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Supporting Information

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Direct Intramolecular Arylation of Aldehydes Promoted by Reaction with IPy_2BF_4/HBF_4: Synthesis of Benzocyclic Ketones

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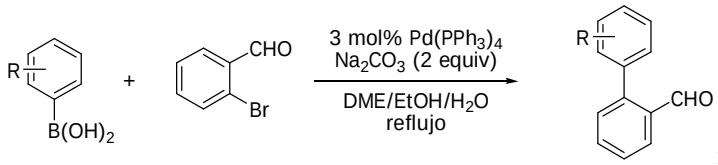
Experimental procedures and spectral and analytical data for all products.

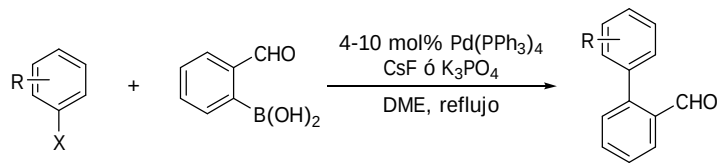
General: All reactions were carried out under an atmosphere of dry N_2 using oven-dried glassware and syringes. Dichloromethane was dried by refluxing over P_2O_5 and distilled under a nitrogen atmosphere. Hexane and EtOAc were obtained from commercial suppliers. IPy_2BF_4 is commercially available (see Galchimia, NovaBiochem or Aldrich catalogues). TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator (Scharlau). Flash column chromatography was carried out on silica gel 60, 230-240 mesh. ^1H NMR (200, 300, 400 MHz) and ^{13}C NMR (50.5, 75.5, 100 MHz) spectra were measured at room temperature on Bruker AC-200, AV-300 and AMX-400 instruments, respectively, with tetramethylsilane ($\delta = 0.0$, ^1H NMR) or $CDCl_3$ ($\delta = 77.00$, ^{13}C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a HP 5987 A, and the intensities are reported as a percentage relative to the base peak after the corresponding *m*/*z* value. High-resolution mass spectra (HRMS) were determined on a Finnigan MAT 95 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 and Carlo Erba 1108 microanalyzers.

Starting Materials:

Scheme S1. Preparation of *orto*-formyl biaryl derivatives by Suzuki coupling reactions



method A



X = I, Br, TfO

method B

2-Formyl derivatives **6, 7** and **10** were prepared by the palladium-catalyzed reaction of 2-bromobenzaldehydes with boronic acids. The substrates **1**,[1] **3**, **5**, **6**, **8**, **12**, **13**, **14**, **15** and **28** were accessible from the parent aryl bromide, iodine or triflate and 2-formylbenzeneboronic acid.

Representative Procedure for Method A. Synthesis of 2-(naphthalene-1-yl)thiophen-3-carboxaldehyde (7) [Chart 1]: To a solution of 2-bromothiophene-3-carboxaldehyde (955 mg, 5.0 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (173 mg, 0.15 mmol, 0.03 equiv) in DME (20mL) is added a degassed solution of naphthalen-1-ylboronic acid (1.06 g, 6.16 mmol, 1.2 equiv) in EtOH (5 mL), followed by a degassed solution of Na_2CO_3 (1.1g, 10 mmol, 2 equiv) in H_2O (5 mL). The resulting heterogeneous mixture is refluxed 15h, before it is diluted with diethyl ether (30 ml). The organic layer is separated, washed with brine, dried over Na_2SO_4, and evaporated. Chromatographic purification of the crude product (hexanes/ethyl acetate, 10/1) affords the aldehyde **7** as a withe solid (0.97 g, 82%).

Representative Procedure for Method B. Synthesis of 2-(1,2-dihydroacenaphthylen-5-yl)benzaldehyde (**12**) [Chart 1]: To a degassed solution containing 5-bromo-1,2-dihydroacenaphthylene (699 mg, 3 mmol, 1.0 equiv), 2-formylbenzeneboronic acid (500 mg, 3.34 mmol, 1.1 equiv) and CsF (1.27g, 8.35 mmol) in DME (20 mL), is added $Pd(PPh_3)_4$ (135 mg, 0.12 mmol) and the resulting mixture is refluxed overnight. For work-up, EtOAc (20 ml) and water (20 ml) are added; the aqueous layer is extracted with EtOAc (3 x 50 mL). The combined organic layers are dried over Na_2SO_4 and evaporated. Chromatographic purification of the product (hexanes/ethyl acetate, 10/1) affords the aldehyde **12** as a white solid (573 mg, 74%).

Preparation of 2,2'-(naphthalene-1,4-diyl)dibenzaldehyde (**14**). A mixture of 1,4-diiodonaphtalene (570 mg, 1.5 mmol),[2] 2-formylbenzeneboronic acid (500 mg, 3.34 mmol), CsF (1.27g, 8.35 mmol) and $Pd(PPh_3)_4$ (135 mg, 0.12 mmol) in DME (20 mL) is stirred at reflux overnight. The resulting yellow solution is worked-up as described in Procedure for Method B, afforded 379 mg of **14** as a white solid (75%).

Preparation of 2,2'-(naphtalene-1,5-diyl)dibenzaldehyde (**15**). To a solution of naphthalene-1,5-diyl bis(trifluoromethanesulfonate) (1.41g, 3.34 mmol) and 2-formylbenzeneboronic acid (1.0 g, 6.68) in DME (30 mL) is added $Pd(PPh_3)_4$ (381 mg, 0.33 mmol) and K_3PO_4 (3.54 g, 16.7 mmol). The suspension is stirred at 80ºC for 48h. The reaction mixture is concentrated *in vacuo* and chromatographic purification of the product with hexanes/ethyl acetate, 10/1 affords the aldehyde **15** as a pale solid (530 mg, 47%).

Preparation of 2-phenylbenzaldehyde (**9**). To a solution of 2-bromobiphenyl (4.66g, 20 mmol) in THF (50mL) at -80ºC is added *n*-BuLi (12.5 mL of a 1.6M solution in hexane, 20 mmol). The resulting yellow solution is stirred at -80ºC for 30 min. DMF (15 mL) is then slowly added and the mixture is stirred for 1h at -80ºC, allowed to warm to rt and stirring is continued for another 30 min. The resulting solution is diluted with CH_2Cl_2 and washed with a saturated aqueous solution of NH_4Cl, dried and concentrated *in vacuo.* Chromatographic purification eluting with 5:1 hexane/EtOAc affords 1.75 g (96%) of **9** as a yellow oil.

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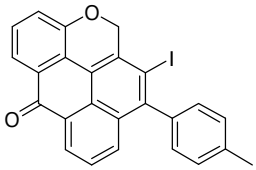
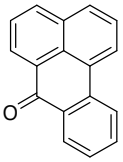
[1] The preparation of 1 is described in reference 9b

[2] Preparation of 1,4-diiodonaphthalene was carried out by diiodination of naphthalene with 2.1 equiv of IPy_2BF_4 and 4 equiv of triflic acid at rt for 15h. The reaction affords1,4-diiodonaphthalene with 69% yield. (J. Barluenga, J. M. González, M. A. García Martín, P. J. Campos *Tetrahedron Lett*. **1993**, *34*, 3893)

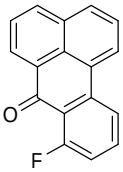
General Procedure for the Synthesis of Compounds 2, 4, 16-27, 29 and 30 [Schemes 1, 2 and Chart 2]: IPy_2BF_4 (0.74 g, 2 mmol, 2 equiv) was dissolved in dry CH_2Cl_2 (10 mL) and stirred for 5 min at rt. The solution was cooled down at -80ºC, then tetrafluoroboric acid (542 μL, 54% solution in diethyl ether, 4 mmol, 4 equiv) was added. After 10 min., the mixture is filtered and the filtrate is maintained at -60ºC in a cryocool apparatus until the aldehyde is added. The resulting mixture is stirred until disappearance of the starting material or no evolution of the reaction (reaction times are given in Table 1, Chart 2 and Schemes 1 and 2). The reaction mixture was poured into 100 g of crushed ice and vigorously stirred, allowing the temperature to rise up to rt. The organic layer was washed with a 5% aqueous solution of $Na_2S_2O_3$ (50 mL), dried over sodium sulfate, and concentrated. The products were purified by column chromatography (silica gel, hexane/EtOAc) to give the ketone. Yields are listed in Table 1, Chart 2 and Schemes 1 and 2.



11-iodo-10-*p*-tolylphenaleno[9,1,2-*cde*]chromen-6(1*H*)-one (2). Yellow solid. R_f = 0.47 (Hexane: EtOAc, 10:1). M.p. 192-194 ºC. ^{1}H NMR (300 MHz, $DCCl_3$): δ = 8.66 (d, *J* =8.0 Hz, 1H), 8.07 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.68 (td, *J* = 8.4, 1.4 Hz, 1H), 7.61 (td, *J* = 8.1, 1.2 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.25 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.24 (dd, J = 8.6, 1.3 Hz, 1H), 5.31 (s, 2H), 2.51 (s, 3H) ppm. ^{13}C NMR (75 MHz, $DCCl_3$): δ = 196.2 (C), 156.8 (C), 144.1 (C), 134.9 (C), 133.1 (C), 132.4 (C), 132.3 (C), 130.5 (2 x CH), 130.0 (C), 129.7 (CH), 129.2 (CH), 129.1 (CH), 128.6 (C), 128.1 (CH), 126.5 (C), 126.3 (CH), 126.1 (C), 125.3 (CH), 123.6 (C), 121.6 (CH), 117.4 (CH), 84.1 (C), 67.9 (CH_2), 21.6 (CH_3) ppm. IR: υ(KBr)/cm^{-1}: 3021, 2915, 1664, 1550, 1499, 815. MS (70 eV, EI): *m/z* (%) = 474 (M^+, 8), 458 (10), 364 (18), 335 (100). HRMS (EI): calcd for $C_{25}H_{15}IO_2$: 474.0111; found: 474.0099.

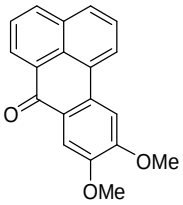


7*H*-Benzo[*de*]anthracen-7-one (**4**). Yellow solid. R_f = 0.42 (Hexane: EtOAc, 3:1). M.p. 143-144 ºC. ^{1}H NMR (300 MHz, $DCCl_3$): δ = 8.76 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.50 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.40 (d, *J* = 7.4 Hz, 1H), 8.31 (dd, *J* = 8.1, 0.5 Hz, 1H), 8.19 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H), 7.74 (td, *J* = 7.4, 1.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.56 (td, *J* = 8.3, 1.0 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $DCCl_3$): δ = 183.7 (CO), 136.0 (C), 134.9 (CH), 133.2 (CH), 132.8 (C), 130.9 (C), 130.0 (CH), 129.6 (CH), 128.3 (C), 128.1 (CH), 127.9 (CH), 127.7 (C), 126.6 (C), 126.4 (2 x CH), 124.0 (CH), 122.9 (CH) ppm IR: υ(KBr)/cm^{-1}: 1644, 1598, 1450, 754. MS (70 eV, EI): *m/z* (%) = 230 (100), 202 (43), 101 (26), 69 (18). HRMS (EI): calcd for $C_{17}H_{10}O$: 230.0732; found: 230.0735. Elemental analisis (%) calcd: C 88.67, H 4.38; found: C 88.50, H 4.39.

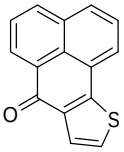


8-fluoro-7*H*-benzo[*de*]anthracen-7-one (**16**). Yellow oil. R_f = 0.40 (Hexane: EtOAc, 3:1). ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 8.1 Hz, 1H), 8.69 (d, *J* = 7.5 Hz, 1H), 8.49 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 9.7 Hz, 1H), 7.77-7.70 (m, 1H), 7.41-7.38 (m, 2H), 6.83 (d, *J* = 9.7 Hz, 1H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 190 2 (CO), 161.4 (C, d, J_{CF} = 235 Hz), 135.9 (C, d, J_{CF} = 8 Hz), 135.6 (CH, d, J_{CF} = 8 Hz) 134.3 (CH), 133.3 (CH), 133.0 (C), 131.6 (C), 130.8 (CH), 130.6 (CH), 128.9 (CH, d, J_{CF} = 4 Hz), 128.7 (C), 127.8 (CH), 127.4

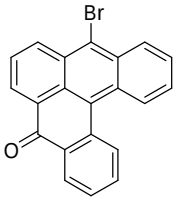
(CH), 127.3 (C), 124.5 (C, d, J_{CF} = 20 Hz), 114.0 (C, d, J_{CF} = 25 Hz) ppm. HRMS (EI): calcd for $C_{17}H_9FO$: 248.0637; found: 248.0639.



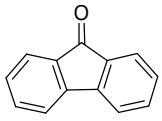
9,10-dimethoxy-7*H*-benzo[*de*]anthracen-7-one (**17**)**.** Yellow solid. R_f = 0.39 (Hexane: EtOAc, 3:1). M.p. 160-162 ºC**.** ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 7.4 Hz, 1H), 8.36 (d, *J* = 7.4 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.67 (td, *J* = 8.0, 2.8 Hz, 1H), 7.47 (td, *J* = 8.8, 1.7 Hz, 1H), 7.16 (s, 1H), 6.97 (s, 1H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 180 0 (CO), 151.4 (C), 140.5 (C), 132.9 (CH), 130.3 (C), 127.7 (CH), 127.0 (C), 126.6 (CH), 126.2 (C), 125.6 (C), 125.2 (C), 124.8 (C), 123.7 (CH), 123.3 (CH), 120.6 (CH), 113.2 (CH), 110.1 (CH), 56.3 (CH_3), 56.2 (CH_3) ppm. IR ν(KBr, cm^{-1}): 1699, 1380, 760. HRMS (EI): calcd for $C_{19}H_{14}O_3$: 290.0943; found: 290.0949.



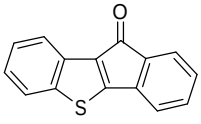
7*H*-phenaleno[1,2-*b*]thiophen-7-one (**18**)**.** Yellow solid. R_f = 0.35 (Hexane: EtOAc, 3:1). M.p. 152-154 ºC**.** ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 7.4 Hz, 1H), 8.11 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.70-7.54 (m, 5H), 7.39 (d, *J* = 5.1 Hz, 1H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 179.9 (C), 149.3 (C), 139.0 (C), 133.5 (CH), 132.7 (C), 132.1 (CH), 131.7 (CH), 130.9 (C), 129.4 (CH), 128.6 (CH), 127.8 (CH), 127.5 (C), 127.1 (CH), 125.6 (C), 120.4 (CH) ppm. HRMS (EI): calcd for $C_{15}H_8OS$: 236.0296; found: 236.0303.



9-bromo-5*H*-dibenzo[*be*]phenalen-5-one (**19**)**.** Yellow solid. R_f = 0.36 (Hexane: EtOAc, 3:1). M.p. 191-192 ºC. ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 7.1 Hz, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 8.27 (d, *J* = 7.7 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 8.01-7.97 (m, 2H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.43-7.29 (m, 4H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 185.2 (CO), 142.3 (C), 138.4 (C), 134.9 (C), 134.1 (CH), 133.5 (C), 133.3 (C), 133.1 (CH), 132.7 (C), 130.6 (CH), 129.9 (CH), 129.3 (C), 128.4 (CH), 127.8 (CH), 127.4 (CH), 126.9 (C), 126.8 (CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 123.1 (C) ppm. HRMS (EI): calcd for $C_{21}H_{11}BrO$: 357.9993; found: 357.9984.

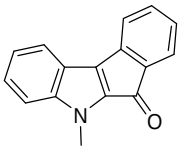


9*H*-fluoren-9-one (**20**)**.** Yellow solid. R_f = 0.53 (Hexane: EtOAc, 10:1). ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 7.65 (dd, J = 7.4, 0.8 Hz, 1H), 7.53-7.45 (m, 2H), 7.32-7.26 (m, 1H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ =193.6 (CO), 144.2 (C), 134.5 (CH), 133.9 (C), 128.9 (CH), 124.0 (CH), 120.2 (CH) ppm. IR ν(KBr, cm^{-1}): 3080, 1726, 1690, 1613, 1430, 1019. HRMS (EI): calcd for $C_{13}H_8O$: 180.0575; found: 180.0577.

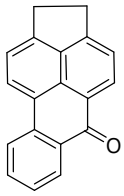


10*H*-benzo[*b*]indeno[2,1-*d*]thiophen-10-one (**21**)**.** Yellow solid. R_f = 0.43 (Hexane: EtOAc, 3:1). M.p. 204-206ºC. ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 8.13 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.86-7.63 (m, 4H), 7.60-7.43 (m, 3H) ppm. ^{13}C (75 MHz,

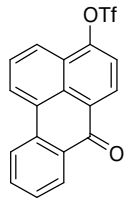
$CDCl_3$): δ = 187.4 (CO), 162.4 (C), 144.2 (C), 138.8 (C), 137.1 (C), 135.0 (C), 133.8 (CH), 132.6 (CH), 129.7 (CH), 126.8 (CH), 125.5 (CH), 123.7 (CH), 123.3 (CH), 123.1 (CH), 120.4 (C) ppm. IR ν(KBr, cm^{-1}): 1720, 1697, 1610. HRMS (EI): calcd for $C_{15}H_8OS$: 236.0296; found: 236.0300.



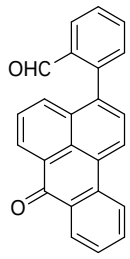
1-methylindeno[2,1-*b*]indol-2(1*H*)-one (**22**)**.** Yellow solid. R_f = 0.62 (Hexane: EtOAc, 3:1). M.p. 147-149ºC. ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 8.9, 1.1 Hz, 1H), 7.36-7.23 (m, 4H), 7.20-7.17 (m, 1H), 7.10-7.08 (m, 1H), 6.99-6.96 (m, 1H), 3.85 (s, 3H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 185.0 (CO), 147.2 (C), 144.1 (C), 140.6 (C), 137.4 (C), 134.1 (CH), 133.7 (C), 126.6 (CH), 126.2 (CH), 123.7 (CH), 122.1 (CH), 121.9 (CH), 121.4 (C), 119.2 (CH), 111.7 (CH), 30.8 (CH_3) ppm. IR ν(KBr, cm^{-1}): 3054, 1704. HRMS (EI): calcd for $C_{16}H_{11}NO$: 233.0841; found: 236.0846.



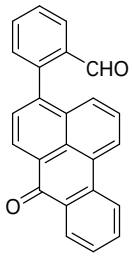
3,4-dihydroindeno[6,7,1-*mna*]anthracen-7-one (**23**)**.** Yellow solid. R_f = 0.66 (Hexane: EtOAc, 3:1). M.p. 145 dec. ^{1}H-RMN (200 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 7.4 Hz, 1H), 8.58 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.40 (d, *J* = 7.4 Hz, 1H), 8.33 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.72-7.69 (m, 1H), 7.56-7.51 (m, 1H), 7.34 (dd, *J* = 7.0, 1.6 Hz, 1H), 3.54 (s, 4H) ppm. ^{13}C (50 MHz, $CDCl_3$): δ = 183.1 (CO), 154.9 (C), 148.8 (C), 138.7 (C), 136.0 (C), 134.5 (C), 133.4 (CH), 132.7 (CH), 132.1 (C), 131.6 (CH), 131.4 (C), 128.4 (CH), 127.5 (CH), 126.0 (C), 125.5 (CH), 123.3 (CH), 122.6 (CH), 31.7 (CH_2), 30.9 (CH_2) ppm. IR ν(KBr, cm^{-1}): 3387, 3054, 1642, 1265, 750. HRMS (EI): calcd for $C_{19}H_{12}O$: 256.0888; found: 256.0882.



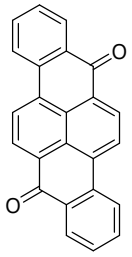
7-oxo-7*H*-benzo[*de*]anthracen-4-yl trifluoromethanesulfonate (**24**)**.** Yellow solid. R_f = 0.36 (Hexane: EtOAc, 3:1). M.p. 212-214ºC. ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 8.83 (d, J = 8.2 Hz, 1H), 8.59-8.55 (m, 2H), 7.84-7.61 (m, 5H), 6.72 (d, J = 9.6 Hz, 1H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 182.2 (CO), 149.9 (C), 135.2 (C), 134.0 (C), 130.4 (CH), 127.7 (2 x C), 126.5 (CH), 126.1 (C), 125.7 (CH), 125.3 (CH), 124.7 (CH), 124.6 (CH), 124.0 (CH), 123.8 (CH), 123.5 (C), 122.1 (C, c, *J* = 180 Hz, CF_3), 119.3 (CH) ppm. HRMS (EI): calcd for $C_{18}H_9F_3O_4S$: 378.0174; found: 378.0183.



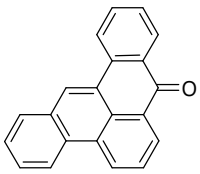
3-(2-Formylphenyl)-7*H*-benzo[*de*]anthracen-7-one (**25**)**.** Yellow solid. R_f = 0.34 (Hexane: EtOAc, 3:1). M.p. 161-163 ºC. ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 9.62 (s, 1H), 8.81 (d, *J* = 7.4 Hz, 1H), 8.52 (d, *J* = 9.1 Hz, 1H), 8.48 (d, *J* = 7.6 Hz, 1H), 8.36 (d, *J* = 8.2 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.79-7.71 (m, 3H), 7.64-7.60 (m, 3H), 7.55 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.46 (dd, *J* = 7.4, 1.1 Hz, 1H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ =191.1 (CHO), 183.6 (CO), 140.4 (C), 139.3 (C), 136.3 (C), 136.0 (CH), 135.0 (C), 134.6 (CH), 134.3 (C), 133.7 (CH), 132.8 (CH), 131.6 (C), 131.4 (C), 130.9 (CH), 130.3 (CH), 129.9 (CH), 128.5 (CH), 128.1 (CH), 127.9 (C), 127.7 (CH), 127.5 (C), 127.2 (CH), 127.1 (CH), 126.6 (CH) ppm. IR ν(KBr, cm^{-1}): 3391, 1693, 1649, 1597, 1316. HRMS (EI): calcd for $C_{24}H_{14}O_2$: 334.0994; found: 334.0986.



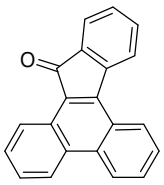
4-(2-Formylphenyl)-7*H*-benzo[*de*]anthracen-7-one (**26**)**.** Yellow solid. R_f = 0.35 (Hexane: EtOAc, 3:1). M.p. 163-165 ºC. ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 9.65 (s, 1H), 8.83 (d, *J* = 7.4 Hz, 1H), 8.54 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.52-8.49 (m, 1H), 8.38 (d, *J* = 8.2 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.80 (dd, J = 7.1, 1.4 Hz, 1H), 7.76-7.73 (m, 2H), 7.69-7.57 (m, 4H), 7.49 (dd, *J* = 7.4, 1.1 Hz, 1H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 191.1 (CHO), 183.6 (CO), 140.3 (C), 137.9 (C), 133.9 (C), 136.7 (CH), 133.5 (CH), 132.5 (C), 132.0 (C), 131.4 (CH), 129.6 (C), 129.5 (C), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.7 (CH), 127.2 (CH), 126.0 (C), 125.7 (CH), 125.3 (CH), 124.9 (CH), 124.3 (CH), 123.8 (C) ppm. HRMS (EI): calcd for $C_{24}H_{14}O_2$: 334.0994; found: 334.0990.



7,14-dihydrodibenzo[*b,i*]pyren-7,14-dione (**27**)**.** Yellow solid. R_f = 0.23 (Hexane: EtOAc, 3:1). M.p. 225-227 ºC. ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 9.69-9.65 (m, 1H), 8.56-8.51 (m, 1H), 7.75 (d, *J* = 7.1 Hz, 1H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.59-7.50 (m, 2H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 183.5 (CO), 136.3 (C), 143.8 (C), 134.6 (C), 134.3 (CH), 132.4 (CH), 130.8 (CH), 130.6 (CH), 130.4 (C), 129.8 (C), 127.6 (CH), 127.2 (CH) ppm. IR (KBr, cm^{-1}): 3001, 1640, 1593, 1458. HRMS (EI): calcd for $C_{24}H_{12}O_2$: 332.0837; found: 332.0811. Elemental analisis (%) calcd C 86.73, H 3.64; found: C 86.64, H 3.65.

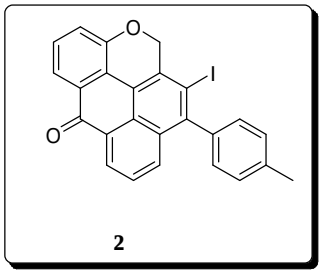


8*H*-benzo[*gh*]tetraphen-8-one (**29**)**.** Yellow solid. R_f = 0.25 (Hexane: EtOAc, 10:1). M.p. 182-184 ºC. ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 8.69-8.61 (m, 3H), 8.64 (s, 1H), 8.47 (dd, J = 7.7, 1.1 Hz, 1H), 8.15 (d, J = 7.4 Hz, 1H), 7.72-7.50 (m, 5H), 7.43 (td, J = 7.6, 1.1 Hz, 1H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 182.5 (CO), 134.2 (C), 133.9 (C), 132.4 (CH), 131.3 (C), 130.3 (C), 129.1 (CH), 128.6 (C), 128.5 (C), 127.9 (C), 127.7 (CH), 127.1 (CH), 126.8 (CH), 126.7 (CH), 126.4 (CH), 125.9 (C), 125.5 (CH), 125.3 (CH), 124.8 (CH), 122.4 (CH), 122.3 (CH) ppm. HRMS (EI): calcd for $C_{21}H_{12}O$: 280.0888; found: 280.0894.

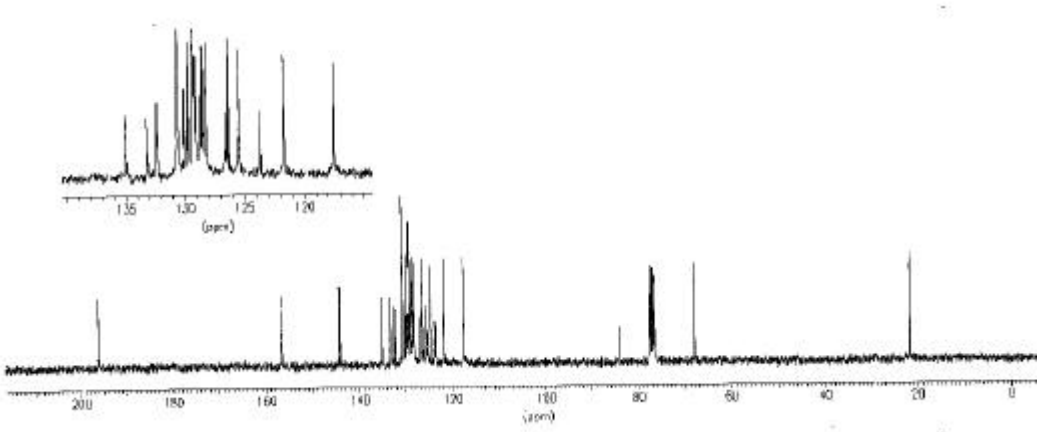


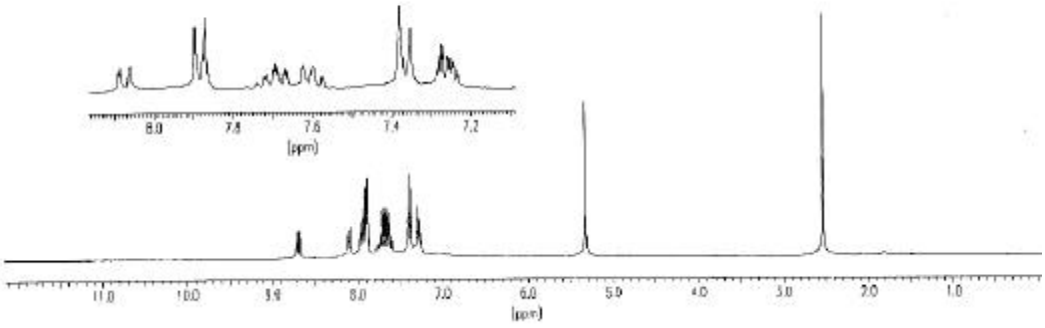
9*H*-indeno[2,1-*l*]phenanthren-9-one (**30**)**.** Yellow solid. R_f = 0.33 (Hexane: EtOAc, 3:1). M.p. 185-187 ºC. ^{1}H-RMN (300 MHz, $CDCl_3$): δ = 9.24 (dd, J = 7.1, 1.2 Hz, 1H), 8.73 (dd, J = 8.2, 1.6 Hz, 1H), 8.69-8.60 (m, 2H), 8.06 (d, J = 7.4 Hz, 1H), 7.81-7.61 (m, 5H), 7.51 (td, J = 7.4, 1.6 Hz, 1H), 7.33 (td, J = 7.8, 0.6 Hz, 1H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 196.5 (CO), 144.8 (C), 144.0 (C), 134.8 (C), 134.5 (C), 134.1 (CH), 131.2 (CH), 129.4 (C), 129.0 (C), 128.6 (C), 127.8 (C), 127.7 (CH), 127.5 (CH), 127.4 (CH), 126.2 (CH), 125.9 (CH), 125.5 (CH), 124.0 (CH), 123.7 (CH), 123.5 (CH), 122.8 (CH) ppm. IR ν(KBr, cm^{-1}): 1696, 1644. HRMS (EI): calcd for $C_{21}H_{12}O$: 280.0888; found: 280.0881.

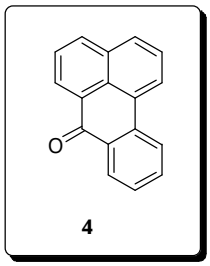
Copies of representative NMR-spectra:



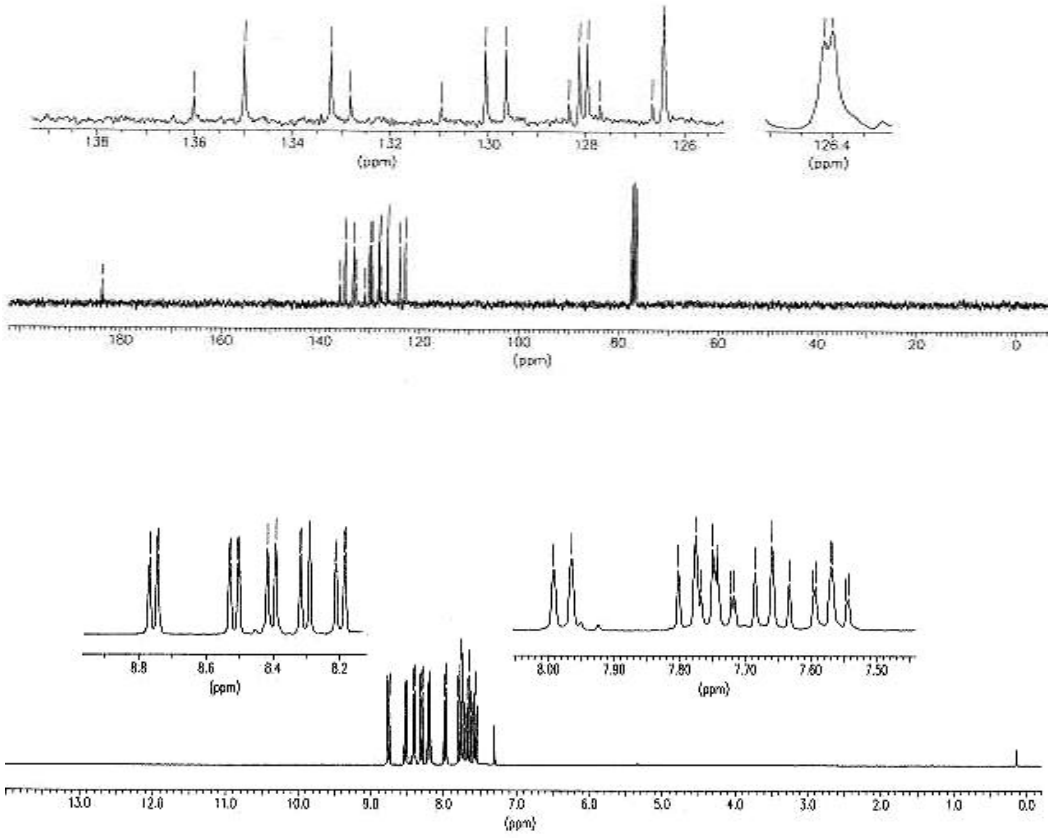
2






O

4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136
134
132
130
128
126
(ppm)
126.4
(ppm)
180
160
140
120
100
80
60
40
20
0
(ppm)
8.8
8.6
8.4
8.2
(ppm)
8.00
7.90
7.80
7.70
7.60
7.50
(ppm)
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12.0
11.0
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8.0
7.0
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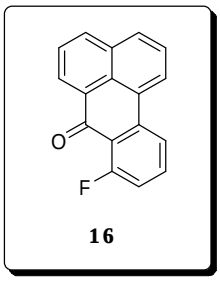
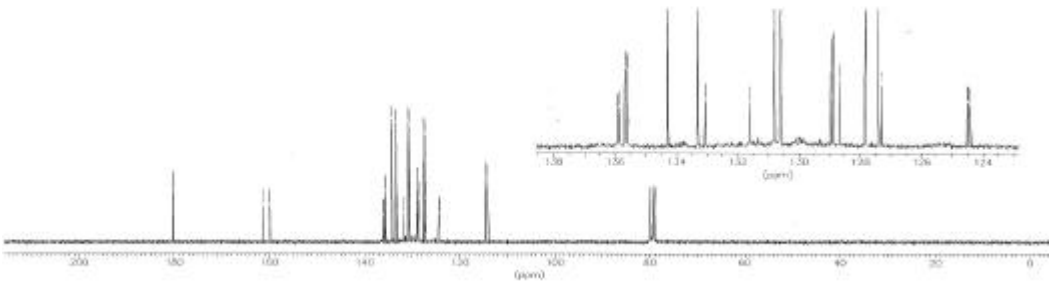
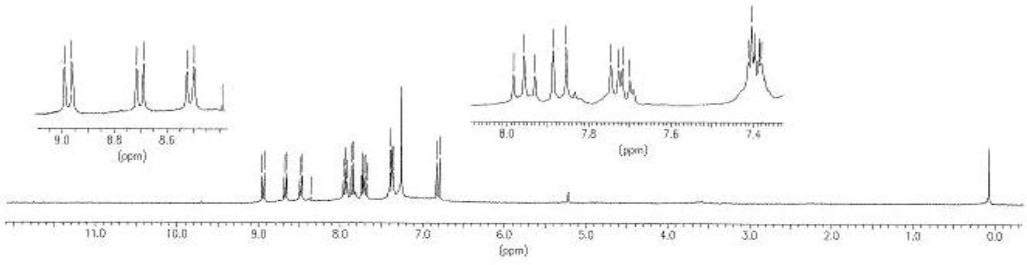
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


O
F

16

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(ppm)
8.0
7.8
7.6
7.4
(ppm)
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8.0
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6.0
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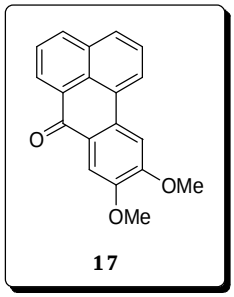
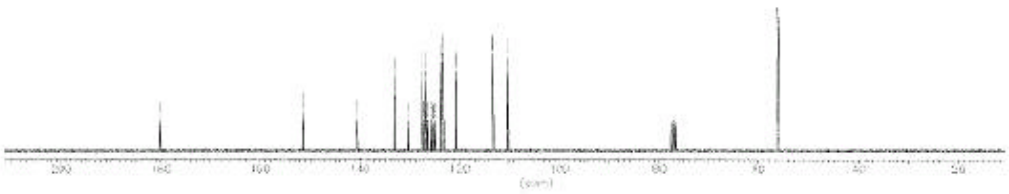
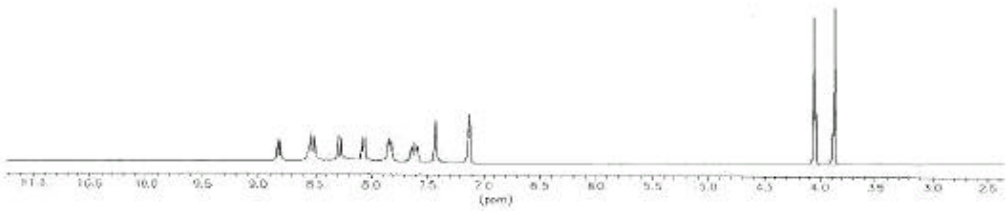
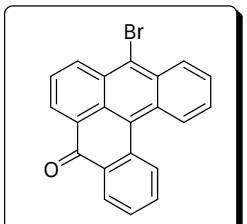
3.0
2.0
1.0
0.0
(ppm)



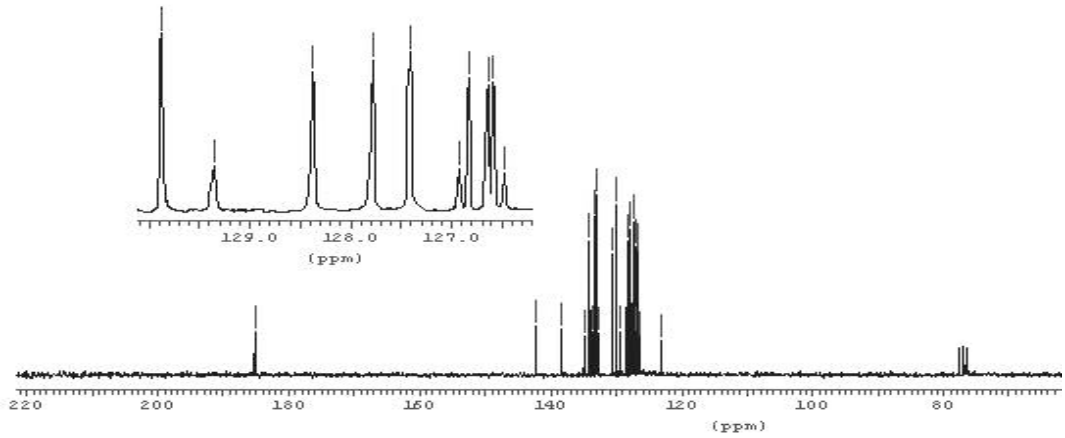
17






Br
O

19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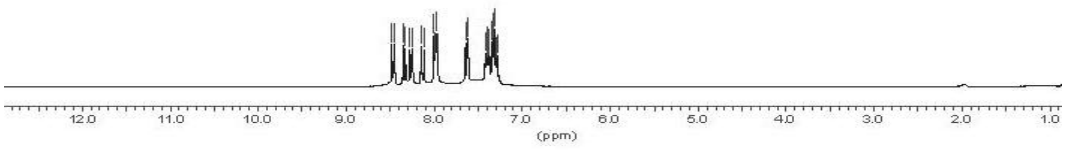
180
160
140
120
100
80
(ppm)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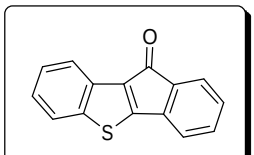
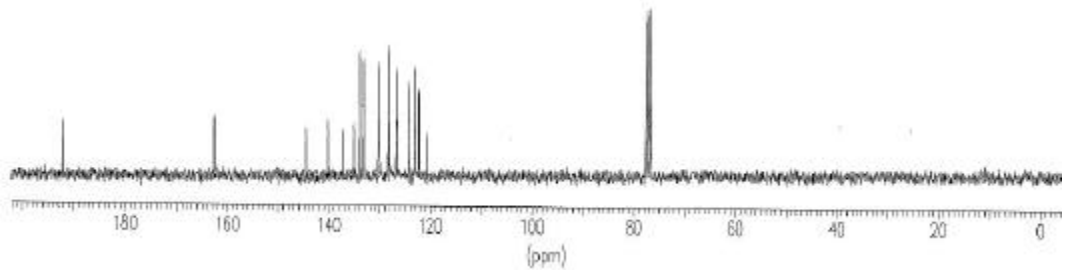
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)


O
S

21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160
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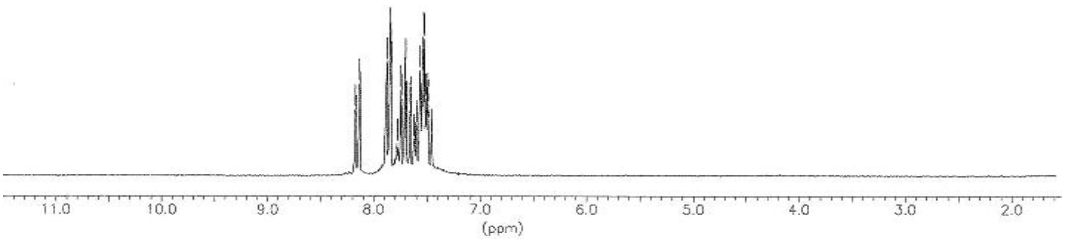
80
60
40
20
0
(ppm)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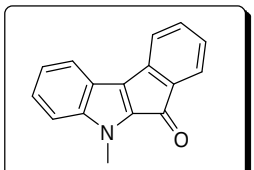
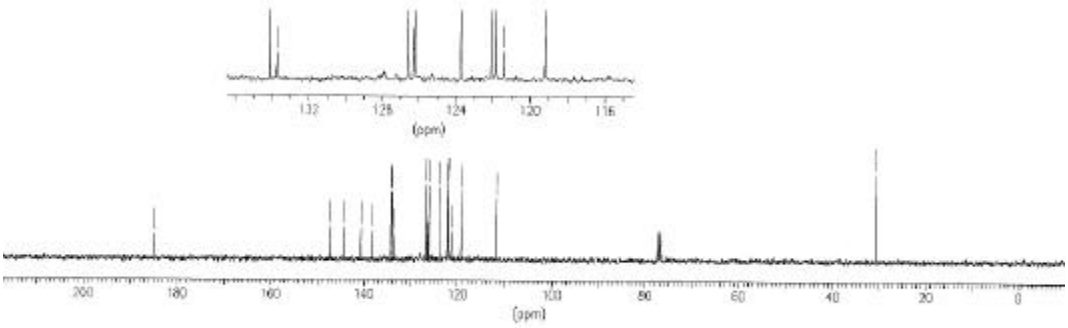
6.0
5.0
4.0
3.0
2.0
(ppm)


N
O

22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128
124
120
116
(ppm)
200
180
160
140
120
100
80
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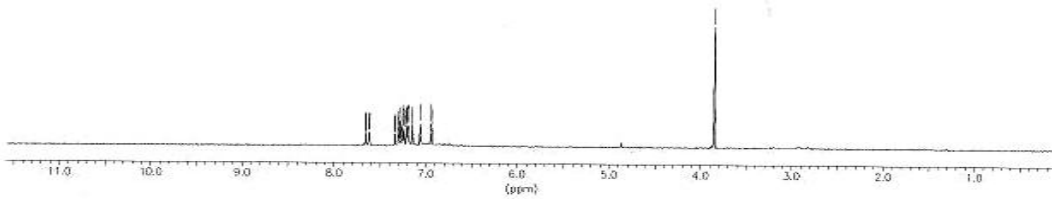
40
20
0
(ppm)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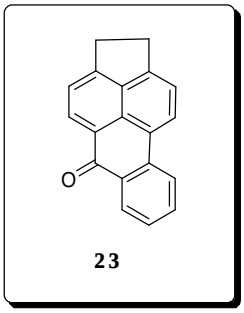
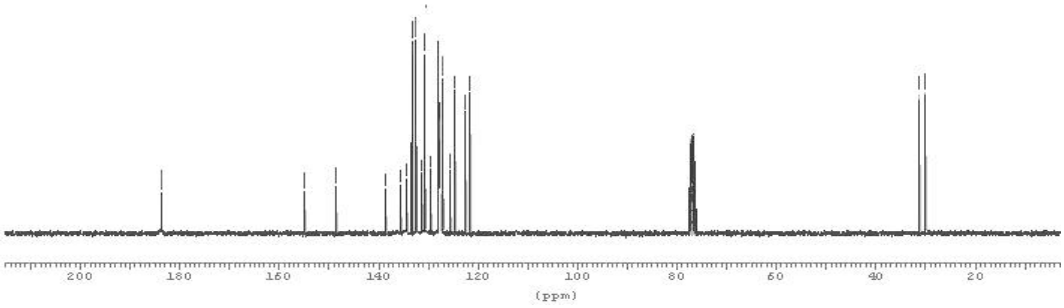
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)


O

23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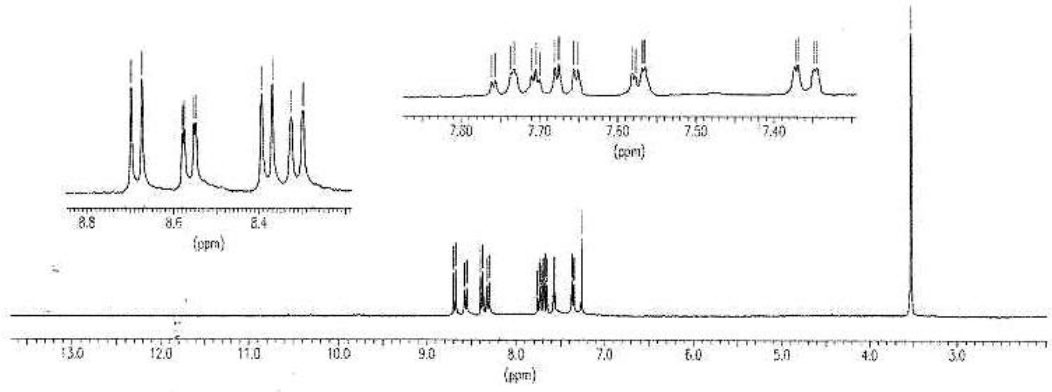
(ppm)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(ppm)
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7.50
7.40
(ppm)
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10.0
9.0
8.0
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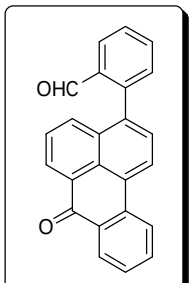
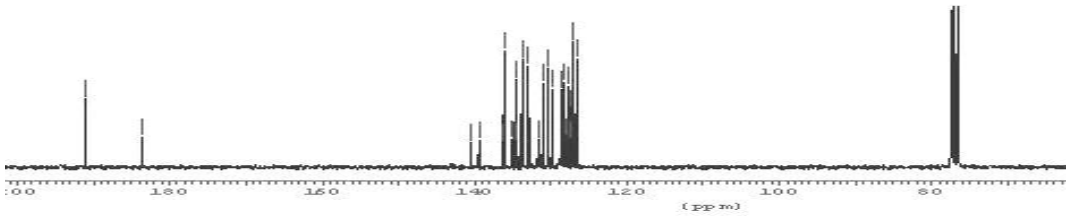
6.0
5.0
4.0
3.0
(ppm)


OHC
O

25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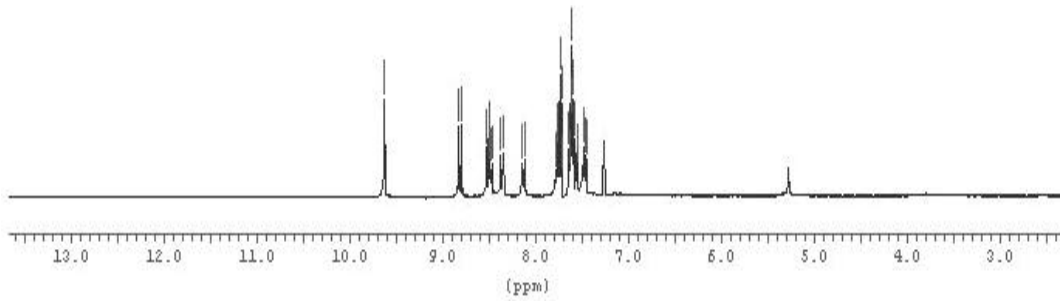
100
80
(ppm)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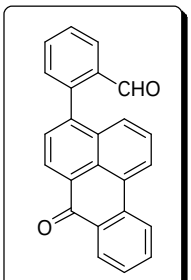
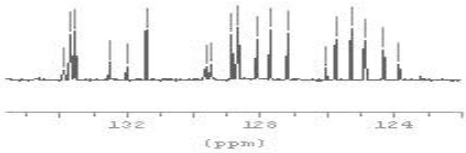
7.0
6.0
5.0
4.0
3.0
(ppm)


CHO
O

26


132
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124
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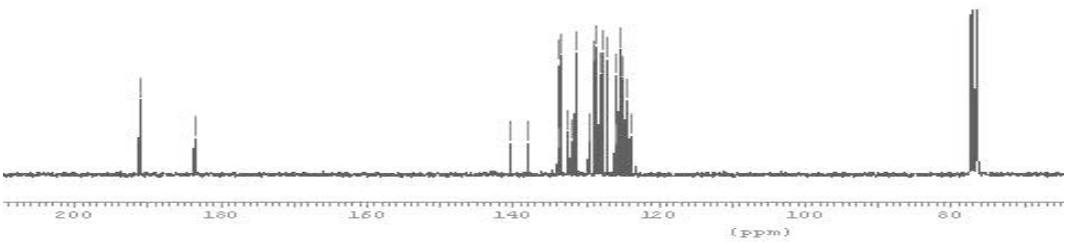
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120
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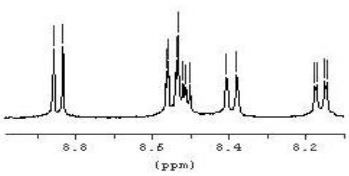
80
(ppm)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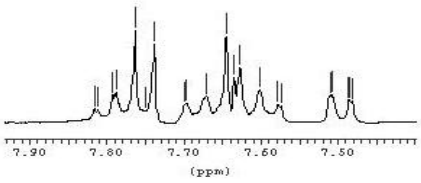
(ppm)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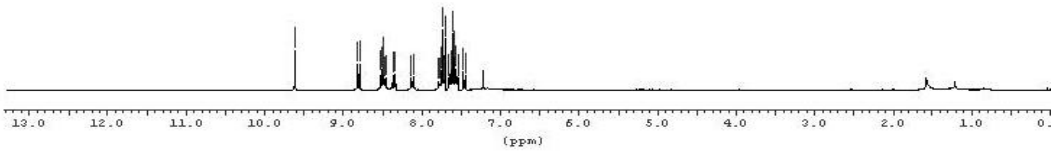
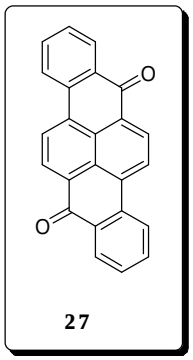
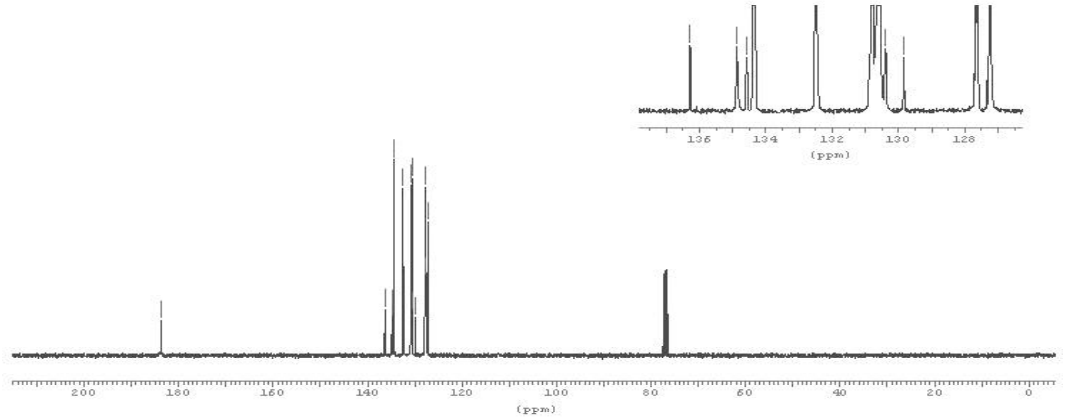
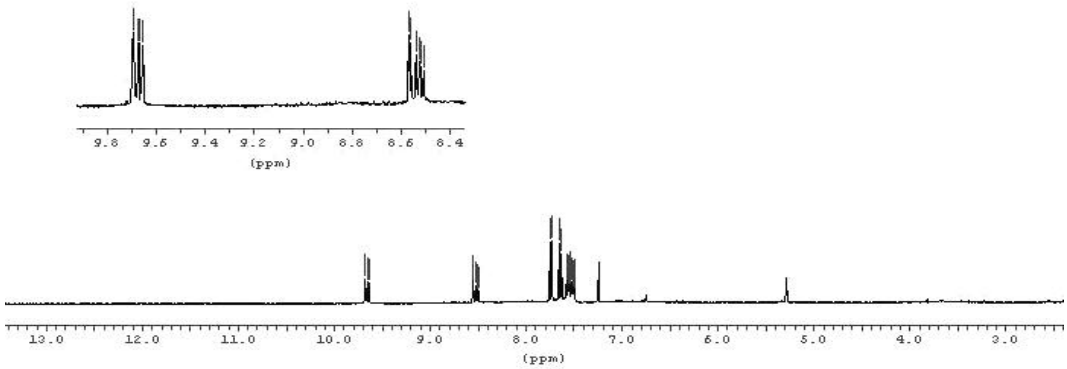
7.50
(ppm)

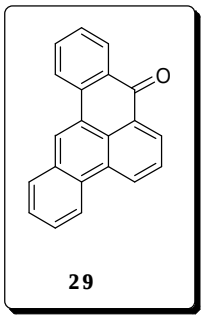

13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)


O
O

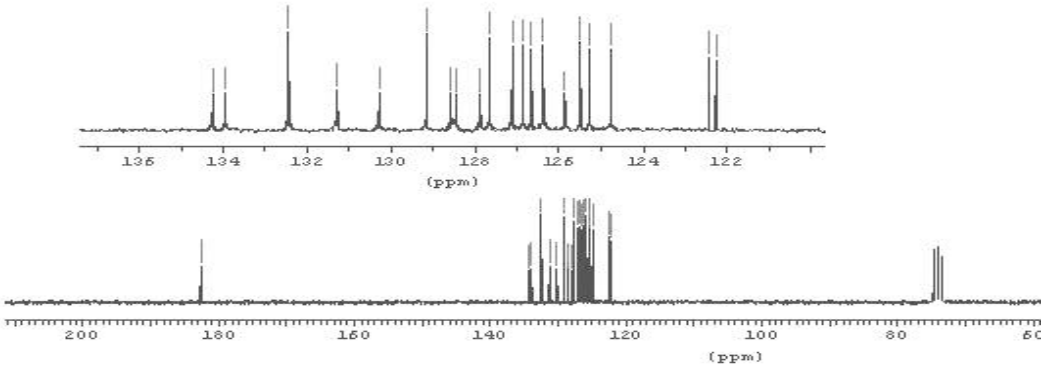
27

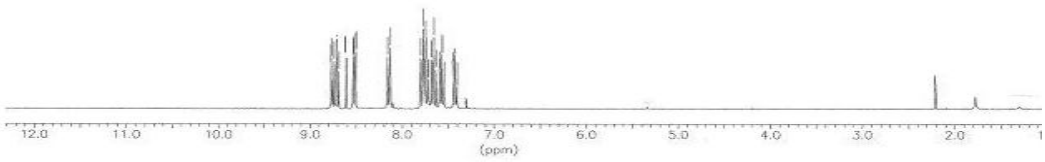

136
134
132
130
128
(ppm)
200
180
160
140
120
100
80
60
40
20
0
(ppm)

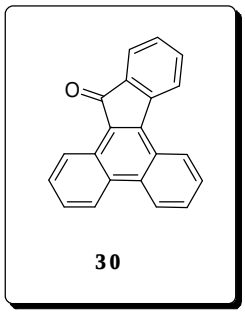

9.8
9.6
9.4
9.2
9.0
8.8
8.6
8.4
(ppm)
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
(ppm)


O

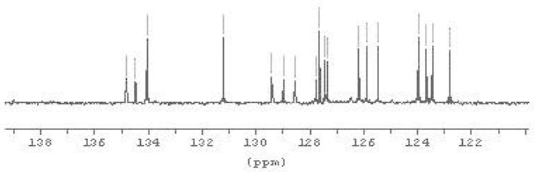
29

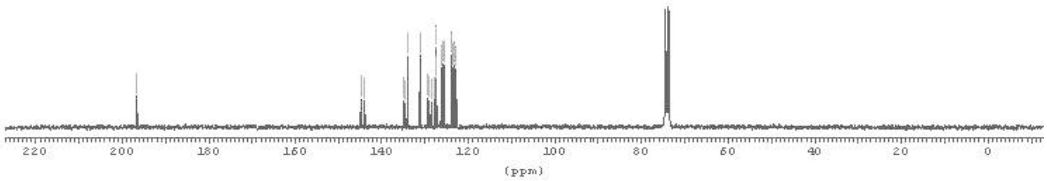

136
134
132
130
128
126
124
122
(ppm)
200
180
160
140
120
100
80
(ppm)

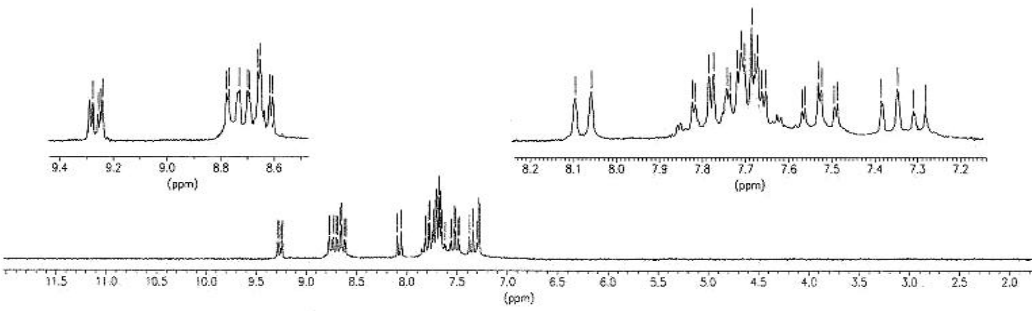

12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
(ppm)


O

30


138
136
134
132
130
128
126
124
122
(ppm)


220
200
180
160
140
120
100
80
60
40
20
0
(ppm)


9.4
9.2
9.0
8.8
8.6
(ppm)
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
(ppm)
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
(ppm)