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Supporting Information

The Reaction of *o*-Alkynylarene and Heteroarene Carboxaldehyde Derivatives with Iodonium Ions and Nucleophiles: A Versatile and Regioselective Synthesis of 1*H*-Isochromene, Naphthalene, Indole, Benzofuran and Benzothiophene Compounds

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Contents

Characterization data and experimental procedures for all compounds.

Experimental section:

General:

All reactions were conducted using oven-dried glassware under an atmosphere of nitrogen. Dichloromethane and 1,2-dichloroethane were distilled before used from CaH_2. Ethanol and the solvents used in column chromatography, hexane and ethyl acetate, were obtained from commercial suppliers and used without further distillation. TLC was performed on aluminium-backed plates coated with silica gel 60 with F254 indicator (Merck). Flash chromatography was carried out on silica gel. NMR spectra were measured at room temperature on Bruker AC-200 MHz, Bruker DPX-300 MHz, Bruker AV-300 MHz and Bruker AV-400 MHz spectrometers. 2D NMR experiments were recorded on a Bruker AV-400 MHz. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (deuterochloroform: δ 7.26 ppm in ^1H spectra, δ 77.00 ppm in ^{13}C spectra). Carbon multiplicities were assigned by DEPT techniques. High-resolution mass spectra were recorded on a Finnigan-Matt 95 mass spectrometer using EI at 70 eV. Infra-red spectra were obtained on a Unicam Mattson 3000 FTIR spectrometer, and only the most significant IR absorptions are given. Elemental analyses were carried out on a Perkin-Elmer 2400 and Carlo Erba 1108 microanalyzers. Melting points were measured on a Buchi-Totoli apparatus.
Crystallographic structure determination for **6g** was performed on a Bruker SMART 1000 diffractometer, Mo_{Ka} radiation (? = 0.71073 Å), at 120 K.

Starting materials:

2-Alkynylbenzaldehydes were prepared by Sonogashira coupling reaction of 2-bromobenzaldehyde with various terminal alkynes.[1] *o*-(alkynyl)arylketones **3a-b** were also prepared by Sonogashira coupling reaction of the corresponding bromine derivatives.

N-tosyl protected 3-alkynylpyrrole-2-carboxaldehydes **7a** (R^1: Ph) and **7b** (R^1: *n*-Bu) were prepared by Sonogashira coupling reaction of 3-bromo-*N*-tosylpyrrole-2-carboxaldehyde with various terminal alkynes;[1] and this brominated pyrrole was

[1] Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 86.

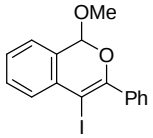
prepared according to literature procedure.[2] 3-phenylethynylfuran-2-carboxaldehyde **26** and 3-alkynylthiophene-2-carboxaldehyde **8a-b** were prepared using procedures already reported in the literature.[3] Enamines **24** were also prepared according previously described procedures.[4]

Commercially available compounds were used as received. IPy_2BF_4 is a commercially available reagent.

General procedure for the synthesis of 4-iodo-1*H*-isochromenes 2, 6, 10 and 12 using IPy_2BF_4 and HBF_4: IPy_2BF_4 (0.37 g, 1 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (10 mL). The solution was cooled at 0ºC and tetrafluoroboric acid, 54% solution in diethyl ether (0.15 mL, 1.1 mmol, 1.1 equiv) was added. After 10 min., the corresponding 2-alkynylbenzaldehyde **1** (1 mmol, 1 equiv) was added and the solution was stirred during 30 min. at room temperature. After this time, the nucleophile (alcohols, silylated compounds **5**, arenes **10** or heteroarenes **12**)(1.2 mmol, 1.2 equiv) was added and the solution was further stirred until disappearance of starting benzaldehyde (reaction times are given in the Main Text). The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and vigorously stirred. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL); dried over sodium sulfate and concentrated. The crude were purified by flash column chromatography (neutral aluminium oxide, hexane/EtOAc) to afford pure compounds **2**, **6, 11** and **13**.

For the reaction of the pyrrole and thiophene derivatives **7a** and **8b**, the same procedure was used to obtain the corresponding bi-heterocyclic compounds **9a-b**.

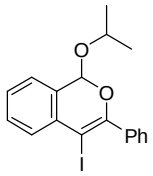
4-Iodo-1-methoxy-3-phenyl-1*H*-isochromene (2a)



Yellow oil. R_f = 0.42 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.79-7.70 (m, 3H), 7.58-7.51 (m, 4H), 7.38 (t, *J* = 7 Hz, 1H), 7.26 (d, *J* = 7 Hz, 1H), 6.11 (s, 1H), 3.74 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 151.6 (C), 137.2 (C), 131.2 (C), 129.9 (CH), 129.8 (CH), 129.6 (CH), 129.2 (CH), 127.8 (CH), 127.7 (CH), 127.0 (C), 125.3 (CH), 99.8 (CH), 73.7 (C-I), 55.9 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}) 3039, 2936, 1052. HRMS (EI) Calcd for $C_{16}H_{13}IO_2$ 363.9960, Found 363.9964.

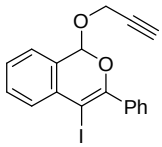
4-Iodo-1-isopropoxy-3-phenyl-1*H*-isochromene (2b)

[2] Ghosez, L.; Franc, C.; Denonne, F.; Cuisinier, C.; Touillaux, R. *Can. J. Chem.* **2001**, *79*, 1827.
[3] Zhang, Y.; Herndon, J. W. *J. Org. Chem.* **2002**, *67*, 4177.
[4] Gilbert, A. *Enamines*, New York, 1998.



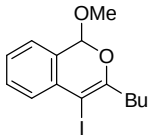
Yellow oil. R_f = 0.45 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.75-7.71 (m, 3H), 7.54-7.44 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.29 (s, 1H), 4.46-4.38 (m, 1H), 1.40 (t, *J*= 6.2 Hz, 6H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 151.8 (C), 137.6 (C), 131.3 (C), 129.7 (CH), 129.5 (CH), 129.4 (CH), 129.0 (CH), 127.8 (CH), 127.7 (C), 127.6 (CH), 124.9 (CH), 96.5 (CH), 73.6 (C-I), 69.9 (CH), 23.3 (CH_3), 21.6 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}) 3063, 2968, 1021, 960. HRMS (FAB+) Calcd for $C_{18}H_{18}IO_2$ (M+H) 393.0352, Found 393.0340. Anal. Calcd for $C_{18}H_{17}IO_2$: C, 55.12%; H, 4.37%, Found: C, 55.13%; H, 4.38%.

4-Iodo-3-phenyl-1-(2-propynyloxy)-1*H*-isochromene (2c)



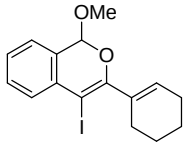
Yellow oil. R_f = 0.57 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.68-7.65 (m, 3H), 7.55-7.48 (m, 4H), 7.38 (td, *J* = 7.4, 1.2 Hz, 1H), 7.28 (dd, *J* = 6.2, 1.2 Hz, 1H), 6.43 (s, 1H), 4.59 (dd, *J* = 15.9, 2.5 Hz, 1H), 4.5 (dd, *J* = 15.9, 2.5 Hz, 1H), 2.6 (t, *J* = 2.5 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 151.3 (C), 137.1 (C), 131.3 (C), 129.9 (CH), 129.8 (CH), 129.6 (CH), 129.2 (CH), 127.8 (2 x CH), 126.5 (C), 125.5 (CH), 96.4 (CH), 78.7 (C), 75.4 (CH), 74.1 (C-I), 54.7 (CH_2) ppm. IR (CH_2Cl_2, cm^{-1}) 3297, 3063, 2150, 1044. HRMS (FAB+) Calcd for $C_{18}H_{13}IO_2$ 387.9960, Found 387.9966. Anal. Calcd for $C_{18}H_{13}IO_2$: C, 55.69%; H, 3.38%, Found: C, 55.91%; H, 3.33%.

3-Butyl-4-iodo-1-metoxy-1*H*-isochromene (2d)



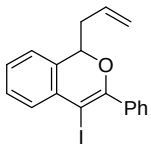
Pale yellow oil. R_f = 0.44 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.50 (d, *J* = 7.9 Hz, 1H), 7.40 (td, *J* = 7.9, 1.3 Hz, 1H), 7.26 (td, *J* = 7.1, 1.3 Hz, 1H), 7.16 (d, *J* = 7.1 Hz, 1H), 5.94 (s, 1H), 3.61 (s, 3H), 2.95-2.64 (m, 2H), 1.78-1.66 (m, 2H), 1.61-1.43 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz): 154.5 (C), 130.8 (C), 129.5 (CH), 128.4 (CH), 126.8 (CH), 126.6 (C), 125.2 (CH), 99.1 (CH), 73.3 (C-I), 55.4 (CH_3), 36.9 (CH_2), 29.3 (CH_2), 22.1 (CH_2), 13.9 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}) 3029, 2956, 1078. HRMS (FAB+) Calcd for $C_{14}H_{17}IO_2$ 344.0273, Found 344.0288. Anal. Calcd for $C_{14}H_{17}IO_2$: C, 48.85%; H, 4.98%, Found: C, 48.05%; H, 5.06%.

3-(Cyclohex-1-enyl)-4-iodo-1-methoxy-1*H*-isochromene (2f)



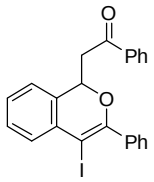
Yellow oil. R_f = 0.43 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.55 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.45 (td, *J* = 7.7, 1.5 Hz, 1H), 7.26 (td, *J* = 7.2, 1.3 Hz, 1H), 7.17 (dd, *J* = 7.2, 1.3 Hz, 1H), 6.10 (broad s, 1H), 5.93 (s, 1H), 3.59 (s, 3H), 2.43-2.20 (m, 4H), 1.83-1.71 (m, 4H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 153.8 (C), 135.2 (C), 132.9 (CH), 131.3 (C), 129.6 (CH), 129.4 (CH), 127.2 (CH), 127.0 (C), 125.2 (CH), 99.4 (CH), 71.9 (C-I), 55.6 (CH_3), 26.7 (CH_2), 24.9 (CH_2), 22.3 (CH_2), 21.6 (CH_2) ppm. IR (CH_2Cl_2, cm^{-1}) 3034, 2926, 1024. HRMS (FAB+) Calcd for $C_{16}H_{17}IO_2$ 368.0273, Found 368.0273.

1-Allyl-4-iodo-3-phenyl-1*H*-isochromene (6a)



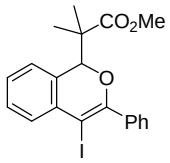
Pale yellow solid (mp = 46ºC, dec). R_f = 0.52 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.75-7.64 (m, 2H), 7.56 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.50-7.45 (m, 3H), 7.43 (td, *J* = 7.7, 1.3 Hz, 1H), 7.29 (td, *J* = 7.5, 1.3 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.07-5.91 (m, 1H), 5.35 (dd, *J* = 7.9, 5.3 Hz, 1H), 5.30-5.23 (m, 2H), 3.02-2.92 (m, 1H), 2.78-2.66 (m, 1H) ppm. ^{13}C-NMR (CDCl3, 75 MHz): 153.8 (C), 136.7 (C), 133.5 (CH), 132.3 (C), 131.1 (C), 130.3 (CH), 129.4 (CH), 129.1 (CH), 128.3 (CH), 127.7 (CH), 127.5 (CH), 123.6 (CH), 118.1 (CH_2), 78.0 (CH), 72.4 (C-I), 38.2 (CH_2) ppm. IR (CH_2Cl_2, cm^{-1}) 3060, 1082. HRMS (FAB+) Calcd for $C_{18}H_{16}IO$ (M+H) 375.0246, Found 375.0247. Anal. Calcd for $C_{18}H_{15}IO$: C, 57.77%; H, 4.04%, Found: C, 56.37%; H, 4.06%.

1-Phenyl-2-(4-iodo-3-phenyl-1*H*-isochromen-1-yl)ethanone (6b)



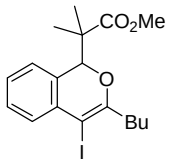
White solid (mp = 68ºC, dec). R_f = 0.25 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.00 (d, *J* = 7.4 Hz, 2H), 7.70-7.25 (m, 11H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.05 (dd, *J* = 7.7, 5.0 Hz, 1H), 3.90 (dd, *J* = 16.7, 7.7 Hz, 1H), 3.50 (dd, *J* = 16.7, 5.0 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 196.5 (C=O), 153.9 (C), 136.7 (C), 136.2 (C), 133.3 (CH), 132.6 (C), 130.9 (C), 130.4 (CH), 129.5 (CH), 129.3 (CH), 128.6 (2 x CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 123.2 (CH), 74.4 (CH), 72.4 (C-I), 42.0 (CH_2) ppm. IR (CH_2Cl_2, cm^{-1}) 3057, 1685, 1087. HRMS (EI) Calcd for $C_{23}H_{17}IO_2$ 452.0273, Found 452.0272.

Methyl 2-(4-iodo-3-phenyl-1*H*-isochromen-1-yl)-2-methylpropanoate (6c)



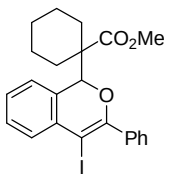
Yellow oil. R_f = 0.35 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.70-7.65 (m, 2H), 7.53 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.48-7.37 (m, 4H), 7.25 (td, *J* = 7.5, 1.3 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 5.65 (s, 1H), 3.75 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75MHz): 175.9 (C=O), 154.7 (C), 136.8 (C), 133.2 (C), 130.0 (CH), 129.4 (CH), 129.2 (CH), 128.8 (CH), 127.7 (CH), 127.1 (CH), 126.1 (C), 125.6 (CH), 82.9 (CH), 72.5 (C-I), 52.2 (CH_3), 49.6 (C), 22.0 (CH_3), 20.3 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}) 3056, 2947, 1727, 1083. HRMS (EI) Calcd for $C_{20}H_{19}IO_3$ 434.0379, Found 434.0378. Anal. Calcd for $C_{20}H_{19}IO_3$: C, 55.31%; H, 4.41%, Found: C, 56.41%; H, 4.39%.

Methyl 2-(4-iodo-3-butyl-1*H*-isochromen-1-yl)-2-methylpropanoate (6d)



Pale yellow oil. R_f = 0.34 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.40-7.17 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 5.46 (s, 1H), 3.73 (s, 3H), 2.71– 2.49 (m, 2H), 1.66-1.55 (m, 2H), 1.48-1.35 (m, 2H), 1.22 (s, 3H), 1.21 (s, 3H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 175.9 (C=O), 157.7 (C), 132.6 (C), 128.6 (CH), 128.0 (CH), 126.4 (CH), 125.9 (C), 125.3 (CH), 82.1 (CH), 72.6 (C-I), 52.1 (CH_3), 49.6 (C), 37.1 (CH_2), 28.5 (CH_2), 22.4 (CH_2), 21.6 (CH_3), 20.3 (CH_3), 13.8 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}) 2960, 1728, 1032. HRMS (EI) Calcd for $C_{18}H_{23}IO_3$ 414.0692, Found 414.0694.

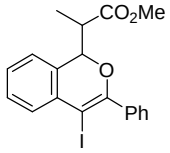
Methyl 1-(4-iodo-3-phenyl-1*H*-isochromen-1-yl)cyclohexanecarboxilate (6e)



Colorless crystals. (mp = 103-104ºC). R_f = 0.39 (Hexane: EtOAc, 10:1). ^{1}HNMR ($CDCl_3$, 200 MHz): 7.78-7.68 (m, 2H), 7.57- 7.36 (m, 5H), 7.25 (td, *J* = 7.2, 1.0 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 5.39 (s, 1H), 3.68 (s, 3H), 2.51-2.46 (m, 1H), 2.33-2.26 (m, 1H), 1.75-1.63 (m, 3H), 1.48-1.07 (m, 5H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 173.9 (C=O), 154.9 (C), 136.9 (C), 132.9 (C), 130.1 (CH), 129.3 (CH), 128.8 (CH), 128.7 (CH), 127.7 (CH), 126.8 (CH), 126.2 (CH), 125.5 (C), 84.5 (CH), 72.5 (C-I), 54.3 (C), 51.9 (CH_3), 31.2 (CH_2), 29.4 (CH_2), 25.3 (CH_2), 23.0 (CH_2), 22.8 (CH_2) ppm. IR (CH_2Cl_2, cm^{-1}) 2938,

1723, 1220. HRMS (EI) Calcd for $C_{23}H_{23}IO_3$ 474.0692, Found 474.0687. Anal. Calcd for $C_{23}H_{23}IO_3$: C, 58.24%; H, 4.89%, Found: C, 58.27%; H, 4.91%.

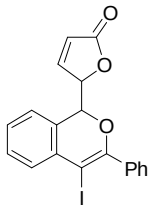
Methyl 2-(4-iodo-3-phenyl-1*H*-isochromen-1-yl)propanoate (6f)



(1:1 mixture of diastereoisomers)

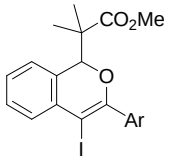
Pale yellow oil. R_f = 0.25 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.72-7.18 (m, 16H), 7.01-6.95 (m, 2H), 5.60 (d, *J* = 6.8 Hz, 1H), 5.49 (d, *J* = 9.8 Hz, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 3.39–3.24 (m, 2H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.09 (d, *J* = 7.2 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 174.7 (C=O), 173.7 (C=O), 154.1 (C), 153.3 (C), 136.8 (C), 136.7 (C), 135.6 (C), 132.4 (C), 131.9 (C), 131.4 (C), 130.0 (2 x CH), 129.45 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 128.9 (CH), 128.7 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.2 (CH), 125.6 (CH), 123.9 (CH), 80.2 (CH), 79.3 (CH), 72.9 (C-I), 72.3 (C-I), 51.85 (CH_3), 51.84 (CH_3), 43.8 (CH), 42.1 (CH), 14.0 (CH_3), 12.6 (CH_3) ppm. HRMS (EI) Calcd for $C_{19}H_{17}IO_3$ 420.0222, Found 420.0229.

3-(4-Iodo-3-phenyl -1*H*-isocromen-1-yl)-3*H*-furan-2-one (6g)



Colorless crystals (mp = 72ºC, dec). R_f = 0.24 (Hexane: EtOAc, 3:1). ^{1}H-RMN ($CDCl_3$, 300 MHz): 7.82-7.78 (m, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.51-7.42 (m, 4H), 7.32 (td, *J* = 7.4, 1.4 Hz, 1H), 7.25 (dd, *J* = 5.7, 1.7 Hz, 1H), 6.97 (dd, *J* = 7.4, 0.6 Hz, 1H), 6.17 (dd, *J* = 5.7, 2 Hz, 1H), 5.57 (dt, *J* = 7.7, 1.7 Hz, 1H), 5.35 (d, *J* = 7.7 Hz, 1H) ppm. ^{13}C-RMN ($CDCl_3$, 75 MHz): 172.2(C=O), 152.8 (C), 151.9 (CH), 135.6 (C), 132.7 (C), 130.6 (CH), 130.0 (CH), 129.9 (CH), 129.8 (CH), 128.1 (CH), 127.8 (CH), 125.2 (C), 124.9 (CH), 123.3 (CH), 81.3 (CH), 79.1 (CH), 72.2 (C-I) ppm. IR (CH_2Cl_2, cm^{-1}): 3021, 1785, 1755. HRMS (IE): Calcd. for $C_{19}H_{13}IO_3$: 415.9904, Found: 415.9909. Anal. calcd. for $C_{19}H_{13}IO_3$: C, 54.83%; H, 3.15%. Found: C, 54.60%; H, 3.25%.

Methyl 2-[4-iodo-3-(4-nitrophenyl)-1*H*-isochromen-1-yl]-2-methylpropanoate (6h)

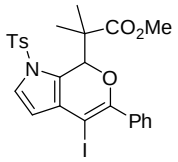


Ar = 4-$NO_2C_6H_4$

Yellow syrup. R_f = 0.56 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.25 (d, *J* = 9.1 Hz, 2H), 7.84 (d, *J* = 9.1 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H),

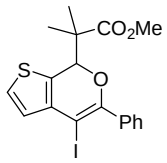
7.31 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.4 Hz, 1H), 5.61 (s, 1H), 3.71 (s, 3H), 1.27 (s, 6H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 175.8 (C=O), 152.3 (C), 147.9 (C), 143.0 (C), 132.3 (C), 131.1 (CH), 129.5 (CH), 129.1 (CH), 127.9 (CH), 126.0 (C), 125.9 (CH), 123.1 (CH), 83.3 (CH), 74.5 (C-I), 52.3 (CH_3), 49.6 (C), 22.3 (CH_3), 20.0 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}): 3076, 2949, 1732. HRMS (FAB+) calcd for $C_{20}H_{19}INO_5$ (M+H) 480.0308, Found 480.0305. Anal. calcd for $C_{20}H_{18}INO_5$: C, 50.12%; H, 3.79%; N, 2.92%, Found: C, 50.29%; H, 3.80%; N, 3.15%.

Methyl 2-(1,7-dihydro-4-iodo-5-phenyl-1-*p*-tosylpyrano[3,4-b]pyrrol-7-yl)-2-methylpropanoate (9a)



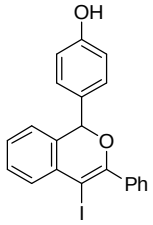
Orange solid (mp 148-150ºC). R_f = 0.41 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.71 (d, *J* = 7.8 Hz, 2H), 7.67-7.65 (m, 2H), 7.40-7.38 (m, 3H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 2.3 Hz, 1H), 6.35 (s, 1H), 6.28 (d, *J* = 2.3 Hz, 1H), 3.76 (s, 3H), 2.39 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 175.6 ($\underline{C}O_2Me$), 150.9 (C), 145.2 (C), 135.1 (C), 134.7 (C), 129.9 (CH), 129.7 (CH), 129.4 (CH), 128.8 (C), 127.5 (CH), 126.5 (CH), 123.8 (CH), 117.5 (C), 115.0 (CH), 79.7 (CH), 60.7 (C-I), 52.4 (CH_3), 50.9 (C), 24.1 (CH_3), 21.5 (CH_3), 19.6 (CH_3) ppm. IR (CH_2Cl_2, cm-1): 1722. HRMS (FAB) Calcd for $C_{25}H_{24}INO_5S$ 577.0420, Found 577.0407. Anal. Calcd. for $C_{25}H_{24}INO_5S$: C, 52.00%; H, 4.19%; N, 2.43%; found C, 51.59%; H, 4.26%; N, 2.11%.

Methyl 2-(4-iodo-5-phenyl-7*H*-thieno[2,3-c]pyran-7-yl)-2-methylpropanoate (9b)



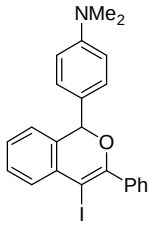
Orange oil. R_f = 0.48 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.70-7.64 (m, 2H), 7.44-7.36 (m, 3H), 7.21 (d, *J* = 5.1 Hz, 1H), 7.11 (d, *J* = 5.1 Hz, 1H), 5.95 (s, 1H), 3.76 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 175.6 (C=O), 151.4 (C), 137.1 (C), 135.5 (C), 129.7 (CH), 129.2 (CH), 128.8 (CH), 127.6 (CH), 123.0 (CH), 122.8 (C), 81.5 (CH), 62.6 (C-I), 52.1 (CH_3), 49.4 (C), 20.7 (CH_3), 20.5 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}) 3053, 1734. HRMS (EI) Calcd for $C_{18}H_{17}IO_3S$ 439.9943, Found 439.9939.

4-(4-Iodo-3-phenyl-1*H*-isochromen-1-yl)phenol (11a)



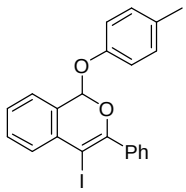
Orange syrup. R_f = 0.29 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.61 (d, *J* = 7.7 Hz, 1H), 7.53-7.46 (m, 2H), 7.41-7.35 (m, 4H), 7.31-7.24 (m, 3H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.24 (s, 1H), 5.49 (broad s, 1H, OH) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 155.9 (C), 154.5 (C), 136.6 (C), 133.3 (C), 131.1 (C), 130.9 (C), 130.2 (CH), 129.9 (CH), 129.3 (CH), 129.0 (CH), 128.5 (CH), 127.7 (CH), 127.6 (CH), 124.8 (CH), 115.3 (CH), 80.2 (CH), 73.2 (C-I) ppm. IR (CH_2Cl_2, cm^{-1}) 3569, 3044, 1174. HRMS (EI) calcd for $C_{21}H_{15}IO_2$ 426.0117, Found 426.0119.

4-(4-Iodo-3-phenyl-1*H*-isochromen-1-yl)-*N*,*N*-dimethylaniline (11b)



White solid (mp = 51ºC, dec). R_f = 0.34 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.61-7.50 (m, 3H), 7.40-7.18 (m, 7H), 6.81-6.73 (m, 3H), 6.22 (s, 1H), 2.98 (s, 6H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 154.6 (C), 150.6 (C), 136.7 (C), 133.4 (C), 131.5 (C), 130.4 (CH), 129.4 (CH), 129.2 (CH), 128.9 (CH), 128.3 (CH), 127.5 (2 x CH), 126.2 (C), 124.8 (CH), 112.1 (CH), 80.6 (CH), 72.9 (C-I), 40.4 (2 x CH3) ppm. IR (CH_2Cl_2, cm^{-1}) 3046, 1612, 1524. HRMS (FAB+) Calcd for $C_{23}H_{21}INO$ (M+H) 454.0668, Found 454.0660. Anal. Calcd for $C_{23}H_{20}INO$: C, 60.94%; H, 4.45%; N, 3.09%, Found: C, 60.40%; H, 4.38%; N, 2.74%.

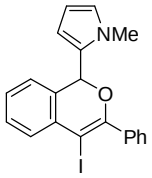
4-Iodo-1-(4-methylphenoxi)-3-phenyl-1*H*-isochromene (11c)



Orange oil. R_f = 0.59 (Hexane:EtOAc, 3:1). ^{1}H-RMN ($CDCl_3$, 300 MHz): 7.70 (d, *J* = 7.9 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54-7.51 (m, 2H), 7.44-7.37 (m, 4H), 7.27 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.19-7.16 (m, 4H), 6.80 (s, 1H), 2.38 (s, 3H) ppm. ^{13}C-RMN ($CDCl_3$, 75 MHz): 154.7 (C), 151.3 (C), 136.6 (C), 131.9 (C), 131.6 (C), 130.4 (CH), 130.1 (CH), 130.0 (CH), 129.9 (CH), 129.2 (CH), 127.9 (CH), 127.6 (CH), 126.3 (C),

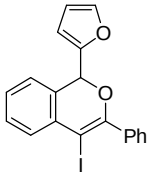
125.5 (CH), 116.7 (CH), 96.7 (CH), 73.6 (C-I), 20.6 (CH_3) ppm. HMRS (FAB+): Calcd. for $C_{22}H_{18}IO_2$ (M+H): 441.0352. Found: 441.0350.

2-(4-Iodo-3-phenyl-1*H*-isochromen-1-yl)-1-methyl-1*H*-pyrrol (13a)



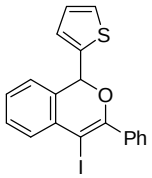
Yellow oil. R_f = 0.37 (Hexane:EtOAc, 3:1). ^{1}H-RMN ($CDCl_3$, 300 MHz): 7.62-7.51 (m, 3H), 7.44-7.20 (m, 5H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.62 (t, *J* = 2.4 Hz, 1H), 6.43-6.41 (m, 1H), 6.27 (broad s, 2H), 3.62 (s, 3H) ppm. ^{13}C-RMN ($CDCl_3$, 75 MHz): 154.3 (C), 137.0 (C), 133.0 (C), 132.0 (C), 130.4 (CH), 129.1 (CH), 128.9 (CH), 128.1 (CH), 127.5 (CH), 127.4 (CH), 124.4 (CH), 122.3 (CH), 122.2 (C), 121.8 (CH), 108.3 (CH), 75.3 (CH), 72.9 (C-I), 36.1 (CH_3) ppm. HMRS (EI): Calcd. for $C_{20}H_{16}INO$: 413.0277. Found: 413.0281.

1-(Furan-2-yl)-4-iodo-3-phenyl-1*H*-isochromene (13b)



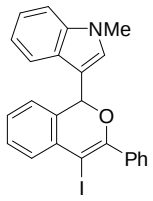
Orange oil. R_f = 0.38 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.68-7.52 (m, 4H), 7.49-7.38 (m, 4H), 7.35-7.29 (m, 1H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.42 (s, 1H), 6.40 (s, 1H), 6.12 (d, *J* = 2.9 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 154.0 (C), 152.6 (C), 143.9 (CH), 137.1 (C), 133.6 (C), 130.9 (CH), 130.1 (CH), 129.9 (CH), 129.6 (CH), 129.2 (C), 128.3 (CH), 128.2 (CH), 125.1 (CH), 111.4 (CH), 111.0 (CH), 73.7 (CH), 73.7 (C-I) ppm. HRMS (EI) Calcd for $C_{19}H_{13}IO_2$: 399.9955, Found 399.9957.

4-Iodo-3-phenyl-1-(thien-2-yl)-1*H*-isochromene (13c)



Reddish oil. R_f = 0.39 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.64-7.56 (m, 3H), 7.49-7.37 (m, 5H), 7.33 (td, *J* = 7.5, 1.1 Hz, 1H), 7.05-7.00 (m, 2H), 6.96-6.94 (m, 1H), 6.58 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 153.3 (C), 142.3 (C), 136.3 (C), 132.4 (C), 130.4 (C), 130.3 (CH), 129.4 (CH), 129.4 (CH), 128.9 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 126.8 (CH), 126.4 (CH), 124.5 (CH), 75.3 (CH), 73.4 (C-I) ppm. HRMS (EI) Calcd for $C_{19}H_{13}IOS$: 415.9726, Found 415.9729.

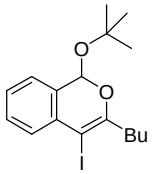
3-(4-Iodo-3-phenyl-1*H*-isochromen-1-yl)-1-methyl-1*H*-indole (13d)



Brown solid (mp = 77ºC, dec). R_f = 0.45 (Hexane: EtOAc, 5:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.88 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.51-7.19 (m, 10H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 10.9 Hz, 2H), 3.76 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 154.5 (C), 137.4 (C), 136.8 (C), 133.4 (C), 131.0 (C), 130.6 (CH), 129.7 (CH), 129.1 (CH), 128.9 (CH), 128.4 (CH), 127.5 (CH), 127.4 (CH), 126.7 (C), 124.5 (CH), 122.1 (CH), 119.9 (CH), 119.7 (CH), 112.8 (C), 109.4 (CH), 74.2 (CH), 72.5 (C-I), 32.8 (CH_3) ppm. HRMS (EI) Calcd for $C_{24}H_{18}INO$: 463.0433, Found: 463.0443.

Reaction of *o*-alkynylbenzaldehyde 1b with IPy_2BF_4 and *tert*-butyl alcohol: *o*-(1-hexynyl)benzaldehyde **1b** (0.19 g, 1 mmol, 1 equiv) was added to a solution of IPy_2BF_4 (0.37 g, 1 mmol, 1 equiv) in dry dichloromethane (10 mL) and the resultant solution was stirred at room temperature for 1 hour. After this time, the *tert*-butyl alcohol (115 µL, 1.2 mmol, 1.2 equiv) was added and the solution was stirred until disappearance of starting benzaldehyde (6 hours). The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and vigorously stirred. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL); dried over sodium sulfate and concentrated. The crude was purified by flash column chromatography (neutral aluminium oxide, hexane/EtOAc) to afford pure compound **2d** (275 mg, 68%).

3-Butyl-1-*tert*-butyl-4-iodo-1*H*-isochromene (2d)



Pale yellow oil. R_f = 0.58 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.42 (d, *J* = 7.1 Hz, 1H), 7.36 (td, *J* = 7.1, 1.1 Hz, 1H), 7.25 (td, *J* = 7.1, 1.1 Hz, 1H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.24 (s, 1H), 2.71 (t, *J* = 7.4 Hz, 2H), 1.70-1.59 (m, 2H), 1.51-1.28 (m with singlet at 1.38, 11H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 155.1 (C), 131.2 (C), 128.7 (CH), 128.1 (CH), 128.0 (C), 126.7 (CH), 124.3 (CH), 92.9 (CH), 75.6 (C), 72.8 (C-I), 36.8 (CH_2), 28.8 (CH_2), 28.7 (CH_3), 21.9 (CH_2), 13.8 (CH_3) ppm. HRMS (EI) Calcd for $C_{17}H_{23}IO_2$: 386.0743, Found 386.0744.

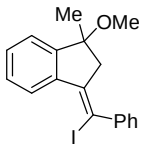
General procedure for the synthesis of 4-iodo-1-methoxy-1*H*-isochromenes 2a-c using IPy_2BF_4 and trimethylborate: Trimethylborate (0.22 mL, 2 mmol, 2 equiv) was added to a solution of IPy_2BF_4 (0.37g, 1 mmol, 1 equiv) in CH_2Cl_2 (10 mL) at 0ºC. After 10 min., the corresponding 2-alkynylbenzaldehyde **1a-c** (1 mmol, 1 equiv) was added and the solution was stirred at room temperature until disappearance of starting aldehyde. The reaction mixture was quenched with saturated aqueous $NaHCO_3$. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL); dried over sodium sulfate and concentrated. The crude was purified by flash column chromatography (neutral aluminium oxide, hexane/EtOAc) to afford pure compounds **2a,d,f**.

Reaction of *o*-(alkynyl)ketones 3a-b with IPy_2BF_4 and alcohols:

a) Using the system IPy_2BF_4/HBF_4: To a stirred solution of IPy_2BF_4 (0.37 g, 1 mmol, 1 equiv) in CH_2Cl_2 (10 mL) at –60ºC was added tetrafluoroboric acid, 54% solution in diethyl ether (0.15 mL, 1.1 mmol, 1.1 equiv). After 10 min., the corresponding *o*-(alkynyl)ketone **3a-b** (1 mmol, 1 equiv) was added. After the mixture was stirred for 30 min., methanol (48 µL, 1.2 mmol, 1.2 equiv) was added and the resulting solution was stirred at –60ºC for 24h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL), dried over sodium sulfate and concentrated. The crude was purified by flash column chromatography (neutral aluminium oxide, hexane/EtOAc) to afford pure compounds **4a-b**.

b) Reaction of 3a using the system $IPy_2BF_4/B(OMe)_3$: Trimethylborate (0.22 mL, 2 mmol, 2 equiv) was added to a solution of IPy_2BF_4 (0.37g, 1 mmol, 1 equiv) in CH_2Cl_2 (10 mL) at -60ºC. After 10 min., 2-(phenylethynyl)acetophenone **3a** was added (0.22 g, 1 mmol, 1 equiv) and the resultant solution was allowed to reach 0ºC for 24h. Then, the reaction mixture was quenched with saturated aqueous $NaHCO_3$; washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL), dried over sodium sulfate and concentrated. Flash column chromatography (neutral aluminium oxide, hexane/EtOAc) gave the pure compound **4a** (182 mg, 48%).

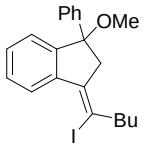
1,3-dihydro-3-[(*E*)-1-iodo-1-phenylmethylene)-1-methoxy-1-methylisobenzofurane (4a)



Pale yellow solid (*unstable*). R_f = 0.43 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.84 (d, *J* = 6.7 Hz, 1H), 7.68-7.50 (m, 4H), 7.47-7.33 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 1H), 3.02 (s, 3H), 1.73 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 150.9 (C), 142.6

(C), 141.7 (C), 133.8 (C), 130.3 (CH), 130.0 (CH), 128.9 (CH), 127.7 (2 x CH), 127.3 (CH), 125.5 (CH), 122.1 (CH), 110.1 (C), 65.9 (C-I), 50.5 (CH_3), 25.6 (CH_3) ppm. LRMS (EI) *m/z* (%) 378(M^+, 29), 347(14), 281(24), 251(M^+ - I, 100), 207(90), 191(35).

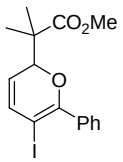
1,3-dihydro-3-[(*E*)-1-iodo-1-phenylmethylene)-1-methoxy-1-phenylisobenzofurane (4b)



Pale yellow oil (*unstable*). R_f = 0.55 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.67 (d, *J* = 7.8 Hz, 1H), 7.59-7.48 (m, 2H), 7.45-7.24 (m, 5H), 7.24 (d, *J* = 7.5 Hz, 1H), 3.21 (s, 3H), 3.09-2.87 (m, 2H), 1.71-1.61 (m, 2H), 1.50-1.38 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 150.5 (C), 142.7 (C), 140.5 (C), 133.0 (C), 129.4 (CH), 128.7 (CH), 128.4 (CH), 128.2 (CH), 125.6 (CH), 124.5 (CH), 123.2 (CH), 109.7 (C), 74.6 (C-I), 50.8 (CH_3), 38.8 (CH_2), 31.2 (CH_2), 21.5 (CH_2), 14.0 (CH_3) ppm. HRMS (EI) Calcd for $C_{21}H_{23}IO$: 418.0794, Found 418.0785.

Reaction of eninal 14 with IPy_2BF_4 and silylketeneacetal 5c: IPy_2BF_4 (0.37 g, 1 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (10 mL). The solution was cooled at 0ºC and tetrafluoroboric acid, 54% solution in diethyl ether (0.15 mL, 1.1 mmol, 1.1 equiv) was added. After 10 min., the eninal **14** (0.16 g, 1 mmol, 1 equiv) was added and the solution was stirred during 30 min. at room temperature. After this time, the silylketenacetal **5c** (243 µL, 1.2 mmol, 1.2 equiv) was added and the solution was further stirred until disappearance of starting aldehyde (1 hour). The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and vigorously stirred. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL); dried over sodium sulfate and concentrated. The crude was purified by flash column chromatography (neutral aluminium oxide, hexane/EtOAc) to afford pure compounds **15a** (23%, 90 mg) and **15b** (31%, 120 mg).

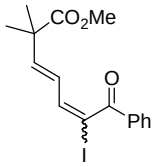
Methyl 2-(5-iodo-6-phenyl-2*H*-piran-2-yl)-2-methylpropanoate (15a)



Yellow oil. R_f = 0.55 (Hexane: EtOAc, 5:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.52-7.48 (m, 2H), 7.40-7.24 (m, 3H), 6.74 (d, *J* = 5.7 Hz, 1H), 4.73 (t, *J* = 5.7 Hz, 1H), 3.75 (broad s, 3H + 1H), 1.37 (s, 3H), 1.24 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 177.3 ($\underline{C}O_2Me$),

153.5 (C), 142.5 (CH), 136.7 (C), 129.6 (CH), 129.3 (CH), 127.9 (CH), 100.8 (CH), 68.8 (C-I), 52.1 (CH_3), 49.5 (CH), 48.1 (C), 22.5 (CH_3), 20.5 (CH_3) ppm. HRMS (EI) Calcd for $C_{16}H_{17}IO_3$: 384.0217, Found: 384.0229.

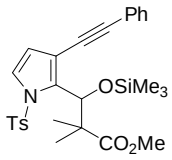
(3*E*,5*E*)-Methyl 2,2-dimethyl-6-iodo-7-oxo-7-phenylhepta-3,5-dienoate (15b)



Yellow oil. R_f = 0.45 (Hexane: EtOAc, 5:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.95 (d, *J* = 7.1 Hz, 2H), 7.64-7.59 (m, 1H), 7.51-7.46 (m, 2H), 7.20 (d, *J* = 10.8 Hz, 1H), 6.09 (d, *J* = 15.4 Hz, 1H), 5.90 (dd, *J* = 15.4, 10.8 Hz, 1H), 3.61 (s, 3H), 1.10 (s, 6H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 192.5 (C=O), 175.6 ($\underline{C}O_2Me$), 145.0 (CH), 143.3 (CH), 134.1 (C), 133.8 (CH), 129.9 (CH), 128.7 (CH), 124.8 (CH), 92.4 (C-I), 52.1 (CH_3), 44.4 (C), 24.5 (2 x CH_3) ppm. IR (CH_2Cl_2, cm^{-1}): 2358, 1733, 1661. HRMS (EI) Calcd for $C_{16}H_{17}IO_3$: 384.0221, Found 384.0217.

Reaction of 3-phenylethynyl-*N*-tosylpyrrole-2-carboxaldehyde 7a with I_2 and silylketeneacetal 5c:[5] Reaction of 3-phenylethynyl-*N*-tosylpyrrole-2-carboxaldehyde **7a** (87 mg, 0.25 mmol, 1 equiv), K_2CO_3 (34 mg, 0.25 mmol, 1 equiv), methyl trimethylsilyl dimethylketene acetal **5c** (61 μL, 0.3 mmol, 1.2 equiv), I_2 (76 mg, 0.3 mmol, 1.2 equiv) in 5 mL of CH_2Cl_2 at room temperature until disappearance of the starting material. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ and water. The solution was extracted with CH_2Cl_2, dried over sodium sulfate and concentrated. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc) to afford the pure compounds **a** (20 mg, 15%) and **b** (50 mg, 45%).

Methyl 2,2-dimethyl-3-{3-(2-phenylethynyl)-1-*p*-tosyl-1H-pyrrol-2-yl}-3-trimethylsilyloxypropanoate (a):

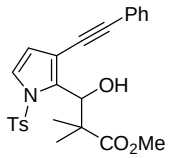


Light brown solid (mp 130-133ºC). R_f = 0.56 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.71 (d, *J* = 12.7 Hz, 2H), 7.44-7.42 (m, 2H), 7.34-7.29 (m, 6H), 6.44 (d, *J* = 5.0 Hz, 1H), 5.82 (s, 1H), 3.74 (s, 3H), 2.42 (s, 3H), 1.37 (s, 3H), 1.18 (s, 3H), -0.24 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 176.7 ($\underline{C}O_2Me$), 145.4 (C), 137.2 (C), 136.2 (C), 131.0 (CH), 130.1 (CH), 128.2 (CH), 127.7 (CH), 127.0 (CH), 123.8 (C), 123.4 (CH), 116.5

[5] Yue, D.; Cà, N. D.; Larock, R. C. *Org. Lett.* **2004**, *6*, 1581.

(CH), 112.2 (C), 92.4 (C), 84.8 (C), 71.6 (CH), 51.8 (C), 51.8 (CH_3), 23.2 (CH_3), 21.5 (CH_3), 19.5 (CH_3), -0.7 (3 x CH_3). IR (CH_2Cl_2, cm-1): 2215, 1726. HRMS (FAB) Calcd for $C_{28}H_{33}NO_5SSi$ 523.1849, Found 523.1853.

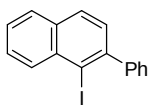
Methyl 3-hydroxy-2,2-dimethyl-3-{3-(2-phenylethynyl)-1-*p*-tosyl-1H-pyrrol-2-yl}propanoate (b):



Yellow oil. R_f = 0.32 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.72 (d, *J* = 8.3 Hz, 2H), 7.51-7.25 (m, 8H), 6.42 (d, *J* = 3.5 Hz, 1H), 5.77 (broad d, *J* = 7.4 Hz, 1H), 3.91 (broad s, 1H, OH), 3.77 (s, 3H), 2.43 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H).
^{13}C-NMR ($CDCl_3$, 50 MHz): 177.1 ($\underline{C}O_2Me$), 145.4 (C), 136.9 (C), 135.7 (C), 131.2 (CH), 130.1 (CH), 128.4 (CH), 128.3 (CH), 126.6 (CH), 123.9 (CH), 122.8 (C), 116.4 (CH), 110.9 (C), 94.1 (C), 83.0 (C), 72.6 (CH), 52.4 (CH_3), 49.9 (C), 24.2 (CH_3), 21.6 (CH_3), 20.2 (CH_3). IR (CH_2Cl_2, cm-1): 3544, 2217, 1731. HRMS (FAB) Calcd for $C_{25}H_{25}NO_5S$ 451.1453, Found 451.1458.

General procedure for the reaction of *o*-(1-hexynyl)benzaldehyde 1b and alkynes 16 using IPy_2BF_4 and HBF_4: IPy_2BF_4 (0.37 g, 1 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (10 mL). The solution was cooled at 0ºC and tetrafluoroboric acid, 54% solution in diethyl ether (0.30 mL, 2.2 mmol, 2.2 equiv) was added. After 10 min., the *o*-(1-hexynyl)benzaldehyde **1b** (0.19 g, 1 mmol, 1 equiv) was added and the solution was stirred during 30 min. at room temperature. After this time, the corresponding alkyne **16** (1.2 mmol, 1.2 equiv) was added and the solution was further stirred at room temperature (reaction times are given in Table 3). The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and vigorously stirred. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL); dried over sodium sulfate and concentrated. The crude were purified by flash column chromatography (silica gel, hexane/EtOAc) to afford pure 1-iodonaphthalenes **17** with variable amounts of the corresponding naphthyl ketones **18** as minor products.

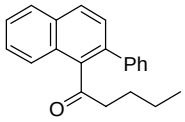
1-Iodo-2-phenylnaphthalene (17a)



Pale yellow oil. R_f = 0.57 (Hexane: EtOAc, 10:1).^{1}H-NMR ($CDCl_3$, 200 MHz): 8.48 (d, *J* = 8.2 Hz, 1H), 7.96-7.84 (m, 2H), 7.75-7.40 (m, 8H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 146.0 (C), 145.9 (C), 134.8 (C), 133.3 (CH), 132.8 (C), 129.4 (CH), 128.3 (CH), 128.1

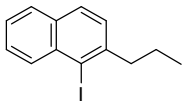
(CH), 128.0 (CH), 127.8 (CH), 127.5 (CH), 126.4 (CH), 104.0 (C-I) ppm. HRMS (EI) Calcd for $C_{16}H_{11}I$: 329.9905, Found 329.9906.

1-(2-Phenylnaphthalen-1-yl)-pentan-1-one: Minor product



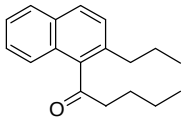
Yellow oil. R_f = 0.37 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.02-7.80 (m, 3H), 7.64-7.46 (m, 8H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.53-1.45 (m, 2H), 1.22-1.08 (m, 2H), 0.76 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 209.9 (C=O), 140.3 (C), 138.4 (C), 135.8 (C), 135.1 (C), 132.4 (C), 129.4 (CH), 129.2 (CH), 128.6 (CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 127.3 (CH), 126.2 (CH), 124.8 (CH), 44.8 (CH_2), 25.6 (CH_2), 21.9 (CH_2), 13.6 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}): 3030, 1692. HRMS (EI) Calcd for $C_{21}H_{20}O$: 288.1514, Found: 288.1518.

1-Iodo-2-propylnaphthalene (17b)



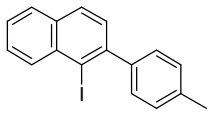
Yellow oil. R_f = 0.52 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.30 (d, *J* = 8.5 Hz, 1H), 7.80-7.75 (m, 2H), 7.61-7.44 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 1H), 3.06-2.98 (m, 2H), 1.82-1.67 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 144.5 (C), 135.1 (C), 132.6 (CH), 132.5 (C), 128.4 (CH), 128.0 (CH), 127.5 (CH), 127.4 (CH), 125.6 (CH), 105.1 (C-I), 44.7 (CH_2), 23.7 (CH_2), 13.9 (CH_3) ppm. HRMS (EI) Calcd for $C_{13}H_{13}I$: 296.0062, Found: 296.0067.

1-(2-Propylnaphthalen-1-yl)pentan-1-one: Minor product



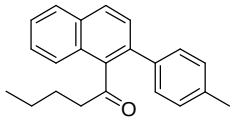
Yellow oil. R_f = 0.32 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.84-7.79 (m, 2H), 7.58-7.42 (m, 3H), 7.38 (d, *J* = 8.5 Hz, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.88-1.67 (m, 4H), 1.53-1.40 (m, 2H), 1.03-0.92 (m, 6H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 210.5 (C=O), 138.6 (C), 134.9 (C), 131.7 (C), 129.2 (C), 128.6 (CH), 128.1 (CH), 127.3 (CH), 126.6 (CH), 125.4 (CH), 124.1 (CH), 45.7 (CH_2), 35.5 (CH_2), 25.6 (CH_2), 24.7 (CH_2), 22.4 (CH_2), 14.1 (CH_3), 13.9 (CH_3) ppm. HRMS (EI) Calcd for $C_{18}H_{22}O$: 254.1671, Found: 254.1668.

1-Iodo-2-*p*-tolylnaphthalene (17c)



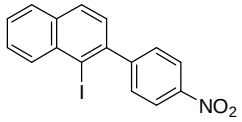
Yellow solid (mp = 84-87ºC). R_f = 0.55 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.47 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.73-7.38 (m, 7H), 2.54 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 146.0 (C), 143.1 (C), 137.2 (C), 134.8 (C), 133.3 (CH), 132.7 (C), 129.3 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 126.3 (CH), 104.1 (C-I), 21.3 (CH_3) ppm. HRMS (EI) Calcd for $C_{17}H_{13}I$: 344.0062, Found: 344.0078.

1-(2-*p*-Tolylnaphthalen-1-yl)pentan-1-one Minor product



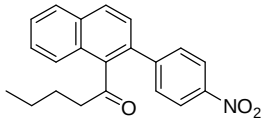
Yellow solid (mp = 98-101ºC). R_f = 0.51 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.01-7.81 (m, 3H), 7.56-7.47 (m, 2H), 7.39-7.20 (m, 5H), 2.44 (s, 3H), 2.31 (t, *J* = 7.2 Hz, 2H), 1.52-1.43 (m, 2H), 1.22-1.02 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 210.1 (C=O), 138.1 (C), 137.7 (C), 137.3 (C), 135.8 (C), 132.3 (C), 129.3 (CH), 129.2 (CH), 129.1 (CH), 128.8 (C), 128.1 (CH), 127.5 (CH), 127.2 (CH), 126.0 (CH), 124.7 (CH), 44.7 (CH_2), 25.7 (CH_2), 21.9 (CH_2), 21.1 (CH_3), 13.5 (CH_3) ppm. HRMS (EI) Calcd for $C_{22}H_{22}O$: 302.1671, Found 302.1671.

1-Iodo-2-(4-nitrophenyl)naphthalene (17d)



Yellow solid (mp = 152-154ºC). R_f = 0.24 (Hexane: EtOAc, 20:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.36 (d, *J* = 8.6 Hz, 3H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.71-7.52 (m, 4H), 7.39 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 152.1 (C), 147.1 (C), 143.7 (C), 134.7 (C), 133.2 (CH), 133.1 (C), 130.6 (CH), 128.9 (CH), 128.5 (CH), 128.3 (CH), 127.1 (CH), 126.5 (CH), 123.2 (CH), 103.2 (C-I) ppm. HRMS (EI) Calcd for $C_{16}H_{10}INO_2$: 374.9756, Found 374.9755.

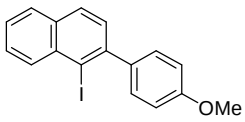
1-[2-(4-Nitrophenyl)naphthalen-1-yl]pentan-1-one: Minor product



Yellow solid (mp = 157-160ºC). R_f = 0.20 (Hexane: EtOAc, 20:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.13 (d, *J* = 8.6 Hz, 2H), 7.86-7.53 (m, 7H), 7.32 (d, *J* = 8.2 Hz, 1H), 2.37 (t, *J* =

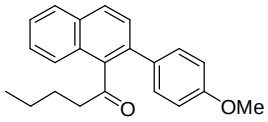
7.4 Hz, 2H), 1.52-1.44 (m, 2H), 1.31-1.10 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 209.1 (C=O), 149.8 (C), 137.4 (C), 136.2 (C), 134.8 (C), 132.5 (CH), 131.1 (C), 129.7 (C), 129.5 (CH), 128.2 (CH), 127.6 (CH), 127.1 (CH), 126.0 (CH), 125.3 (CH), 122.8 (CH), 42.1 (CH_2), 26.1 (CH_2), 23.2 (CH_2), 13.1 (CH_3) ppm. HRMS (EI) Calcd for $C_{21}H_{19}NO_3$: 333.1365, Found 333.1361.

1-Iodo-2-(4-methoxyphenyl)naphthalene (17e)



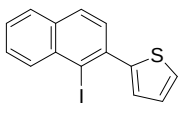
Yellow solid (mp = 85-88ºC). R_f = 0.62 (Hexane: EtOAc, 3:1).^{1}H-NMR ($CDCl_3$, 300 MHz): 8.40 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.69-7.62 (m, 1H), 7.60-7.53 (m, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 158.9 (C), 145.7 (C), 138.5 (C), 134.9 (C), 133.4 (CH), 132.7 (C), 130.6 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 126.3 (CH), 113.2 (CH), 104.5 (C-I), 55.2 (CH_3) ppm. HRMS (EI) Calcd for $C_{17}H_{13}IO$: 360.0011, Found 360.0015. Anal. Calcd for $C_{17}H_{13}IO$: C, 56.69%; H, 3.64%; Found: C, 57.03%; H, 3.11%.

1-[2-(4-Methoxyphenyl)naphthalen-1-yl]-pentan-1-one: Minor product



Yellow solid (mp = 96-99ºC). R_f = 0.57 (Hexane: EtOAc, 3:1).^{1}H-NMR ($CDCl_3$, 300 MHz): 8.01-7.80 (m, 3H), 7.61-7.45 (m, 3H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.54-1.42 (m, 2H), 1.19-1.10 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 210.2 (C=O), 159.4 (C), 138.0 (C), 135.5 (C), 132.6 (C), 132.2 (C), 130.5 (CH), 129.2 (C), 129.1 (CH), 128.1 (CH), 127.5 (CH), 127.2 (CH), 126.0 (CH), 124.6 (CH), 114.1 (CH), 55.3 (CH_3), 44.7 (CH_2), 25.7 (CH_2), 22.0 (CH_2), 13.6 (CH_3) ppm. HRMS (EI) Calcd for $C_{22}H_{22}O_2$: 318.1620, Found 318.1617.

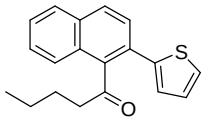
2-(1-Iodonaphthalen-2-yl)thiophene (17f)



Yellow solid (mp = 514-56ºC). R_f = 0.52 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.39 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.69-7.54 (m, 3H), 7.48 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.26-7.23 (m, 1H), 7.19 (dd, *J* = 5.1, 3.7 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 146.8 (C), 138.9 (C), 135.7 (C), 133.8 (CH), 133.2 (C), 128.4 (CH),

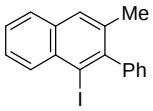
128.3 (CH), 128.2 (2 x CH), 128.1 (CH), 126.8 (CH), 126.6 (CH), 125.9 (CH), 105.9 (C-I) ppm. HRMS (EI) Calcd for $C_{14}H_9IS$: 335.9470, Found 335.9464.

1-[2-(Thiophen-2-yl)naphthalen-1-yl]pentan-1-one: Minor product



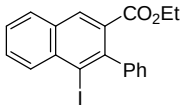
Pale brown solid (mp = 61-64ºC). R_f = 0.37 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.95-7.90 (m, 2H), 7.81-7.78 (m, 1H), 7.64-7.54 (m, 3H), 7.46 (dd, *J* = 4.5, 1.8 Hz, 1H), 7.15-7.12 (m, 2H), 2.49 (t, *J* = 7.4 Hz, 2H), 1.64-1.54 (m, 2H), 1.30-1.18 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 209.8 (C=O), 152.2 (C), 141.4 (C), 138.3 (C), 132.6 (C), 129.2 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.5 (CH), 127.4 (CH), 127.0 (CH), 126.4 (CH), 124.8 (CH), 44.4 (CH_2), 25.8 (CH_2), 22.0 (CH_2), 13.7 (CH_3) ppm. HRMS (EI) Calcd for $C_{19}H_{18}OS$: 294.1078, Found 294.1089.

1-Iodo-3-methyl-2-phenylnaphthalene (17g)



White solid (mp = 89-92ºC). R_f = 0.71 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.28 (d, *J* = 7.4 Hz, 1H), 7.79-7.62 (m, 2H), 7.59-7.43 (m, 5H), 7.22 (dd, *J* = 7.9, 1.4 Hz, 2H), 2.25 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz): 146.9 (C), 145.8 (C), 134.9 (C), 133.5 (2 x C), 133.2 (CH), 128.9 (CH), 128.6 (CH), 128.3 (CH), 127.4 (CH), 127.3 (CH), 127.0 (CH), 126.5 (CH), 106.0 (C-I), 22.8 (CH_3) ppm. HRMS (EI) Calcd for $C_{17}H_{13}I$: 344.0062, Found 344.0068. Anal. Calcd for $C_{17}H_{13}I$: C, 59.32%; H, 3.81%; Found: C, 59.42%; H, 3.96%.

4-Iodo-3-phenylnaphthalene-2-carboxylic acid ethyl ester (17h)

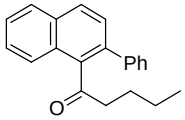


Pale yellow solid (mp = 93-96ºC). R_f = 0.38 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.37 (s, 1H), 8.36 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H) 7.71-7.64 (m, 1H), 7.61-7.55 (m, 1H), 7.52-7.41 (m, 3H), 7.31-7.25 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.00 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 167.1 (C=O), 145.2 (C), 143.7 (C), 135.8 (C), 133.4 (CH), 131.8 (C), 130.7 (CH), 130.3 (C), 129.7 (CH), 129.3 (CH), 129.0 (CH), 127.5 (CH), 127.4 (CH), 127.2 (CH), 107.8 (C-I), 61.0 (CH_2), 13.5 (CH_3). IR (CH_2Cl_2, cm^{-1}): 3020, 1715. HRMS (EI) Calcd for $C_{19}H_{15}IO_2$: 402.0117, Found

402.0125. Anal. Calcd for $C_{19}H_{15}IO_2$: C, 56.74%; H, 3.76%; Found: C, 56.54%; H, 4.05%.

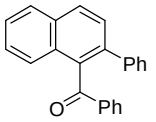
General procedure for the reaction of *o*-alkynylbenzaldehyde 1 and alkenes 19-20 using IPy_2BF_4 and HBF_4: To a stirred solution of IPy_2BF_4 (0.37 g, 1 mmol, 1 equiv) in CH_2Cl_2 (10 mL) at 0ºC was added tetrafluoroboric acid, 54% solution in diethyl ether (0.15 mL, 1.1 mmol, 1.1 equiv). After 10 min., the corresponding *o*-(alkynyl)benzaldehyde **1** (1 mmol, 1 equiv) was added. After the mixture was stirred for 30 min. at room temperature, the corresponding alkene **19-20** (1.2 mmol, 1.2 equiv) was added and the resulting solution was stirred at room temperature until disappearance of starting benzaldehyde (reactions times are given in Tables 4 and 5). The reaction mixture was quenched with saturated aqueous $NaHCO_3$. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL), dried over sodium sulfate and concentrated. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc) to afford pure compounds **18**.

1-(2-Phenylnaphthalen-1-yl)pentan-1-one (18a).



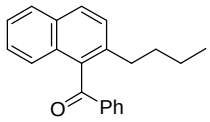
Yellow oil. R_f = 0.37 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.02-7.80 (m, 3H), 7.64-7.46 (m, 8H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.53-1.45 (m, 2H), 1.22-1.08 (m, 2H), 0.76 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 209.9 (C=O), 140.3 (C), 138.4 (C), 135.8 (C), 135.1 (C), 132.4 (C), 129.4 (CH), 129.2 (CH), 128.6 (CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 127.3 (CH), 126.2 (CH), 124.8 (CH), 44.8 (CH_2), 25.6 (CH_2), 21.9 (CH_2), 13.6 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}): 3030, 1692. HRMS (EI) Calcd for $C_{21}H_{20}O$: 288.1514, Found: 288.1518.

Phenyl-(2-phenylnaphthalen-1-yl)methanone (18b)



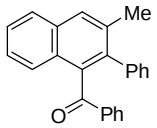
Yellow solid (mp = 117-120ºC). R_f = 0.42 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.07 (d, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.72-7.67 (m, 2H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.60-7.39 (m, 5H), 7.32-7.21 (m, 5H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 199.5 (C=O)), 140.1 (C), 137.8 (C), 137.3 (C), 137.6 (C), 133.1 (CH), 132.3 (C), 130.5 (C), 129.4 (CH), 129.35 (CH), 129.3 (CH), 128.1 (CH), 18.05 (CH), 128.0 (CH), 127.4 (CH), 127.3 (CH), 127.1 (CH), 126.2 (CH), 125.4 (CH). IR (CH_2Cl_2, cm^{-1}): 3050, 1664. HRMS (EI) Calcd. for $C_{23}H_{16}O$: 308.1201, Found: 308.1208.

Phenyl-(2-butylnaphthalen-1-yl)methanone (18c)



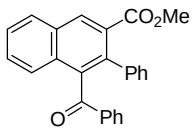
Yellow oil. R_f = 0.41 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.98-7.81 (m, 4H), 7.61-7.37 (m, 7H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.75-1.54 (m, 2H), 1.41-1.19 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz): 200.2 (C=O), 137.8 (C), 137.2 (C), 135.5 (C), 133.6 (CH), 131.6 (C), 130.6 (C), 129.7 (CH), 128.9 (CH), 128.6 (CH), 127.9 (CH), 127.3 (CH), 126.5 (CH), 125.4 (CH), 33.35 (CH_2), 33.3 (CH_2), 22.5 (CH_2), 13.7 (CH_3) ppm. HRMS (EI) Calcd for $C_{21}H_{20}O$: 288.1514, Found: 288.1512.

(3-Methyl-2-phenylnaphthalen-1-yl)-phenylmethanone (18d)



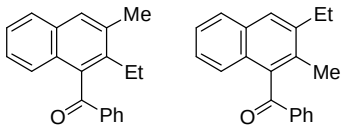
White solid (mp = 152-155ºC). R_f = 0.35 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.96-7.88 (m, 2H), 7.75-7.59 (m, 3H), 7.56-7.32 (m, 4H), 7.29-7.04 (m, 6H), 2.35 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 199.4 (C=O) , 138.1 (2 x C), 137.9 (C), 136.8 (C), 134.0 (C), 132.9 (CH), 132.6 (C), 129.2 (CH), 129.0 (CH), 128.9 (C), 128.0 (2 x CH), 127.6 (CH), 127.3 (CH), 127.0 (CH), 126.2 (CH), 126.1 (CH), 125.2 (CH), 20.9 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}): 3052, 1667. HRMS (EI) Calcd for $C_{24}H_{18}O$: 322.1358, Found 322.1360. Anal. Calcd for $C_{24}H_{18}O$: C, 89.41%; H, 5.63%; Found: C, 89.78%; H, 5.35%.

4-Benzoyl-3-phenylnaphthalene-2-carboxylic acid methyl ester (18e)



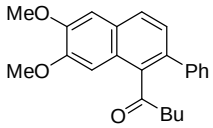
Yellow solid (mp = 151-153ºC). R_f = 0.52 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.56 (s, 1H), 8.07 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.72-7.67 (m, 1H), 7.65-7.50 (m, 5H), 7.46-7.41 (m, 1H), 7.31-6.82 (m, 6H), 3.64 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 198.3 (C=O), 167.9 ($\underline{C}O_2Me$), 138.0 (C), 137.9 (C), 137.5 (C), 135.6 (C), 133.1 (CH), 131.5 (CH), 131.3 (C), 131.2 (C), 129.3 (C), 129.1 (2 x CH), 128.9 (CH), 128.1 (2 x CH), 127.3 (CH), 127.1 (CH), 126.9 (CH), 125.2 (CH), 51.9 (CH_3). IR (CH_2Cl_2, cm^{-1}): 3028, 1728. HRMS (EI) Calcd for $C_{25}H_{18}O_3$: 366.1256, Found 366.1256. Anal. Calcd for $C_{25}H_{18}O_3$: C, 81.95%; H, 4.95%; Found: C, 82.15%; H, 4.67%.

Mixture of regioisomers: (2-Ethyl-3-methylnaphthalen-1-yl)(phenyl)methanone (major product) and (2-Ethyl-3-methylnaphthalen-4-yl)(phenyl)methanone (minor product) (18f)



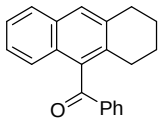
Yellow oil. R_f = 0.42 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.93-7.76 (m, 7H), 7.63-7.55 (m, 2), 7.51-7.39 (m, 7H), 7.36-7.28 (m, 2H), 2.86 (c, *J* = 7.5 Hz, 2H, *major*), 2.59 (s, 3H, *min*or), 2.31 (s, 3H, *major*), 1.40 (t, *J* = 7.5 Hz, 3H, *major*), 1.16 (t, *J* = 7.5 Hz, 3H, *min*or) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 200.8 (C=O), 200.4 (C=O), 140.7 (C), 137.7 (C), 137.5 (C), 136.4 (C), 135.9 (C), 134.5 (C), 133.6 (2 x CH), 131.9 (C), 131.8 (C), 131.1 (C), 129.7 (CH), 129.6 (CH), 129.4 (C), 129.3 (CH), 129.1 (C), 128.7 (CH), 128.6 (CH), 127.4 (CH), 127.1 (CH), 126.8 (CH), 125.7 (CH), 125.6 (CH), 125.4 (CH), 125.3 (CH), 124.7 (CH), 124.5 (CH), 26.2 (CH_2), 24.2 (CH_2), 19.5 (CH_3), 16.4 (CH_3), 14.5 (CH_3), 14.1 (CH_3) ppm. HRMS (EI) Calcd for $C_{20}H_{18}O$: 274.1358, Found 274.1354.

1-(2,3-Dimethoxi-6-phenylnaphthalen-5-yl)pentan-1-one (18g)



Orange oil. R_f = 0.40 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.80 (d, *J* = 8.3 Hz, 1H), 7.50-7.37 (m, 6H), 7.19 (t, *J* = 6.6 Hz, 2H), 4.04 (s, 3H), 3.99 (s, 3H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.51-1.40 (m, 2H), 1.18-1.05 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 210.4 (C=O), 150.3 (C), 149.5 (C), 140.6 (C), 136.7 (C), 134.6 (C), 129.2 (CH), 128.4 (CH), 127.5 (CH), 127.4 (CH), 125.6 (CH), 124.7 (C), 106.3 (CH), 103.3 (CH), 55.7 (2 x CH_3), 44.6 (CH_2), 25.8 (CH_2), 21.8 (CH_2), 13.5 (CH_2) ppm. HRMS (EI) Calcd for $C_{23}H_{24}O_3$: 348.1725, Found 348.1725.

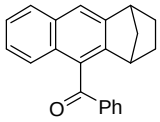
Phenyl-(1,2,3,4-tetrahydroanthracen-9-yl)-methanone (18h)



Pale yellow solid (mp = 157-160ºC). R_f = 0.45 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.85 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.69 (s, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50-7.28 (m, 5H), 3.10-2.80 (m, 2H), 2.76-2.50 (m, 2H), 1.96-1.75 (m, 4H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 200.6 (C=O), 137.3 (C), 135.7 (2 x C), 133.6 (CH), 132.6 (C), 131.6 (C), 129,5 (CH), 129.0 (C), 128.7 (CH), 127.9 (CH), 127.3 (CH), 125.5 (CH), 125.2 (CH), 124.5 (CH), 30.0 (CH_2), 27.1 (CH_2), 22.75 (CH_2), 22.7 (CH_2) ppm. IR

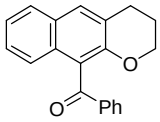
(CH_2Cl_2, cm^{-1}): 3060, 1657. HRMS (EI) Calcd for $C_{21}H_{18}O$: 286.1358, Found 286.1358. Anal. Calcd for $C_{25}H_{18}O$: C, 88.08%; H, 6.34%; Found: C, 88.58%; H, 6.09%.

3-Benzoyltetracycle[10.2.1.$0^{2,11}$.$0^{4,9}$]pentadeca-2,4,6,8,10-pentaene (18i)



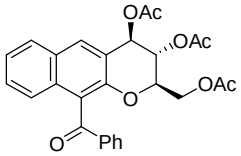
Yellow solid (mp = 126-128ºC). R_f = 0.47 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.92-7.88 (m, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.71 (s, 1H), 7.66-7.57 (m, 2H), 7.50-7.40 (m, 3H), 7.37-7.31 (m, 1H), 3.56 (s, 1H), 3.29 (s, 1H), 2.02-1.96 (m, 1H), 1.89-1.85 (m, 2H), 1.63-1.60 (m, 1H), 1.38-1.29 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 198.7 (C=O), 146.5 (C), 145.2 (C), 138.1 (C), 133.5 (CH), 132.5 (C), 129.8 (CH), 129.6 (C), 128.5 (CH), 127.9 (CH), 125.5 (CH), 125.2 (CH), 125.1 (CH), 119.9 (CH), 47.9 (CH_2), 43.1 (CH), 42.0 (CH), 27.5 (CH_2), 26.7 (CH_2) ppm. HRMS (EI) Calcd for $C_{22}H_{18}O$: 298.1358, Found 298.1362.

(3,4-Dihydro-2*H*-benzo[*g*]chromen-10-yl)(phenyl)methanone (18j)



Orange solid (mp = 125-127ºC, dec). R_f = 0.32 (Hexane: EtOAc, 5:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.92-7.85 (m, 2H), 7.85 (m, 1H), 7.69 (s, 1H), 7.65-7.44 (m, 4H), 7.36-7.30 (m, 2H), 4.19 (t, *J* = 5.4 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H), 2.13-2.05 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 198.0 (C=O), 150.4 (C), 137.8 (C), 133.3 (CH), 133.1 (C), 130.7 (C), 130.3 (C), 129.6 (2 x CH), 128.5 (CH), 127.3 (CH), 126.3 (CH), 123.9 (C), 123.7 (CH), 123.6 (CH), 66.9 (CH_2), 25.6 (CH_2), 22.1 (CH_2) ppm. HRMS (EI) Calcd for $C_{20}H_{16}O_2$: 288.1150, Found 288.1154.

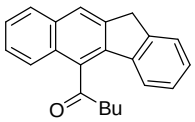
(2*S*,3*S*,4*R*)-(3,4-Diacetoxi-2-acetoximethyl-3,4-dihydro-2*H*-benzo[*g*]chromen-10-yl)(phenyl)methanone (18k)



Pale yellow solid (mp = 119-122ºC). R_f = 0.45 (Hexane: EtOAc, 1:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.87-7.79 (m, 4H), 7.59-7.52 (m, 2H), 7.46-7.35 (m, 4H), 6.32 (d, *J* = 6.2 Hz, 1H), 5.37 (t, *J* = 6.5 Hz, 1H), 4.44-4.38 (m, 1H), 4.27 (dd, *J* = 12.2, 5.9 Hz, 1H), 4.09 (dd, *J* = 12.2, 3.4 Hz, 1H), 2.19 (s, 3H), 2.06 (s, 3H), 1.80 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 196.3 (C=O), 170.3 ($\underline{C}O_2R$), 170.2 (CO_2R), 169.4 (CO_2R), 147.6 (C), 137.7 (C), 133.5 (CH), 131.7 (C), 130.7 (CH), 129.3 (CH), 128.8 (C), 128.5 (CH), 128.2

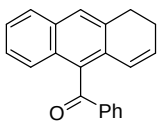
(CH), 128.1 (CH), 124.8 (CH), 123.9 (CH), 122.2 (C), 120.4 (C), 74.5 (CH), 68.4 (CH), 67.2 (CH), 61.7 (CH_2), 20.9 (CH_3), 20.6 (CH_3), 20.3 (CH_3) ppm. IR (CH_2Cl_2, cm^{-1}) 3064, 2962, 1745, 1669, 1370, 1232. HRMS (EI) Calcd for $C_{27}H_{24}O_8$: 476.1471, Found 476.1463. Anal. Calcd for $C_{27}H_{24}O_8$: C, 68.06%; H, 5.08%; Found: C, 67.71%; H, 4.67%.

1-(11*H*-Benzo[*b*]fluoren-5-yl)pentan-1-one (18l)



Pale yellow solid (mp = 200ºC, dec). R_f = 0.45 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.01 (s, 1H), 7.93-7.86 (m, 1H), 7.75-7.70 (m, 1H), 7.64-7.58 (m, 2H), 7.55-7.51 (m, 2H), 7.41 (dd, *J* = 5.7, 3.1 Hz, 2H), 4.13 (s, 2H), 3.07 (t, *J* = 7.4 Hz, 2H), 1.99-1.89 (m, 2H), 1.57-1.45 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 210.3 (C=O), 144.2 (C), 140.9 (C), 139.2 (C), 134.8 (C), 132.9 (C), 132.5 (C), 128.6 (C), 128.2 (CH), 127.9 (CH), 127.1 (CH), 126.2 (CH), 125.7 (CH), 125.3 (CH), 124.2 (CH), 124.0 (CH), 122.6 (CH), 45.2 (CH_2), 36.1 (CH_2), 25.5 (CH_2), 22.3 (CH_2), 13.9 (CH_3) ppm. HRMS (EI) Calcd for $C_{22}H_{20}O$: 300.1514, Found 300.1515.

(7,8-Dihydroantracen-10-yl)(phenyl)methanone (18m)

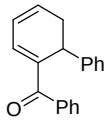


Pale yellow solid (mp = 133-135ºC). R_f = 0.5 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.91-7.87 (m, 2H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.68 (s, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52-7.40 (m, 4H), 7.36-7.29 (m, 1H), 6.45 (d, *J* = 9.7 Hz, 1H), 6.19-6.12 (m, 1H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.48-2.40 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 199.9 (C=O), 137.6 (C), 133.8 (C), 133.7 (CH), 132.3 (2 x C), 131.9 (CH), 129.7 (CH), 129.4 (C), 128.6 (CH), 127.4 (CH), 126.6 (CH), 125.8 (CH), 125.7 (CH), 125.1 (CH), 124.7 (CH), 28.1 (CH_2), 23.1 (CH_2) ppm. HRMS (EI) Calcd for $C_{21}H_{16}O$: 284.1195, Found 284.1195.

Reaction of eninal 14 with alkenes using IPy_2BF_4 and HBF_4: IPy_2BF_4 (0.37g, 1 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (10 mL). The solution was cooled at 0ºC and tetrafluoroboric acid, 54% solution in diethyl ether (0.15 mL, 1.1 mmol, 1.1 equiv) was added. After 10 min., the eninal **14** (0.16 g, 1 mmol, 1 equiv) was added and the solution was stirred during 30 min. at room temperature. After this time, the corresponding alkene **19a**/**20a** (1.2 mmol, 1.2 equiv) was added and the solution was further stirred until disappearance of starting aldehyde. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and vigorously stirred. The organic layer

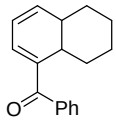
was washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL); dried over sodium sulfate and concentrated. The crude were purified by flash column chromatography (silica gel, hexane/EtOAc) to afford the corresponding diene **21** or **22**.

Phenyl-(6-phenylcyclohexa-1,3-dien-1-yl)methanone (21)



Pale yellow oil. R_f = 0.48 (Hexane: EtOAc, 5:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.65 (d, *J* = 7.1 Hz, 2H), 7.55-7.18 (m, 8H), 6.85 (d, *J* = 5.1 Hz, 1H), 6.24-6.11 (m, 2H), 4.37 (dd, *J* = 10.2, 2.9 Hz, 1H), 3.01 (dd, *J* = 18.5, 10.2 Hz, 1H), 2.74 (dt, *J* = 18.5, 4.5 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 196.7 (C=O), 143.0 (C), 138.6 (C), 136.9 (CH), 132.9 (CH), 131.3 (CH), 128.9 (CH), 128.5 (C), 128.3 (CH), 128.0 (CH), 127.1 (CH), 126.5 (CH), 123.7 (CH), 35.2 (CH), 31.9 (CH_2) ppm. IR (CH_2Cl_2, cm^{-1}) 3064, 1658. HRMS (EI) Calcd for $C_{19}H_{16}O$: 260.1201, Found 260.1203.

Phenyl-(1,2,3,4,4a,8a-hexahydronaphthalen-8-yl)methanone (22)

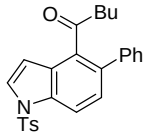


Pale yellow oil. R_f = 0.56 (Hexane: EtOAc, 5:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.65-7.60 (m, 2H), 7.56-7.38 (m, 3H), 6.59 (d, *J* = 5.5 Hz, 1H), 6.18-6.00 (m, 2H), 2.94-2.67 (m, 2H), 1.91-1.56 (m, 4H), 1.51-1.26 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 197.3 (C=O), 140.4 (CH), 140.3 (C), 139.0 (C), 136.6 (CH), 131.1 (CH), 128.8 (CH), 127.9 (CH), 124.2 (CH), 35.6 (CH), 33.4 (CH), 29.7 (CH_2), 24.7 (CH_2), 24.1 (CH_2), 22.6 (CH_2) ppm. HRMS (EI) Calcd for $C_{17}H_{18}O$: 238.1358, Found 238.1356.

General procedure for the synthesis of benzoheterocycles 23, 27 and 28 using IPy_2BF_4 and HBF_4: IPy_2BF_4 (112 mg, 0.3 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (5 mL). The solution was cooled at 0ºC and tetrafluoroboric acid, 54% solution in diethyl ether (45 μL, 0.33 mmol, 1.1 equiv) was added. After 10 min., the corresponding *N*-tosyl protected 3-alkynylpyrrole-2-carboxaldehyde **7a-b**, 3-phenylethynylfuran-2-carboxaldehyde **26** or 3-alkynylthiophene-2-carboxaldehyde **8a-b** (0.3 mmol, 1 equiv) was added and the solution was stirred during 30 min. at room temperature. After this time, the alkene **19**/**20** was added and the solution was further stirred until disappearance of starting material as determined by TLC analysis (reaction times are given in Tables 6 and 7). The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and vigorously stirred. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (20 mL) and water (20 mL); dried over sodium

sulfate and concentrated. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc) to afford the pure compounds.

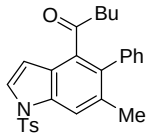
1-(5-Phenyl-1-*p*-tosyl-1H-indol-4-yl)-1-pentanone (23a):



Brown oil. R_f = 0.38 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.12 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 3.7 Hz, 1H), 7.46-7.39 (m, 6H), 7.30-7.27 (m, 2H), 6.76 (d, *J* = 3.7 Hz, 1H), 2.40 (s, 3H), 2.17 (t, *J* = 7.6 Hz, 2H), 1.45-1.35 (m, 2H), 1.10-1.00 (m, 2H), 0.70 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 207.9 (C=O), 145.2 (C), 140.3 (C), 135.0 (C), 134.9 (C), 134.1 (C), 133.3 (C), 129.9 (CH), 129.1 (CH), 128.6 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 126.8 (CH), 126.5 (CH), 114.7 (CH), 108.0 (CH), 43.3 (CH_2), 26.4 (CH_2), 21.9 (CH_2), 21.5 (CH_3), 13.5 (CH_3). IR (CH_2Cl_2, cm-1): 1682. HRMS (EI) Calcd for $C_{26}H_{25}NO_3S$ 431.1555, Found 431.1561.

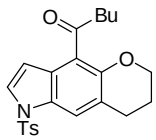
1-(6-Methyl-5-phenyl-1-*p*-tosyl-1H-indol-4-yl)-1-pentanone (23b):



Pale yellow syrup. R_f = 0.52 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.98 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.43-7.30 (m, 5H), 7.25-7.22 (m, 2H), 6.62 (d, *J* = 3.7 Hz, 1H), 2.42 (s, 3H), 2.31 (s, 3H), 2.04 (t, *J* = 7.7 Hz, 2H), 1.35-1.25 (m, 2H), 1.06-0.94 (m, 2H), 0.68 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 207.9 (C=O), 145.0 (C), 139.1 (C), 135.2 (C), 134.3 (C), 134.1 (C), 133.1 (C), 130.1 (CH), 129.9 (CH), 129.6 (CH), 129.1 (C), 128.3 (CH), 127.6 (CH), 126.8 (CH), 126.3 (C), 115.5 (CH), 107.8 (CH), 43.4 (CH_2), 26.1 (CH_2), 22.0 (CH_2), 21.6 (CH_3), 21.5 (CH_3), 13.6 (CH_3). HRMS (EI) Calcd for $C_{27}H_{27}NO_3S$ 445.1712, Found 445.1716.

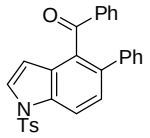
1-(1,6,7,8-Tetrahydro-1-*p*-tosylpyrano[2,3-f]indol-4-yl)-1-pentanone (23c):



Orange syrup. R_f = 0.34 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.09 (s, 1H), 7.79-7.76 (m, 2H), 7.66 (d, *J* = 3.6 Hz, 1H), 7.46 (d, *J* = 3.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.94-3.83 (m, 1H), 3.58-3.45 (m, 1H), 3.06-3.01 (m, 2H), 2.98-2.93 (m, 2H), 2.37 (s, 3H), 2.04-1.99 (m, 2H), 1.80-1.70 (m, 2H), 1.48-1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 201.4 (C=O), 145.0 (C), 138.3 (C), 135.9 (C), 135.1 (C), 129.8 (CH), 129.6 (C), 128.1 (C), 127.6 (C), 126.7 (CH), 125.8 (CH), 117.6 (CH), 109.9 (CH), 66.4 (CH_2), 39.1 (CH_2), 26.4 (CH_2), 25.4 (CH_2), 22.4 (CH_2), 21.5 (CH_3), 19.7 (CH_3), 13.9 (CH_3). HRMS (EI) Calcd for $C_{23}H_{25}NO_4S$ 411.1499, Found 411.1493.

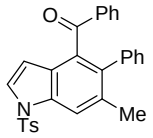
Phenyl(5-phenyl-1-*p*-tosyl-1H-indol-4-yl)methanone (23d):



Pale yellow solid (mp 90-94ºC). R_f = 0.34 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.16 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.63-7.57 (m, 3H), 7.47-7.15 (m, 11H), 6.55 (d, *J* = 3.5 Hz, 1H), 2.40 (s, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 197.6 (C=O), 145.2 (C), 139.9 (C), 137.1 (C), 135.9 (C), 134.9 (C), 133.9 (C), 132.9 (CH), 130.9 (C), 129.9 (CH), 129.6 (C), 129.5 (CH), 129.2 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 127.1 (CH), 126.8 (CH), 126.4 (CH), 114.8 (CH), 107.9 (CH), 21.5 (CH_3). IR (CH_2Cl_2, cm-1): 1660. HRMS (EI) Calcd for $C_{28}H_{31}NO_3S$ 451.1237, Found 451.1241. Elemental analysis calcd (%) for $C_{28}H_{31}NO_3S$: C 74.48, H 4.69, N 3.10; found C 74.25, H 4.72, N 3.05.

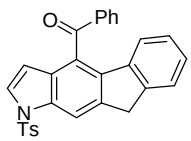
(6-Methyl-5-phenyl-1-*p*-tosyl-1H-indol-4-yl)(phenyl)methanone (23e):



Yellow syrup. R_f = 0.30 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.03 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.54-7.51 (m, 3H), 7.44-7.38 (m, 1H), 7.32-7.24 (m, 5H), 7.22-7.15 (m, 2H), 7.13-7.04 (m, 2H), 6.39 (d, *J* = 3.7 Hz, 1H), 2.42 (s, 3H), 2.29 (s, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 197.9 (C=O), 145.1 (C), 138.4 (C), 137.6 (C), 135.4 (C), 135.1 (C), 133.9 (C), 133.4 (2 x C), 132.9 (CH), 132.3 (C), 130.0 (CH), 129.9 (CH), 129.4 (CH), 127.9 (CH), 127.7 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 115.5 (CH), 107.7 (CH), 21.6 (CH_3), 21.4 (CH_3). HRMS (EI) Calcd for $C_{29}H_{23}NO_3S$ 465.1399, Found 465.1398.

(1,9-Dihydro-1-*p*-tosylindeno[1,2-f]indol-4-yl)(phenyl)methanone (23g):

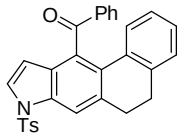


Yellow syrup. R_f = 0.37 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.29 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.55-7.53 (m,

2H), 7.47-7.42 (m, 2H), 7.32-7.21 (m, 4H), 7.15-7.09 (m, 1H), 6.38 (d, *J* = 3.7 Hz, 1H), 4.08 (s, 2H), 2.38 (s, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 197.4 (C=O), 145.2 (C), 143.7 (C), 141.4 (C), 139.4 (C), 136.8 (C), 135.0 (C), 134.5 (C), 134.0 (CH), 133.9 (C), 130.1 (CH), 129.9 (2 x CH), 128.8 (CH), 128.3 (C), 126.9 (CH), 126.7 (2 x CH), 126.0 (C), 124.8 (CH), 122.7 (CH), 111.3 (CH), 107.9 (CH), 36.8 (CH_2), 21.5 (CH_3). HRMS (EI) Calcd for $C_{29}H_{21}NO_3S$ 463.1242, Found 463.1232.

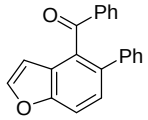
(6,8-Dihydro-8-*p*-tosyl-5H-naphtho[1,2-f]indol-11-yl)(phenyl)methanone (23h):



Yellow solid (mp 124-126ºC). R_f = 0.41 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.09 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 3.7 Hz, 1H), 7.46-7.26 (m, 6H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.17 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 3.06-3.01 (m, 2H), 2.92-2.88 (m, 2H), 2.41 (s, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 198.5 (C=O), 145.1 (C), 138.5 (C), 137.0 (C), 136.7 (2 x C), 135.1 (C), 133.8 (C), 133.1 (CH), 131.6 (C), 129.9 (CH), 129.5 (CH), 129.3 (C), 129.0 (C), 128.5 (CH), 128.3 (CH), 127.4 (CH), 127.3 (CH), 126.8 (CH), 126.7 (CH), 126.3 (CH), 113.8 (CH), 108.2 (CH), 30.8 (CH_2), 29.6 (CH_2), 21.5 (CH_3). HRMS (EI) Calcd for $C_{30}H_{23}NO_3S$ 477.1399, Found 477.1398. Elemental analysis calcd (%) for $C_{30}H_{23}NO_3S$: C 75.45, H 4.85, N 2.93; found C 75.12, H 4.96, N 3.11.

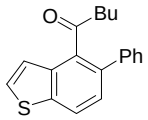
Phenyl(5-phenylbenzofuran-4-yl)methanone (27):



Light yellow oil. R_f = 0.62 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.72-7.62 (m, 4H), 7.46-7.16 (m, 9H), 6.70 (s, 1H).

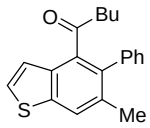
^{13}C-NMR ($CDCl_3$, 75 MHz): 197.5 (C=O), 154.1 (C), 146.3 (CH), 140.2 (C), 137.4 (C), 136.0 (C), 133.2 (C), 132.8 (CH), 130.9 (C), 129.6 (CH), 129.4 (CH), 128.1 (CH), 128.0 (CH), 127.0 (CH), 126.4 (CH), 113.0 (CH), 106.3 (CH). IR (CH_2Cl_2, cm-1): 1657. HRMS (EI) Calcd for $C_{21}H_{14}O_2$ 298.0988, Found 298.0979.

1-(5-Phenylbenzo[b]thiophen-4-yl)-1-pentanone (28a):



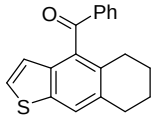
Brown solid (mp 60-62ºC). R_f = 0.45 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.98 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 5.7 Hz, 1H), 7.48-7.40 (m, 7H), 2.21 (t, *J* = 7.7 Hz, 2H), 1.49-1.39 (m, 2H), 1.16-1.04 (m, 2H), 0.70 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 208.8 (C=O), 140.3 (C), 139.4 (C), 136.6 (C), 135.9 (C), 135.4 (C), 129.2 (CH), 128.6 (CH), 128.2 (CH), 127.7 (CH), 125.9 (CH), 123.5 (CH), 122.8 (CH), 43.8 (CH_2), 26.2 (CH_2), 21.9 (CH_2), 13.5 (CH_3). IR (CH_2Cl_2, cm-1): 1693. HRMS (EI) Calcd for $C_{19}H_{18}OS$ 294.1078, Found 294.1075.

1-(6-Methyl-5-phenylbenzo[*b*]thiophen-4-yl)pentan-1-one (28b)



Yellow oil. R_f = 0.42 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.87 (s, 1H), 7.52-7.40 (m, 4H), 7.34-7.26 (m, 3H), 2.32 (s, 3H), 2.21 (t, *J* = 7.7 Hz, 2H), 1.41-1.30 (m, 2H), 1.14-1.01 (m, 2H), 0.77 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 208.6 (C=O), 139.6 (C), 138.9 (C), 137.2 (C), 134.8 (C), 134.5 (C), 132.5 (C), 130.2 (CH), 128.3 (CH), 127.6 (CH), 126.8 (CH), 124.1 (CH), 122.5 (CH), 43.9 (CH_2), 25.9 (CH_2), 22.0 (CH_2), 20.9 (CH_3), 13.6 (CH_3) ppm. HRMS (EI) Calcd for $C_{20}H_{20}OS$: 308.1235, Found 308.1231.

Phenyl-(5,6,7,8-tetrahydronaphtho[2,3-*b*]thiophen-4-yl)methanone (28c)

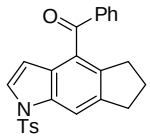


Yellow oil. R_f = 0.42 (Hexane: EtOAc, 10:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.85 (d, *J* = 7.1 Hz, 2H), 7.71 (s, 1H), 7.64-7.57 (m, 1H), 7.50-7.41 (m, 3H), 6.90 (d, *J* = 5.7 Hz, 1H), 3.02-2.96 (m, 2H), 2.72-2.66 (m, 2H), 1.87-1.75 (m, 4H) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): 199.2 (C=O), 138.6 (C), 137.2 (C), 137.1 (C), 135.8 (C), 133.7 (CH), 133.2 (C), 132.5 (C), 129.7 (CH), 128.7 (CH), 126.2 (CH), 123.2 (CH), 121.8 (CH), 30.1 (CH_2), 27.0 (CH_2), 22.9 (CH_2), 22.7 (CH_2) ppm. HRMS (EI) Calcd for $C_{19}H_{16}OS$: 292.0916, Found 292.0910.

Procedure for the synthesis of the indole 23f using IPy_2BF_4 and HBF_4: IPy_2BF_4 (115 mg, 0.31 mmol, 1 equiv) was dissolved in dry 1,2-dichloroethane (5 mL) in a sealed tube. The solution was cooled at 0ºC and tetrafluoroboric acid, 54% solution in diethyl ether (21 µL, 0.15 mmol, 0.5 equiv) was added. After 10 min., 3-phenylethynyl-*N*-tosylpyrrole-2-carboxaldehyde **7a** (108 mg, 0.31 mmol, 1 equiv) was added and the solution was stirred during 30 min. at room temperature. After this time, cyclopentene **20g** (110 µL, 1.24 mmol, 4 equiv) was added and the solution was

further stirred at 60ºC for 2 hours. The reaction mixture was allowed to reach room temperature and then was quenched with saturated aqueous $NaHCO_3$ and vigorously stirred. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (25 mL) and water (25 mL); dried over sodium sulfate and concentrated. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc) to afford 47 mg (37%) of the pure compound **23f**.

(1,5,6,7-Tetrahydro-1-*p*-tosylcyclopenta[f]indol-4-yl)(phenyl)methanone (23f):

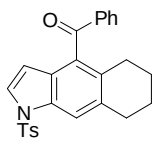


Brown solid (mp 98-100ºC). R_f = 0.38 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.99 (s, 1H), 7.78- 7.75 (m, 4H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.48-7.42 (m, 3H), 7.28-7.24 (m, 2H), 6.36 (d, *J* = 3.7 Hz, 1H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.74 (t, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 2.11-2.01 (m, 2H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 197.1 (C=O), 144.9 (C), 142.6 (C), 139.2 (C), 137.9 (C), 135.2 (C), 134.3 (C), 133.2 (CH), 129.9 (CH), 129.7 (CH), 128.5 (CH), 128.4 (C), 127.3 (C), 126.7 (CH), 126.4 (CH), 111.6 (CH), 108.2 (CH), 32.8 (CH_2), 31.9 (CH_2), 26.2 (CH_2), 21.5 (CH_3). HRMS (EI) Calcd for $C_{25}H_{21}NO_3S$ 415.1242, Found 415.1248.

General procedure for the synthesis of the indoles 23i and 23j using IPy_2BF_4: IPy_2BF_4 (115 mg, 0.31 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (5 mL) and 3-phenylethynyl-*N*-tosylpyrrole-2-carboxaldehyde **7a** (108 mg, 0.31 mmol, 1 equiv) was added at room temperature. After stirring the solution for 30 min, the corresponding enamine was added: 199 µL (1.24 mmol, 4 equiv) of 1-pyrrolidino-1-cyclohexene **24a** or 224 mg (1.24 mmol, 4 equiv) of 1-pyrrolidino-1-hexene **24b**; and the solution was further stirred at room temperature for 12 hours. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and vigorously stirred. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (25 mL) and water (25 mL); dried over sodium sulfate and concentrated. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc) to afford 41 mg (31%) of the pure compound **23i** or 70 mg (43%) of the pure compound **23j**.

(5,6,7,8-Tetrahydro-1-*p*-tosyl-1H-benzo[f]indol-4-yl)(phenyl)methanone (23i):

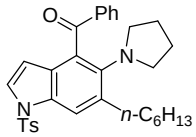


Light brown syrup. R_f = 0.36 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.82 (s, 1H), 7.78-7.62 (m, 3H), 7.59-7.57 (m, 1H), 7.47-7.41 (m, 3H), 7.28-7.24 (m, 3H), 6.20

(d, *J* = 3.7 Hz, 1H), 3.01-2.97 (m, 2H), 2.65-2.60 (m, 2H), 2.38 (s, 3H), 1.82-1.71 (m, 4H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 198.4 (C=O), 144.9 (C), 137.1 (C), 135.0 (C), 134.9 (C), 133.6 (CH), 133.1 (C), 131.2 (C), 129.9 (C), 129.8 (CH), 129.7 (CH), 128.6 (CH), 128.8 (C), 126.7 (CH), 126.4 (CH), 114.5 (CH), 107.4 (CH), 30.5 (CH_2), 26.9 (CH_2), 22.8 (CH_2), 22.6 (CH_2), 21.5 (CH_3). HRMS (EI) Calcd for $C_{26}H_{23}NO_3S$ 429.1393, Found 429.1394.

{6-Hexyl-5-(pyrrolidin-1-yl)-1-*p*-tosyl-1H-indol-4-yl}(phenyl)methanone (23j):



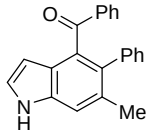
Orange syrup. R_f = 0.54 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.93 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.71-7.68 (m, 2H), 7.57-7.51 (m, 1H), 7.46 (d, *J* = 3.7 Hz, 1H), 7.43-7.38 (m, 2H), 7.28-7.24 (m, 2H), 6.36 (d, *J* = 3.7 Hz, 1H), 2.96-2.91 (m, 4H), 2.70-2.64 (m, 2H), 2.39 (s, 3H), 1.68-1.63 (m, 2H), 1.54-1.53 (m, 4H), 1.35-1.34 (m, 6H), 0.9 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 197.9 (C=O), 145.0 (C), 141.2 (C), 139.7 (C), 138.4 (C), 135.1 (C), 132.7 (CH), 132.1 (C), 131.8 (C), 129.8 (CH), 128.9 (CH), 128.1 (CH), 127.8 (C), 126.8 (CH), 126.7 (CH), 115.7 (CH), 107.4 (CH), 51.9 (CH_2), 32.0 (CH_2), 31.7 (CH_2), 31.0 (CH_2), 29.4 (CH_2), 25.7 (CH_2), 22.6 (CH_2), 21.5 (CH_3), 14.1 (CH_3). HRMS (EI) Calcd for $C_{32}H_{36}N_2O_3S$ 528.2441, Found 528.2425.

Reaction of 3-phenylethynyl-*N*-tosylpyrrole-2-carboxaldehyde 7a with I_2 and styrene 19a: Reaction of 3-phenylethynyl-*N*-tosylpyrrole-2-carboxaldehyde **7a** (87 mg, 0.25 mmol, 1 equiv), K_2CO_3 (34 mg, 0.25 mmol, 1 equiv), styrene **19a** (34 µL, 0.3 mmol, 1.2 equiv), I_2 (76 mg, 0.3 mmol, 1.2 equiv) in 5 mL of CH_2Cl_2 at room temperature until disappearance of the starting material. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ and water. The solution was extracted with CH_2Cl_2, dried over sodium sulfate and concentrated. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc) to afford pure compound **23d** (70 mg, 62%). This compound has been characterized above.

Procedure for the synthesis of the compound 25: A mixture of the N-tosyl protected indole **23e** (30 mg, 0.065 mmol, 1 equiv) in 5 mL of ethanol and 15% ethanolic NaOH (85 µL, 0.32 mmol, 5 equiv) was stirred at reflux temperature for 3h. The solution was concentrated in vacuo and the residue was dissolved in CH_2Cl_2 and washed with water. The organic phase was dried and concentrated to give 17 mg (85%) of the pure indole **25**.

(6-Methyl-5-phenyl-1H-indol-4-yl)(phenyl)methanone (25):



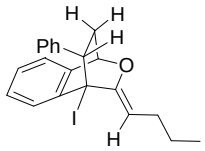
Brown solid (mp 164-166ºC). R_f = 0.27 (Hexane: EtOAc, 3:1). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.34 (broad s, 1H), 7.65-7.62 (m, 2H), 7.44-7.41 (m, 2H), 7.31-7.25 (m, 2H), 7.19-7.17 (m, 6H), 6.31 (s, 1H), 2.30 (s, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): 199.1 (C=O), 139.6 (C), 138.4 (C), 135.3 (C), 132.4 (CH), 131.6 (C), 130.5 (CH), 130.3 (C), 129.5 (CH), 127.8 (CH), 127.5 (CH), 126.5 (CH), 124.7 (CH), 124.5 (C), 113.2 (CH), 101.9 (CH), 21.1 (CH_3). IR (CH_2Cl_2, cm-1): 3335, 1651. HRMS (EI) Calcd for $C_{22}H_{17}NO$ 311.1304, Found 311.1305. Elemental analysis calcd (%) for $C_{22}H_{17}NO$: C 84.86, H 5.50, N 4.50; found C 84.81, H 5.56, N 4.38.

Procedure for the synthesis of compound III:

IPy_2BF_4 (0.37 g, 1 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (4 mL) and *o*-(1-hexynyl)benzaldehyde **1b** (0.19 g, 1 mmol, 1 equiv) was added at room temperature. After stirring the solution for 6 hours, styrene **19a** was added (114 μL, 1 mmol, 1 equiv) and the solution was further stirred at room temperature for 3 days. Solvent was removed under pressure to afford the pure compound **III** as an orange solid in quantitative yield.

10-Butenilydene-1-iodo-9-oxa-11-phenyl-tricycle[6.2.2.0^{2,7}]dodeca-2,4,6-triene (III)

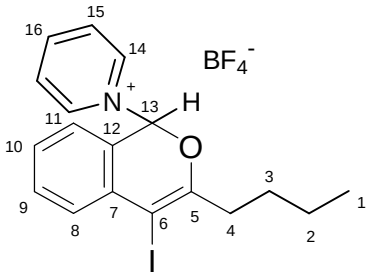


Orange solid (mp = 65ºC, dec). ^{1}H-NMR ($CDCl_3$, 400 MHz): 7.48 (td, *J* = 7.4, 1.3 Hz, 1H), 7.39 (td, *J* = 7.6, 1.3 Hz, 1H), 7.35 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 8.0, 7.5 Hz, 2H), 6.34 (broad s, 1H), 5.47 (dd, *J* = 3.9, 1.2 Hz, 1H), 5.43 (t, *J* = 7.1 Hz, 1H), 3.65 (dd, *J* = 10.3, 4.3 Hz, 1H), 2.96 (ddd, *J* = 10.3, 7.2, 3.9 Hz, 1H), 2.03 (m, 3H), 1.40 (sextet, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): 150.8 (C), 144.2 (C), 138.5 (C), 137.1 (C), 131.4 (CH), 129.0 (CH), 128.7 (CH), 128.4 (CH), 127.5 (CH), 127.0 (CH), 121.8 (CH), 104.0 (CH), 73.1 (CH), 56.6 (C), 52.1 (CH), 39.3 (CH_2), 27.7 (CH_2), 22.9 (CH_2), 13.7 (CH_3) ppm. HRMS (EI) Calcd for $C_{21}H_{21}IO$: 416.0637, Found 416.0634.

Structure elucidation of Intermediates I and III by 1D- and 2D-NMR:

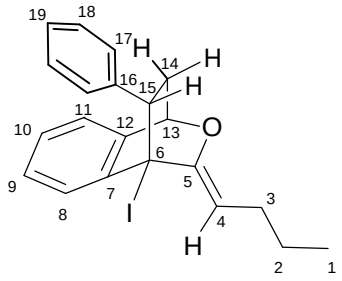
Intermediate **I**



Site	^{13}C-NMR (ppm)	DEPT	^{1}H-NMR (ppm)	COSY	HMBC
1	13.5	CH_3	0.83 (3H, t , *J* = 7.3 Hz)	H-2	C-2, C-3
2	21.9	CH_2	1.16 (2H, bs)	H-1	
3	28.6	CH_2	1.31 (2H, quintet, *J* = 7.4 Hz)	H-2, H-4	C-1, C-2, C-4, C-5
4	36.1	CH_2	2.67 (2H, bs)	H-3	C-3, C-5, C-6
5	153.8	C			
6	74.8	C			
7	118.6	C			
8	133.1	CH	7.72 (2H, m)	H-9	C-6
9	129.5	CH	7.54 (1H, ddd, *J* = 8.2, 6.9, 2.0 Hz)		C-7, C-11
10	128.3	CH	7.63 (1H, d, *J* = 7.5 Hz)	H-9	C-8, C-12
11	130.2	CH	7.72 (2H, m)	H-9	C-7, C-13
12	131.7	C			
13	93.0	CH	7.90 (1H, s)		C-5, C-7, C-10, C-11, C-12
14	142.7[1]	CH	[2]		
15	138.0[1]	CH	[2]		
16	124.5[1]	CH	[2]		

[1] Broad signals. [2] The pyridine protons appear as broad signals over the aromatic zone: 8.1 – 7.7 and 7.6 – 7.3 ppm.

Intermediate **III**



Site	^{13}C-NMR (ppm)	DEPT	^{1}H-NMR (ppm)	COSY	HMBC
1	13.7	CH_3	0.93 (3H, t, *J* = 7.3 Hz)	H-2	C-2, C-3
2	22.9	CH_2	1.40 (2H, sextet, *J* = 7.3 Hz)	H-1, H-3	C-1, C-3, C-4
3	27.7	CH_2	2.03 (3H, m)	H-2	C-1, C-2, C-4, C-5
4	104.0	CH	5.43 (1H, t, *J* = 7.1 Hz)	H-3	C-5, C-6
5	150.8	C			
6	56.6	C			
7	137.1	C			
8	121.8	CH	7.35 (2H, m)	H-9, H-10	C-6, C-7, C-9, C-10, C-15
9	128.4	CH	7.48 (1H, td, *J* = 7.4, 1.3 Hz)	H-10	C-11, C-12
10	128.7	CH	7.39 (1H, td, *J* = 7.6, 1.3 Hz)	H-8, H-11	C-7, C-8
11	131.4	CH	7.35 (2H, m)	H-9	C-7, C-8, C-9, C-10
12	138.5	C			
13	52.1	CH	3.65 (1H, dd, *J* = 10.3, 4.3 Hz)	H-14	C-6, C-7, C-10, C-16
14	39.3	CH_2	2.03 (3H, m) 2.96 (1H, ddd, *J* = 10.3, 7.2, 3.9 Hz)	H-13, H-15	C-12, C-15
15	73.1	CH	5.47 (1H, dd, *J* = 3.9, 1.2 Hz)	H-14	C-5, C-6, C-7, C-13
16	144.2	C			
17	129.0	CH	6.34 (bs, 2H)	H-18	
18	127.5	CH	7.09 (2H, t, *J* = 8.0, 7.5 Hz)	H-17, H-19	C-16, C-19
19	127.0	CH	7.17 (1H, t, *J* = 7.3 Hz)	H-18	C-16, C-17