Supplementary Material

$PhI(OAc)_2$-BF_3-OEt_2 Mediated Domino Imine Activation, Intramolecular C-C Bond Formation and β-Elimination: New Approach for the synthesis of Fluorenones, Xanthones and Phenanthridines †

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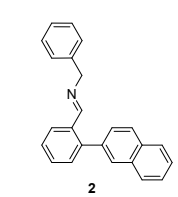
Contents for supporting information:

General information

All reagents were purchased from commercial suppliers and used without further purification. IR spectra of the compounds were recorded on Perkin-Elmer AC-1 spectrometer. ^{1}H NMR spectra were run on Bruker Advance DPX 300 MHz spectrometer in $CDCl_3$ and TMS was used as internal standard. ESI mass spectra were recorded on JEOL SX 102/DA-6000. Silica gel 60-120 and 230-400 mesh was used as stationary phase to isolate the compounds. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Dichloromethane (DCM) and 1,2-dichloroethane (DCE) was distilled over calcium hydride. Aldimines (**2**, **12-19**, **29**, **32**, **37-39** and **46-48**) were prepared from condensation of the corresponding aldehydes with amines according to the literature method.[1]

Structers of Aldimines (2, 12-19, 29, 32, 37-39 and 46-48)



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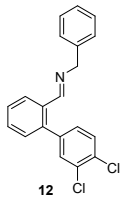

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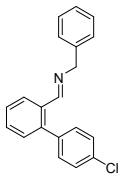

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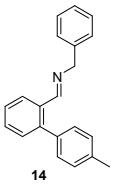

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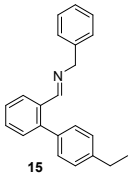

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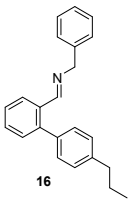

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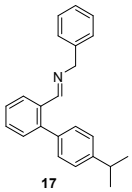

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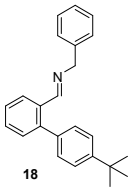

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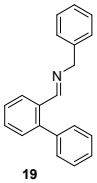

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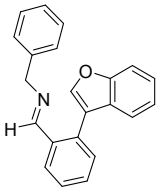

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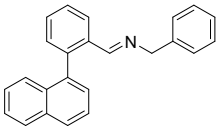

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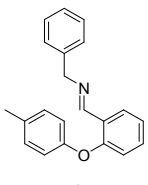

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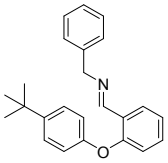

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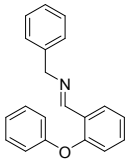

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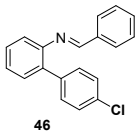

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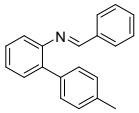

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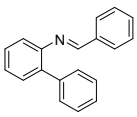
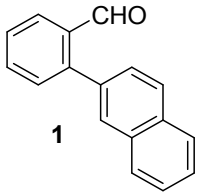


48

General procedure (I) for synthesis of biaryl-2-carbaldehydes

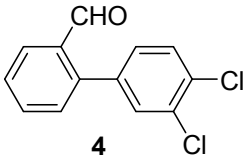
5 mmol of 2-bromobenzaldehyde, 6 mmol of arylboronic acid and 0.5 mmol of $Pd(PPh_3)_4$ were taken in a round bottom flask. 10 ml of DMF was added in the reaction mixture and stirred for 2 min. 10 ml of 2(M) Na_2CO_3 solution was then added and then refluxed for 4-8 h at 80 ^oC. The reaction mixture was extracted with ethyl acetate (2 x 10 mL). The combined ethyl acetate layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by column chromatography on silica gel (60-120 mesh) using ethyl acetate/hexane as eluent.

Spectroscopic data of biaryl-2-carbaldehydes



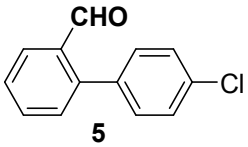
1

2-(naphthalen-2-yl)benzaldehyde **(1):** Following the general procedure (**I**), **1** was prepared from naphthalen-2-ylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil 373 mg (59% yield); IR (KBr): ν_{max} 3058, 3020, 2860, 1695 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 7.98-7.85 (m, 4H), 7.72-7.60 (m, 1H), 7.58-7.56 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 192.4 (C), 145.9 (C), 135.2 (C), 134.0 (C), 133.6 (CH), 133.0 (C), 132.8 (C), 131.0 (CH), 129.5 (CH), 128.2 (CH), 128.2 (CH), 127.9 (CH), 127.8 (CH), 127.8 (CH), 127.7 (CH), 126.9 (CH), 126.7 (CH); MS (ESI): *m/z* = 233.1 $(M+H)^+$. The compound was previously reported by Larock et al.[2]



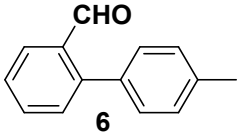
4

3',4'-dichlorobiphenyl-2-carbaldehyde **(4):** Following the general procedure (**I**), **4** was prepared from 3,4-dichlorophenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 80 : 20). Yellow solid 412 mg (61% yield); m.p. 136-138 ^oC; IR (KBr): 3035, 2850, 1692, 777, 766 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.15 (s, 1H), 7.94 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.77 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.72-7.63 (m, 3H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 7.4, 1.3 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 193.2 (C), 139.3 (C), 137.4 (C), 137.4 (C), 135.0 (CH), 134.2 (C), 131.9 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 127.0 (CH), 126.3 (CH), 126.1 (CH); MS (ESI): *m/z* = 251.1 $(M+H)^+$.



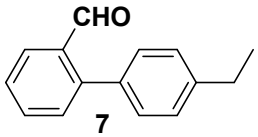
5

4'-chlorobiphenyl-2-carbaldehyde **(5):** Following the general procedure (**I**), **5** was prepared from 4-chlorophenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil[3] 383 mg (67% yield). Spectroscopic data was identical with that previously reported.[3]



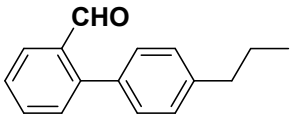
6

4'-methylbiphenyl-2-carbaldehyde **(6):** Following the general procedure (**I**), **6** was prepared from 4-methylphenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil[4] 382 mg (72% yield). Spectroscopic data was identical with that previously reported.[4]



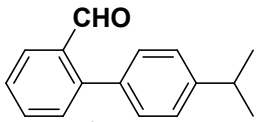
7

4'-ethylbiphenyl-2-carbaldehyde **(7):** Following the general procedure (**I**), **7** was prepared from 4-ethylphenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 407 mg (68% yield); IR (Neat): 3020, 2965, 2930, 2845, 1698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.04 (d, *J* = 6.9 Hz, 1H), 7.68-7.62 (m, 1H), 7.52-7.46 (m, 2H), 7.33 (brs, 4H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 192.6 (C), 146.0 (C), 135.0 (C), 133.8 (C), 133.5 (CH), 130.8 (CH), 130.1 (2CH), 127.9 (2CH), 127.5 (CH), 28.6 (CH_2), 15.5 (CH_3); MS (ESI): *m/z* 211.1 $(M+H)^+$.



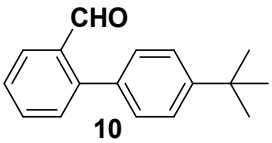
8

4'-propylbiphenyl-2-carbaldehyde **(8):** Following the general procedure (**I**), **8** was prepared from 4-propylphenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 450 mg (74% yield); IR (Neat): 3032, 2945, 2862, 1696 cm^{-1}; MS (ESI): *m/z* 225.1 $(M+H)^+$; ^{1}H- and ^{13}C-NMR data was identical with that previously reported.[5]



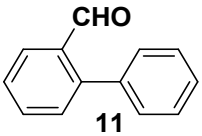
9

4'-isopropylbiphenyl-2-carbaldehyde **(9):** Following the general procedure (**I**), **9** was prepared from 4-isopropylphenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil[6] 405 mg (68% yield). Spectroscopic data was identical with that previously reported.[6]



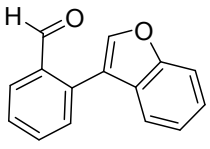
10

4'-tert-butylbiphenyl-2-carbaldehyde **(10):** Following the general procedure (**I**), **10** was prepared from 4-tertbutylphenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil[7] 445 mg (69% yield). Spectroscopic data was identical with that previously reported.[7]



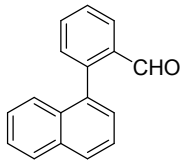
11

Biphenyl-2-carbaldehyde **(11):** Following the general procedure (**I**), **11** was prepared from phenylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil[8] 344 mg (69% yield). Spectroscopic data was identical with that previously reported.[9]



28

2-(benzofuran-3-yl)benzaldehyde **(28):** Following the general procedure (**I**), **28** was prepared from benzofuran-3-ylboronic acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 85 : 15). Pale yellow oil[2] 410 mg (68% yield). Spectroscopic data was identical with that previously reported.[2]



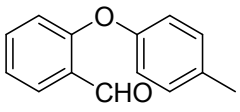
31

2-(naphthalen-1-yl)benzaldehyde **(31):** Following the general procedure (**I**), **31** was prepared from naphthalen-1-ylboronic acid acid and 2-bromo benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). White solid[10] 362 mg (58% yield); m.p.: 88-90^{o}C (lit[10] m.p. 87-88^{o}C). Spectroscopic data was identical with that previously reported.[10]

General procedure (II) for synthesis of the 2-(aryloxy)benzaldehydes[11]

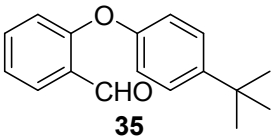
To a solution of DMA (10 mL) containing 2-fluorobenzaldehyde (5.0 mmol) and hydroxy benzene derivative (5.0 mmol), was added K_2CO_3 (5.0 mmol) and the reaction mixture was stirred for 2 h at 170 ^{o}C under an Argon atmosphere. It was then cooled to room temperature and after usual workup and concentration, crude mixture was purified by column chromatography on silica gel (60-120 mesh) using ethyl acetate/hexane as eluent.

Spectroscopic data of 2-(aryloxy)benzaldehydes



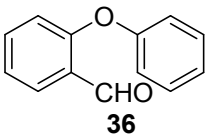
34

2-(p-tolyloxy)benzaldehyde **(34):** Following the general procedure (**II**), **34** was prepared from 4-methylphenol and 2-fluro benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil[12] 512 mg (60% yield). Spectroscopic data was identical with that previously reported.[12]



35

2-(4-tert-butylphenoxy)benzaldehyde **(35):** Following the general procedure (**II**), **35** was prepared from 4-tertbutylphenol and 2-flurobenzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil[2] 650 mg (65% yield). Spectroscopic data was identical with that previously reported.[2]



36

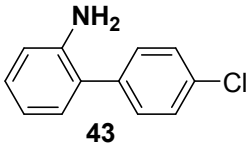
2-phenoxybenzaldehyde **(36):** Following the general procedure (**II**), **36** was prepared from phenol and 2-fluro benzaldehyde and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil[13] 496 mg (62% yield). Spectroscopic data was identical with that previously reported.[13]

General procedure (III) for synthesis of biaryl-2-amines[14]

To a 100 mL round bottom flask, aryl boronic acid (3.0 mmol), K_2CO_3 (8.0 mmol), and $Pd(PPh_3)_4$ (0.2 mmol) were dissolved in 15 mL of toluene followed by the addition of 3 mL of H_2O and 5 mL of EtOH. 2-Bromoaniline (2.0 mmol) was then added and the resulting mixture was heated at 100 ^{o}C for 16 h. After cooling to room temperature, the reaction mixture was diluted

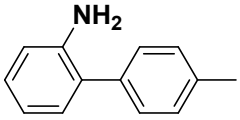
with 30 mL of saturated aqueous NH_4Cl and 30 mL of CH_2Cl_2. The aqueous phase was extracted with an additional 2 × 30 mL of CH_2Cl_2, and the combined organic layers were washed with 30 mL of water and 30 mL of saturated aqueous $NaHCO_3$. The organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo and purified by column chromatography on silica gel (60-120 mesh) using ethyl acetate/hexane as eluent.

Spectroscopic data of biaryl-2-amines



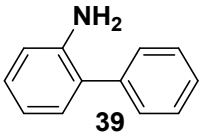
43

4'-chlorobiphenyl-2-amine **(43):** Following the general procedure (**III)**, **43** was prepared from 4-chlorophenylboronic acid and 2-bromo aniline and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 80 : 20). Yellow oil[15] 410 mg (69% yield). Spectroscopic data was identical with that previously reported.[15]



44

4'-methylbiphenyl-2-amine **(44):** Following the general procedure (**III)**, **44** was prepared from 4-methylphenylboronic acid and 2-bromo aniline and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 80 : 20). Brown oil[16] 332 mg (62% yield). Spectroscopic data was identical with that previously reported.[16]



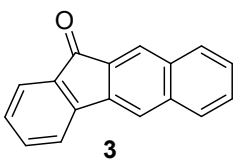
39

biphenyl-2-amine **(45):** Following the general procedure (**III)**, **45** was prepared from phenylboronic acid and 2-bromo aniline and purified by column chromatography on silica gel (60-120 mesh) using (hexane : EtOAc = 80 : 20). Brown solid[17] 310 mg (63% yield). mp. 51-54 ^oC (lit[17] m.p. 52-54 ^oC); Spectroscopic data was identical with that previously reported.[17]

General procedure (IV) for synthesis of fluorenones, anthranone and xanthones

Aldimine (0.25 mmol) was dissolved in DCE (1.0 ml) and added in mixture of $PhI(OAc)_2$ (0.375 mmol) and BF_3-OEt_2 (0.375 mmol) in DCE (3 ml). The resulting reaction mixture was stirred at room temperature for 5 min and then was refluxed for 24-30 h at 80 ^oC and then cooled to room temperature. 1N HCl (2 ml) was added and stirred for 2-6 h at room temperature. Diluted with H_2O and extracted with diethyl ether (2 x 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to afford the residue, which was purified by column chromatography on silica gel (230-400 mesh) using ethyl acetate/hexane as the eluent to provide the desired product.

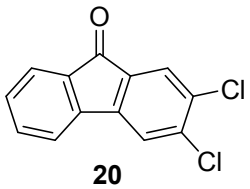
Spectroscopic data of fluorenones, anthranone and xanthones



3

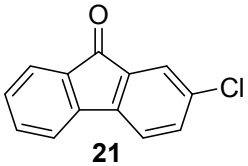
11H-benzo[b]fluoren-11-one **(3):** Following the general procedure (**IV)**, **3** was prepared from aldimine **2** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow solid[18] (60 mg, 61% yield); m.p.: 142-144 ^oC (lit.[18] m.p. 141-142 ^oC); IR (KBr): ν_{max} 3042, 1710, 1604, 895 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.89-7.86 (m, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.57-7.53 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 193.1 (C), 144.8 (C), 138.5 (C), 136.9 (C), 136.2

(C), 135.0 (CH), 133.9 (C), 132.7 (C), 130.8 (CH), 129.1 (CH), 128.8 (CH), 128.7 (CH), 126.6 (CH), 125.6 (CH), 124.4 (CH), 120.8 (CH), 119.0 (CH); MS (ESI): *m/z* = 231.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{17}H_{10}O$: 230.0732, found: 231.0734 $(M+H)^+$. Spectroscopic data was compared with that previously reported.[18]



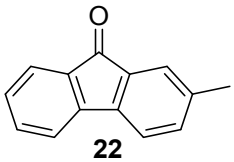
20

2,3-dichloro-9H-fluoren-9-one **(20):** Following the general procedure (**IV**), **20** was prepared from aldimine **12** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 85 : 15). Yellow solid (64 mg, 65% yield); m.p.: 134-136 °C; IR (KBr): ν_{max} 1712, 1602, 777 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.61 (s, 1H), 7.57 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.49 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.43-7.37 (m, 1H), 7.31-7.25 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 195.9 (C), 143.8 (C), 142.5 (C), 140.4 (C), 136.9 (C), 136.1 (C), 135.7 (C), 133.9 (C), 129.5 (CH), 128.3 (CH), 125.8 (CH), 123.0 (CH), 122.2 (CH); MS (ESI): *m/z* = 249.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{13}H_6Cl_2O$: 247.9796, found: 248.9798 $(M+H)^+$.



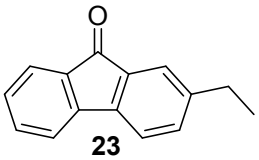
21

2-chloro-9H-fluoren-9-one **(21):** Following the general procedure (**IV**), **21** was prepared aldimine **13** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow solid[19] 58 mg (59% yield). m.p.: 120-121 °C (lit.[19] mp 118-120 °C); Spectroscopic data was identical with that previously reported.[19]



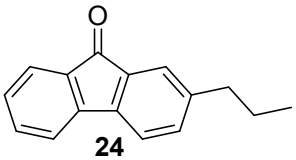
22

2-methyl-9H-fluoren-9-one **(22):** Following the general procedure (**IV**), **22** was prepared from aldimine **14** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow solid[19] 56 mg (57% yield). m.p.: 92-94 °C (lit.[19] mp 92 °C); Spectroscopic data was identical with that previously reported.[19]



23

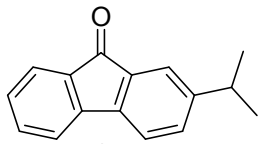
2-ethyl-9H-fluoren-9-one **(23):** Following the general procedure (**IV**), **23** was prepared from aldimine **15** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil 56 mg (57% yield); IR (Neat): 1720, 1600, 1485, 1440 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.64-7.58 (m, 2H), 7.50-7.41 (m, 3H), 7.30-7.22 (m, 2H), 2.72 (q, *J* = 6.8 Hz, 2H), 1.30 (t, *J*=6.6 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 194.2 (C), 144.9 (C), 141.2 (C), 139.8 (C), 135.9 (C), 135.4 (C), 134.7 (CH), 134.5 (CH), 128.5 (CH), 125.7 (CH), 125.2 (CH), 121.5 (CH), 121.1 (CH), 28.7 (CH_2), 13.0 (CH_3); MS (ESI): *m/z* = 209.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{15}H_{12}O$: 208.0888, found: 209.0887 $(M+H)^+$.



24

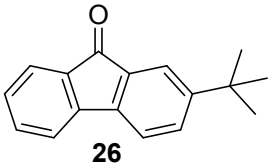
2-propyl-9H-fluoren-9-one **(24):** Following the general procedure (**IV**), **24** was prepared from aldimine **16** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil 54 mg (55% yield); IR (Neat): 2935, 1722, 1605, 1480, 1450 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J* = 1.3 Hz, 1H), 7.58 (dd, *J* = 7.3, 1.5 Hz,

1H), 7.51-7.46 (m, 2H), 7.43-7.34 (m, 2H), 7.31-7.26 (m, 1H), 2.54 (t, *J* = 7.4 Hz, 2H), 1.78-1.67 (m, 2H), 1.05 (t, *J* = 6.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 194.4 (C), 144.1 (C), 141.4 (C), 139.2 (C), 135.6 (C), 134.8 (C), 134.2 (CH), 133.6 (CH), 128.8 (CH), 128.3 (CH), 125.8 (CH), 121.8 (CH), 121.4 (CH), 38.6 (CH_2), 24.5 (CH_2), 13.0 (CH_3); MS (ESI): *m/z* = 223.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{16}H_{14}O$: 222.1045, found: 223.1044 $(M+H)^+$.



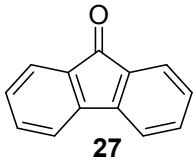
25

2-isopropyl-9H-fluoren-9-one **(25):** Following the general procedure (**IV**), **25** was prepared from aldimine **17** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil (57 mg, 58% yield); IR (Neat): 1710, 1612, 1380 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 1.3 Hz, 1H), 7.63 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.51-7.47 (m, 3H), 7.38 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.31-7.25 (m, 1H), 3.23-3.11 (m, 1H), 1.33 (d, *J* = 6.4 Hz, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 194.2 (C), 144.9 (C), 143.2 (C), 141.6 (C), 139.1 (C), 135.4 (C), 134.5 (CH), 130.3 (CH), 127.5 (CH), 125.1 (CH), 121.9 (CH), 121.1 (CH), 119.1 (CH), 34.3 (C), 23.2 ($2CH_3$); MS (ESI): *m/z* = 223.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{16}H_{14}O$: 222.1045, found: 223.1042 $(M+H)^+$.



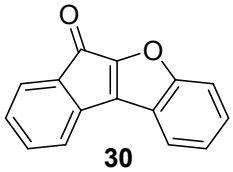
26

2-tert-butyl-9H-fluoren-9-one **(26):** Following the general procedure (**IV**), **26** was prepared from aldimine **18** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil (54 mg, 55% yield); IR (Neat): 1712, 1595, 1385 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 1.4 Hz, 1H), 7.59 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.47-7.33 (m, 4H), 7.27-7.22 (m, 1H), 1.35 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 194.3 (C), 151.9 (C), 144.3 (C), 141.7 (C), 138.4 (C), 135.5 (C), 134.6 (CH), 130.9 (CH), 128.7 (CH), 125.2 (CH), 122.9 (CH), 121.3 (CH), 119.9 (CH), 35.0 (C), 31.4 ($3CH_3$); MS (ESI): *m/z* = 237.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{17}H_{16}O$: 236.1201, found: 237.1211 $(M+H)^+$.



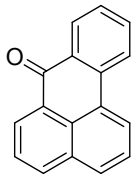
27

9H-fluoren-9-one **(27):** Following the general procedure (**IV**), **27** was prepared from aldimine **19** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow solid[20] 46 mg (47% yield). m.p.: 82-85 °C (lit.[20] mp 82-83 °C); Spectroscopic data was identical with that previously reported.[20]



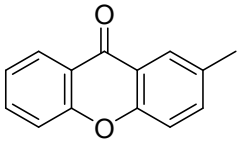
30

6H-benzo[d]indeno[2,1-b]furan-6-one **(30)** Following the general procedure (**IV**), **30** was prepared from aldimine **29** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Orange yellow solid[21] (42 mg, 66% yield); m.p.: 110-112 °C (lit.[21] m.p. 109-110 °C); IR (KBr): ν_{max} 3025, 1720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 7.9, 0.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.61-7.47 (m, 1H), 7.45-7.17 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.6 (C), 163.2 (C), 155.9 (C), 144.9 (C), 141.0 (C), 135.3 (C), 135.2 (CH), 128.4 (2CH), 127.9 (C), 121.8 (CH), 120.8 (CH), 120.1 (CH), 116.8 (CH), 112.6 (CH); MS (ESI): *m/z* = 221.2 $(M+H)^+$; HRMS (ESI) calculated for $C_{15}H_{18}O_2$: 220.0524, found: 221.0525 $(M+H)^+$. Spectroscopic data was compared with that previously reported.[21]



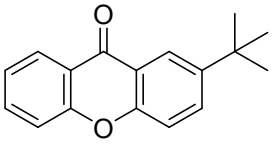
33

7H-benzo[de]anthracen-7-one **(33)** Following the general procedure (**IV)**, **33** was prepared from aldimine **31** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow solid[18] (44 mg, 68% yield); m.p.: 160-162 ^{o}C (lit.[18] m.p. 162-1664 ^{o}C); IR (KBr): ν_{max} 3040, 1650, 1597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (d, *J* = 7.6 Hz, 1H), 8.52 (d, *J* = 7.2 Hz, 1H), 8.45 (d, *J* = 7.2 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.88-7.72 (m, 2H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.8 (C), 136.1 (C), 135.1 (CH), 133.5 (CH), 133.0 (C), 131.3 (C), 130.2 (CH), 129.7 (CH), 128.5 (C), 128.2 (CH), 128.1 (CH), 127.9 (C), 126.8 (C), 126.5 (CH), 126.5 (CH), 124.1 (CH), 123.0 (CH); MS (ESI): *m/z* = 231.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{17}H_{10}O$: 230.0732, found: 231.0733 $(M+H)^+$. Spectroscopic data was compared with that previously reported.[18]



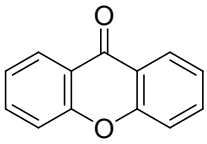
40

2-methyl-9H-xanthen-9-one **(40):** Following the general procedure (**IV)**, **40** was prepared from aldimine **37** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Pale yellow oil[22] 76 mg (74% yield). IR (KBr): ν_{max} 3060, 2920, 2864, 1658 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.27 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.05 (s, 1H), 7.72-7.67 (m, 1H), 7.49-7.38 (m, 3H), 7.33 (d, *J* = 7.5 Hz, 1H), 2.41 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 177.3 (C), 156.4 (C), 154.3 (C), 136.3 (CH), 134.8 (CH), 133.4 (C), 126.1 (CH), 125.7 (CH), 123.5 (CH), 121.9 (C), 119.2 (C), 118.7 (CH), 118.3 (CH), 20.8 (CH_3); MS (ESI): *m/z* = 211.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{14}H_{10}O_2$: 210.0681, found: 211.0685 $(M+H)^+$. Spectroscopic data was compared with that previously reported.[2]



41

2-tert-butyl-9H-xanthen-9-one **(41):** Following the general procedure (**IV)**, **35** was prepared from aldimine **38** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). Yellow oil[23] (67 mg, 68% yield); IR (Neat): ν_{max} 2965, 2867, 1661 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.32-8.28 (m, 2H), 7.77 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.72-7.67 (m, 1H), 7.49-7.43 (m, 2H), 7.39-7.33 (m, 1H), 1.40 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 177.4 (C), 156.5 (C), 154.9 (C), 147.6 (C), 134.8 (CH), 133.5 (CH), 127.4 (CH), 123.7 (CH), 122.7 (CH), 122.0 (C), 121.3 (C), 118.1 (CH), 117.8 (CH), 35.4 (C), 31.7 ($3CH_3$); MS (ESI): *m/z* = 253.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{17}H_{16}O_2$: 252.1150, found: 253.1155 $(M+H)^+$. Spectroscopic data was compared with that previously reported.[2]

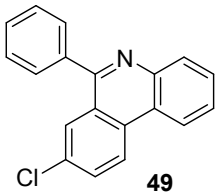


42

9H-xanthen-9-one **(42):** Following the general procedure (**IV)**, **42** was prepared from aldimine **39** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 90 : 10). White solid[24] 53 mg (54% yield). m.p.: 172-174 ^{o}C (lit.[24] m.p. 176-177 ^{o}C); IR (KBr): ν_{max} 2920, 2870, 1655, 1458 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.30 (d, *J* = 7.9 Hz, 2H), 7.69-7.64 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 177.2 (C), 156.2 (C), 134.8 (2CH), 126.6 (2CH), 124.1 (2CH), 121.7 (C), 118.0 (2CH); MS (ESI): *m/z* =197.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{13}H_8O_2$: 196.0524, found: 197.0525 $(M+H)^+$. Spectroscopic data was identical with that previously reported.[24]

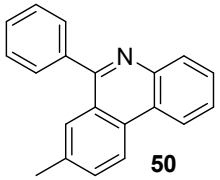
General procedure (V) for synthesis of phenanthridines

Aldimine (0.25 mmol) was dissolved in DCE (1 ml) and added in a mixture of $PhI(OAc)_2$ (0.375 mmol) and BF_3-OEt_2 (0.375 mmol) in DCE (3 ml). The resulting reaction mixture was stirred at room temperature for 5 min and then was refluxed for 30 h at 80 °C and then cooled to room temperature. Diluted with H_2O and extracted with diethyl ether (2 x 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure to afford the residue, which was purified by column chromatography on silica gel (230-400 mesh) using ethyl acetate/hexanes as the eluent to provide the desired product.



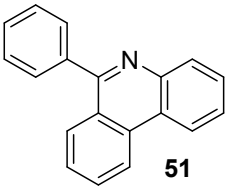
49

8-chloro-6-phenylphenanthridine **(49):** Following the general procedure (**V**), **49** was prepared from aldimine **46** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 80 : 20). White solid (57 mg, 58% yield); m.p.: 143-145 °C; IR (Neat): 3062, 2990, 2927, 1606, 1510, 1495, 1466, 1455, 1354, 1250, 1235, 1170, 1032, 830, 777, 735, 726 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.55 (d, *J* = 7.7 Hz, 1H), 8.51 (d, *J* = 7.7 Hz, 1H), 8.33 (d, *J* = 7.3 Hz, 1H), 7.88 (s, 1H), 7.66-7.58 (m, 5H), 7.56-7.54 (m, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 160.1 (C), 144.2 (C), 139.9 (C), 135.3 (C), 132.6 (C), 131.6 (CH), 130.8 (CH), 129.5 (CH), 128.9 (2CH), 128.8 (CH), 128.7 (2CH), 127.9 (CH), 127.3 (CH), 125.7 (C), 124.2 (C), 122.2 (CH), 121.6 (CH); MS (ESI): *m/z* = 290.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{20}H_{12}ClN$: 289.0658, found: 290.0655 $(M+H)^+$.



50

8-methyl-6-phenylphenanthridine **(50):** Following the general procedure (**V**), **50** was prepared from aldimine **47** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 80 : 20). Yellow oil[25] (56 mg, 57% yield); IR (Neat): ν_{max} 3060, 2920, 1580, 1562, 1460, 1365, 1230, 766, 733, 703 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.58 (d, *J* = 8.2 Hz, 1H), 8.48 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.87 (s, 1H), 7.75-7.65 (m, 5H), 7.59-7.52 (m, 3H), 2.51 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.3 (C), 143.8 (C), 139.8 (C), 137.1 (C), 132.3 (CH), 131.2 (C), 130.2 (CH), 129.5 (CH), 128.7 (2CH), 128.5 (CH), 128.4 (2CH), 128.2 (CH), 127.2 (CH), 125.3 (C), 124.0 (C), 122.0 (CH), 121.5 (CH), 21.7 (CH_3); MS (ESI): *m/z* = 270.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{20}H_{15}N$: 269.1204, found: 270.1206 $(M+H)^+$. Spectroscopic data was compared with that previously reported.[25]



51

6-phenylphenanthridine **(51):** Following the general procedure (**V**), **51** was prepared from aldimine **48** and purified by column chromatography on silica gel (230-400 mesh) using (hexane : EtOAc = 80 : 20). White solid[26] 49 mg (48% yield). m.p.: 105-106 °C (lit.[26] mp 109 °C); IR (KBr): ν_{max} 3058, 3020, 2926, 2851, 1560, 1482, 1458, 1444, 1361, 1330, 1300, 1228, 1135, 1073, 1029, 956, 784, 763, 727, 701, 672 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 7.7 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.86-7.56 (m, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.2 (C), 143.7 (C), 139.8 (C), 133.3 (C), 130.5 (CH), 130.2 (CH), 129.7 (2CH), 128.8 (C), 128.8 (CH), 128.7 (CH), 128.3 (CH), 127.0 (CH), 126.7 (CH), 125.2 (C), 123.6 (C), 122.1 (CH), 121.9 (CH); MS (ESI): *m/z* = 256.1 $(M+H)^+$; HRMS (ESI) calculated for $C_{19}H_{13}N$: 255.1048, found: 256.1044 $(M+H)^+$. Spectroscopic data was compared with that previously reported.[26]

References:

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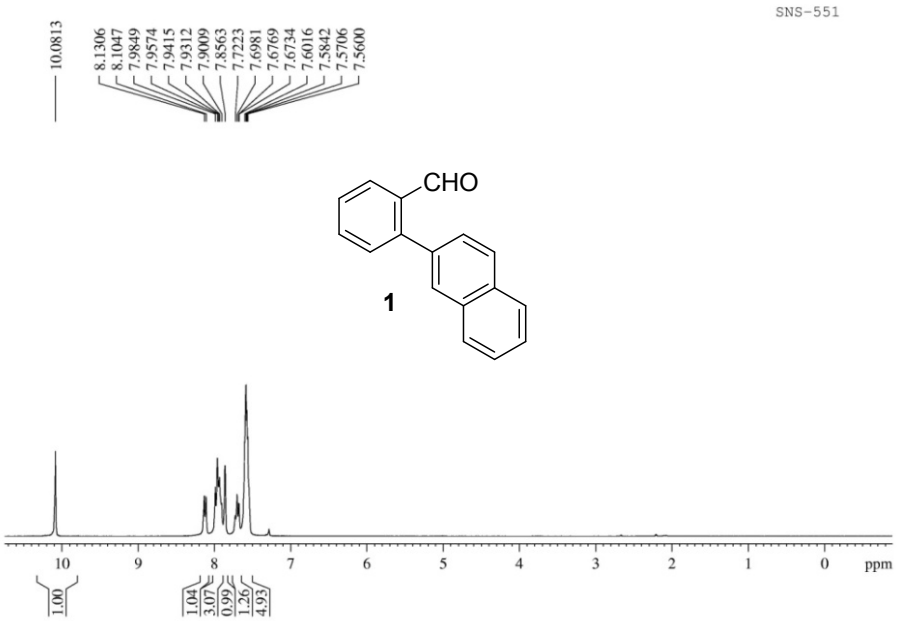

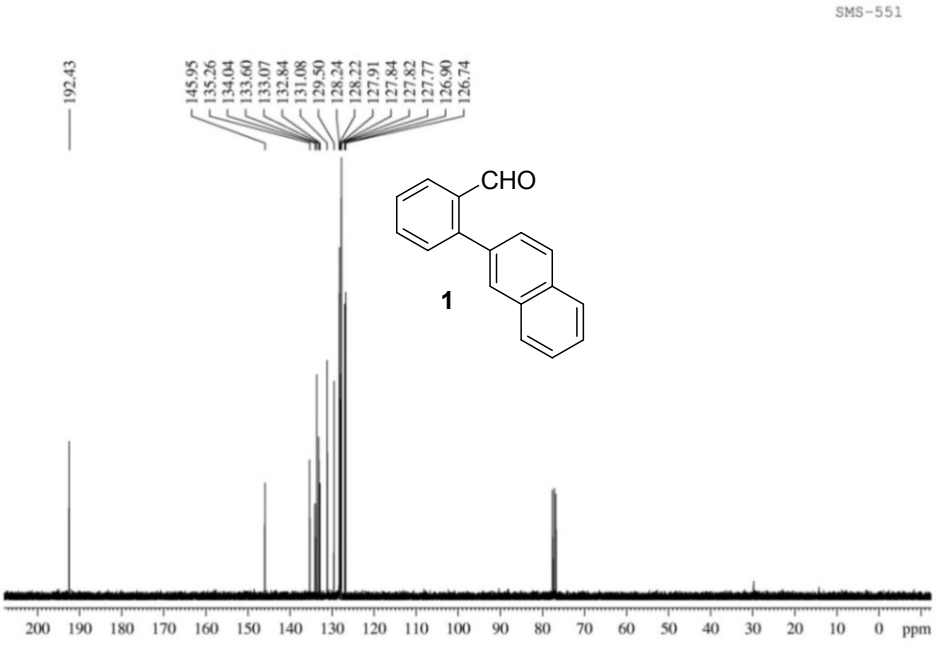

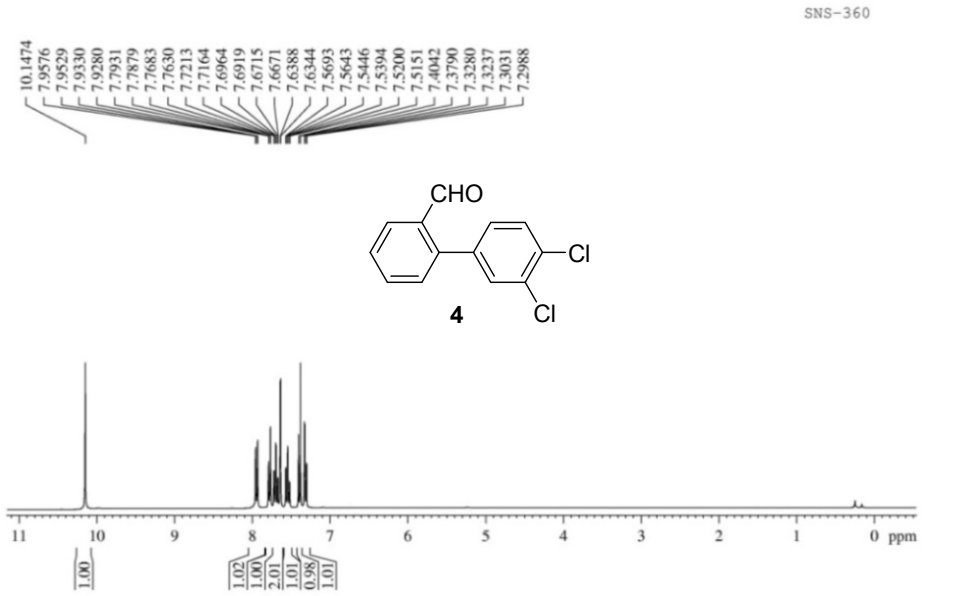
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7.7931
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7.7683
7.7630
7.7213
7.7164
7.6964
7.6919
7.6715
7.6671
7.6388
7.6344
7.5693
7.5643
7.5446
7.5394
7.5200
7.5151
7.4042
7.3790
7.3280
7.3237
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Cl
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11
10
9
8
7
6
5
4
3
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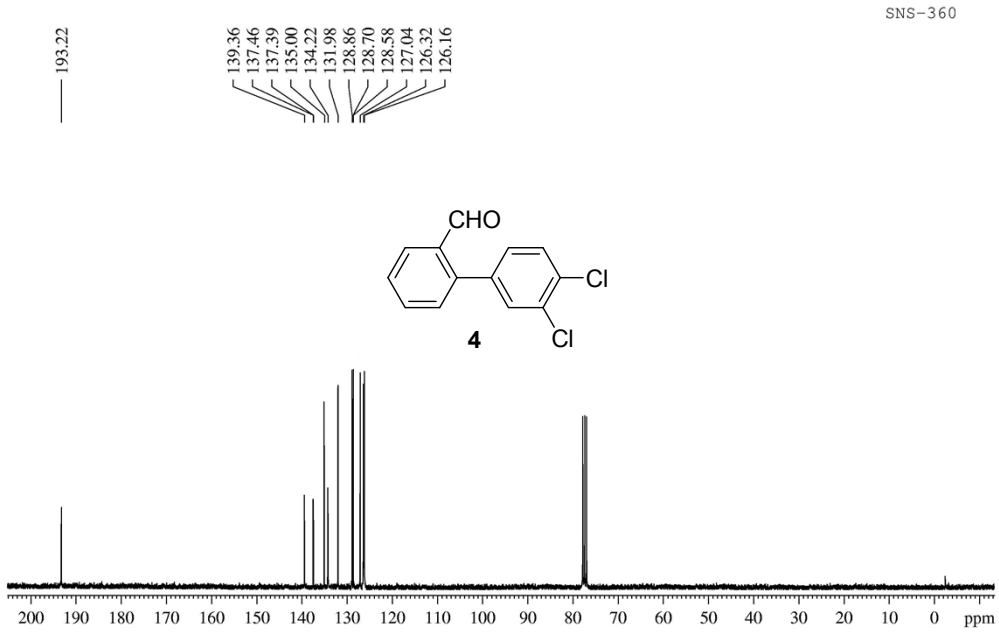
1.00
2.01
1.01
0.98
1.01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126.16
CHO
Cl
Cl
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200
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170
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150
140
130
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110
100
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80
70
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50
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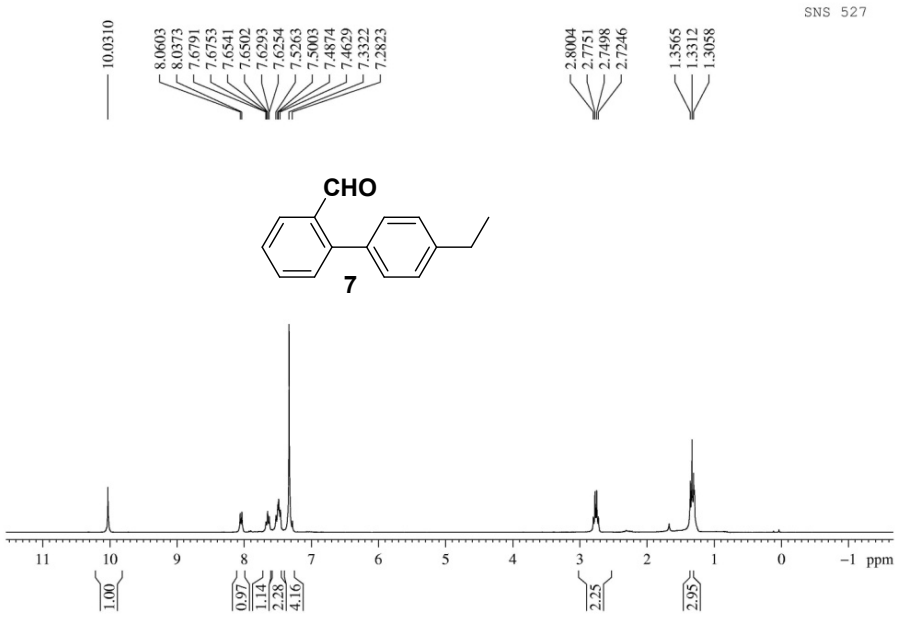
30
20
10
0
ppm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7.6254
7.5263
7.5003
7.4874
7.4629
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7.2823
2.8004
2.7751
2.7498
2.7246
1.3565
1.3312
1.3058
CHO
7
11
10
9
8
7
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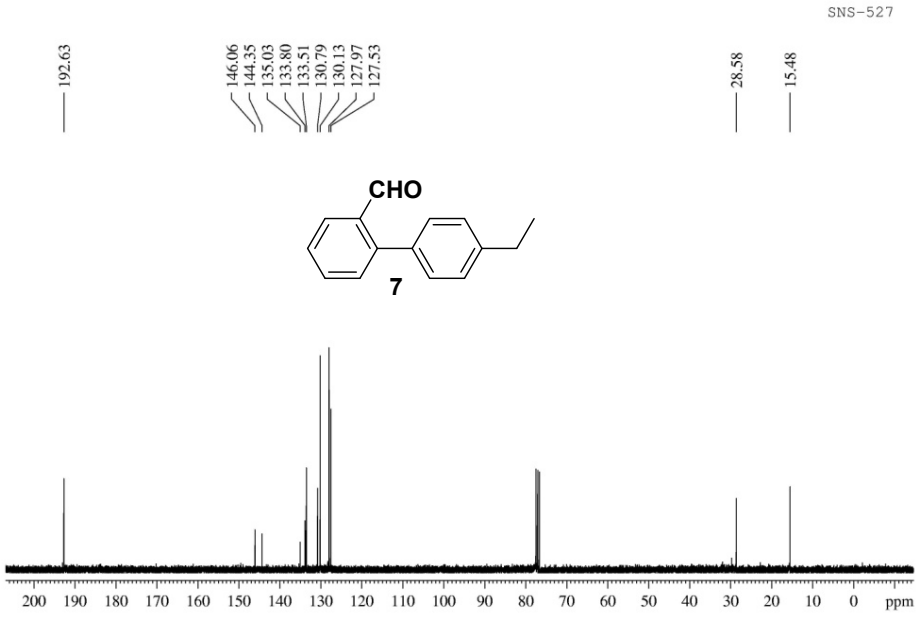
2.95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180
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30
20
10
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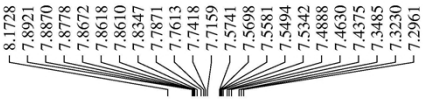
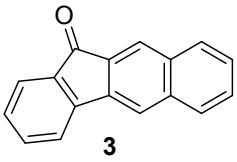
ppm

SNS-551 P





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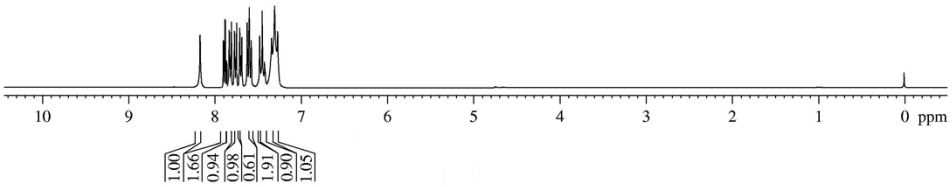

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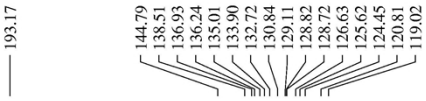

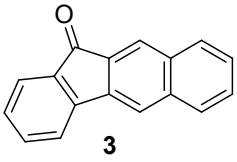

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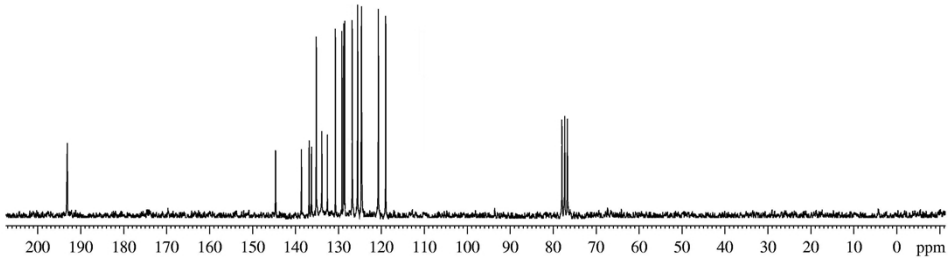

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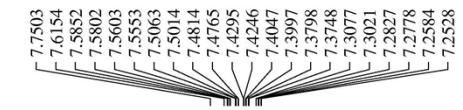

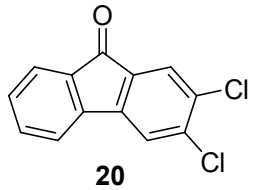

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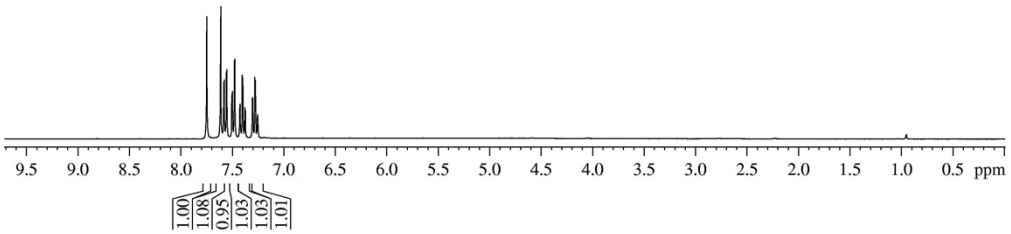

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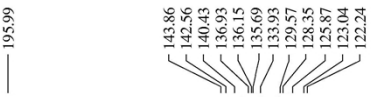

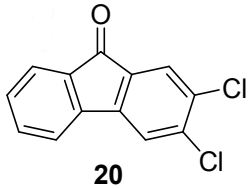

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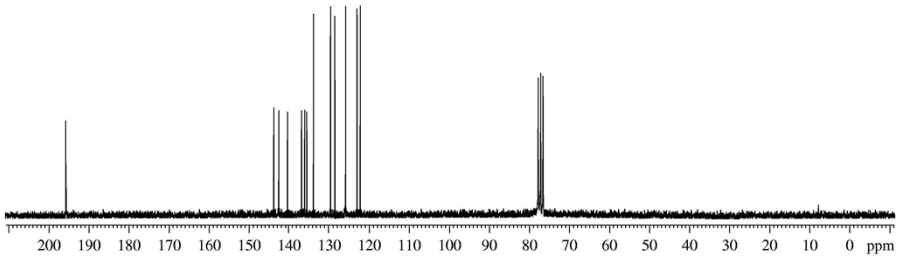

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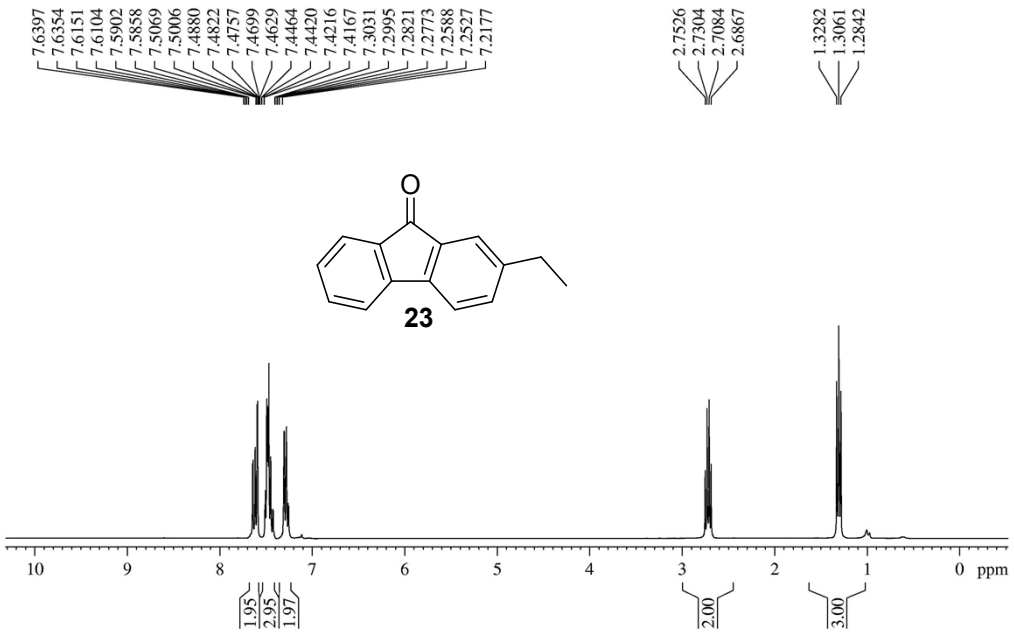

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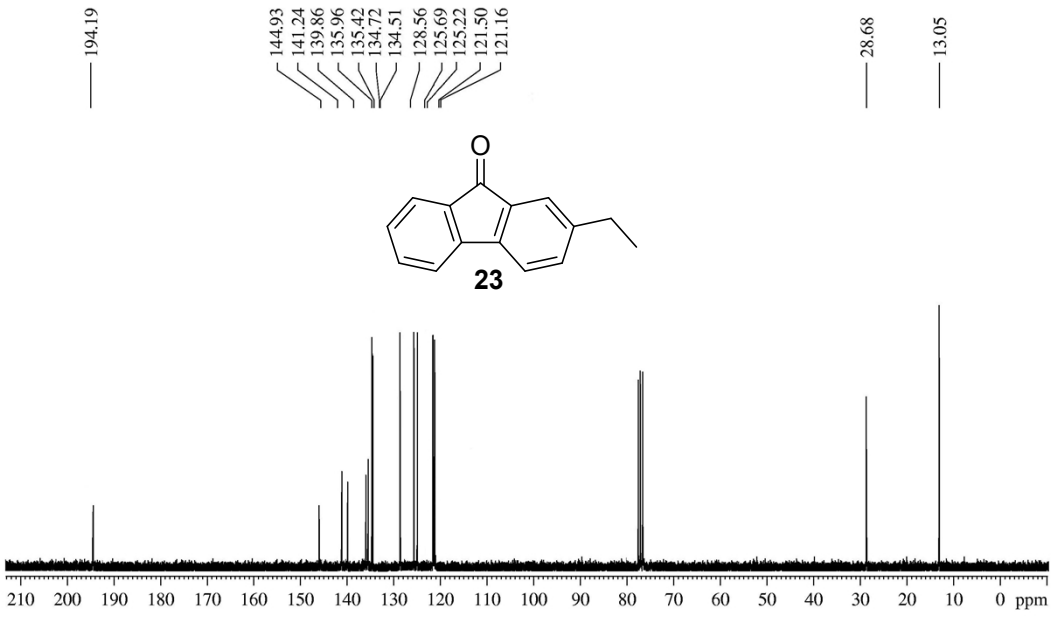

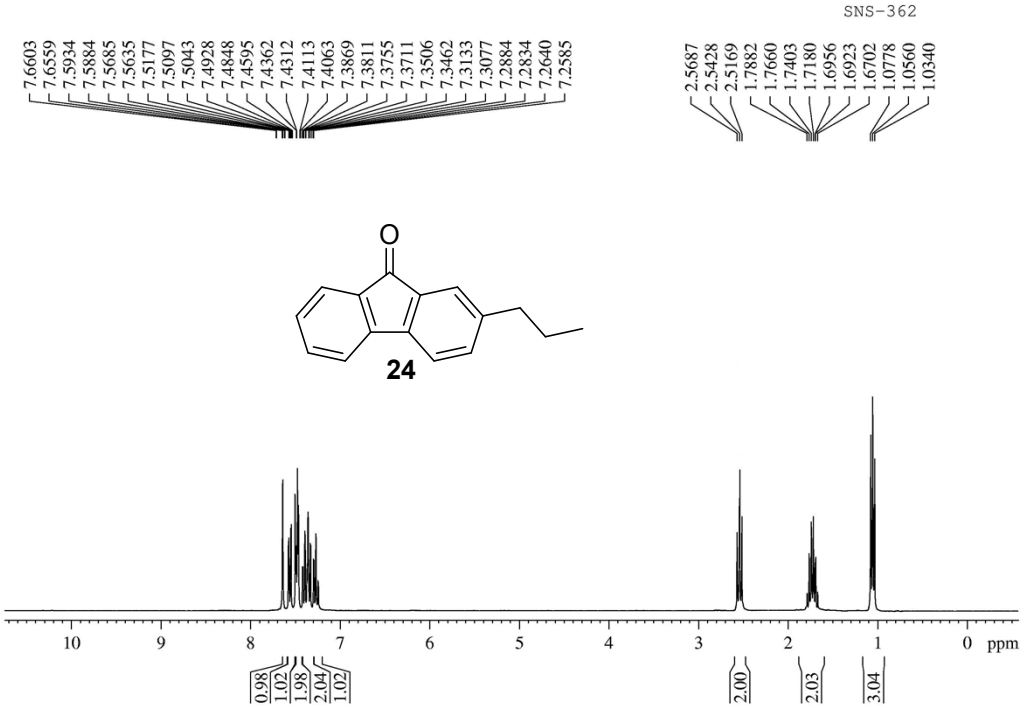
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7.4312
7.4113
7.4063
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1.6923
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8
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6
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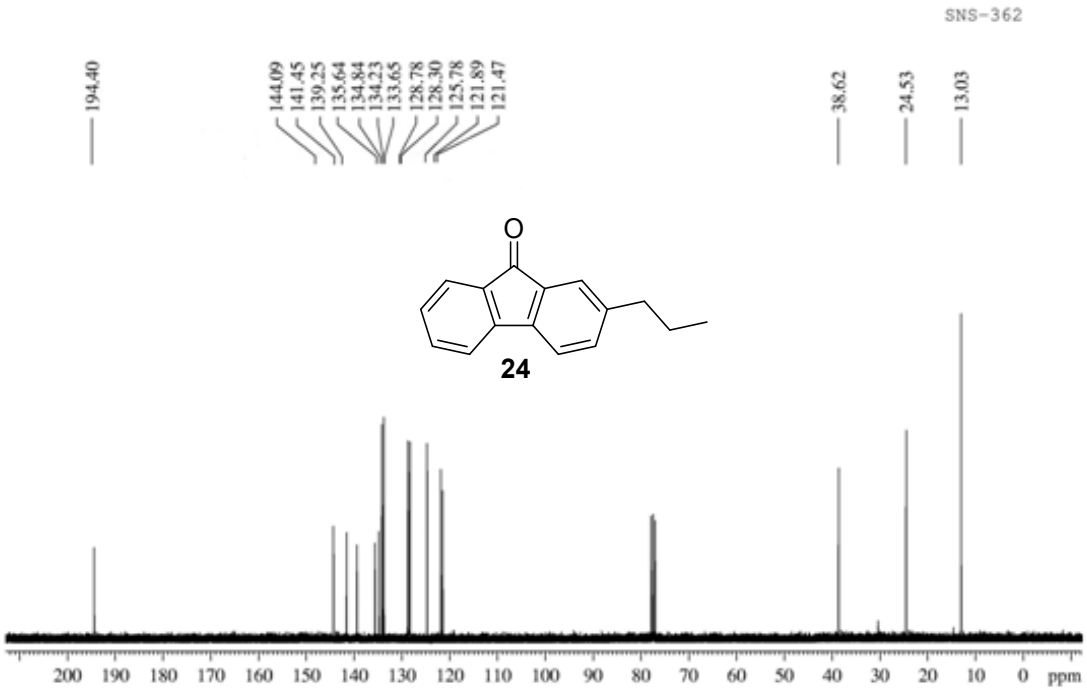
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121.47
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13.03
O
24
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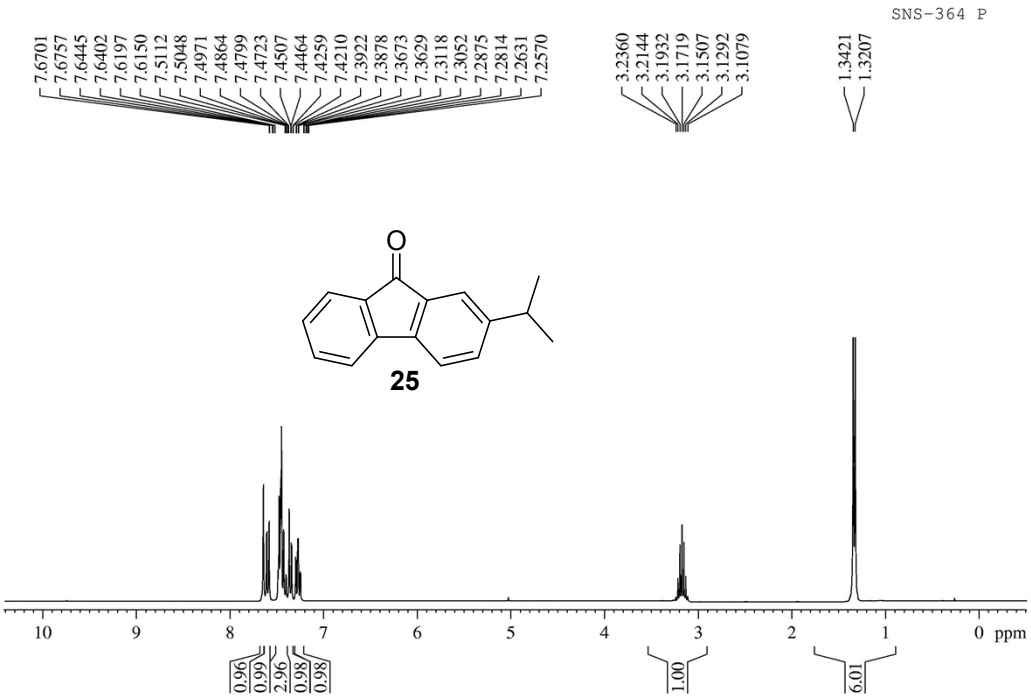
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10
9
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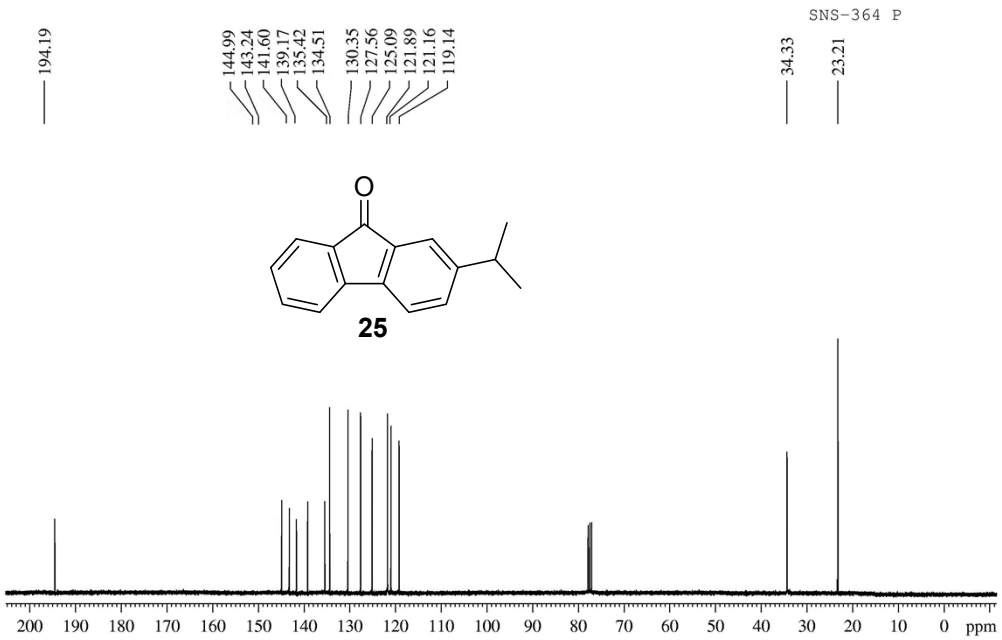
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O
25
200
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10
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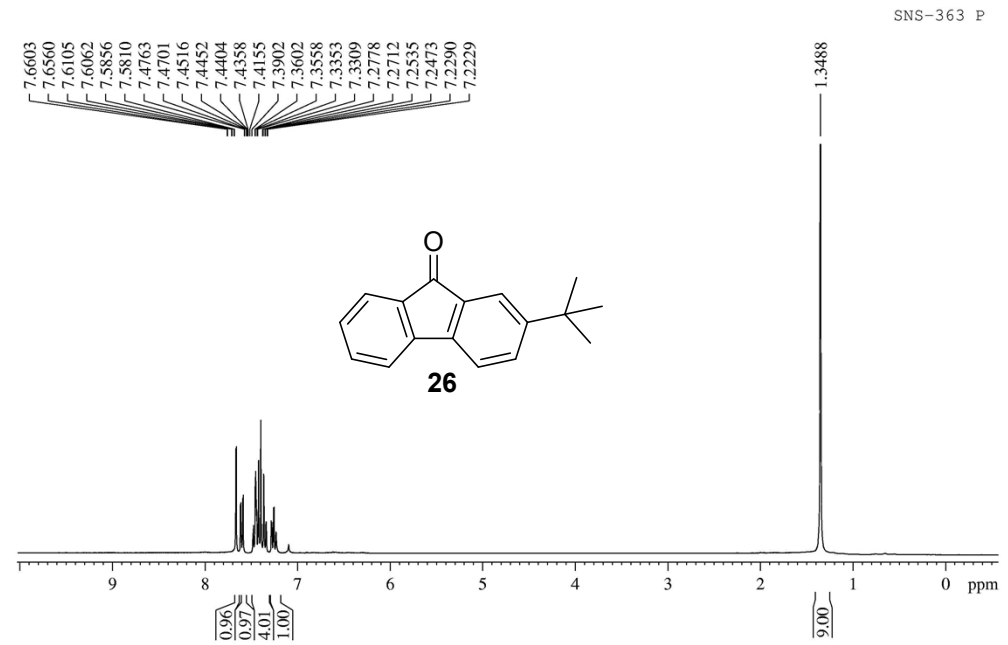
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7.3353
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7.2778
7.2712
7.2535
7.2473
7.2290
7.2229
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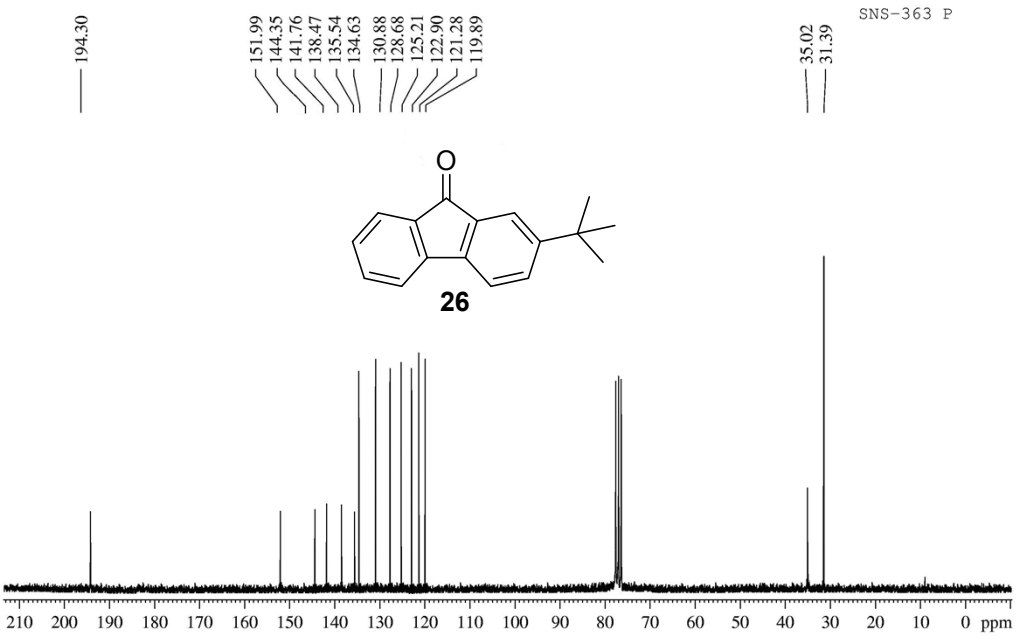
9.00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125.21
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119.89
35.02
31.39
O
26
210
200
190
180
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150
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110
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70
60
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30
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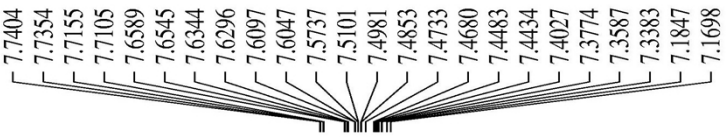
10
0 ppm



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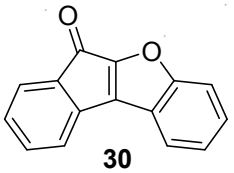

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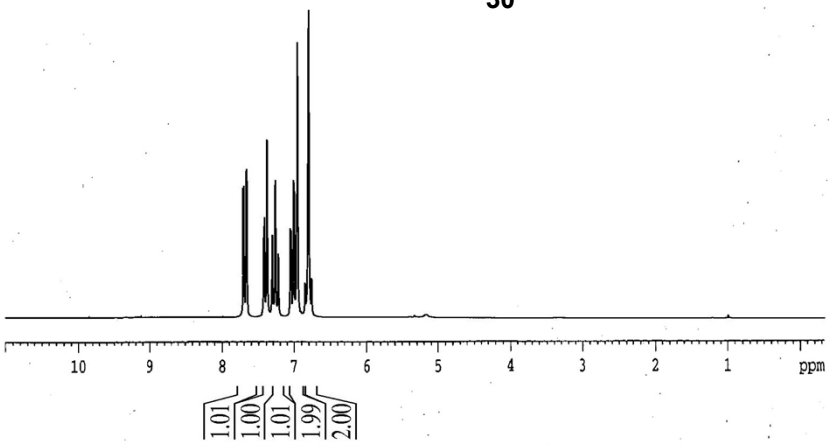
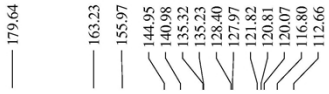
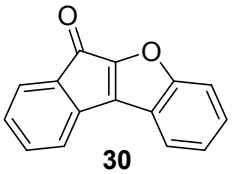




SN-TN-2



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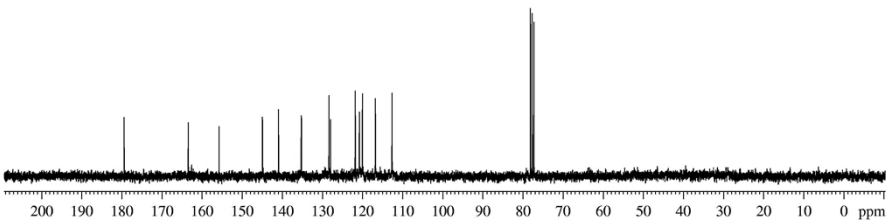
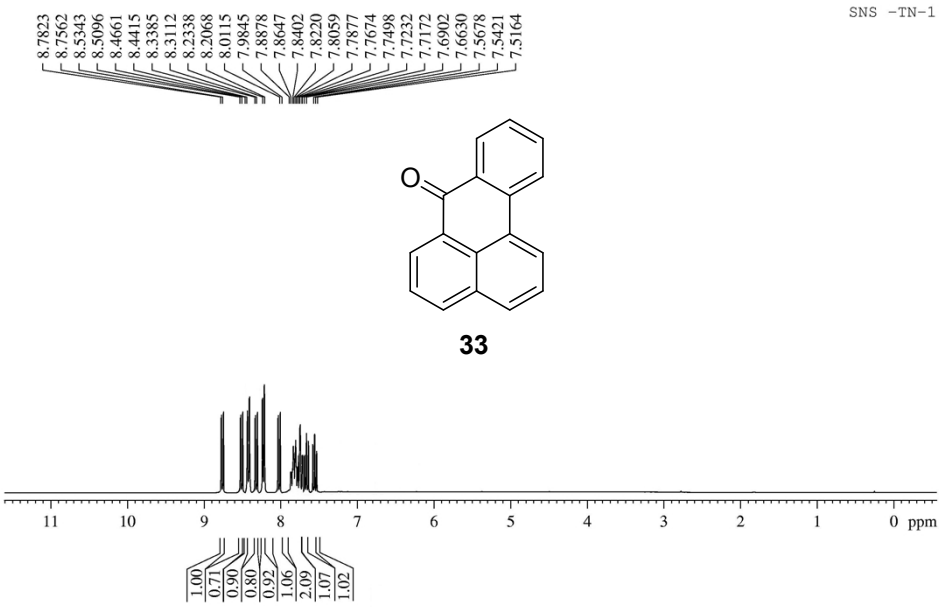
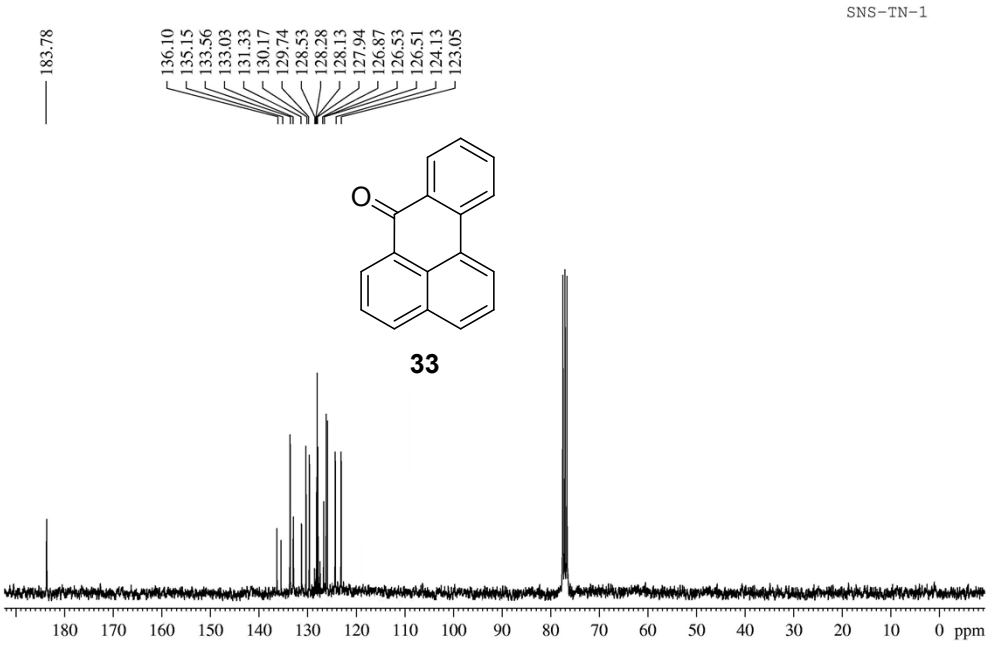
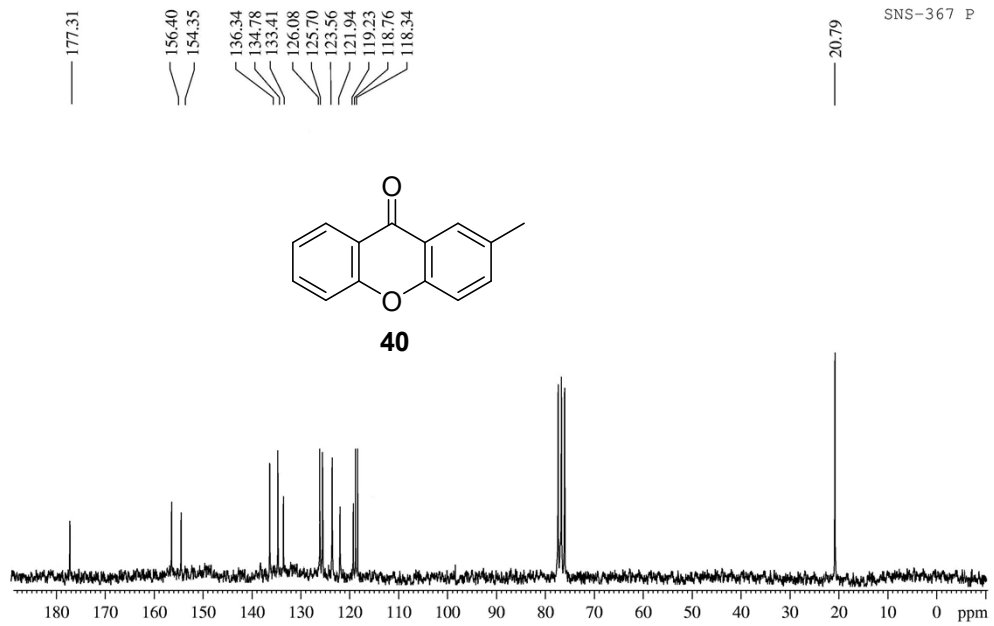



SNS -TN-1
8.7823
8.7562
8.5343
8.5096
8.4661
8.4415
8.3385
8.3112
8.2338
8.2068
8.0115
7.9845
7.8878
7.8647
7.8402
7.8220
7.8059
7.7877
7.7674
7.7498
7.7232
7.7172
7.6902
7.6630
7.5678
7.5421
7.5164
O
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
0.71
0.90
0.80
0.92
1.06
2.09
1.07
1.02

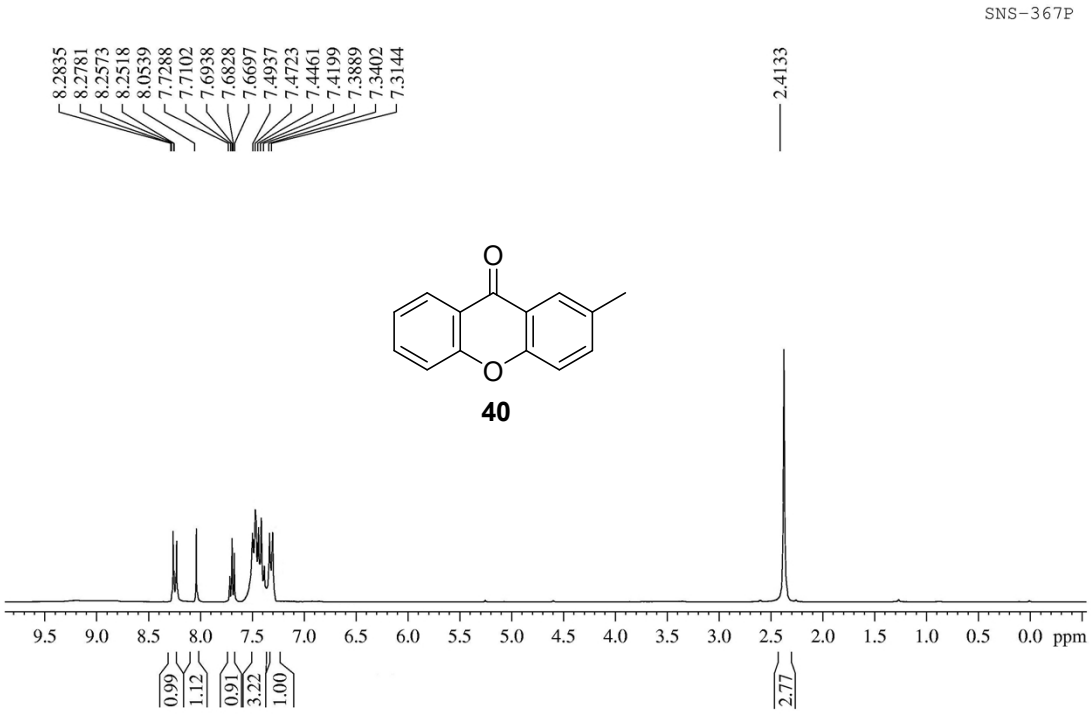
33


SNS-TN-1
183.78
136.10
135.15
133.56
133.03
131.33
130.17
129.74
128.53
128.28
128.13
127.94
126.87
126.53
126.51
124.13
123.05
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

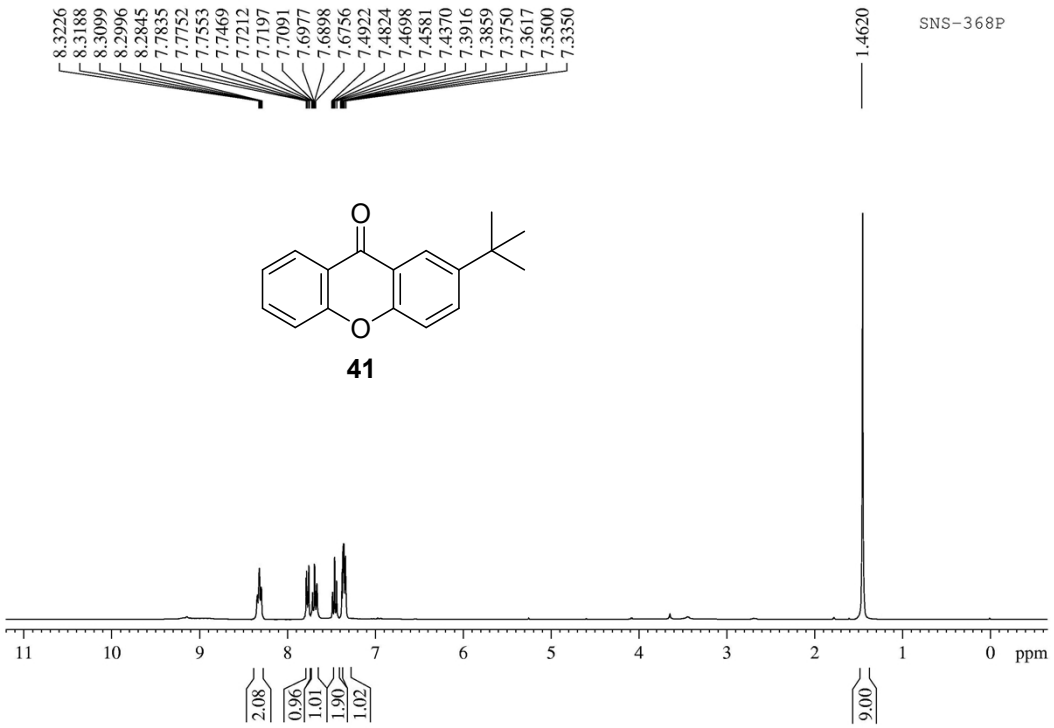
33

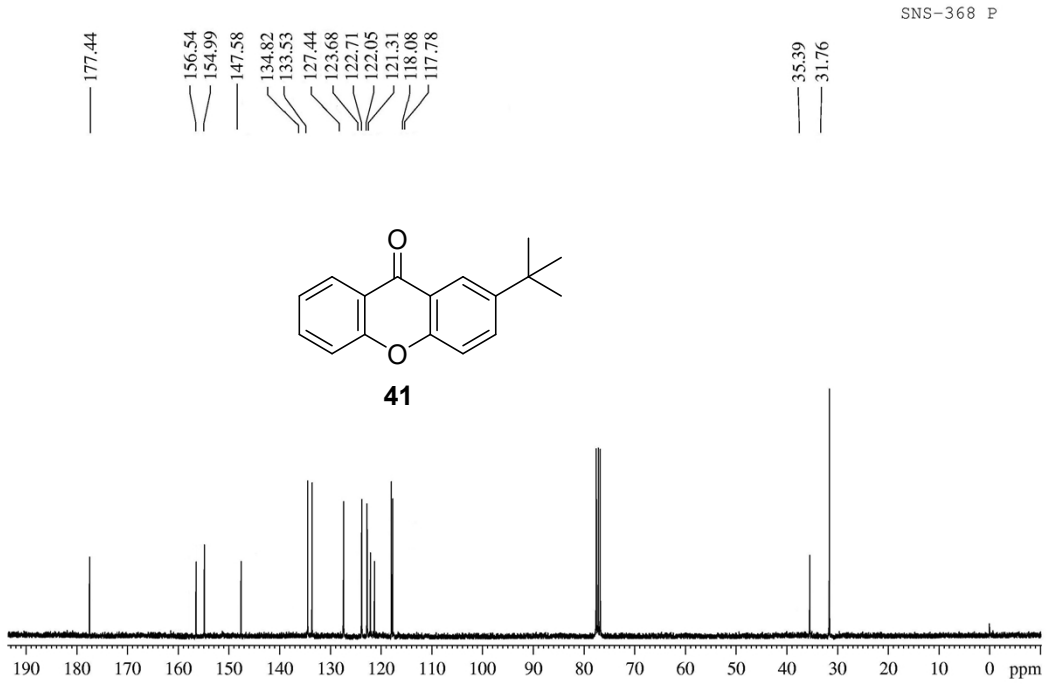

SNS-367 P
177.31
156.40
154.35
136.34
134.78
133.41
126.08
125.70
123.56
121.94
119.23
118.76
118.34
20.79
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

40

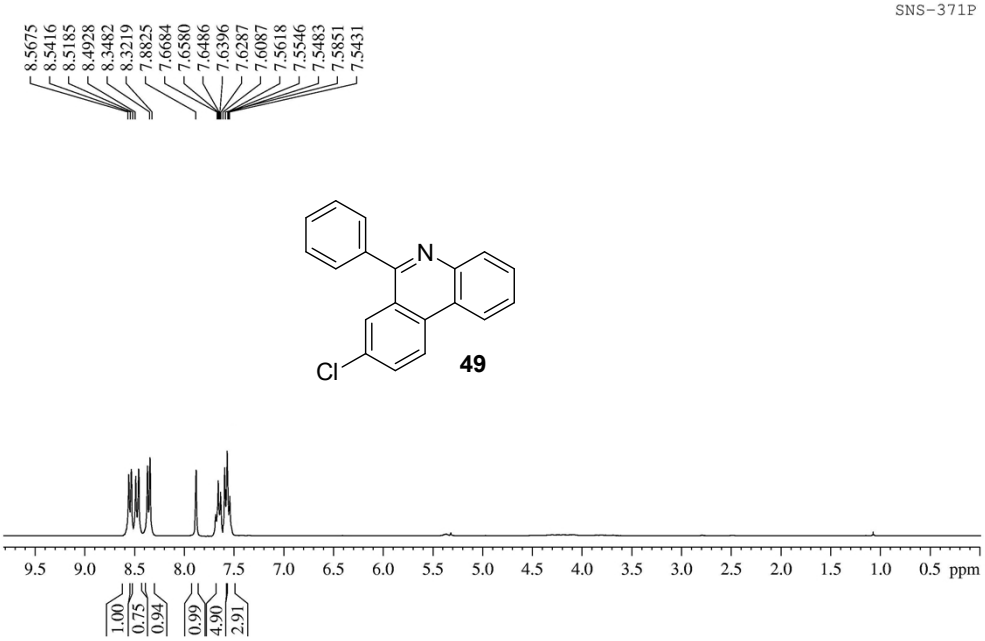

SNS-367P
8.2835
8.2781
8.2573
8.2518
8.0539
7.7288
7.7102
7.6938
7.6828
7.6697
7.4937
7.4723
7.4461
7.4199
7.3889
7.3402
7.3144
2.4133
O
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.99
1.12
0.91
3.22
1.00
2.77

40

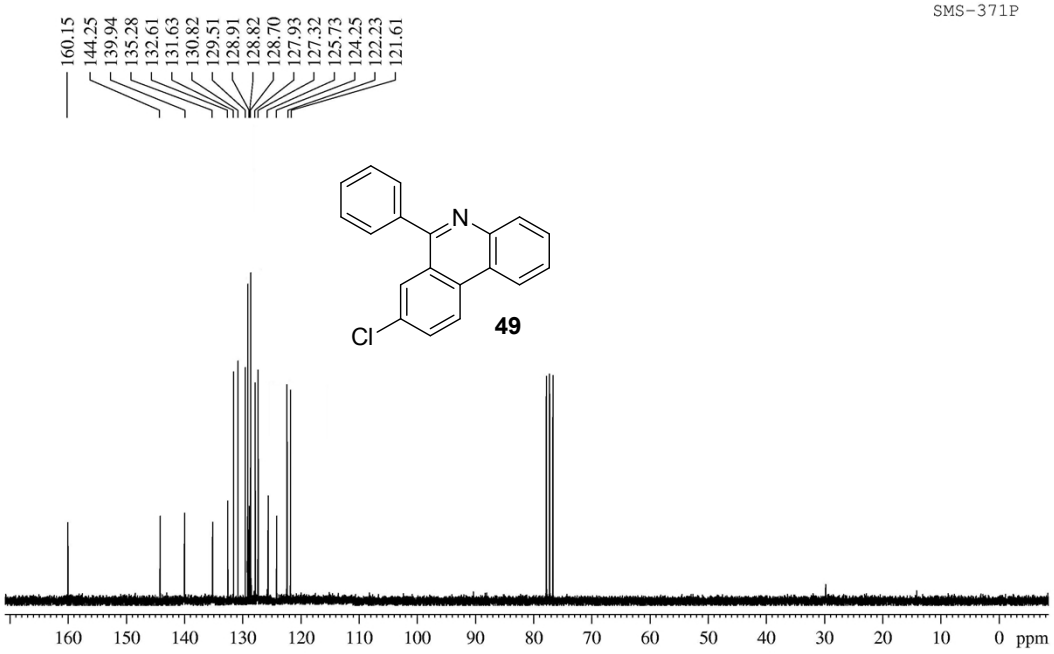

8.3226
8.3188
8.3099
8.2996
8.2845
8.2835
7.7752
7.7553
7.7469
7.7212
7.7197
7.7091
7.6977
7.6898
7.6756
7.4922
7.4824
7.4698
7.4581
7.4370
7.3916
7.3859
7.3750
7.3617
7.3500
7.3350
1.4620
SNS-368P
O
O
41
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.08
0.96
1.01
1.90
1.02
9.00

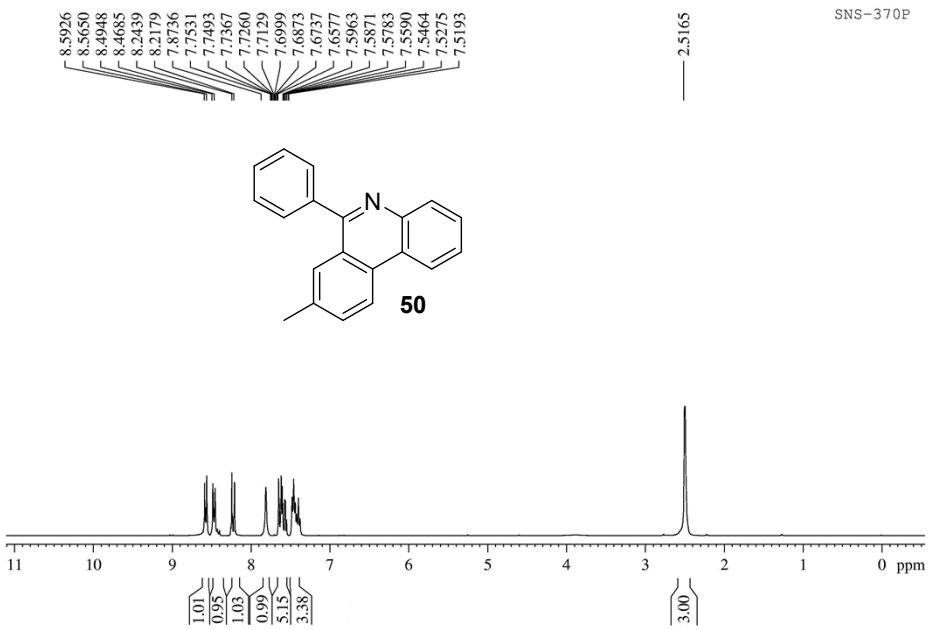

SNS-368 P
177.44
156.54
154.99
147.58
134.82
133.53
127.44
123.68
122.71
122.05
121.31
118.08
117.78
35.39
31.76
O
O
41
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

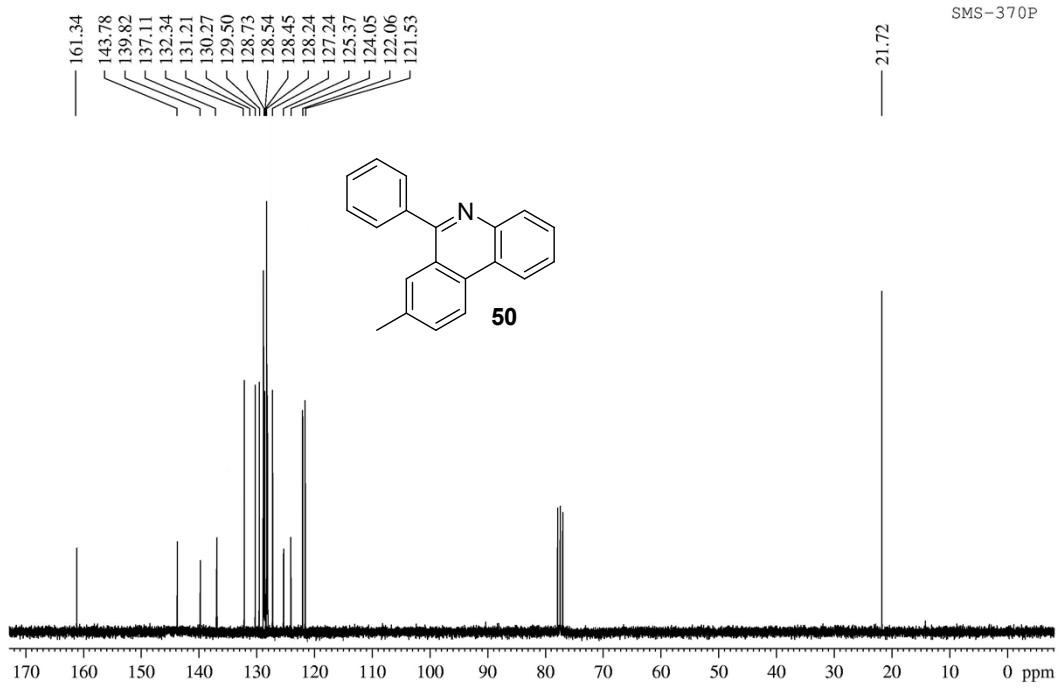
SNS-371P

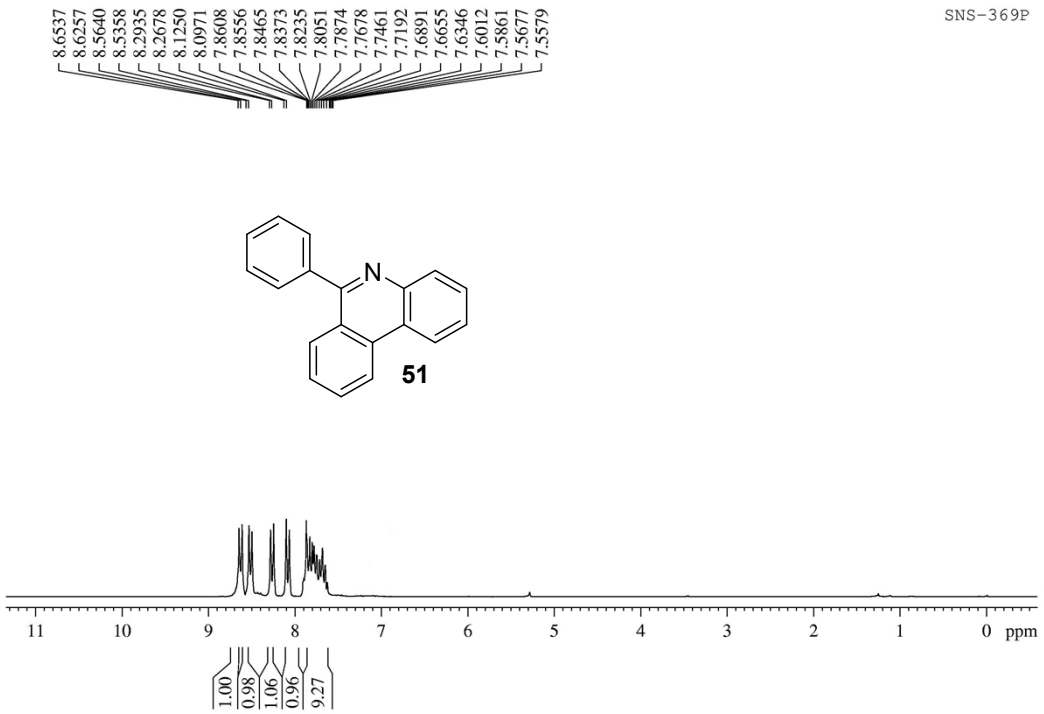


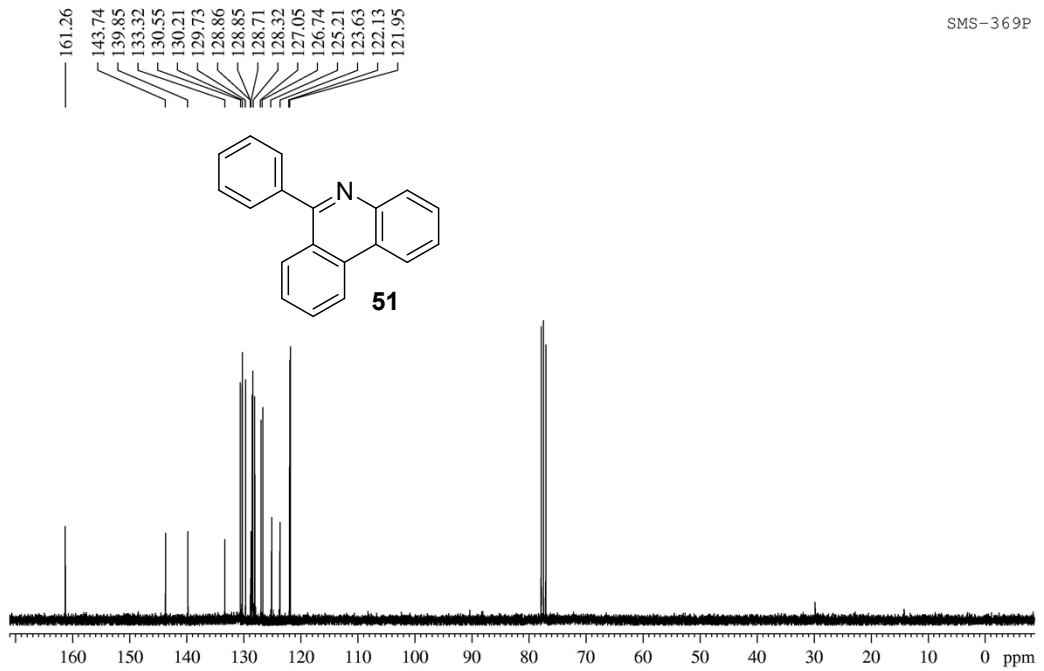
SMS-371P




SNS-370P
8.5926
8.5650
8.4948
8.4685
8.2439
8.2179
7.8736
7.7531
7.7493
7.7367
7.7260
7.7129
7.6999
7.6873
7.6737
7.6577
7.5963
7.5871
7.5783
7.5590
7.5464
7.5275
7.5193
2.5165
N
50
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.01
0.95
1.03
0.99
5.15
3.38
3.00


SMS-370P
161.34
143.78
139.82
137.11
132.34
131.21
130.27
129.50
128.73
128.54
128.45
128.24
127.24
125.37
124.05
122.06
121.53
21.72
N
50
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


SNS-369P
8.6537
8.6257
8.5640
8.5358
8.2935
8.2678
8.1250
8.0971
7.8608
7.8556
7.8465
7.8373
7.8235
7.8051
7.7874
7.7678
7.7461
7.7192
7.6891
7.6655
7.6346
7.6012
7.5861
7.5677
7.5579
N
51
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
0.98
1.06
0.96
9.27


SMS-369P
161.26
143.74
139.85
133.32
130.55
130.21
129.73
128.86
128.85
128.71
128.32
127.05
126.74
125.21
123.63
122.13
121.95
N
51
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm