Supporting Information

Redox-neutral rhodium(III)-catalyzed [4+1] annulation of *N*-aryl phthalazinediones with alkynes

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General Information

If not otherwise specified, the reagents were obtained from commercial sources and used directly without purification. Heating source: all the reactions that require heating were carried out in an oil bath. Analytical thin-layer chromatography (TLC): HSGF 254 (0.15-0.2 mm thickness). Detection under UV light at 254 nm. Column chromatography: separations were carried out on silica gel FCP 200-300. Yields refer to isolated yields. Melting point apparatus: a micro melting point apparatus, values are uncorrected. Nuclear magnetic resonance (NMR) apparatus: a Brucker 400, 500 or 600 MHz instrument. Chemical shifts (δ) are given in ppm. Proton coupling patterns were recorded as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). HRMS (high-resolution mass) were measured on a Thermo Scientific LTQ Orbitrap Discovery (Bremen, Germany). The linear ion trap (LTQ) part of the hybrid MS system was equipped with electrospray ionization (ESI) probe and operated in both positive and negative ion modes.

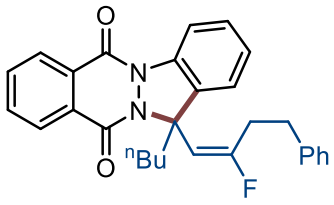
Preparation of the Starting Materials

All the 2-phenyl-2,3-dihydrophthalazine-1,4-diones substrates were prepared according to the literature procedure and their characterization data were in accordance with the published ones.[1,2] All the α,α-difluoromethylene alkyne substrates were prepared according to the literature procedure and their characterization data were in accordance with the published ones.[3,4]

General Procedure for the Rh(III)-Catalyzed [4+1] Annulation

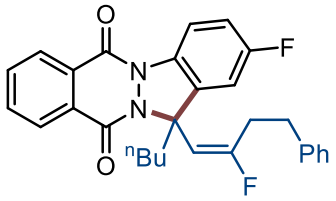
To a mixture of 2-arylphthalazine-1,4-diones **1** (0.25 mmol), $[Cp^*RhCl_2]_2$ (5 mol%) and KF (0.25 mmol) in a 25 mL Schlenk tube was added a solution of alkynes **2** (0.325 mmol) in MeOH (4.0 mL). Then the tube was capped with septa, and the resulting mixture was stirred at appropriate temperature for appropriate time indicated in Scheme 2. After removal of the solvent, the residue was purified by flash chromatography on silica gel to provide the desired products **3**.

Characterization Data of Products 3

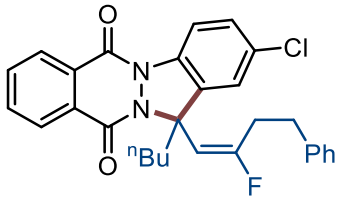


(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3a): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 15:1) on silica gel to provide the product as a colorless viscous oil (95.5 mg, yield 84%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.47 (d, *J* = 8.1 Hz, 1H), 8.42-8.39 (m, 1H), 8.33-8.28 (m, 1H), 7.88-7.83 (m, 2H), 7.52-7.47 (m, 1H), 7.33-7.30 (m, 1H), 7.21-7.19 (m, 1H), 6.98-6.92 (m, 2H), 6.80-6.74 (m, 1H), 6.66 (d, *J* = 7.0 Hz, 2H), 5.99 (d, *J* = 22.4 Hz, 1H), 2.99-2.93 (m, 1H), 2.49-2.43 (m, 1H), 2.30-2.25 (m, 1H), 1.99-1.94 (m, 1H), 1.92-1.83 (m, 1H), 1.79-1.69 (m, 1H), 1.24-1.09 (m, 2H), 0.97-0.90 (m,

1H), 0.88-0.82 (m, 1H), 0.70 (t, J = 7.3 Hz, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 163.3 (d, $J_{C\text{-}F}$ = 255.6 Hz), 154.7, 154.0, 140.0, 136.1, 133.7, 133.4, 131.2, 129.71, 129.70, 129.2, 128.3, 128.1, 127.7, 127.6, 126.9, 126.0, 122.5, 115.9, 111.3 (d, $J_{C\text{-}F}$ = 29.1 Hz), 70.9 (d, $J_{C\text{-}F}$ = 14.7 Hz), 39.6, 31.8 (d, $J_{C\text{-}F}$ = 26.7 Hz), 31.3, 25.1, 22.2, 13.9; **^{19}F NMR (565 MHz, CDCl$_3$)** δ -95.9; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{29}H_{28}FN_2O_2^+$ 455.2129; Found 455.2136.

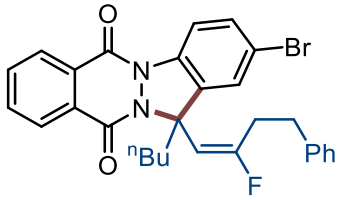


(*E*)-13-butyl-2-fluoro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3b): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 15:1) on silica gel to provide the product as a light yellow viscous oil (68.2 mg, yield 57%). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.44 (dd, J = 8.9, 4.5 Hz, 1H), 8.41-8.38 (m, 1H), 8.32-8.26 (m, 1H), 7.89-7.84 (m, 2H), 7.19-7.16 (m, 1H), 6.98-6.94 (m, 2H), 6.85 (dd, J = 7.5, 2.6 Hz, 1H), 6.80-6.76 (m, 1H), 6.69 (d, J = 7.3 Hz, 2H), 5.93 (d, J = 22.0 Hz, 1H), 3.00-2.93 (m, 1H), 2.52-2.47 (m, 1H), 2.39-2.34 (m, 1H), 1.97-1.88 (m, 2H), 1.85-1.75 (m, 1H), 1.23-1.12 (m, 2H), 0.95-0.88 (m, 1H), 0.72-0.65 (m, 4H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 163.3 (d, $J_{C\text{-}F}$ = 256.5 Hz), 161.1 (d, $J_{C\text{-}F}$ = 247.6 Hz), 154.5, 154.0, 139.8, 133.8, 133.6, 133.3 (d, $J_{C\text{-}F}$ = 8.4 Hz), 132.3 (d, $J_{C\text{-}F}$ = 2.2 Hz), 129.6, 129.0, 128.3, 128.0, 127.8, 127.5, 126.1, 117.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 116.7 (d, $J_{C\text{-}F}$ = 23.5 Hz), 111.0 (d, $J_{C\text{-}F}$ = 29.7 Hz), 109.9 (d, $J_{C\text{-}F}$ = 25.4 Hz), 70.7 (dd, $J_{C\text{-}F}$ = 14.8, 2.4 Hz), 39.5, 31.9 (d, $J_{C\text{-}F}$ = 26.8 Hz), 31.2, 25.0, 22.2, 13.9; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -95.4, -113.2; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{29}H_{27}F_2N_2O_2^+$ 473.2035; Found 473.2035.

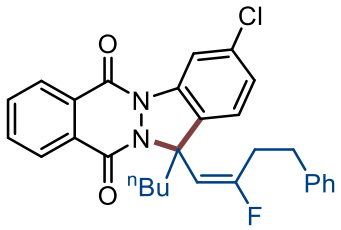


(*E*)-13-butyl-2-chloro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3c): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 15:1) on silica gel to provide the product as a light yellow viscous oil (55.0 mg, yield 45%). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.41-8.37 (m, 2H), 8.31-8.28 (m, 1H), 7.89-7.84 (m, 2H), 7.48-7.41 (m, 1H), 7.18-7.16 (m, 1H), 6.98-6.94 (m, 2H), 6.80-6.76 (m, 1H), 6.69 (d, J = 7.7 Hz, 2H), 5.93 (d, J = 22.1 Hz, 1H), 2.99-2.93 (m, 1H), 2.54-2.48 (m, 1H), 2.38-2.32 (m, 1H), 1.96-1.88 (m, 2H), 1.84-1.74 (m, 1H), 1.24-1.13 (m, 2H), 0.96-0.89 (m, 1H), 0.75-0.68 (m, 4H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 163.4 (d, $J_{C\text{-}F}$ = 256.5 Hz), 154.7, 153.9, 139.8, 134.6, 133.9, 133.6, 133.1, 132.2, 129.9, 129.5, 129.1, 128.3, 128.0, 127.8, 127.6, 126.2, 122.7, 116.9, 111.0 (d, $J_{C\text{-}F}$ = 29.7 Hz), 70.7 (d, $J_{C\text{-}F}$ = 14.8 Hz), 39.6, 32.0 (d, $J_{C\text{-}F}$ = 26.9 Hz), 31.3, 25.1, 22.2, 13.9; **^{19}F NMR**

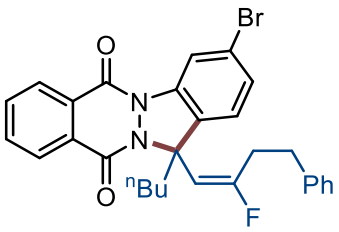
(565 MHz, $CDCl_3$) δ -95.3; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{29}H_{27}ClFN_2O_2^+$ 489.1740; Found 489.1746.



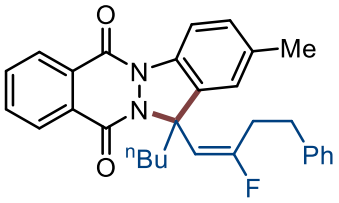
(*E*)-2-bromo-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3d): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 15:1) on silica gel to provide the product as a light yellow viscous oil (78.7 mg, yield 59%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.41-8.37 (m, 1H), 8.33 (d, *J* = 8.6 Hz, 1H), 8.31-8.27 (m, 1H), 7.90-7.84 (m, 2H), 7.60 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.00-6.92 (m, 2H), 6.81-6.75 (m, 1H), 6.69 (d, *J* = 7.3 Hz, 2H), 5.93 (d, *J* = 22.1 Hz, 1H), 3.05-2.86 (m, 1H), 2.58-2.43 (m, 1H), 2.39-2.30 (m, 1H), 1.98-1.88 (m, 2H), 1.84-1.73 (m, 1H), 1.24-1.14 (m, 2H), 0.95-0.86 (m, 1H), 0.75-0.68 (m, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.4 (d, $J_{C\text{-}F}$ = 256.8 Hz), 154.7, 153.8, 139.8, 135.1, 133.9, 133.6, 133.4, 132.8, 129.5, 129.2, 128.3, 128.0, 127.8, 127.6, 126.2, 125.6, 119.6, 117.2, 111.0 (d, $J_{C\text{-}F}$ = 29.5 Hz), 70.6 (d, $J_{C\text{-}F}$ = 14.6 Hz), 39.6, 32.0 (d, $J_{C\text{-}F}$ = 26.6 Hz), 31.3, 25.1, 22.2, 14.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -95.2; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{29}H_{27}BrFN_2O_2^+$ 533.1234; Found 533.1243.



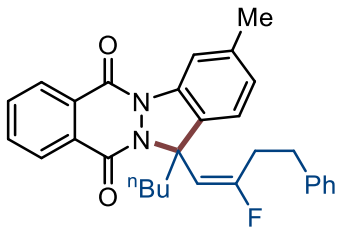
(*E*)-13-butyl-3-chloro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3e): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 12:1) on silica gel to provide the product as a light yellow viscous oil (69.7 mg, yield 57%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (d, *J* = 1.9 Hz, 1H), 8.42-8.36 (m, 1H), 8.33-8.25 (m, 1H), 7.89-7.85 (m, 2H), 7.25 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 7.02-6.91 (m, 2H), 6.82-6.74 (m, 1H), 6.69 (d, *J* = 7.5 Hz, 2H), 5.95 (d, *J* = 22.2 Hz, 1H), 2.96-2.90 (m, 1H), 2.52-2.46 (m, 1H), 2.38-2.33 (m, 1H), 1.95-1.90 (m, 1H), 1.90-1.76 (m, 2H), 1.24-1.10 (m, 2H), 0.96-0.87 (m, 1H), 0.74-0.66 (m, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.3 (d, $J_{C\text{-}F}$ = 256.4 Hz), 154.9, 153.9, 139.8, 136.8, 135.4, 134.0, 133.6, 129.6, 129.4, 129.2, 128.4, 128.1, 127.8, 127.7, 127.0, 126.1, 123.3, 116.1, 111.2 (d, $J_{C\text{-}F}$ = 29.3 Hz), 70.8 (d, $J_{C\text{-}F}$ = 14.8 Hz), 39.6, 32.0 (d, $J_{C\text{-}F}$ = 26.7 Hz), 31.2, 25.0, 22.2, 13.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.7; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{29}H_{27}ClFN_2O_2^+$ 489.1740; Found 489.1741.



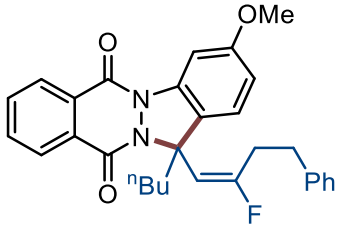
(*E*)-3-bromo-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3f): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 12:1) on silica gel to provide the product as a light yellow viscous oil (66.7 mg, yield 50%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.65 (d, *J* = 1.8 Hz, 1H), 8.41-8.36 (m, 1H), 8.32-8.26 (m, 1H), 7.89-7.85 (m, 2H), 7.40 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.03-6.96 (m, 3H), 6.82-6.76 (m, 1H), 6.72-6.66 (m, 2H), 5.94 (d, *J* = 22.2 Hz, 1H), 2.97-2.89 (m, 1H), 2.53-2.46 (m, 1H), 2.38-2.32 (m, 1H), 1.95-1.77 (m, 3H), 1.23-1.11 (m, 2H), 0.96-0.89 (m, 1H), 0.74-0.66 (m, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.3 (d, $J_{C\text{-}F}$ = 256.4 Hz), 154.9, 153.9, 139.8, 137.0, 134.0, 133.6, 130.2, 129.9, 129.4, 129.2, 128.4, 128.1, 127.8, 127.7, 126.1, 123.6, 123.2, 118.8, 111.1 (d, $J_{C\text{-}F}$ = 29.5 Hz), 70.8 (d, $J_{C\text{-}F}$ = 14.8 Hz), 39.5, 32.0 (d, $J_{C\text{-}F}$ = 26.8 Hz), 31.2, 25.0, 22.2, 13.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.7; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{29}H_{27}BrFN_2O_2^+$ 533.1234; Found 533.1229.



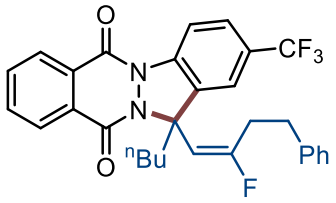
(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-2-methyl-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3h): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 20:1) on silica gel to provide the product as a light yellow viscous oil (91.4 mg, yield 78%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.42-8.38 (m, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.32-8.28 (m, 1H), 7.87-7.82 (m, 2H), 7.29 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.02 (s, 1H), 6.99-6.93 (m, 2H), 6.83-6.73 (m, 1H), 6.67 (d, *J* = 7.1 Hz, 2H), 5.96 (d, *J* = 22.3 Hz, 1H), 3.00-2.94 (m, 1H), 2.49-2.43 (m, 1H), 2.42 (s, 3H), 2.31-2.25 (m, 1H), 1.97-1.91 (m, 1H), 1.90-1.83 (m, 1H), 1.81-1.71 (m, 1H), 1.24-1.10 (m, 2H), 0.96-0.87 (m, 1H), 0.74-0.67 (m, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.2 (d, $J_{C\text{-}F}$ = 255.6 Hz), 154.4, 154.0, 140.0, 137.0, 134.0, 133.5, 133.4, 131.4, 130.4, 129.8, 129.1, 128.3, 128.0, 127.6, 127.5, 126.0, 122.8, 115.7, 111.3 (d, $J_{C\text{-}F}$ = 29.0 Hz), 70.9 (d, $J_{C\text{-}F}$ = 14.8 Hz), 39.6, 31.8 (d, $J_{C\text{-}F}$ = 26.6 Hz), 31.4, 25.1, 22.2, 21.5, 13.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -96.0; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{30}H_{30}FN_2O_2^+$ 469.2286; Found 469.2294.



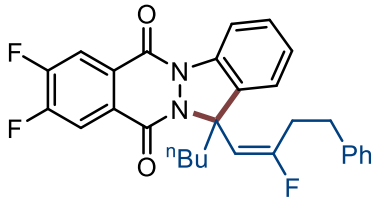
(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-3methyl-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3i): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 20:1) on silica gel to provide the product as a light yellow viscous oil (83.2 mg, yield 71%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.41-8.38 (m, 1H), 8.33-8.27 (m, 2H), 7.87-7.83 (m, 2H), 7.12 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.99-6.94 (m, 2H), 6.80-6.76 (m, 1H), 6.66 (d, *J* = 7.0 Hz, 2H), 5.98 (d, *J* = 22.4 Hz, 1H), 2.97-2.90 (m, 1H), 2.49 (s, 3H), 2.48-2.44 (m, 1H), 2.31-2.26 (m, 1H), 1.98-1.93 (m, 1H), 1.90-1.72 (m, 2H), 1.23-1.09 (m, 2H), 0.96-0.88 (m, 1H), 0.75-0.71 (m, 1H), 0.70 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.2 (d, J_{C-F} = 255.6 Hz), 154.7, 154.0, 140.1, 140.0, 136.3, 133.6, 133.4, 129.7, 129.2, 128.4, 128.2, 128.1, 127.7, 127.6, 127.5, 126.0, 122.1, 116.3, 111.4 (d, J_{C-F} = 28.9 Hz), 70.8 (d, J_{C-F} = 14.8 Hz), 39.6, 31.8 (d, J_{C-F} = 26.5 Hz), 31.4, 25.1, 22.2, 21.9, 13.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -96.1; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{30}H_{30}FN_2O_2^+$ 469.2286; Found 469.2292.



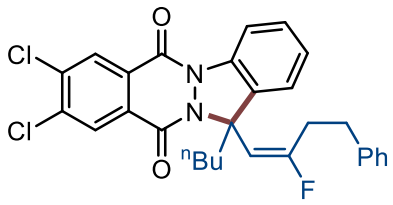
(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-3-methoxy-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3j): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1) on silica gel to provide the product as a light yellow viscous oil (88.4 mg, yield 73%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.40-8.37 (m, 1H), 8.32-8.27 (m, 1H), 8.09 (d, *J* = 2.4 Hz, 1H), 7.87-7.83 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.97-6.94 (m, 2H), 6.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.78-6.73 (m, 1H), 6.70 (d, *J* = 7.3 Hz, 2H), 5.97 (d, *J* = 22.6 Hz, 1H), 3.92 (s, 3H), 2.95-2.89 (m, 1H), 2.51-2.45 (m, 1H), 2.32 (ddd, *J* = 13.8, 8.7, 5.6 Hz, 1H), 1.96-1.91 (m, 1H), 1.90-1.73 (m, 2H), 1.23-1.11 (m, 2H), 0.96-0.89 (m, 1H), 0.77-0.72 (m, 1H), 0.70 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.2 (d, J_{C-F} = 255.4 Hz), 160.8, 154.8, 153.9, 140.0, 137.2, 133.7, 133.4, 129.6, 129.2, 128.2, 128.1, 127.7, 127.5, 126.0, 122.9, 122.8, 114.1, 111.4 (d, J_{C-F} = 28.5 Hz), 100.8, 70.7 (d, J_{C-F} = 14.9 Hz), 55.9, 39.6, 31.8 (d, J_{C-F} = 26.6 Hz), 31.4, 25.1, 22.2, 13.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -96.0; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{30}H_{30}FN_2O_3^+$ 485.2235; Found 485.2232.



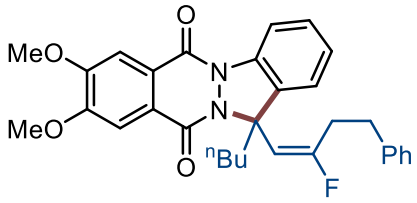
(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-2-(trifluoromethyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3l): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 10:1) on silica gel to provide the product as a colorless viscous oil (23.5 mg, yield 18%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.55 (d, J = 8.5 Hz, 1H), 8.42-8.39 (m, 1H), 8.32-8.29 (m, 1H), 7.90-7.87 (m, 2H), 7.77 (d, J = 8.5 Hz, 1H), 7.47 (s, 1H), 6.95-6.91 (m, 2H), 6.74-6.71 (m, 1H), 6.66 (d, J = 7.9 Hz, 2H), 5.97 (d, J = 22.0 Hz, 1H), 3.01-2.95 (m, 1H), 2.54-2.48 (m, 1H), 2.31-2.27 (m, 1H), 1.99-1.87 (m, 2H), 1.77-1.68 (m, 1H), 1.22-1.15 (m, 2H), 0.97-0.90 (m, 1H), 0.73-0.64 (m, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.5 (d, $J_{C\text{-}F}$ = 256.7 Hz), 155.2, 153.9, 139.7, 138.5, 134.2, 133.7, 132.2, 129.3, 129.2, 128.9 (q, $J_{C\text{-}F}$ = 33.2 Hz), 128.3, 127.9, 127.9, 127.8, 127.4 (q, $J_{C\text{-}F}$ = 3.9 Hz), 126.2, 125.5 (q, $J_{C\text{-}F}$ = 271.3 Hz), 119.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 115.9, 111.1 (d, $J_{C\text{-}F}$ = 29.7 Hz), 70.8 (d, $J_{C\text{-}F}$ = 14.8 Hz), 39.7, 32.0 (d, $J_{C\text{-}F}$ = 26.9 Hz), 31.2, 25.1, 22.2, 13.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -61.9, -95.0; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{30}H_{27}F_4N_2O_2^+$ 523.2003; Found 523.2007.



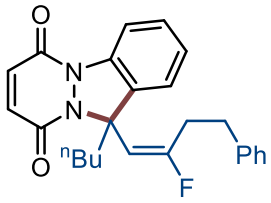
(*E*)-13-butyl-8,9-difluoro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3m): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 20:1) on silica gel to provide the product as a colorless viscous oil (68.7 mg, yield 56%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.42 (d, J = 8.0 Hz, 1H), 8.16 (dd, J = 9.7, 7.3 Hz, 1H), 8.04 (dd, J = 9.8, 7.4 Hz, 1H), 7.53-7.49 (m, 1H), 7.34 (td, J = 7.6, 1.0 Hz, 1H), 7.21-7.18 (m, 1H), 7.00-6.95 (m, 2H), 6.83-6.78 (m, 1H), 6.72-6.67 (m, 2H), 5.96 (d, J = 22.3 Hz, 1H), 2.91 (ddd, J = 13.8, 12.4, 4.6 Hz, 1H), 2.53-2.46 (m, 1H), 2.32-2.26 (m, 1H), 2.01-1.93 (m, 1H), 1.92-1.81 (m, 1H), 1.74-1.65 (m, 1H), 1.24-1.13 (m, 2H), 0.92-0.86 (m, 1H), 0.78-0.72 (m, 1H), 0.71 (t, J = 7.3 Hz, 3H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -95.3, -126.5 (d, $J_{C\text{-}F}$ = 21.1 Hz), -127.1 (d, $J_{C\text{-}F}$ = 21.1 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.4 (d, $J_{C\text{-}F}$ = 256.2 Hz), 152.9, 152.2, 139.9, 135.9, 131.1, 129.9, 128.6 (d, $J_{C\text{-}F}$ = 11.9 Hz), 128.5 (d, $J_{C\text{-}F}$ = 11.9 Hz), 128.3, 128.1, 127.2, 126.0, 122.6, 116.7 (d, $J_{C\text{-}F}$ = 20.5 Hz), 116.6, 116.5 (d, $J_{C\text{-}F}$ = 20.5 Hz), 115.9, 111.1 (d, $J_{C\text{-}F}$ = 29.5 Hz), 71.3 (d, $J_{C\text{-}F}$ = 14.9 Hz), 39.5, 31.8 (d, $J_{C\text{-}F}$ = 26.8 Hz), 31.2, 25.1, 22.2, 13.9; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{29}H_{26}F_3N_2O_2^+$ 491.1941; Found 491.1944.



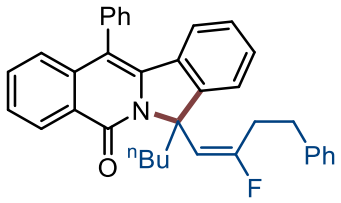
(*E*)-13-butyl-8,9-dichloro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13H-indazolo[1,2-*b*]phthalazine-6,11-dione (3n): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 20:1) on silica gel to provide the product as a colorless viscous oil (66.7 mg, yield 51%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49-8.41 (m, 2H), 8.33 (s, 1H), 7.50 (td, *J* = 7.9, 1.2 Hz, 1H), 7.34 (td, *J* = 7.6, 1.0 Hz, 1H), 7.21-7.18 (m, 1H), 7.00-6.93 (m, 2H), 6.82-6.75 (m, 1H), 6.72-6.66 (m, 2H), 5.96 (d, *J* = 22.3 Hz, 1H), 2.95-2.86 (m, 1H), 2.56-2.46 (m, 1H), 2.33-2.25 (m, 1H), 2.01-1.93 (m, 1H), 1.93-1.81 (m, 1H), 1.78-1.66 (m, 1H), 1.22-1.08 (m, 2H), 0.90-0.84 (m, 1H), 0.78-0.72 (m, 1H), 0.69 (t, *J* = 7.4 Hz, 3H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -95.4; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.4 (d, $J_{C\text{-}F}$ = 256.3 Hz), 152.9, 152.2, 139.9, 139.0, 138.8, 135.8, 131.1, 129.9, 129.7, 129.5, 129.0, 128.4, 128.3, 128.1, 127.3, 126.0, 122.6, 116.0, 111.1 (d, $J_{C\text{-}F}$ = 29.5 Hz), 71.3 (d, $J_{C\text{-}F}$ = 14.9 Hz), 39.5, 31.8 (d, $J_{C\text{-}F}$ = 26.8 Hz), 31.2, 25.1, 22.2, 13.9; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{29}H_{26}Cl_2FN_2O_2^+$ 523.1350; Found 523.1351.



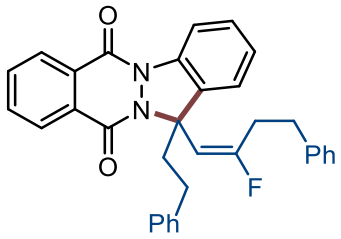
(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-8,9-dimethoxy-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3o): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 6:1) on silica gel to provide the product as a colorless viscous oil (57.9 mg, yield 45%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.44 (d, *J* = 8.1 Hz, 1H), 7.76 (s, 1H), 7.69 (s, 1H), 7.52-7.44 (m, 1H), 7.33-7.27 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.05-6.98 (m, 2H), 6.93-6.86 (m, 1H), 6.67 (d, *J* = 7.4 Hz, 2H), 5.97 (d, *J* = 22.2 Hz, 1H), 4.07 (s, 3H), 4.05 (s, 3H), 2.97 (td, *J* = 13.2, 4.6 Hz, 1H), 2.49-2.39 (m, 1H), 2.32-2.23 (m, 1H), 2.04-1.92 (m, 1H), 1.89-1.81 (m, 1H), 1.81-1.71 (m, 1H), 1.22-1.09 (m, 2H), 0.99-0.90 (m, 1H), 0.87 (d, *J* = 7.0 Hz, 1H), 0.71 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.4 (d, $J_{C\text{-}F}$ = 254.0 Hz), 154.6, 154.03, 153.96, 153.8, 140.1, 136.4, 131.3, 129.7, 128.3, 128.1, 126.7, 126.1, 124.0, 123.7, 122.5, 115.8, 111.1 (d, $J_{C\text{-}F}$ = 28.0 Hz), 108.1, 107.9, 70.9 (d, $J_{C\text{-}F}$ = 14.0 Hz), 56.8, 56.7, 39.7, 31.5, 31.8 (d, $J_{C\text{-}F}$ = 26.8 Hz), 25.1, 22.3, 14.0; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -95.9; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{31}H_{32}FN_2O_4^+$ 515.2341; Found 515.2347.



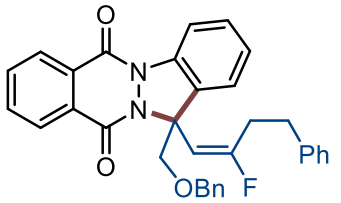
(*E*)-11-butyl-11-(2-fluoro-4-phenylbut-1-en-1-yl)-11*H*-pyridazino[1,2-*a*]indazole-6,9-dione (3p): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 8:1) on silica gel to provide the product as a yellow solid (45.5 mg, yield 45%), m. p. 89-91°C.**^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.35 (d, *J* = 8.2 Hz, 1H), 7.49-7.45 (m, 1H), 7.34-7.30 (m, 1H), 7.18-7.13 (m, 3H), 7.13-7.09 (m, 1H), 6.90 (d, *J* = 10.2 Hz, 1H), 6.79 (d, *J* = 10.2 Hz, 1H), 6.75 (d, *J* = 7.1 Hz, 2H), 5.88 (d, *J* = 22.0 Hz, 1H), 2.92-2.84 (m, 1H), 2.53-2.47 (m, 1H), 2.31-2.26 (m, 1H), 1.95-1.89 (m, 1H), 1.83-1.76 (m, 2H), 1.24-1.10 (m, 2H), 0.92-0.83 (m, 1H), 0.73 (t, *J* = 7.3 Hz, 3H), 0.68-0.61 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.4 (d, $J_{C\text{-}F}$ = 256.7 Hz), 153.8, 153.3, 140.0, 135.7, 135.2, 131.0, 129.8, 128.6, 128.3, 127.4, 126.4, 122.4, 115.6, 110.2 (d, $J_{C\text{-}F}$ = 29.6 Hz), 71.4 (d, $J_{C\text{-}F}$ = 14.8 Hz), 39.0, 31.7 (d, $J_{C\text{-}F}$ = 26.7 Hz), 31.4, 25.0, 22.2, 13.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -95.0; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{25}H_{26}FN_2O_2^+$ 405.1973; Found 405.1977.



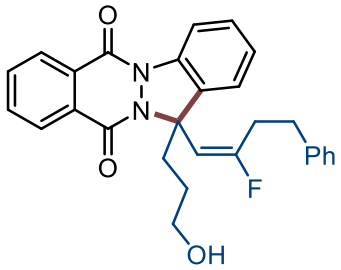
(*E*)-7-butyl-7-(2-fluoro-4-phenylbut-1-en-1-yl)-12-phenylisoindolo[2,1-*b*]isoquinolin-5(7*H*)-one (3q): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 20:1) on silica gel to provide the product as a colorless viscous oil (28.3 mg, yield 22%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.52 (d, *J* = 8.0 Hz, 1H), 7.63-7.51 (m, 5H), 7.50-7.48 (m, 1H), 7.43-7.41 (m, 1H), 7.37-7.34 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.10-7.07 (m, 1H), 7.05-7.00 (m, 4H), 6.56 (d, *J* = 7.0 Hz, 2H), 6.31 (d, *J* = 8.0 Hz, 1H), 6.08 (d, *J* = 21.8 Hz, 1H), 3.27-3.21 (m, 1H), 2.32-2.27 (m, 1H), 2.13-2.07 (m, 2H), 1.76-1.61 (m, 2H), 1.24-1.09 (m, 2H), 0.88-0.78 (m, 1H), 0.70 (t, *J* = 7.3 Hz, 3H), 0.57-0.49 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 161.7 (d, $J_{C\text{-}F}$ = 254.2 Hz), 160.0, 146.7, 140.6, 138.6, 138.1, 135.2, 133.2, 132.2, 131.3, 131.1, 130.1, 129.6, 129.6, 128.6, 128.2, 128.1, 127.8, 126.6, 126.0, 125.2, 123.8, 122.6, 114.4, 110.7 (d, $J_{C\text{-}F}$ = 27.6 Hz), 70.7 (d, $J_{C\text{-}F}$ = 13.7 Hz), 38.7, 31.7, 31.7 (d, $J_{C\text{-}F}$ = 27.2 Hz), 24.6, 22.3, 14.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -97.8; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{36}H_{33}FNO^+$ 514.2541; Found 514.2546.



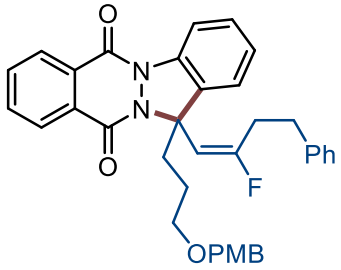
(*E*)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13-phenethyl-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3r): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 12:1) on silica gel to provide the product as a light yellow viscous oil (75.4 mg, yield 60%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.51 (d, *J* = 8.1 Hz, 1H), 8.34-8.29 (m, 1H), 8.22-8.15 (m, 1H), 7.83-7.77 (m, 2H), 7.57-7.52 (m, 1H), 7.38-7.34 (m, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.01-6.97 (m, 2H), 6.97-6.94 (m, 2H), 6.88 (d, *J* = 6.8 Hz, 2H), 6.83-6.79 (m, 1H), 6.79-6.75 (m, 1H), 6.67 (d, *J* = 7.1 Hz, 2H), 6.02 (d, *J* = 22.4 Hz, 1H), 3.55-3.48 (m, 1H), 2.50-2.44 (m, 1H), 2.32-2.23 (m, 3H), 2.18-2.12 (m, 1H), 1.93-1.84 (m, 1H), 1.81-1.71 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.2 (d, $J_{C\text{-}F}$ = 255.9 Hz), 154.8, 154.0, 139.9, 139.6, 136.4, 133.4, 133.2, 130.6, 130.0, 129.7, 129.0, 128.3, 128.2, 128.14, 128.07, 127.5, 127.3, 126.9, 126.0, 125.8, 122.6, 116.0, 111.4 (d, $J_{C\text{-}F}$ = 29.3 Hz), 70.6 (d, $J_{C\text{-}F}$ = 14.9 Hz), 40.0, 31.8 (d, $J_{C\text{-}F}$ = 26.6 Hz), 31.3, 29.8; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.7; **HRMS** (ESI) m/z: $[M + Na]^+$ Calculated for $C_{33}H_{27}FN_2O_2Na^+$ 525.1949; Found 525.1954.



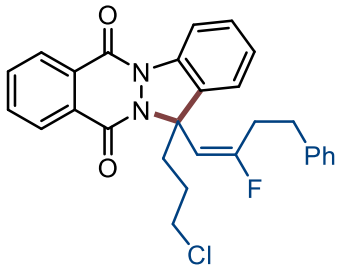
(*E*)-13-((benzyloxy)methyl)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3s): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 8:1) on silica gel to provide the product as a yellow viscous oil (38.9 mg, yield 30%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.49 (d, *J* = 8.2 Hz, 1H), 8.40 (dd, *J* = 7.3, 1.8 Hz, 1H), 8.25 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.87-7.82 (m, 2H), 7.54-7.51 (m, 1H), 7.31-7.29 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.15-7.11 (m, 3H), 6.97-6.94 (m, 2H), 6.92-6.89 (m, 2H), 6.79-6.76 (m, 1H), 6.66 (d, *J* = 7.5 Hz, 2H), 5.81 (d, *J* = 21.5 Hz, 1H), 4.52 (d, *J* = 9.4 Hz, 1H), 4.38-4.31 (m, 2H), 3.85 (d, *J* = 9.4 Hz, 1H), 2.50-2.45 (m, 1H), 2.32-2.27 (m, 1H), 1.96-1.87 (m, 1H), 1.85-1.76 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.4 (d, $J_{C\text{-}F}$ = 257.3 Hz), 154.7, 154.4, 139.9, 137.5, 136.6, 133.5, 133.4, 130.0, 129.9, 129.9, 129.2, 128.3, 128.3, 128.1, 127.7, 127.6, 127.6, 127.4, 126.6, 126.1, 122.8, 115.8, 106.8 (d, $J_{C\text{-}F}$ = 30.0 Hz), 73.3, 72.2, 70.4 (d, $J_{C\text{-}F}$ = 14.8 Hz), 32.1 (d, $J_{C\text{-}F}$ = 26.4 Hz), 31.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -94.2; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{33}H_{28}FN_2O_3^+$ 519.2078; Found 519.2083.



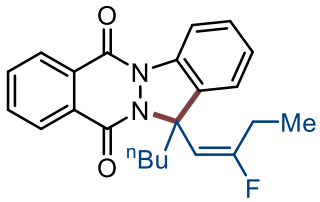
(*E*)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13-(3-hydroxypropyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3t): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 2:1) on silica gel to provide the product as a yellow viscous oil (51.5 mg, yield 45%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.44 (d, *J* = 8.1 Hz, 1H), 8.39-8.36 (m, 1H), 8.28-8.23 (m, 1H), 7.87-7.81 (m, 2H), 7.50-7.46 (m, 1H), 7.32-7.29 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.96-6.91 (m, 2H), 6.76-6.72 (m, 1H), 6.65 (d, *J* = 7.5 Hz, 2H), 5.98 (d, *J* = 22.3 Hz, 1H), 3.49-3.40 (m, 2H), 3.05-2.98 (m, 1H), 2.48-2.42 (m, 1H), 2.30-2.25 (m, 1H), 2.11-2.06 (m, 1H), 1.91-1.83 (m, 1H), 1.77-1.68 (m, 1H), 1.23-1.16 (m, 1H), 1.07-0.99 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.4 (d, $J_{C\text{-}F}$ = 255.9 Hz), 154.6, 154.1, 139.8, 136.1, 133.7, 133.5, 130.7, 129.9, 129.6, 129.0, 128.2, 128.0, 127.6, 127.6, 127.0, 126.0, 122.5, 115.9, 111.1 (d, $J_{C\text{-}F}$ = 29.5 Hz), 70.7 (d, $J_{C\text{-}F}$ = 15.1 Hz), 61.8, 36.2, 31.8 (d, $J_{C\text{-}F}$ = 26.7 Hz), 31.3, 26.3; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -95.4; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{28}H_{26}FN_2O_3^+$ 457.1922; Found 457.1927.



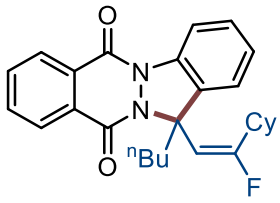
(*E*)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13-(3-((4-methoxybenzyl)oxy)propyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3u): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 4:1) on silica gel to provide the product as a yellow viscous oil (119.7 mg, yield 83%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.46 (d, *J* = 8.2 Hz, 1H), 8.41-8.39 (m, 1H), 8.31-8.27 (m, 1H), 7.87-7.82 (m, 2H), 7.51-7.47 (m, 1H), 7.32-7.29 (m, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.98-6.93 (m, 2H), 6.83-6.81 (m, 2H), 6.79-6.74 (m, 1H), 6.67 (d, *J* = 7.1 Hz, 2H), 6.00 (d, *J* = 22.3 Hz, 1H), 4.25 (s, 2H), 3.77 (s, 3H), 3.30-3.24 (m, 2H), 3.05-2.99 (m, 1H), 2.49-2.44 (m, 1H), 2.31-2.26 (m, 1H), 2.13-2.07 (m, 1H), 1.93-1.84 (m, 1H), 1.80-1.70 (m, 1H), 1.30-1.22 (m, 1H), 1.14-1.06 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.3 (d, $J_{C\text{-}F}$ = 255.9 Hz), 159.2, 154.6, 154.0, 139.9, 136.1, 133.6, 133.4, 130.8, 130.3, 129.8, 129.7, 129.3, 129.1, 128.3, 128.0, 127.6, 127.6, 126.9, 126.0, 122.6, 115.9, 113.8, 111.2 (d, $J_{C\text{-}F}$ = 29.3 Hz), 72.6, 70.7 (d, $J_{C\text{-}F}$ = 14.9 Hz), 69.1, 55.3, 36.4, 31.8 (d, $J_{C\text{-}F}$ = 26.9 Hz), 31.3, 23.5; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.6; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{36}H_{24}FN_2O_4^+$ 577.2497; Found 577.2499.



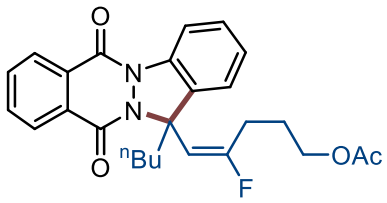
(*E*)-13-(3-chloopropyl)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3v): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 8:1) on silica gel to provide the product as a light yellow viscous oil (86.9 mg, yield 73%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.46 (d, *J* = 8.2 Hz, 1H), 8.42-8.38 (m, 1H), 8.33-8.25 (m, 1H), 7.88-7.84 (m, 2H), 7.54-7.48 (m, 1H), 7.35-7.31 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.00-6.90 (m, 2H), 6.77-6.73 (m, 1H), 6.67 (d, *J* = 7.3 Hz, 2H), 6.00 (d, *J* = 22.4 Hz, 1H), 3.39-3.30 (m, 2H), 3.14-3.05 (m, 1H), 2.49-2.44 (m, 1H), 2.32-2.26 (m, 1H), 2.24-2.17 (m, 1H), 1.93-1.84 (m, 1H), 1.79-1.69 (m, 1H), 1.52-1.43 (m, 1H), 1.24-1.16 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.5 (d, $J_{C\text{-}F}$ = 256.0 Hz), 154.7, 154.1, 139.8, 136.0, 133.8, 133.6, 130.3, 130.1, 129.7, 129.0, 128.3, 128.0, 127.7, 127.6, 127.0, 126.0, 122.6, 116.0, 111.0 (d, $J_{C\text{-}F}$ = 29.8 Hz), 70.4 (d, $J_{C\text{-}F}$ = 14.9 Hz), 44.0, 37.1, 31.8 (d, $J_{C\text{-}F}$ = 27.0 Hz), 31.3, 26.4; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.0; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{28}H_{25}ClFN_2O_2^+$ 475.1583; Found 475.1586.



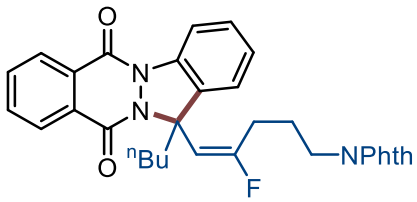
(*E*)-13-butyl-13-(2-fluorobut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3w): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 12:1) on silica gel to provide the product as a light yellow viscous oil (58.7 mg, yield 62%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.47-8.41 (m, 2H), 8.38-8.35 (m, 1H), 7.88-7.84 (m, 2H), 7.48-7.45 (m, 1H), 7.34-7.30 (m, 1H), 7.27-7.25 (m, 1H), 5.87 (d, *J* = 21.5 Hz, 1H), 3.03-2.97 (m, 1H), 2.02-1.97 (m, 1H), 1.65-1.45 (m, 2H), 1.25-1.12 (m, 2H), 1.02-0.93 (m, 1H), 0.77-0.72 (m, 1H), 0.70 (t, *J* = 7.4 Hz, 3H), 0.57 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.5 (d, $J_{C\text{-}F}$ = 257.0 Hz), 154.9, 154.1, 136.0, 133.8, 133.5, 131.6, 129.6, 129.6, 129.2, 127.7, 127.6, 126.8, 122.4, 115.8, 109.8 (d, $J_{C\text{-}F}$ = 29.3 Hz), 71.1 (d, $J_{C\text{-}F}$ = 14.5 Hz), 39.7, 25.1, 22.7 (d, $J_{C\text{-}F}$ = 27.6 Hz), 22.2, 13.9, 9.6; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -97.0; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{23}H_{24}FN_2O_2^+$ 379.1816; Found 379.1819.



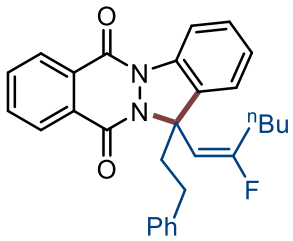
(*E*)-13-butyl-13-(2-cyclohexyl-2-fluorovinyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3x): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 32:1) on silica gel to provide the product as a light yellow viscous oil (82.2 mg, yield 76%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.46 (d, J = 8.1 Hz, 1H), 8.45-8.42 (m, 1H), 8.38-8.34 (m, 1H), 7.88-7.84 (m, 2H), 7.49-7.45 (m, 1H), 7.33-7.30 (m, 1H), 7.26-7.25 (m, 1H), 5.77 (d, J = 21.4 Hz, 1H), 3.04-2.99 (m, 1H), 2.03-1.98 (m, 1H), 1.42-1.31 (m, 4H), 1.22-0.98 (m, 6H), 0.90-0.84 (m, 2H), 0.80-0.74 (m, 1H), 0.71 (t, J = 7.4 Hz, 3H), 0.58-0.44 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 167.8 (d, $J_{C\text{-}F}$ = 260.8 Hz), 154.8, 154.1, 136.1, 133.9, 133.5, 132.0, 129.6, 129.4, 129.2, 127.6, 127.6, 126.7, 122.4, 115.7, 109.0 (d, $J_{C\text{-}F}$ = 29.2 Hz), 71.2 (d, $J_{C\text{-}F}$ = 14.6 Hz), 39.6, 39.0 (d, $J_{C\text{-}F}$ = 25.3 Hz), 28.61, 27.8, 25.8 (d, $J_{C\text{-}F}$ = 26.6 Hz), 25.3 (d, $J_{C\text{-}F}$ = 23.3 Hz), 22.3, 14.0; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -107.2; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{27}H_{30}FN_2O_2^+$ 433.2286; Found 433.2293.



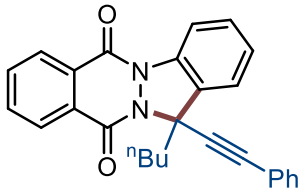
(*E*)-5-(13-butyl-6,11-dioxo-6,11-dihydro-13*H*-indazolo[1,2-*b*]phthalazin-13-yl)-4-fluoropent-4-en-1-yl acetate (3y): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 10:1) on silica gel to provide the product as a light yellow viscous oil (63.1 mg, yield 56%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.46 (d, J = 8.1 Hz, 1H), 8.44-8.41 (m, 1H), 8.38-8.33 (m, 1H), 7.88-7.85 (m, 2H), 7.49-7.46 (m, 1H), 7.35-7.32 (m, 1H), 7.26 (d, J = 8.0 Hz, 1H), 5.95 (d, J = 21.7 Hz, 1H), 3.62-3.55 (m, 2H), 3.02-2.97 (m, 1H), 2.02-1.97 (m, 1H), 1.88 (s, 3H), 1.74-1.65 (m, 1H), 1.64-1.54 (m, 1H), 1.47-1.39 (m, 1H), 1.34-1.26 (m, 1H), 1.25-1.12 (m, 2H), 1.01-0.93 (m, 1H), 0.77-0.72 (m, 1H), 0.70 (t, J = 7.3 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 170.9, 163.4 (d, J = 256.1 Hz), 154.8, 154.1, 136.1, 133.9, 133.6, 131.4, 129.8, 129.6, 129.1, 127.7, 127.6, 126.9, 122.4, 115.8, 111.2 (d, J = 28.9 Hz), 70.9 (d, J = 14.4 Hz), 63.3, 39.7, 26.2 (d, J = 27.3 Hz), 25.1, 24.5, 22.2, 20.9, 13.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.9; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{26}H_{28}FN_2O_4^+$ 451.2028; Found 451.2035.



(*E*)-13-butyl-13-(5-(1,3-dioxoisoindolin-2-yl)-2-fluoropent-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3z): The reaction mixture was subjected directly to flash chromatography (100% DCM) on silica gel to provide the product as a yellow viscous oil (63.1 mg, yield 47%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.43-8.40 (m, 1H), 8.36-8.33 (m, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.88-7.84 (m, 2H), 7.81-7.78 (m, 2H), 7.76-7.72 (m, 2H), 7.27-7.24 (m, 1H), 7.23-7.20 (m, 1H), 7.17-7.14 (m, 1H), 5.94 (d, J = 21.8 Hz, 1H), 3.37-3.25 (m, 1H), 3.25-3.17 (m, 1H), 2.98-2.90 (m, 1H), 2.00-1.95 (m, 1H), 1.74-1.66 (m, 1H), 1.58-1.47 (m, 2H), 1.33-1.26 (m, 1H), 1.22-1.09 (m, 2H), 0.99-0.90 (m, 1H), 0.75-0.70 (m, 1H), 0.68 (t, J = 7.4 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 168.1, 163.3 (d, $J_{C\text{-}F}$ = 256.4 Hz), 154.7, 154.2, 135.9, 134.0, 133.8, 133.5, 132.1, 131.0, 129.6, 129.6, 129.1, 127.7, 127.7, 126.7, 123.5, 122.4, 115.5, 111.0 (d, $J_{C\text{-}F}$ = 28.8 Hz), 70.9 (d, $J_{C\text{-}F}$ = 14.4 Hz), 39.6, 37.3, 27.2 (d, $J_{C\text{-}F}$ = 27.2 Hz), 25.0, 24.7, 22.2, 13.9; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -95.3; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{32}H_{29}FN_3O_4^+$ 538.2137; Found 538.2145.



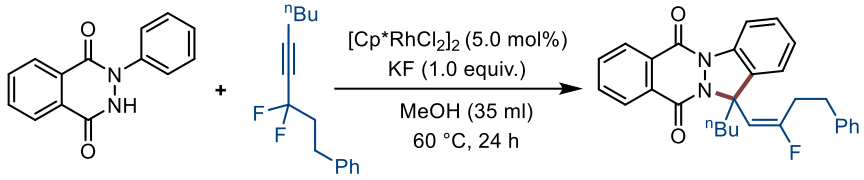
(*E*)-13-(2-fluorohex-1-en-1-yl)-13-phenethyl-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3aa): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 16:1) on silica gel to provide the product as a light yellow viscous oil (52.3 mg, yield 46%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.50 (d, J = 8.2 Hz, 1H), 8.35 (dd, J = 7.2, 2.0 Hz, 1H), 8.28-8.21 (m, 1H), 7.83-7.79 (m, 2H), 7.54-7.50 (m, 1H), 7.39-7.36 (m, 1H), 7.31 (d, J = 7.3 Hz, 1H), 7.02-6.98 (m, 2H), 6.90 (d, J = 7.4 Hz, 2H), 6.85-6.79 (m, 1H), 5.91 (d, J = 21.7 Hz, 1H), 3.58-3.51 (m, 1H), 2.34-2.26 (m, 2H), 2.23-2.18 (m, 1H), 1.56-1.48 (m, 2H), 1.11-1.03 (m, 1H), 0.98-0.90 (m, 1H), 0.85-0.70 (m, 2H), 0.46 (t, J = 7.3 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.9 (d, $J_{C\text{-}F}$ = 257.0 Hz), 154.9, 154.1, 139.7, 136.3, 133.5, 133.3, 131.0, 130.0, 129.5, 129.0, 128.2, 127.5, 127.4, 126.9, 125.8, 122.6, 116.0, 110.3 (d, $J_{C\text{-}F}$ = 29.7 Hz), 70.7 (d, $J_{C\text{-}F}$ = 14.8 Hz), 40.2, 29.9, 29.0 (d, $J_{C\text{-}F}$ = 26.8 Hz), 27.3, 22.2, 13.5; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -94.7; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{29}H_{28}FN_2O_2^+$ 455.2129; Found 455.2134.



13-butyl-13-(phenylethynyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3ab'): The reaction mixture was subjected directly to flash chromatography (Petroleum/EtOAc: 20:1) on silica gel to provide the product as a yellow viscous oil (36.6 mg, yield 36%).**^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.46 (d, J = 8.0 Hz, 1H), 8.45-8.39 (m, 2H), 7.88-7.84 (m, 2H), 7.53-7.48 (m, 2H), 7.45-7.42 (m,

2H), 7.38-7.35 (m, 1H), 7.29-7.25 (m, 3H), 3.26-3.18 (m, 1H), 2.41-2.32 (m, 1H), 1.32-1.20 (m, 2H), 1.19-1.11 (m, 1H), 0.99-0.91 (m, 1H), 0.78 (t, J = 7.3 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 154.8, 154.7, 135.8, 133.7, 133.6, 132.2, 130.0, 129.8, 129.7, 129.3, 128.9, 128.3, 127.8, 127.6, 126.7, 122.6, 122.1, 116.1, 86.2, 85.6, 67.4, 38.9, 25.5, 22.2, 14.0; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{27}H_{23}N_2O_2^+$ 407.1754; Found 407.1757.

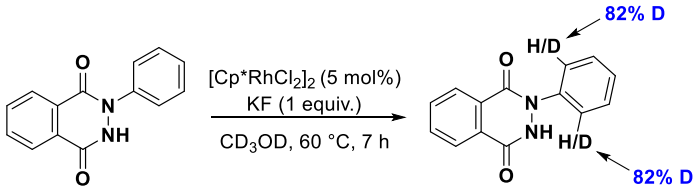
Gram Scale Synthesis of Compound 3a



1a, 5 mmol **2a,** 6.5 mmol **3a,** 1.82 g, 80%

To a mixture of *N*-phenyl 2,3-dihydrophthalazine-1,4-dione **1a** (5 mmol), $[Cp^*RhCl_2]_2$ (5 mol%) and KF (5 mmol) in a 100 mL flask was added a solution of **2a** (6.5 mmol) in MeOH (40.0 mL). Then the flask was capped with septa, and the resulting mixture was stirred at 60 °C in an oil bath for 24 h. After removal of the solvent, the residue was purified by flash chromatography on silica gel to provide the desired products **3a** as a yellow oil (1.82 g, yield 80%).

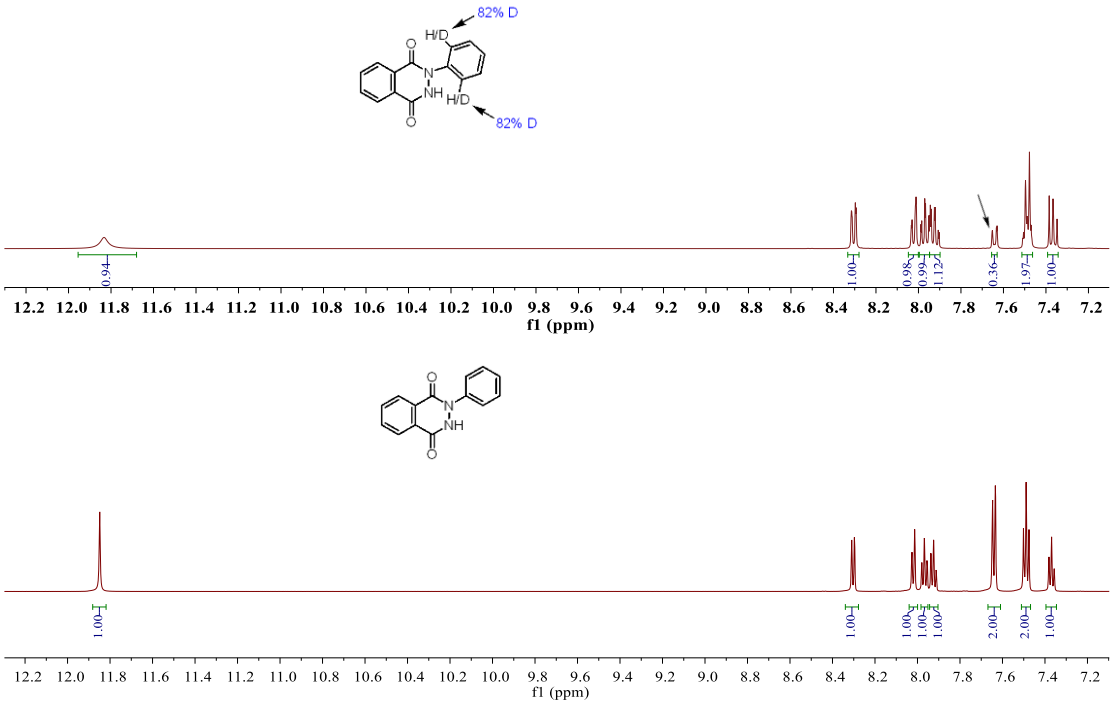
Deuterium Incorporation Experiments of Rh(III)-Catalyzed [4+1] Annulation



1a **1a-D**

To a mixture of **1a** (0.25 mmol), $[Cp^*RhCl_2]_2$ (5 mol%) and KF (0.25 mmol) in a 25 mL Schlenk tube was added CD_3OD (4.0 mL). Then the tube was capped with septa, and the resulting mixture was stirred at 60 °C in an oil bath for 7 h. After removal of the solvent, the residue was purified by flash chromatography (Petroleum/EtOAc = 2:1) on silica gel to give the product. *Found H/D exchange occurred on the phenyl ring at the ortho-position (82% D).*

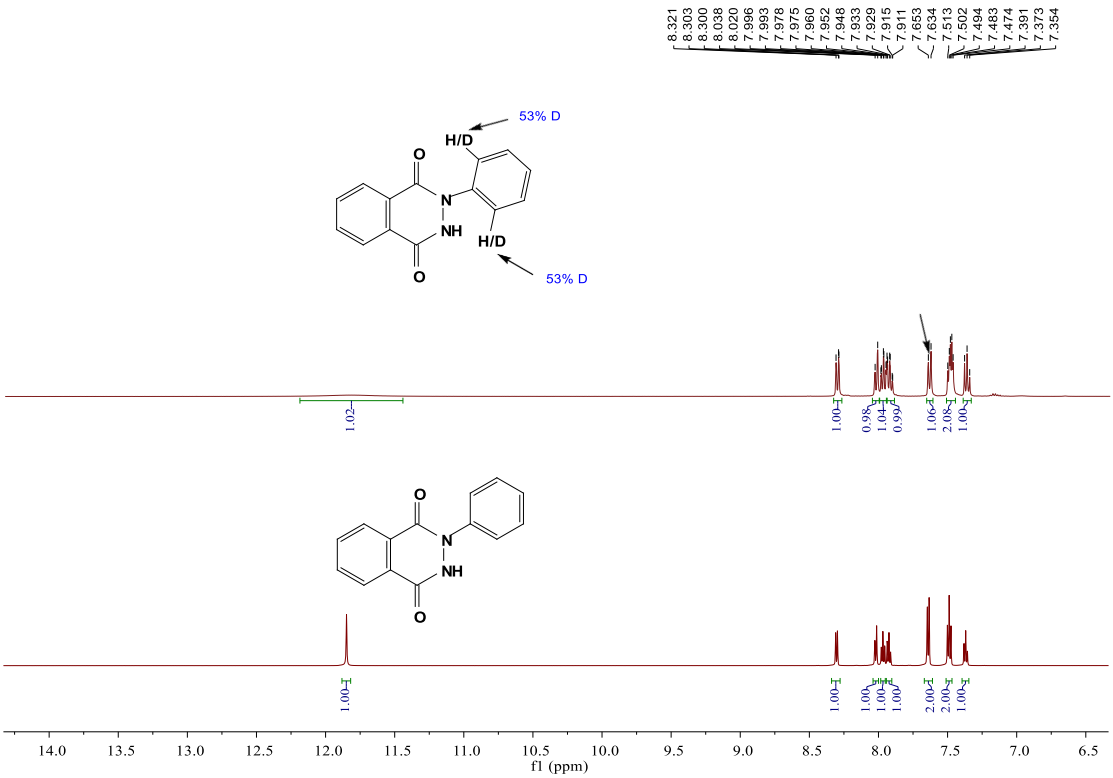
^{1}H NMR of the product **1a-D** of this reaction.



Determination of the KIE

(1) The intermolecular competition experiment

To a mixture of **1a** (0.25 mmol), **1a-D** (0.25 mmol, 82% D), $[Cp^*RhCl_2]_2$ (5 mol%) and KF (0.25 mmol) in a 10 mL flask was added a solution of **2a** (0.325 mmol) in MeOH (4.0 mL). Then the flask was capped with septa, and the resulting mixture was stirred at 60 °C in an oil bath for 1.0 h. After removal of the solvent, the residue was purified by flash chromatography on silica gel to provide the starting material (**1a** and **1a-D**) and product **3a**. The mixture of the starting materials (**1a** and **1a-D**) was analyzed by ^{1}H NMR. A kinetic isotopic effect of this reaction was determined to be k_H/k_D = 0.73 (0.47/0.53*0.82).



(2) Two parallel reactions for KIE value measurement

To a mixture of **1a** (0.25 mmol), $[Cp^*RhCl_2]_2$ (5 mol%) and KF (0.25 mmol) in a 10.0 mL flask was added a solution of **2a** (0.325 mmol) in MeOH (4.0 mL). Then the flask was capped with septa, and the resulting mixture was stirred at 60 °C in an oil bath for 1.0 h. After removal of the solvent, the residue was purified by flash chromatography on silica gel to provide the product **3a** (14 mg, yield 12%).

To a mixture of **1a-D** (0.25 mmol, 82% D), $[Cp^*RhCl_2]_2$ (5 mol%) and KF (0.25 mmol) in a 10.0 mL flask was added a solution of **2a** (0.325 mmol) in MeOH (4.0 mL). Then the flask was capped with septa, and the resulting mixture was stirred at 60 °C in an oil bath for 1.0 h. After removal of the solvent, the residue was purified by flash chromatography on silica gel to provide the product **3a** (14.5 mg, yield 13%).

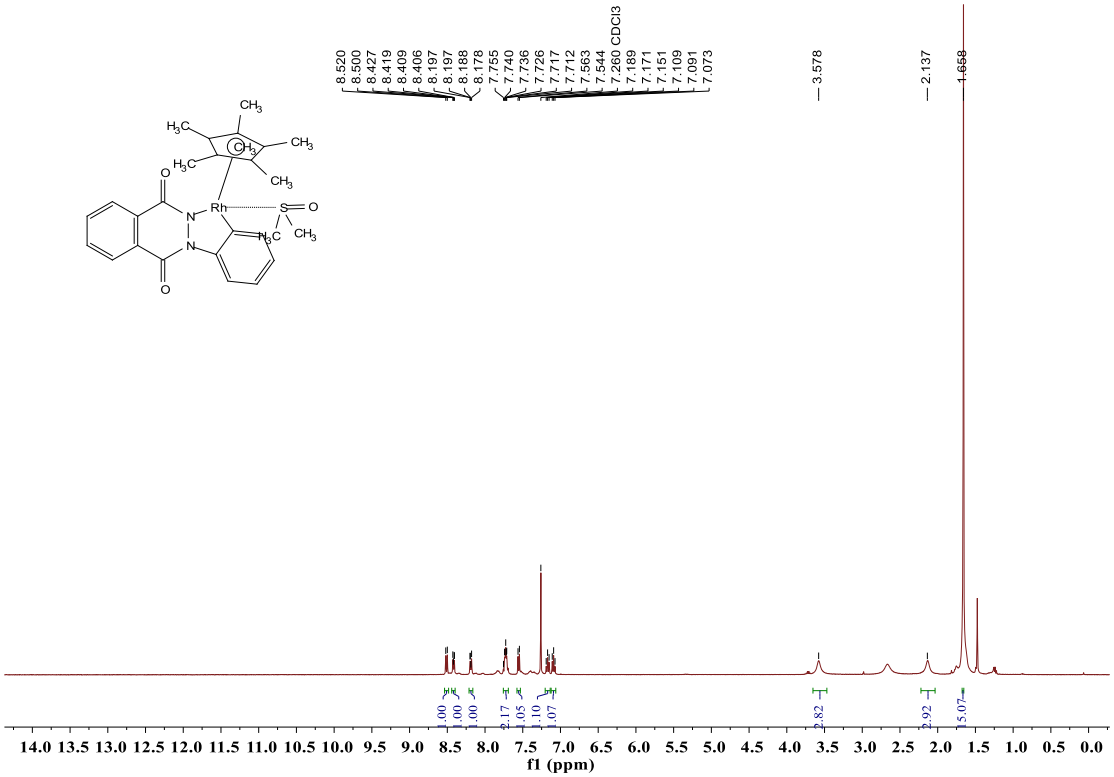
A kinetic isotopic effect of these two reactions was determined to be k_H/k_D =0.79 (14/14.5*0.82).

Synthetic procedure for Rh-complex

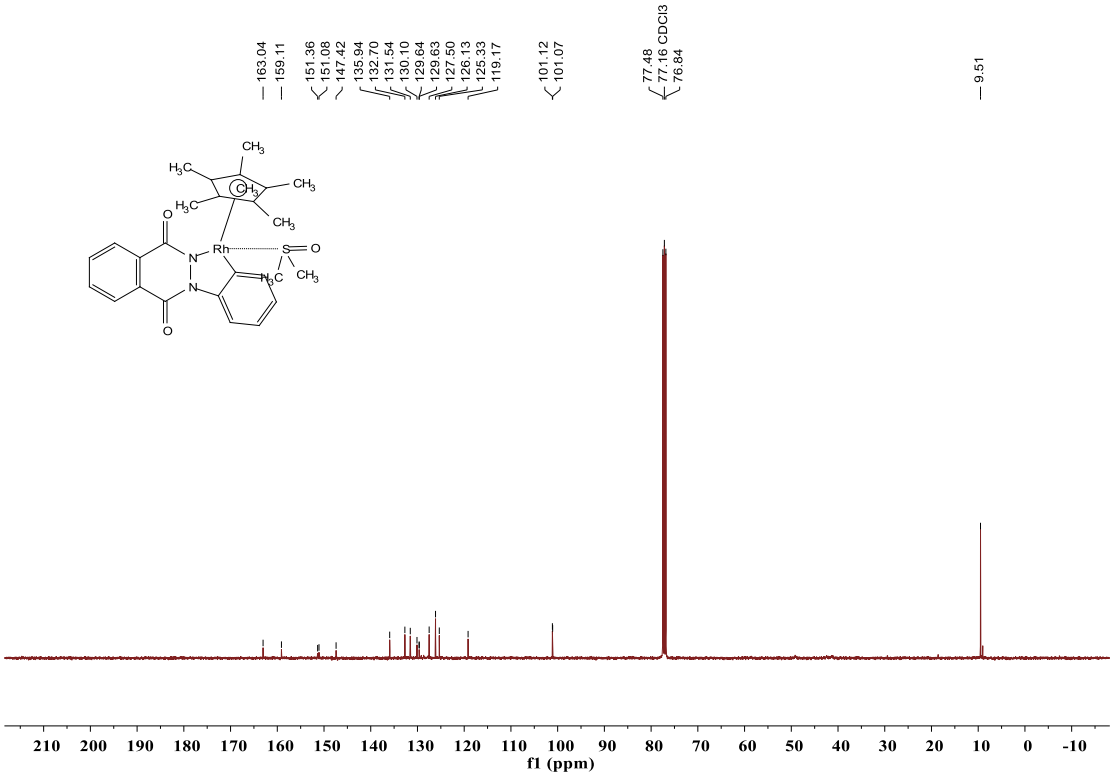
(3) Procedure for the Synthesis of [Cp*Rh(Phthalazine-dione)DMSO] Complex (**4a**)] [5]

To a sealed tube with a screwcap, **1a** (0.1 mmol), $[Cp^*RhCl_2]_2$ (1.0 equiv), NaOAc (5 equiv), and DCM (2.5 mL) were added. The tube was tightly capped after purging with N_2 gas, and the reaction was allowed to stir at 25 °C for 12 h. The reaction mixture was filtered through Celite pad and washed with DCM. The filtrate was concentrated to reduce the volume to 0.5 mL. Then DMSO (0.5 mL) was added, and the resulting mixture was allowed to settle down for 12 h. Later, the reaction mixture was quenched with water and extracted with DCM (3 × 15 mL). The organic layers were combined, dried over anhydrous sodium sulfate and concentrated under reduced pressure to afford the desired complex **4a** in 68% yield.

[Cp*Rh(Phthalazine-dione)DMSO] Complex (**4a**). Orange solid (38 mg, 68%). Mp 171−172 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 (d, *J* = 8.2 Hz, 1H), 8.44-8.40 (m, 1H), 8.21-8.16 (m, 1H), 7.76-7.69 (m, 2H), 7.55 (d, J = 7.4 Hz, 1H), 7.20-7.14 (m, 1H), 7.12-7.06 (m, 1H), 3.58 (s, 3H), 2.14 (s, 3H), 1.66 (s, 15H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.0, 159.1, 151.4, 151.1, 147.4, 135.9, 132.7, 131.5, 130.1, 129.6, 129.6, 127.5, 126.1, 125.3, 119.2, 101.1, 101.1, 9.5; **HRMS** (ESI) m/z: $[M + H]^+$ Calculated for $C_{24}H_{24}N_2O_2Rh$ $C_{29}H_{28}FN_2O_2^+$ 475.0887; Found 475.0889.

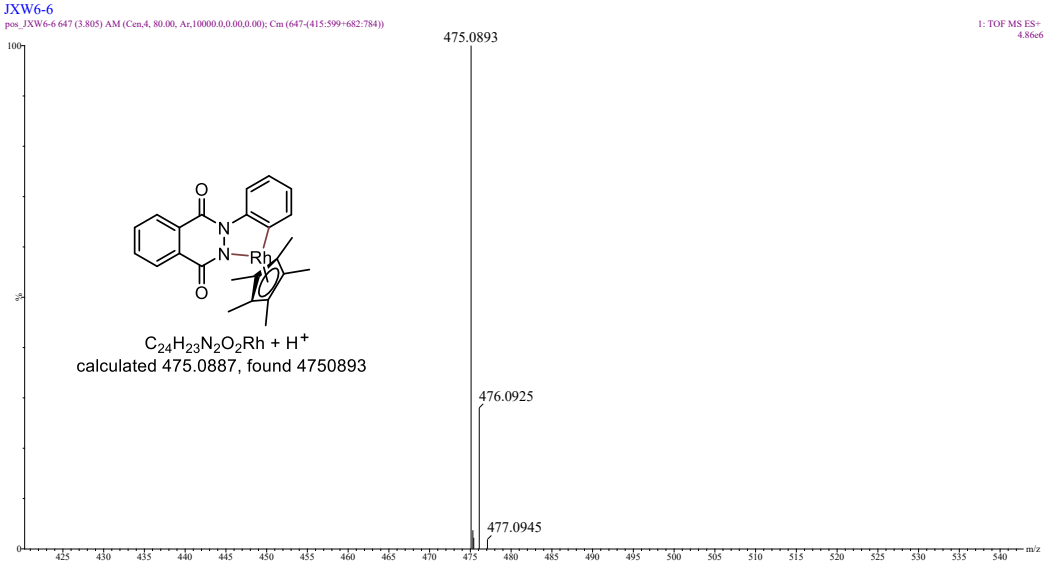


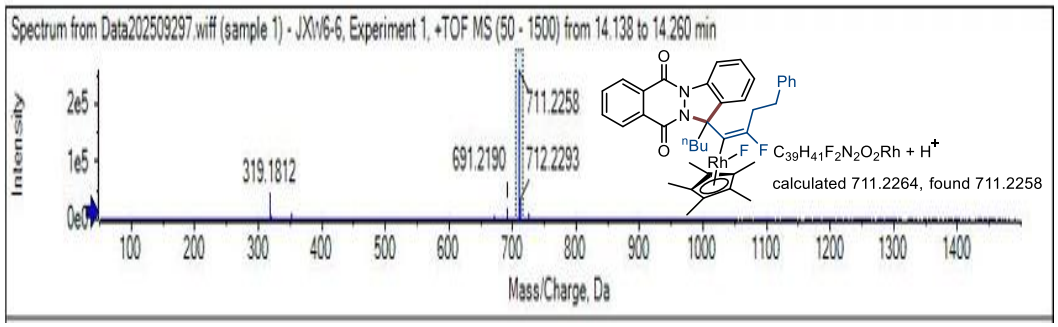
^{1}H NMR spectra of **4a**

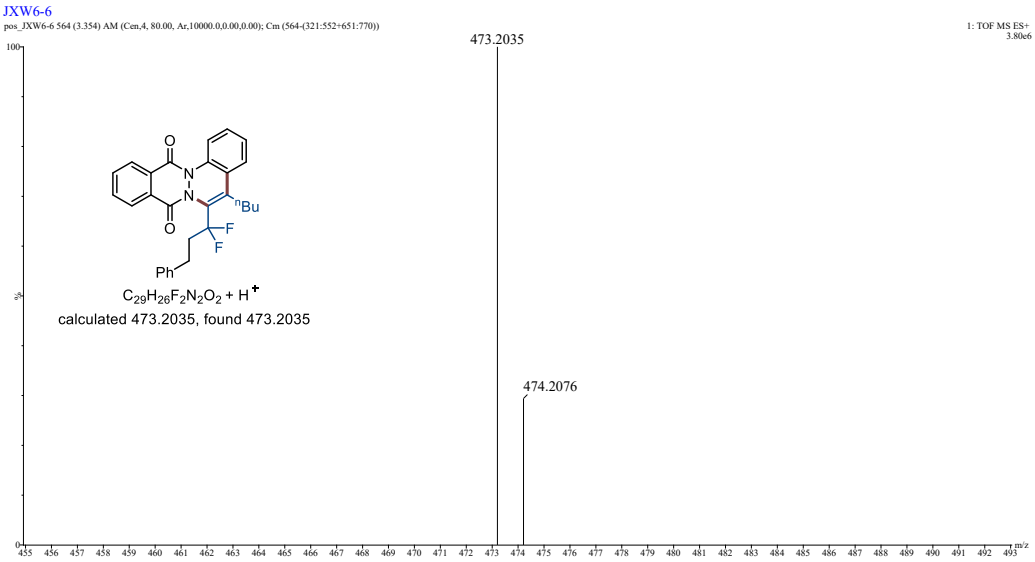


^{13}C NMR spectra of **4a**

Possible Intermediates and Side Products Trapped by HRMS

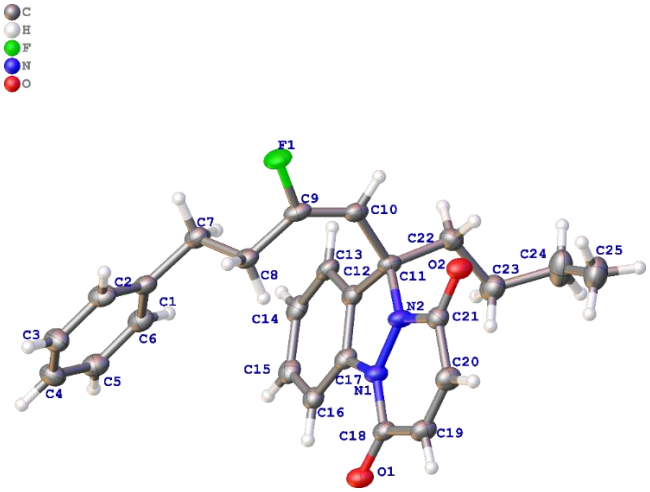






X-ray Data of Compound 3p

Deposition Data: CCDC 2469480 (ellipsoid contour at 30% probability level)



A suitable crystal of compound **3p** was obtained by slowly volatilizing a solution of **3p** in chloroform and methanol at ambient temperature. A colorless crystal of **3p** was mounted on a glass fiber at a random orientation. The data were collected by a diffractometer Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation (1.54178 Å) by using a ω scan mode. The structures were solved by direct methods using Olex2 software, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with XL using a full-matrix least squares procedure based on F^2. The weighted R factor, wR and goodness-of-fit S values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on the parent atoms.

Table S1 Crystal data and structure refinement for 3p.

Identification code	**3p**
Empirical formula	$C_{25}H_{25}FN_2O_2$
Formula weight	404.47
Temperature/K	100.1(5)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.086(2)
b/Å	8.3538(9)
c/Å	22.882(4)
α/°	90
β/°	94.994(14)
γ/°	90
Volume/Å^3	2111.1(6)
Z	4
ρ_{calc}g/cm^3	1.273
μ/mm^{-1}	0.704
F(000)	856.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.756 to 147.88
Index ranges	-13 ≤ h ≤ 13, -7 ≤ k ≤ 10, -28 ≤ l ≤ 19
Reflections collected	8224
Independent reflections	4139 [R_{int} = 0.0959, R_{sigma} = 0.1241]
Data/restraints/parameters	4139/9/283
Goodness-of-fit on F^2	0.974
Final R indexes [I>=2σ (I)]	R_1 = 0.0655, wR_2 = 0.1475
Final R indexes [all data]	R_1 = 0.1181, wR_2 = 0.1891
Largest diff. peak/hole / e Å^{-3}	0.25/-0.29

Crystal structure determination of 3p

Crystal Data for $C_{25}H_{25}FN_2O_2$ (M =404.47 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 11.086(2) Å, b = 8.3538(9) Å, c = 22.882(4) Å, β = 94.994(14)°, V = 2111.1(6) Å^3, Z = 4, T = 100.1(5) K, μ(Cu Kα) = 0.704 mm^{-1}, *Dcalc* = 1.273 g/cm^3, 8224 reflections measured (7.756° ≤ 2Θ ≤ 147.88°), 4139 unique (R_{int} = 0.0959, R_{sigma} = 0.1241) which were used in all calculations. The final R_1 was 0.0655 (I > 2σ(I)) and wR_2 was 0.1891 (all data).

CCDC 2469480 contains the supplementary crystallographic data for compound **3p**. These data can be also obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

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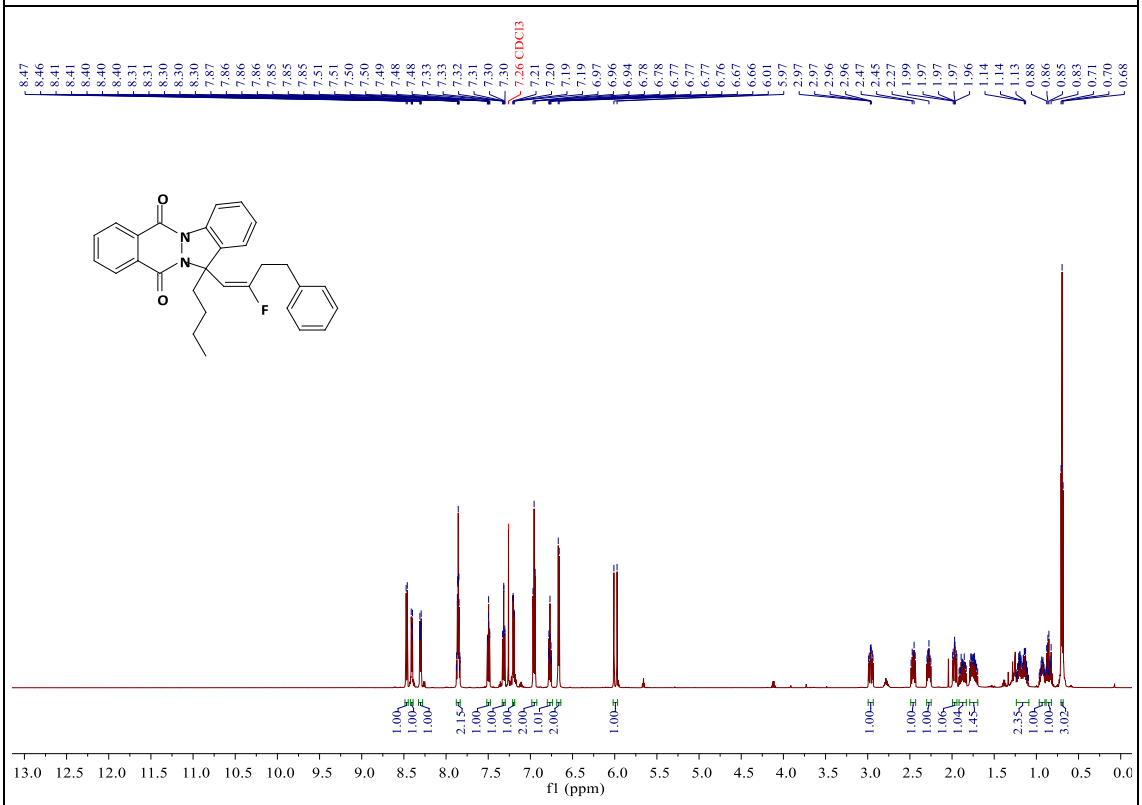
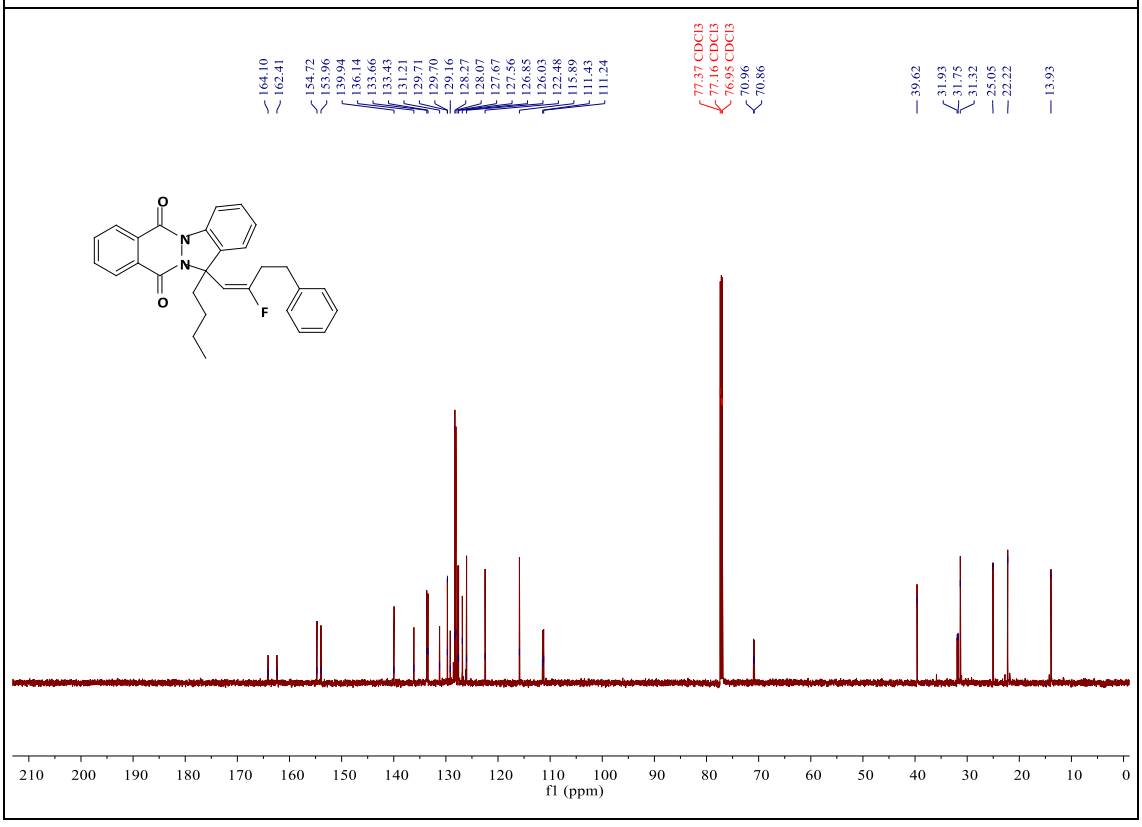
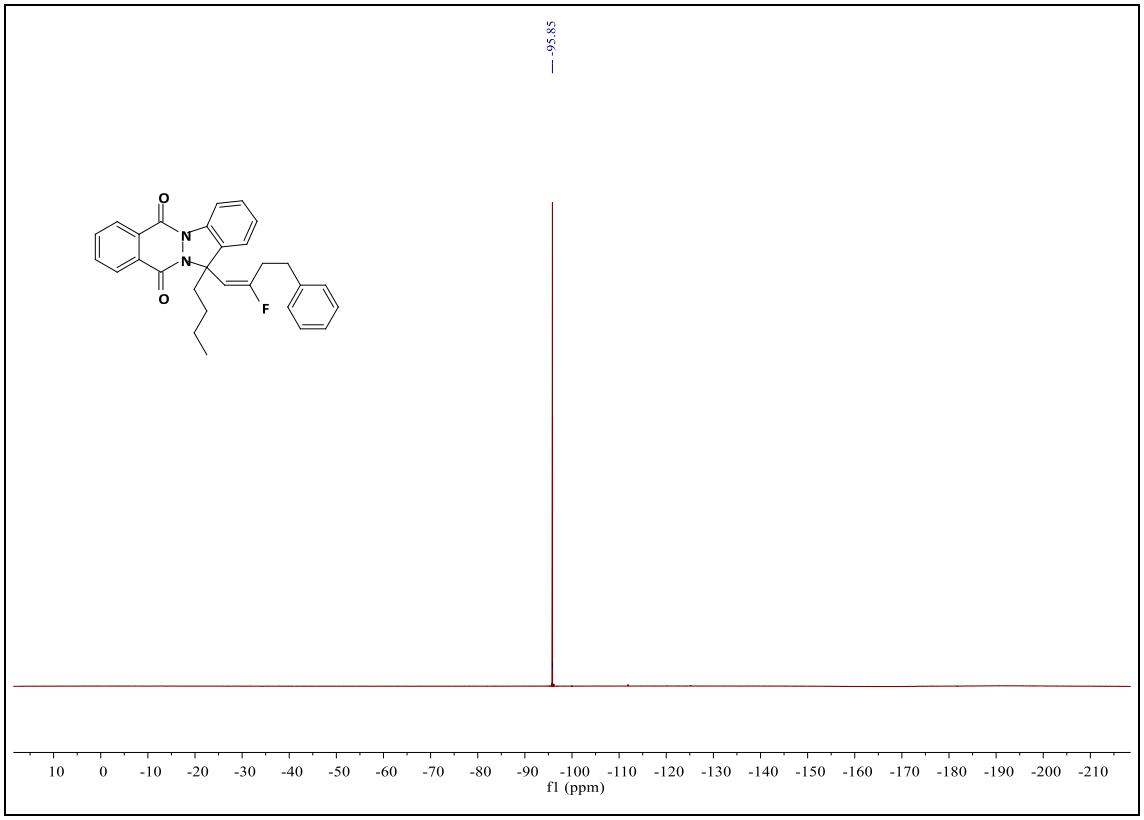
2. S. Rajkumar, S. A. Savarimuthu, R.-S. Kumaran, C. M. Nagarajad and T. Gandhi, *Chem. Commun.,* 2016, **52**, 2509–2512.
3. X. Wu, P. Li, Y. Lu, J. Qiao, J. Zhao, X. Jia, H. Ni, L. Kong, X. Zhang and F. Zhao, *Adv. Synth. Catal*., 2020, **362**, 2953–2960.
4. C.-Q. Wang, L. Ye, C. Feng and T.-P. Loh, *J. Am. Chem. Soc*., 2017, **139**, 1762−1765.
5. P. Karishma, C. K. Mahesha, S. K. Mandal and R. Sakhuja, *J. Org. Chem.,* 2021, **86**, 2734−274.

Copies for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3a)



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O
N
N
O
F
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0
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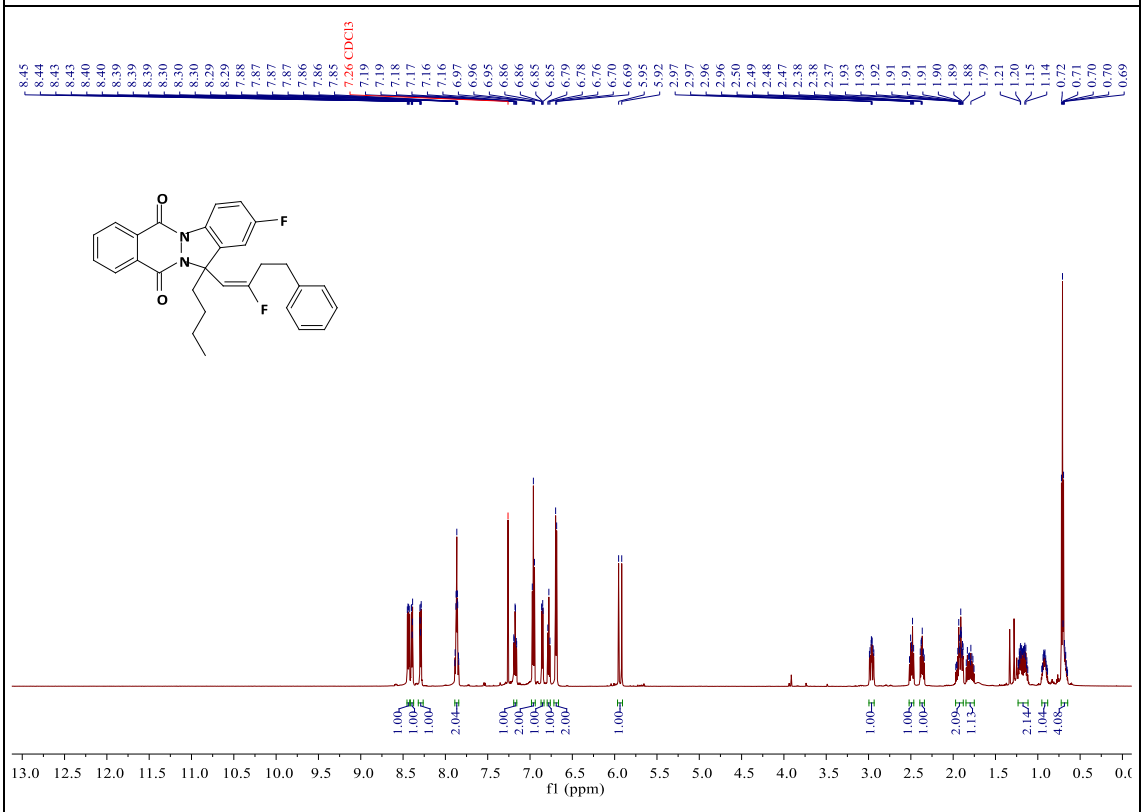
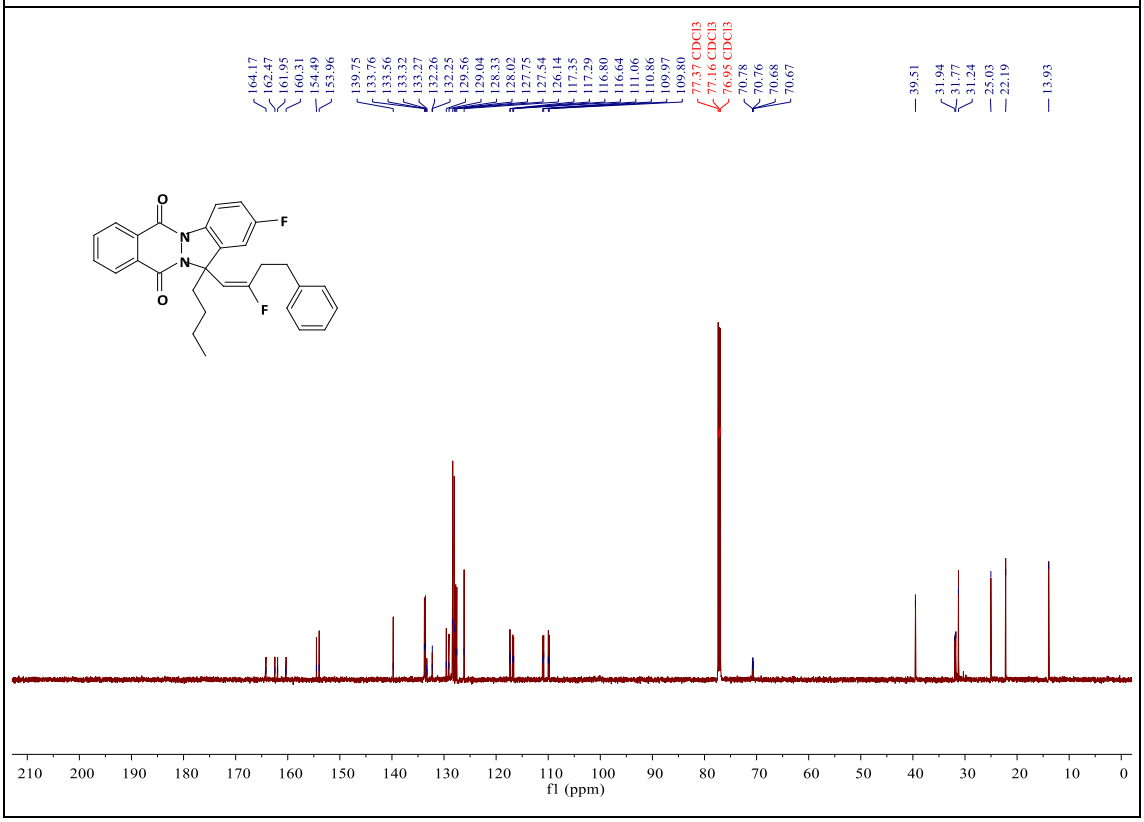
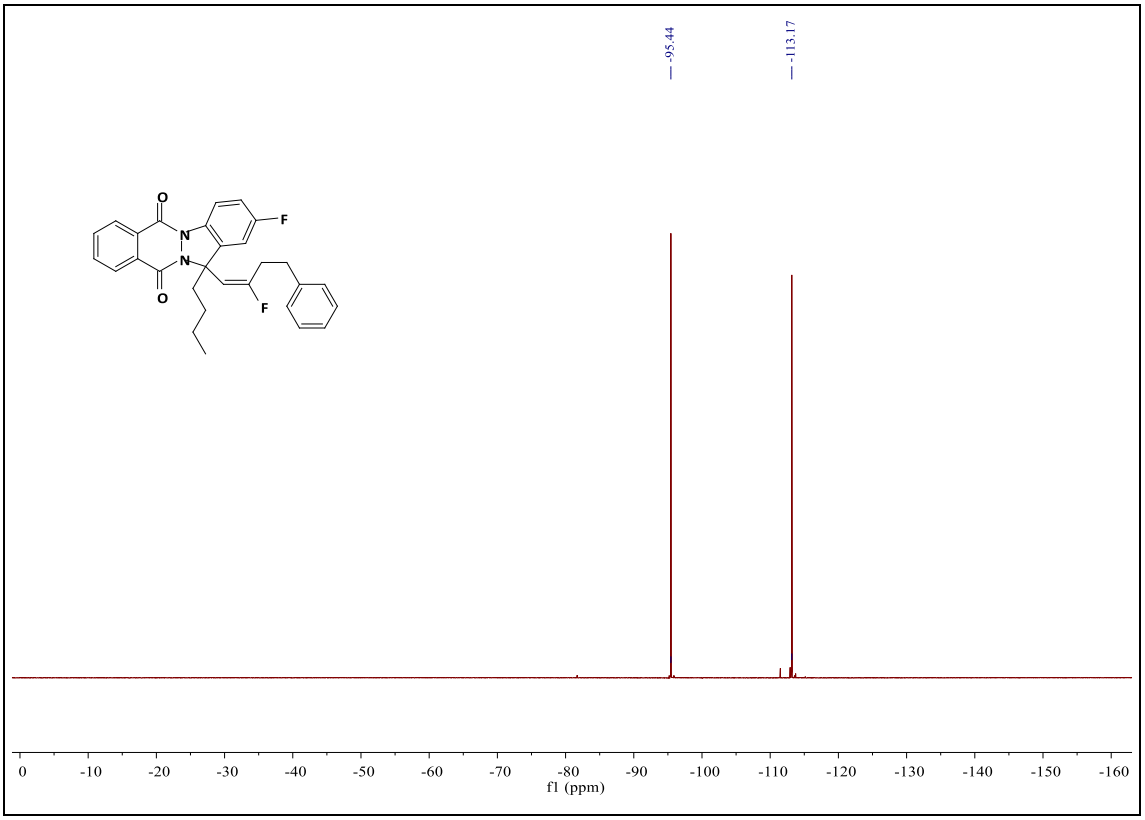
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

(*E*)-13-butyl-2-fluoro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3b)



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F
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-40
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-60
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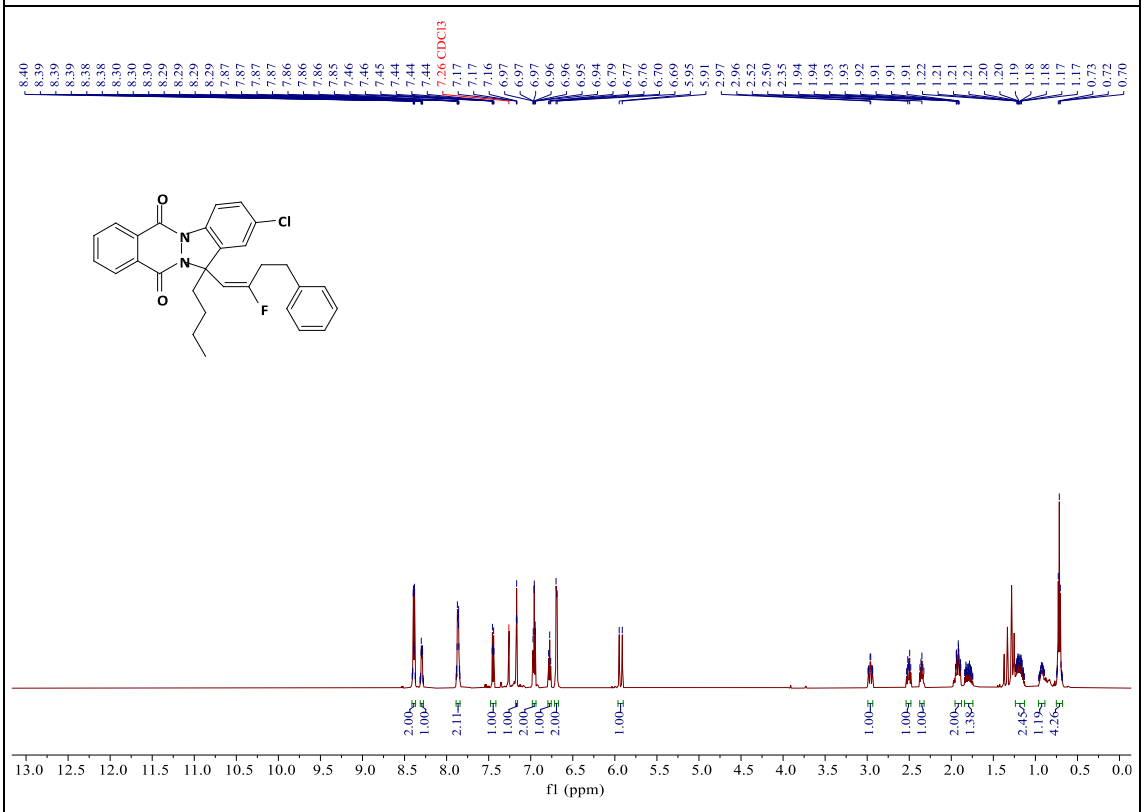
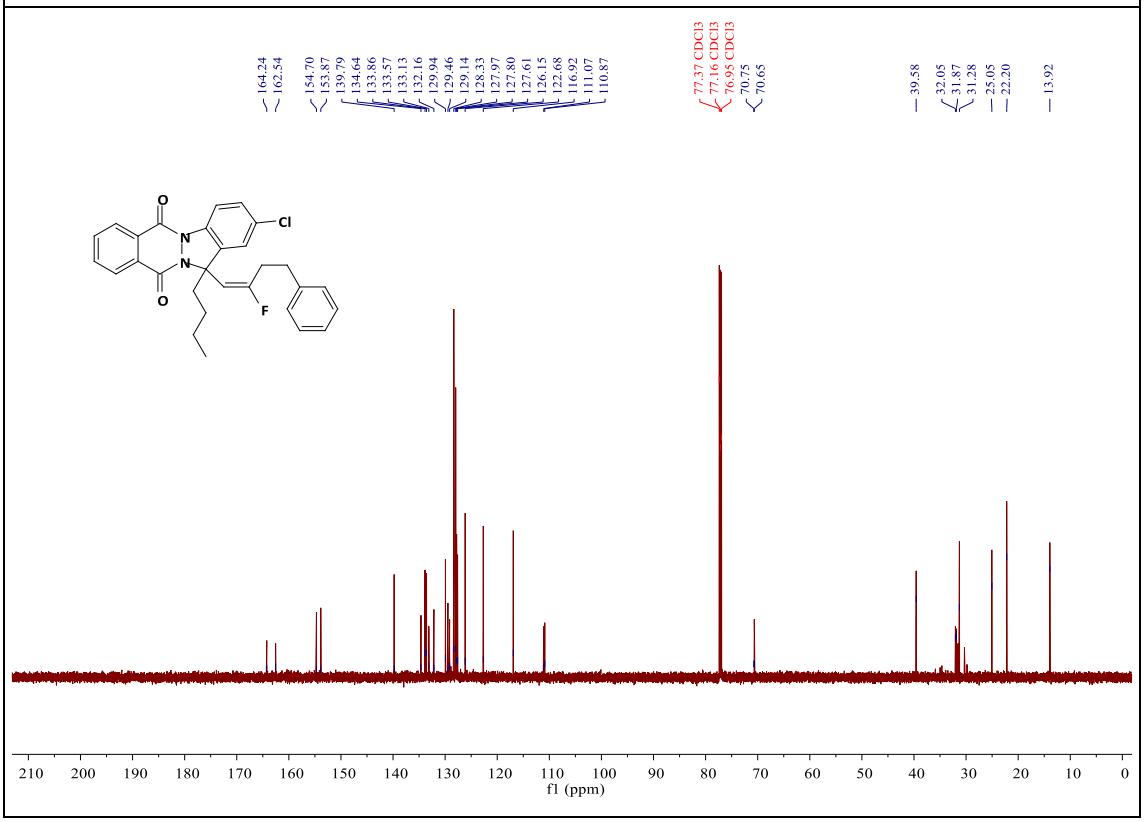
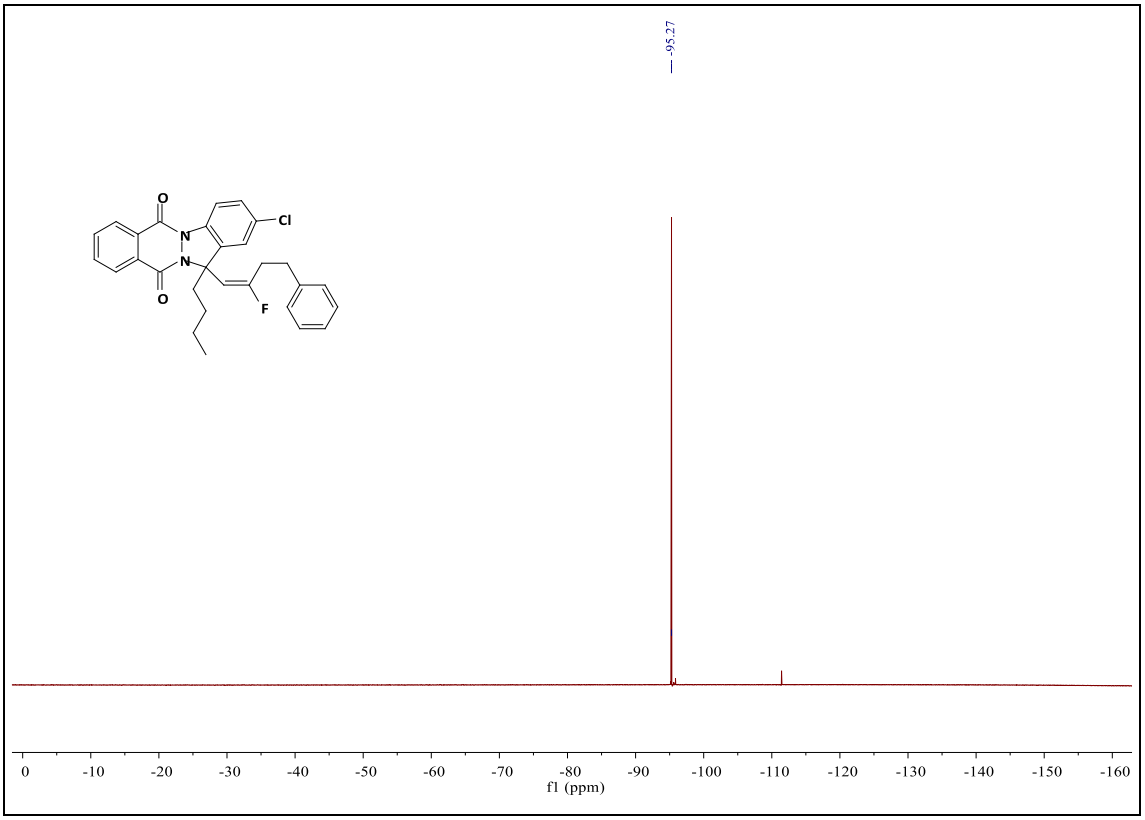
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

(*E*)-13-butyl-2-chloro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3c)



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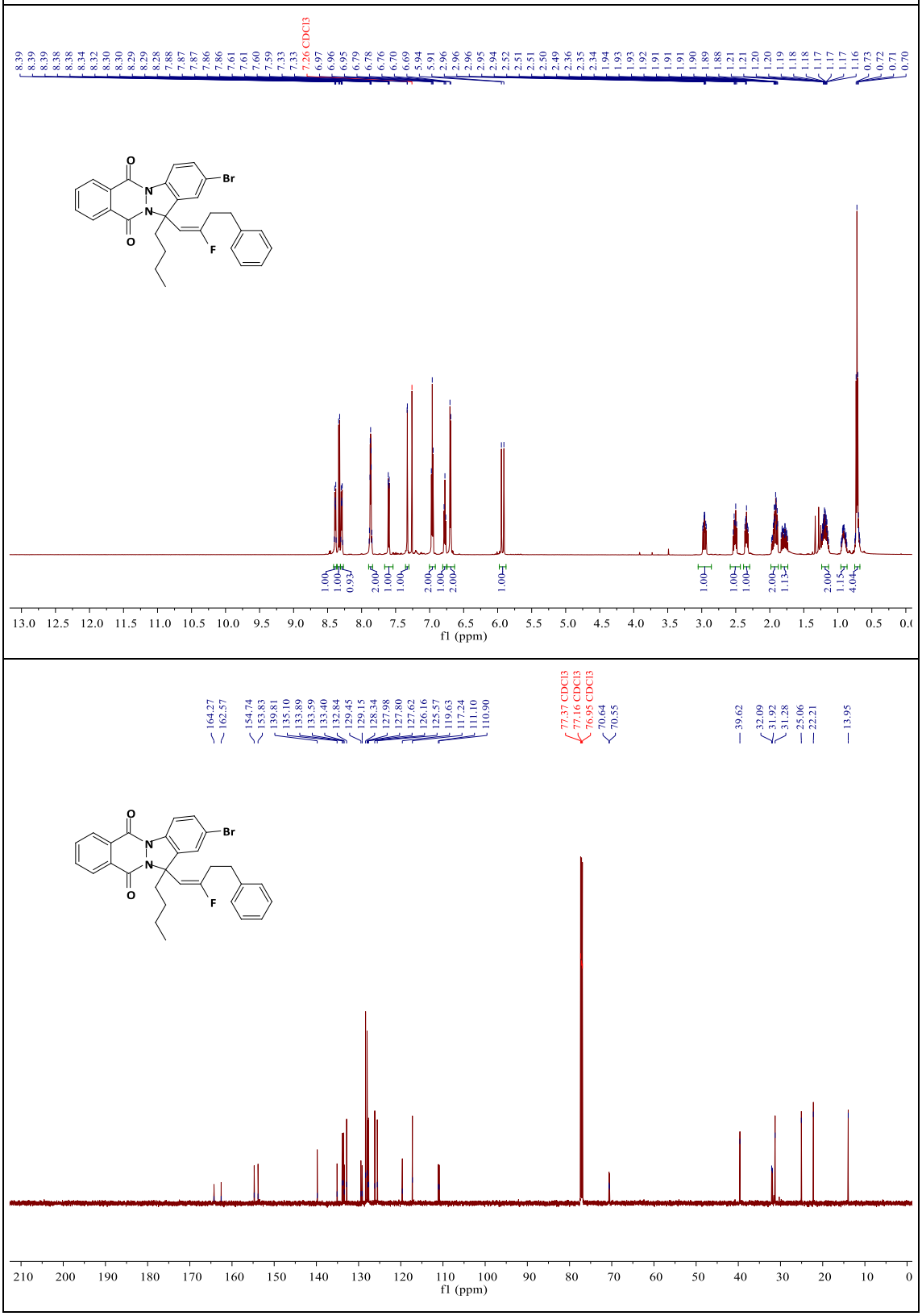
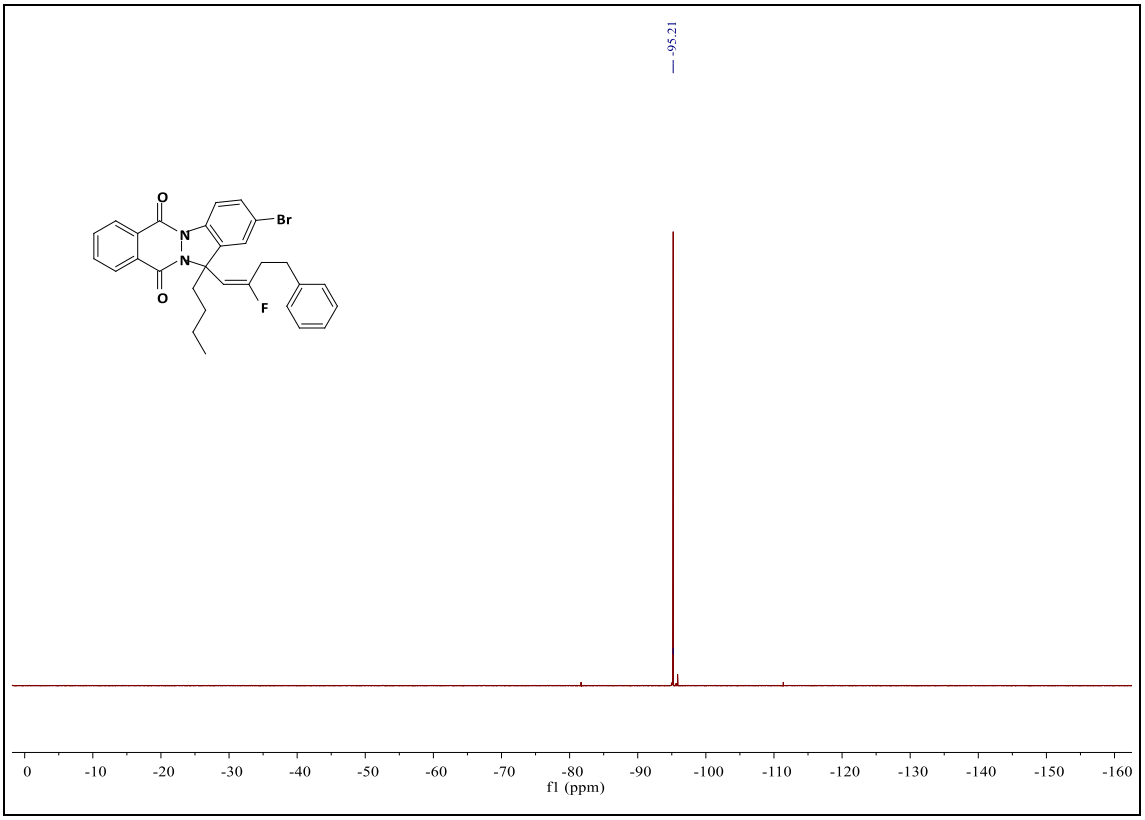
-110
-120
-130
-140
-150
-160
f1 (ppm)

(*E*)-2-bromo-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3d)

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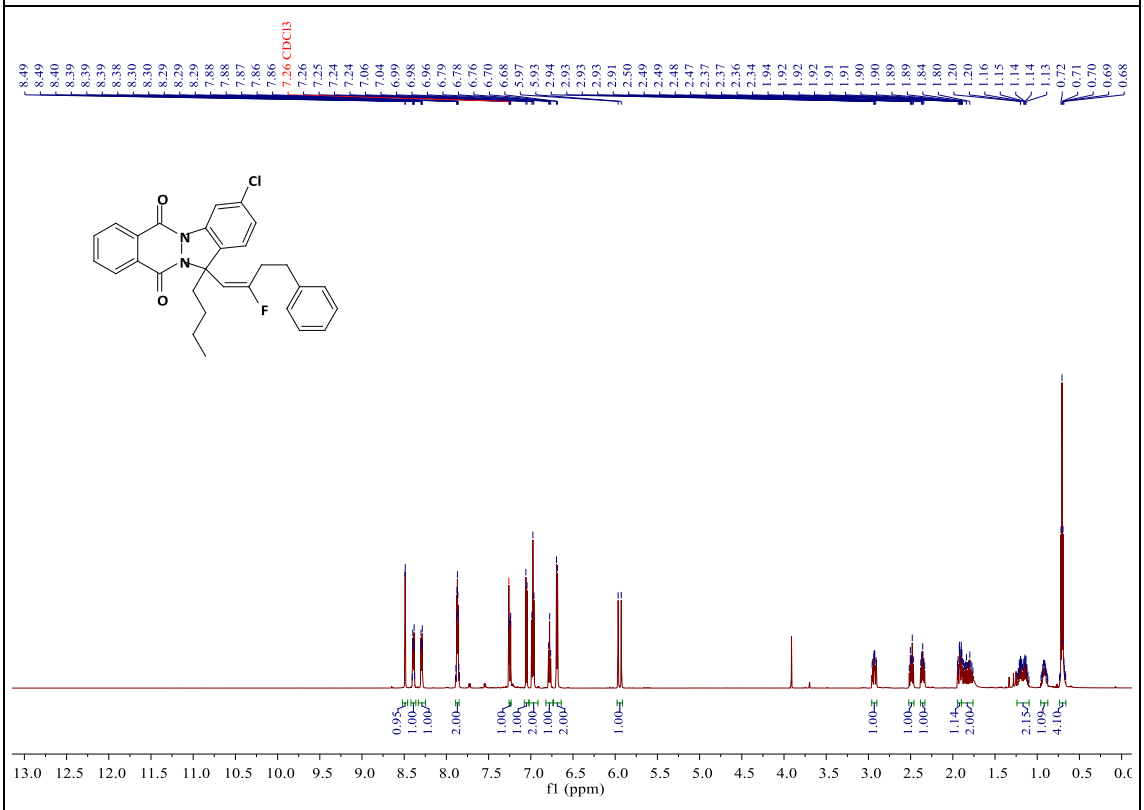
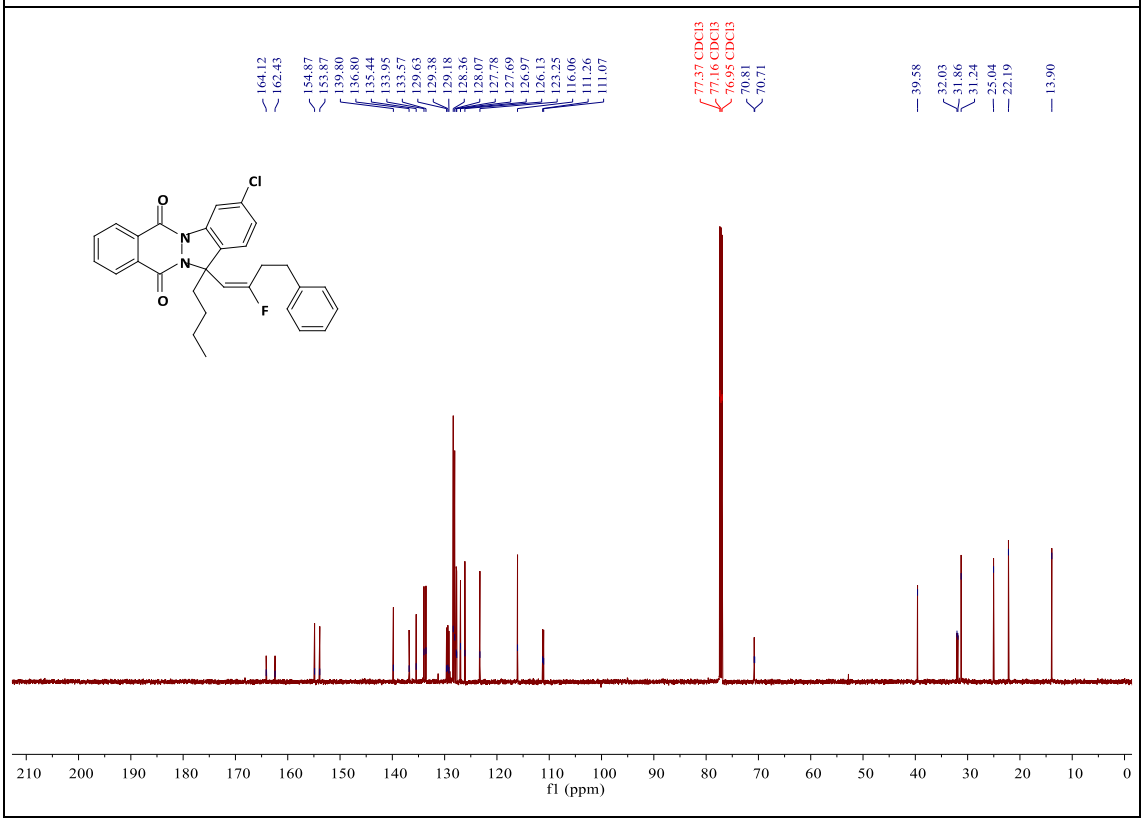
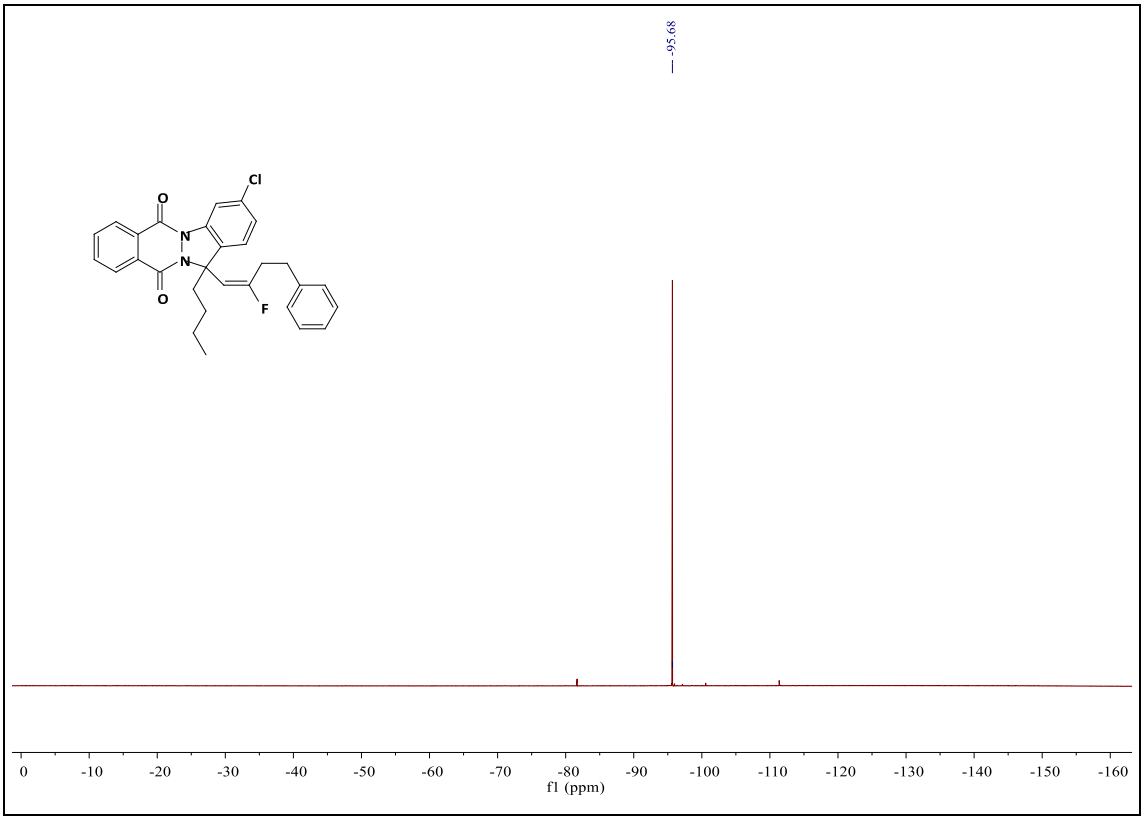
O
N
N
O
Br
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

(*E*)-13-butyl-3-chloro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3e)



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-110
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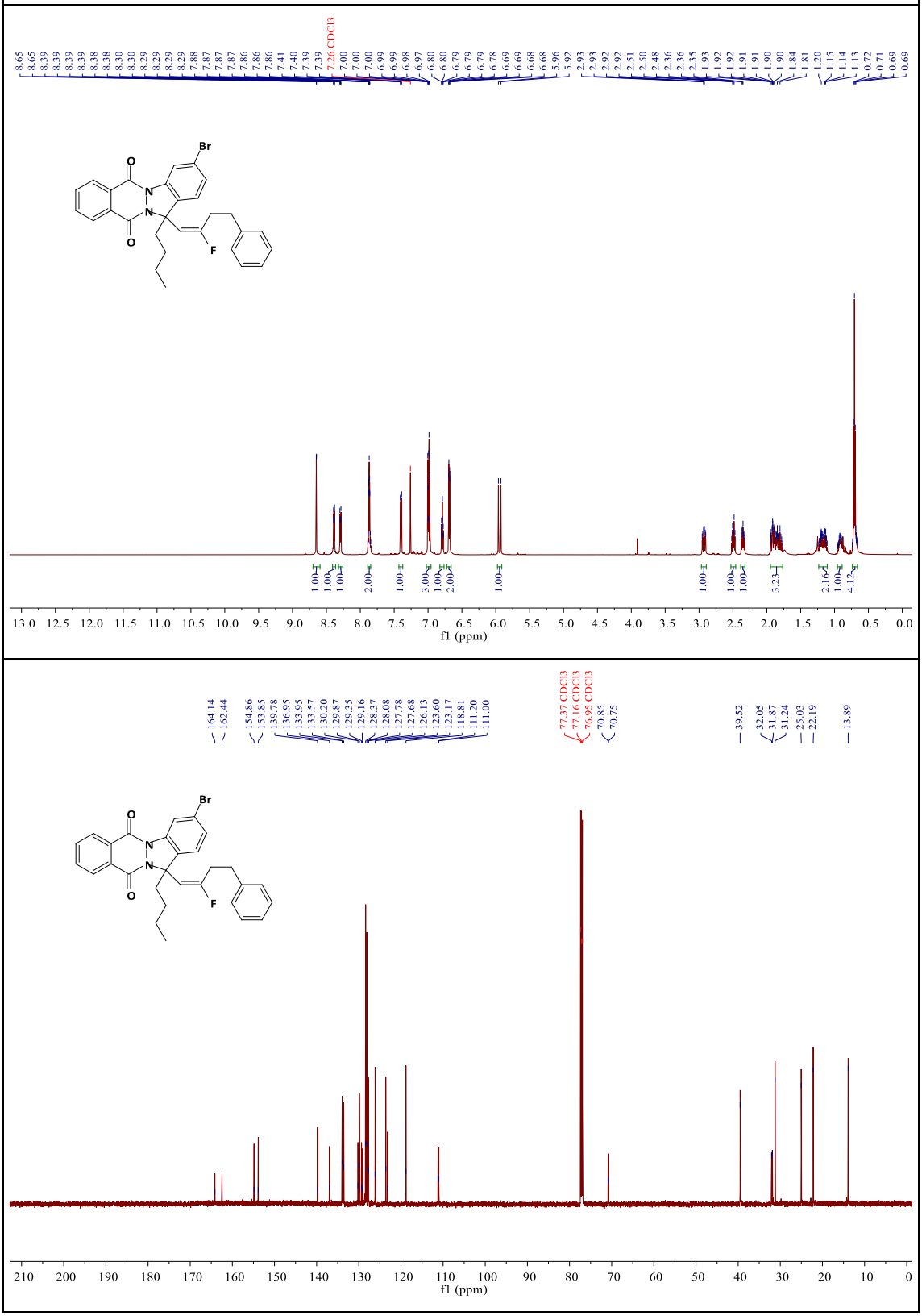
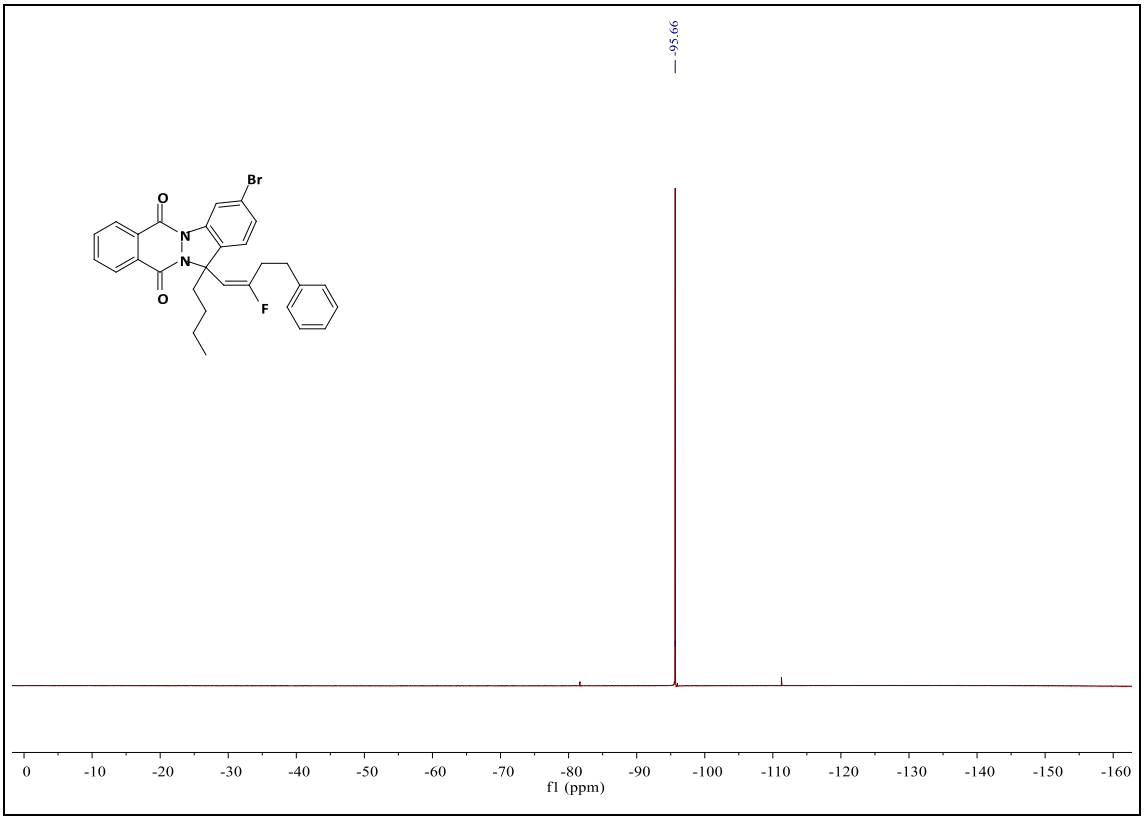
-130
-140
-150
-160
f1 (ppm)

(*E*)-3-bromo-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3f)

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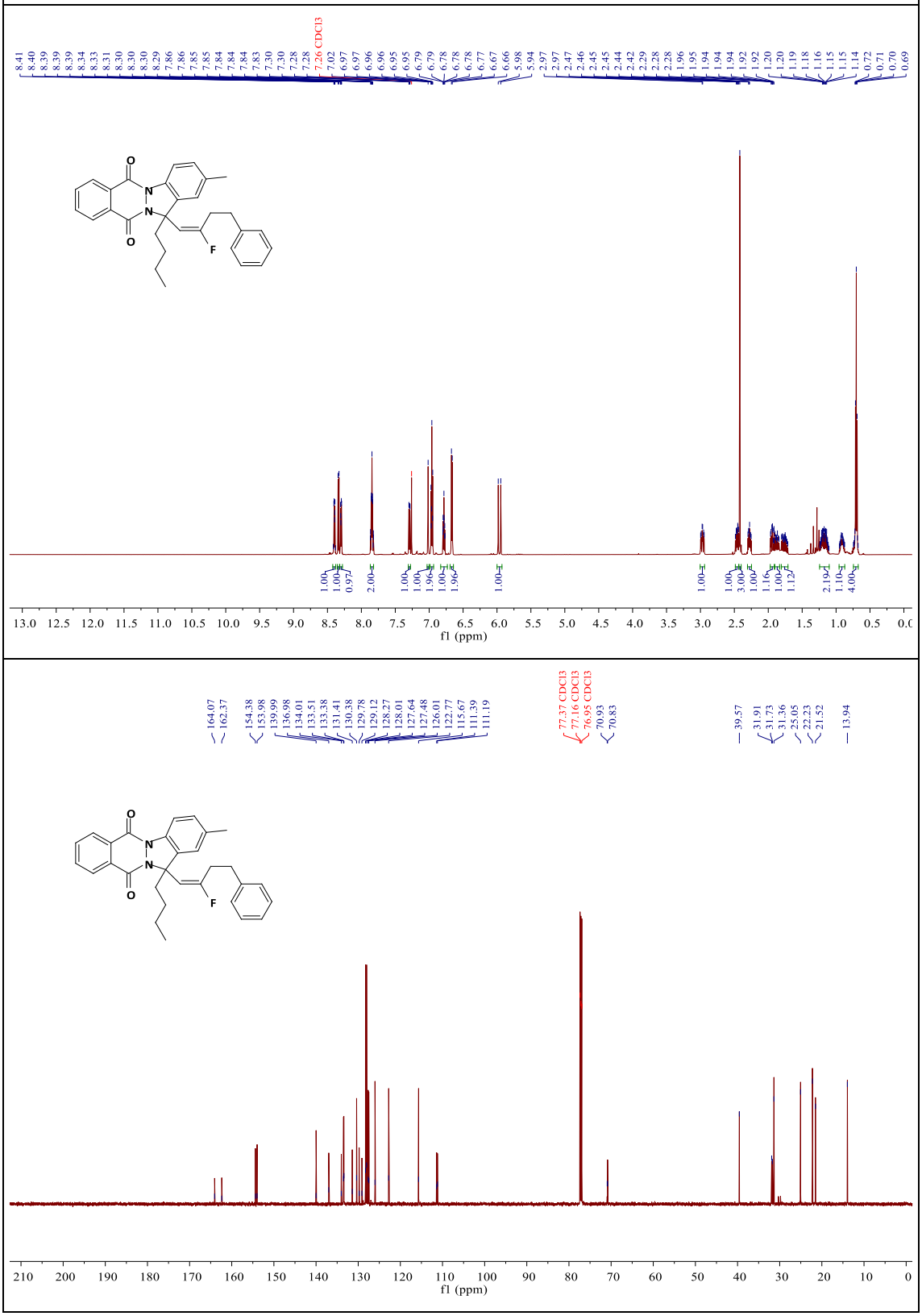
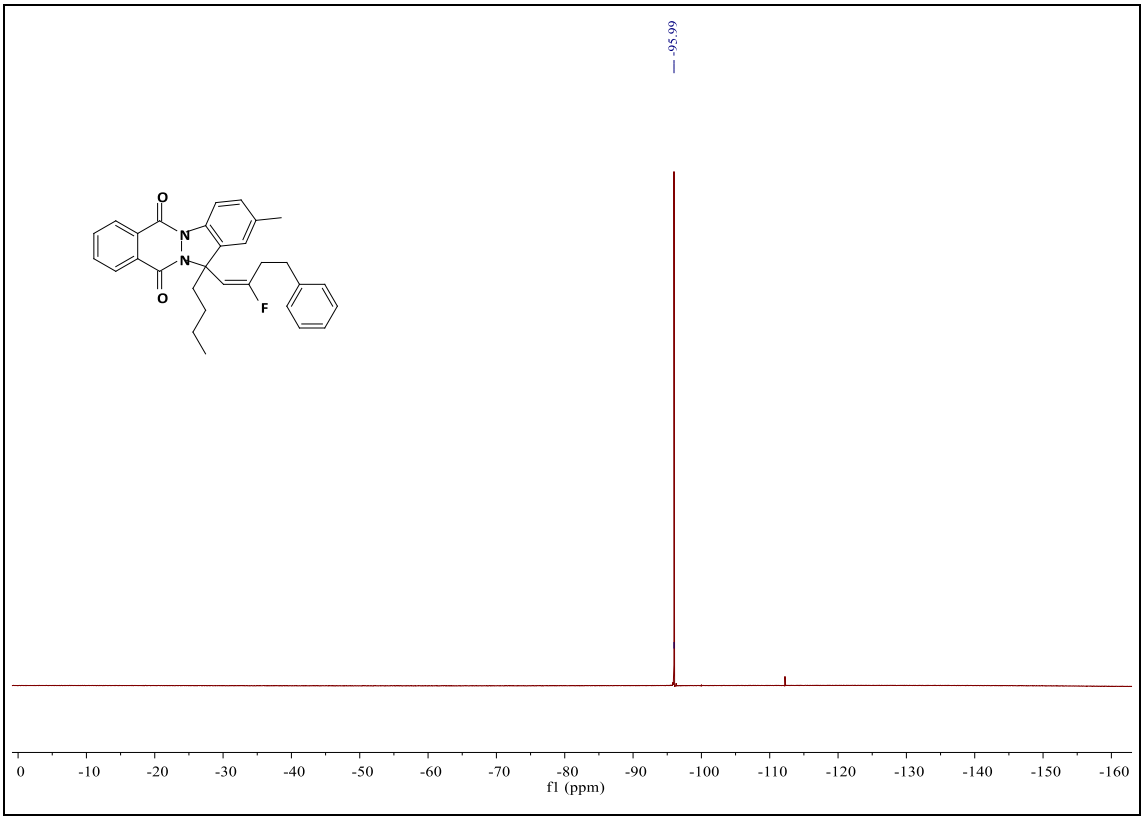
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-2-methyl-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3h)

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-110
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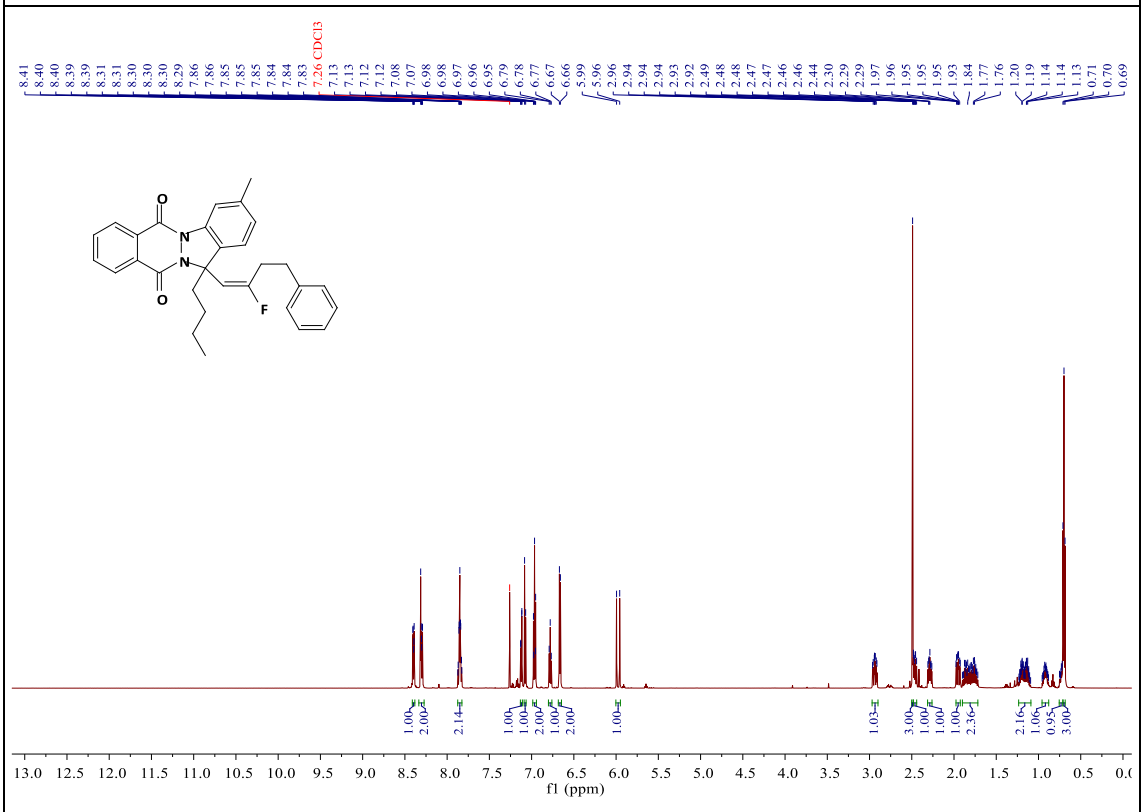
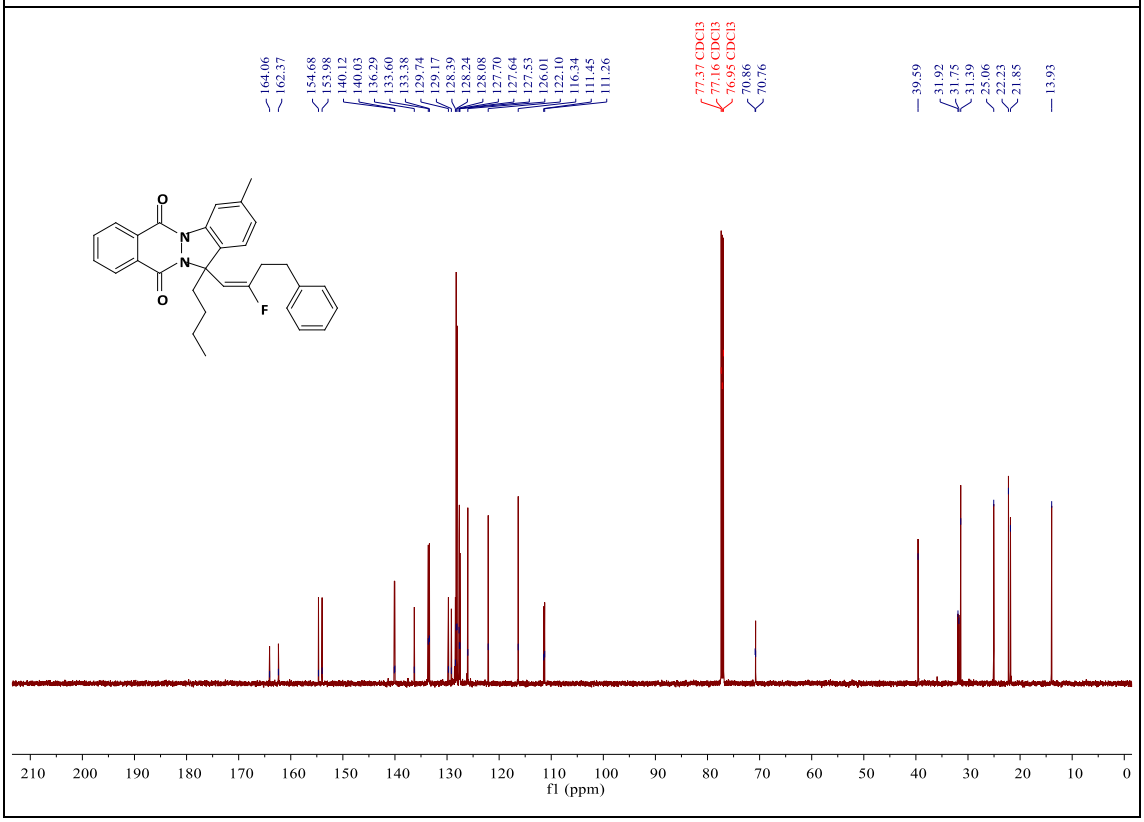
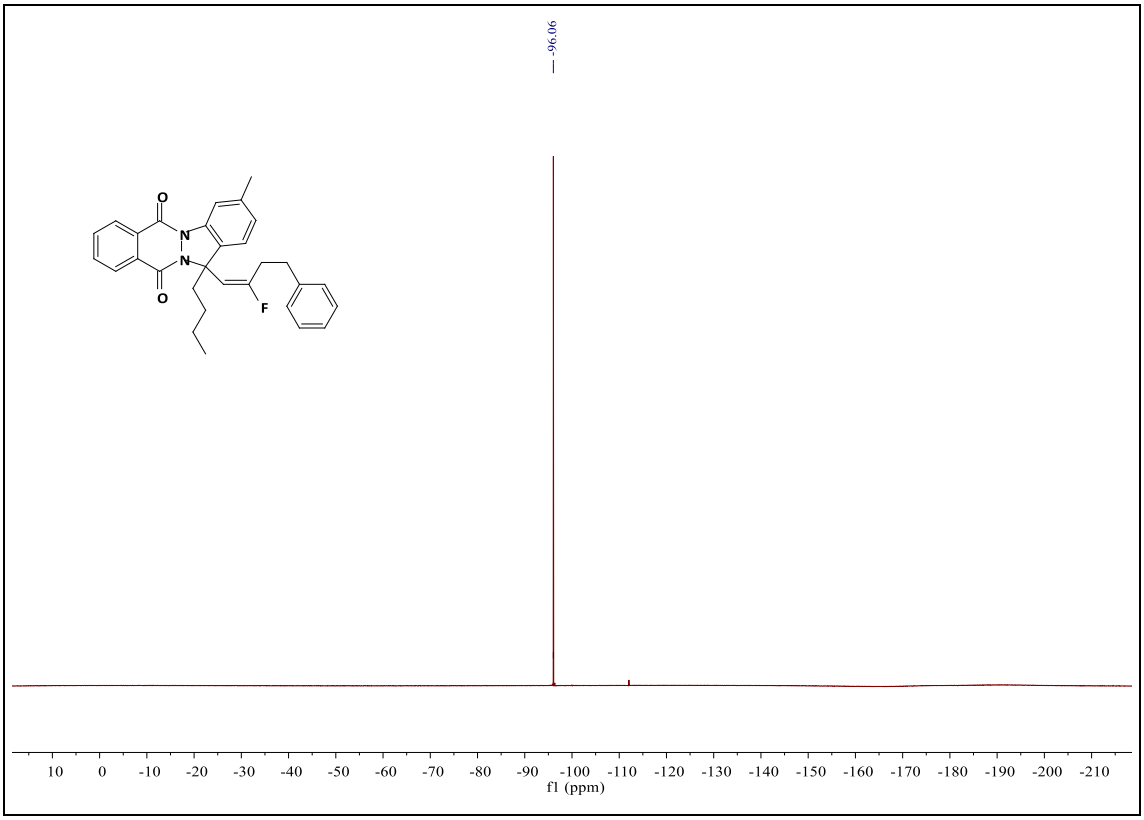
-130
-140
-150
-160
f1 (ppm)

(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-3-methyl-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3i)



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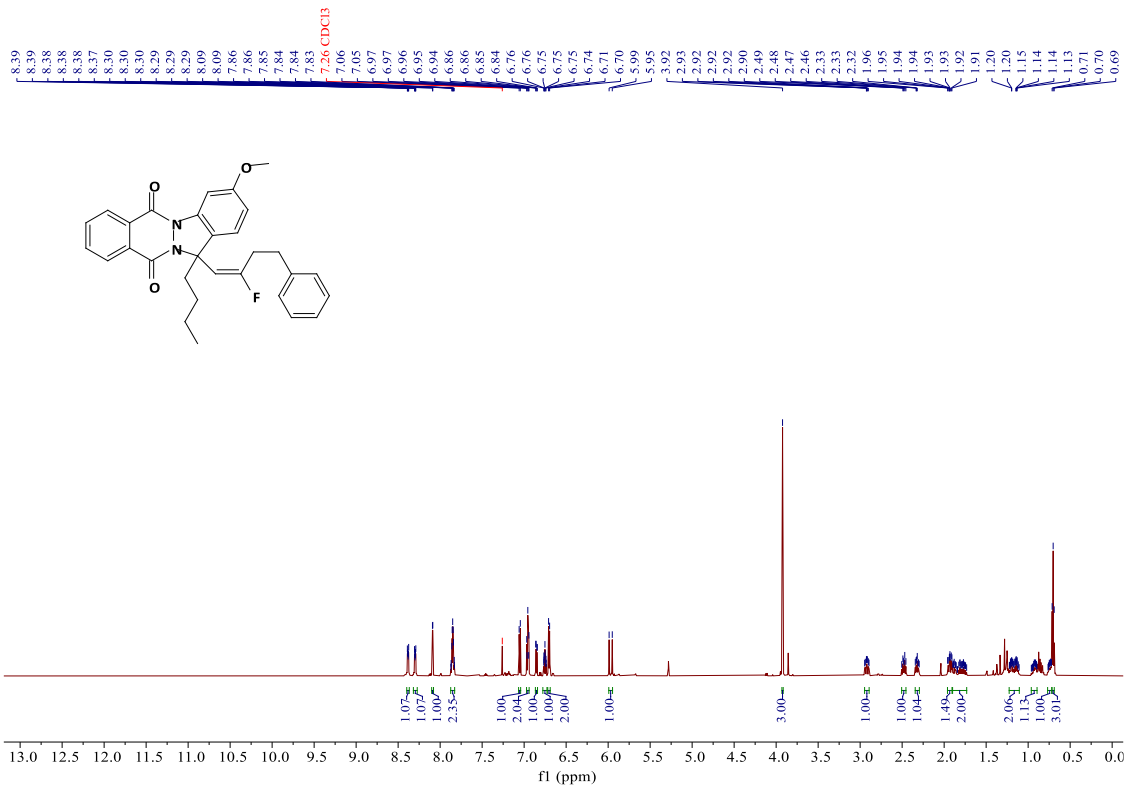
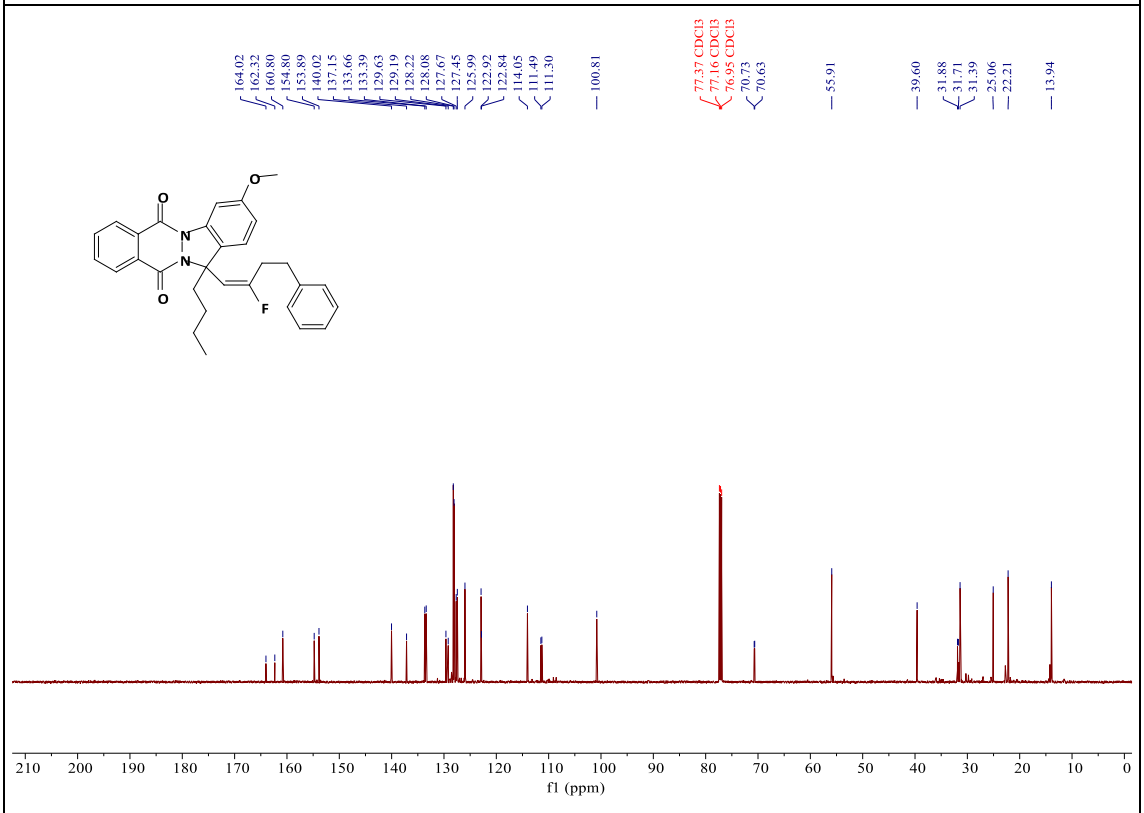
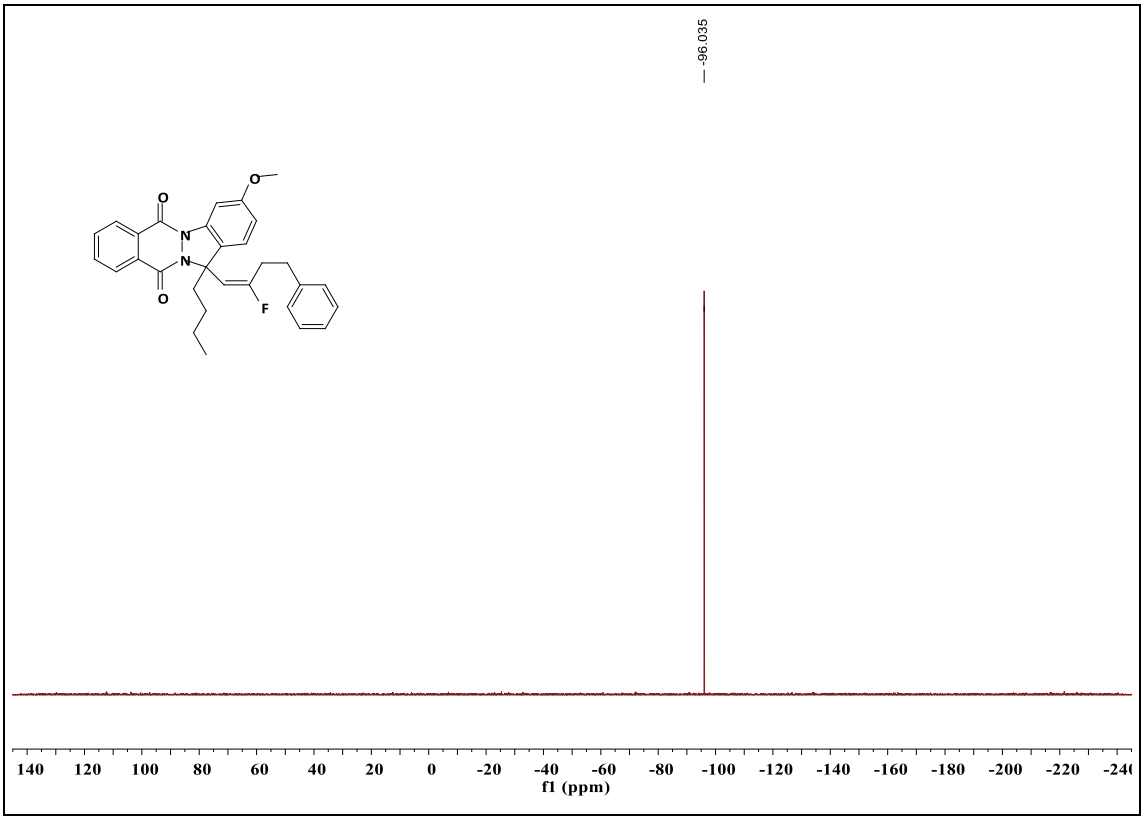
N
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-3-methoxy-13*H*-indazolo[1,2-b]phthalazine-6,11-dione (3j)



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O
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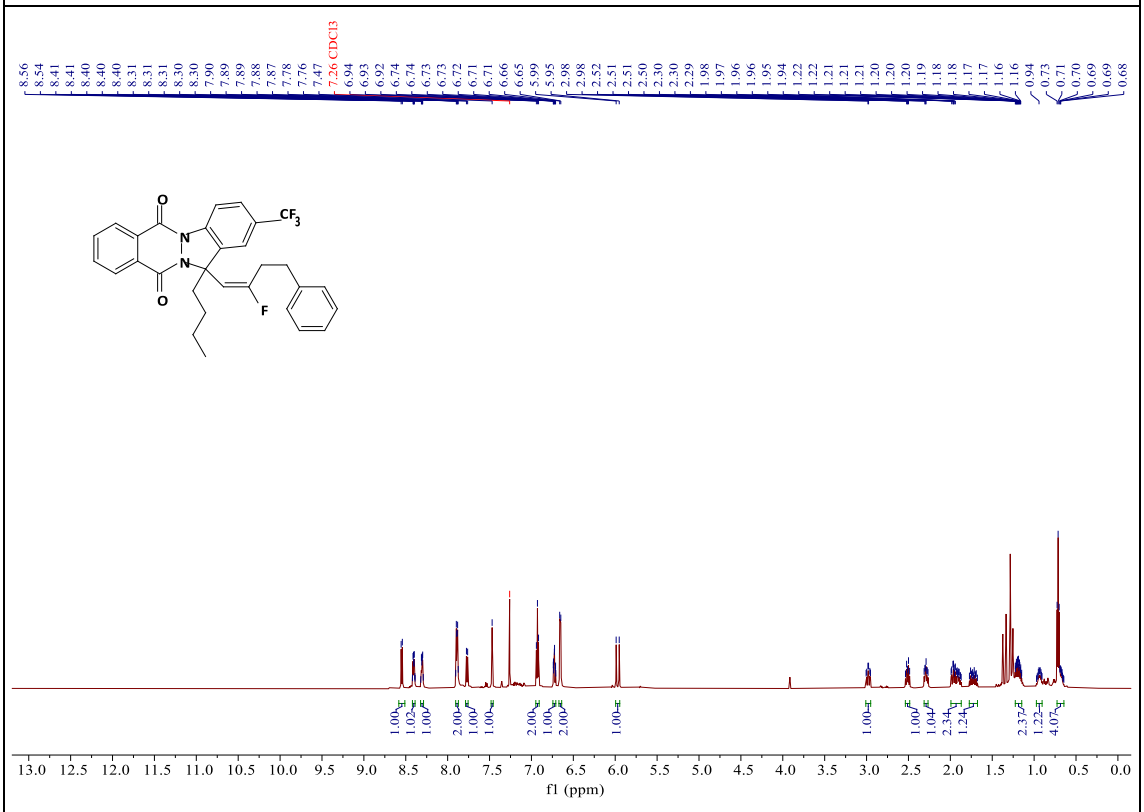
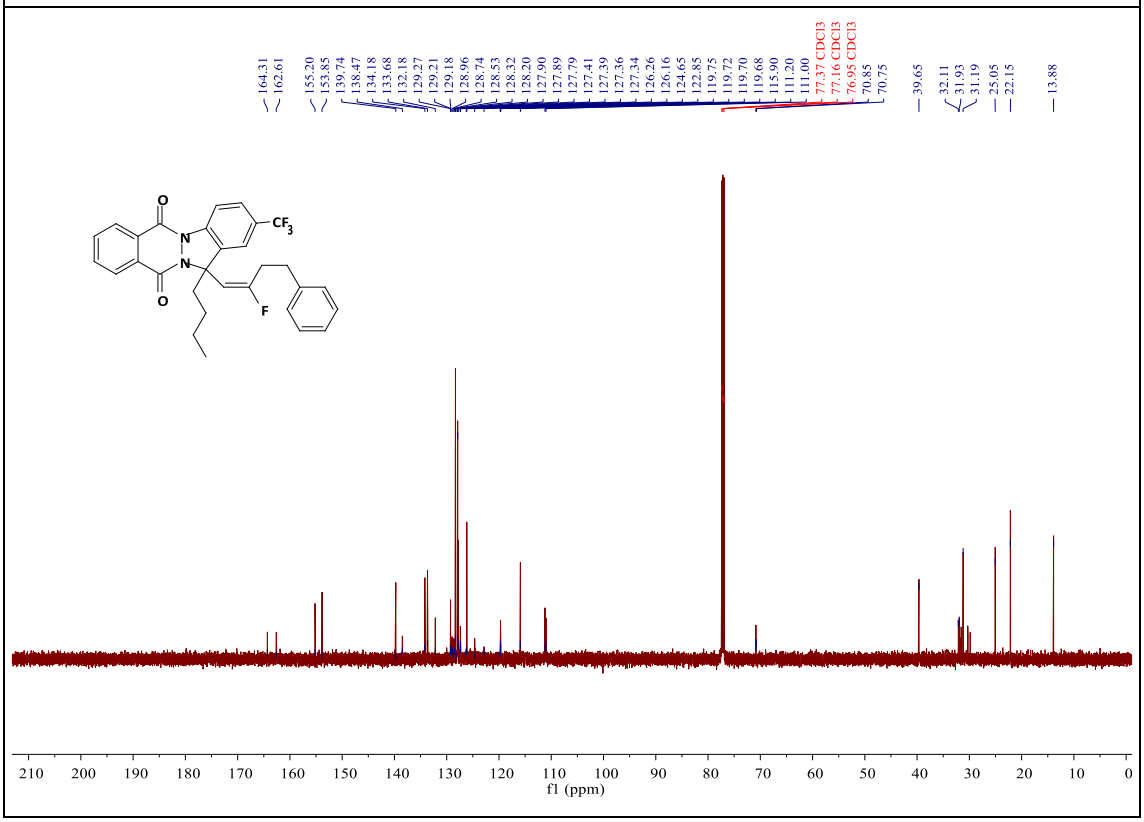
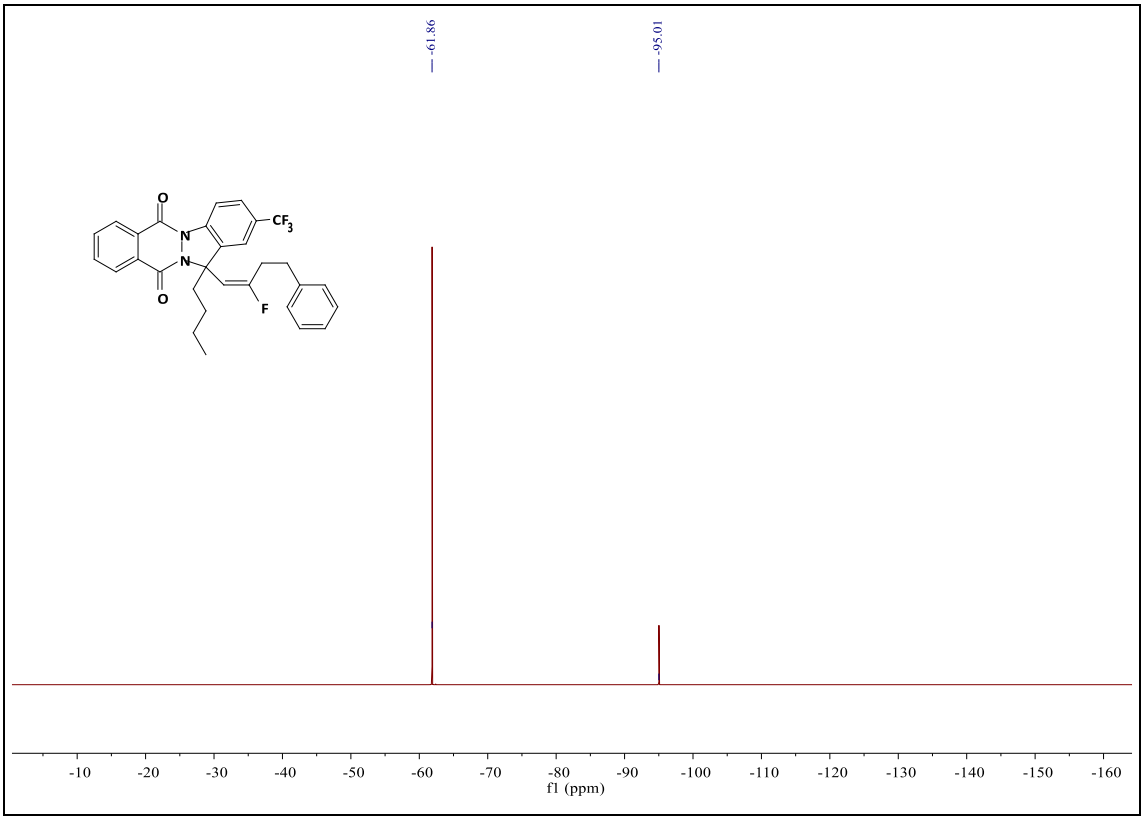
N
N
O
F
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220
f1 (ppm)

(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-2-(trifluoromethyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3l)



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N
O
CF3
F
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-30
-40
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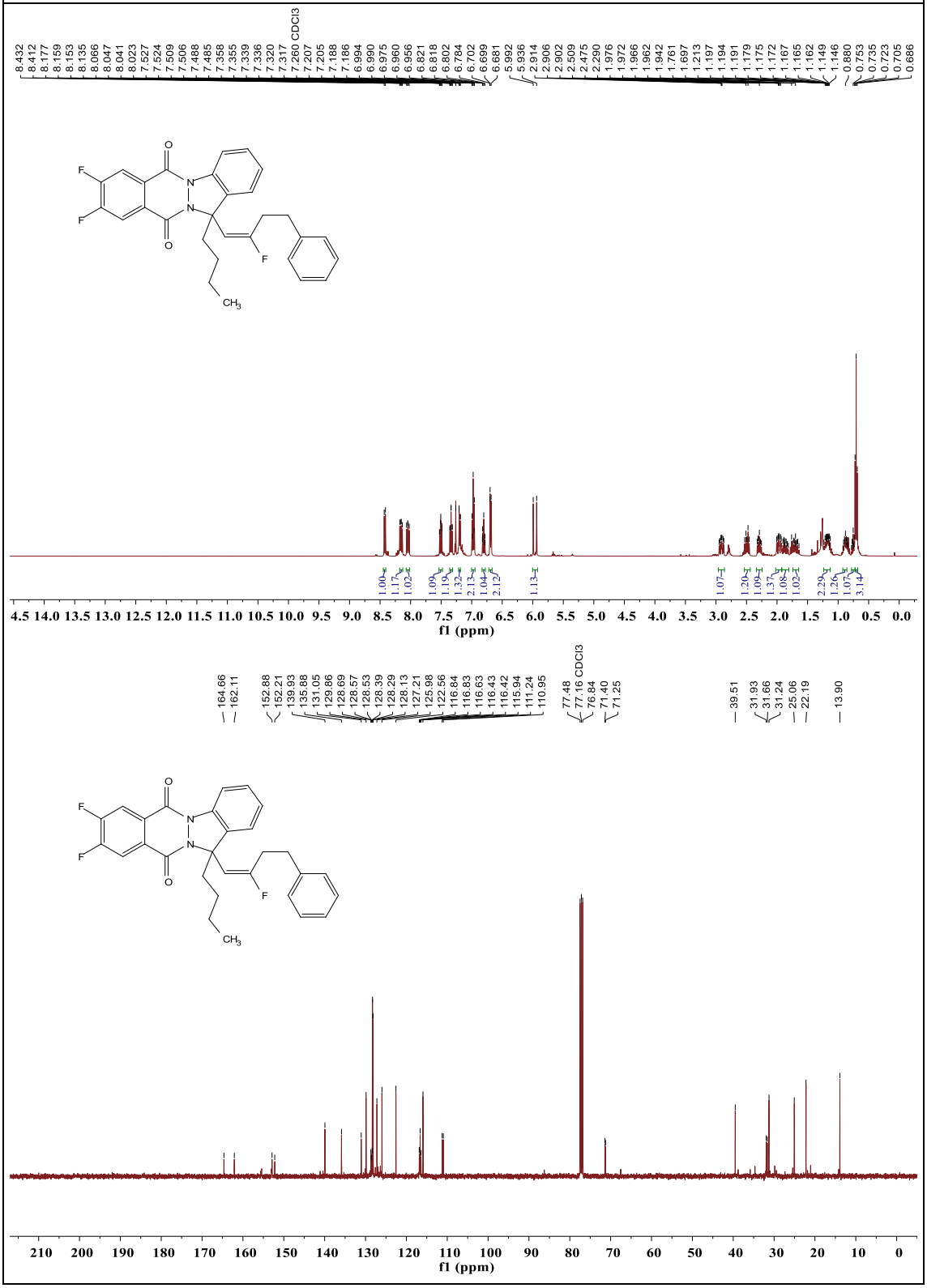
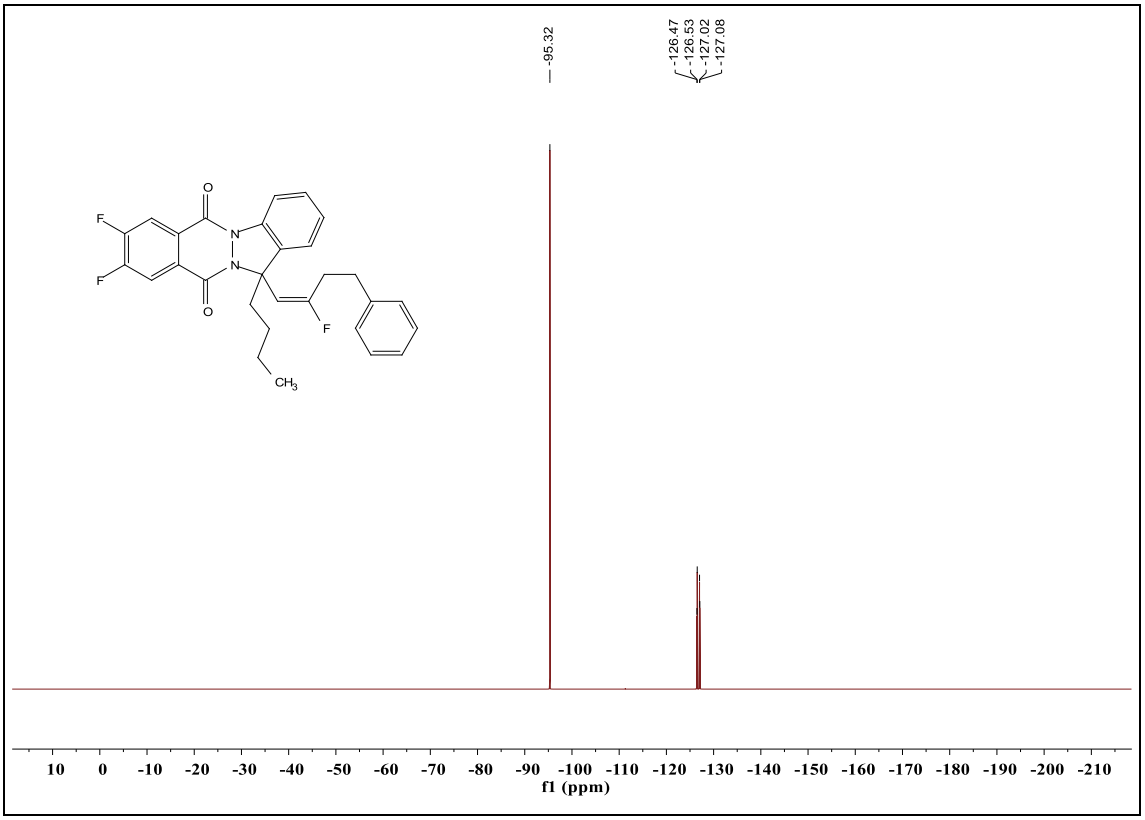
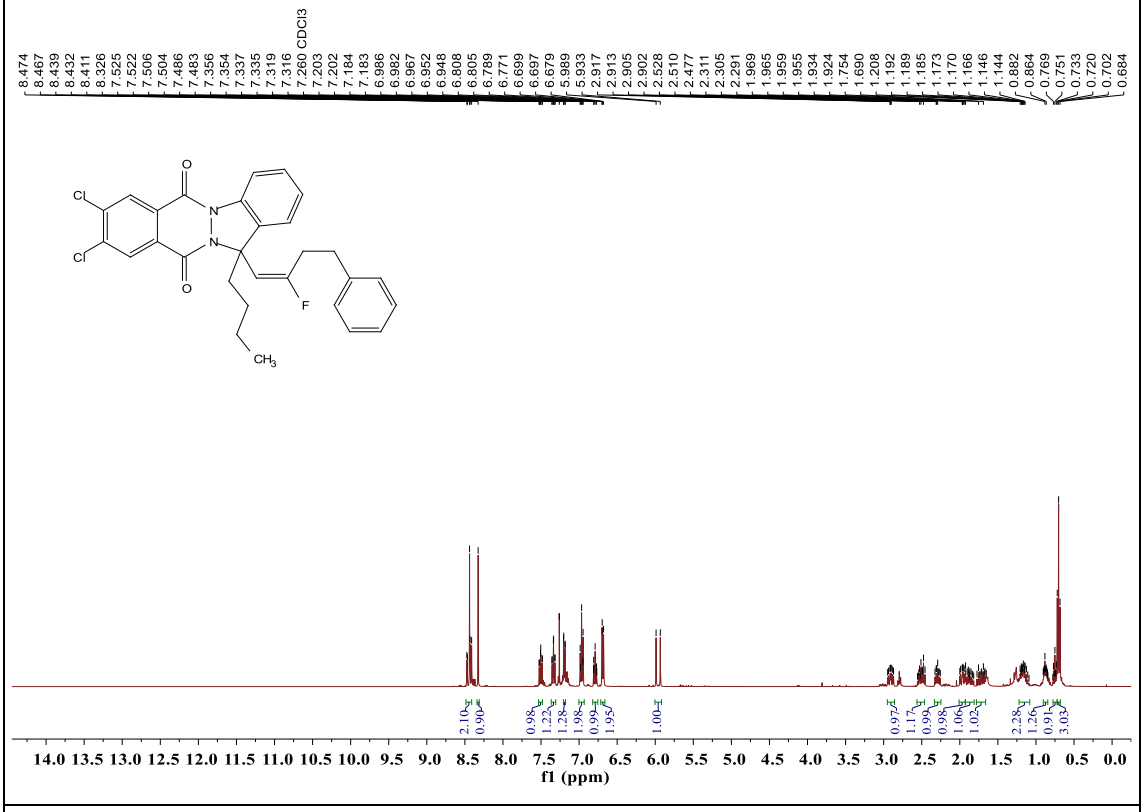
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

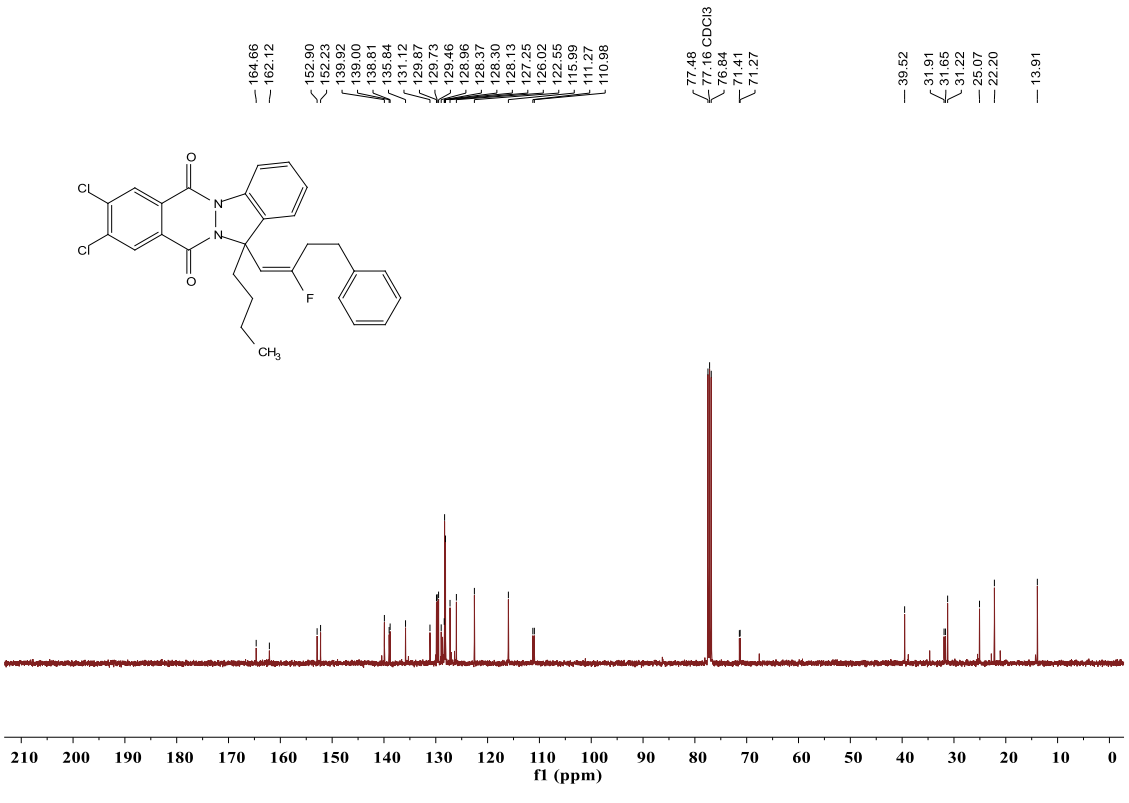
(*E*)-13-butyl-8,9-difluoro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3m)

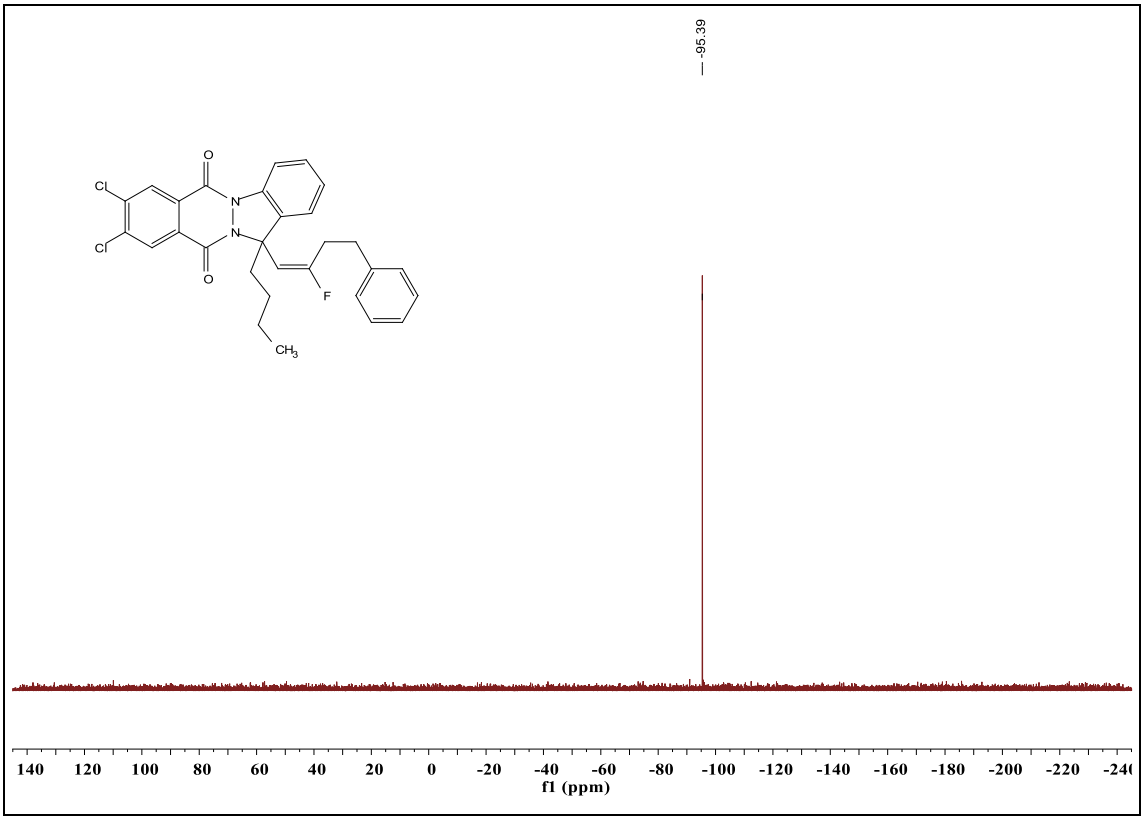



-95.32
-126.47
-126.53
-127.02
-127.08
O
F
F
N
N
O
F
CH3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

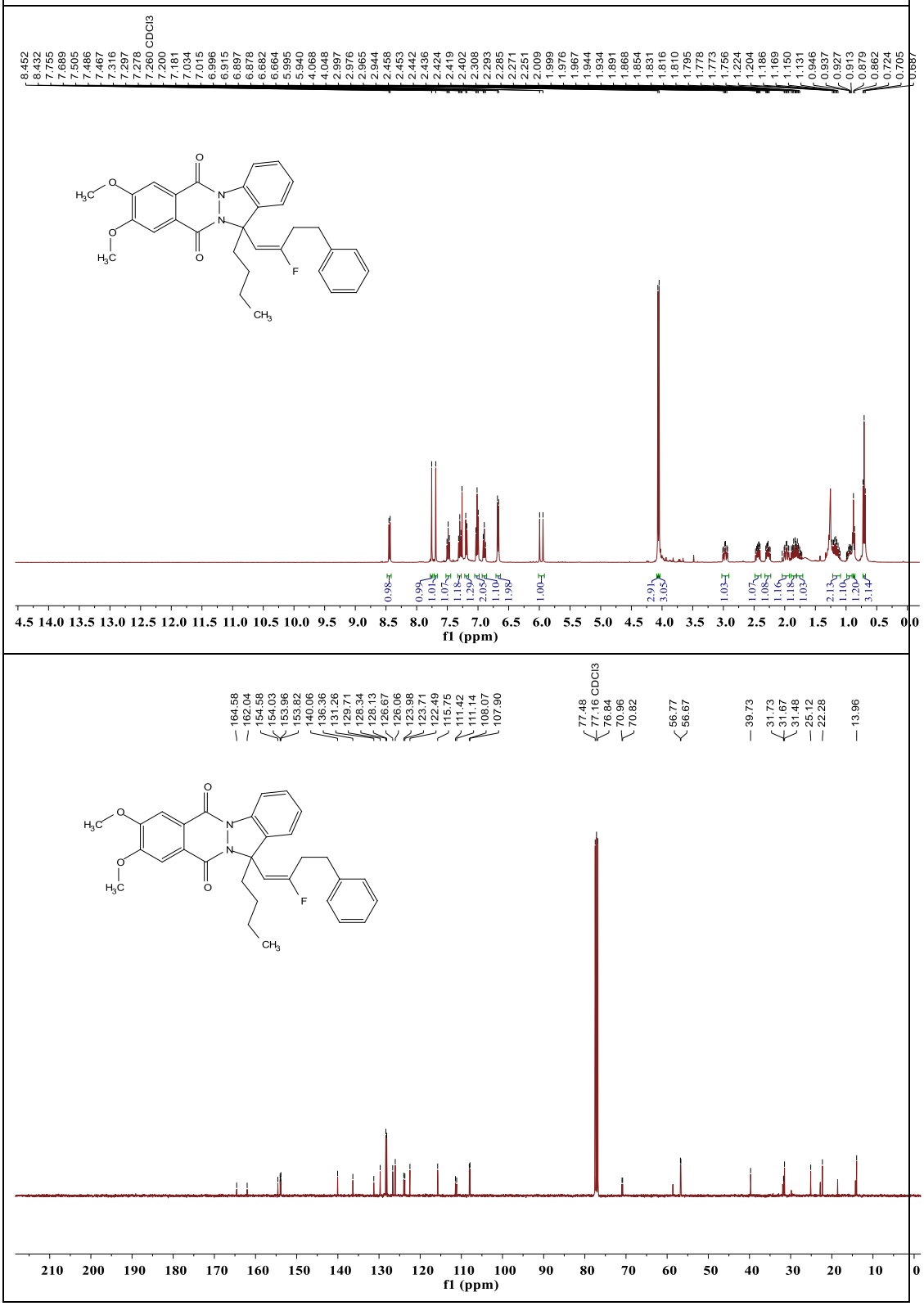
(*E*)-13-butyl-8,9-dichloro-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13H-indazolo[1,2-*b*]phthalazine-6,11-dione (3n)

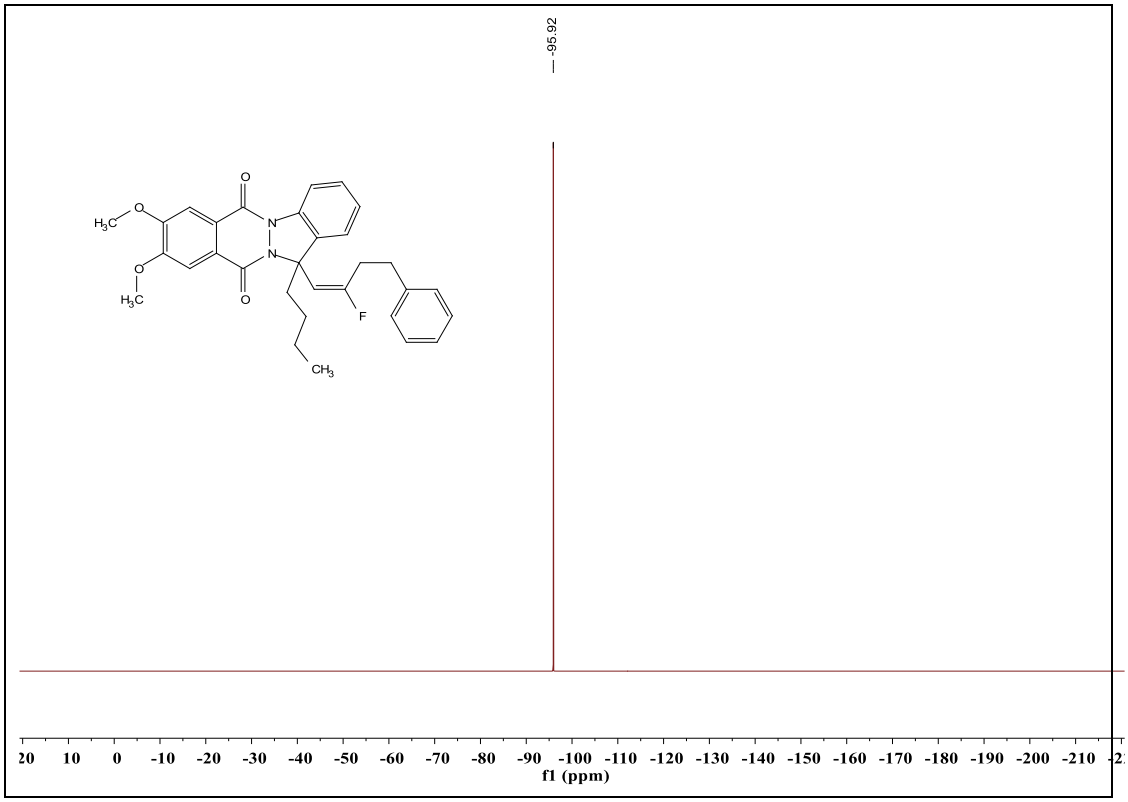




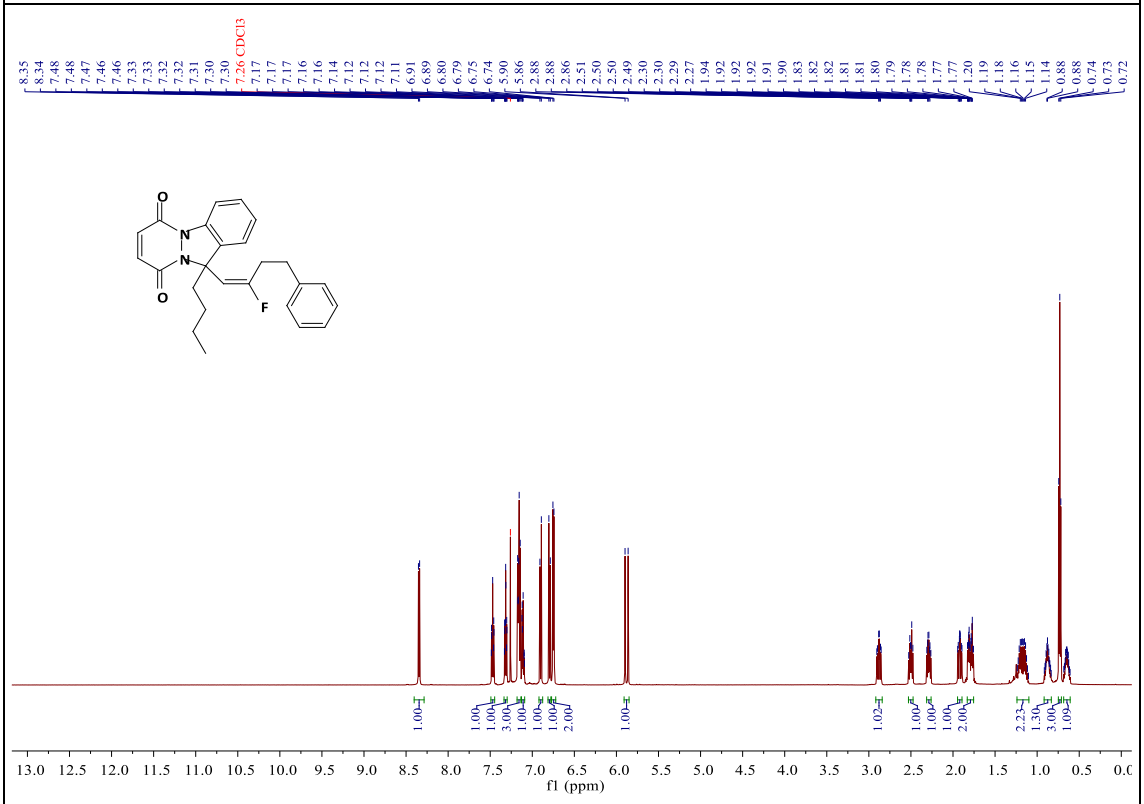

-95.39
O
Cl
Cl
N
N
O
F
CH3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220
f1 (ppm)

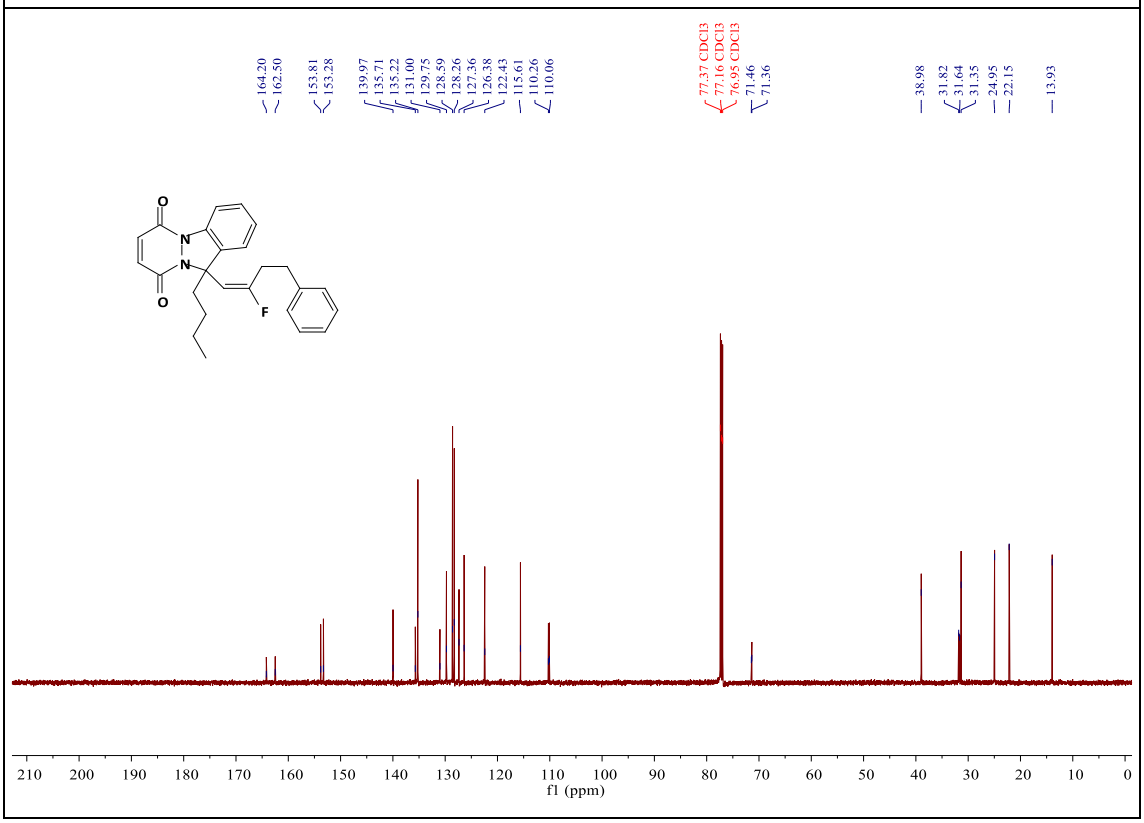
(*E*)-13-butyl-13-(2-fluoro-4-phenylbut-1-en-1-yl)-8,9-dimethoxy-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3o)

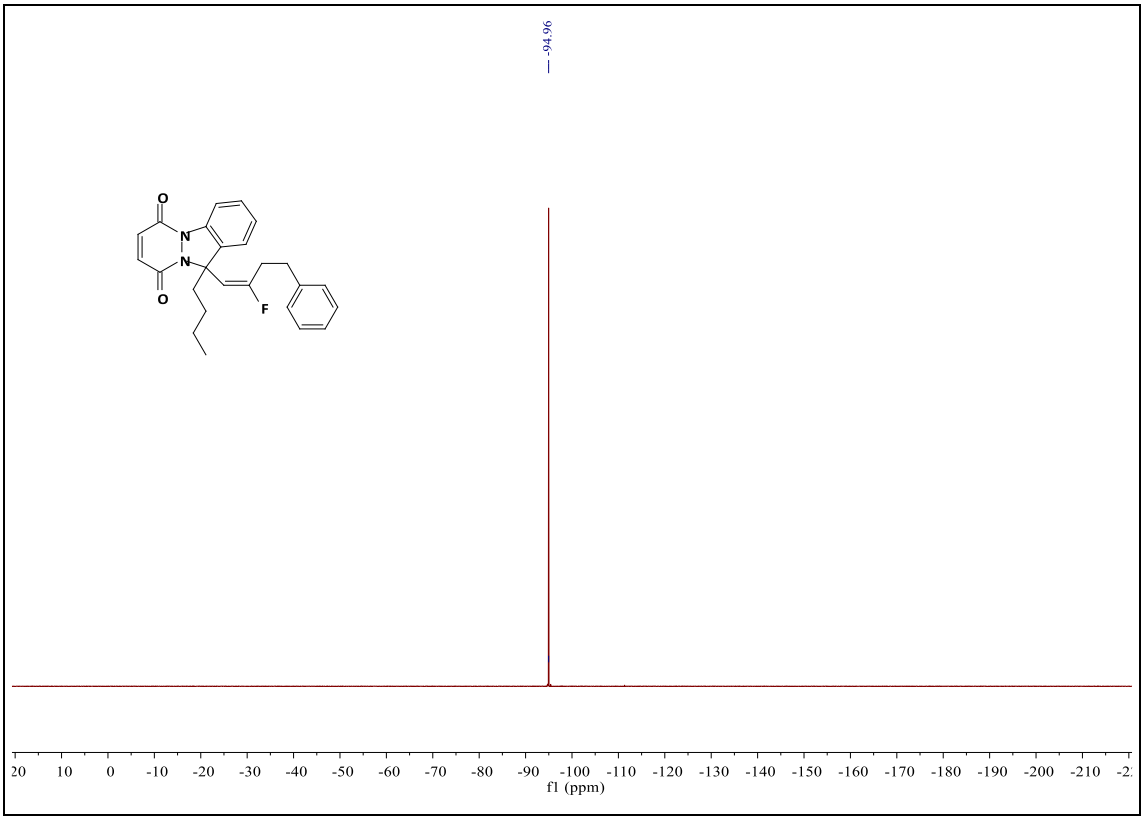



-95.92
O
O
H3C
O
H3C
N
N
O
F
CH3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

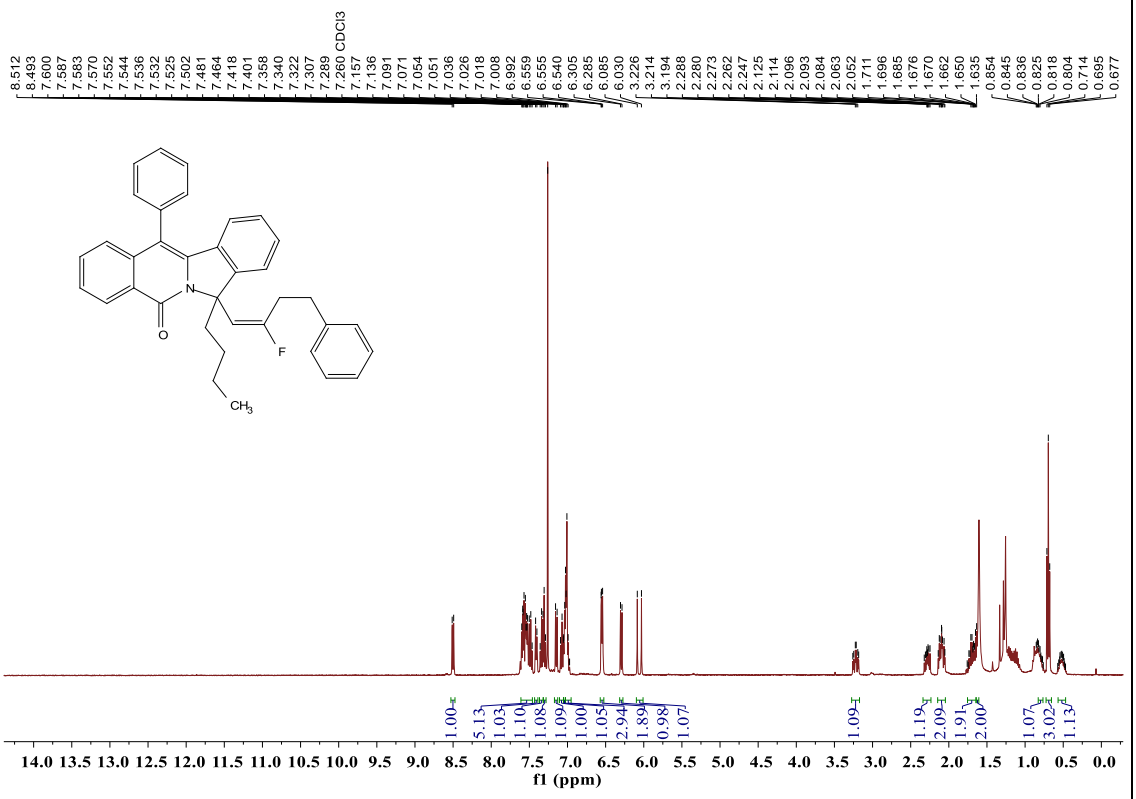
(*E*)-11-butyl-11-(2-fluoro-4-phenylbut-1-en-1-yl)-11*H*-pyridazino[1,2-a]indazole-6,9-dione (3p)

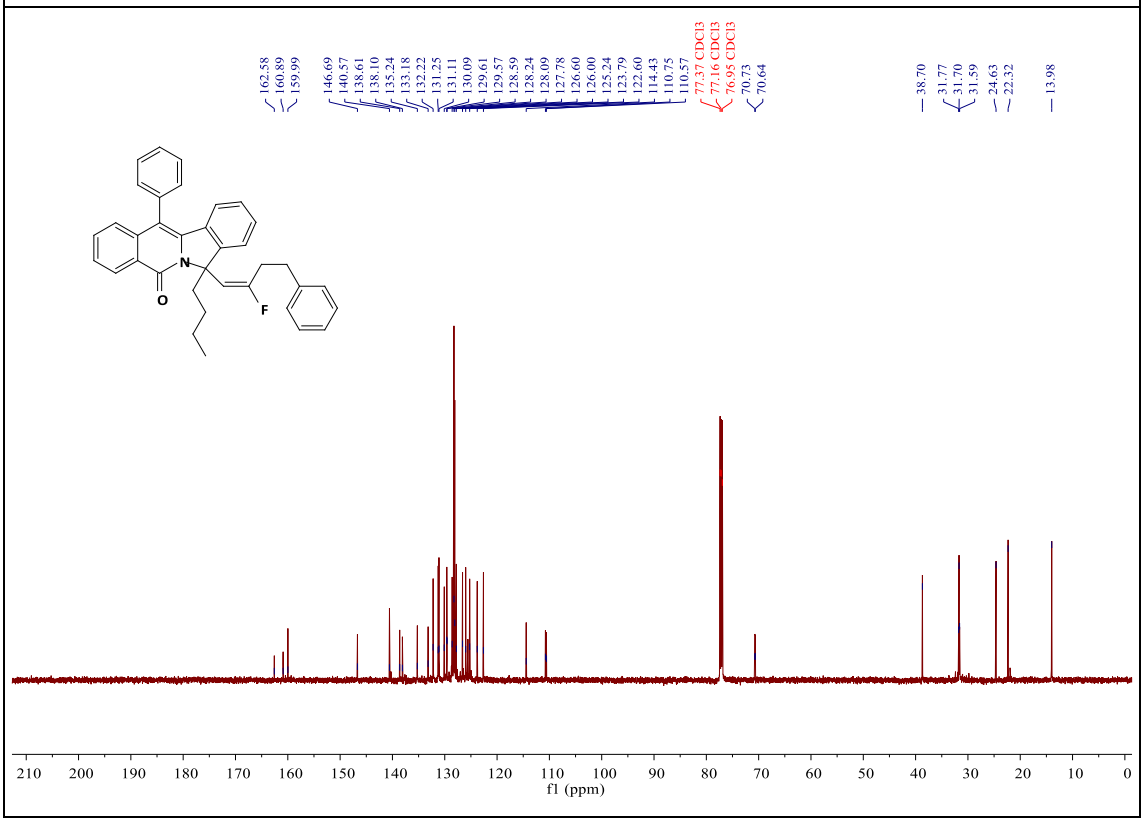


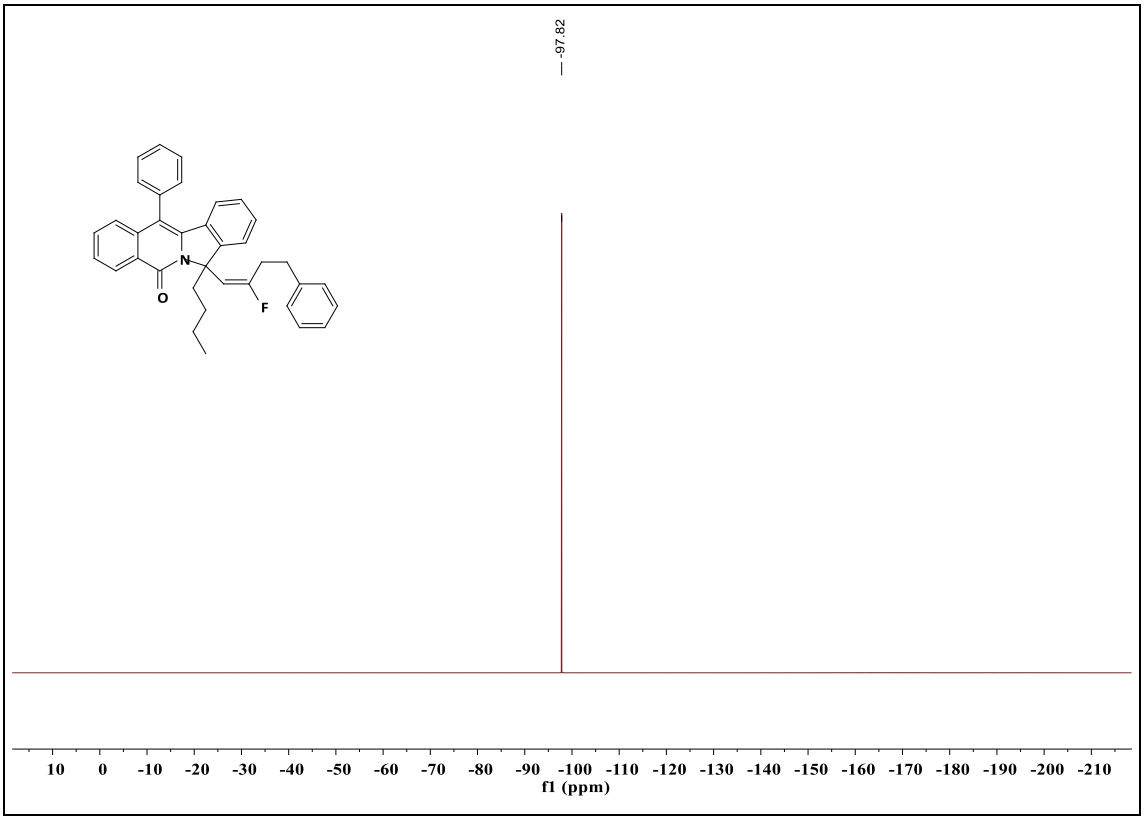



-94.96
O
N
N
O
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

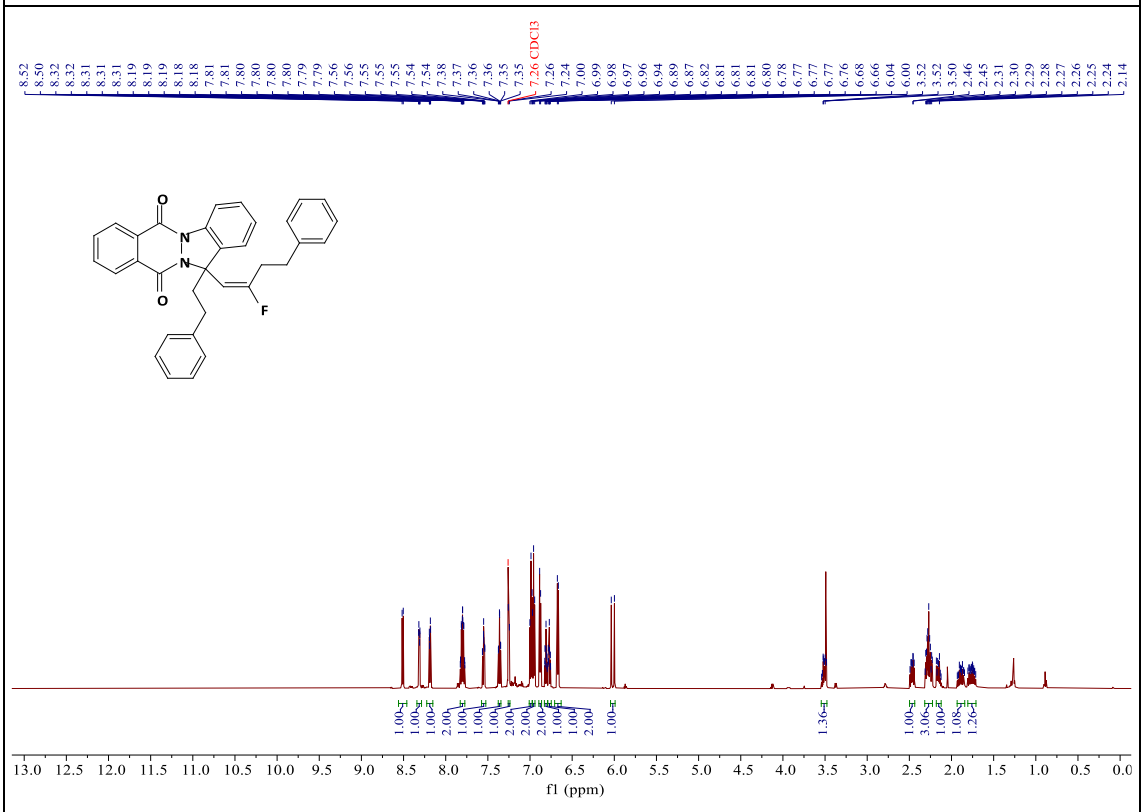
(*E*)-7-butyl-7-(2-fluoro-4-phenylbut-1-en-1-yl)-12-phenylisoindolo[2,1-*b*]isoquinolin-5(7*H*)-one (3q)

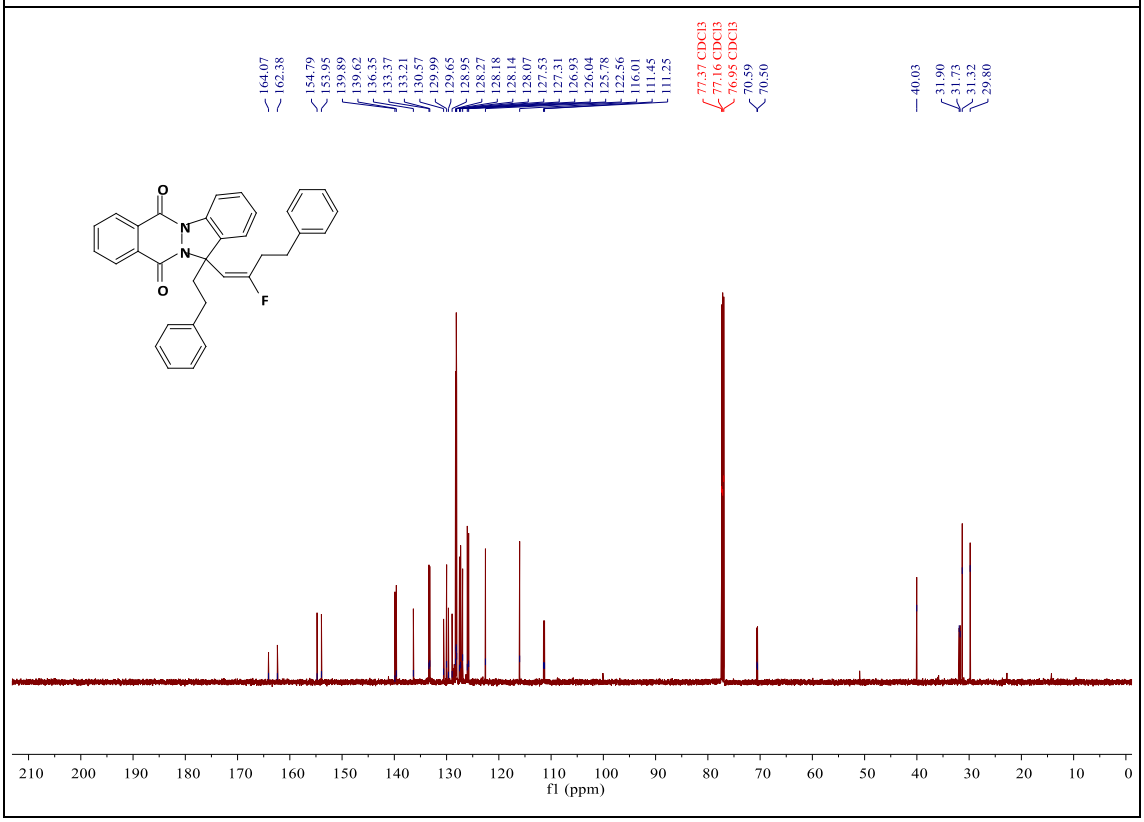


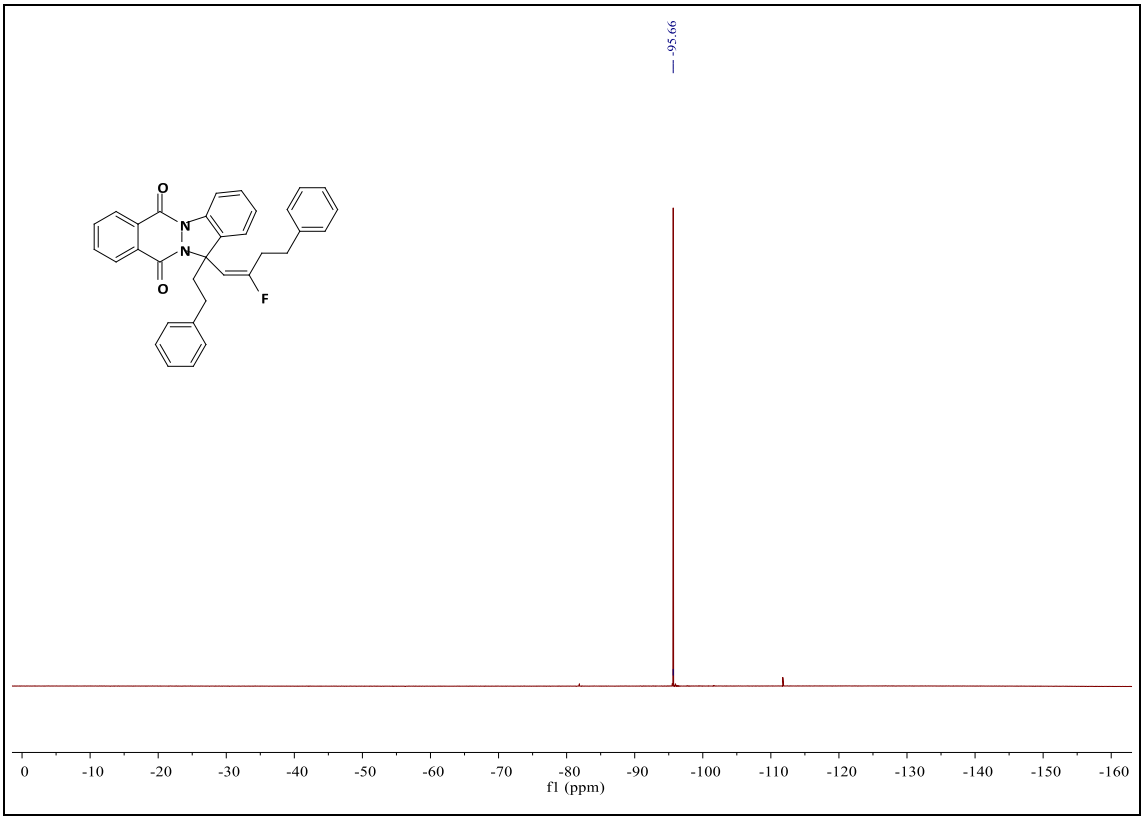



-97.82
N
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

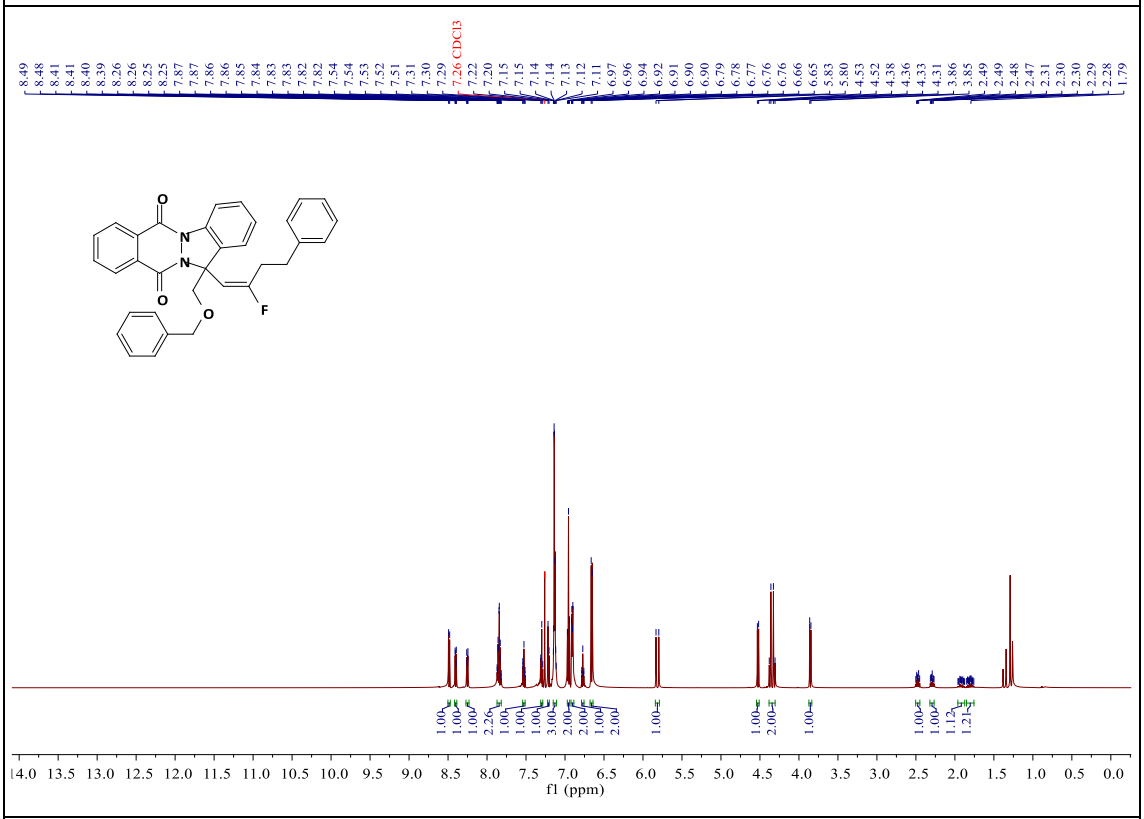
(*E*)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13-phenethyl-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3r)

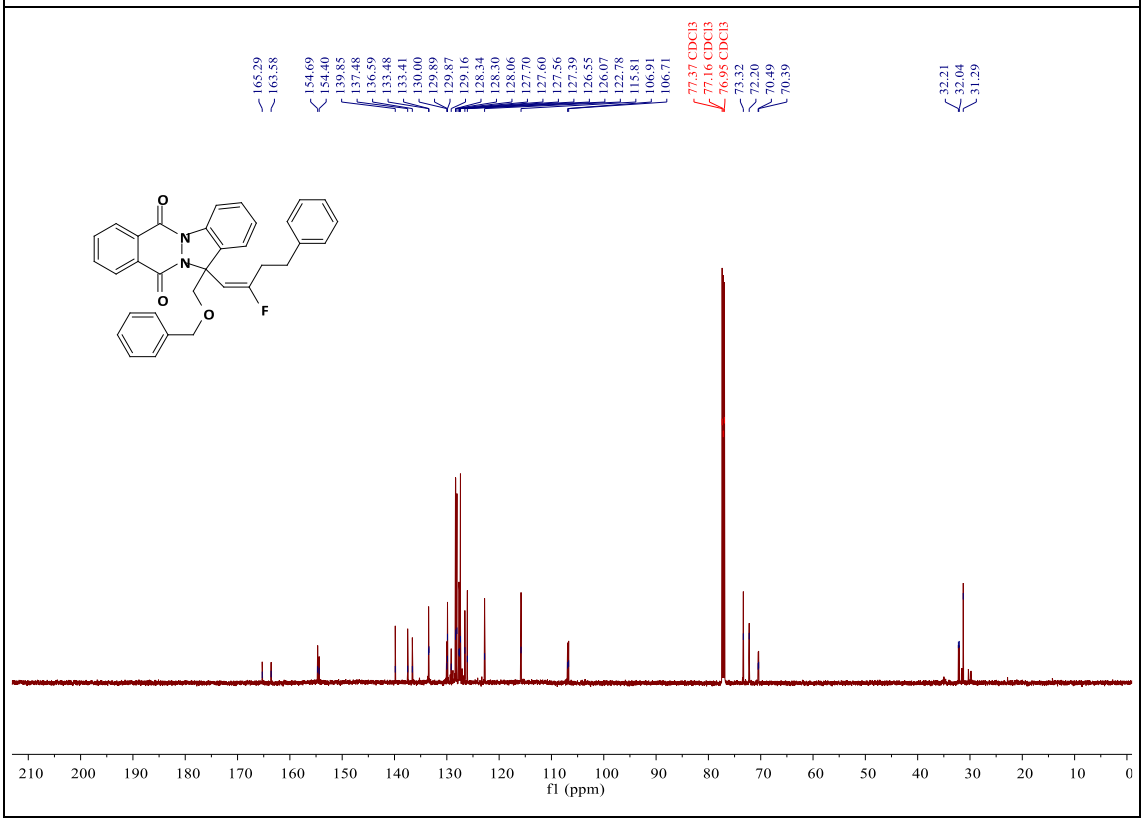


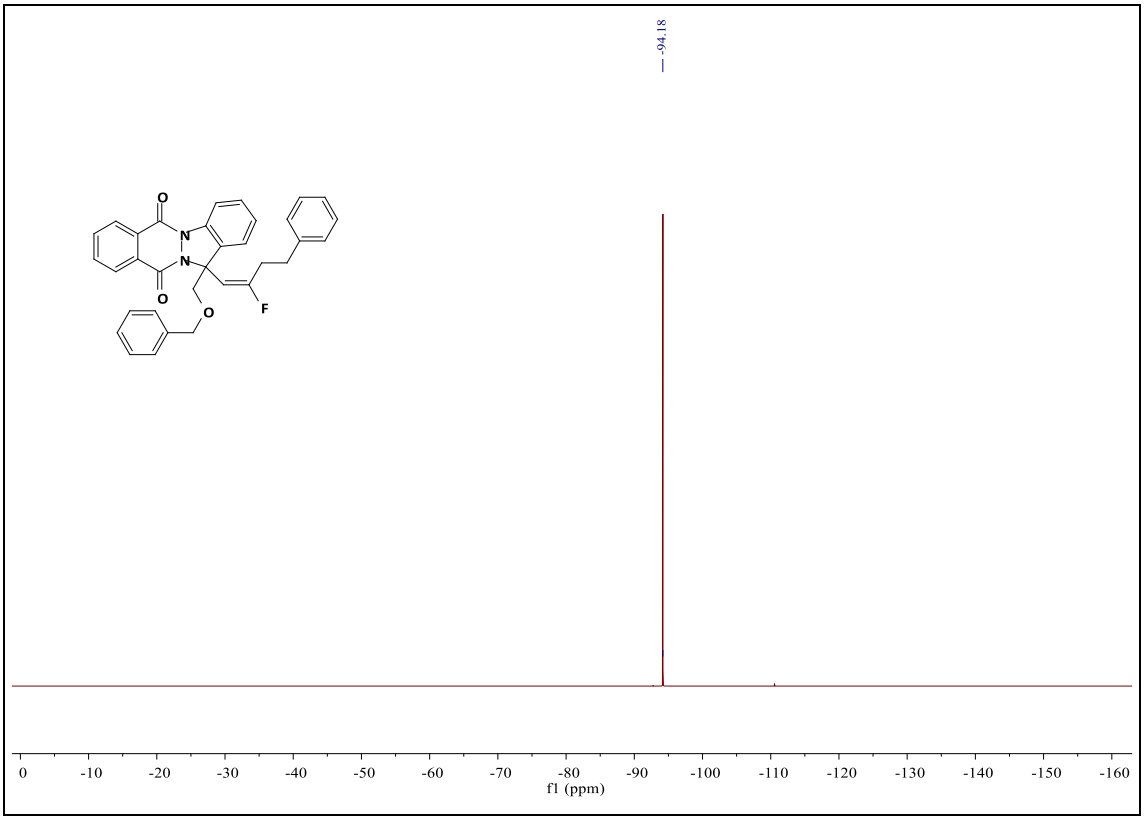



-95.66
O
N
N
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

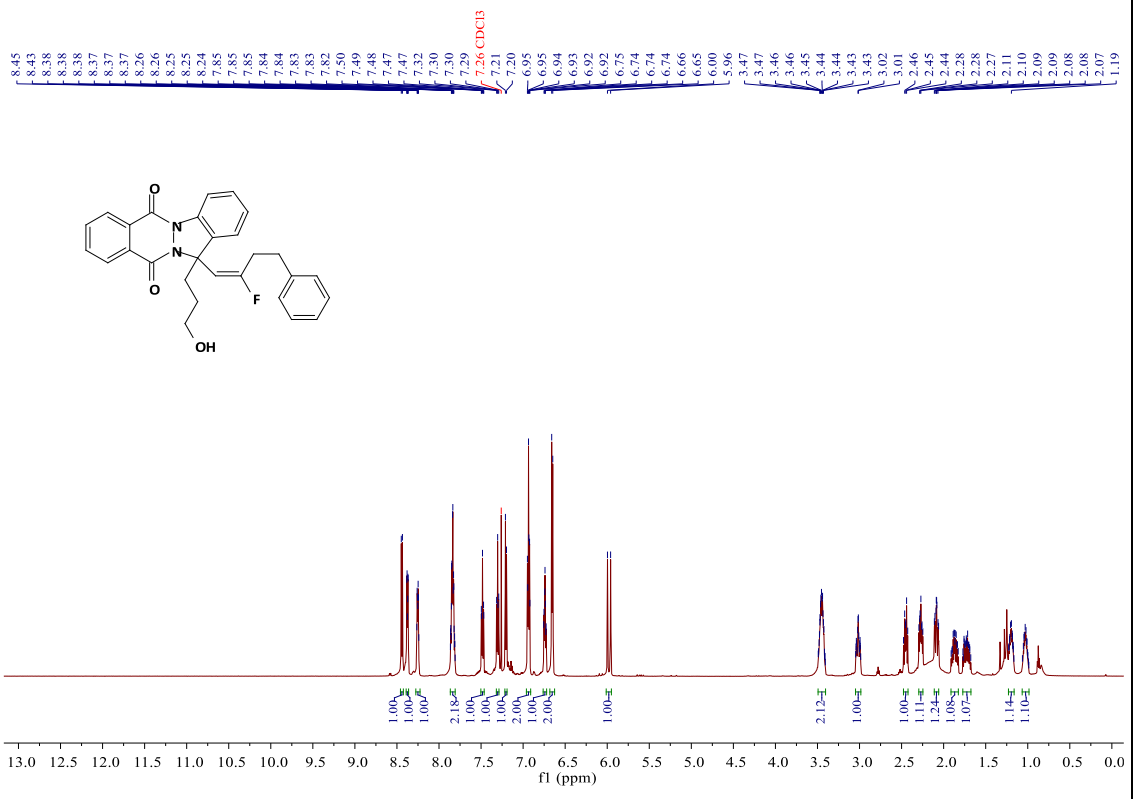
(*E*)-13-((benzyloxy)methyl)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3s)

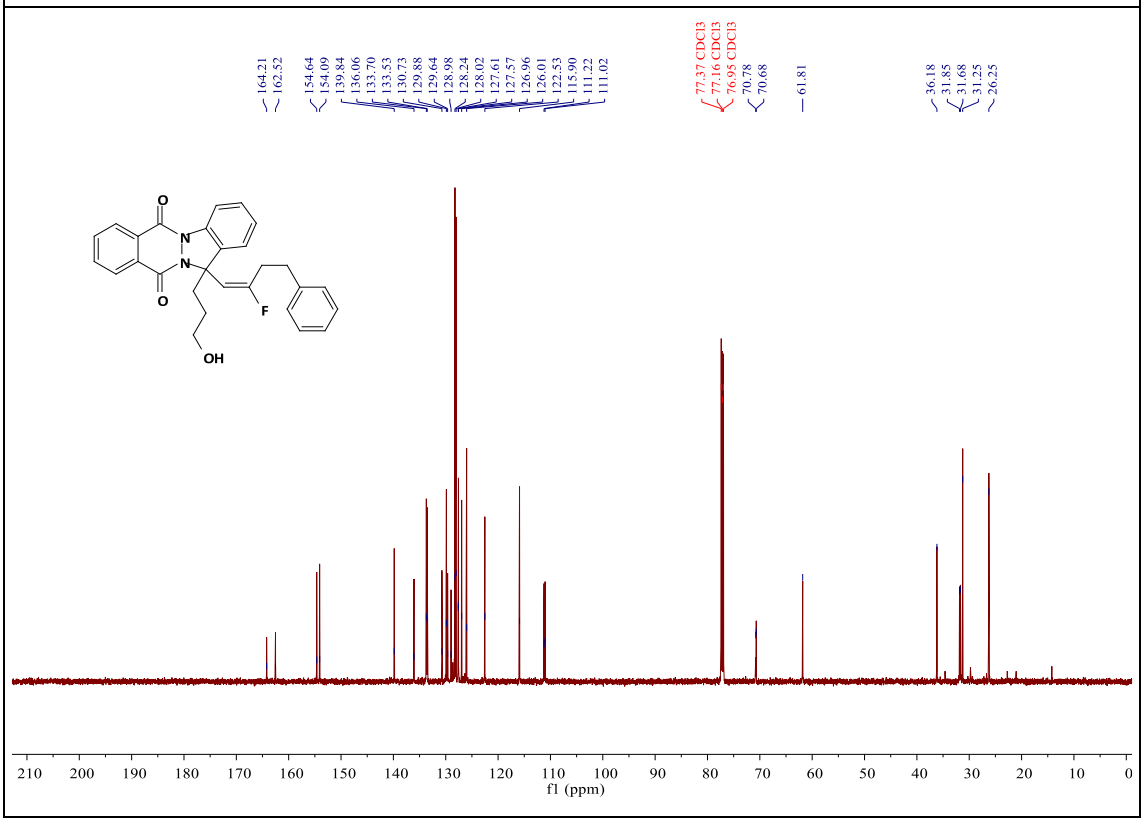


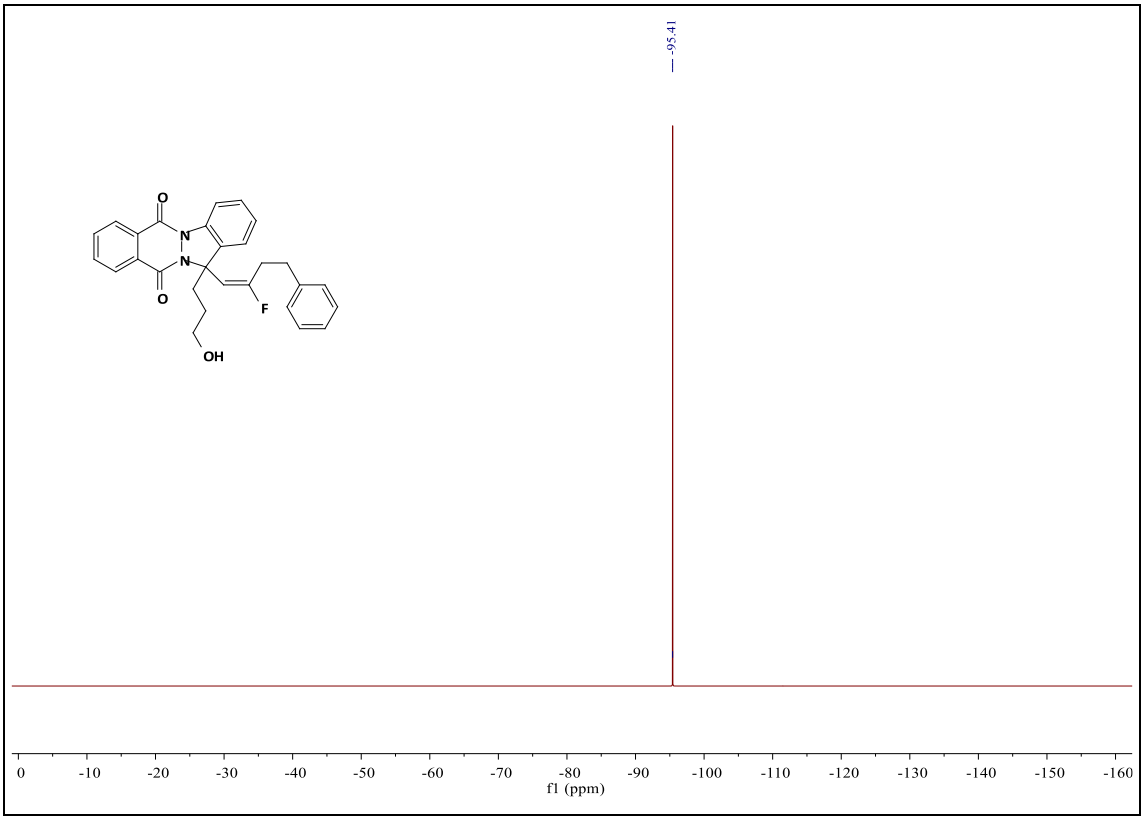



-94.18
O
N
N
O
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

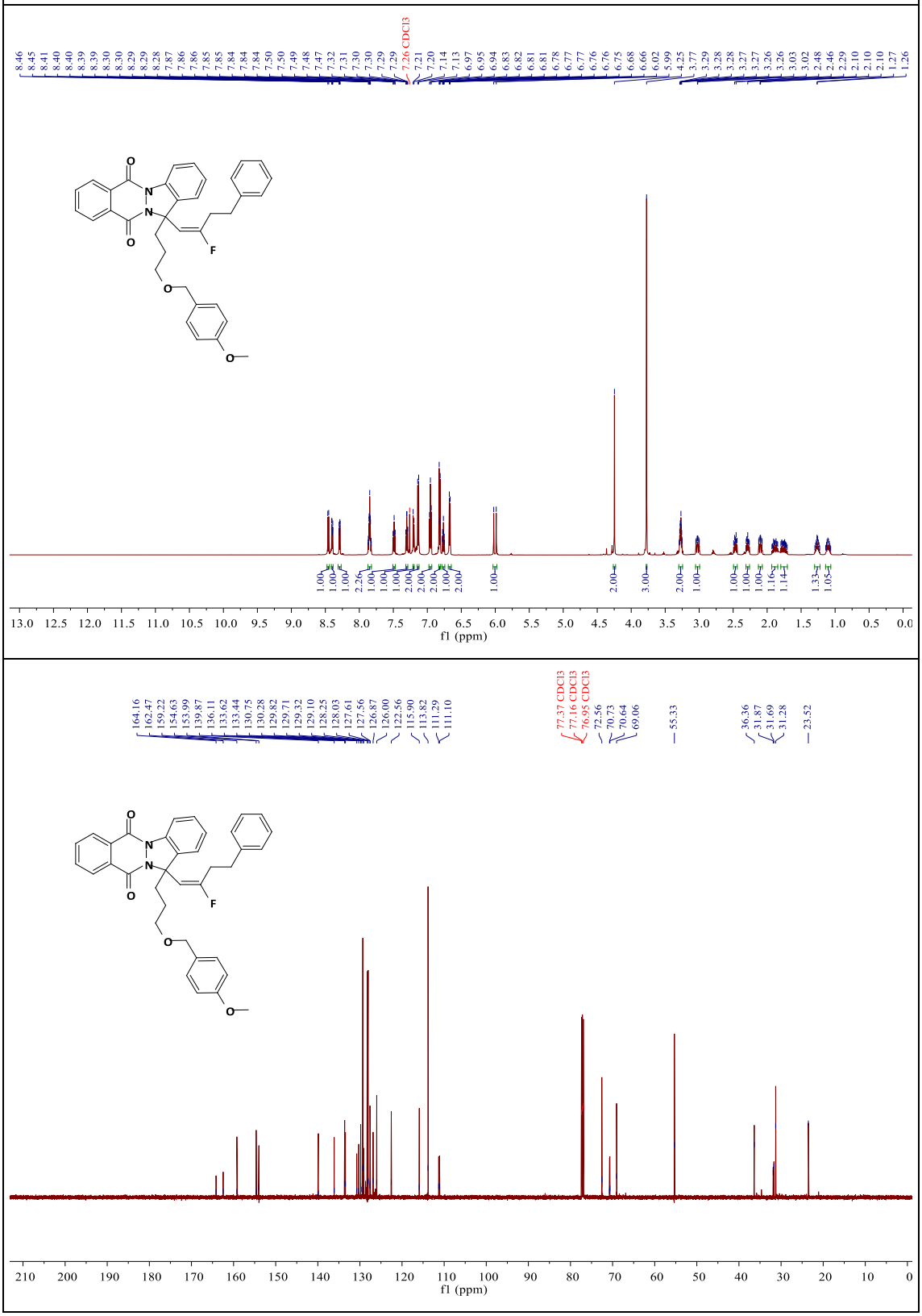
(*E*)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13-(3-hydroxypropyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3t)

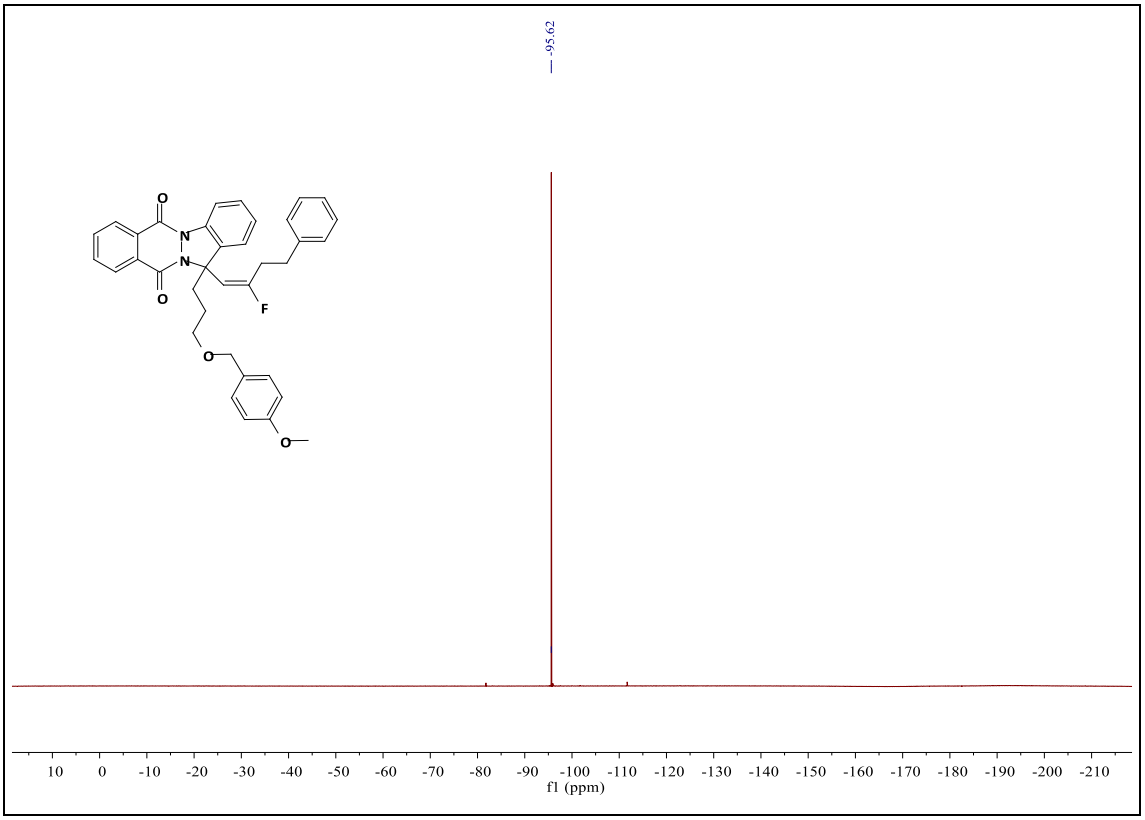




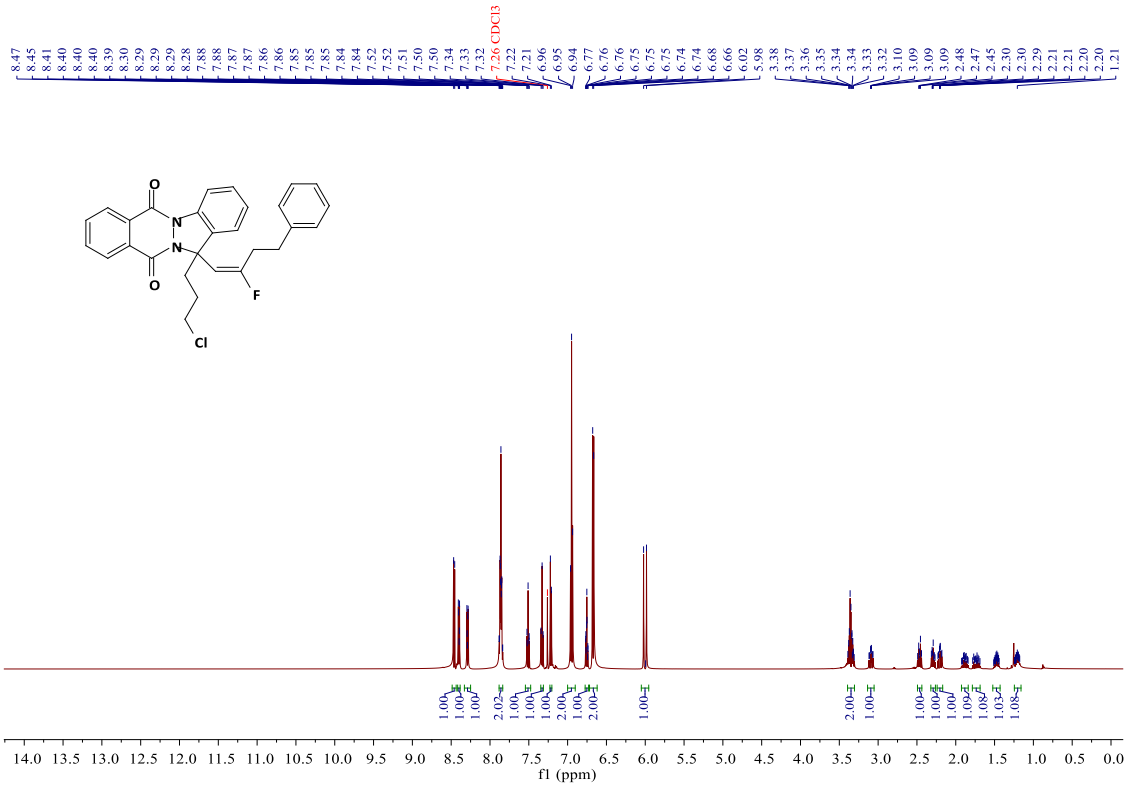

-95.41
O
N
N
O
F
OH
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

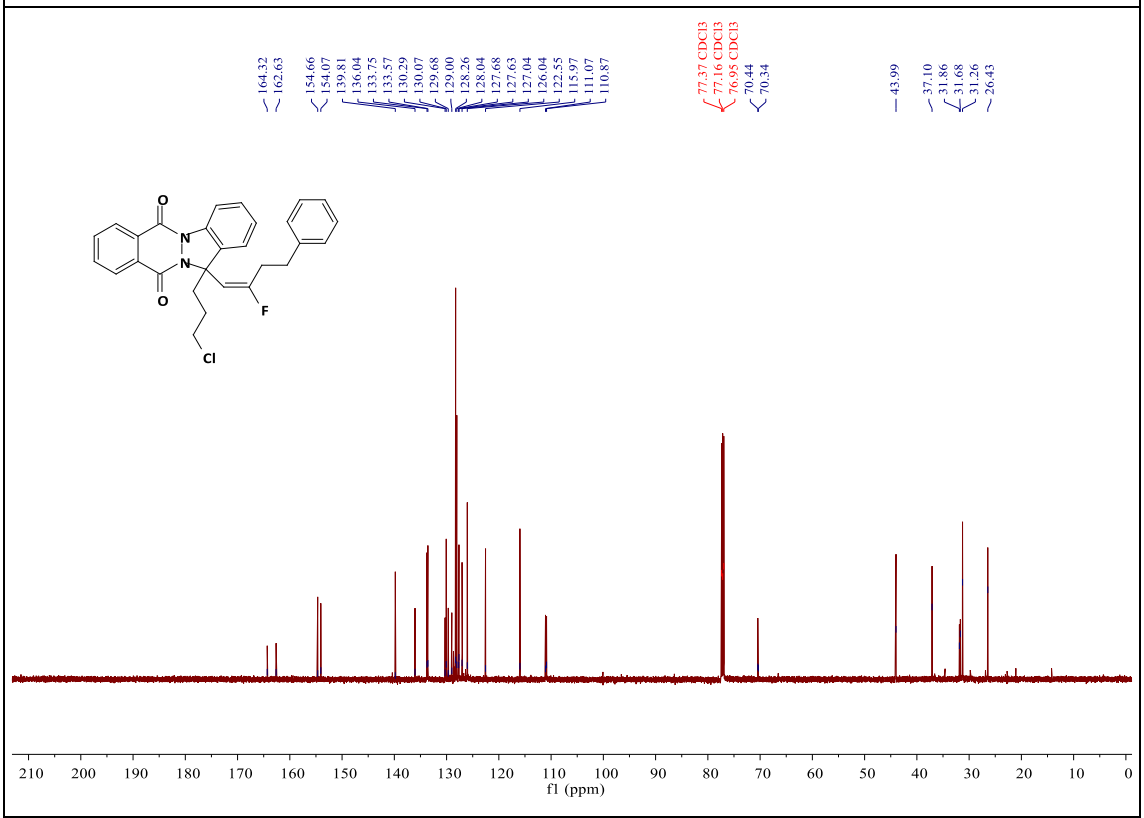
(*E*)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13-(3-((4-methoxybenzyl)oxy)propyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3u)

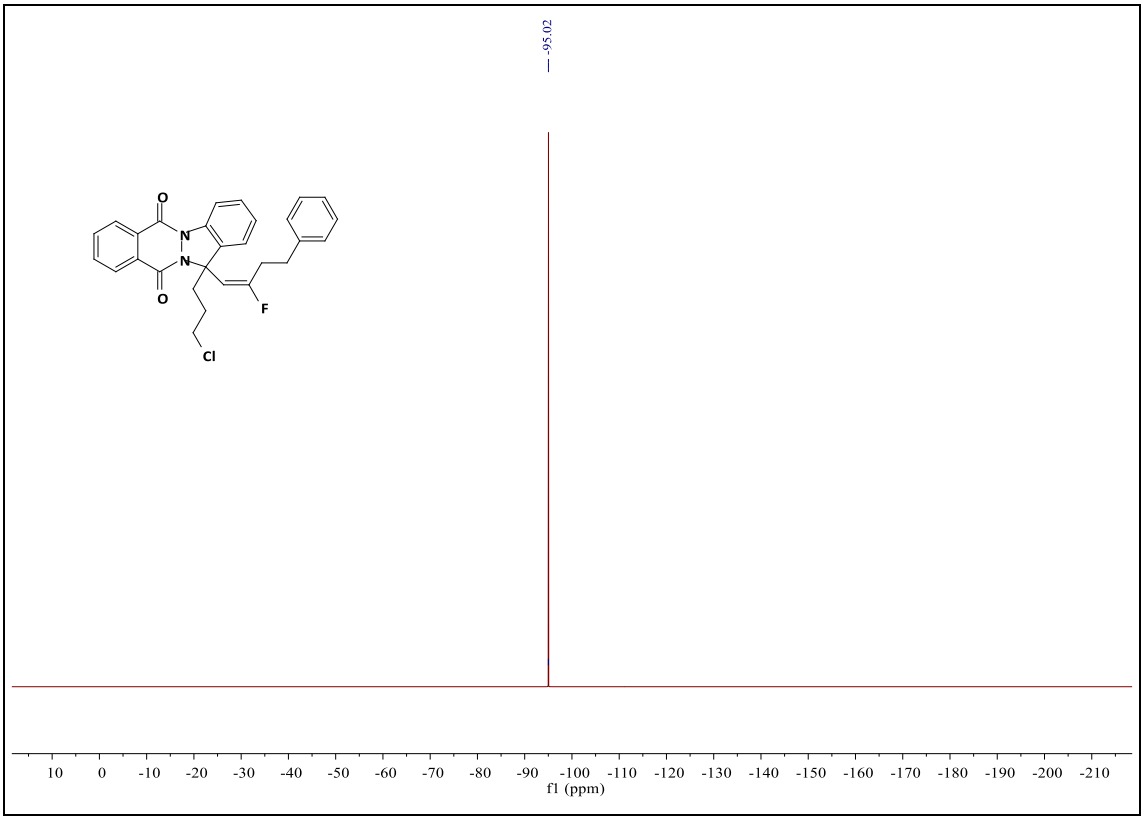



-95.62
O
N
N
O
F
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

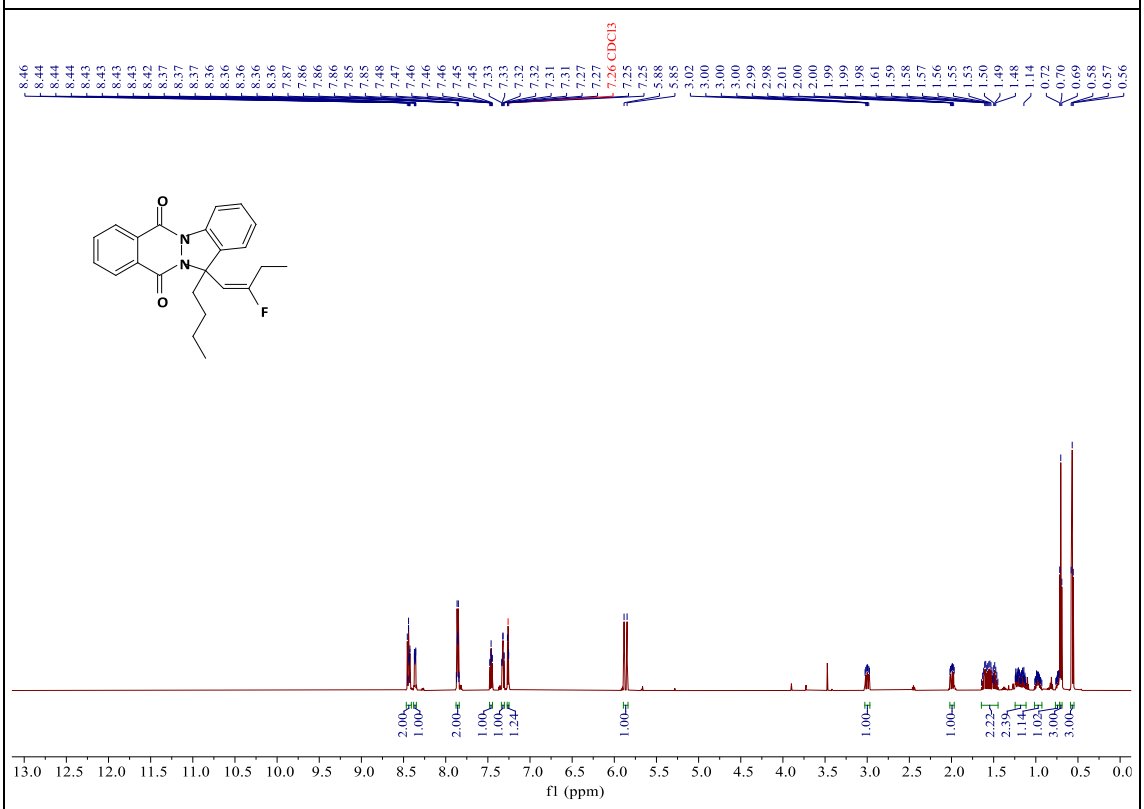
(*E*)-13-(3-chloropropyl)-13-(2-fluoro-4-phenylbut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3v)

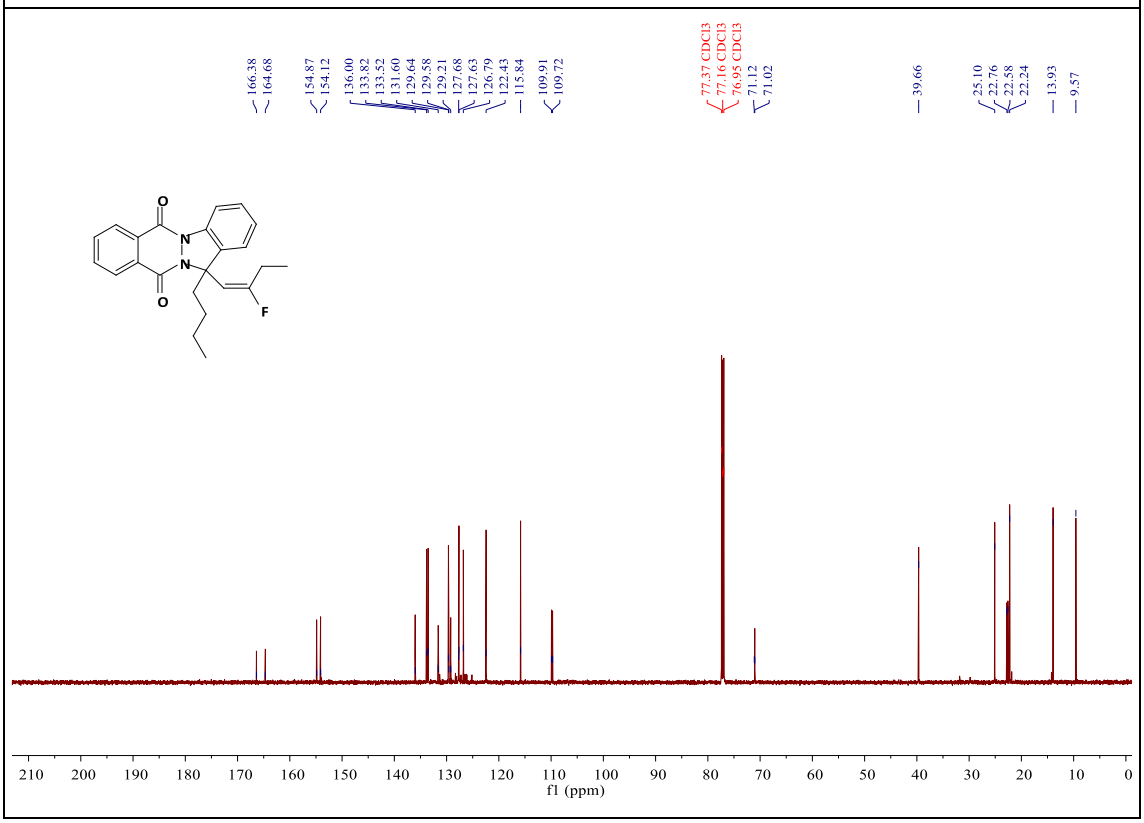


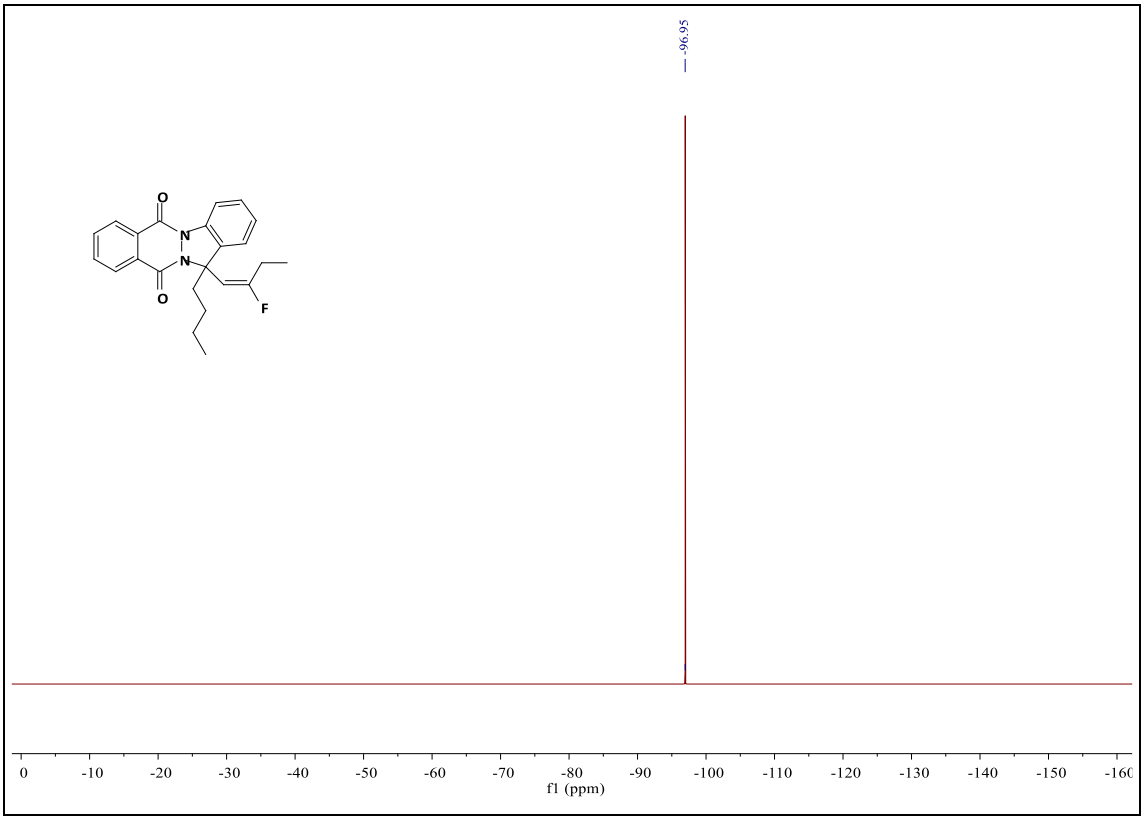



-95.02
O
N
N
O
F
Cl
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

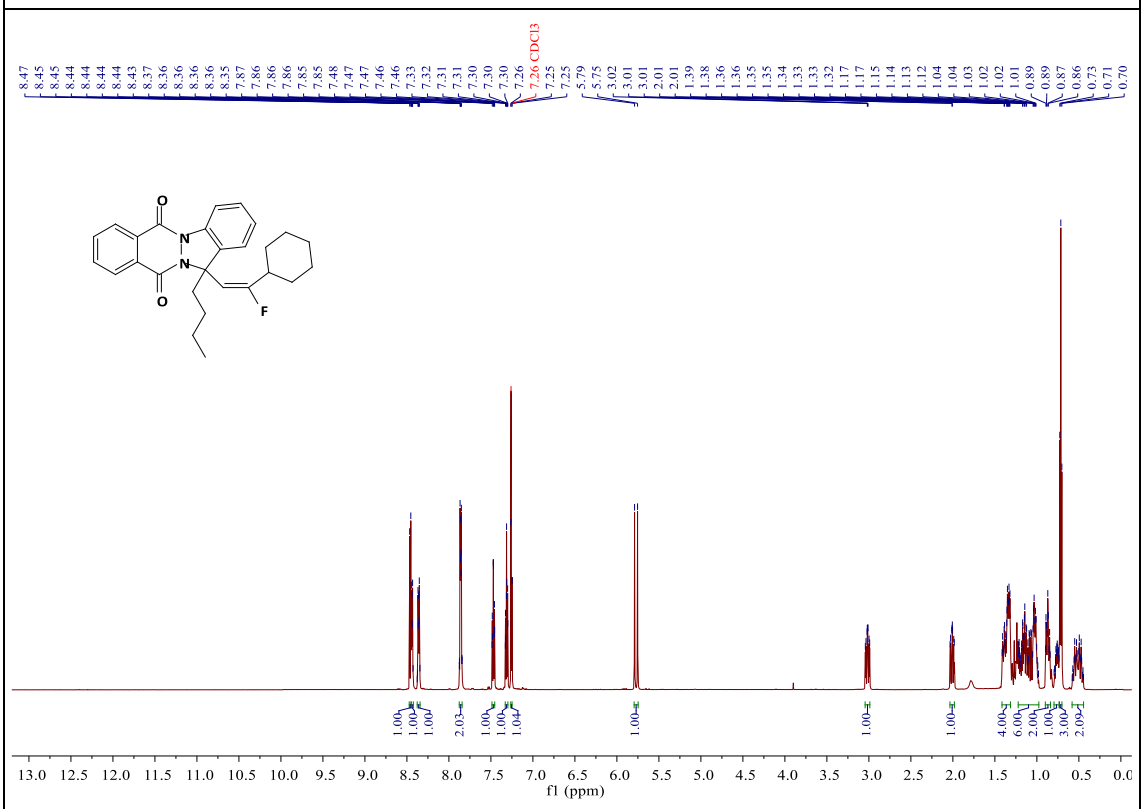
(*E*)-13-butyl-13-(2-fluorobut-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3w)

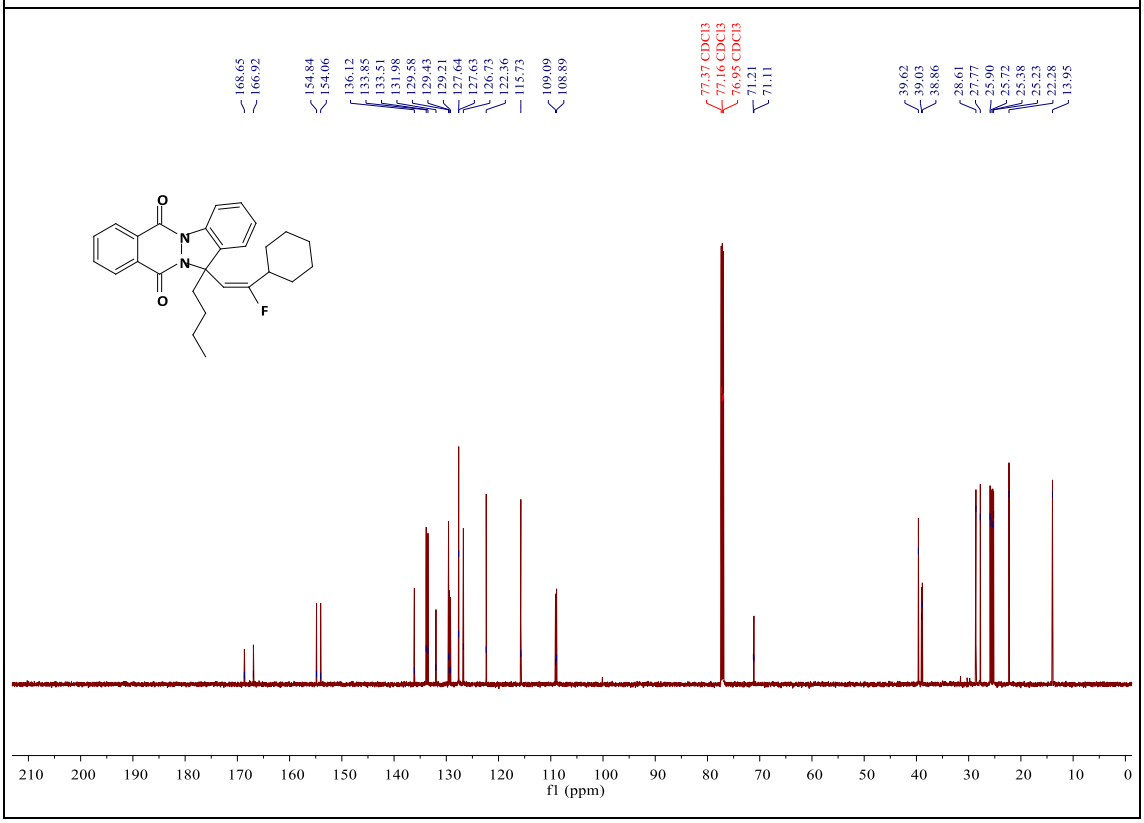


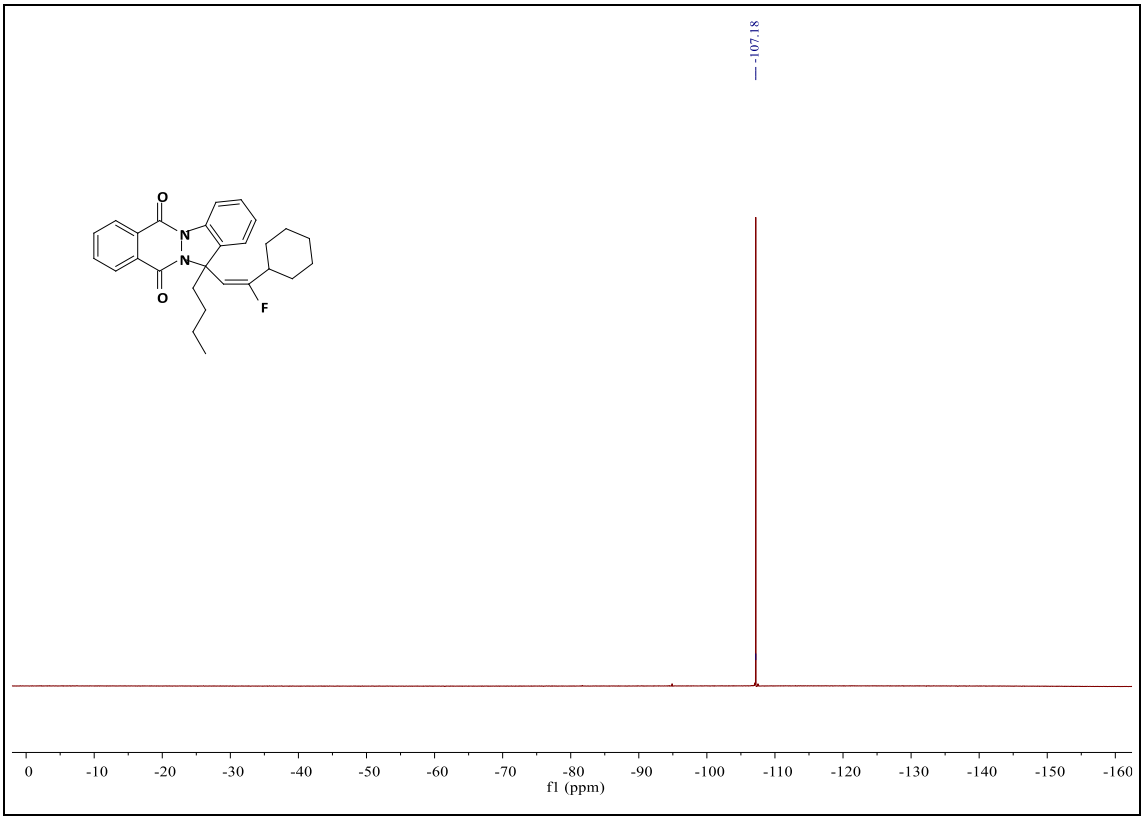



-96.95
O
N
N
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

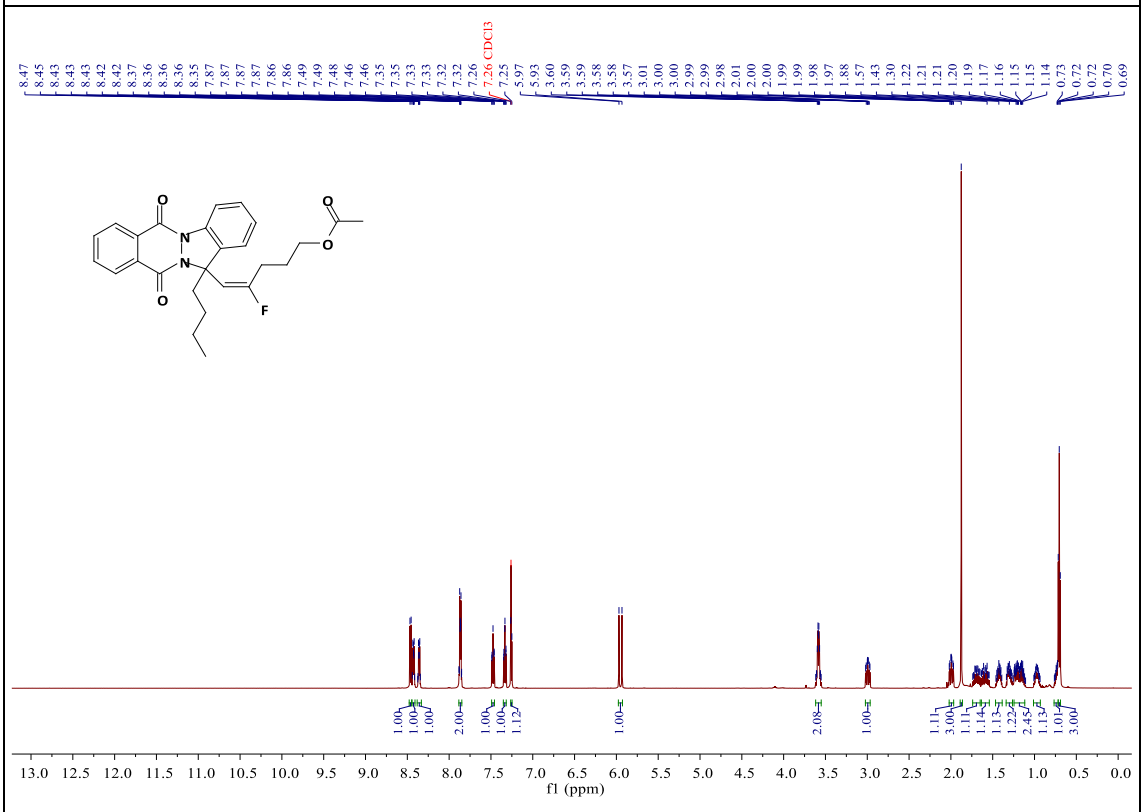
(*E*)-13-butyl-13-(2-cyclohexyl-2-fluorovinyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3x)

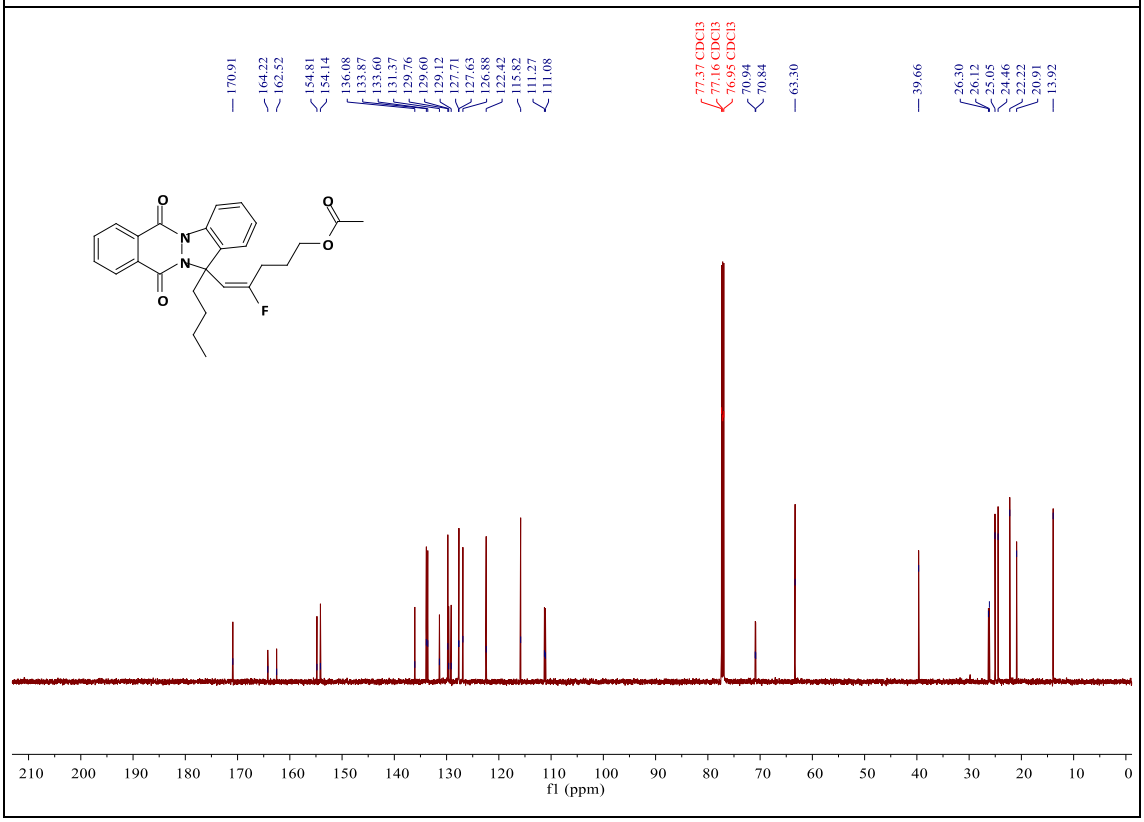


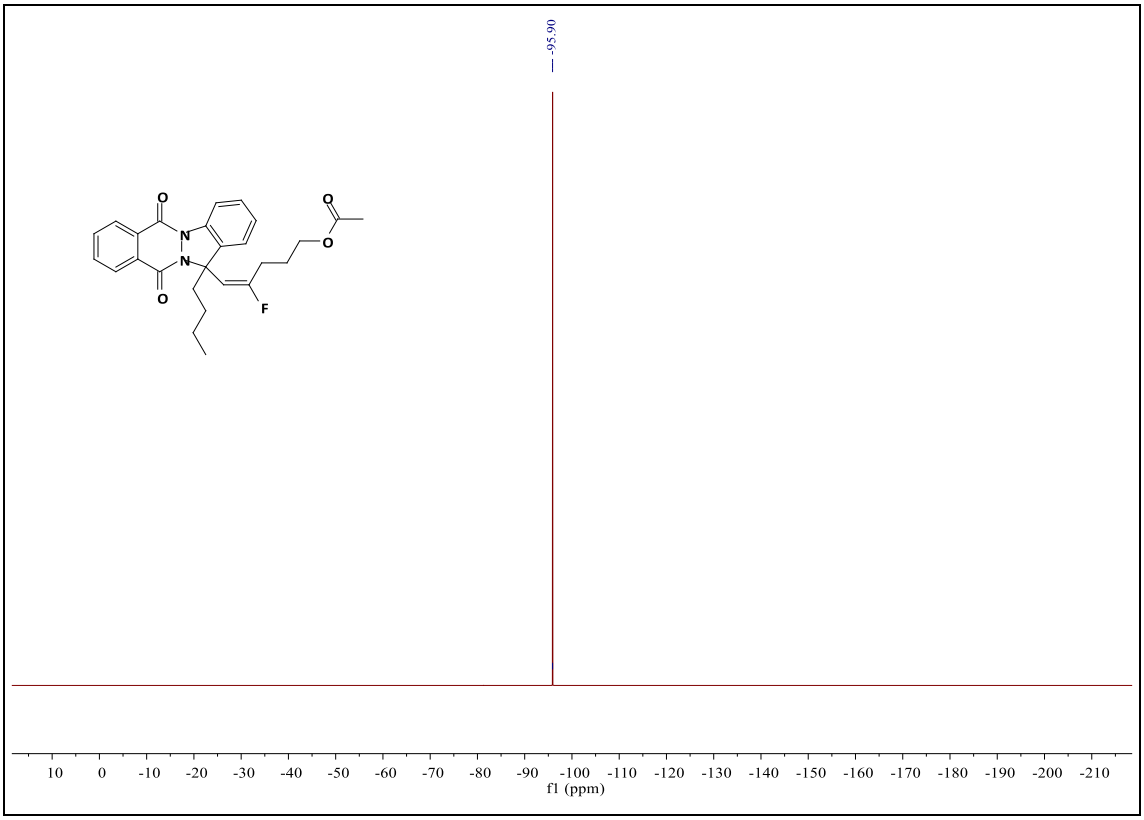



-107.18
O
N
N
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

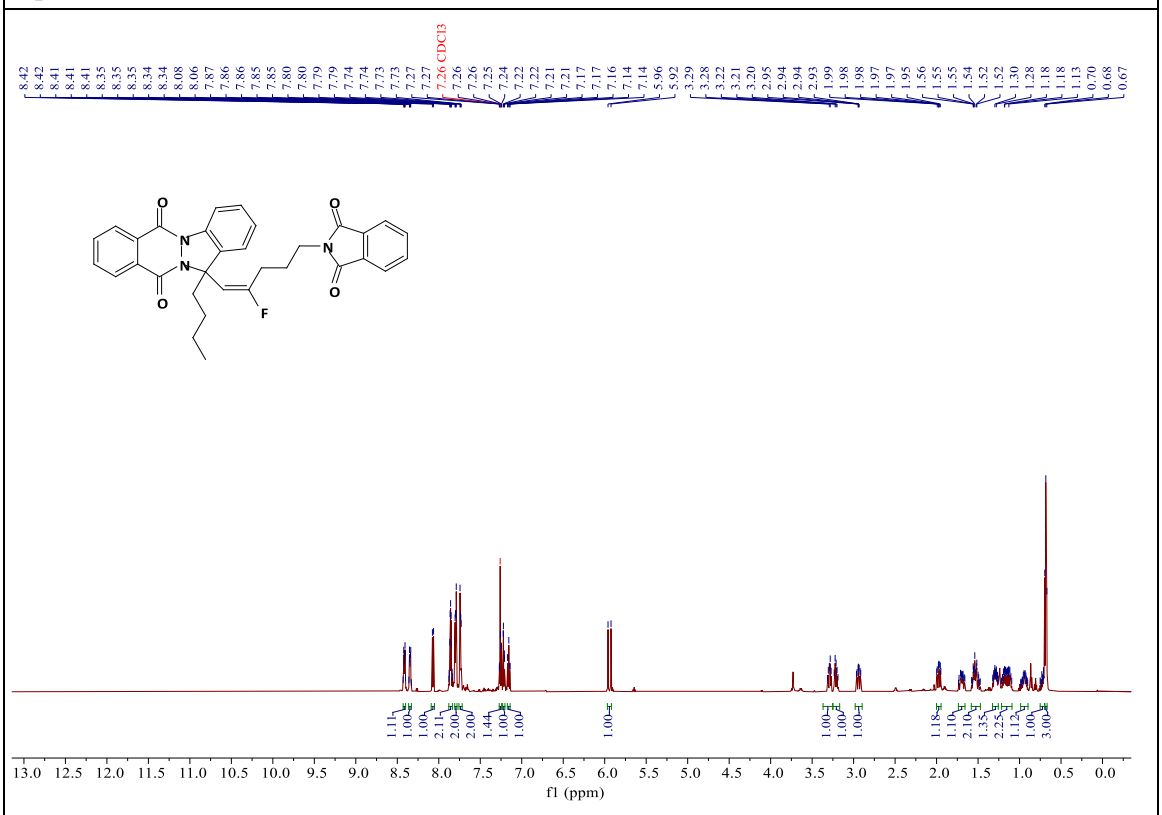
(*E*)-5-(13-butyl-6,11-dioxo-6,11-dihydro-13*H*-indazolo[1,2-*b*]phthalazin-13-yl)-4-fluoropent-4-en-1-yl acetate (3y)

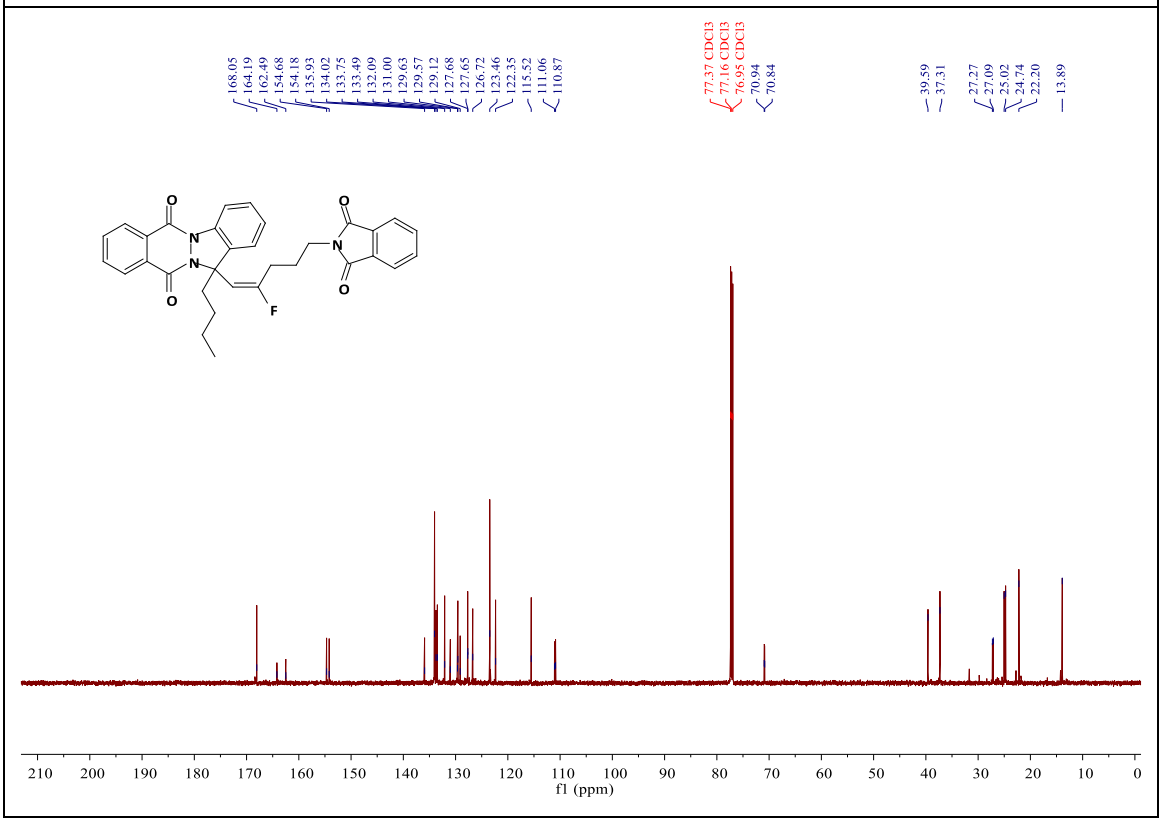


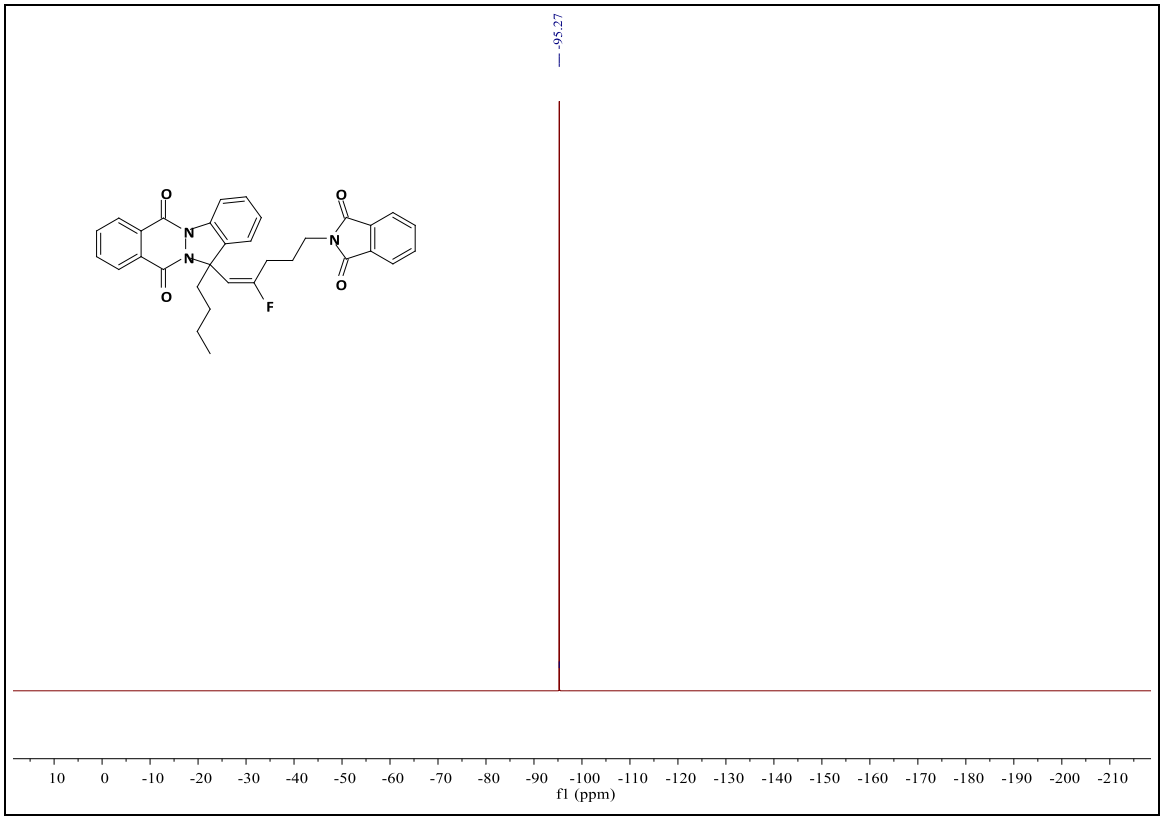



-95.90
O
O
N
N
O
O
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

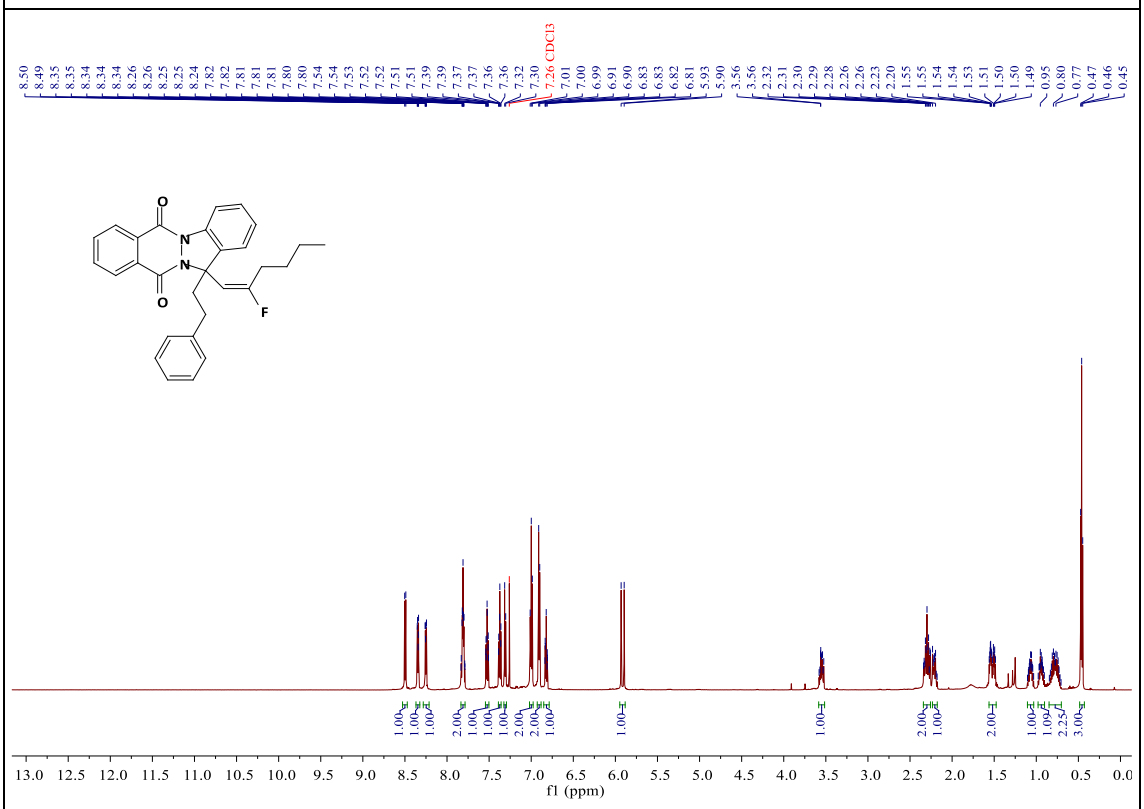
(*E*)-13-butyl-13-(5-(1,3-dioxoisoindolin-2-yl)-2-fluoropent-1-en-1-yl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3z)

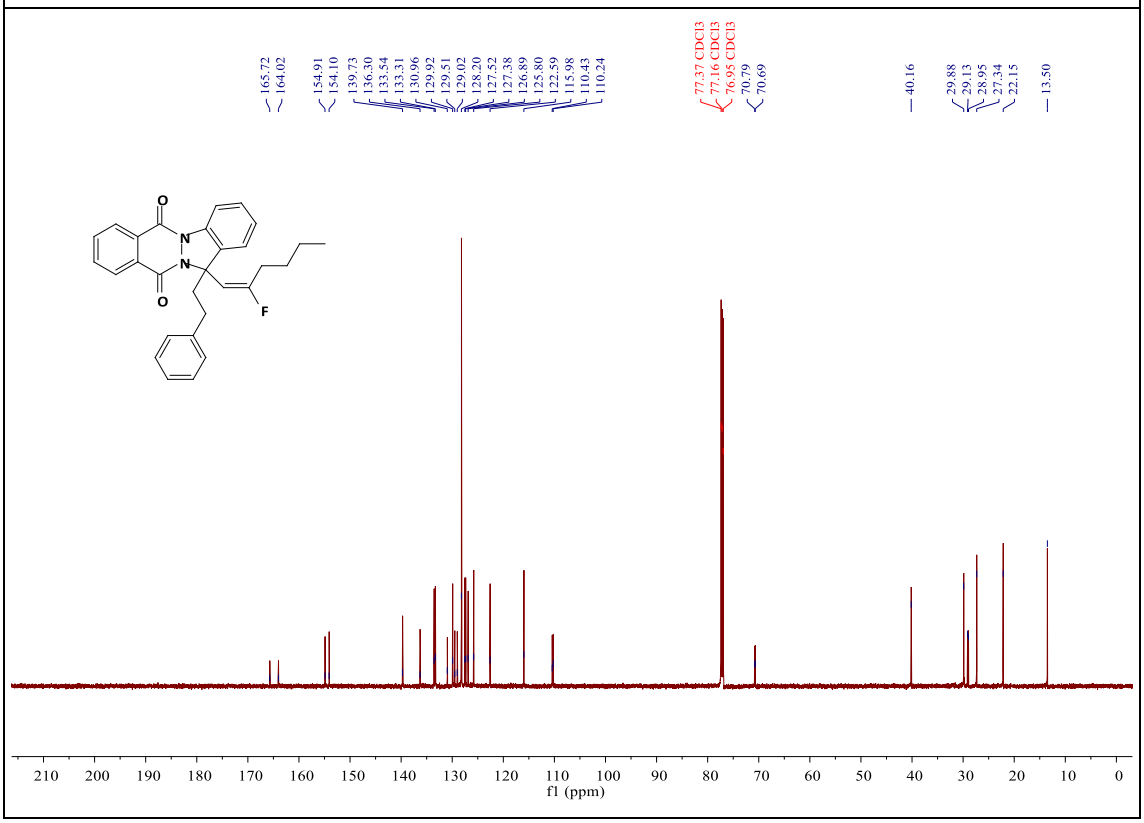


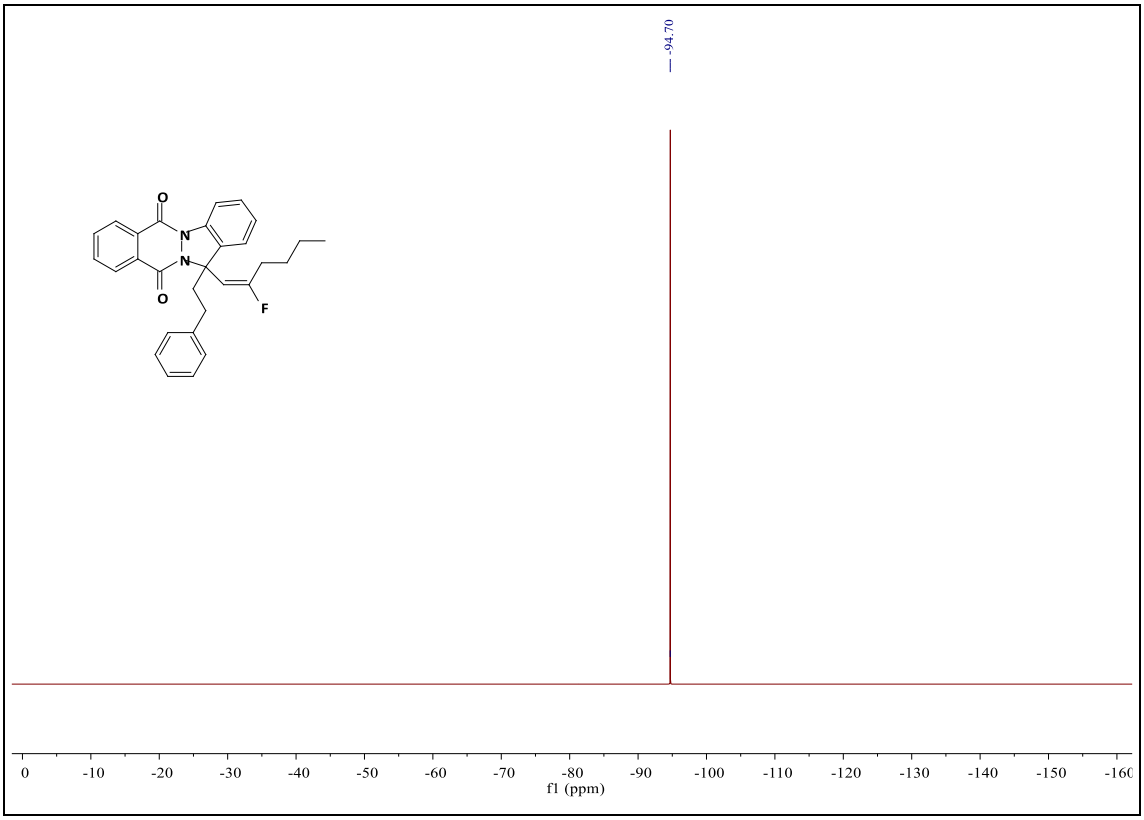



-95.27
O
N
N
O
O
N
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

(*E*)-13-(2-fluorohex-1-en-1-yl)-13-phenethyl-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3aa)






-94.70
O
N
N
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

13-butyl-13-(phenylethynyl)-13*H*-indazolo[1,2-*b*]phthalazine-6,11-dione (3ab')