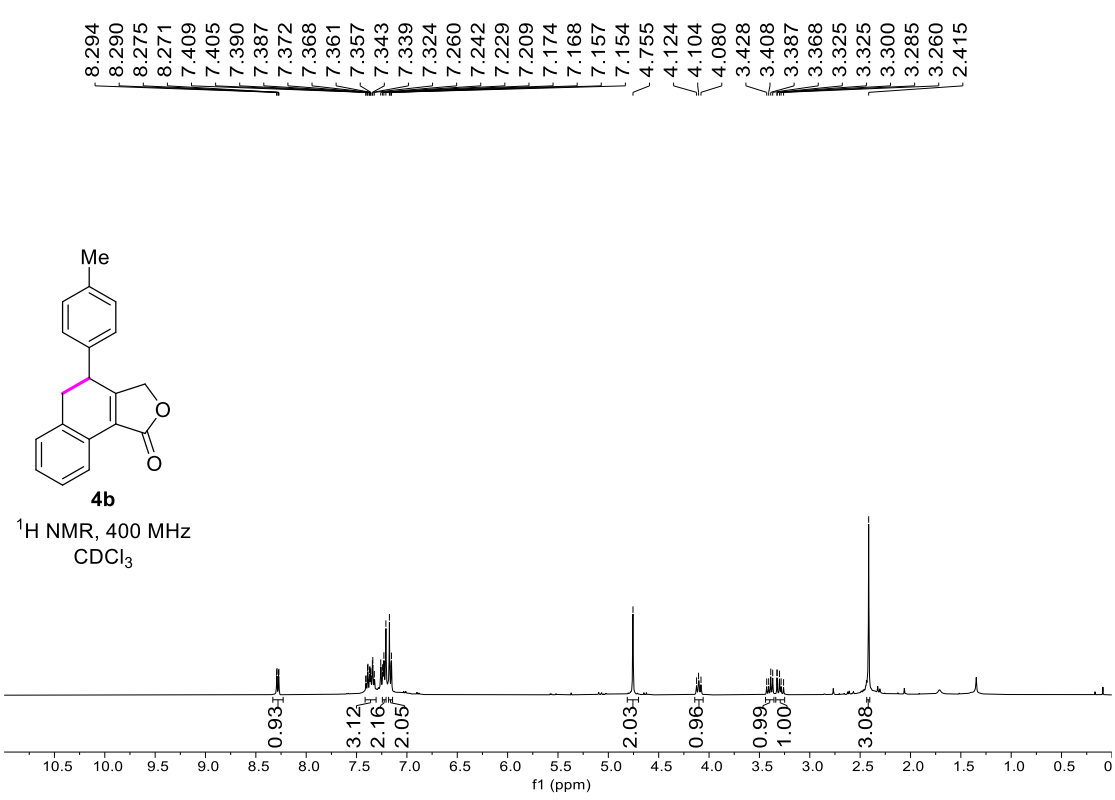

8.206
8.187
7.324
7.306
7.299
7.284
7.260
7.256
7.246
7.240
7.200
7.196
7.177
7.156
4.674
4.069
4.047
4.025
3.368
3.349
3.328
3.308
3.260
3.236
3.220
3.196
O
O
4a
1H NMR, 400 MHz
CDCl3
0.94
3.07
2.14
3.12
1.98
1.02
0.96
0.88
f1 (ppm)




**4a**

$^{13}$C NMR, 100 MHz

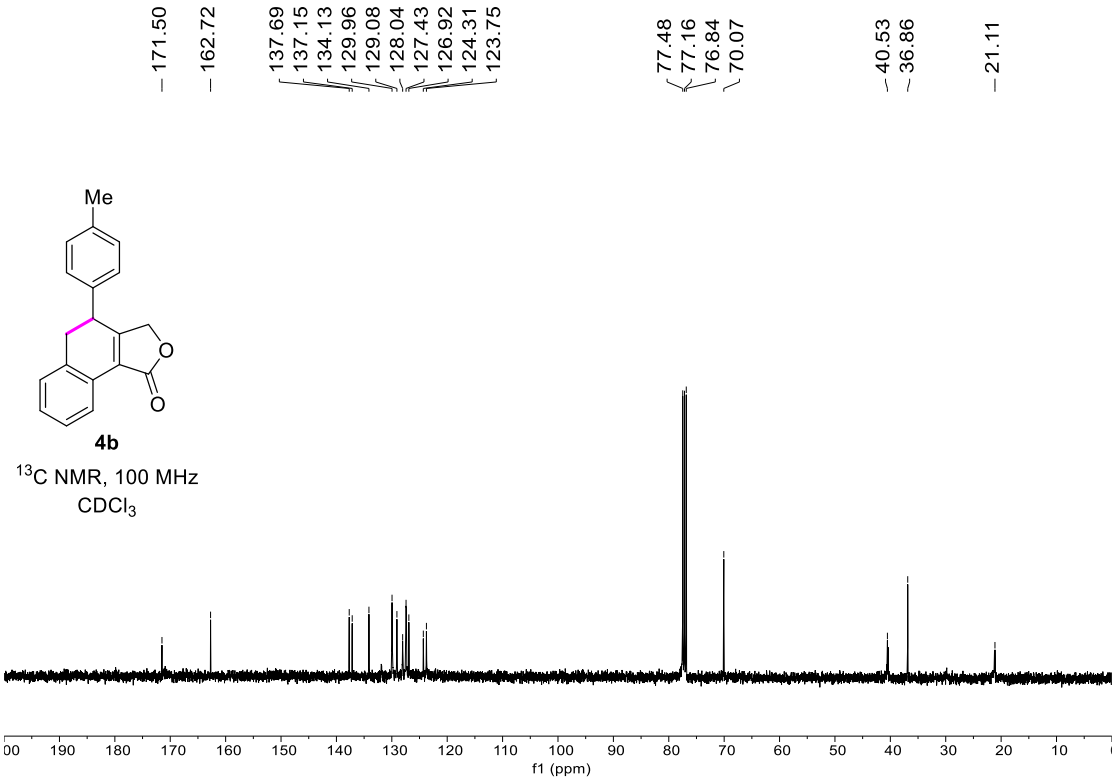
$CDCl_3$

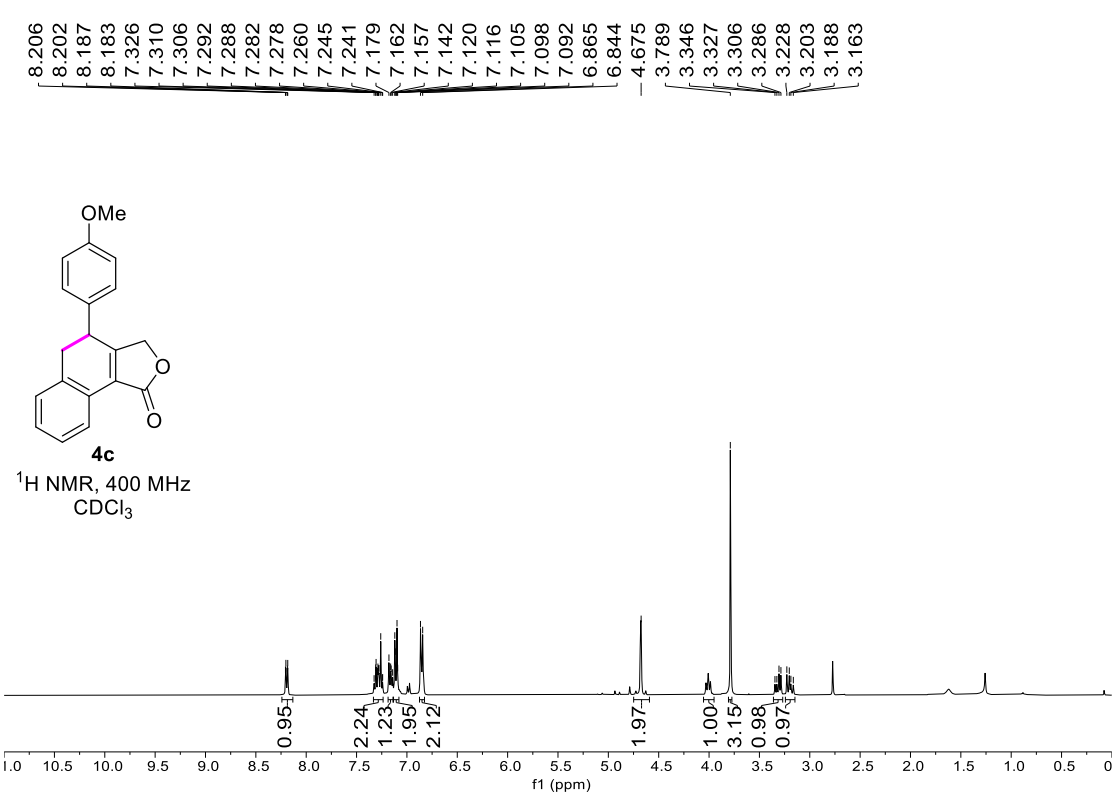


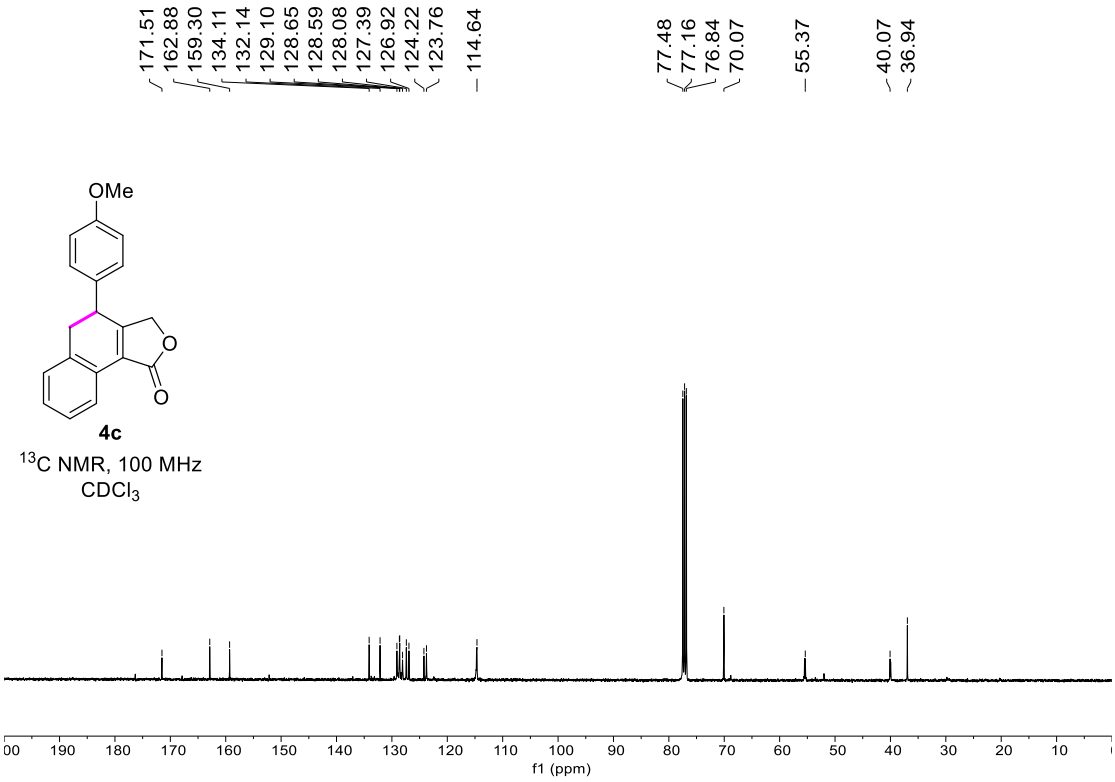

**4b**

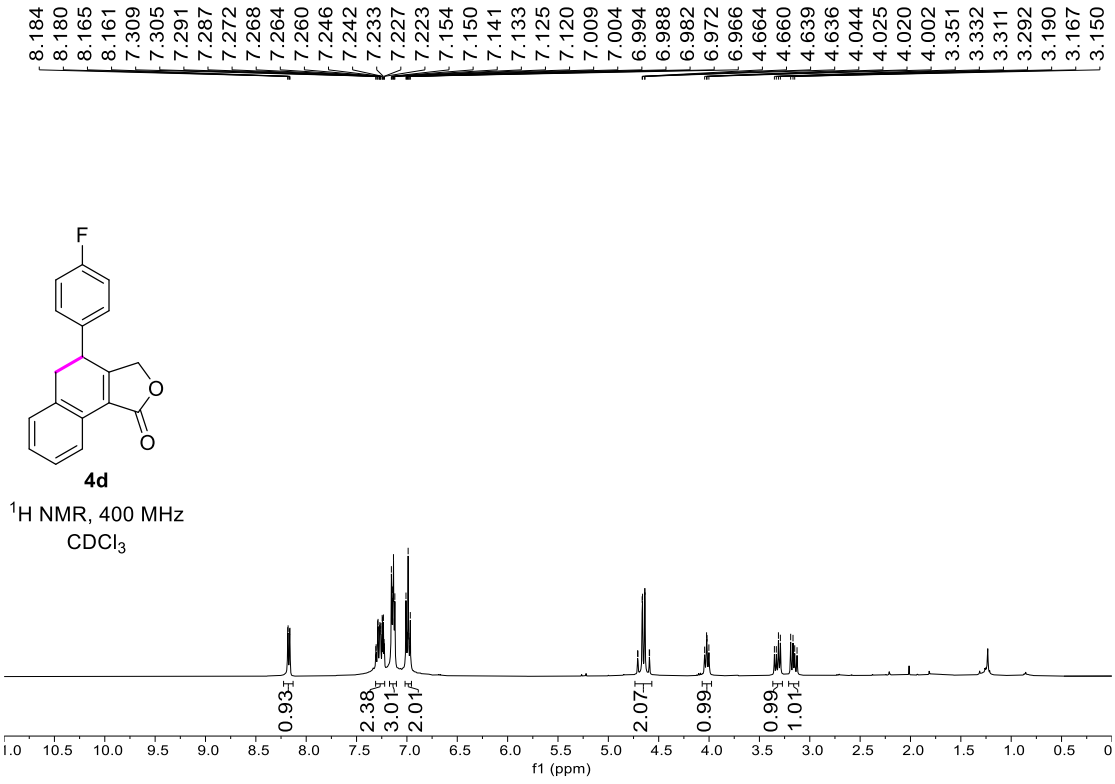
$^{1}$H NMR, 400 MHz

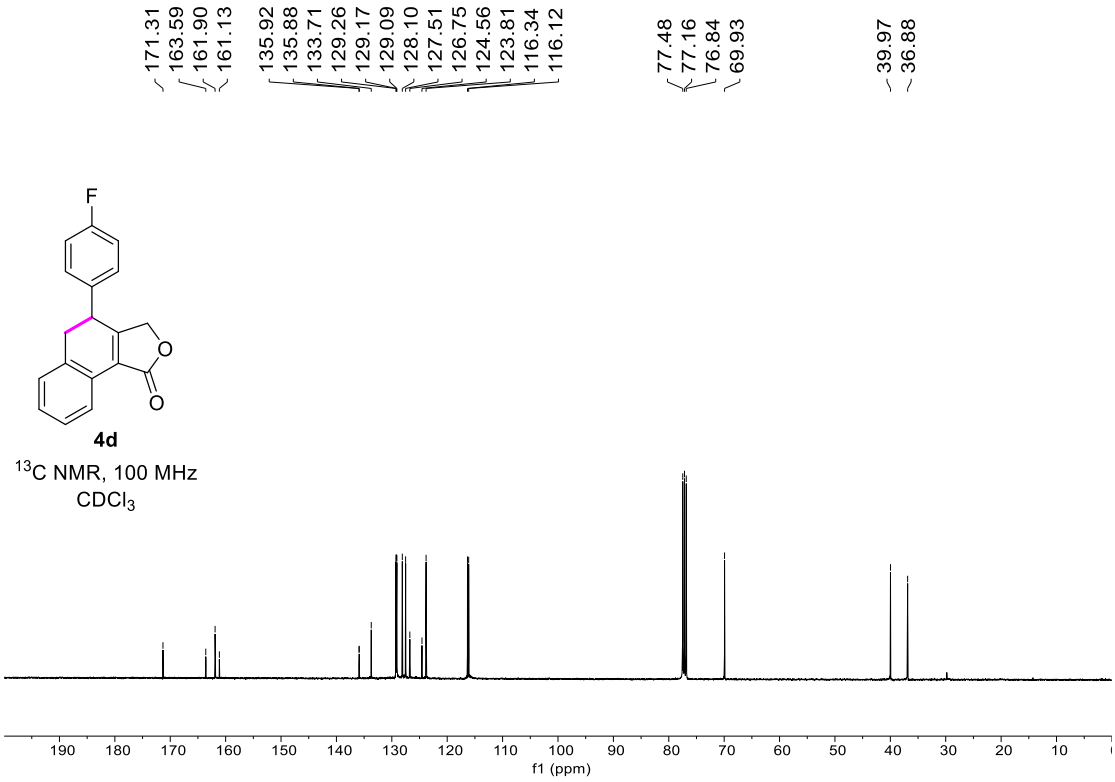
$CDCl_3$

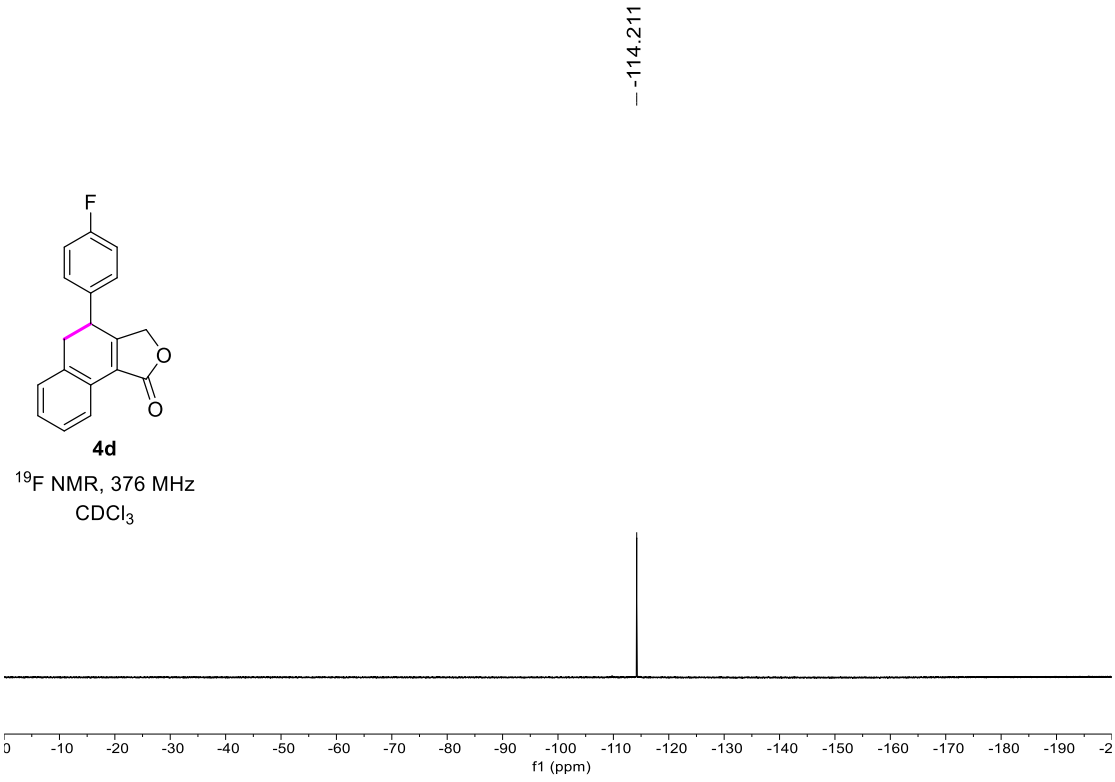

171.50
162.72
137.69
137.15
134.13
129.96
129.08
128.04
127.43
126.92
124.31
123.75
77.48
77.16
76.84
70.07
40.53
36.86
21.11
Me
O
O
4b
13C NMR, 100 MHz
CDCl3
f1 (ppm)

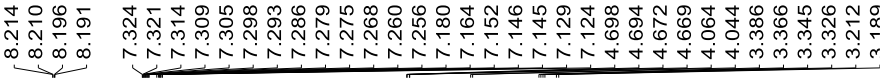

8.206
8.202
8.187
8.183
7.326
7.310
7.306
7.292
7.288
7.282
7.278
7.260
7.245
7.241
7.179
7.162
7.157
7.142
7.120
7.116
7.105
7.098
7.092
6.865
6.844
4.675
3.789
3.346
3.327
3.306
3.286
3.228
3.203
3.188
3.163
OMe
O
O
4c
1H NMR, 400 MHz
CDCl3
0.95
2.24
1.23
1.95
2.12
1.97
1.00
3.15
0.98
0.97
f1 (ppm)

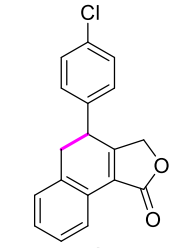

171.51
162.88
159.30
134.11
132.14
129.10
128.65
128.59
128.08
127.39
126.92
124.22
123.76
114.64
77.48
77.16
76.84
70.07
55.37
40.07
36.94
OMe
O
O
4c
13C NMR, 100 MHz
CDCl3
f1 (ppm)


8.184
8.180
8.165
8.161
7.309
7.305
7.291
7.287
7.272
7.268
7.264
7.260
7.246
7.242
7.233
7.227
7.223
7.154
7.150
7.141
7.133
7.125
7.120
7.009
7.004
6.994
6.988
6.982
6.972
6.966
4.664
4.660
4.639
4.636
4.044
4.025
4.020
4.002
3.351
3.332
3.311
3.292
3.190
3.167
3.150
F
O
O
4d
1H NMR, 400 MHz
CDCl3
0.93
2.38
3.01
2.01
2.07
0.99
0.99
1.01
f1 (ppm)


171.31
163.59
161.90
161.13
135.92
135.88
133.71
129.26
129.17
129.09
128.10
127.51
126.75
124.56
123.81
116.34
116.12
77.48
77.16
76.84
69.93
39.97
36.88
F
O
O
4d
13C NMR, 100 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-114.211
F
O
O
4d
19F NMR, 376 MHz
CDCl3
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

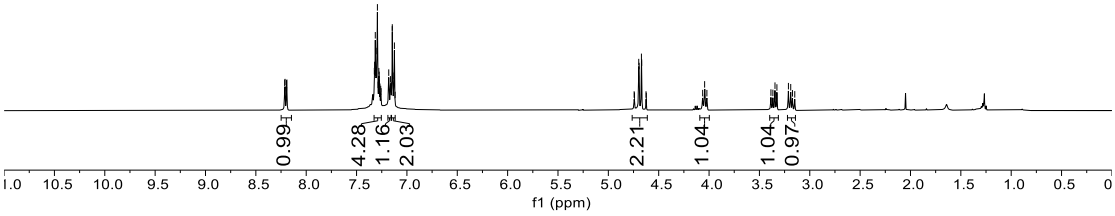


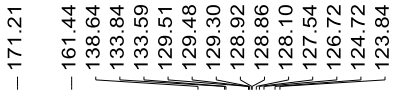



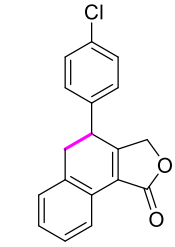

**4e**

$^{1}$H NMR, 400 MHz

$CDCl_3$



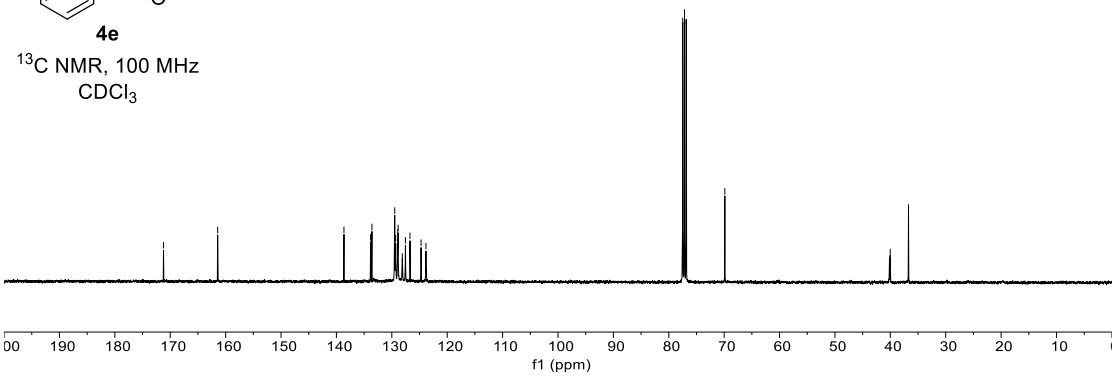



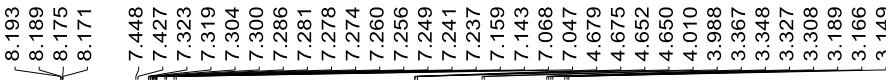



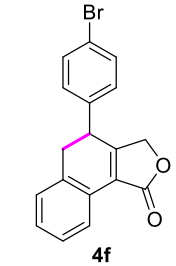

**4e**

$^{13}$C NMR, 100 MHz

$CDCl_3$

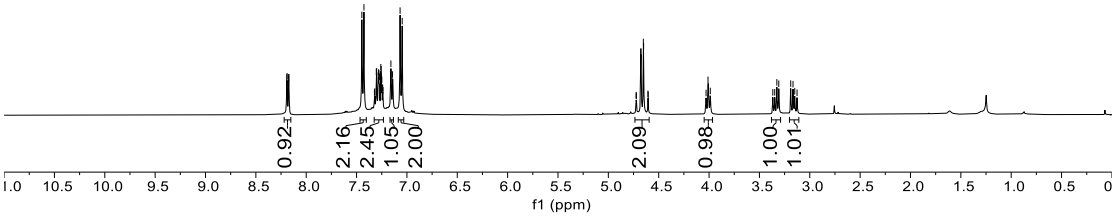


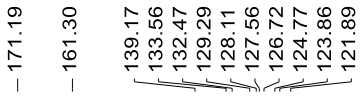


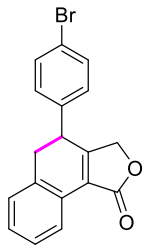




**4f**

$^{1}$H NMR, 400 MHz
$CDCl_3$

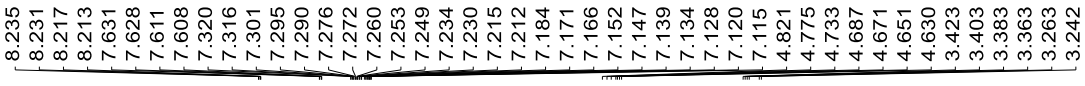


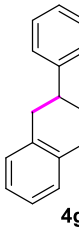




**4f**

$^{13}$C NMR, 100 MHz
$CDCl_3$

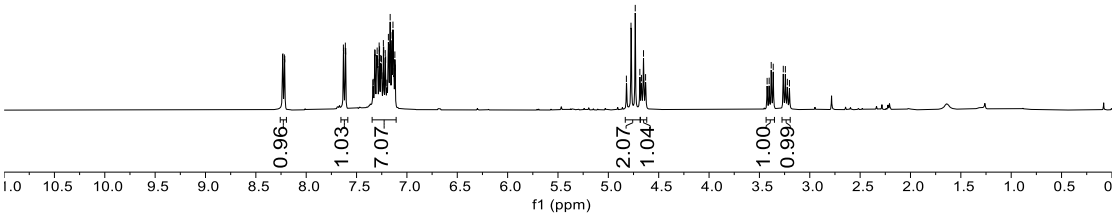


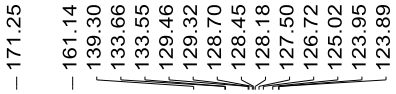



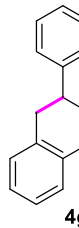

**4g**

$^{1}$H NMR, 400 MHz

$CDCl_3$



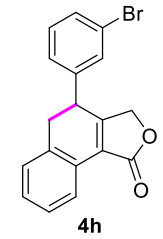




**4g**

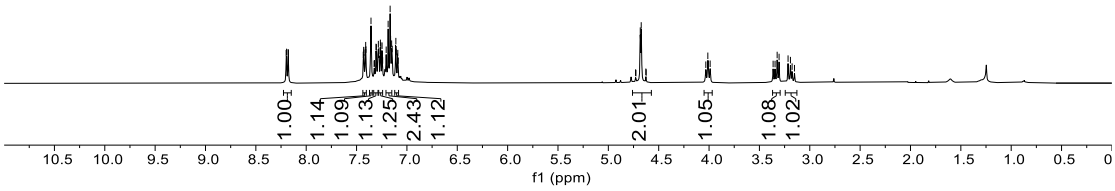
$^{13}$C NMR, 100 MHz

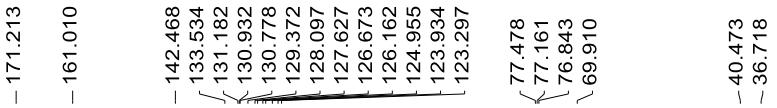
$CDCl_3$

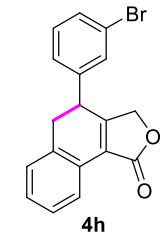




**4h**

$^{1}$H NMR, 400 MHz
$CDCl_3$

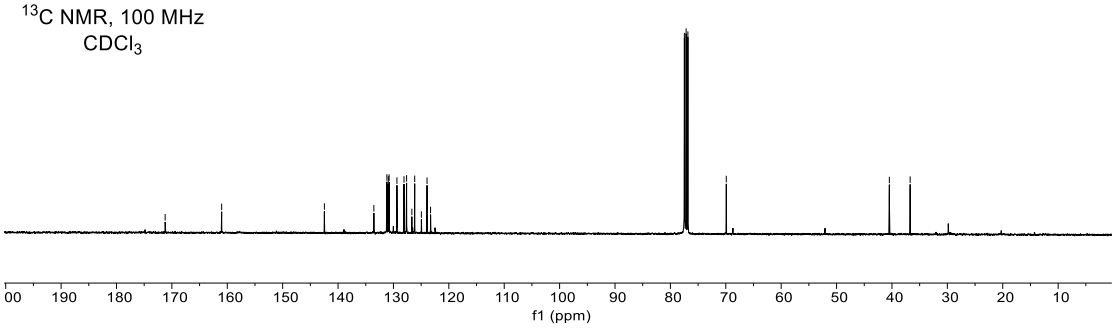


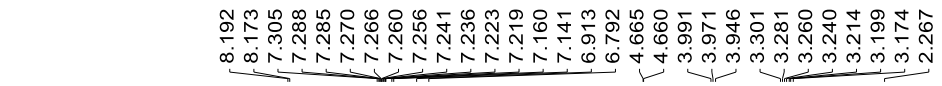



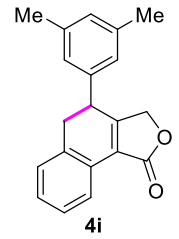




**4h**

$^{13}$C NMR, 100 MHz
$CDCl_3$





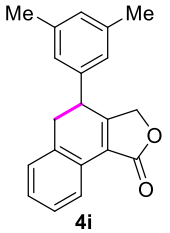




**4i**

$^{1}$H NMR, 400 MHz
$CDCl_3$

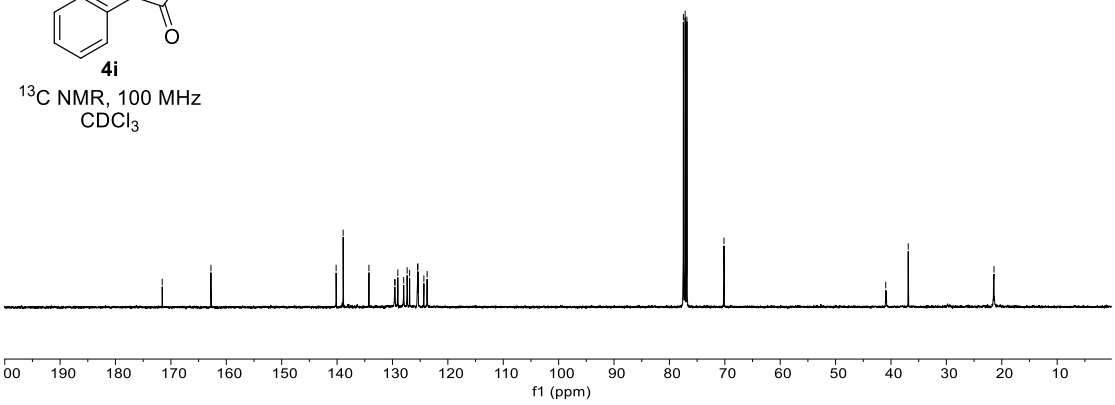


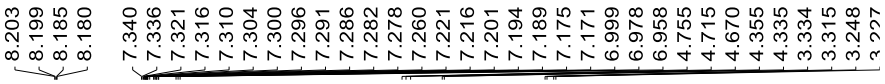


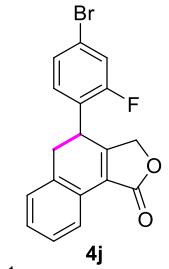



**4i**

$^{13}$C NMR, 100 MHz
$CDCl_3$



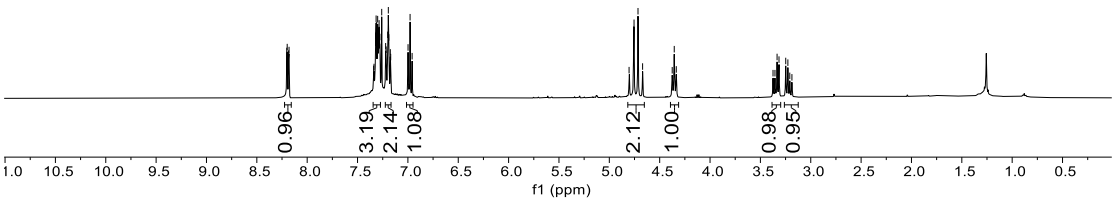


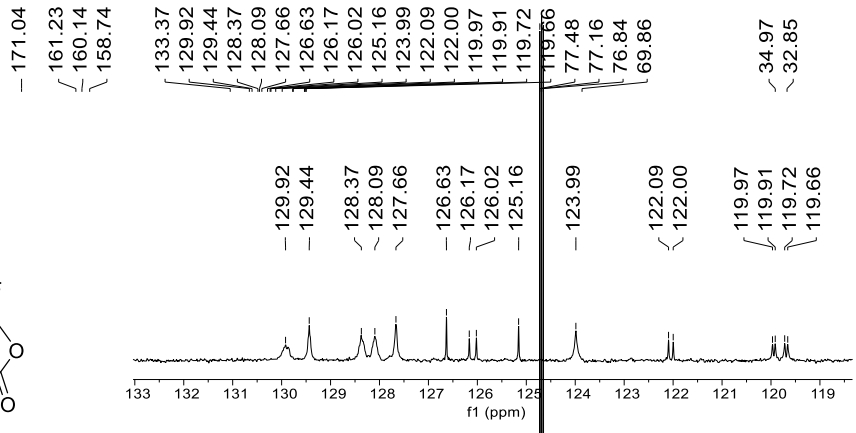



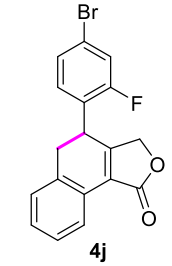

**4j**

$^{1}$H NMR, 400 MHz

$CDCl_3$



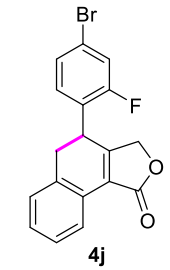




**4j**

$^{13}$C NMR, 100 MHz

$CDCl_3$

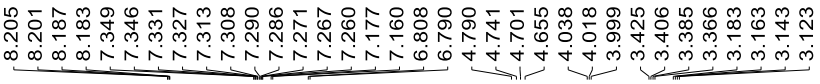


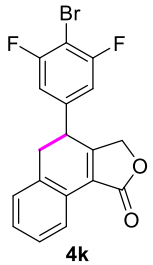

**4j**

$^{19}$F NMR, 376 MHz

$CDCl_3$



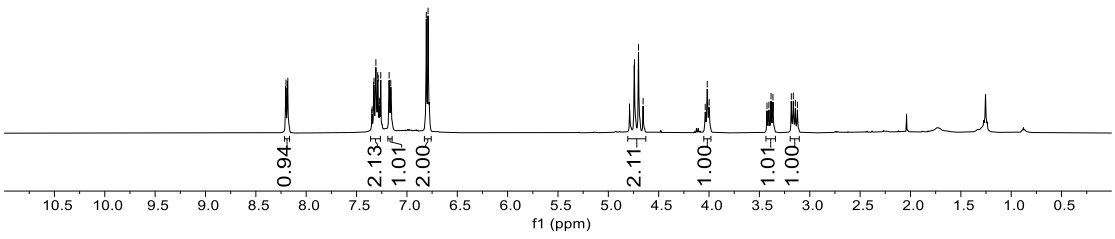



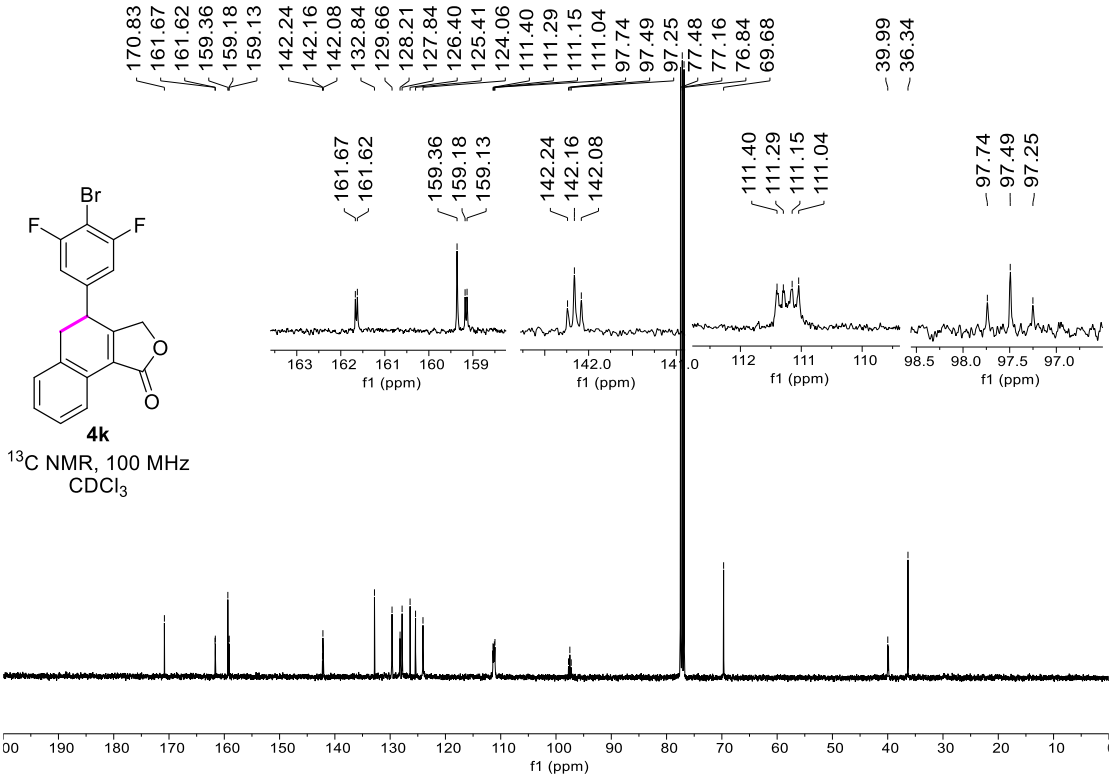



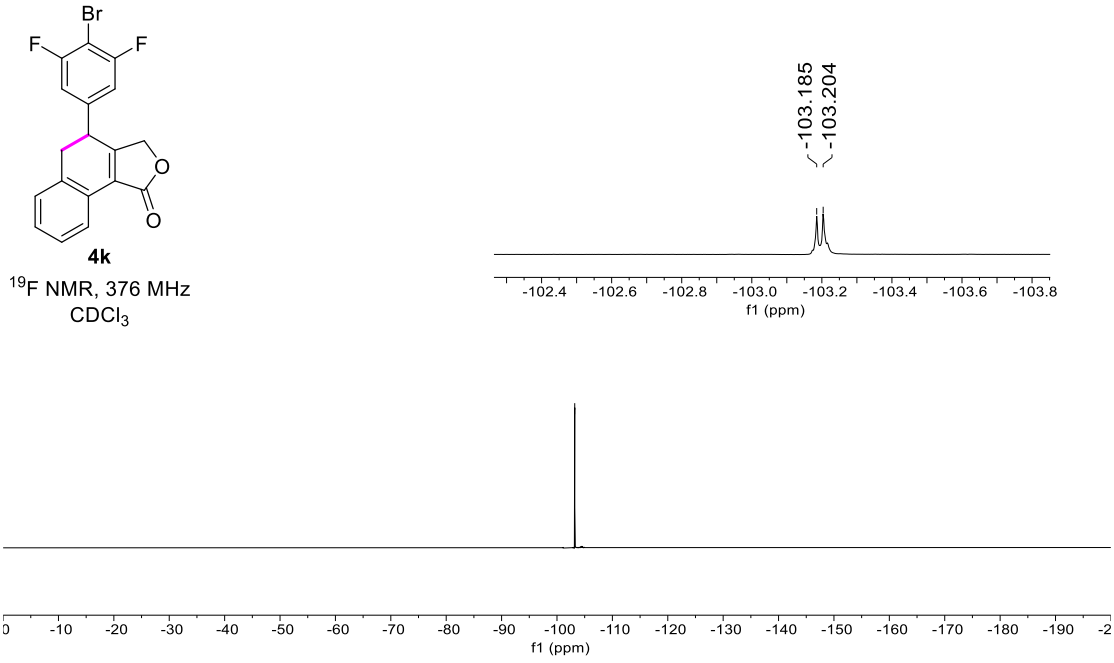

**4k**

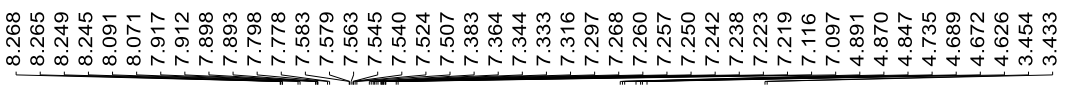
$^{1}$H NMR, 400 MHz

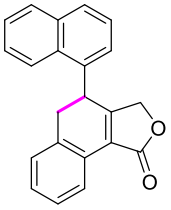
$CDCl_3$




170.83
161.67
161.62
159.36
159.18
159.13
142.24
142.16
142.08
132.84
129.66
128.21
127.84
126.40
125.41
124.06
111.40
111.29
111.15
111.04
97.74
97.49
97.25
77.48
77.16
76.84
69.68
39.99
36.34
Br
F
F
O
O
4k
13C NMR, 100 MHz
CDCl3
f1 (ppm)


-103.185
-103.204
Br
F
F
O
O
4k
19F NMR, 376 MHz
CDCl3
f1 (ppm)

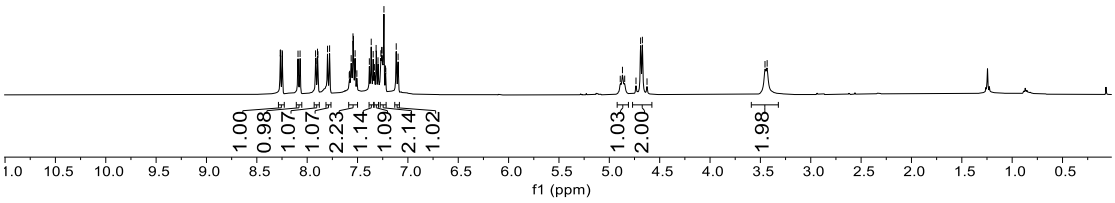


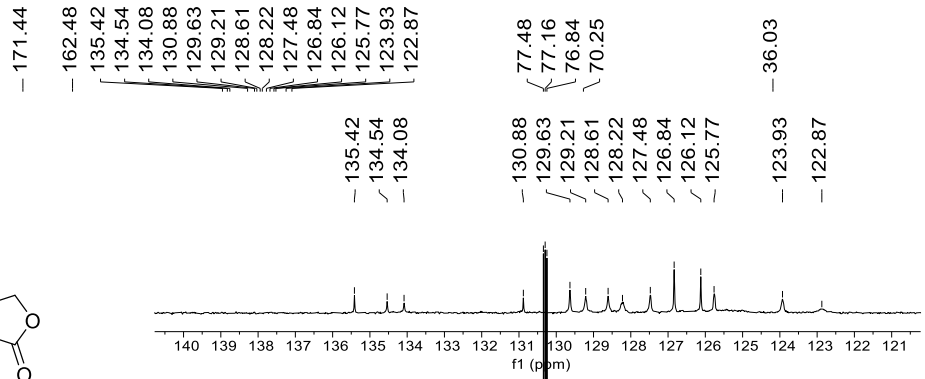



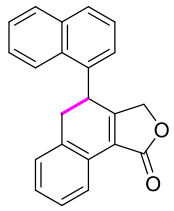
**4l**

$^{1}$H NMR, 400 MHz

$CDCl_3$



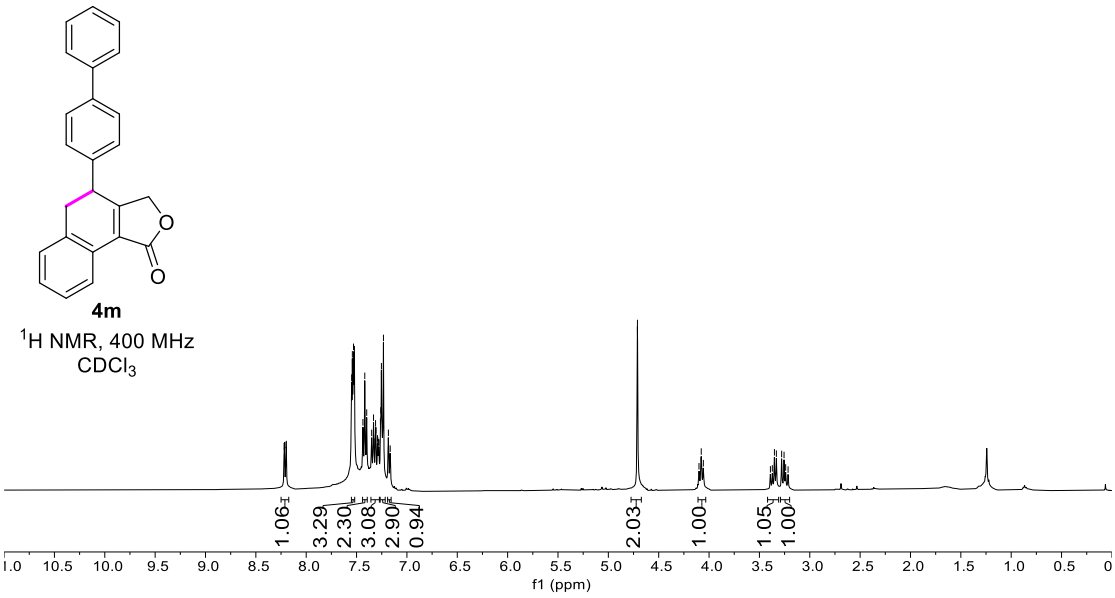



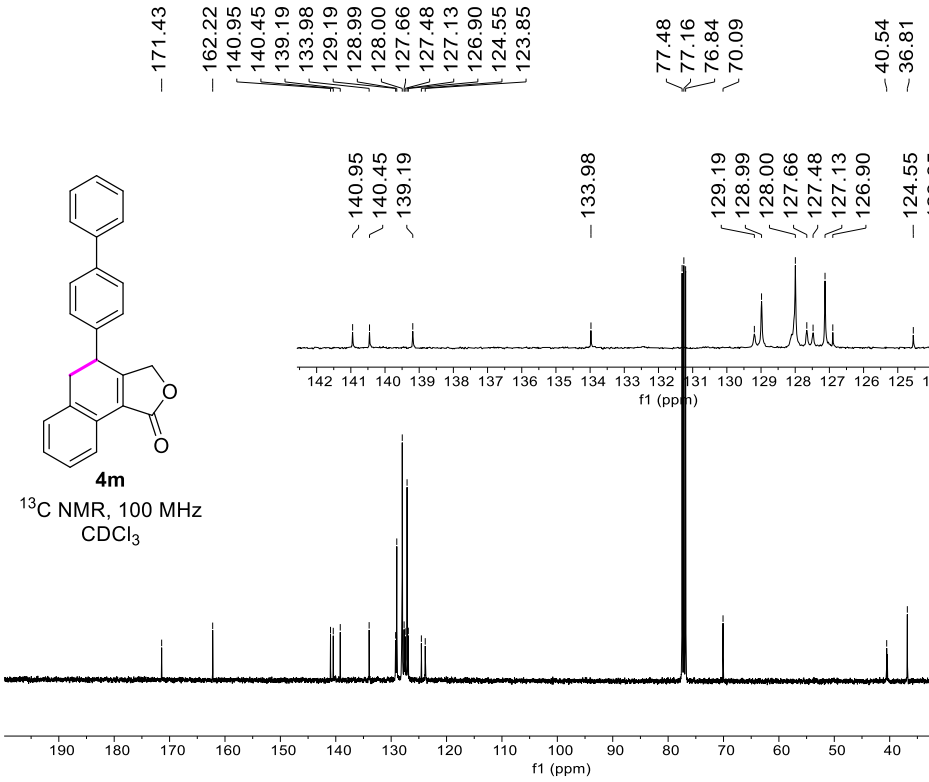
**4l**

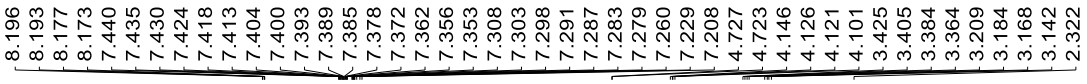
$^{13}$C NMR, 100 MHz

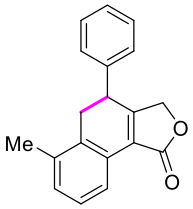
$CDCl_3$


8.220
8.216
8.201
8.197
7.549
7.542
7.530
7.521
7.437
7.419
7.399
7.350
7.331
7.326
7.311
7.307
7.292
7.289
7.281
7.277
7.263
7.260
7.253
7.233
7.184
7.166
4.711
4.100
4.078
4.057
3.391
3.372
3.351
3.332
3.279
3.255
3.239
3.215


4m
1H NMR, 400 MHz
CDCl3
1.06
3.29
2.30
3.08
2.90
0.94
2.03
1.00
1.05
1.00
f1 (ppm)


171.43
162.22
140.95
140.45
139.19
133.98
129.19
128.99
128.00
127.66
127.48
127.13
126.90
124.55
123.85
77.48
77.16
76.84
70.09
40.54
36.81
4m
13C NMR, 100 MHz
CDCl3
f1 (ppm)

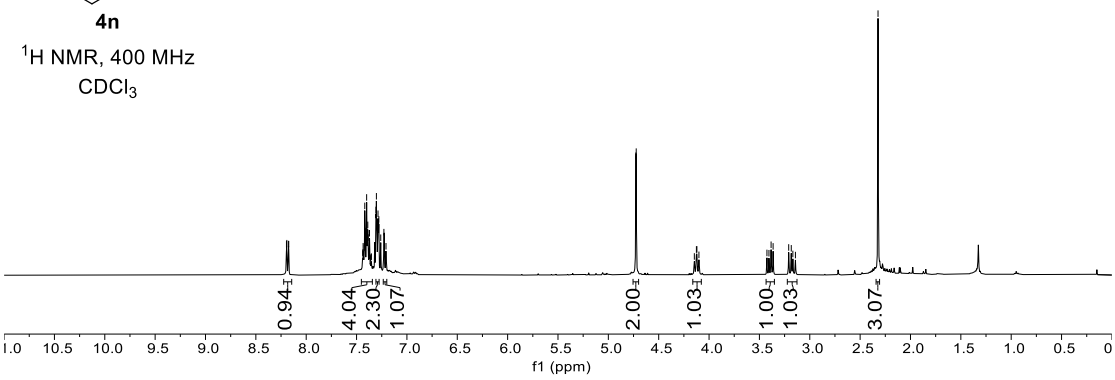


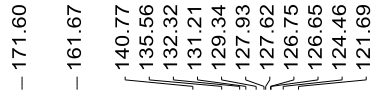



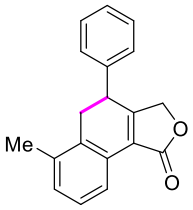

**4n**

$^{1}$H NMR, 400 MHz

$CDCl_3$



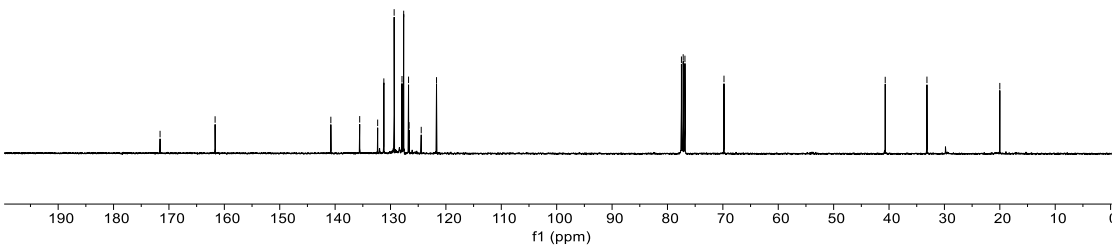



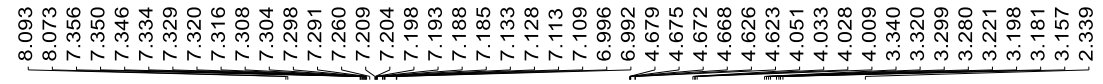



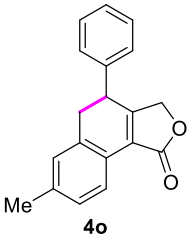

**4n**

$^{13}$C NMR, 100 MHz

$CDCl_3$

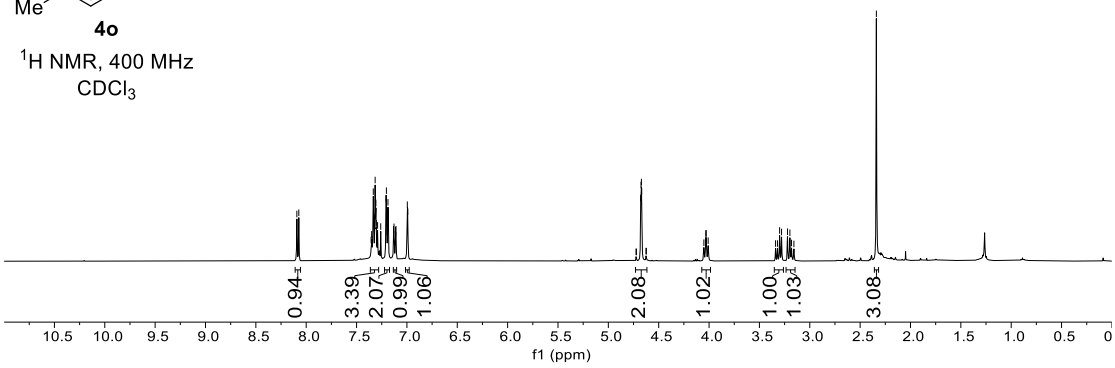




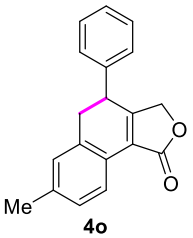




**4o**

$^{1}$H NMR, 400 MHz
$CDCl_3$

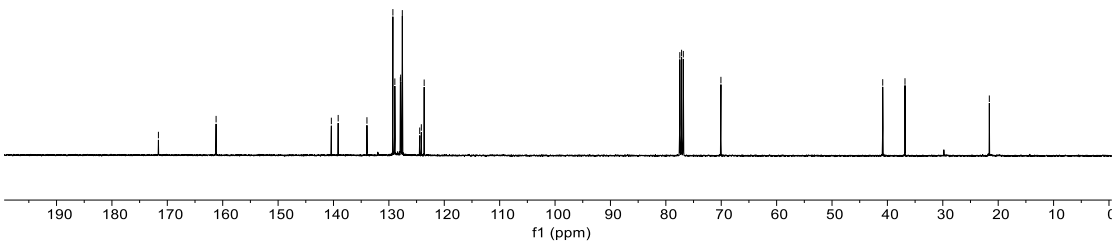


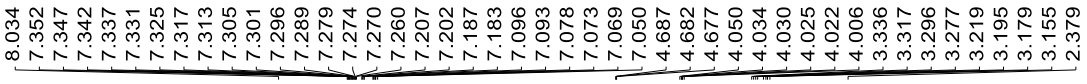


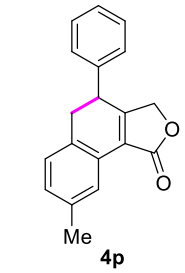



**4o**

$^{13}$C NMR, 100 MHz
$CDCl_3$

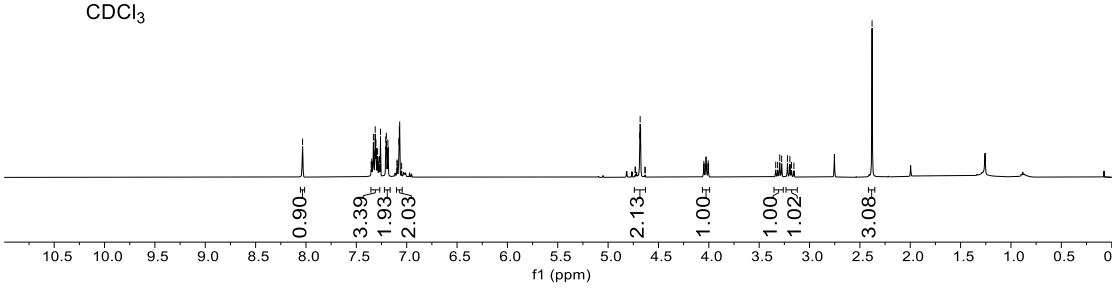




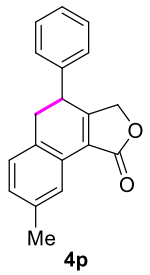




**4p**

$^{1}$H NMR, 400 MHz
$CDCl_3$

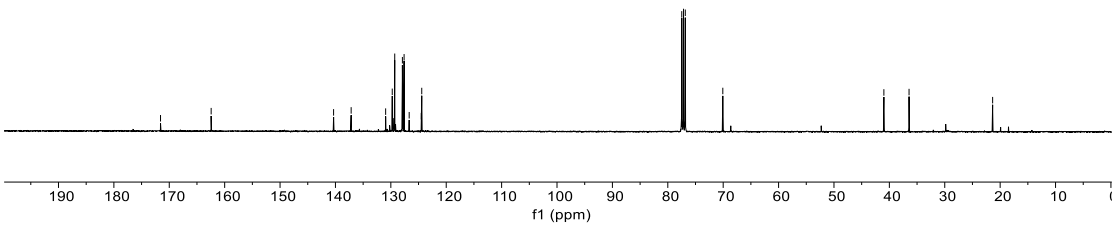


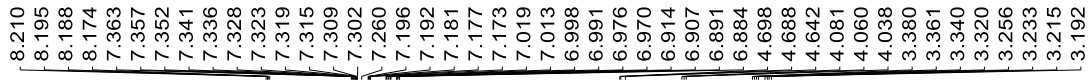


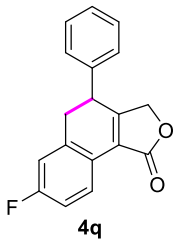



**4p**

$^{13}$C NMR, 100 MHz
$CDCl_3$



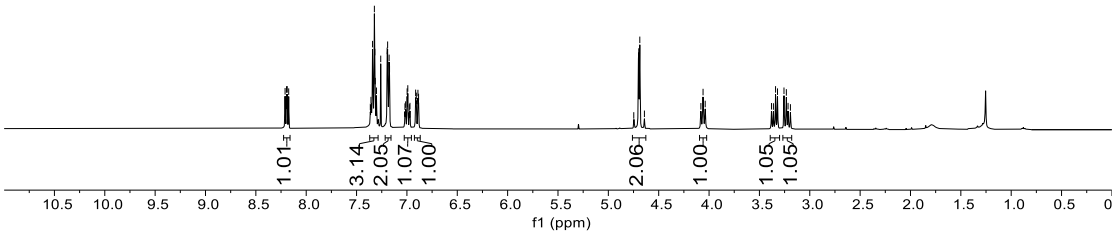


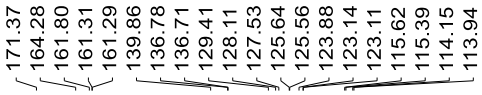



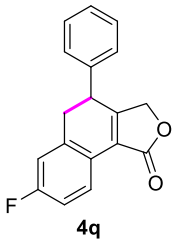

**4q**

$^{1}$H NMR, 400 MHz

$CDCl_3$



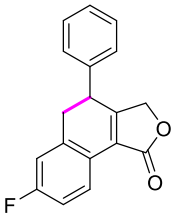




**4q**

$^{13}$C NMR, 100 MHz

$CDCl_3$

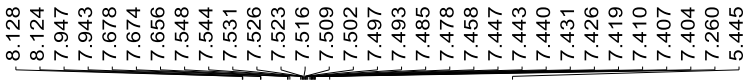


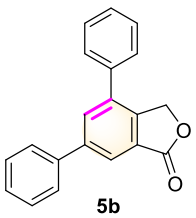
**4q**

$^{19}$F NMR, 376 MHz

$CDCl_3$



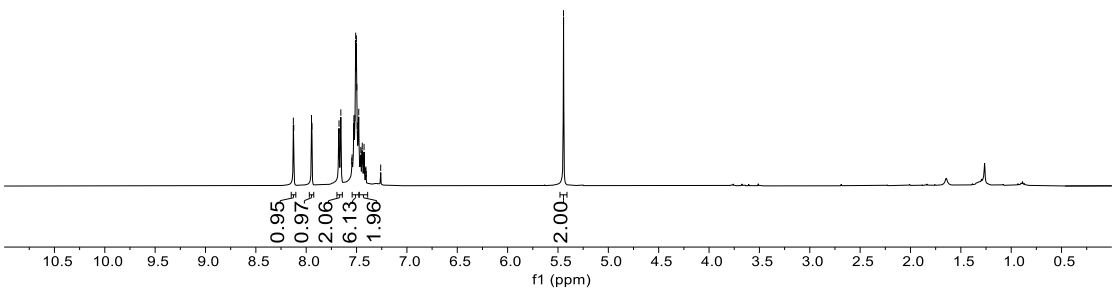



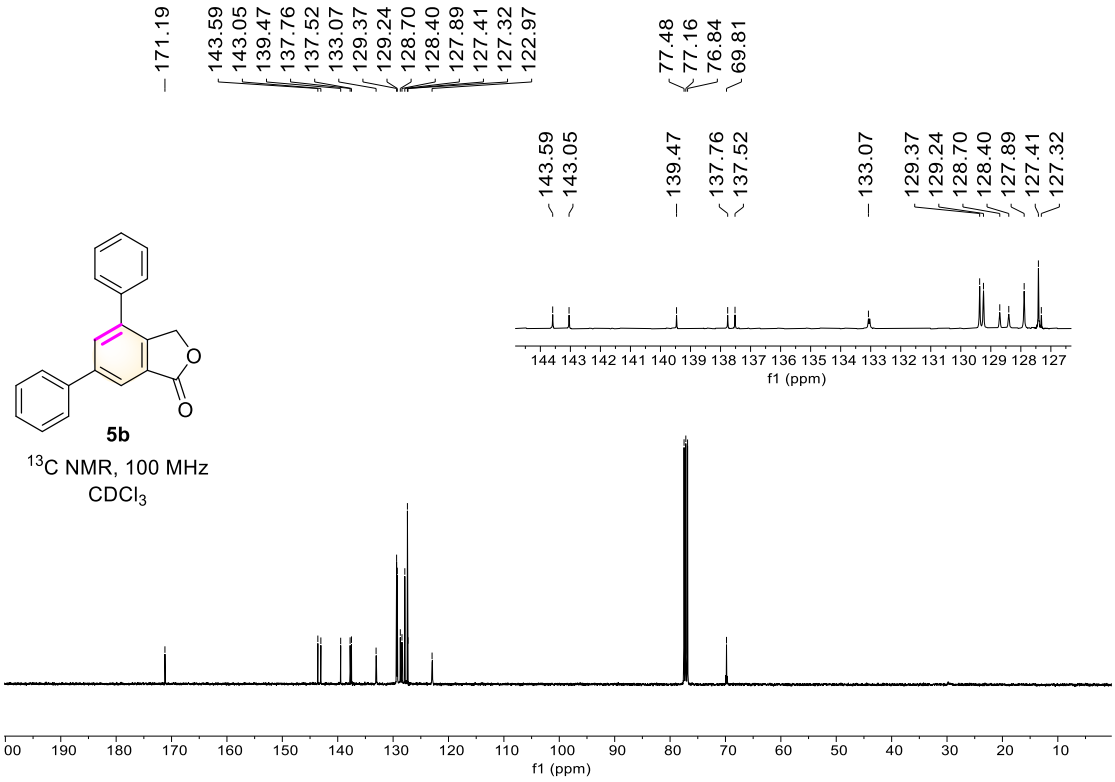



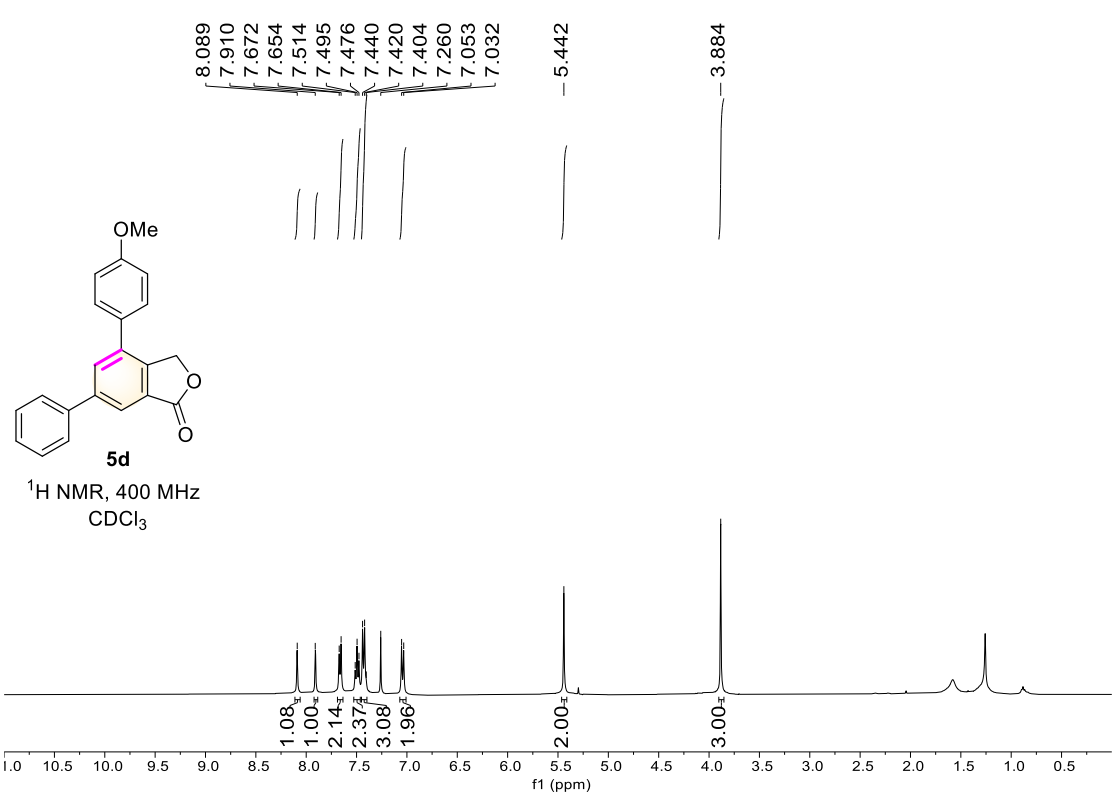
**5b**

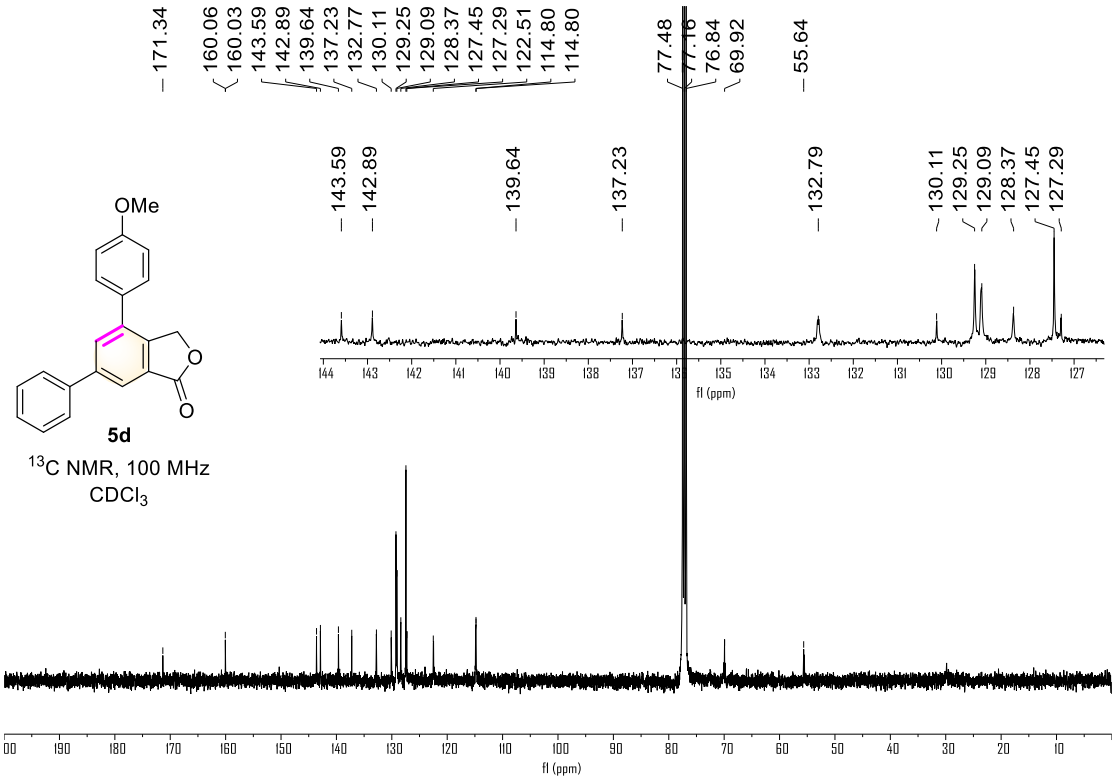
$^{1}$H NMR, 400 MHz

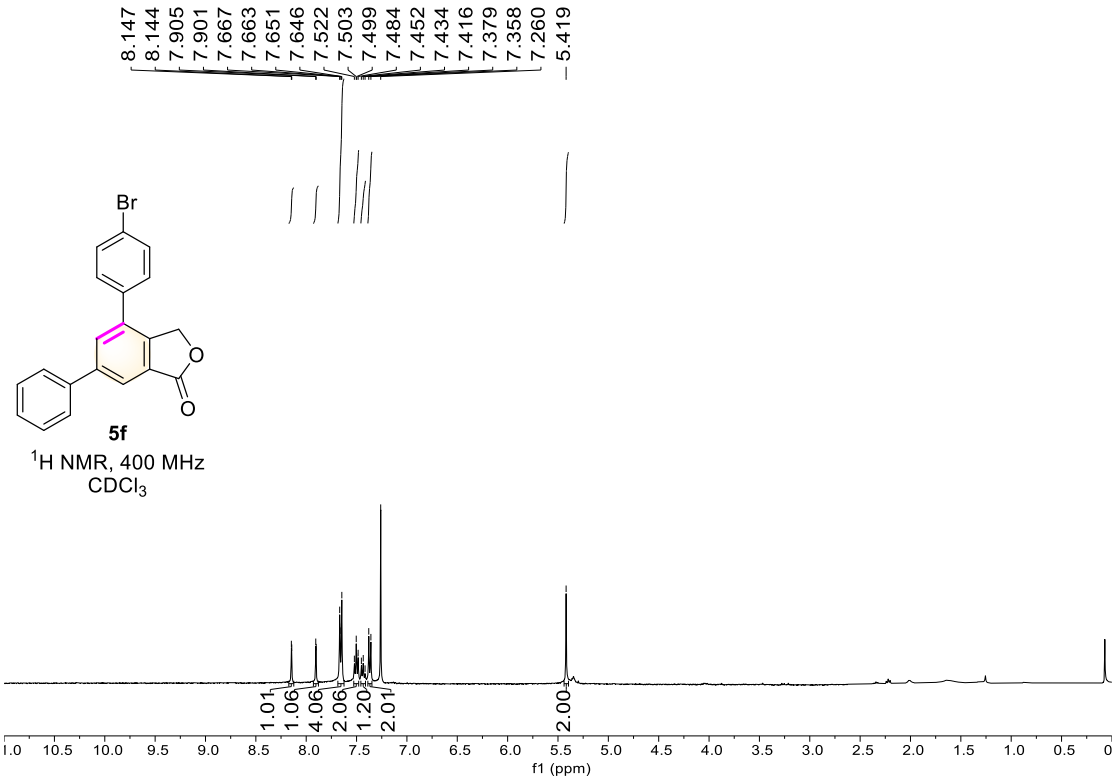
$CDCl_3$

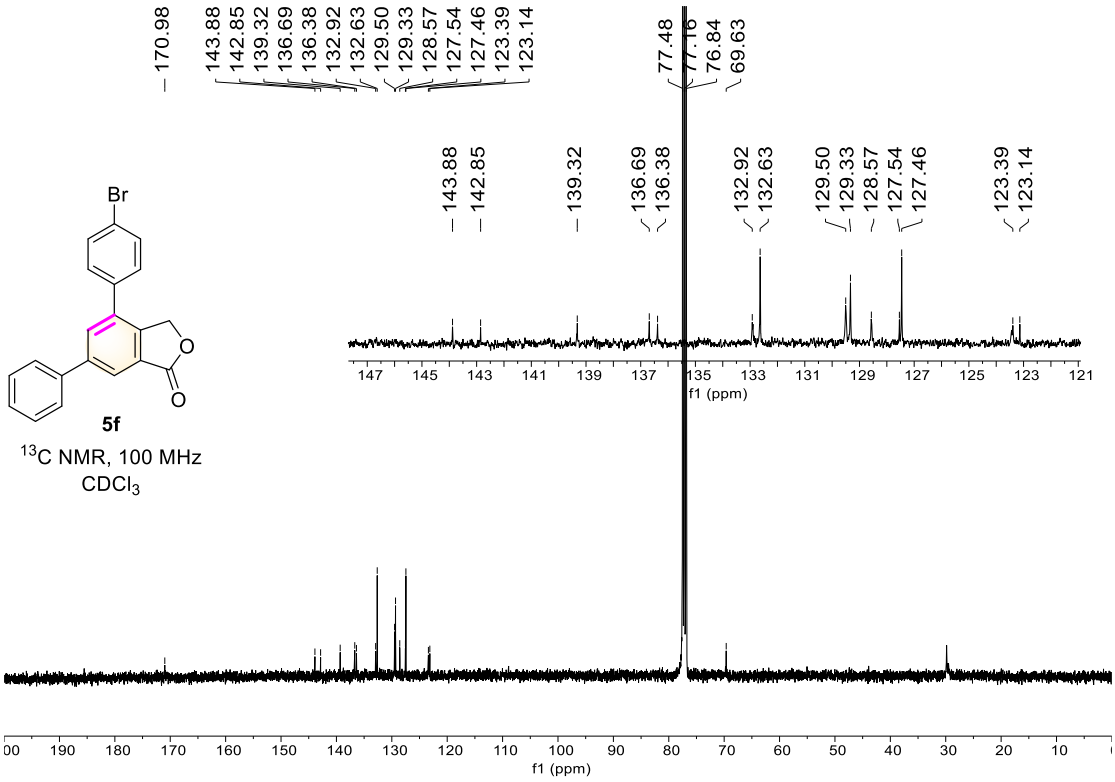



171.19
143.59
143.05
139.47
137.76
137.52
133.07
129.37
129.24
128.70
128.40
127.89
127.41
127.32
122.97
77.48
77.16
76.84
69.81
O
O
5b
13C NMR, 100 MHz
CDCl3
f1 (ppm)


8.089
7.910
7.672
7.654
7.514
7.495
7.476
7.440
7.420
7.404
7.260
7.053
7.032
5.442
3.884
OMe
O
O
5d
1H NMR, 400 MHz
CDCl3
1.08
1.00
2.14
2.37
3.08
1.96
2.00
3.00
f1 (ppm)


171.34
160.06
160.03
143.59
142.89
139.64
137.23
132.77
130.11
129.25
129.09
128.37
127.45
127.29
122.51
114.80
114.80
77.48
77.16
76.84
69.92
55.64
OMe
O
O
5d
13C NMR, 100 MHz
CDCl3
f1 (ppm)

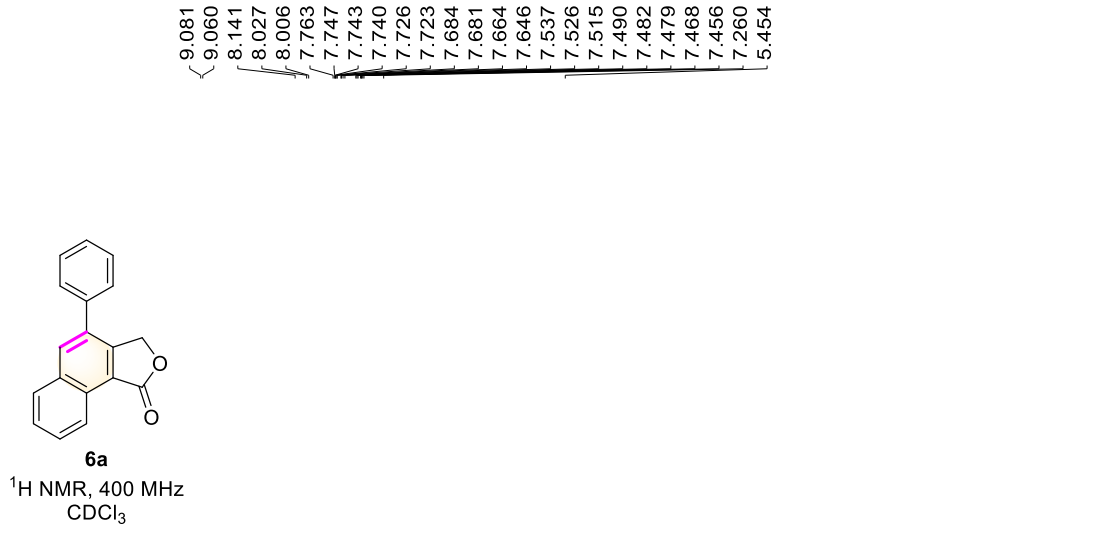

8.147
8.144
7.905
7.901
7.667
7.663
7.651
7.646
7.522
7.503
7.499
7.484
7.452
7.434
7.416
7.379
7.358
7.260
5.419
Br
O
O
5f
1H NMR, 400 MHz
CDCl3
1.01
1.06
4.06
2.06
1.20
2.01
2.00
f1 (ppm)




**5f**

$^{13}$C NMR, 100 MHz

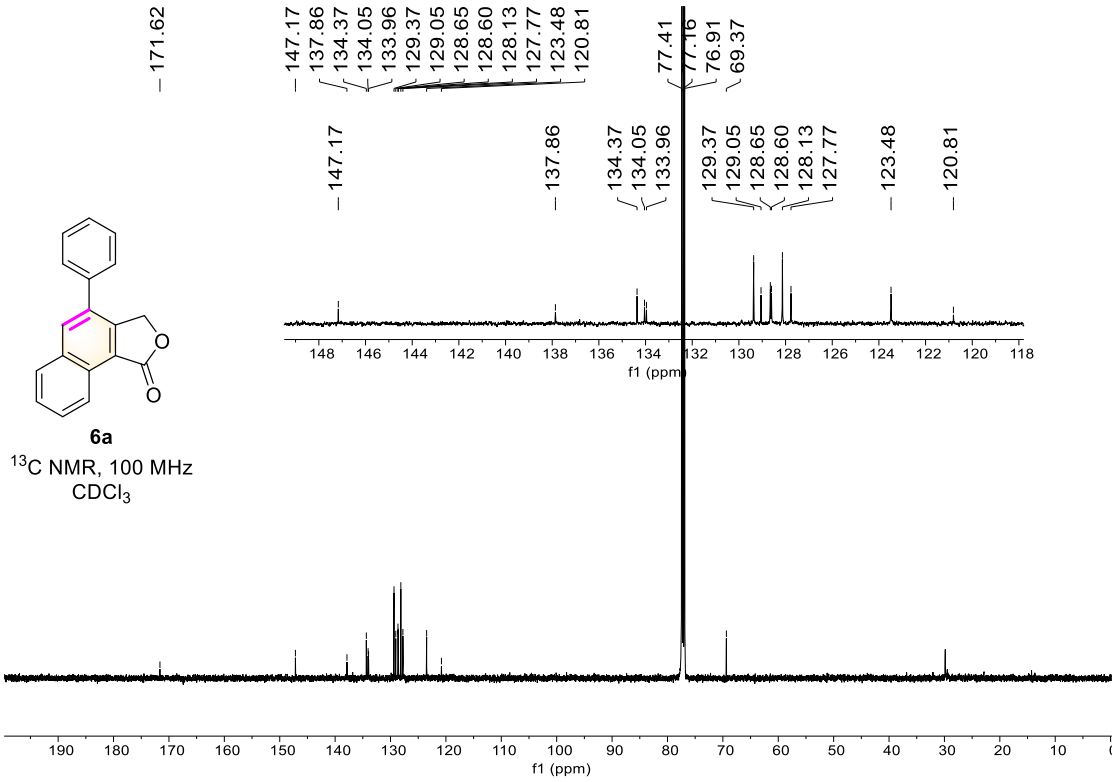
$CDCl_3$




**6a**

$^{1}$H NMR, 400 MHz

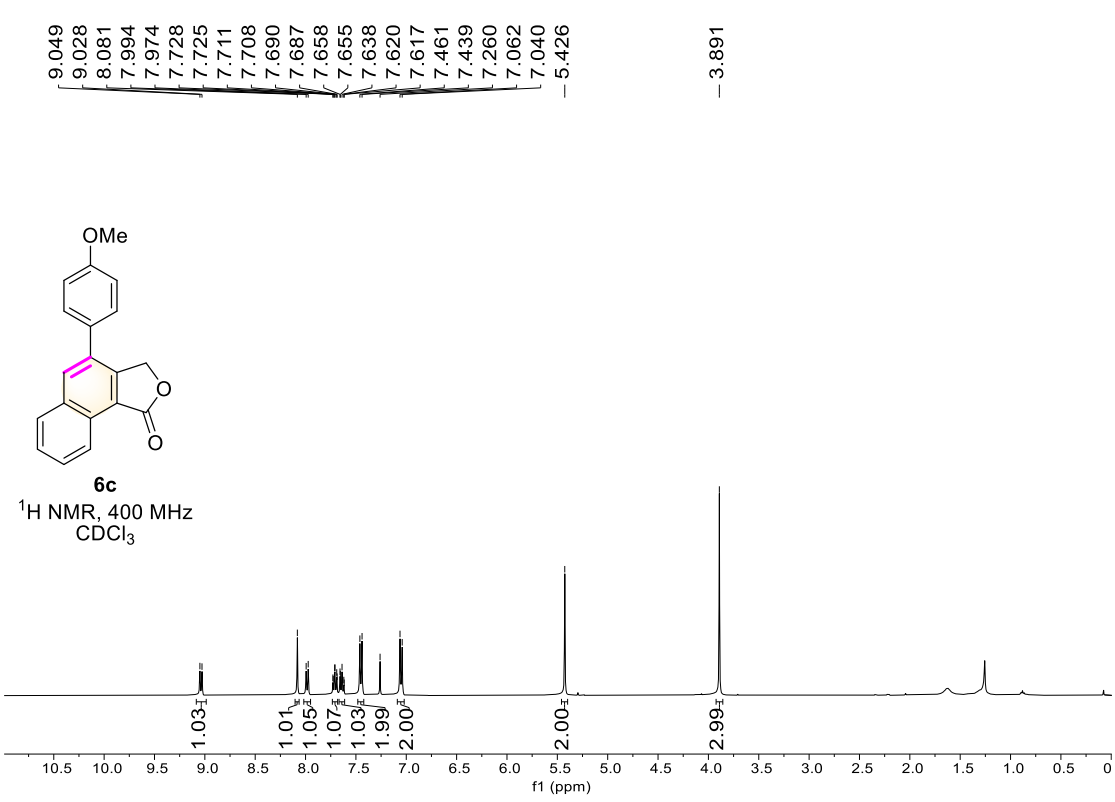
$CDCl_3$




**6a**

$^{13}C$ NMR, 100 MHz

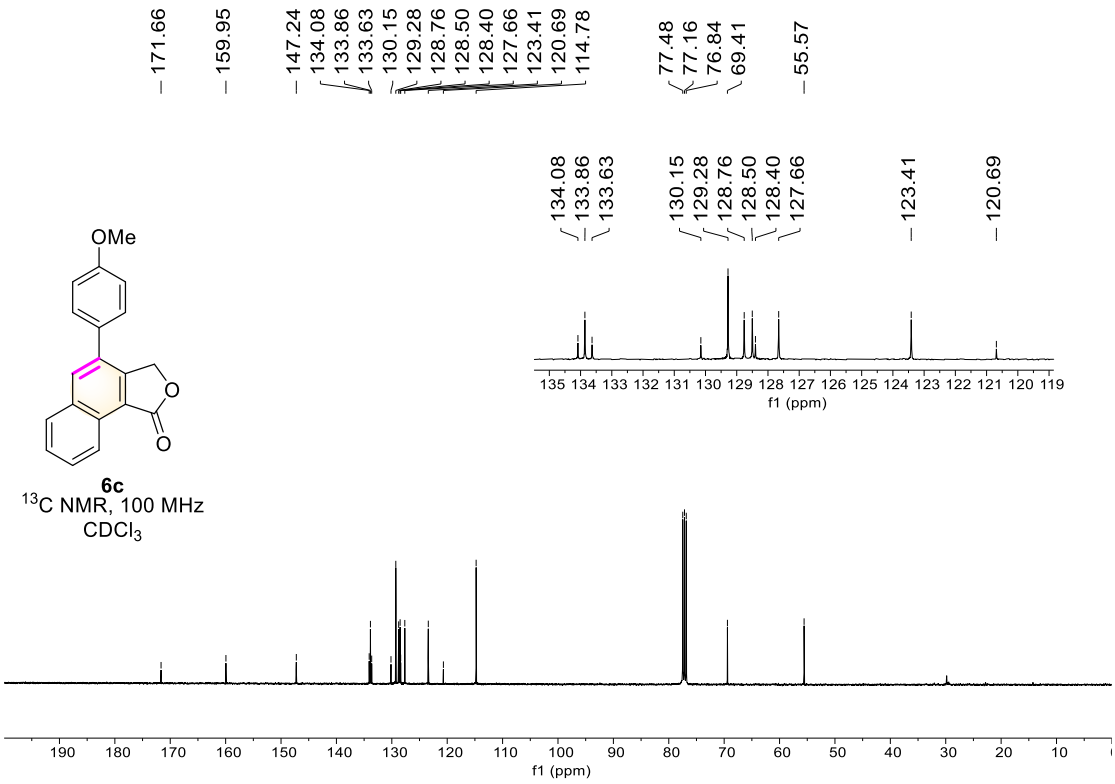
$CDCl_3$

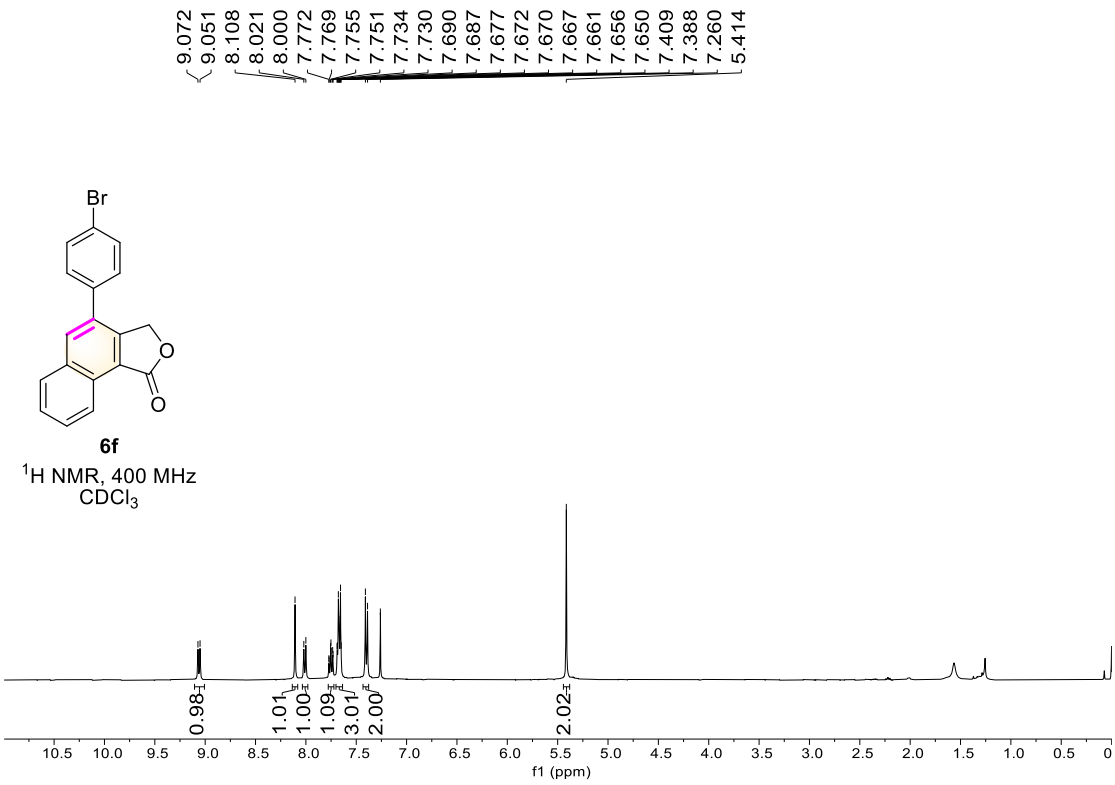


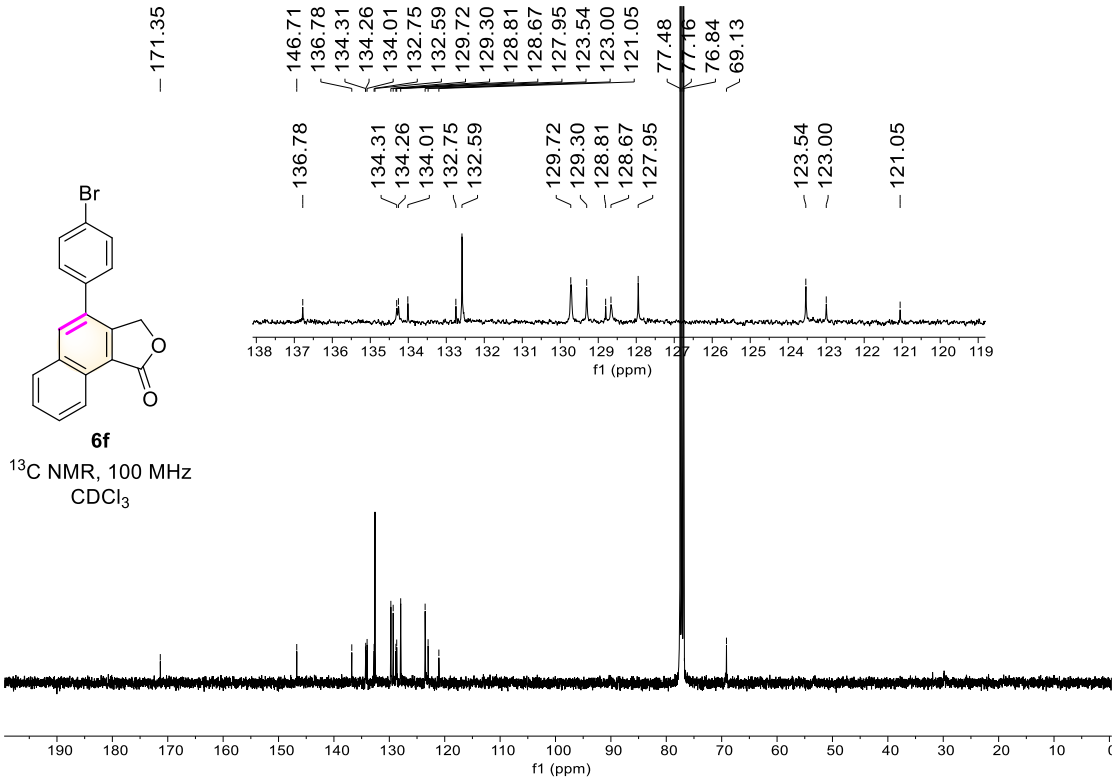

**6c**

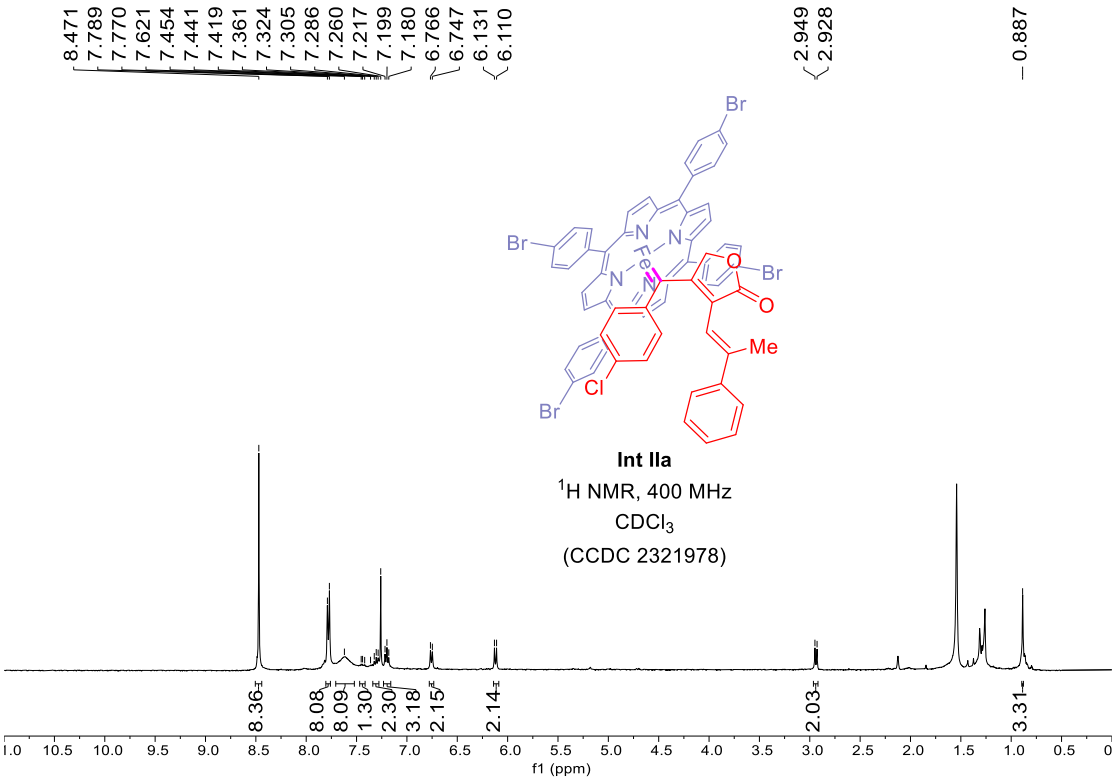
$^{1}H$ NMR, 400 MHz

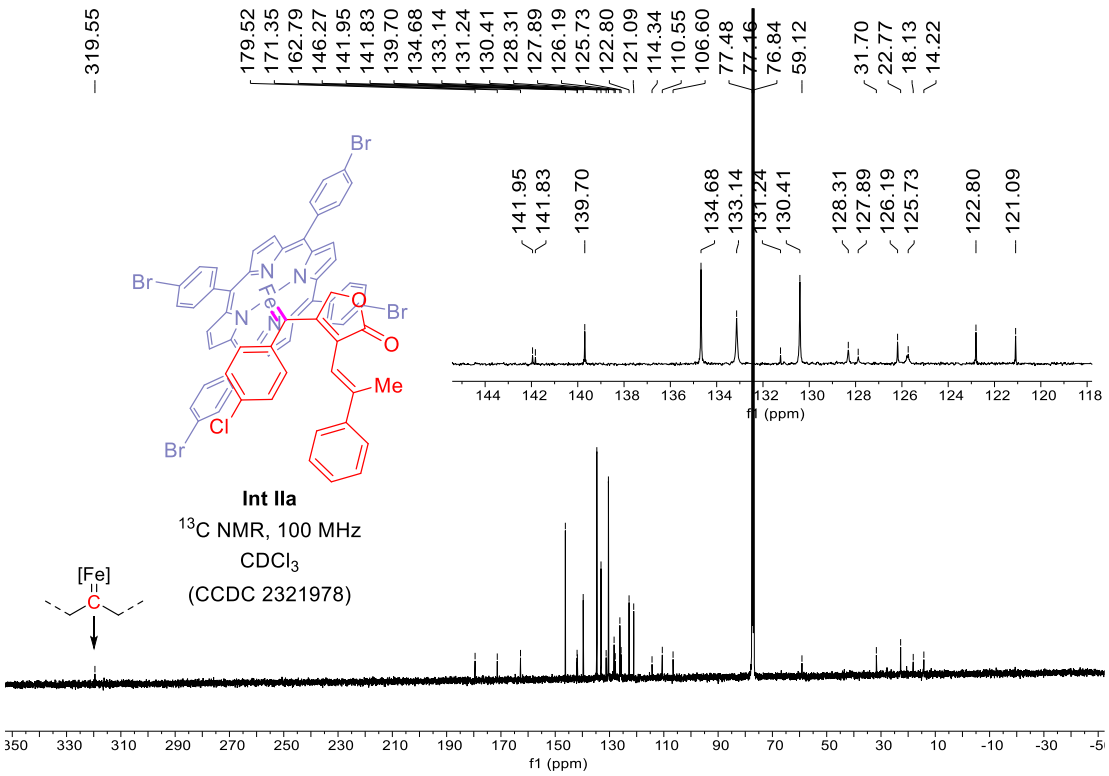
$CDCl_3$


171.66
159.95
147.24
134.08
133.86
133.63
130.15
129.28
128.76
128.50
128.40
127.66
123.41
120.69
114.78
77.48
77.16
76.84
69.41
55.57
OMe
O
O
6c
13C NMR, 100 MHz
CDCl3
f1 (ppm)


9.072
9.051
8.108
8.021
8.000
7.772
7.769
7.755
7.751
7.734
7.730
7.690
7.687
7.677
7.672
7.670
7.667
7.661
7.656
7.650
7.409
7.388
7.260
5.414
Br
O
O
6f
1H NMR, 400 MHz
CDCl3
0.98
1.01
1.00
1.09
3.01
2.00
2.02
f1 (ppm)


171.35
146.71
136.78
134.31
134.26
134.01
132.75
132.59
129.72
129.30
128.81
128.67
127.95
123.54
123.00
121.05
77.48
77.16
76.84
69.13
Br
O
O
6f
13C NMR, 100 MHz
CDCl3
f1 (ppm)


8.471
7.789
7.770
7.621
7.454
7.441
7.419
7.361
7.324
7.305
7.286
7.260
7.217
7.199
7.180
6.766
6.747
6.131
6.110
2.949
2.928
0.887
Br
Br
Br
Cl
Fe
N
O
Me
Int IIa
1H NMR, 400 MHz
CDCl3
(CCDC 2321978)
8.36
8.08
8.09
1.30
2.30
3.18
2.15
2.14
2.03
3.31
f1 (ppm)



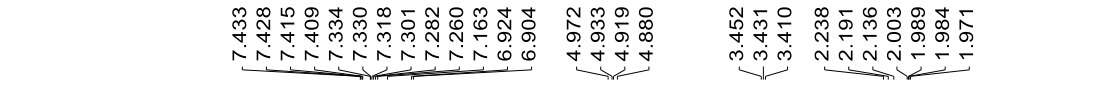

**Int IIa**

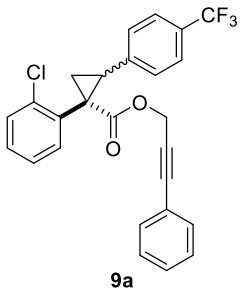
$^{13}$C NMR, 100 MHz

$CDCl_3$

(CCDC 2321978)



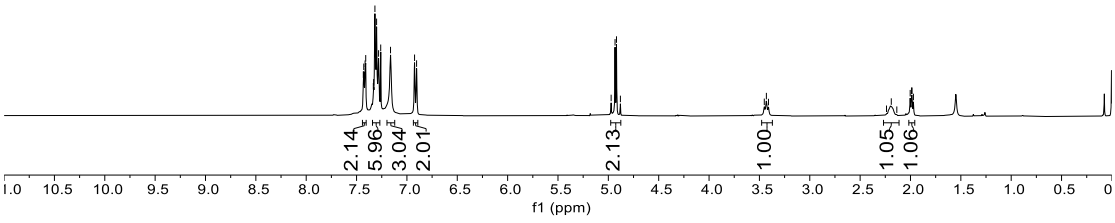



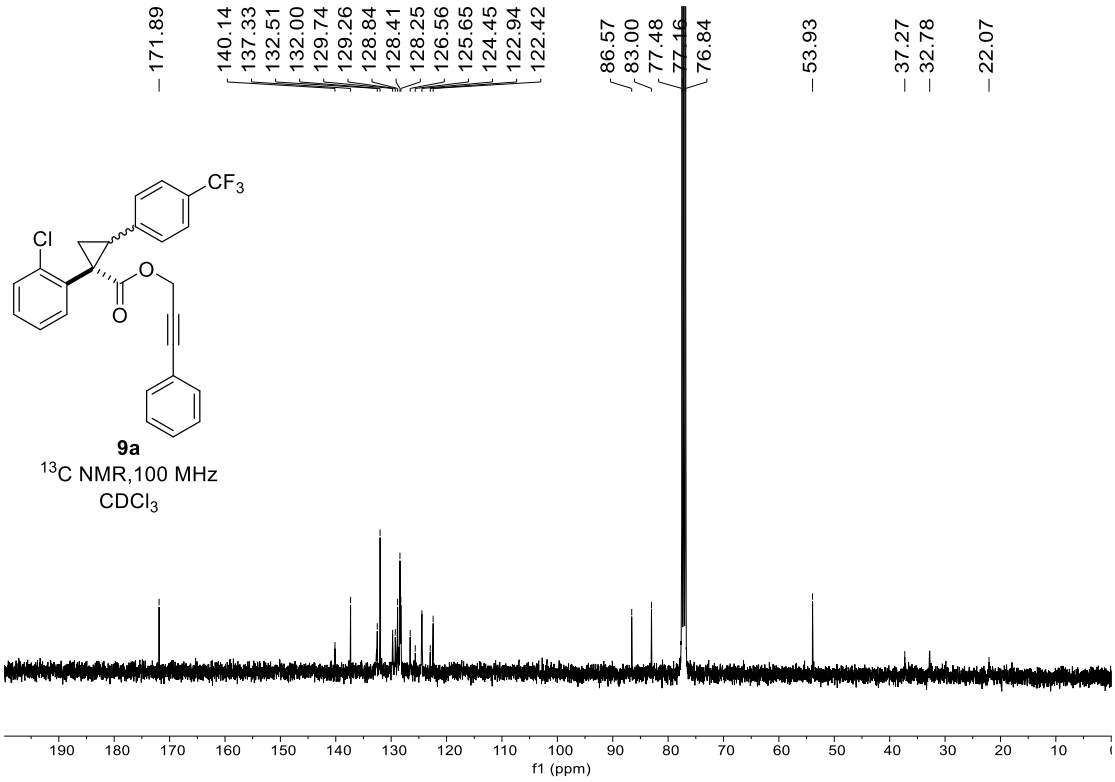



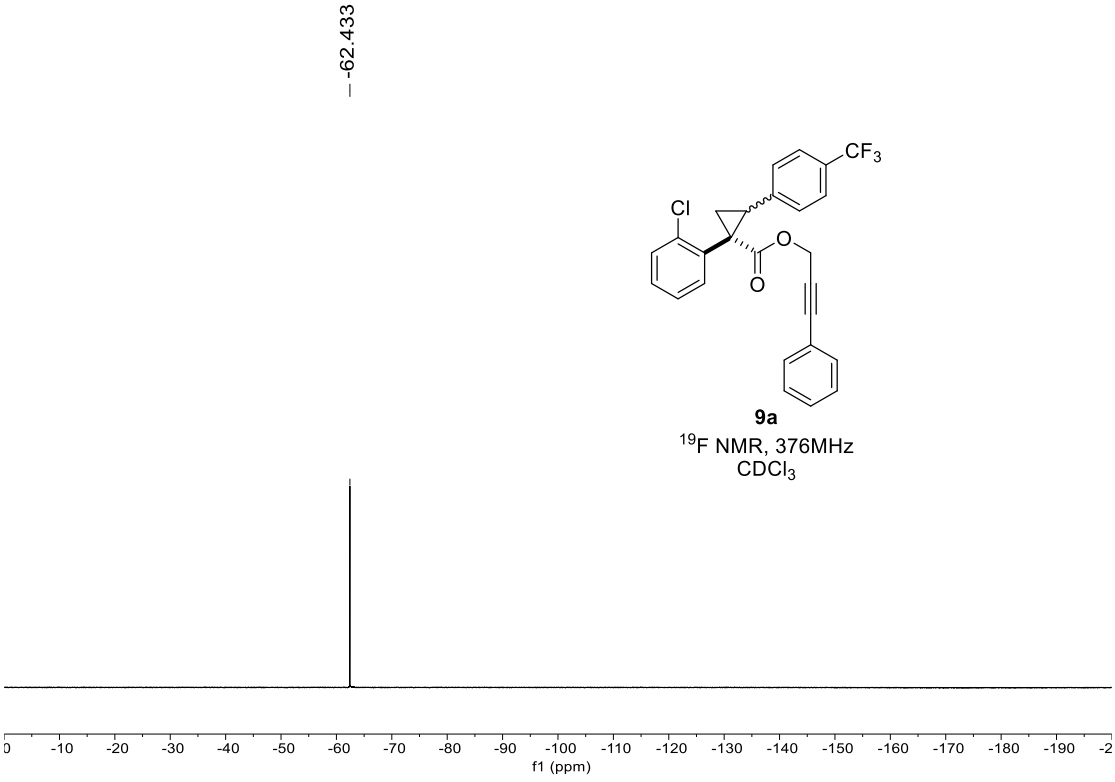

**9a**

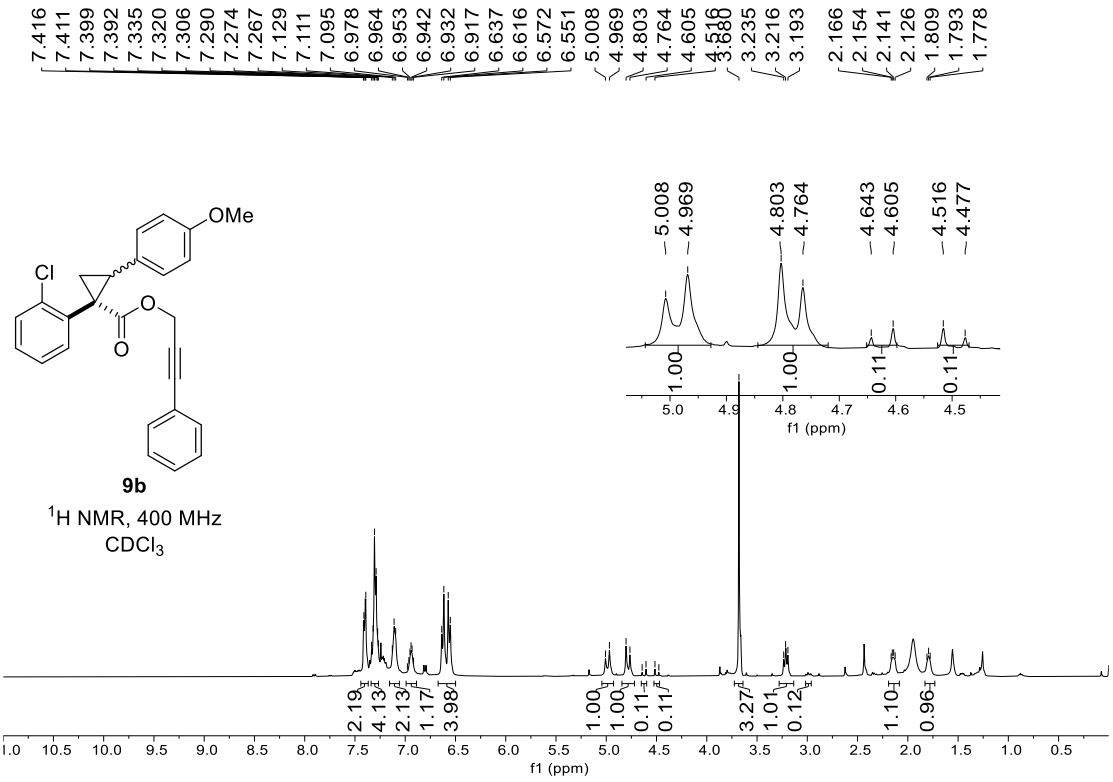
$^{1}$H NMR, 400 MHz

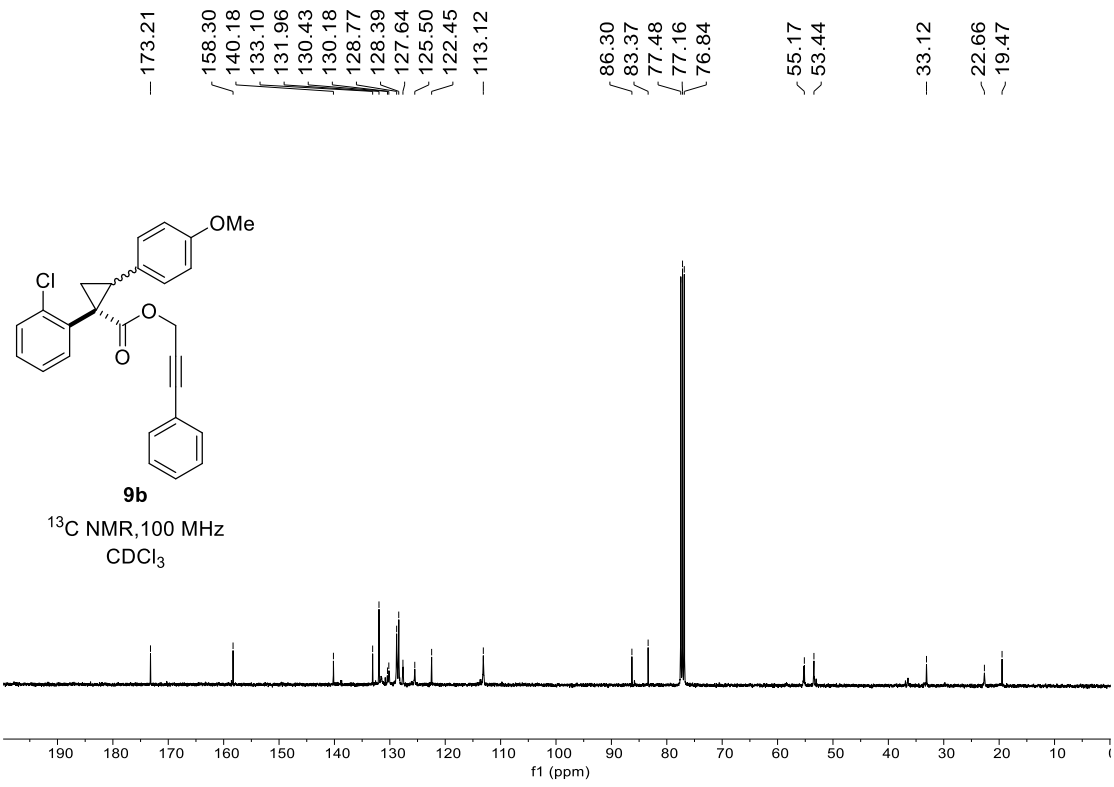
$CDCl_3$




171.89
140.14
137.33
132.51
132.00
129.74
129.26
128.84
128.41
128.25
126.56
125.65
124.45
122.94
122.42
86.57
83.00
77.48
77.16
76.84
53.93
37.27
32.78
22.07
CF3
Cl
O
O
9a
13C NMR,100 MHz
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

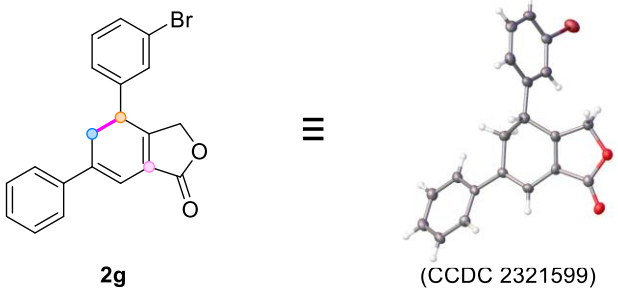

-62.433
CF3
Cl
O
O
9a
19F NMR, 376MHz
CDCl3
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)


7.416
7.411
7.399
7.392
7.335
7.320
7.306
7.290
7.274
7.267
7.129
7.111
7.095
6.978
6.964
6.953
6.942
6.932
6.917
6.637
6.616
6.572
6.551
5.008
4.969
4.803
4.764
4.605
4.516
3.880
3.235
3.216
3.193
2.166
2.154
2.141
2.126
1.809
1.793
1.778
OMe
Cl
O
O
9b
1H NMR, 400 MHz
CDCl3
5.008
4.969
4.803
4.764
4.643
4.605
4.516
4.477
1.00
1.00
0.11
0.11
f1 (ppm)
2.19
4.13
2.13
1.17
3.98
1.00
1.00
0.11
0.11
3.27
1.01
0.12
1.10
0.96
f1 (ppm)


173.21
158.30
140.18
133.10
131.96
130.43
130.18
128.77
128.39
127.64
125.50
122.45
113.12
86.30
83.37
77.48
77.16
76.84
55.17
53.44
33.12
22.66
19.47
OMe
Cl
O
O
9b
13C NMR,100 MHz
CDCl3
f1 (ppm)

## Single-Crystal X-ray Diffraction

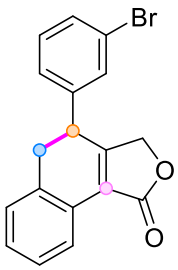
***Single-Crystal X-ray Diffraction of 2g.***




**2g** ≡ (CCDC 2321599)

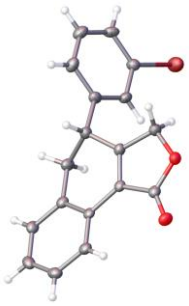
| | | | |
|---|---|---|---|
| Bond precision: | C-C = 0.0067 Å | | Wavelength = 1.54184 |
| Cell: | a = 9.9225(2) | b = 11.6881(3) | c = 15.1944(3) |
| | alpha = 110.104(2) | beta = 102.399(2) | gamma = 100.788(2) |
| Temperature | | 100 K | |
| | Calculated | | Reported |
| Volume | 1549.40(7) | | 1549.39(6) |
| Space group | *P -1* | | *P -1* |
| Hall group | *-P 1* | | *-P 1* |
| Moiety formula | $C_{20}H_{15}BrO_2$ | | $C_{20}H_{15}BrO_2$ |
| Sum formula | $C_{20}H_{15}BrO_2$ | | $C_{20}H_{15}BrO_2$ |
| Mr | 367.22 | | 367.23 |
| Dx, g/cm$^{-3}$ | 1.574 | | 1.574 |
| Z | 4 | | 4 |
| Mu (mm$^{-1}$) | 3.670 | | 3.670 |
| F000 | 744.0 | | 744.0 |
| F000' | 743.06 | | |
| h, k, lmax | 11, 13, 17 | | 11, 13, 17 |
| Nref | 5283 | | 5193 |
| Tmin, Tmax | 0.676, 0.746 | | 0.592, 1.000 |
| Tmin' | 0.549 | | |
| Correction method= # Reported T Limits: Tmin = 0.592 Tmax = 1.000 | | | |
| AbsCorr = MULTI-SCAN | | | |
| Data completeness = 0.983 | | Theta (max) = 65.089 | |
| R (reflections) = 0.0541 (4479) | | wR2 (reflections) = 0.1412 (5193) | |
| S = 1.052 | | Npar= 415 | |

***Single-Crystal X-ray Diffraction of 4h.***




**4h**

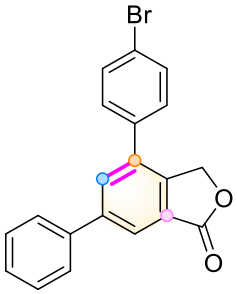
≡



(CCDC 2351137)

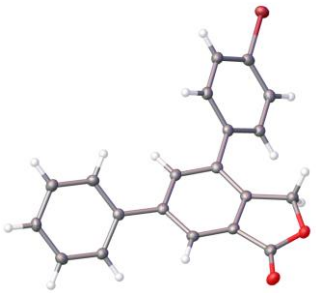
| | | | |
|---|---|---|---|
| Bond precision: | C-C = 0.0040 Å | | Wavelength = 1.54184 |
| Cell: | a = 7.3007(2) | b = 9.1847(2) | c = 21.3007(5) |
| | alpha = 90 | beta = 89.975(2) | gamma = 90 |
| Temperature | | 100 K | |
| | Calculated | | Reported |
| Volume | 1428.31(6) | | 1428.31(6) |
| Space group | *P2$_1$/n* | | *P12$_1$/n1* |
| Hall group | *-P 2yn* | | *-P 2yn* |
| Moiety formula | $C_{18}H_{13}BrO_2$ | | $C_{18}H_{13}BrO_2$ |
| Sum formula | $C_{18}H_{13}BrO_2$ | | $C_{18}H_{13}BrO_2$ |
| Mr | 341.18 | | 341.19 |
| Dx, g/cm$^{-3}$ | 1.587 | | 1.587 |
| Z | 4 | | 4 |
| Mu (mm$^{-1}$) | 3.930 | | 3.930 |
| F000 | 688.0 | | 688.0 |
| F000' | 686.93 | | |
| h, k, lmax | 9, 11, 26 | | 9, 11, 26 |
| Nref | 2982 | | 2898 |
| Tmin, Tmax | 0.431, 0.456 | | 0.634, 1.000 |
| Tmin' | 0.326 | | |
| Correction method= # Reported T Limits: Tmin = 0.634 Tmax = 1.000 | | | |
| AbsCorr = MULTI-SCAN | | | |
| Data completeness = 0.972 | | Theta(max) = 75.560 | |
| R (reflections) = 0.0418 (2846) | | wR2 (reflections) = 0.1053 (2898) | |
| S = 1.079 | | Npar = 190 | |

***Single-Crystal X-ray Diffraction of 5f.***




**5f**

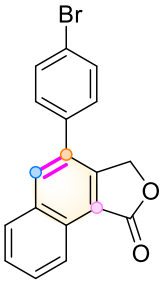
≡



(CCDC 2321605)

| | | | |
|---|---|---|---|
| Bond precision: | C-C = 0.0020 Å | | Wavelength = 1.54184 |
| Cell: | a = 16.4382(2) | b = 7.3302(1) | c = 25.4467(3) |
| | alpha = 90 | beta = 90 | gamma = 90 |
| Temperature | | 100 K | |
| | Calculated | | Reported |
| Volume | 3066.21(7) | | 3066.21(7) |
| Space group | *P b c a* | | *P b c a* |
| Hall group | *-P 2ac 2ab* | | *-P 2ac 2ab* |
| Moiety formula | $C_{20}H_{13}BrO_2$ | | $C_{20}H_{13}BrO_2$ |
| Sum formula | $C_{20}H_{13}BrO_2$ | | $C_{20}H_{13}BrO_2$ |
| Mr | 365.20 | | 365.21 |
| Dx, g/cm$^{-3}$ | 1.582 | | 1.582 |
| Z | 8 | | 8 |
| Mu (mm$^{-1}$) | 3.709 | | 3.709 |
| F000 | 1472.0 | | 1472.0 |
| F000' | 1470.13 | | |
| h, k, lmax | 20, 9, 31 | | 20, 9, 31 |
| Nref | 3150 | | 3059 |
| Tmin, Tmax | 0.539, 0.831 | | 0.695, 1.000 |
| Tmin' | 0.454 | | |
| Correction method= # Reported T Limits: Tmin = 0.695 Tmax = 1.000 | | | |
| AbsCorr = MULTI-SCAN | | | |
| Data completeness = 0.971 | | Theta(max) = 74.790 | |
| R (reflections) = 0.0242 (2901) | | wR2 (reflections) = 0.0658 (3059) | |
| S = 1.068 | | Npar = 209 | |

***Single-Crystal X-ray Diffraction of 6f.***



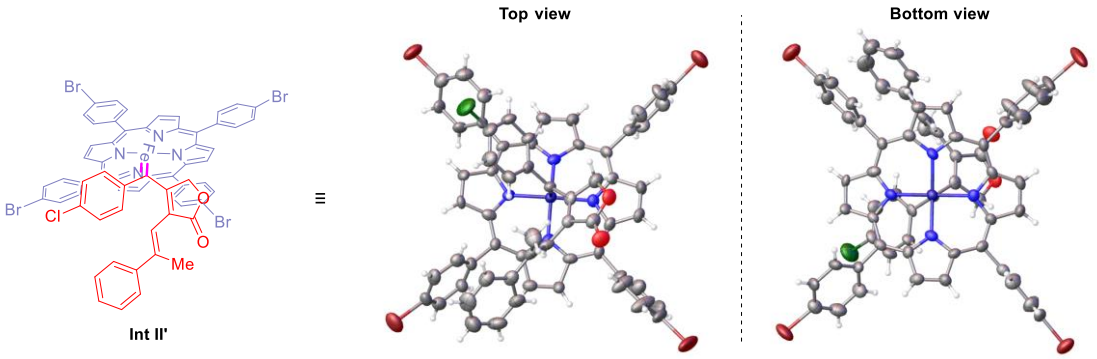

**6f**

≡

(CCDC 2351106)

| | | | |
|---|---|---|---|
| Bond precision: | C-C = 0.0122 Å | | Wavelength = 1.54184 |
| Cell: | a = 9.6930(4) | b = 9.7666(3) | c = 14.6505(4) |
| | alpha = 87.001(2) | beta = 86.137(3) | gamma = 75.644(3) |
| Temperature | | 100 K | |
| | Calculated | | Reported |
| Volume | 1339.66(8) | | 1339.66(8) |
| Space group | *P -1* | | *P -1* |
| Hall group | *-P 1* | | *-P 1* |
| Moiety formula | $C_{18}H_{11}BrO_2$ | | 2 ($C_{18}H_{11}BrO_2$) |
| Sum formula | $C_{18}H_{11}BrO_2$ | | $C_{36}H_{22}Br_2O_4$ |
| Mr | 339.17 | | 678.35 |
| Dx, g/cm$^{-3}$ | 1.682 | | 1.682 |
| Z | 4 | | 2 |
| Mu (mm$^{-1}$) | 4.190 | | 4.190 |
| F000 | 680.0 | | 680.0 |
| F000' | 678.93 | | |
| h, k, lmax | 11, 11, 17 | | 11, 11, 17 |
| Nref | 4754 | | 4732 |
| Tmin, Tmax | 0.288, 0.433 | | 0.676, 1.000 |
| Tmin' | 0.185 | | |
| Correction method= # Reported T Limits: Tmin = 0.676 Tmax = 1.000 | | | |
| AbsCorr = MULTI-SCAN | | | |
| Data completeness = 0.995 | | Theta(max) = 66.592 | |
| R (reflections) = 0.1056 (4084) | | wR2 (reflections) = 0.2836 (4732) | |
| S = 1.190 | | Npar = 379 | |

***Single-Crystal X-ray Diffraction of Int IIa.***




(CCDC 2321978)

| | | | |
|---|---|---|---|
| Bond precision: | C-C = 0.0020 Å | | Wavelength = 1.54184 |
| Cell: | a = 16.4382(2) | b = 7.3302(1) | c = 25.4467(3) |
| | alpha = 90 | beta = 90 | gamma = 90 |
| Temperature | | 100 K | |
| | Calculated | | Reported |
| Volume | 3066.21(7) | | 3066.21(7) |
| Space group | *P b c a* | | *P b c a* |
| Hall group | *-P 2ac 2ab* | | *-P 2ac 2ab* |
| Moiety formula | $C_{20}H_{13}BrO_2$ | | $C_{20}H_{13}BrO_2$ |
| Sum formula | $C_{20}H_{13}BrO_2$ | | $C_{20}H_{13}BrO_2$ |
| Mr | 365.20 | | 365.21 |
| Dx, g/cm$^{-3}$ | 1.582 | | 1.582 |
| Z | 8 | | 8 |
| Mu (mm$^{-1}$) | 3.709 | | 3.709 |
| F000 | 1472.0 | | 1472.0 |
| F000' | 1470.13 | | |
| h, k, lmax | 20, 9, 31 | | 20, 9, 31 |
| Nref | 3150 | | 3059 |
| Tmin, Tmax | 0.539, 0.831 | | 0.695, 1.000 |
| Tmin' | 0.454 | | |
| Correction method= # Reported T Limits: Tmin = 0.695 Tmax = 1.000 | | | |
| AbsCorr = MULTI-SCAN | | | |
| Data completeness = 0.971 | | Theta(max) = 74.790 | |
| R (reflections) = 0.0242 (2901) | | wR2 (reflections) = 0.0658 (3059) | |
| S = 1.068 | | Npar = 209 | |

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