Electronic Supporting Information

Preparation of iodonium ylides: Probing the fluorination of 1,3-dicarbonyl compounds with a fluoroiodane

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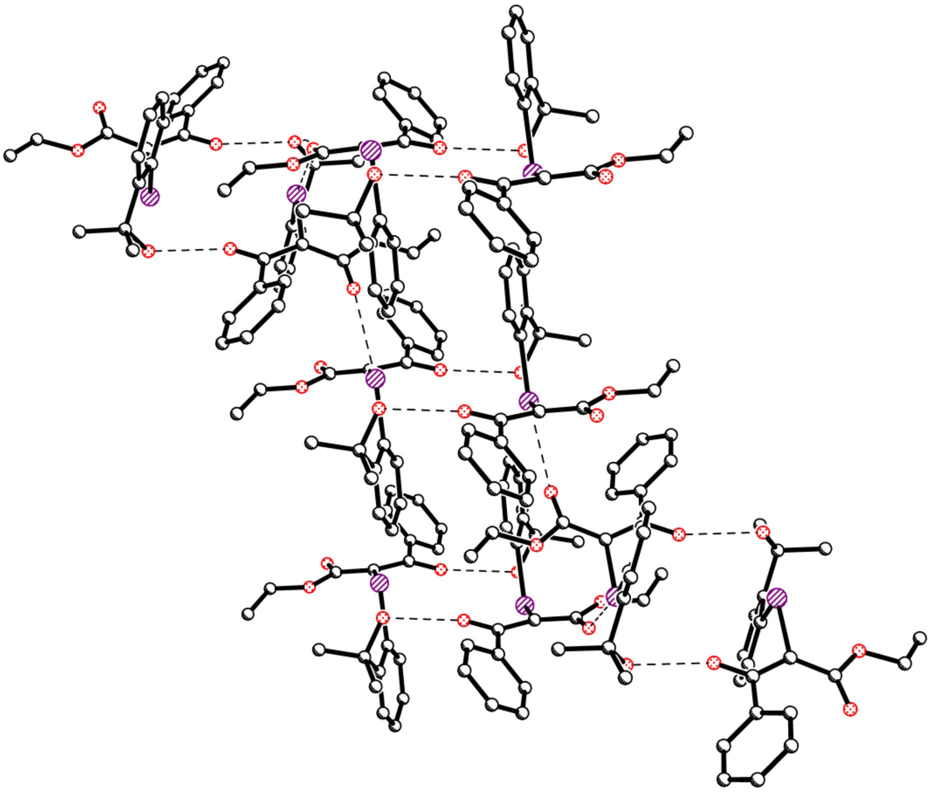
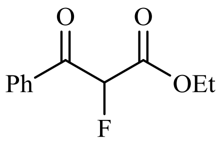


Figure 4 Solid-state packing diagram of iodonium ylide **8** showing intermolecular hydrogen bonding between O(1) and O(2)’ (2.654(5) Å) and intermolecular I(1)-O(3)’’ interactions (2.975(4) Å)

Experimental

The ^{1}H, ^{19}F and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX 400 spectrometer at 400.13, 376.46 and 100.62 MHz respectively unless otherwise stated when the ^{1}H and ^{13}C{^{1}H} were recorded on a Bruker AV 500 spectrometer at 500.13 and 125.76 MHz respectively. The ^{1}H, ^{19}F and ^{13}C{^{1}H} NMR spectra were referenced to external $SiMe_4$ (^{1}H), external $CFCl_3$ (^{19}F) and to external $SiMe_4$ (^{13}C) using the high frequency positive convention. Elemental analyses were performed by the Elemental Analysis Service at the University of North London. Electron impact (EI) mass spectra were recorded on a Kratos concept 1 H, double focussing, forward geometry mass spectrometer, Atmospheric Solids Analysis Probe (ASAP) mass spectra were recorded on a Xevo QTof mass spectrometer (Waters) and Electrospray (ES) mass spectra were obtained by LC-MS using a Xevo QTof mass spectrometer (Waters) coupled to an Acquity LC system (Waters) with an Acquity UPLC BEH C18 column (2.1 x 50 mm). X-ray crystallography data were collected on a Bruker Apex SMART 2000 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

Procedure for the fluorination of ethyl 3-oxo-3-phenylpropanoate 5 (Table 1, Entries 1 and 2)



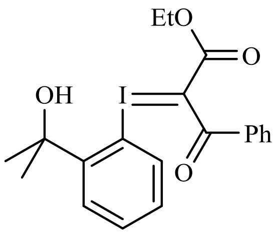
The flask was charged with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.400 g, 1.44 mmol), dry dichloromethane (1.2 mL), $Et_3N.3HF$ (0.31 mL, 1.92 mmol) and ethyl 3-oxo-3-phenylpropanoate **5** (0.12 mL, 0.72 mmol). The flask was then sealed and heated to 40 ^{o}C (oil bath temperature) for 24 h. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give the crude product which was analysed by ^{1}H and ^{19}F NMR spectroscopy. In Entry 1 the crude product was purified by column chromatography on silica gel using 5 % ethyl acetate in hexane to give ethyl 2-fluoro-3-oxo-3-phenylpropanoate **6** as a yellow oil (0.095 g, 63%). The characterisation data is in agreement with the literature.[3a] δ_H ($CDCl_3$) 1.17 (3H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 4.21 (2H, m_{AB}, dq, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 7.0 Hz, OCH_AH_B), 5.80 (1H, d, $^2J_{HF}$ = 50.0 Hz, CHF), 7.42 (2H, t, $^3J_{HH}$ = 8.0 Hz, ArH), 7.55 (1H, t, $^3J_{HH}$ = 8.0 Hz, ArH), 7.95 (2H, d, $^3J_{HH}$ = 8.0 Hz, ArH); δ_F ($CDCl_3$) -190.4 (s); δ_C ($CDCl_3$) 14.5 (CH_3), 62.9 (CH_2), 90.0 (d, $^1J_{CF}$ = 197.2 Hz, CH), 128.8 (CH), 129.5 (CH), 133.4 (C), 134.5 (CH), 164.9 (d, $^2J_{CF}$ = 24.1 Hz, CO), 189.5 (d, $^2J_{CF}$ = 20.1 Hz, CO); *m/z* (ASAP) 211.0760 (MH^+, $C_{11}H_{12}FO_3$ requires 211.0770, 100 %).

Procedure for the fluorination of ethyl 3-oxo-3-phenylpropanoate 5 (Table 1, Entry 3)

The flask was charged with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.400 g, 1.44 mmol), dry dichloromethane (1.2 mL) and ethyl 3-oxo-3-phenylpropanoate **5** (0.12 mL, 0.72 mmol). The flask was then sealed and heated to 40 ^{o}C (oil bath temperature) for 24 h. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give the crude product which was analysed by ^{1}H and ^{19}F NMR spectroscopy. The crude product was purified by column chromatography on silica gel using 5 % ethyl acetate in hexane to give ethyl 2-fluoro-3-oxo-3-phenylpropanoate **6** as a yellow oil (0.015 g, 10%).

Procedure for the reaction of ethyl 3-oxo-3-phenylpropanoate 5 with fluoroiodane 1 under basic conditions (Table 1, Entries 4-6)

A small Schlenk flask was charged with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **1** (0.44 g, 1.58 mmol), the required amount of spray-dried potassium fluoride, dry CH_3CN (1.3 mL) and ethyl 3-oxo-3-phenylpropanoate **5** (0.14 mL, 0.79 mmol) under nitrogen. The flask was sealed and stirred at the required temperature (oil bath

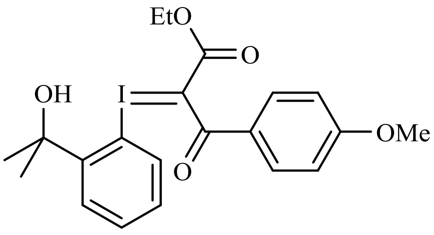


temperature) for 24 hours. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give the crude product which was analysed by ^{1}H and ^{19}F NMR spectroscopy. In Entry 6 purification by column chromatography (10% ethyl acetate in petroleum ether 40-60 then 100% EtOAc) followed by washing with diethyl ether gave iodonium ylide **8** as a white solid (0.15 g, 42%). Crystals suitable for X-ray crystallography were grown by slow evaporation of a diethyl ether solution containing the iodonium ylide. mp 126-127 °C. (Found: C, 53.00; H, 4.69. Calc. for $C_{20}H_{21}IO_4$: C, 53.11; H, 4.68%). δ_H ($CDCl_3$, 500 MHz) 0.88 (3H, t, $^{3}J_{HH}$ = 7.3 Hz, OCH_2CH_3), 1.48 (6H, s, 2 x CH_3), 3.89 (2H, q, $^{3}J_{HH}$ = 7.3 Hz, OCH_2CH_3), 6.57 (1H, br s, OH), 7.22-7.25 (2H, m, ArH), 7.36-7.41 (4H, m, ArH), 7.53 (3H, m, ArH); δ_C ($CDCl_3$, 126 MHz) 14.0 (CH_3), 29.8 (2 x CH_3), 60.3 (CH_2), 73.6 (C), 78.5 (C=I), 109.8 (ArCI), 127.27 (CH), 127.30 (CH), 127.4 (CH), 127.9 (CH), 129.2 (CH), 129.5 (CH), 129.7 (CH), 140.7 (C), 146.6 (C), 166.2 (CO), 189.1 (CO); *m/z* (ES) 475.0376 (MNa^+, $C_{20}H_{21}IO_4Na$ requires 475.0382, 35 %), 453.0578 (MH^+, $C_{20}H_{22}IO_4$ requires 453.0563, 100%), 407.0136 (20%).

Preparation of iodonium ylide 8 from hydroxyiodane 2 and ethyl 3-oxo-3-phenylpropanoate 5

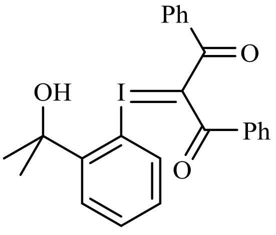
Ethyl 3-oxo-3-phenylpropanoate **5** (0.62 mL, 3.60 mmol) was added to a solution of 1-hydroxy-3,3-dimethyl-1,3-dihydro-λ^{3}-benzo[d][1,2]iodoxole **2** (2.00 g, 7.19 mmol) stirring in dry DCM (7.6 mL) under nitrogen in a small Schlenk flask. The flask was then sealed and stirred at 40 °C for 24 hours. After cooling to room temperature, the reaction mixture was concentrated on a rotary evaporator to give a pale yellow oil (2.82 g). Purification by column chromatography (10% EtOAc in petroleum ether 40-60 then 100% EtOAc) followed by washing with diethyl ether gave iodonium ylide **8** as a white solid (1.37 g, 84%).

Preparation of iodonium ylide 10 from hydroxyiodane 2 and ethyl 3-(4-methoxyphenyl)-3-oxo-propanoate



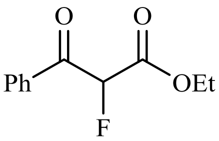
Ethyl 3-(4-methoxyphenyl)-3-oxo-propanoate (0.34 mL, 1.80 mmol) was added to a solution of 1-hydroxy-3,3-dimethyl-1,3-dihydro-λ^{3}-benzo[d][1,2]iodoxole **2** (1.00 g, 3.60 mmol) stirring in dry DCM (3.8 mL) under nitrogen in a Schlenk flask. The flask was then sealed and stirred at 40 °C for 24 hours. After cooling to room temperature, the reaction mixture was concentrated on a rotary evaporator to give a yellow solid (1.49 g). Purification by column chromatography (10% EtOAc in petroleum ether then 100% EtOAc) followed by trituration with diethyl ether gave iodonium ylide **10** as a pale yellow solid (0.39 g, 45%). mp 128-129 ^{o}C. (Found C, 52.37; H, 4.75. Calc. for $C_{21}H_{23}IO_5$: C, 52.30; H, 4.81%). δ_H ($CDCl_3$) 0.91 (3H, t, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 1.48 (6H, s, 2 x CH_3), 3.85 (3H, s, OCH_3), 3.90 (2H, q, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 6.62 (1H, s, OH), 6.88 (2H, d, $^3J_{HH}$ = 8.8 Hz, ArH), 7.17-7.22 (2H, m, ArH), 7.33 (1H, t, $^3J_{HH}$ = 7.7 Hz, ArH), 7.51 (1H, d, $^3J_{HH}$ = 7.7 Hz, ArH), 7.56 (2H, d, $^3J_{HH}$ = 8.8 Hz, ArH); δ_C ($CDCl_3$) 14.2 (CH_3), 29.9 (2 x CH_3), 55.3 (OCH_3), 60.2 (CH_2), 73.5 (C), 77.7 (C=I), 110.0 (CI), 112.6 (CH), 127.2 (CH), 127.5 (CH), 129.5 (CH), 129.7 (CH), 130.4 (CH), 132.5 (C), 146.6 (C), 160.9 (C), 166.3 (CO), 188.3 (CO). *m/z* (ES) 483.0691 (MH^+, $C_{21}H_{24}IO_5$ requires 483.0669, 100%), 437.0263 (M-OEt, 40%), 221.0823 ($C_{12}H_{13}O_4^+$, 60%), 193.0865 ($C_{10}H_9O_4$, 60%).

Preparation of iodonium ylide 11 from hydroxyiodane 2 and 1,3-diphenylpropane-1,3-dione



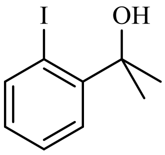
A solution of 1,3-diphenylpropane-1,3-dione (0.43 g, 1.93 mmol) and 1-hydroxy-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **2** (1.07 g, 3.86 mmol) in dry DCM (4.1 mL) was stirred at 40 ^{o}C for 24 hours under a nitrogen atmosphere in a Schlenk flask. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give a yellow solid (1.53 g). Purification by column chromatography (10% ethyl acetate in petroleum ether then 100% ethyl acetate) followed by washing with diethyl ether gave iodonium ylide **11** as a yellow solid (0.57 g, 61%). mp 149-150 ^{o}C. (Found: C, 59.45; H, 4.45. Calc. for $C_{24}H_{21}IO_3$: C, 59.52; H, 4.37%). δ_H ($CDCl_3$) 1.49 (6H, s, 2 x CH_3), 6.66 (1H, s, OH), 6.98 (4H, t, $^3J_{HH}$ = 7.7 Hz, ArH), 7.04-7.08 (2H, m, ArH), 7.16-7.21 (2H, m, ArH), 7.29-7.33 (5H, m, ArH), 7.63 (1H, dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.1 Hz, ArH); δ_C ($CDCl_3$) 29.8 (CH_3), 73.6 (C), 98.3 (C=I), 110.0 (CI), 127.2 (CH), 127.4 (2 x CH), 128.0 (CH), 129.3 (CH), 129.7 (CH), 129.8 (CH), 139.6 (C), 146.8 (C), 189.6 (CO); *m/z* (ES) 485.0610 (MH^+, $C_{24}H_{22}IO_3$ requires 485.0614, 100%).

Procedure for the fluorination of iodonium ylide 8 with TREAT-HF (Table 3, Entry 1)



TREAT-HF (0.19 mL, 1.19 mmol) was added to a solution of iodonium ylide **8** (0.200 g, 0.44 mmol) stirring in dry DCM (0.73 mL) in a small

Schlenk flask under nitrogen. The flask was sealed and stirred at 40 °C for 24 hours. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give a pale yellow oil (0.402 g). Purification by column chromatography (5% EtOAc in hexane) gave ethyl 2-fluoro-3-oxo-3-phenylpropanoate **6** as a pale yellow oil (0.033 g, 36%) in addition to 2-(2-iodophenyl)propan-2-ol as a pale yellow oil (0.062 g, 54 %).

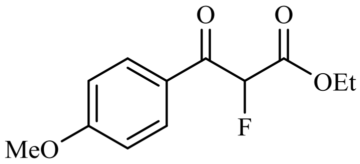


The characterisation data for 2-(2-iodophenyl)propan-2-ol is in agreement with the literature.[15] δ_H ($CDCl_3$) 1.64 (6H, s, 2 x CH_3), 2.63 (1H, br s, OH), 6.77 (1H, td, ${}^3J_{HH}$ = 7.8 Hz, ${}^4J_{HH}$ = 2.0 Hz, ArH), 7.20 (1H, td, ${}^3J_{HH}$ = 7.8 Hz, ${}^4J_{HH}$ = 1.4 Hz, ArH), 7.51 (1H, dd, ${}^3J_{HH}$ = 7.8 Hz, ${}^4J_{HH}$ = 2.0 Hz, ArH), 7.83 (1H, dd, ${}^3J_{HH}$ = 7.8 Hz, ${}^4J_{HH}$ = 1.4 Hz, ArH); δ_C ($CDCl_3$) 28.5 (CH_3), 72.5 (C), 92.1 (CI), 125.6 (CH), 127.0 (CH), 127.5 (CH), 141.6 (CH), 147.5 (C); m/z (EI) 261.98491 (M^+, $C_9H_{11}IO$ requires 261.98519, 30 %), 247 ($(M - CH_3)^+$, 100%).

Procedure for the fluorination of iodonium ylide 8 with TBAF (Table 3, Entry 2)

A small Schlenk flask was charged with a solution of iodonium ylide **8** (0.200 g, 0.44 mmol) in TBAF (1.2 mL, 1.2 mmol, 1.0 M in THF) under nitrogen. The flask was sealed and stirred at 40 °C for 24 hours. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give a pale yellow oil. Analysis of the crude reaction mixture by ^1H and ^{19}F NMR spectroscopy revealed a complex mixture of products and so, purification was not attempted.

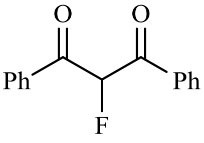
Procedure for the fluorination of iodonium ylide 10 with TREAT-HF (Table 3, Entry 3)



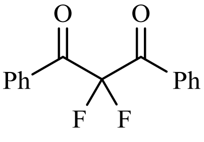
TREAT-HF (0.18 mL, 1.12 mmol) was added to a solution of iodonium ylide **10** (0.200 g, 0.41 mmol) stirring in dry DCM (0.75 mL) in a small Schlenk flask under nitrogen. The flask was sealed and stirred at 40 °C for 24 hours. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give a yellow oil (0.443 g). Purification by column chromatography (17% EtOAc in petroleum ether 40-60) gave 2-(2-iodophenyl)propan-2-ol as a pale yellow oil (0.099 g, 92%) and ethyl 2-fluoro-3-(4-methoxyphenyl)-3-oxopropanoate as a colourless oil (0.027 g, 28%). The characterisation data for ethyl 2-fluoro-3-(4-methoxyphenyl)-3-oxopropanoate is in agreement with the literature.[16] δ_H ($CDCl_3$) 1.19 (3H, t, ${}^3J_{HH}$ = 7.5 Hz, OCH_2CH_3), 3.82 (3H, s, OMe), 4.22 (2H, m_{AB}, dq, ${}^2J_{HH}$ = 10.6 Hz, ${}^3J_{HH}$ = 7.5 Hz, OCH_AH_B), 5.74 (1H, d, ${}^2J_{HF}$ = 48.4 Hz, CHF), 6.89 (2H, d, ${}^3J_{HH}$ = 9.0 Hz, ArH), 7.96 (2H, d, ${}^3J_{HH}$ = 9.0 Hz, ArH); δ_F

($CDCl_3$) -189.5 (s); δ_C ($CDCl_3$) 13.0 (CH_3), 54.6 (CH_3), 61.6 (CH_2), 89.2 (d, ${}^1J_{CF}$ = 197.6 Hz, CH), 113.1 (CH), 125.3 (C), 131.0 (d, ${}^4J_{CF}$ = 3.1 Hz, CH), 163.6 (C), 164.2 (d, ${}^2J_{CF}$ = 24.1 Hz, CO), 186.8 (d, ${}^2J_{CF}$ = 20.8 Hz, CO); *m/z* (ES^+) 241.0880 (MH^+, $C_{12}H_{14}FO_4$ requires 241.0876, 60%), 135.0452 (100).

Procedure for the fluorination of iodonium ylide 11 with TREAT-HF (Table 3, Entry 4)

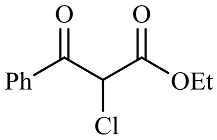


TREAT-HF (0.18 mL, 1.11 mmol) was added to a solution of iodonium ylide **11** (0.200 g, 0.41 mmol) stirring in dry DCM (0.75 mL) under nitrogen in a small Schlenk flask. The flask was then sealed and stirred at 40 °C for 24 hours. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator. Purification by column chromatography using 10% EtOAc in petroleum ether 40-60 gave a mixture of 2-fluoro-1,3-diphenylpropane-1,3-dione, 2,2-difluoro-1,3-diphenylpropane-1,3-dione and 1,3-diphenylpropane-1,3-dione (0.072 g). Further elution gave 2-(2-iodophenyl)propan-2-ol (0.072 g, 67%). 2-Fluoro-1,3-diphenyl-propane-1,3-dione exists as a mixture of tautomers (54% keto: 46% enol) and the characterisation data is in agreement with the literature.[3a] δ_H ($CDCl_3$, 500 MHz) 6.53 (1H, d, ${}^2J_{HF}$ = 49.1 Hz, keto CHF), 7.46-7.51 (4H keto + 4H enol, m, ArH), 7.54-7.57 (2H, m, enol ArH), 7.60 (2H, t, ${}^3J_{HH}$ = 7.4 Hz, keto ArH), 8.02 (4H, d, ${}^3J_{HH}$ = 8.5 Hz, enol ArH), 8.09 (4H, d, ${}^3J_{HH}$ = 8.3 Hz, keto ArH), 17.74 (1H, d, ${}^4J_{HF}$ = 3.1 Hz, enol OH); δ_F ($CDCl_3$, 376 MHz) -168.6 (s, enol), -186.7 (s, keto); δ_C ($CDCl_3$, 126 MHz) 96.6 (d, ${}^1J_{CF}$ = 198.9 Hz, keto CH), 128.5 (enol CH), 128.8 (keto CH), 129.1 (d, ${}^4J_{CF}$ = 8.5 Hz, enol CH), 129.8 (d, ${}^4J_{CF}$ = 3.3 Hz, keto CH), 132.4 (enol CH), 133.2 (d, ${}^3J_{CF}$ = 5.1 Hz, enol C), 133.6 (d, ${}^3J_{CF}$ = 1.9 Hz, keto, C), 134.5 (keto, CH), 144.2 (d, ${}^1J_{CF}$ = 235.4 Hz, enol CF), 176.0 (d, ${}^2J_{CF}$ = 21.5 Hz, enol CO), 191.2 (d, ${}^2J_{CF}$ = 20.1 Hz, keto CO); m/z (ASAP) 243.0824 (MH^+, $C_{15}H_{12}O_2F$ requires 243.0821, 100 %).

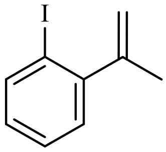


The characterisation data for 2,2-difluoro-1,3-diphenylpropane-1,3-dione is in agreement with the literature.[17] δ_H ($CDCl_3$) 7.41 (4H, t, ${}^3J_{HH}$ = 8.0 Hz, ArH), 7.56 (2H, t, ${}^3J_{HH}$ = 8.0 Hz, ArH), 8.00 (4H, d, ${}^3J_{HH}$ = 8.0 Hz, ArH); δ_F ($CDCl_3$) -102.6 (s); δ_C ($CDCl_3$) 112.7 (t, ${}^1J_{CF}$ = 265.1 Hz, CF_2), 128.9 (CH), 130.3 (CH), 131.6 (C), 135.0 (CH), 187.4 (t, ${}^2J_{CF}$ = 27.4 Hz, CO); *m/z* (EI) 260 (M^+, 28%), 105 (100), 77 (88).

Procedure for the reaction of iodonium ylide 8 with hydrochloric acid (Table 4, Entry 1)

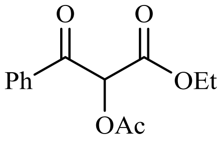


Concentrated hydrochloric acid (0.1 mL, 1.19 mmol) was added to a solution of iodonium ylide **8** (0.200 g, 0.44 mmol) stirring in dry DCM (0.9 mL) under nitrogen in a small Schlenk flask. The flask was then sealed and stirred at 40 °C for 24 hours. After cooling the reaction mixture to room temperature, DCM was added (5 mL) followed by water (5 mL). The organic layer was separated and the aqueous layer was extracted with more DCM (3 x 5 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated on a rotary evaporator to give a colourless oil (0.198 g). Purification by column chromatography (100% petroleum ether 40-60) gave 1-iodo-2-(prop-1-en-2-yl)benzene as a colourless oil (0.059 g, 55%). Further elution with 5% EtOAc in petroleum ether 40-60 gave ethyl 2-chloro-3-oxo-3-phenyl-propanoate as a colourless oil (0.095 g, 83%) and 2-(2-iodophenyl)propan-2-ol as a pale yellow oil (0.034 g, 29%). The characterisation data for ethyl 2-chloro-3-oxo-3-phenylpropanoate is in agreement with the literature.[18] δ_H ($CDCl_3$) 1.16 (3H, t, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 4.21 (2H, q, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 5.54 (1H, s, CH), 7.42 (2H, t, $^3J_{HH}$ = 7.4 Hz, ArH), 7.55 (1H, t, $^3J_{HH}$ = 7.4 Hz, ArH), 7.92 (2H, d, $^3J_{HH}$ = 7.4 Hz, ArH); δ_C ($CDCl_3$) 13.9 (CH_3), 58.0 (CH), 63.2 (CH_2), 128.9 (CH), 129.2 (CH), 133.4 (C), 134.3 (CH), 165.3 (CO), 188.3 (CO); *m/z* (ASAP) 227.0467 ($M^{35}ClH^+$, $C_{11}H_{12}ClO_3$ requires 227.0475, 100%), 229.0460 ($M(^{37}Cl)H^+$, 30%).



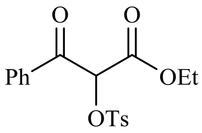
The characterisation data for 1-iodo-2-(prop-1-en-2-yl)benzene is in agreement with the literature.[19] δ_H ($CDCl_3$) 1.98 (3H, dd, $^4J_{HH}$ = 1.4 Hz, $^4J_{HH}$ = 1.1 Hz, CH_3), 4.79-4.81 (1H, m, alkene CH), 5.12-5.14 (1H, m, alkene CH), 6.83 (1H, td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, ArH), 7.07 (1H, dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, ArH), 7.20 (1H, td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, ArH), 7.74 (1H, dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, ArH); δ_C ($CDCl_3$) 23.9 (CH_3), 97.0 (CI), 116.1 (CH_2), 128.1 (CH), 128.4 (CH), 128.5 (CH), 139.2 (CH), 148.4 (C), 148.9 (C); *m/z* (ASAP) 244.9816 (MH^+, $C_9H_{10}I$ requires 244.9827, 100%).

Procedure for the reaction of iodonium ylide 8 with acetic acid (Table 4, Entry 2)



Glacial acetic acid (0.068 mL, 1.19 mmol) was added to a solution of iodonium ylide **8** (0.200 g, 0.44 mmol) stirring in dry DCM (0.9 mL) under nitrogen in a small Schlenk flask. The flask was then sealed and stirred at 40 °C for 24 hours. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give a colourless oil (0.221 g). Purification by column chromatography using 10% EtOAc in petroleum ether 40-60 gave 2-(2-iodophenyl)propan-2-ol as a pale yellow oil (0.099 g, 86%) and ethyl 2-acetoxy-3-oxo-3-phenylpropanoate as a colourless oil (0.099 g, 93%). The characterisation data for ethyl 2-acetoxy-3-oxo-3-phenylpropanoate is in agreement with the literature.[20] δ_H ($CDCl_3$) 1.21 (3H, t, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 2.22 (3H, s, $COCH_3$), 4.25 (2H, q, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 6.33 (1H, s, CH), 7.50 (2H, t, $^3J_{HH}$ = 7.6 Hz, ArH), 7.63 (1H, t, $^3J_{HH}$ = 7.6 Hz, ArH), 8.00 (2H, d, $^3J_{HH}$ = 7.6 Hz, ArH); δ_C ($CDCl_3$) 13.9 (CH_3), 20.5 (CH_3), 62.4 (CH_2), 74.5 (CH), 128.8 (CH), 129.2 (CH), 134.2 (CH), 134.2 (C), 165.1 (CO), 169.5 (CO), 189.6 (CO); *m/z* (ASAP) 251.0924 (MH^+, $C_{13}H_{15}O_5$ requires 251.0919, 100%).

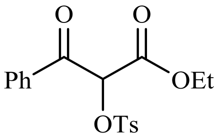
Procedure for the reaction of iodonium ylide 8 with $TsOH.H_2O$ (Table 4, Entry 3)



A small Schlenk flask was charged with iodonium ylide **8** (0.150 g, 0.33 mmol), $TsOH.H_2O$ (0.170 g, 0.90 mmol) and dry DCM (0.75 mL) under nitrogen. The flask was sealed and stirred at 40 °C for 24 hours. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give a white solid (0.268 g). Purification by column chromatography (14% EtOAc in petroleum ether 40-60) gave 1-iodo-2-(prop-1-en-2-yl)benzene as a colourless oil (0.075 g, 93%) and ethyl 3-oxo-3-phenyl-2-(tosyloxy)propanoate (0.086 g, 72%). The characterisation data for ethyl 3-oxo-3-phenyl-2-(tosyloxy)propanoate is in agreement with the literature.[21] δ_H ($CDCl_3$) 1.10 (3H, t, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 2.36 (3H, s, $ArCH_3$), 4.10 (2H, m_{AB}, dq, $^2J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 7.1 Hz, OCH_AH_B), 5.92 (1H, s, CH), 7.22 (2H, d, $^3J_{HH}$ = 8.4 Hz, ArH), 7.38 (2H, t, $^3J_{HH}$ = 7.5 Hz, ArH), 7.53 (1H, t, $^3J_{HH}$ = 7.5 Hz, ArH), 7.71 (2H, d, $^3J_{HH}$ = 8.4 Hz, ArH), 7.85 (2H, d, $^3J_{HH}$ = 7.7 Hz, ArH); δ_C ($CDCl_3$) 13.8 (CH_3), 21.7 (CH_3), 62.9 (CH_2), 78.1 (CH), 128.4 (CH), 128.8 (CH), 129.4 (CH), 129.9 (CH), 132.5 (C), 133.4 (C), 134.4 (CH), 145.6 (C), 164.2 (CO), 188.3 (CO); m/z (ASAP) 363.0905 (MH^+, $C_{18}H_{19}O_6S$ requires 363.0902, 100%), 317.0449 ($(M – OEt)^+$, 38%).

Note: Ethyl 3-oxo-3-phenyl-2-(tosyloxy)propanoate exists as both keto and enol tautomers (93% keto : 7% enol) in $CDCl_3$. Full characterisation of the enol tautomer by ^1H NMR spectroscopy is not possible because many of the peaks in the aromatic region are obscured and it was not possible to obtain ^{13}C NMR data for the enol tautomer since it represents such a low percentage of the total sample. Partial ^1H NMR data is given: δ_H ($CDCl_3$) 1.25 (3H, t, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 2.25 (3H, s, $ArCH_3$), 4.23 (2H, q, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 6.92 (2H, d, $^3J_{HH}$ = 8.3 Hz, ArH), 7.11 (2H, t, $^3J_{HH}$ = 7.8 Hz, ArH), 11.91 (br s, enol OH).

Preparation of ethyl 3-oxo-3-phenyl-2-(tosyloxy)propanoate using tosyliodane 4



A small Schlenk flask was charged with 1-tosyloxy-3,3-dimethyl-1,3-dihydro-λ^3-benzo[d][1,2]iodoxole **4** (0.400 g, 0.93 mmol), ethyl 3-oxo-3-phenylpropanoate **5** (0.080 mL, 0.46 mmol) and dry DCM (1.0 mL). The flask was sealed and stirred at 40 ^{o}C for 24 hours. After cooling the reaction mixture to room temperature, it was concentrated on a rotary evaporator to give a yellow oily solid (0.474 g). Purification by column chromatography using 20% EtOAc in hexane gave ethyl 3-oxo-3-phenyl-2-(tosyloxy)propanoate as a yellow oil (0.129 g, 77%).

Crystallographic data for iodonium ylide 8

$C_{20}H_{21}IO_4$, M = 452.27, monoclinic, space group P2(1)/n, a = 15.062(3) Å, b = 8.1555(15) Å, c = 15.606(3) Å, α = 90°, β = 104.717(4)°, γ = 90°, U = 1854.1(6) Å^3 (by least-squares refinement), T = 150(2) K, graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, Z = 4, D_{calc} = 1.620 mg m^{-3}, F(000) = 904, dimensions 0.16 mm x 0.11 mm x 0.04 mm, μ(Mo Kα) = 1.748 mm^{-1}, empirical absorption correction, maximum and minimum transmission factors of 0.928 and 0.673 respectively, Bruker APEX 2000 CCD diffractometer, data collection range 1.68 < θ < 26.00°, $-18 \leq h \leq 18$, $-10 \leq k \leq 10$, $-19 \leq l \leq 18$, no crystal decay was detected; 14049 reflections were measured and 3635 were unique (R_{int} = 0.1203), final R_1 = 0.0497, wR_2 = 0.0763 (0.0841 and 0.0841 respectively for all the data). The final residual Fourier map showed peaks of 0.737 and -1.008 e Å^{-3}.

Structure solution and refinement

The data was collected on a Bruker APEX 2000 CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least squares cycles on F^2 for all data, using SHELXTL version 6.10.[22] All hydrogen atoms were included in calculated positions (C-H = 0.95-0.98 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 Ueq(C) for methyl H atoms and 1.2 Ueq(C) for all other H atoms. All non hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with The Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC

1036695. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

15 P. Eisenberger, I. Kieltsch, R. Koller, K. Stanek, A. Togni, *Org. Synth.*, 2011, **88**, 168.

16 M. Baumann, I. R. Baxendale, L. J. Martin, S. V. Ley, *Tetrahedron*, 2009, **65**, 6611.

17 G. Stavber, M. Zupan, M. Jereb, S. Stavber, *Org. Lett.*, 2004, **6**, 4973.

18 Z. He, H. Li, Z. Li, *J. Org. Chem.*, 2010, **75**, 4636.

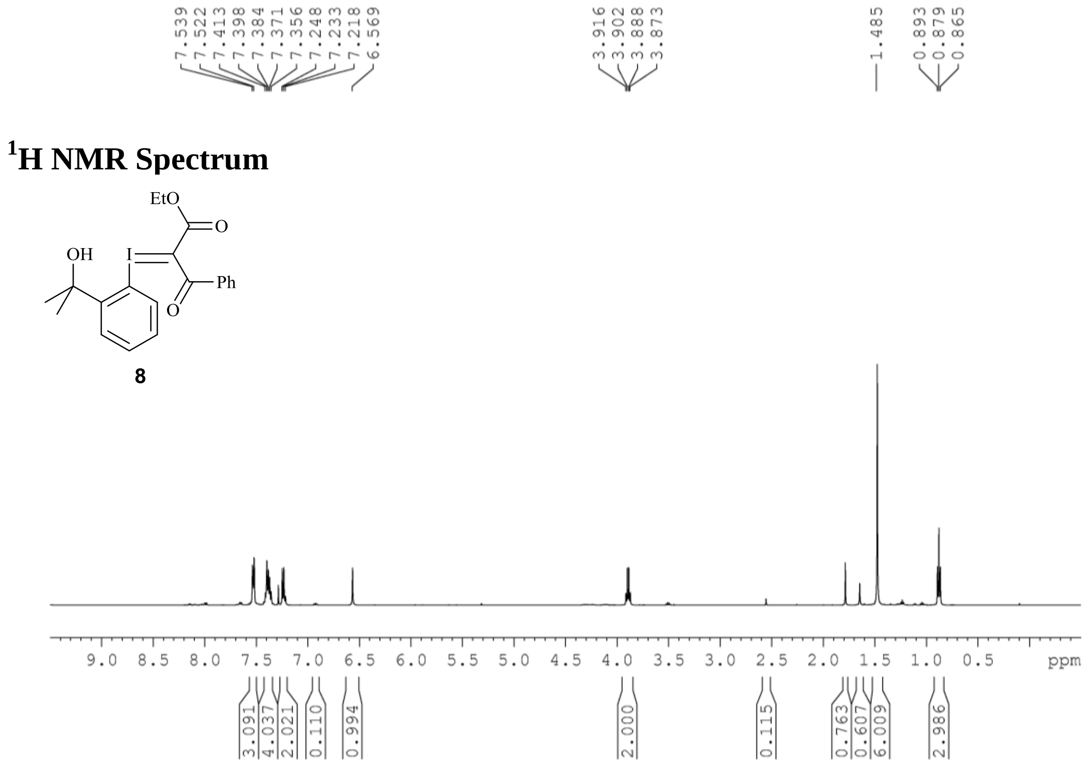
19 X. Jia, D. A. Petrone, M. Lautens, *Angew. Chem. Int. Ed.*, 2012, **51**, 9870.

20 M. Ochiai, Y. Takeuchi, T. Katayama, T. Sueda, K. Miyamoto, *J. Am. Chem. Soc.*, 2005, **127**, 12244.

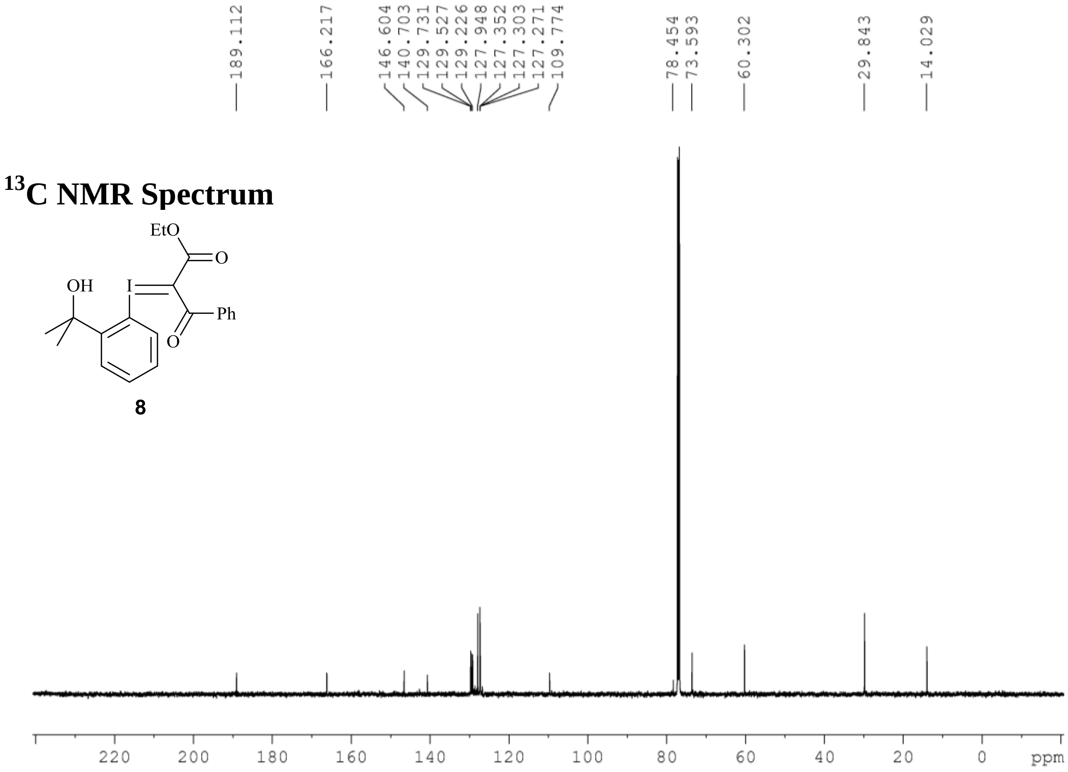
21 A. Tanaka, K. Moriyama, H. Togo, *Synlett*, 2011, 1853.

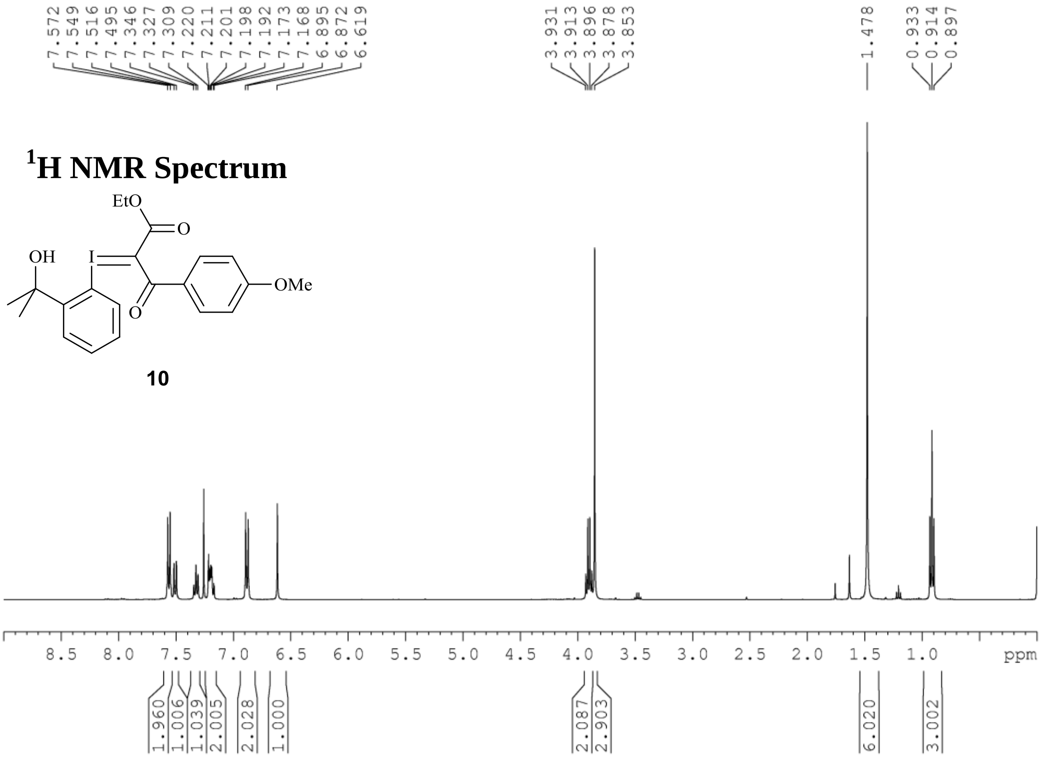
22 G. M. Sheldrick, SHELXTL Version 6.10, Bruker AXS, Inc., Maddison, Wisconsin, USA, 2000.

^{1}H NMR Spectrum



^{13}C NMR Spectrum




^{1}H NMR Spectrum
EtO
O
OH
I
O
OMe
10
7.572
7.549
7.516
7.495
7.346
7.327
7.309
7.220
7.211
7.201
7.198
7.192
7.173
7.168
6.895
6.872
6.619
3.931
3.913
3.896
3.878
3.853
1.478
0.933
0.914
0.897
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
ppm
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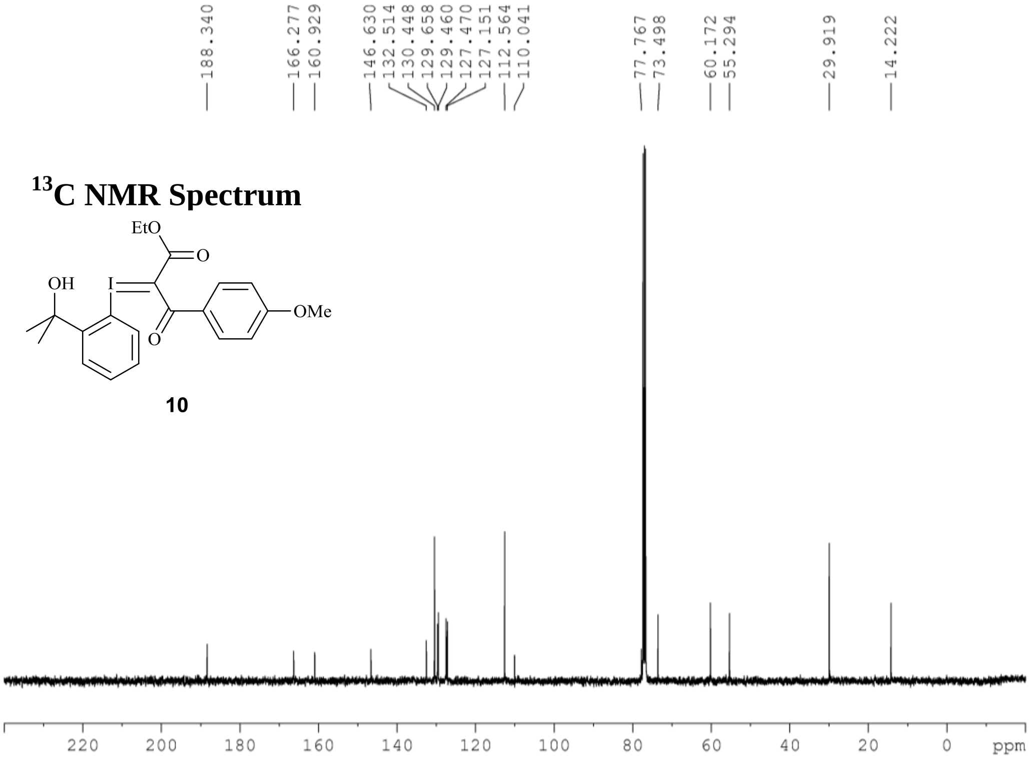
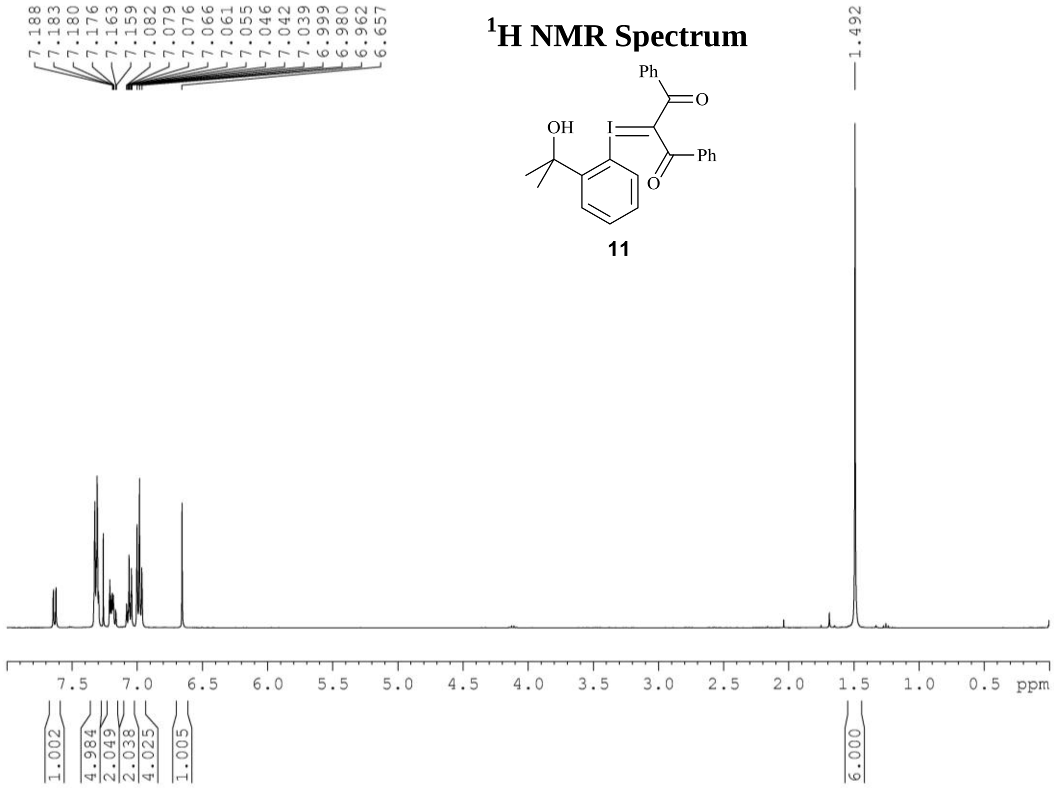
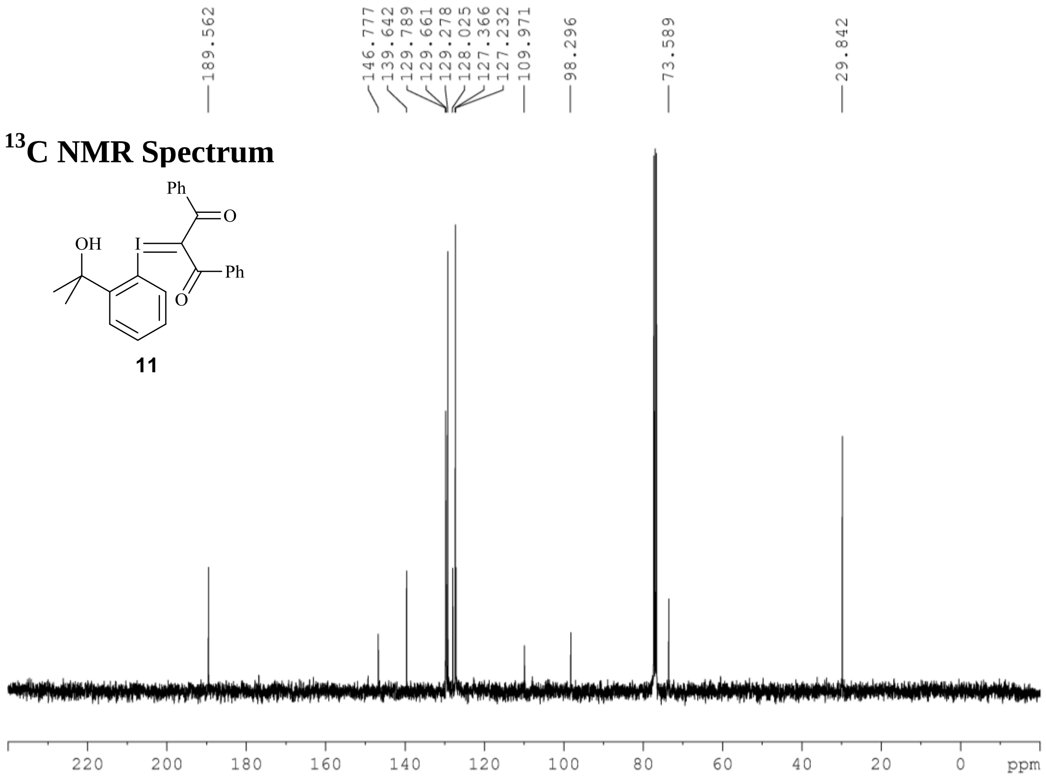
1.006
1.039
2.005
2.028
1.000
2.087
2.903
6.020
3.002


^{13}C NMR Spectrum
EtO
O
OH
I
O
OMe
10
188.340
166.277
160.929
146.630
132.514
130.448
129.658
129.460
127.470
127.151
112.564
110.041
77.767
73.498
60.172
55.294
29.919
14.222
220
200
180
160
140
120
100
80
60
40
20
0
ppm



^{1}H NMR Spectrum

11



^{13}C NMR Spectrum

11