Supporting Information

Ligand-Free Nickel-Catalyzed Arylation Cascades for Accessing Pyrrolopyridin-2-one, Pyranoindole-2,7-dione, and Indolin-2-one Frameworks with Mechanistic Insights

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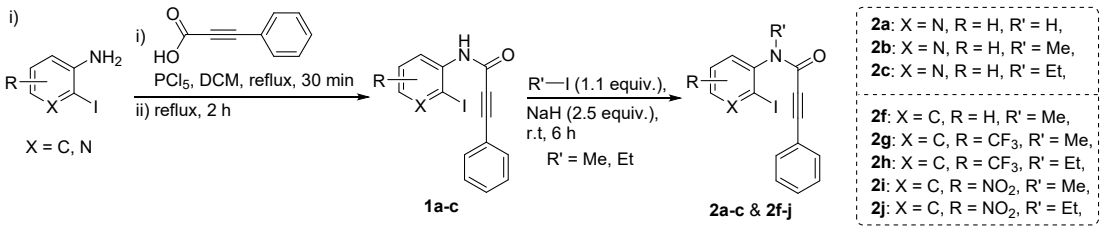
Experimental section:

1) General information - materials and equipments:

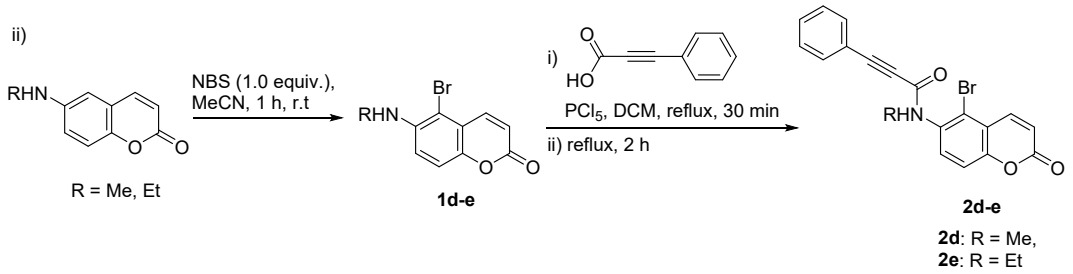
NMR spectra were recorded on a Bruker-Daltonics Avance-300 & Avance-400 spectrometer operating at 300 MHz, 400 MHz (^{1}H) or 75 MHz, 100 MHz (^{13}C), with the residual protic solvent used as the internal standard. ^{1}H-NMR data are reported as follows: δ, chemical shift; coupling constants (J are given in Hertz, Hz), and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), brs (broad singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), dt (doublet of triplet) and m (multiplet). Silica gel (60-120 mesh) and (230-400 mesh) were used for chromatographic separation. Petroleum-ether refers to the fraction between 60 ^{o}C and 80 ^{o}C. ESI mass spectral analysis was done using LCQ-ORBITRAP-XL instrument. Electron paramagnetic resonance (EPR) spectra were recorded in standard quartz EPR tubes using JEOL JES-FA200 X-band spectrometer, and simulation was performed using Easy Spin software.

2) Preparation of substrates:



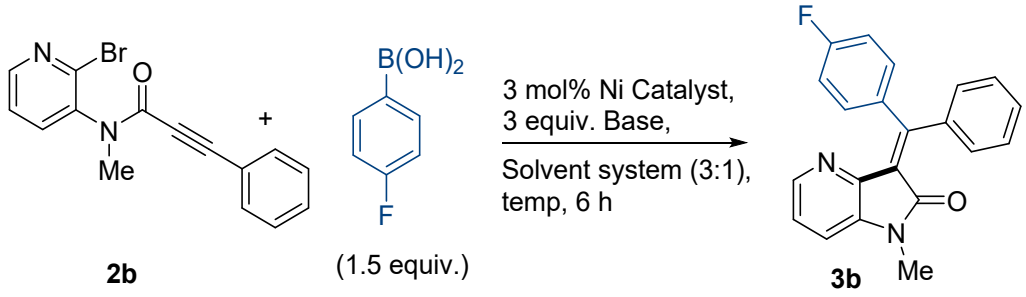
To a stirred solution of propiolic acid in dry dichloromethane (DCM), phosphorus pentachloride (PCl_5) was added portionwise at room temperature, and the reaction mixture was heated under reflux for 30 min. After cooling to room temperature, the corresponding 2-iodo-3-aminobenzene or 2-iodo-3-aminopyridine was added in one portion, and the mixture was again heated under reflux for 2 h. Upon completion (monitored by TLC), the reaction was cooled and carefully quenched with saturated aqueous sodium bicarbonate solution. The organic layer was separated, and the aqueous phase was extracted with dichloromethane. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The resulting crude amide was dissolved in dry DMF or THF, and sodium hydride (NaH, 60% dispersion in mineral oil) was added at 0 °C under an inert atmosphere. After stirring for 15-20 min, the appropriate alkyl iodide (R′ = Me or Et) was added, and the reaction mixture was allowed to warm to room temperature and stirred for 6 h. The reaction was then quenched with saturated aqueous ammonium chloride

solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography using hexane/ethyl acetate as eluent afforded the desired N-alkylated substrates **2a-c** and **2f-j** as solids.



6-N-alkylated coumarin was dissolved in acetonitrile and stirred at room temperature for 5 min. *N*-Bromosuccinimide was then added in one portion, and the reaction mixture was stirred at room temperature for 1 h. After completion (monitored by TLC), the solvent was removed under reduced pressure, and the crude brominated coumarin was used directly in the next step without further purification. Separately, propiolic acid was dissolved in dry dichloromethane, phosphorus pentachloride (PCl_5) was added portionwise at room temperature, and the reaction mixture was heated under reflux for 30 min. After cooling to room temperature, the brominated coumarin was added in one portion, and the reaction mixture was again heated under reflux for 2 h. Upon completion, the reaction was cooled and carefully quenched with saturated aqueous sodium bicarbonate solution. The organic layer was separated, and the aqueous phase was extracted with dichloromethane. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography using hexane/ethyl acetate as eluent afforded the desired N-alkylated brominated coumarin amide products **2d-e**.

3) Optimization table:



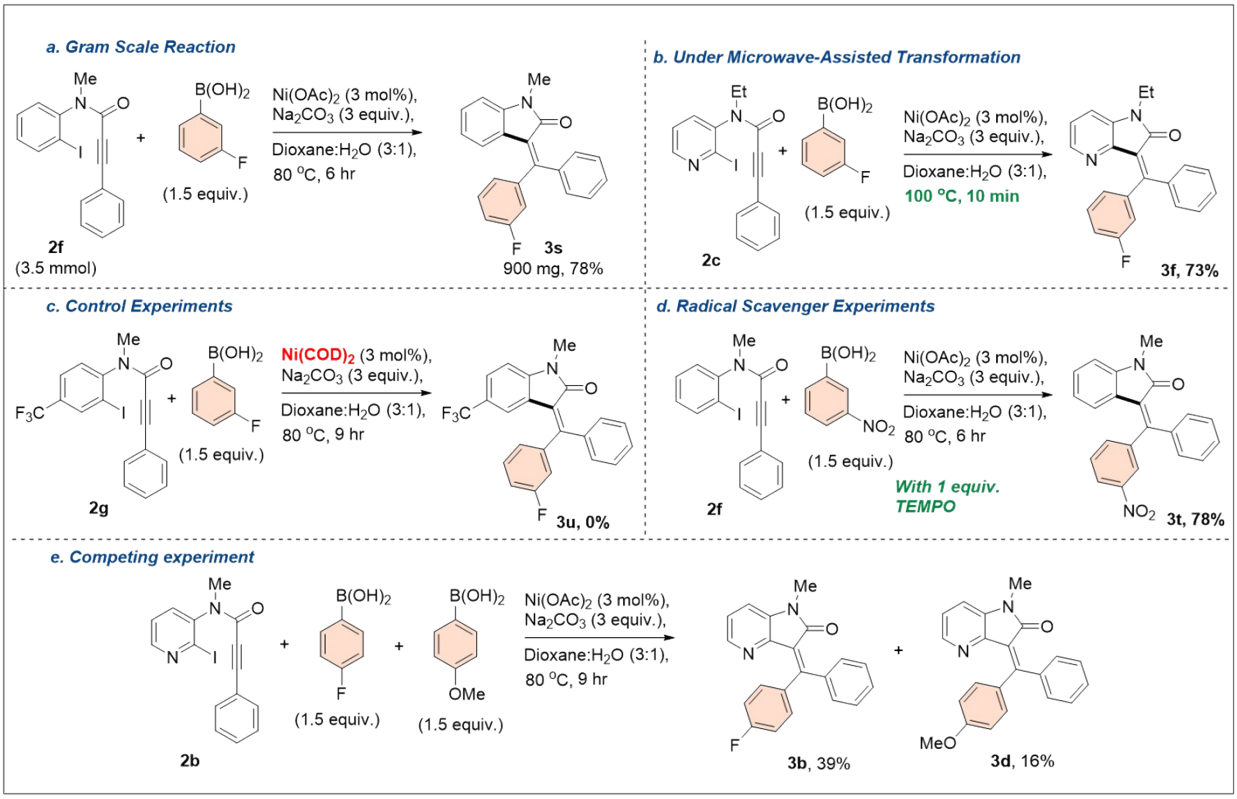
2b (1.5 equiv.) **3b**

Entry	*Catalyst (1 mol%)*	*Base (3 equiv.)*	*Solvent (3:1)*	*Temperature (°C)*	*Time (h)*	*Yield (%)*
1.	$Ni(acac)_2$	Na_2CO_3	Dioxane:H_2O	80 °C	6	trace
2.	$Ni(PPh_3)_2Cl_2$	Na_2CO_3	Dioxane:H_2O	80 °C	6	5
3.	$NiCl_2$	Na_2CO_3	Dioxane:H_2O	80 °C	6	trace
4.	$NiBr_2$	Na_2CO_3	Dioxane:H_2O	80 °C	6	trace
5.	**$Ni(OAc)_2$**	**Na_2CO_3**	**Dioxane:H_2O**	**80 °C**	**6**	**75**
6.	$Ni(COD)_2$	Na_2CO_3	Dioxane:H_2O	80 °C	6	nr
7.	$Ni(PPh_3)_4$	Na_2CO_3	Dioxane:H_2O	80 °C	6	nr
8.	$Ni(dppf)Cl_2$	Na_2CO_3	Dioxane:H_2O	80 °C	6	trace
9.	$NiCl_2$glyme	Na_2CO_3	Dioxane:H_2O	80 °C	6	22
10.	$Ni(OAc)_2$	Cs_2CO_3	Dioxane:H_2O	80 °C	6	32
11.	$Ni(OAc)_2$	K_2CO_3	Dioxane:H_2O	80 °C	6	56
12.	$Ni(OAc)_2$	$NaHCO_3$	Dioxane:H_2O	80 °C	6	44
13.	$Ni(OAc)_2$	NEt_3	Dioxane:H_2O	80 °C	6	20
14.	$Ni(OAc)_2$	^{t}BuOK	Dioxane:H_2O	80 °C	6	34
15.	$Ni(OAc)_2$	Na_2CO_3	DMF:H_2O	80 °C	6	trace

16.	$Ni(OAc)_2$	Na_2CO_3	THF:H_2O	80 ^oC	6	trace
17.	$Ni(OAc)_2$	Na_2CO_3	Toluene:H_2O	80 ^oC	6	9
18.	$Ni(OAc)_2$	Na_2CO_3	Dioxane	80 ^oC	6	nr
19.	$Ni(OAc)_2$	-	Dioxane:H_2O	80 ^oC	6	nr
20.[a]	$Ni(OAc)_2$	Na_2CO_3	Dioxane:H_2O	80 ^oC	6	58
21.	$Ni(OAc)_2$	Na_2CO_3	Dioxane:H_2O	120 ^oC	6	58
22.	$Ni(OAc)_2$	Na_2CO_3	Dioxane:H_2O	50 ^oC	6	32
23.	$Ni(OAc)_2$	Na_2CO_3	Dioxane:H_2O	80 ^oC	3	40

Table S1. Optimization of reaction conditions for the nickel-catalyzed tandem carbocyclization-arylation reaction. [a = 10 mol% $Ni(OAc)_2$ was used]

4) Control experiments:

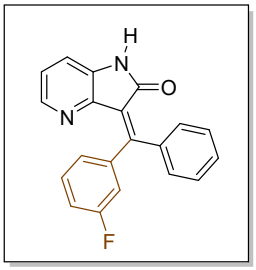


Scheme S1. Control experiments and mechanistic studies.

5) General procedure for the products 3a-3ae:

(*E*)-3-((3-fluorophenyl)(phenyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3a):

N-(2-bromopyridin-3-yl)-3-phenylpropiolamide, **2a** (100 mg, 0.33 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-fluorophenyl)boronic acid (69 mg, 0.49 mmol), Na_2CO_3 (105 mg, 0.99 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 ^oC for 7 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL × 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3a**.

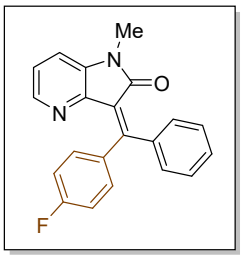


Brown gummy; yield = 77% (80 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.82 (m, 2H), 7.56 – 7.64 (m, 2H), 7.43 – 7.53 (m, 5H), 7.27 – 7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5 (d, *J* = 2.0 Hz), 163.5 (d, *J* = 22.8 Hz), 161.1 (d, *J* = 22.5 Hz), 157.7 (dd, *J* = 3.7, 2.2 Hz), 143.8 (d, *J* = 3.7 Hz), 142.5, 142.4, 141.9 (d, *J* = 7.7 Hz), 139.6, 139.2, 135.8 (d, *J* = 1.8 Hz), 131.4, 130.9, 130.3, 130.0, 129.3 (dd, *J* = 16.1, 8.1 Hz), 127.9, 127.8, 127.1 (d, *J* = 3.0 Hz), 126.5 (d, *J* = 2.9 Hz), 123.6 (d, *J* = 4.8 Hz), 123.0 (d, *J* = 3.0 Hz), 118.4, 118.2, 117.7, 117.5, 117.0, 116.7, 116.5, 116.3, 115.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.7 (s, 1F); HRMS (ESI $[M+H]^+$) for $C_{20}H_{13}FN_2O$ calcd. 317.1090; found 317.1096.

(*E*)-3-((4-fluorophenyl)(phenyl)methylene)-1-methyl-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3b):

N-(2-bromopyridin-3-yl)-*N*-methyl-3-phenylpropiolamide, **2b** (100 mg, 0.32 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-fluorophenyl)boronic acid (66 mg, 0.47 mmol), Na_2CO_3 (102 mg, 0.96 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 ^oC for 6 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl

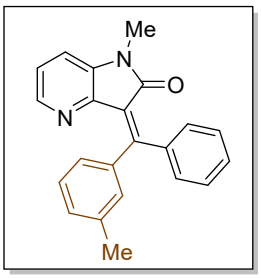
acetate (10 mL × 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3b**.



White gummy; yield = 75% (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (ddd, *J* = 8.7, 4.9, 1.6 Hz, 2H), 7.35 – 7.45 (m, 10H), 7.28 – 7.32 (m, 4H), 7.01 – 7.10 (m, 8H), 3.23 (s, 3H), 3.21 (s, 3H) (E and Z isomer at 1:1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.8, 162.6, 158.1, 158.0, 143.9, 143.8, 142.3, 142.1, 140.2, 139.7, 137.9, 137.8, 136.1, 135.6, 133.8, 133.7, 132.9, 132.9, 131.5, 130.6, 130.2, 129.8, 128.0, 122.7 (d, *J* = 12.0 Hz), 122.5 (d, J = 10.2 Hz), 115.1, 114.9, 114.9, 114.7, 113.5, 113.5, 77.4, 77.0, 76.7, 25.6 (*E* and *Z* isomer at 1:1); ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.0 (s, 1F), -110.8 (s, 1F); HRMS (ESI $[M+H]^+$) for $C_{21}H_{15}FN_2O$ calcd. 331.1247; found 331.1246.

(*E*)-1-methyl-3-(phenyl(m-tolyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3c):

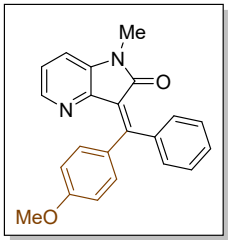
N-(2-bromopyridin-3-yl)-*N*-methyl-3-phenylpropiolamide, **2b** (100 mg, 0.32 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of *m*-tolylboronic acid (64 mg, 0.47 mmol), Na_2CO_3 (102 mg, 0.96 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 6 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL × 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3c**.



Yellow gummy; yield = 75% (78 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.98 (m, 2H), 7.28 – 7.47 (m, 11H), 7.15 – 7.26 (m, 6H), 7.00 – 7.10 (m, 5H), 3.22 (s, 3H), 3.21 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H) (E and Z isomer at 1:1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 166.0, 159.8, 159.8, 144.1, 144.1, 142.3, 142.2, 140.5, 140.5, 140.0, 139.8, 138.0, 137.6, 137.3, 132.1, 131.5, 131.0, 131.0, 130.6, 130.6, 130.0, 129.7, 128.8, 127.9, 127.8, 127.8, 127.7, 127.6, 122.6, 122.6, 122.5, 122.4, 113.5, 113.5, 25.7, 25.6, 21.6, 21.6 (*E* and *Z* isomer at 1:1); HRMS (ESI [M+Na]$^+$) for $C_{22}H_{18}N_2O$ calcd. 349.1317; found 349.1315.

(*E*)-3-((4-methoxyphenyl)(phenyl)methylene)-1-methyl-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3d):

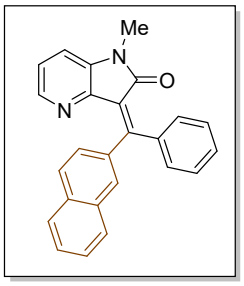
N-(2-bromopyridin-3-yl)-*N*-methyl-3-phenylpropiolamide, **2b** (100 mg, 0.32 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-methoxyphenyl)boronic acid (71 mg, 0.47 mmol), Na_2CO_3 (102 mg, 0.96 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 ^{o}C for 6 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL × 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3d**.



Yellow gummy; yield = 77% (84 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.92 (dd, *J* = 4.3, 2.2 Hz, 1H), 7.34 – 7.47 (m, 10H), 7.28 – 7.31 (m, 4H), 6.99 – 7.08 (m, 4H), 6.85 – 6.93 (m, 4H), 3.86 (s, 3H), 3.86 (s, 3H), 3.24 (s, 3H), 3.21 (s, 3H), (*E* and *Z* isomer at 1:1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.2, 161.7, 161.6, 159.8, 159.6, 144.6, 144.3, 142.2, 142.1, 140.9, 140.4, 137.6, 137.5, 134.2, 133.4, 132.2, 132.0, 131.8, 130.9, 130.1, 129.7, 128.0, 127.8, 122.4, 122.2, 121.4, 121.1, 113.4, 113.3, 113.3, 113.1, 55.4, 55.4, 25.7, 25.6 (*E* and *Z* isomer at 1:1); HRMS (ESI [M+Na]$^+$) for $C_{22}H_{18}N_2O_2$ calcd. 365.1266; found 365.1284.

(*E*)-1-methyl-3-(naphthalen-2-yl(phenyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3e):

N-(2-bromopyridin-3-yl)-*N*-methyl-3-phenylpropiolamide, **2b** (100 mg, 0.32 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of naphthalen-2-ylboronic acid (81 mg, 0.47 mmol), Na_2CO_3 (102 mg, 0.96 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 6 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL × 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3e**.

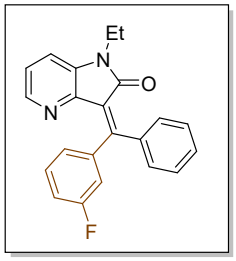


Orange solid; m.p. 152 - 154 °C; yield = 72% (83 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.99 (m, 6H), 7.71 – 7.80 (m, 4H), 7.34 – 7.56 (m, 16H), 7.02 – 7.07 (m, 4H), 3.24 (s, 3H). 3.22 (s, 3H) (E and Z isomer at 1:1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 166.0, 159.4, 144.1, 144.0, 142.3, 142.3, 140.6, 140.1, 138.2, 138.1, 138.0, 137.5, 134.3, 134.1, 133.0, 132.8, 132.2, 131.8, 130.9, 130.2, 129.9, 129.1, 129.0, 128.9, 128.5, 128.0, 127.9, 127.8, 127.8, 127.3, 127.2, 127.1, 127.0, 126.2, 122.8, 122.7, 113.6, 113.5, 29.8, 25.7; HRMS (ESI $[M+H]^+$) for $C_{25}H_{18}N_2O$ calcd. 363.1497; found 363.1501.

(*E*)-1-ethyl-3-((3-fluorophenyl)(phenyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3f):

N-(2-bromopyridin-3-yl)-*N*-ethyl-3-phenylpropiolamide, **2c** (100 mg, 0.30 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-fluorophenyl)boronic acid (63 mg, 0.45 mmol), Na_2CO_3 (95 mg, 0.90 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 7 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude

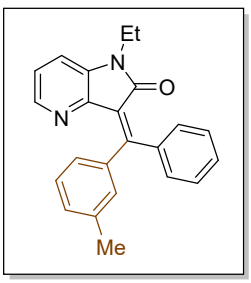
product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3f**.



Yellow solid; m.p. 148 - 150 °C; yield = 79% (81 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 4.4, 1.3 Hz, 1H), 7.30 – 7.47 (m, 6H), 7.10 – 7.16 (m, 2H), 7.03 – 7.07 (m, 2H), 3.77 (q, *J* = 7.2 Hz, 2H), 1.26 (td, *J* = 7.1, 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 163.7, 163.5, 161.3, 161.0, 157.2, 157.1, 157.1, 157.1, 143.8, 143.7, 142.6, 142.5, 142.2, 142.0, 142.0, 139.8, 139.3, 137.4, 131.4, 130.5, 130.2, 129.9, 129.5, 129.4, 129.3, 129.2, 128.0, 127.8, 127.0, 127.0, 126.2, 126.2, 123.3 (d, *J* = 5.3 Hz), 123.0 (d, *J* = 2.3 Hz), 118.3, 118.1, 117.5, 117.2, 116.8, 116.6, 116.4, 116.2, 113.7, 77.5, 77.2, 76.8, 34.3, 12.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.5 (s, 1F), -113.8 (s, 1F); HRMS (ESI $[M+H]^+$) for $C_{22}H_{17}FN_2O$ calcd. 345.1403; found 345.1402.

(*E*)-1-ethyl-3-(phenyl(m-tolyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3g):

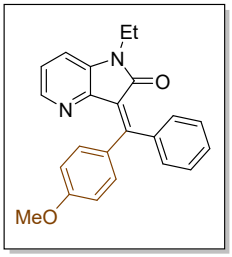
N-(2-bromopyridin-3-yl)-*N*-ethyl-3-phenylpropiolamide, **2c** (100 mg, 0.30 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of *m*-tolylboronic acid (61 mg, 0.45 mmol), Na_2CO_3 (95 mg, 0.90 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 7 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3g**.



Yellow solid; m.p. 156 - 158 °C; yield = 74% (75 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.96 (m, 2H), 7.29 – 7.46 (m, 12H), 7.16 – 7.25 (m, 6H), 7.02 – 7.05 (m, 4H), 3.77 (qd, *J* = 7.2, 1.3 Hz, 4H), 2.34 (s, 3H), 2.32 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 6H) (*E* and *Z* isomer at 1:1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.7, 159.7, 144.3, 142.1, 142.1, 140.6, 140.5, 140.1, 139.9, 137.6, 137.3, 137.1, 132.2, 131.5, 131.1, 131.0, 130.7, 130.6, 130.0, 129.7, 128.8, 127.9, 127.8, 127.7, 127.6, 122.6, 122.5, 113.5, 113.5, 34.3, 21.6, 12.8 (E and Z isomer at 1:1); HRMS (ESI $[M+H]^+$) for $C_{23}H_{20}N_2O$ calcd. 341.1654; found 341.1652.

(*E*)-1-ethyl-3-((4-methoxyphenyl)(phenyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-b]pyridin-2-one (3h):

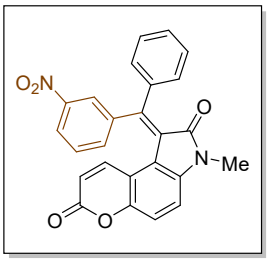
N-(2-bromopyridin-3-yl)-*N*-ethyl-3-phenylpropiolamide, **2c** (100 mg, 0.30 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-methoxyphenyl)boronic acid (68 mg, 0.45 mmol), Na_2CO_3 (95 mg, 0.90 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 7 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3h**.



Brown solid; m.p. 160 - 162 °C; yield = 77% (82 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 4.1, 2.4 Hz, 1H), 7.91 (dd, *J* = 4.4, 2.0 Hz, 0.8 H), 7.34 – 7.47 (m, 8.8H), 7.29 – 7.31 (m, 3.4H), 6.98 – 7.07 (m, 3.5H), 6.85 – 6.92 (m, 3.5H), 3.86 (s, 3H), 3.86 (s, 2.4H), 3.74 – 3.82 (m, 3.6H), 1.26 (dt, *J* = 8.5, 7.2 Hz, 5.4H) (*E* and *Z* isomer at 5:4); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 161.6, 161.6, 159.6, 159.5, 144.7, 144.4, 141.9, 141.8, 140.9, 140.4, 136.7, 136.6, 134.2, 133.5, 132.2, 132.0, 131.8, 130.9, 130.0, 129.8, 129.7, 128.3, 127.9, 127.7, 122.3, 122.1, 121.4, 121.2, 113.4, 113.3, 113.2, 113.1, 55.4, 34.3, 34.2, 12.9, 12.8 (*E* and *Z* isomer at 5:4); HRMS (ESI $[M+H]^+$) for $C_{23}H_{20}N_2O_2$ calcd. 357.1603; found 357.1602.

(*E*)-3-methyl-1-((3-nitrophenyl)(phenyl)methylene)-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3i):

N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-methyl-3-phenylpropiolamide, **2d** (100 mg, 0.26 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-nitrophenyl)boronic acid (65 mg, 0.39 mmol), Na_2CO_3 (83 mg, 0.78 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3i**.

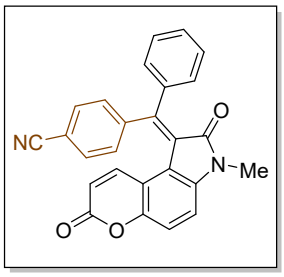


Brown solid; m.p. 172 - 174 °C; yield = 74% (82 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 - 8.35 (m, 1H), 8.19 (t, *J* = 2.0 Hz, 1H), 7.66 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.37 – 7.48 (m, 3H), 7.24 – 7.30 (m, 3H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.76 (d, *J* = 10.0 Hz, 1H), 5.79 (d, *J* = 9.6 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 160.0, 154.1, 150.5, 148.0, 141.4, 141.0, 140.8, 139.8, 137.3, 131.3, 131.1, 130.1, 128.8, 126.4, 126.3, 124.8, 118.6, 118.6, 116.0, 113.7, 111.4, 77.5, 77.2, 76.8, 26.4; HRMS (ESI $[M+Na]^+$) for $C_{25}H_{16}N_2O_5$ calcd. 447.0957; found 447.0958.

(*E*)-4-((3-methyl-2,7-dioxo-2,3-dihydropyrano[3,2-*e*]indol-1(7*H*)-ylidene)(phenyl)methyl)benzonitrile (3j):

N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-methyl-3-phenylpropiolamide, **2d** (100 mg, 0.26 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-cyanophenyl)boronic acid (56 mg, 0.39 mmol), Na_2CO_3 (83 mg, 0.78 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The

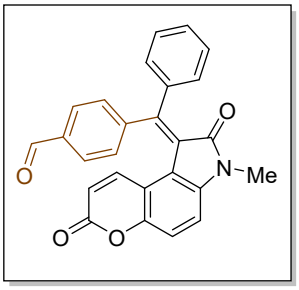
crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3j**.



Yellow solid; m.p. 158 - 160 °C; yield = 72% (76 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.72 (m, 2H), 7.62 – 7.66 (m, 0.6H), 7.35 – 7.46 (m, 6.2H), 7.21 – 7.30 (m, 4.4H), 7.01 (d, *J* = 8.7 Hz, 0.3H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.76 (dd, *J* = 10.0, 0.8 Hz, 0.3H), 6.74 (dd, *J* = 10.0, 0.8 Hz, 1H), 5.87 (d, *J* = 10.0 Hz, 0.3H), 5.78 (d, *J* = 10.0 Hz, 1H), 3.22 (s, 1H), 3.21 (s, 3H) (*E* and *Z* isomer at 3:1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 160.0, 159.7, 154.8, 150.5, 146.2, 144.7, 141.1, 141.0, 140.9, 139.8, 139.4, 138.9, 133.1, 132.2, 131.9, 131.7, 131.7, 131.2, 131.0, 130.0, 128.2, 126.2, 118.7, 118.6, 118.6, 116.3, 116.0, 113.8, 113.7, 113.5, 113.3, 111.5, 111.4, 26.4 (*E* and *Z* isomer at 3:1); HRMS (ESI $[M+H]^+$) for $C_{26}H_{16}N_2O_3$ calcd. 405.1239; found 405.1238.

(*E*)-4-((3-methyl-2,7-dioxo-2,3-dihydropyrano[3,2-*e*]indol-1(7*H*)-ylidene)(phenyl)methyl)benzaldehyde (3k):

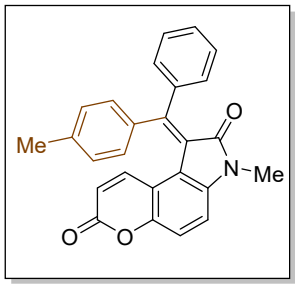
N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-methyl-3-phenylpropiolamide, **2d** (100 mg, 0.26 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-formylphenyl)boronic acid (58 mg, 0.39 mmol), Na_2CO_3 (83 mg, 0.78 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3k**.



Brown solid; m.p. 180 - 182 °C; yield = 75% (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 10.02 (s, 0.4H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 0.8H), 7.35 – 7.52 (m, 7.8H), 7.23 – 7.32 (m, 6H), 7.00 (d, *J* = 8.5 Hz, 0.4H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.80 (d, *J* = 9.6 Hz, 0.4H), 6.77 (d, *J* = 10.0 Hz, 1H), 5.78 (d, *J* = 10.0 Hz, 1H), 5.77 (d, *J* = 9.9 Hz, 0.4H), 3.23 (s, 1.2H), 3.21 (s, 3H) (*E* and *Z* isomer at 5:2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 191.2, 166.5, 166.3, 160.0, 159.8, 155.7, 155.7, 150.5, 150.4, 147.6, 146.3, 141.1, 141.0, 140.9, 139.9, 139.6, 139.2, 137.1, 136.9, 132.2, 131.9, 131.7, 131.3, 130.9, 130.5, 129.9, 129.2, 128.1, 125.9, 118.7, 118.4, 118.3, 116.0, 115.9, 113.7, 113.4, 111.3, 111.3, 26.4 (*E* and *Z* isomer at 5:2); HRMS (ESI $[M+H]^+$) for $C_{26}H_{17}NO_4$ calcd. 408.1236; found 408.1240.

(*E*)-3-methyl-1-(phenyl(p-tolyl)methylene)-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3l):

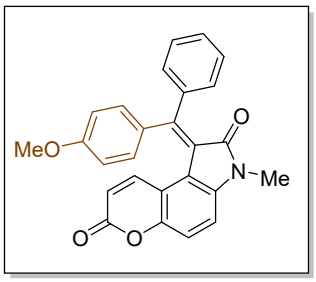
N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-methyl-3-phenylpropiolamide, **2d** (100 mg, 0.26 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of *p*-tolylboronic acid (53 mg, 0.39 mmol), Na_2CO_3 (83 mg, 0.78 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3l**.



Brown solid; m.p. 158 - 160 °C; yield = 77% (78 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.54 (m, 7H), 7.32 – 7.39 (m, 8H), 7.26 (s, 4H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 10.0 Hz, 1H), 6.94 (d, *J* = 10.0 Hz, 1H), 5.90 (d, *J* = 10.0 Hz, 1H), 5.87 (d, *J* = 10.0 Hz, 1H), 3.34 (s, 3H), 3.33 (s, 3H), 2.55 (s, 3H), 2.47 (s, 3H) (*E* and *Z* isomer at 1:1); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 166.6, 160.3, 160.2, 158.6, 158.6, 150.3, 150.3, 141.7, 141.2, 141.2, 140.4, 140.3, 140.2, 140.1, 140.0, 138.8, 136.9, 132.0, 131.8, 131.7, 131.7, 130.6, 130.5, 130.2, 129.5, 128.6, 127.8, 124.1, 124.0, 119.7, 117.3, 117.2, 115.4, 115.2, 113.2, 113.2, 111.0, 110.9, 77.6, 77.2, 76.7, 26.3, 26.3, 21.8, 21.5 (*E* and *Z* isomer at 1:1); HRMS (ESI $[M+H]^+$) for $C_{26}H_{19}NO_4$ calcd. 410.1392; found 410.1390.

(*E*)-1-((4-methoxyphenyl)(phenyl)methylene)-3-methyl-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3m):

N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-methyl-3-phenylpropiolamide, **2d** (100 mg, 0.26 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-methoxyphenyl)boronic acid (59 mg, 0.39 mmol), Na_2CO_3 (83 mg, 0.78 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3m**.

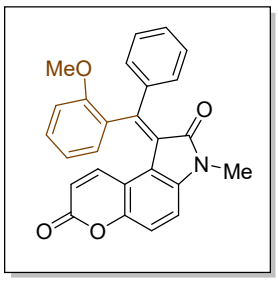


Red solid; m.p. 167 - 169 °C; yield = 79% (84 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.52 (m, 1H), 7.36 – 7.43 (m, 4H), 7.30 – 7.34 (m, 5H), 7.26 – 7.28 (m, 3H), 7.21 (dt, *J* = 8.9, 2.9 Hz, 4H), 6.91 – 7.01 (m, 5H), 6.82 – 6.86 (m, 2.6H), 5.84 (d, *J* = 10.0 Hz, 0.9H), 5.74 (d, *J* = 10.0 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 2.7H), 3.24 (s, 3H), 3.21 (s, 2.7H) (*E* and *Z* isomer at 10:9); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 166.7, 162.2, 161.6, 160.4, 160.3, 158.5, 158.4, 150.3, 150.3, 141.7, 140.4, 140.2, 140.1, 140.1, 139.9, 134.4, 133.8, 133.6, 132.0, 131.9,

131.7, 130.7, 130.7, 129.5, 127.9, 123.3, 123.2, 120.1, 120.0, 117.0, 116.9, 115.3, 115.3, 115.0, 113.2, 113.0, 113.0, 111.0, 110.9, 55.6, 55.4, 26.4, 26.3 (*E* and *Z* isomer at 10:9); HRMS (ESI $[M+H]^+$) for $C_{26}H_{19}NO_4$ calcd. 410.1392; found 410.1390.

(*E*)-1-((2-methoxyphenyl)(phenyl)methylene)-3-methyl-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3n):

N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-methyl-3-phenylpropiolamide, **2d** (100 mg, 0.26 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (2-methoxyphenyl)boronic acid (59 mg, 0.39 mmol), Na_2CO_3 (83 mg, 0.78 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3n**.

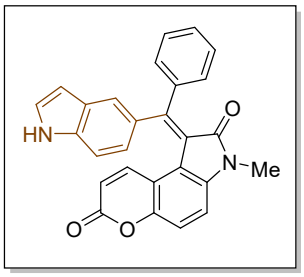


Orange solid; m.p. 162 - 164 °C; yield = 77% (82 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.46 (m, 1H), 7.22 – 7.35 (m, 6H), 7.08 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.95 – 7.02 (m, 3H), 6.80 (d, *J* = 10.0 Hz, 1H), 5.76 (d, *J* = 10.0 Hz, 1H), 3.64 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 160.4, 158.0, 153.1, 150.3, 141.7, 140.7, 140.6, 131.6, 131.1, 131.1, 130.0, 129.9, 129.9, 129.6, 129.3, 125.7, 120.5, 119.2, 117.4, 115.3, 113.7, 111.4, 111.0, 55.8, 26.2; HRMS (ESI $[M+H]^+$) for $C_{26}H_{19}NO_4$ calcd. 432.1212; found 432.1210.

(*E*)-1-((1H-indol-5-yl)(phenyl)methylene)-3-methyl-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3o):

N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-methyl-3-phenylpropiolamide, **2d** (100 mg, 0.26 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (1*H*-indol-5-yl)boronic acid (63 mg, 0.39 mmol), Na_2CO_3 (83 mg, 0.78 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL

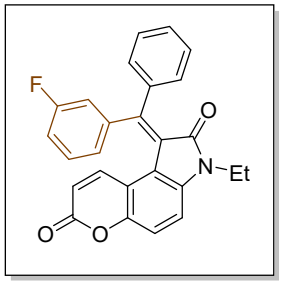
round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3o**.



Brown solid; m.p. 173 - 175 °C; yield = 73% (79 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.36 – 7.51 (m, 5H), 7.19 – 7.31 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.77 (d, *J* = 10.0 Hz, 1H), 6.46 (s, 1H), 5.52 (d, *J* = 10.0 Hz, 1H), 3.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 161.0, 160.6, 150.3, 141.0, 140.9, 140.1, 136.9, 133.4, 130.6, 128.7, 127.8, 126.1, 125.8, 125.5, 123.1, 120.6, 116.8, 114.7, 113.2, 112.3, 110.9, 103.9, 26.3; HRMS (ESI $[M+H]^+$) for $C_{27}H_{18}N_2O_3$ calcd. 419.1396; found 419.1391.

(*E*)-3-ethyl-1-((3-fluorophenyl)(phenyl)methylene)-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3p):

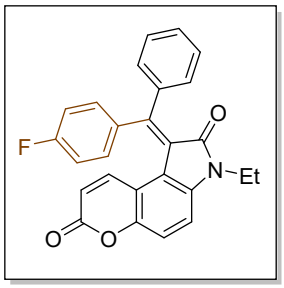
N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-ethyl-3-phenylpropiolamide, **2e** (100 mg, 0.25 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-fluorophenyl)boronic acid (52 mg, 0.38 mmol), Na_2CO_3 (80 mg, 0.76 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3p**.



Red solid; m.p. 168 - 170 °C; yield = 77% (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.52 (m, 1H), 7.29 – 7.45 (m, 9H), 7.23 – 7.26 (m, 4H), 7.15 – 7.19 (m, 2H), 7.06 – 7.11 (m, 2H), 7.00 (dt, *J* = 8.2, 2.3 Hz, 3H), 6.95 (dt, *J* = 9.5, 2.1 Hz, 1H), 6.86 (d, *J* = 9.6 Hz, 1H), 6.79 (d, *J* = 10 Hz, 1H) (*E* and *Z* isomer at 1:1); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 166.1, 162.1, 161.5, 160.4, 160.3, 158.3, 158.2, 150.1, 150.1, 141.7, 140.4, 140.2, 140.1, 139.2, 139.0, 134.4, 133.8, 133.5, 132.0, 131.9, 131.7, 130.6, 130.6, 129.4, 127.8, 123.3 (d, *J* = 5.5 Hz), 120.2 (d, *J* = 7.9 Hz), 116.9, 116.8, 115.2, 115.1, 114.9, 113.1, 111.0, 110.9, 55.5, 41.0, 34.8, 34.7, 12.9 (*E* and *Z* isomer at 1:1); ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.5 (s, 1F), -113.4 (s, 1F); HRMS (ESI $[M+H]^+$) for $C_{27}H_{20}O_4S$ calcd. 441.1161; found 441.1160.

(*E*)-3-ethyl-1-((4-fluorophenyl)(phenyl)methylene)-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3q):

N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-ethyl-3-phenylpropiolamide, **2e** (100 mg, 0.25 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-fluorophenyl)boronic acid (52 mg, 0.38 mmol), Na_2CO_3 (80 mg, 0.76 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3q**.

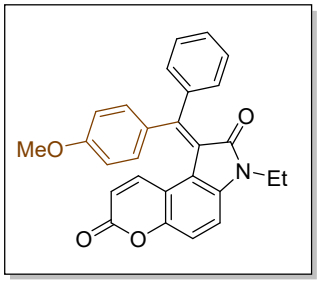


Yellow solid; yield = 80% (82 mg); m.p. 176 - 178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.91 (m, 1H), 7.27 - 7.36 (m, 5H), 7.02 - 7.22 (m, 6H), 6.95 (td, *J* = 7.3, 1.6 Hz, 1H), 6.85

(td, J = 7.3, 1.3 Hz, 1H), 6.68 - 6.72 (m, 2H), 3.71 (s, 3H) (*E* and *Z* isomer at 1:1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.1, 165.1, 160.3, 160.2, 156.8, 156.7, 150.3, 150.3, 141.7, 140.0 (d, J = 10.1 Hz), 139.8 (d, J = 3.1 Hz), 139.6, 137.9, 134.2, 134.1, 133.9, 133.8, 131.9, 131.7, 130.8, 129.7, 128.0, 124.8, 124.7, 119.6, 117.7, 117.6, 117.0, 116.7, 115.7, 115.6, 115.2, 115.0, 113.6, 113.4, 111.3, 111.2, 35.0, 34.9, 29.8, 13.0 (*E* and *Z* isomer at 1:1); ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.0 (s, 1F), -109.3 (s, 1F); HRMS (ESI $[M+Na]^+$) for $C_{27}H_{19}FO_4S$ calcd. 434.1168; found 434.1164.

(*E*)-3-ethyl-1-((4-methoxyphenyl)(phenyl)methylene)-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3r):

N-(5-bromo-2-oxo-2*H*-chromen-6-yl)-*N*-ethyl-3-phenylpropiolamide, **2e** (100 mg, 0.25 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-methoxyphenyl)boronic acid (59 mg, 0.38 mmol), Na_2CO_3 (80 mg, 0.76 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3r**.

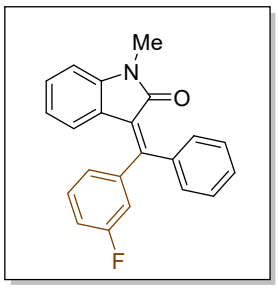


Yellow solid; m.p. 170 - 172 °C; yield = 80% (85 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.52 (m, 4H), 7.31 – 7.37 (m, 6H), 7.17 – 7.28 (m, 6H), 7.00 (t, J = 9.8 Hz, 3H), 6.92 – 6.94 (m, 2H), 6.85 (dd, J = 9.3, 4.9 Hz, 3H), 5.83 (d, J = 10.0 Hz, 1H), 5.73 (d, J = 10.0 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.74 – 3.81 (m, 4H), 1.26 (q, J = 7.2 Hz, 6H) (*E* and *Z* isomer at 1:1); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 166.1, 162.1, 161.5, 160.4, 160.3, 158.3, 158.2, 150.1, 150.1, 141.7, 140.4, 140.2, 140.1, 139.2, 139.0, 134.4, 133.8, 133.5, 132.0, 131.9, 131.7, 130.6, 130.6, 129.4, 127.8, 123.3, 123.2, 120.3, 120.2, 116.9, 116.8, 115.2, 115.1, 114.9, 113.1, 113.1, 111.0, 110.9, 77.6, 77.4, 77.2, 76.7, 55.5, 55.4, 55.4, 41.0, 34.8, 34.7,

29.7, 12.9, 12.9 (*E* and *Z* isomer at 1:1); HRMS (ESI $[M+H]^+$) for $C_{27}H_{21}NO_4$ calcd. 424.1549; found 424.1549.

(*E*)-3-((3-fluorophenyl)(phenyl)methylene)-1-methylindolin-2-one (3s):

N-(2-iodophenyl)-*N*-methyl-3-phenylpropiolamide, **2f** (100 mg, 0.28 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-fluorophenyl)boronic acid (58 mg, 0.42 mmol), Na_2CO_3 (89 mg, 0.84 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3s**.

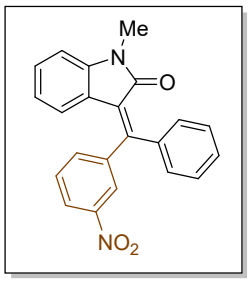


Yellow solid; m.p. 163 - 165 °C; yield = 82% (75 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.46 (m, 6H), 7.13 – 7.23 (m, 3H), 7.04 (dd, *J* = 9.3, 2.0 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.73 (t, *J* = 7.7 Hz, 1H), 6.46 (d, *J* = 7.7 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.4, 161.9, 152.6, 152.6, 143.6, 143.4, 143.4, 139.4, 130.7 (d, *J* = 8.3 Hz), 130.0, 129.3, 129.2, 128.0, 125.1, 125.1, 124.8, 123.3, 122.9, 121.6, 116.3 (t, *J* = 21.6 Hz), 107.9, 77.5, 77.2, 76.8, 26.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.7 (s, 1F); HRMS (ESI $[M]^+$) for $C_{22}H_{16}FNO$ calcd. 322.1216; found 322.1222.

(*E*)-1-methyl-3-((3-nitrophenyl)(phenyl)methylene)indolin-2-one (3t):

N-(2-iodophenyl)-*N*-methyl-3-phenylpropiolamide, **2f** (100 mg, 0.28 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-nitrophenyl)boronic acid (70 mg, 0.42 mmol), Na_2CO_3 (89 mg, 0.84 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried

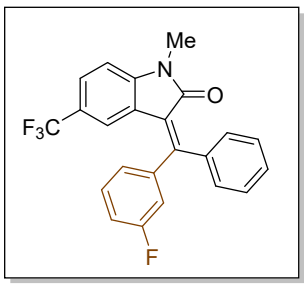
over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3t**.



Yellow solid; m.p. 110 - 112 °C; yield = 80% (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.34 (m, 1H), 8.19 (t, *J* = 2.0 Hz, 1H), 7.73 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.37 – 7.43 (m, 3H), 7.32 – 7.36 (m, 2H), 7.20 – 7.24 (m, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.70 (td, *J* = 7.7, 1.1 Hz, 1H), 6.33 (d, *J* = 7.7 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 150.7, 148.8, 143.8, 142.9, 138.9, 135.6, 130.2, 130.0, 129.8, 129.6, 128.3, 125.8, 124.5, 124.0, 122.9, 122.3, 121.7, 108.3, 26.0; HRMS (ESI $[M+H]^+$) for $C_{22}H_{16}N_2O_3$ calcd. 357.1239; found 357.1234.

(*E*)-3-((3-fluorophenyl)(phenyl)methylene)-1-methyl-5-(trifluoromethyl)indolin-2-one (3u):

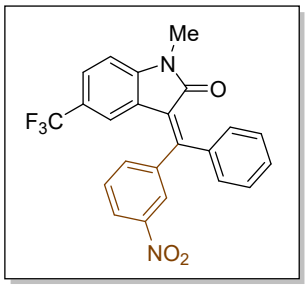
N-(2-iodo-4-(trifluoromethyl)phenyl)-*N*-methyl-3-phenylpropiolamide, **2g** (100 mg, 0.23 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-fluorophenyl)boronic acid (49 mg, 0.35 mmol), Na_2CO_3 (73 mg, 0.69 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3u**.



Brown solid; m.p. 164 - 166 °C; yield = 76% (69 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.48 (m, 7H), 7.14 – 7.23 (m, 2H), 7.00 (ddd, *J* = 9.2, 2.6, 1.5 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 1.7 Hz, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 164.4, 161.9, 155.1, 145.7, 142.5 (d, *J* = 7.2 Hz), 138.6, 130.9 (d, *J* = 8.3 Hz), 130.2, 130.0, 129.9, 128.0, 126.2 (d, *J* = 4.2 Hz), 124.9 (d, *J* = 3.2 Hz), 123.5, 123.0, 120.2, 116.5 (dd, *J* = 37.4, 21.5 Hz), 107.6, 77.4, 77.0, 76.7, 26.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.0 (s, 3F), -111.3 (s, 1F); HRMS (ESI $[M+H]^+$) for $C_{23}H_{15}F_4NO$ calcd. 398.1168; found 398.1187.

(*E*)-1-methyl-3-((3-nitrophenyl)(phenyl)methylene)-5-(trifluoromethyl)indolin-2-one (3v):

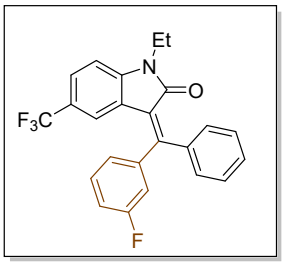
N-(2-iodo-4-(trifluoromethyl)phenyl)-*N*-methyl-3-phenylpropiolamide, **2g** (100 mg, 0.23 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-nitrophenyl)boronic acid (57 mg, 0.35 mmol), Na_2CO_3 (73 mg, 0.69 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3v**.



Yellow solid; m.p. 170 - 172 °C; yield = 75% (73 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dt, *J* = 8.1, 1.7 Hz, 1H), 8.17 (t, *J* = 2.0 Hz, 1H), 7.65 – 7.74 (m, 2H), 7.39 – 7.48 (m, 4H), 7.33 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.52 (d, *J* = 1.7 Hz, 1H), 3.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 153.3, 148.9, 146.1, 142.2, 138.2, 135.5, 130.4 (d, *J* = 3.9 Hz), 130.2, 128.4, 126.9 (d, *J* = 3.9 Hz), 124.6 (d, *J* = 6.5 Hz), 124.5, 124.2, 122.6, 119.9, 119.9, 108.0, 26.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.1 (s, 3F); HRMS (ESI $[M+H]^+$) for $C_{23}H_{15}F_3N_2O_3$ calcd. 425.1113; found 425.1108.

(*E*)-1-ethyl-3-((3-fluorophenyl)(phenyl)methylene)-5-(trifluoromethyl)indolin-2-one (3w):

N-ethyl-*N*-(2-iodo-4-(trifluoromethyl)phenyl)-3-phenylpropiolamide, **2h** (100 mg, 0.22 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-fluorophenyl)boronic acid (47 mg, 0.34 mmol), Na_2CO_3 (70 mg, 0.66 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 ^oC for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3w**.

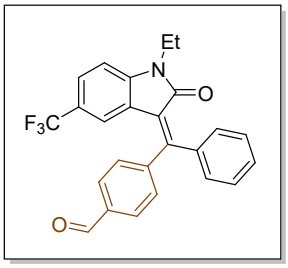


Orange solid; m.p. 168 - 170 ^oC; yield = 76% (69 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.51 (m, 7H), 7.07 – 7.22 (m, 2H), 6.98 – 7.05 (m, 1H), 6.87 (d, J = 8.3 Hz, 1H), 6.59 – 6.62 (m, 1H), 3.80 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 165.0, 161.7, 155.0, 145.0, 142.7 (d, J = 7.4 Hz), 138.7, 131.0 (d, J = 8.3 Hz), 130.2, 130.0, 129.4, 129.1, 128.1, 126.3 (d, J = 4.1 Hz), 125.0 (d, J = 3.2 Hz), 123.9, 123.7, 123.5, 123.4, 120.5 (d, J = 4.1 Hz), 116.6 (dd, J = 26.4, 21.7 Hz), 107.7, 34.8, 12.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.0 (s, 3F), -111.3 (s, 1F); HRMS (ESI $[M+Na]^+$) for : $C_{24}H_{17}F_4NO$ calcd. 434.1144; found 434.1140.

(*E*)-4-((1-ethyl-2-oxo-5-(trifluoromethyl)indolin-3-ylidene)(phenyl)methyl)benzaldehyde (3x):

N-ethyl-*N*-(2-iodo-4-(trifluoromethyl)phenyl)-3-phenylpropiolamide, **2h** (100 mg, 0.22 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-formylphenyl)boronic acid (51 mg, 0.34 mmol), Na_2CO_3 (70 mg, 0.66 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 ^oC for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and

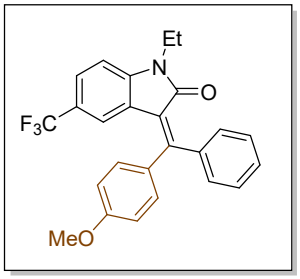
extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3x**.



Yellow solid; m.p. 164 - 166 °C; yield = 71% (66 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.11 (s, 1H), 10.04 (s, 0.2H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 0.4H), 7.52 (dd, *J* = 8.3, 1.9 Hz, 2.8H), 7.30 – 7.48 (m, 7.6H), 6.87 (d, *J* = 8.2 Hz, 1.2H), 6.67 (d, *J* = 1.8 Hz, 0.2H), 6.56 (d, *J* = 1.7 Hz, 1H), 3.80 (q, *J* = 7.2 Hz, 2.4H), 1.27 (t, *J* = 7.3 Hz, 4.2H) (*E* and *Z* isomer at 5:1); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.8, 191.4, 165.9, 154.6, 146.5, 145.6, 145.0, 139.6, 138.4, 136.8, 136.4, 130.5, 130.4, 130.1, 130.0, 129.4 (d, *J* = 4.3 Hz), 129.3, 128.9, 128.1, 126.4 (d, *J* = 3.8 Hz), 125.9, 123.9, 123.8, 123.4, 123.0, 122.3, 120.3 (d, *J* = 4.0 Hz), 107.7, 107.7, 77.5, 77.0, 76.6, 34.7, 12.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.1 (s, 3F); HRMS (ESI $[M+H]^+$) for $C_{25}H_{18}F_3NO_2$ calcd. 422.1368; found 422.1366.

(*E*)-1-ethyl-3-((4-methoxyphenyl)(phenyl)methylene)-5-(trifluoromethyl)indolin-2-one (3y):

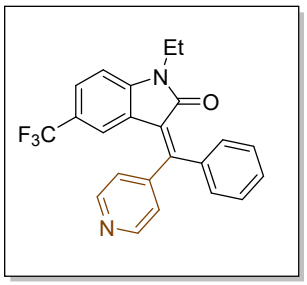
N-ethyl-*N*-(2-iodo-4-(trifluoromethyl)phenyl)-3-phenylpropiolamide, **2h** (100 mg, 0.22 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (4-methoxyphenyl)boronic acid (52 mg, 0.34 mmol), Na_2CO_3 (70 mg, 0.66 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3y**.



Brown solid; m.p. 160 - 162 °C; yield = 77% (72 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.45 (m, 6H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.96 – 6.99 (m, 2H), 6.93 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.89 (s, 3H), 3.82 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 161.3, 157.3, 144.5 (d, *J* = 1.4 Hz), 139.8, 132.7, 131.7, 130.6, 129.7, 127.9, 126.2, 125.5 (q, *J* = 4.0 Hz), 124.1, 123.5, 123.1, 122.6, 122.2, 119.9 (q, *J* = 4.0 Hz), 116.0, 114.7, 114.4, 107.4, 55.5, 34.6, 12.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.8 (S, 3F); HRMS (ESI $[M+Na]^+$) for $C_{25}H_{20}F_3NO_2$ calcd. 446.1344; found 446.1348.

(*E*)-1-ethyl-3-(phenyl(pyridin-4-yl)methylene)-5-(trifluoromethyl)indolin-2-one (3z):

N-ethyl-*N*-(2-iodo-4-(trifluoromethyl)phenyl)-3-phenylpropiolamide, **2h** (100 mg, 0.22 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of pyridin-4-ylboronic acid (42 mg, 0.34 mmol), Na_2CO_3 (70 mg, 0.66 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3z**.

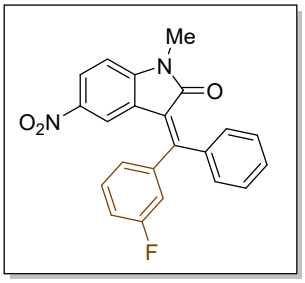


Brown solid; m.p. 177- 179 °C; yield = 78% (67 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 2H), 7.37 – 7.52 (m, 5H), 7.31 – 7.34 (m, 2H), 7.27 (d, *J* = 4.7 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.64 (s, 1H), 3.79 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 152.8, 151.0, 148.4, 145.3, 138.0, 130.1, 130.0, 129.6, 128.8, 128.3, 126.9,

124.1, 123.5, 122.7, 120.5, 108.0, 34.9, 12.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.1 (s, 3F). HRMS (ESI $[M+H]^+$) for $C_{23}H_{17}F_3N_2O$ calcd. 395.1371; found 395.1373.

(*E*)-3-((3-fluorophenyl)(phenyl)methylene)-1-methyl-5-nitroindolin-2-one (3aa):

N-(2-iodo-4-nitrophenyl)-*N*-methyl-3-phenylpropiolamide, **2i** (100 mg, 0.25 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-fluorophenyl)boronic acid (51 mg, 0.37 mmol), Na_2CO_3 (78 mg, 0.74 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3aa**.

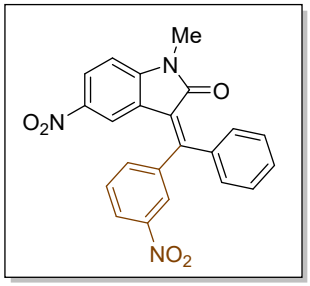


Brown solid; yield = 74% (69 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.38 – 7.52 (m, 4H), 7.34 – 7.37 (m, 2H), 7.24 – 7.30 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 9.2, 2.2 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 3.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 165.0, 161.7, 156.9 (d, *J* = 2.0 Hz), 148.0, 142.8, 142.2 (d, *J* = 7.4 Hz), 138.4, 131.3, 131.2, 130.4, 130.3, 128.2, 125.5, 125.0, 124.9, 123.3, 122.7, 118.9, 117.5, 117.2, 116.6, 116.3, 107.4, 77.6, 77.2, 76.7, 26.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.6 (s, 3F); HRMS (ESI $[M+H]^+$) for $C_{22}H_{15}FN_2O_3$ calcd. 375.1145; found 375.1143.

(*E*)-1-methyl-5-nitro-3-((3-nitrophenyl)(phenyl)methylene)indolin-2-one (3ab):

N-(2-iodo-4-nitrophenyl)-*N*-methyl-3-phenylpropiolamide, **2i** (100 mg, 0.25 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (3-nitrophenyl)boronic acid (62 mg, 0.37 mmol), Na_2CO_3 (78 mg, 0.74 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10

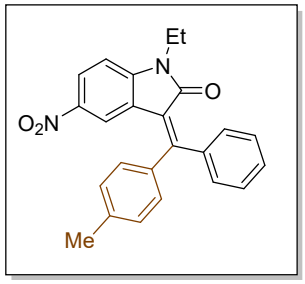
mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3ab**.



Yellow solid; m.p. 170 - 172 °C; yield = 71% (71 mg); ^{1}H NMR (400 MHz, $CDCl_3$) 7.40 – 7.44 (m, 1H), 8.15 – 8.19 (m, 2H), 7.72 – 7.74 (m, 2H), 7.40 – 7.51 (m, 3H), 7.32 – 7.35 (m, 2H), 7.20 (d, *J* = 2.2 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 3.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 155.0, 149.0, 148.3, 142.7, 141.7, 137.9, 135.3, 130.7, 130.7, 130.3, 128.5, 126.0, 125.0, 124.5, 123.6, 122.7, 118.5, 107.7, 26.6; HRMS (ESI $[M+H]^+$) for $C_{22}H_{15}N_3O_5$ calcd. 402.1090; found 402.1088.

(*E*)-1-ethyl-5-nitro-3-(phenyl(p-tolyl)methylene)indolin-2-one (3ac):

N-ethyl-*N*-(2-iodo-4-nitrophenyl)-3-phenylpropiolamide, **2j** (100 mg, 0.24 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of *p*-tolylboronic acid (48 mg, 0.36 mmol), Na_2CO_3 (76 mg, 0.72 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3ac**.

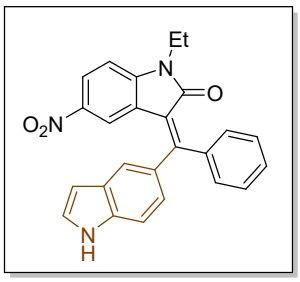


Orange solid; m.p. 156 - 158 °C; yield = 78% (72 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.13 (m, 1H), 7.34 – 7.59 (m, 5H), 7.27 – 7.32 (m, 3H), 7.19 – 7.22 (m, 2H), 6.85 (dd, *J* =

8.7, 2.5 Hz, 1H), 3.83 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 159.4, 147.0, 142.5, 141.0, 139.3, 137.3, 130.8, 130.6, 130.4, 130.1, 130.0, 129.6, 129.5, 129.4, 128.8, 128.0, 125.0, 124.9, 124.1, 121.8, 118.9, 107.1, 107.1, 35.0, 21.7, 12.9; HRMS (ESI $[M+H]^+$) for $C_{24}H_{20}N_2O_3$ calcd. 407.1372; found 407.1368.

(*E*)-3-((1H-indol-5-yl)(phenyl)methylene)-1-ethyl-5-nitroindolin-2-one (3ad):

N-ethyl-*N*-(2-iodo-4-nitrophenyl)-3-phenylpropiolamide, **2j** (100 mg, 0.24 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of (1*H*-indol-5-yl)boronic acid (58 mg, 0.36 mmol), Na_2CO_3 (76 mg, 0.72 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3ad**.

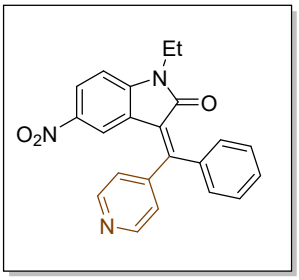


Orange solid; m.p. 160 - 162 °C; yield = 71% (70 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.09 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.55 (s, 1H), 7.38 – 7.49 (m, 6H), 7.26 – 7.29 (m, 2H), 7.19 – 7.22 (m, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.55 (s, 1H), 3.85 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.5, 146.8, 142.4, 140.3, 137.1, 131.7, 130.9, 130.1, 128.4, 127.9, 125.8, 124.7, 124.6, 124.2, 123.8, 121.0, 118.6, 111.7, 106.9, 103.8, 35.0, 29.8, 13.0; HRMS (ESI $[M+Na]^+$) for $C_{25}H_{19}N_3O_3$ calcd. 432.1324; found 432.1319.

(*E*)-1-ethyl-5-nitro-3-(phenyl(pyridin-4-yl)methylene)indolin-2-one (3ae):

N-ethyl-*N*-(2-iodo-4-nitrophenyl)-3-phenylpropiolamide, **2j** (100 mg, 0.24 mmol) was dissolved in 1,4-Dioxane (3 mL) followed by addition of pyridin-4-ylboronic acid (44 mg,

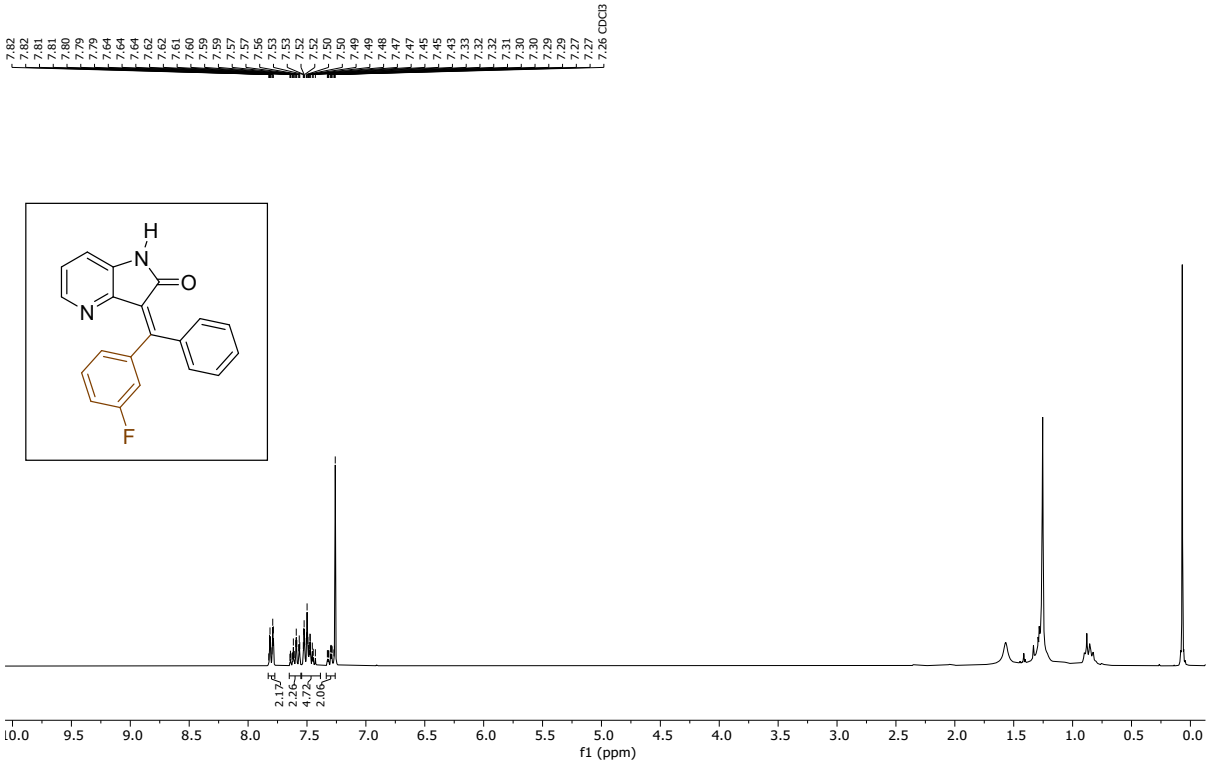
0.36 mmol), Na_2CO_3 (76 mg, 0.72 mmol), $Ni(OAc)_2$ and distilled water (1 mL) and heated in a pre-heated oil bath under continuous stirring at 90 °C for 5 h in a 10 mL round-bottom flask fitted with a septum. Upon completion of the reaction, as monitored by TLC, the reaction mixture was cooled. The reaction mixture was washed and extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel with hexane:ethyl acetate as eluent to give pure product **3ae**.

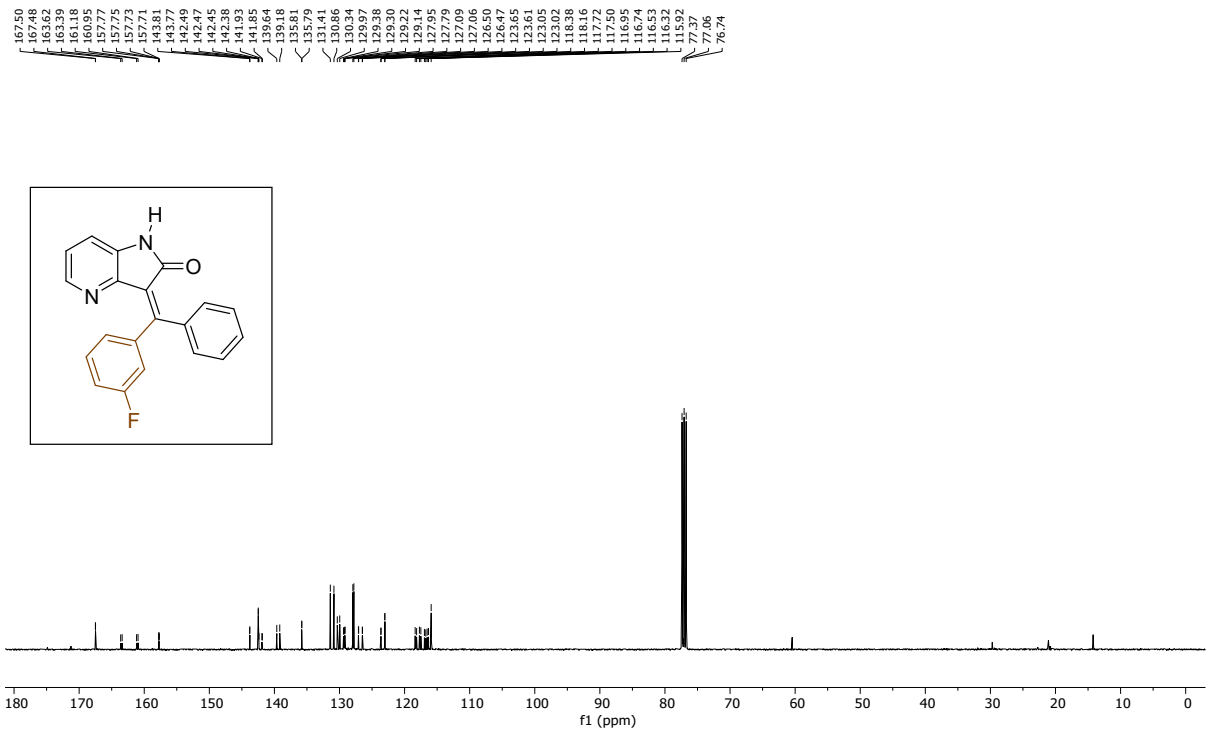


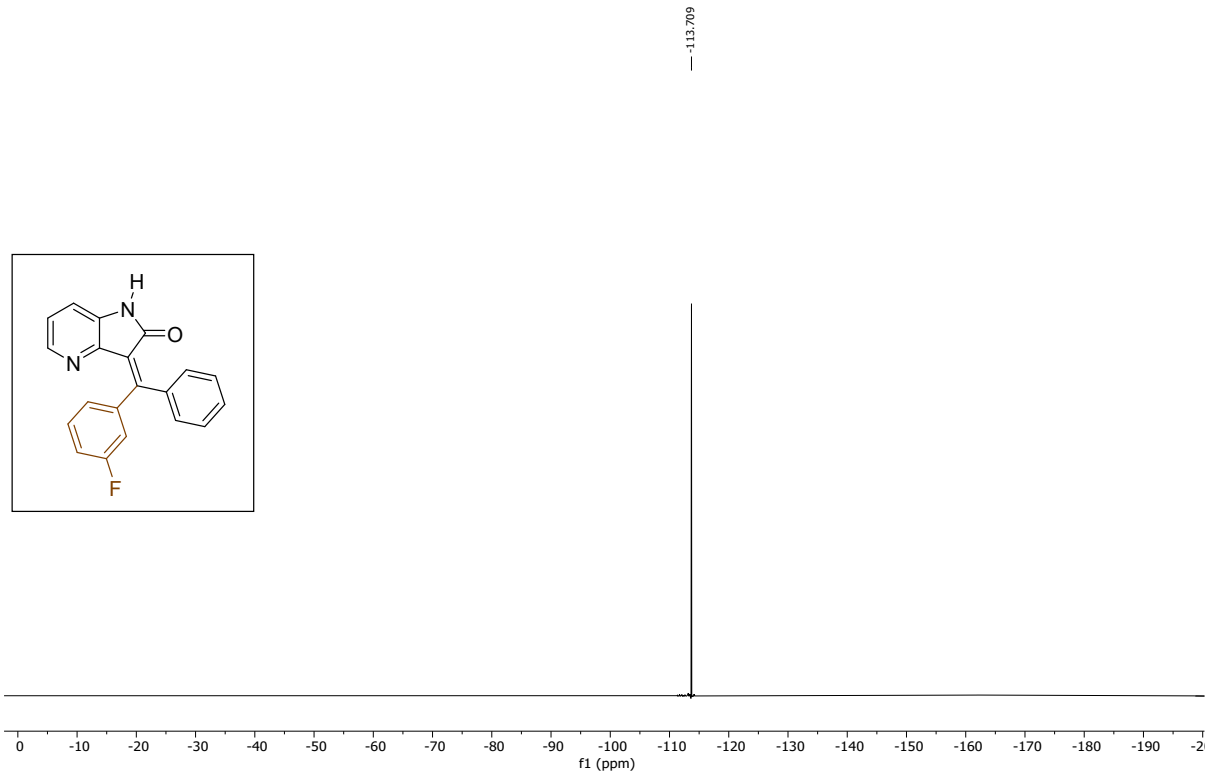
Yellow solid; m.p. 156 - 158 °C; yield = 73% (65 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.9 Hz, 2H), 8.16 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.50 – 7.59 (m, 3H), 7.35 (d, *J* = 2.2 Hz, 1H), 7.30 – 7.32 (m, 2H), 7.24 – 7.26 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 1H), 3.81 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 154.3, 149.9, 147.6, 147.1, 142.7, 138.7, 130.7, 129.8, 128.7, 126.1, 123.9, 123.7, 122.9, 119.4, 107.6, 35.1, 12.8; HRMS (ESI $[M+H]^+$) for $C_{22}H_{17}N_3O_3$ calcd. 372.1348; found 372.1341.

6) ^{1}H and ^{13}C-NMR spectra of compounds 3a-3ae:

Figure S1. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-3-((3-fluorophenyl)(phenyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3a) in $CDCl_3$.



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O
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F
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-40
-50
-60
-70
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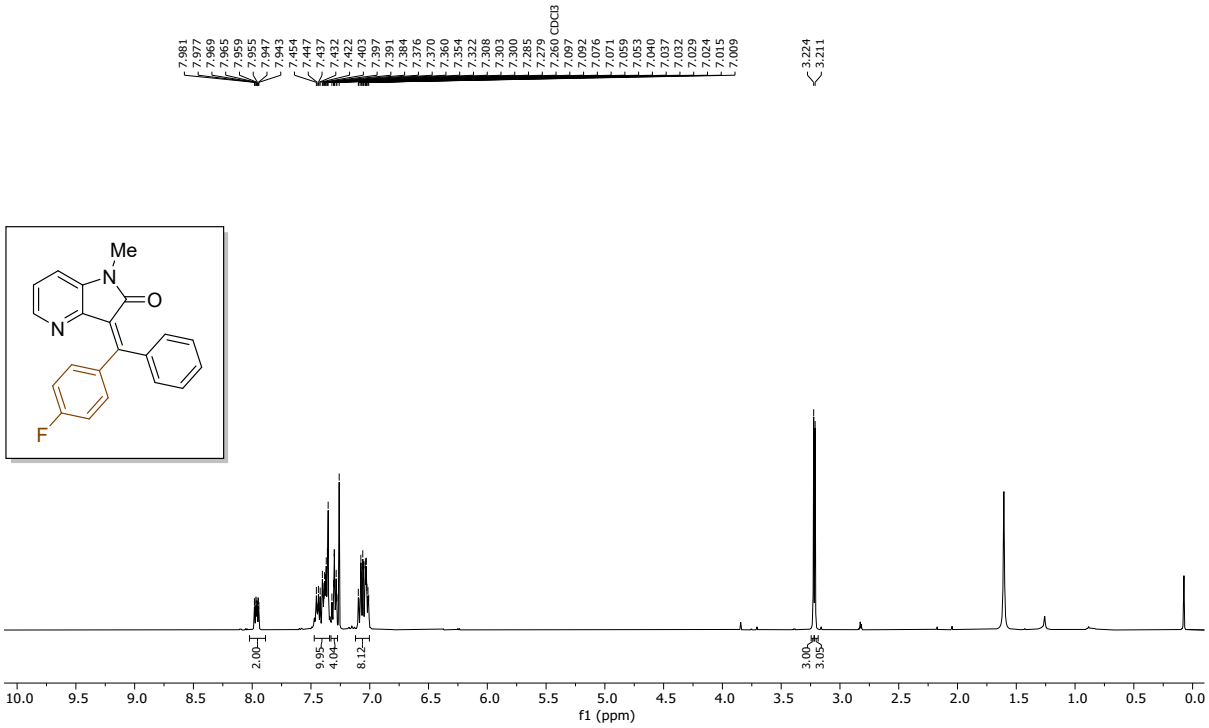
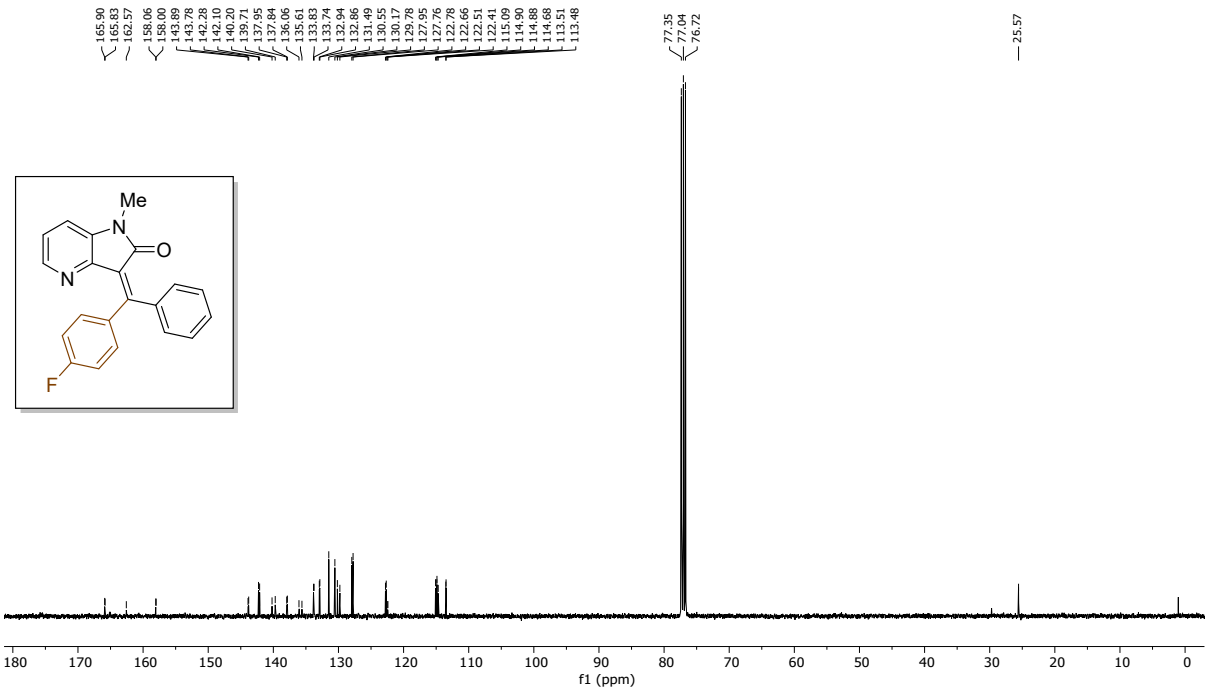
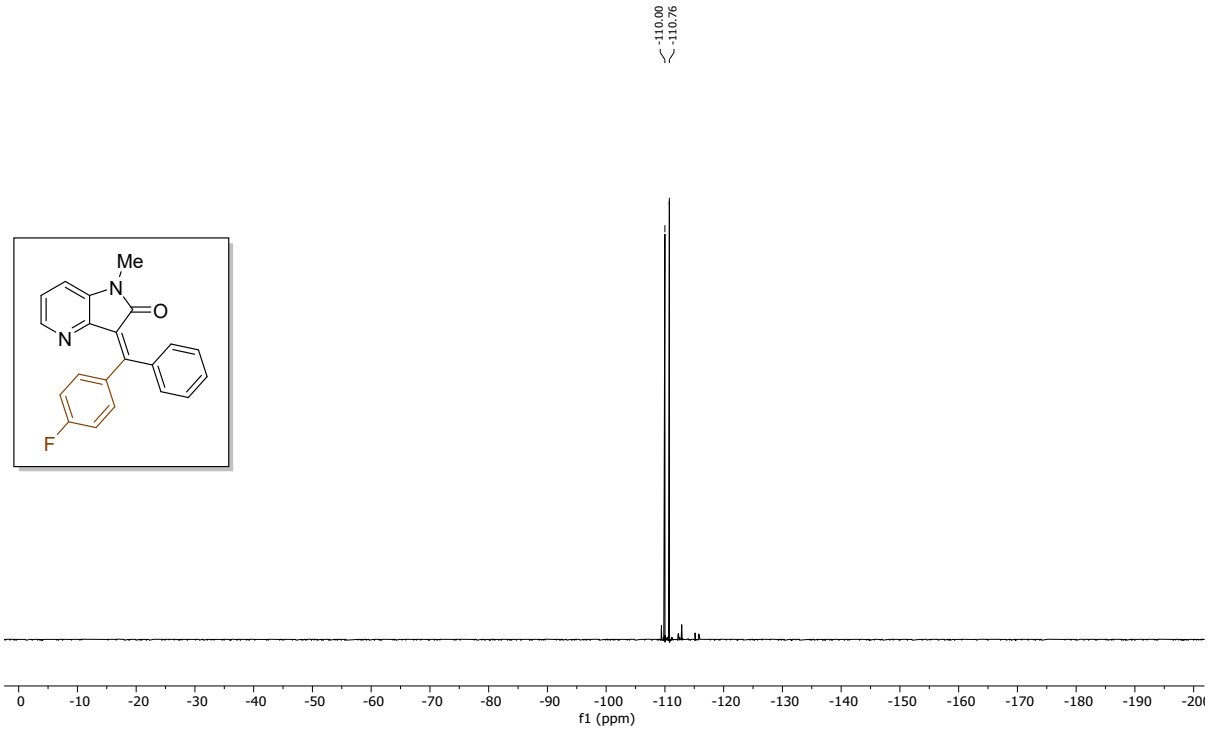
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Figure S2. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-3-((4-fluorophenyl)(phenyl)methylene)-1-methyl-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3b) in $CDCl_3$.



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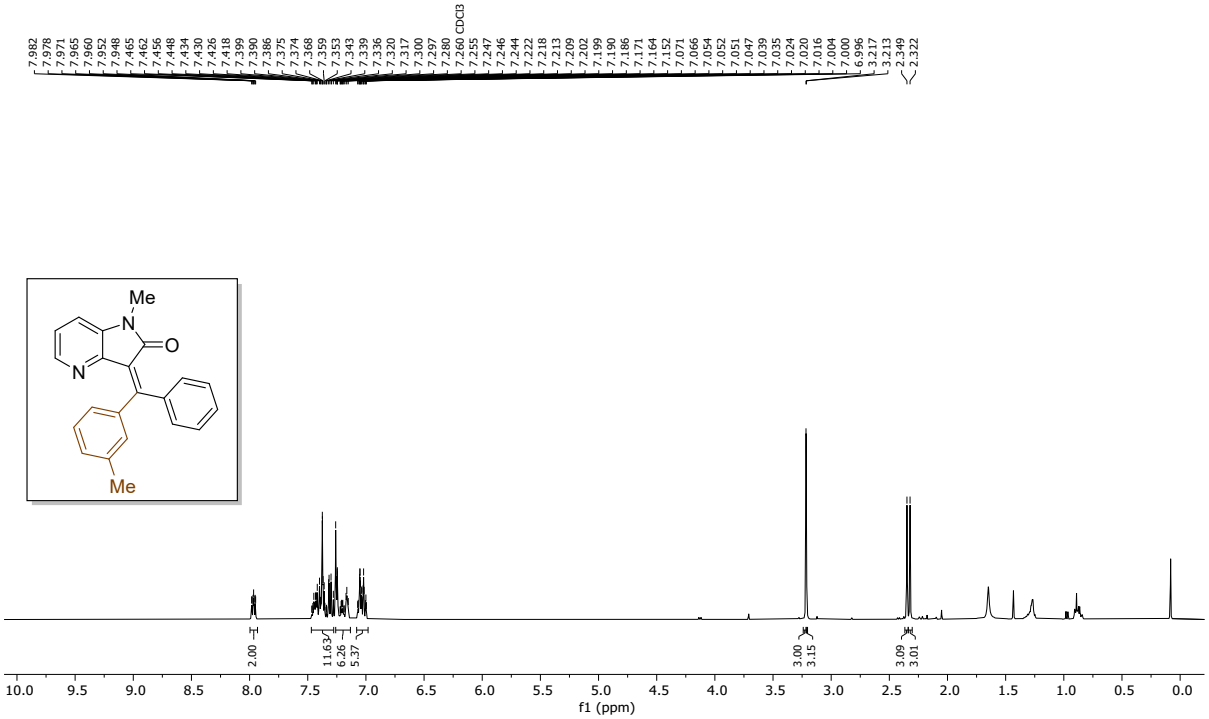
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Figure S3. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-1-methyl-3-(phenyl(m-tolyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3c) in $CDCl_3$.



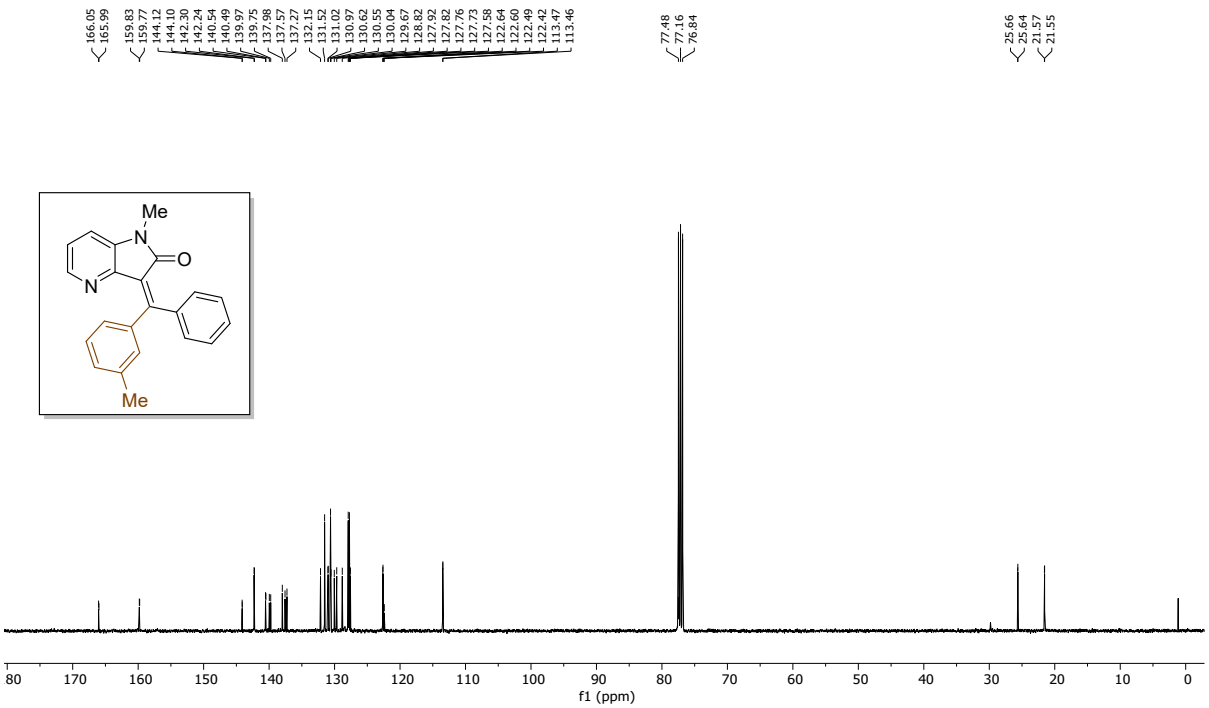
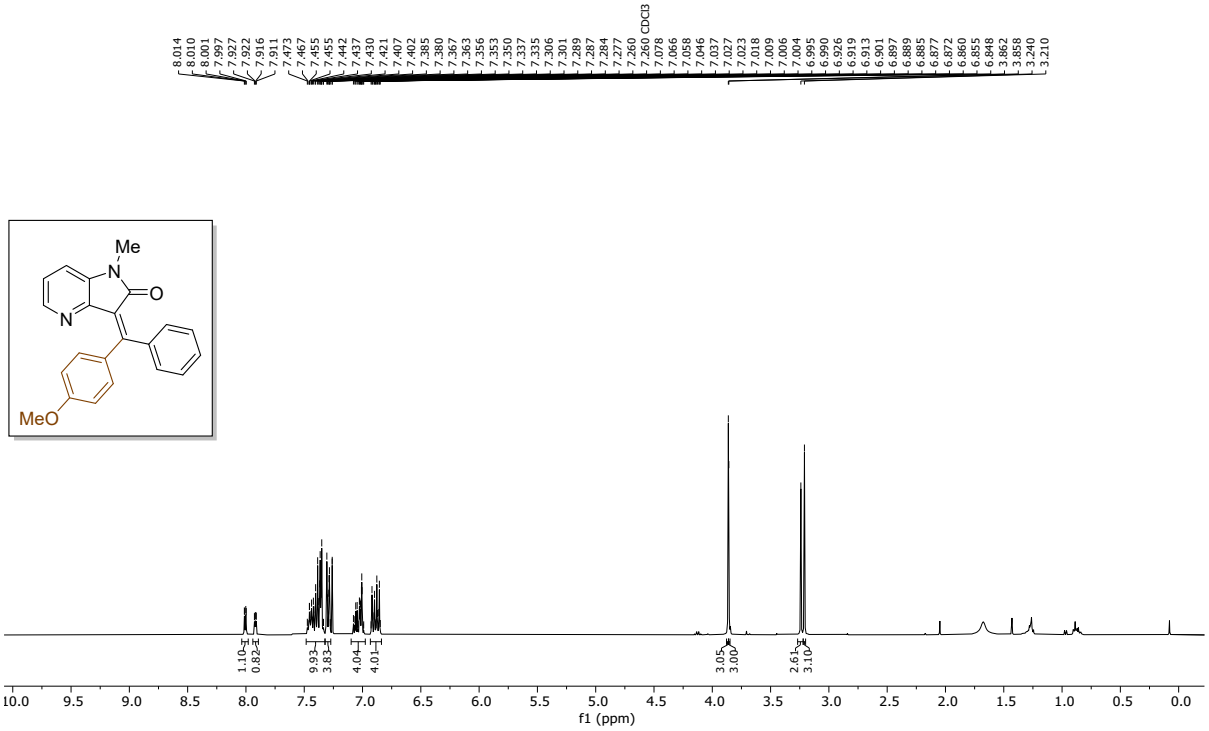


Figure S4. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-3-((4-methoxyphenyl)(phenyl)methylene)-1-methyl-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-*2*-one (3d) in $CDCl_3$.



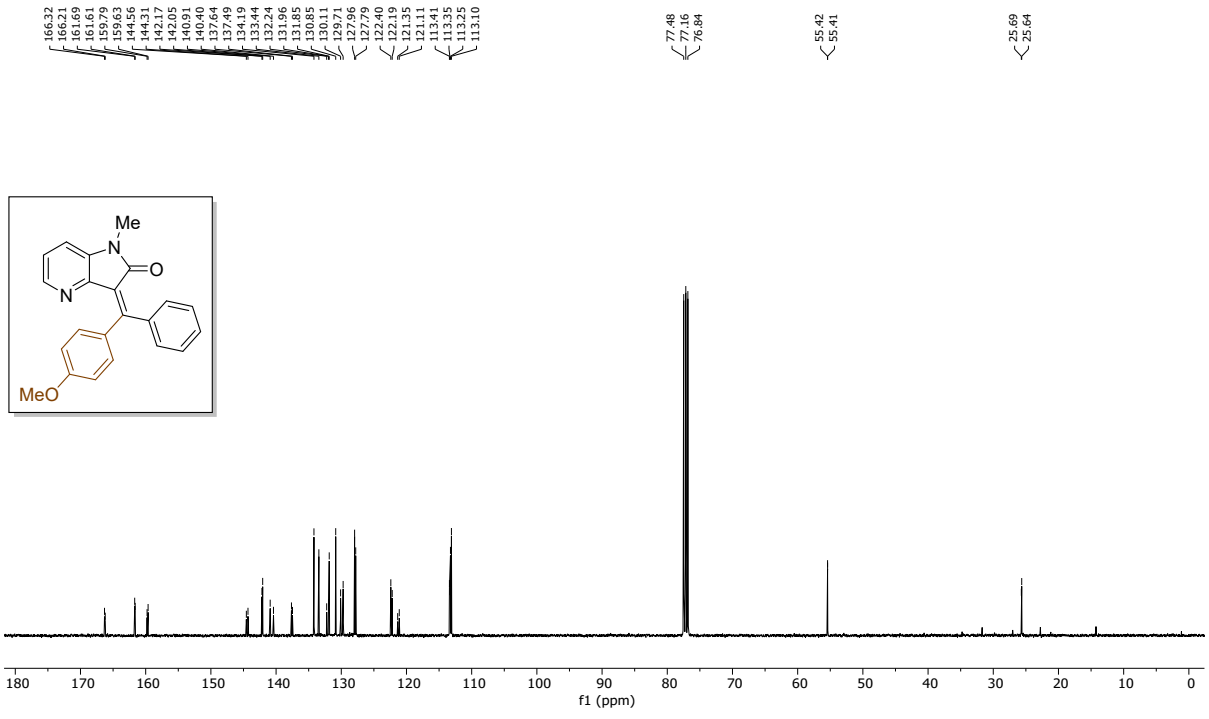


Figure S5. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-1-methyl-3-(naphthalen-2-yl(phenyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3e) in $CDCl_3$.

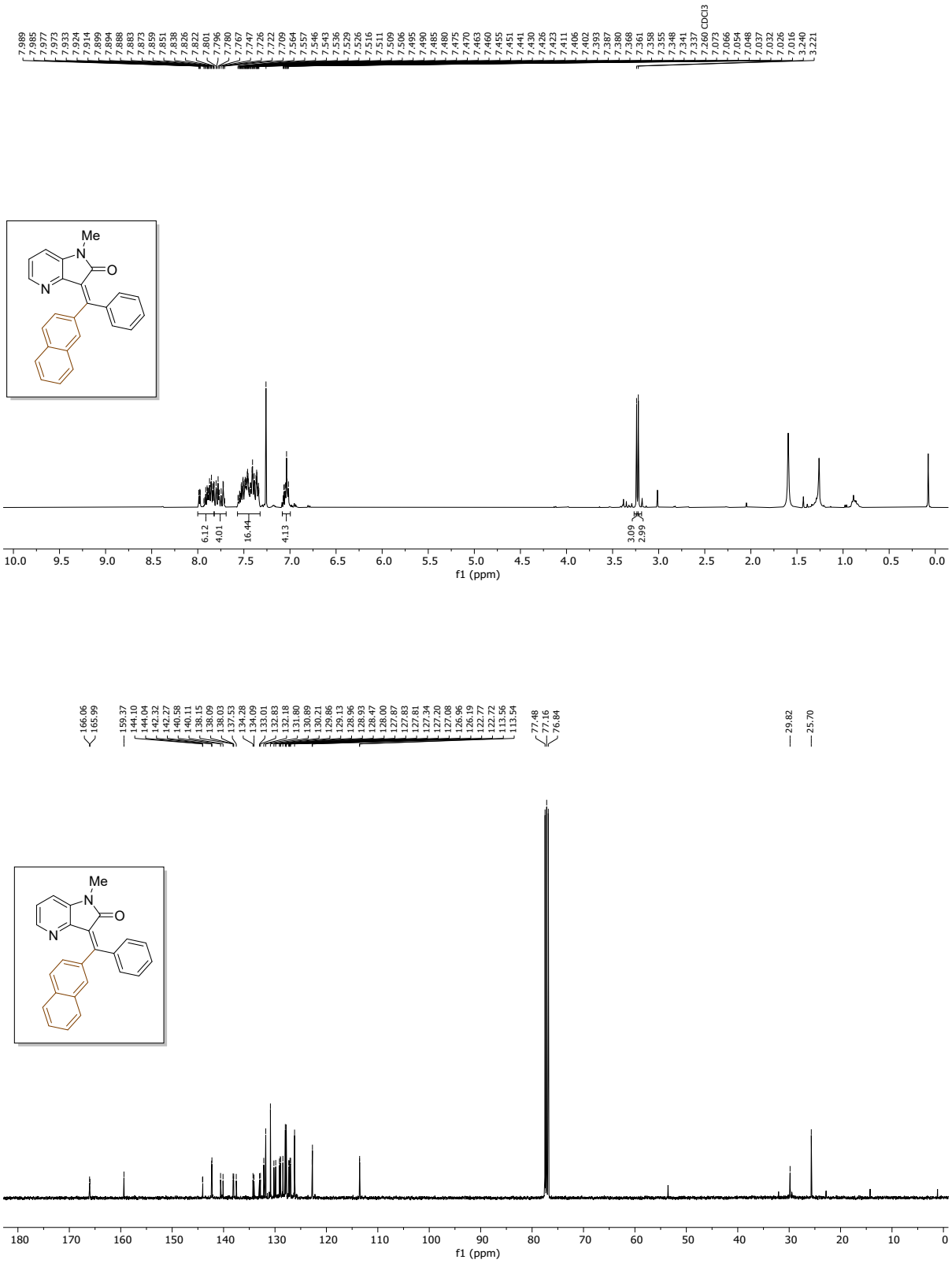
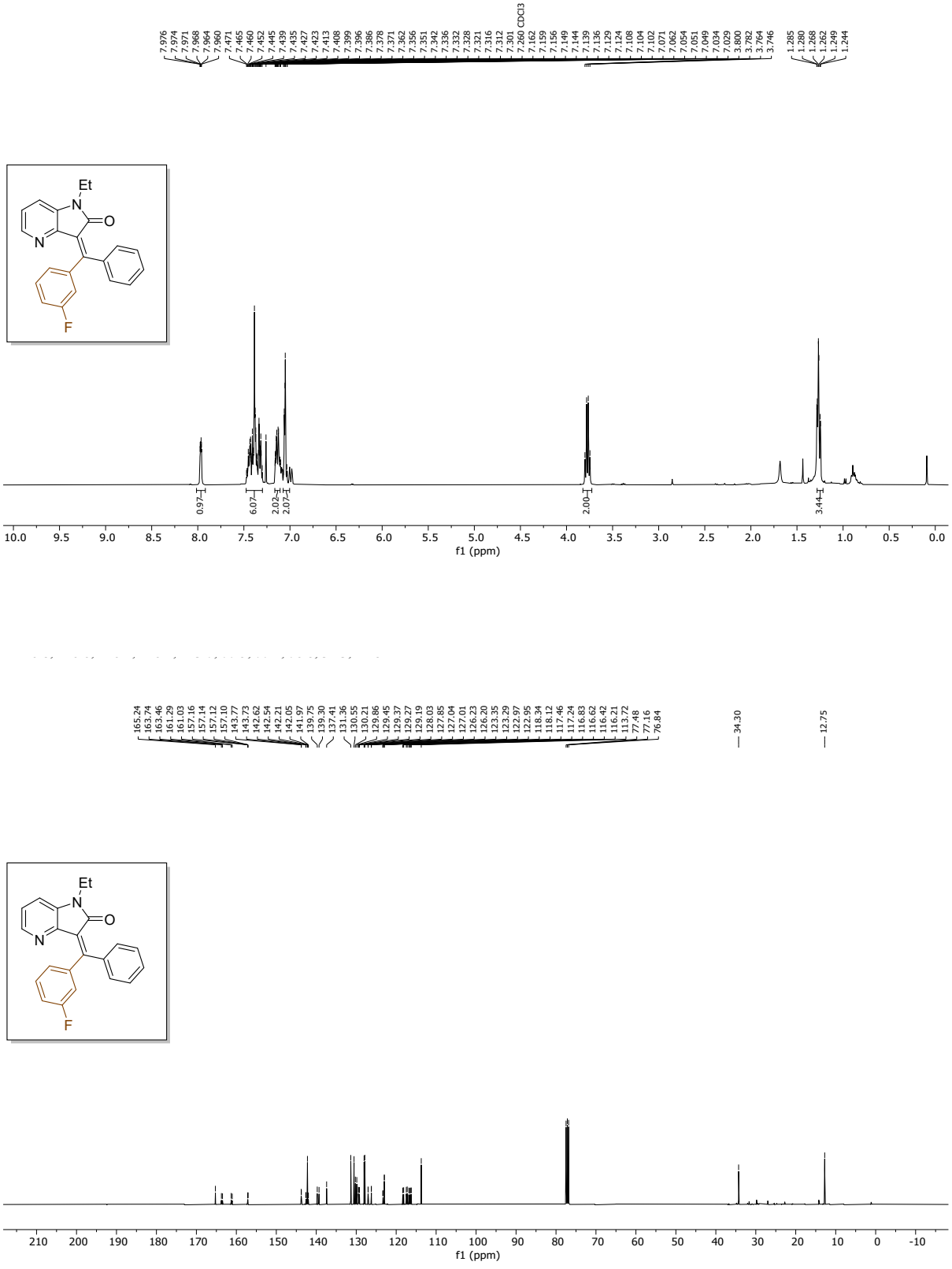
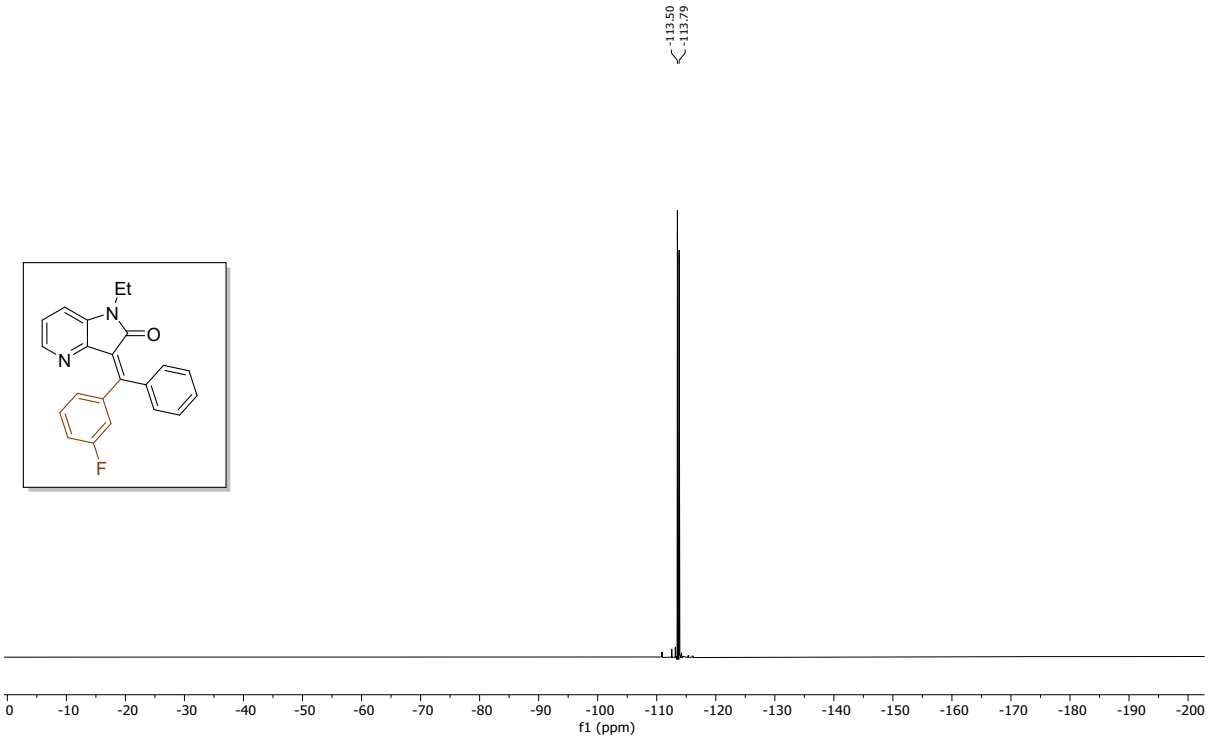


Figure S6. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-1-ethyl-3-((3-fluorophenyl)(phenyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3f) in $CDCl_3$.

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O
N
F
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-30
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-50
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-70
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-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

Figure S7. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-1-ethyl-3-(phenyl(m-tolyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3g) in $CDCl_3$.

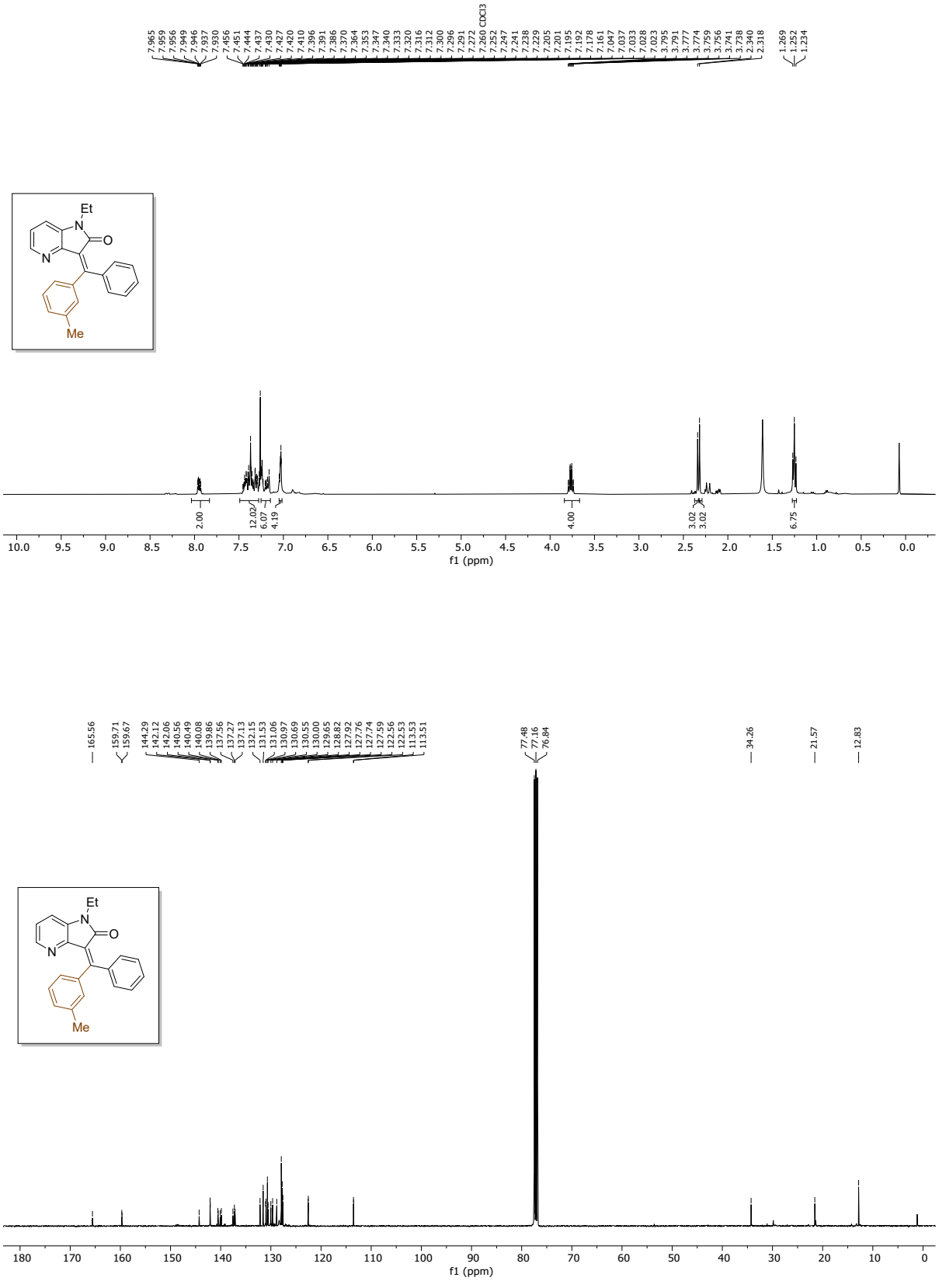


Figure S8. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-1-ethyl-3-((4-methoxyphenyl)(phenyl)methylene)-1,3-dihydro-2*H*-pyrrolo[3,2-*b*]pyridin-2-one (3h) in $CDCl_3$.

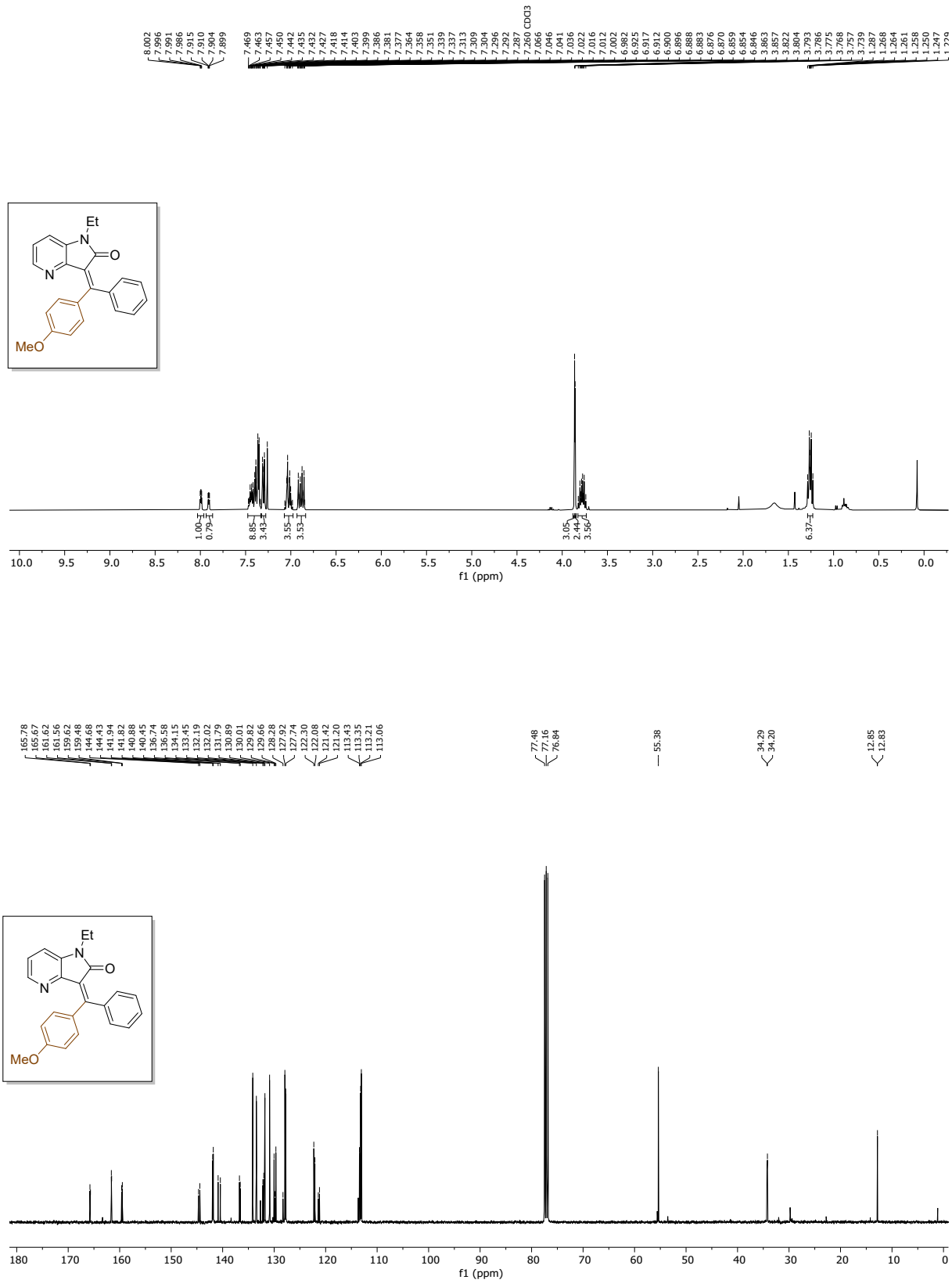
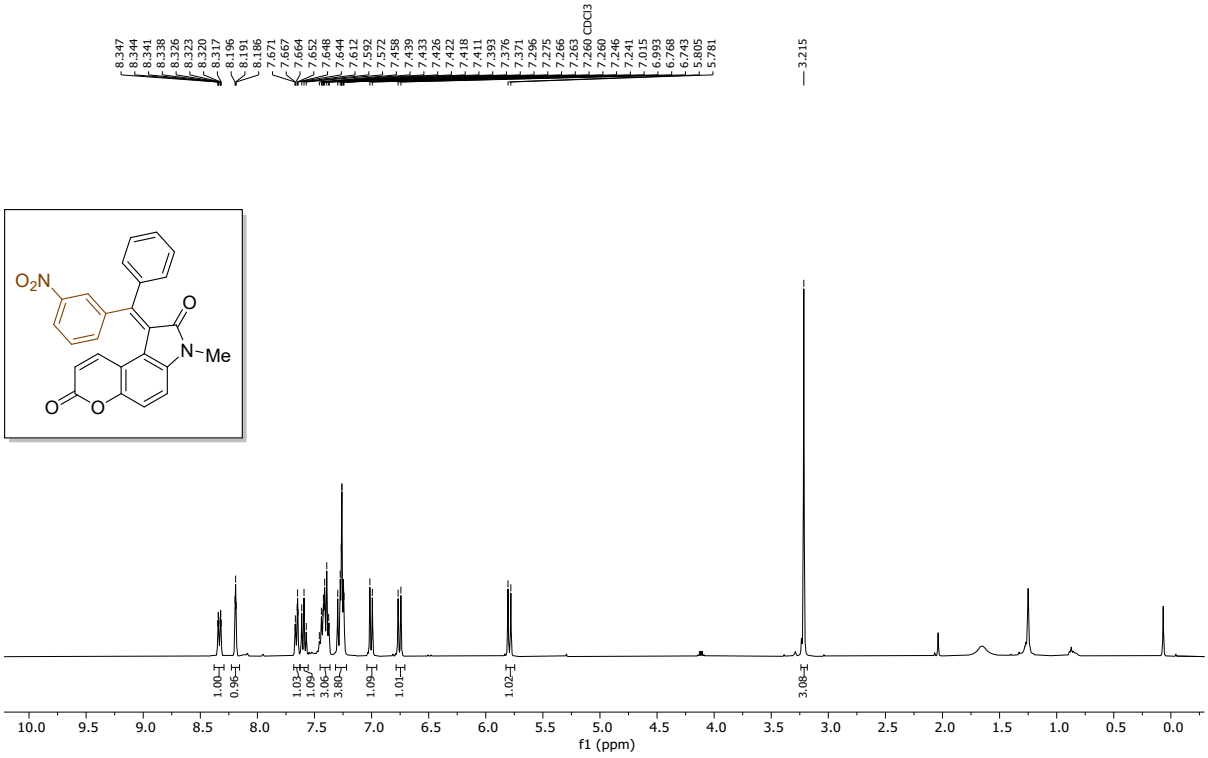


Figure S9. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-3-methyl-1-((3-nitrophenyl)(phenyl)methylene)-1,3-dihydropyrano[3,2-e]indole-2,7-dione (3i) in $CDCl_3$.



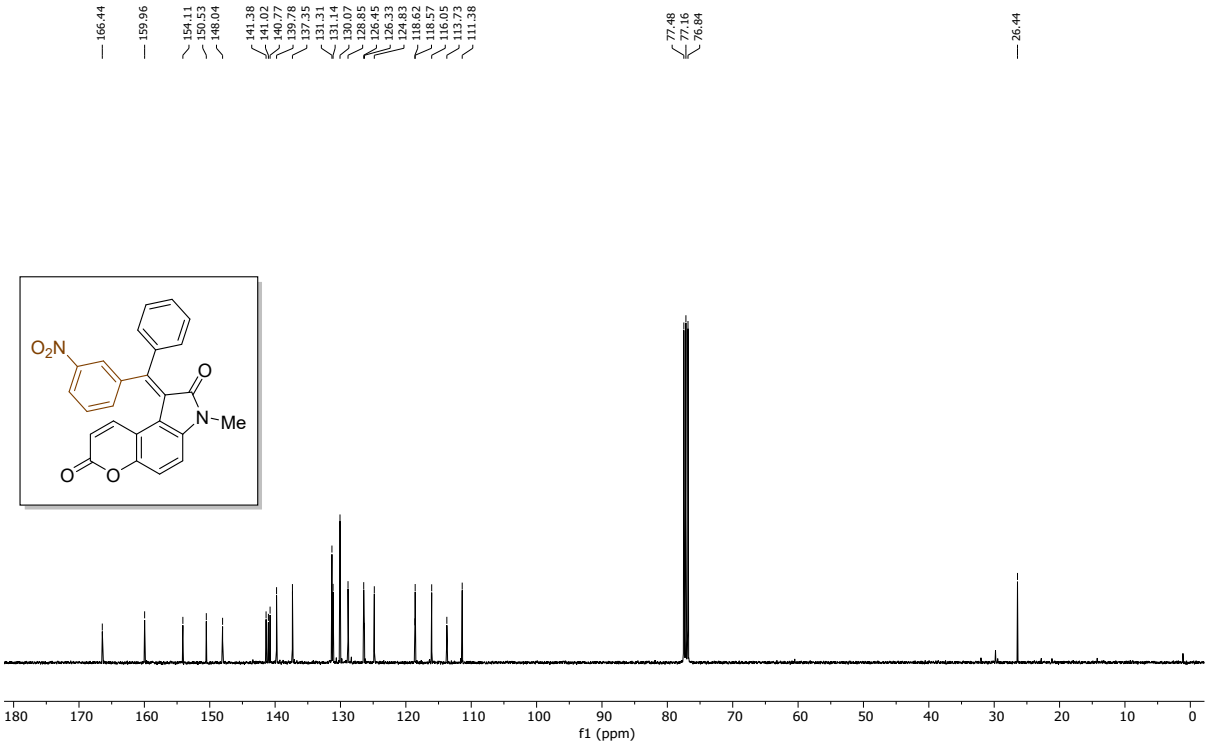
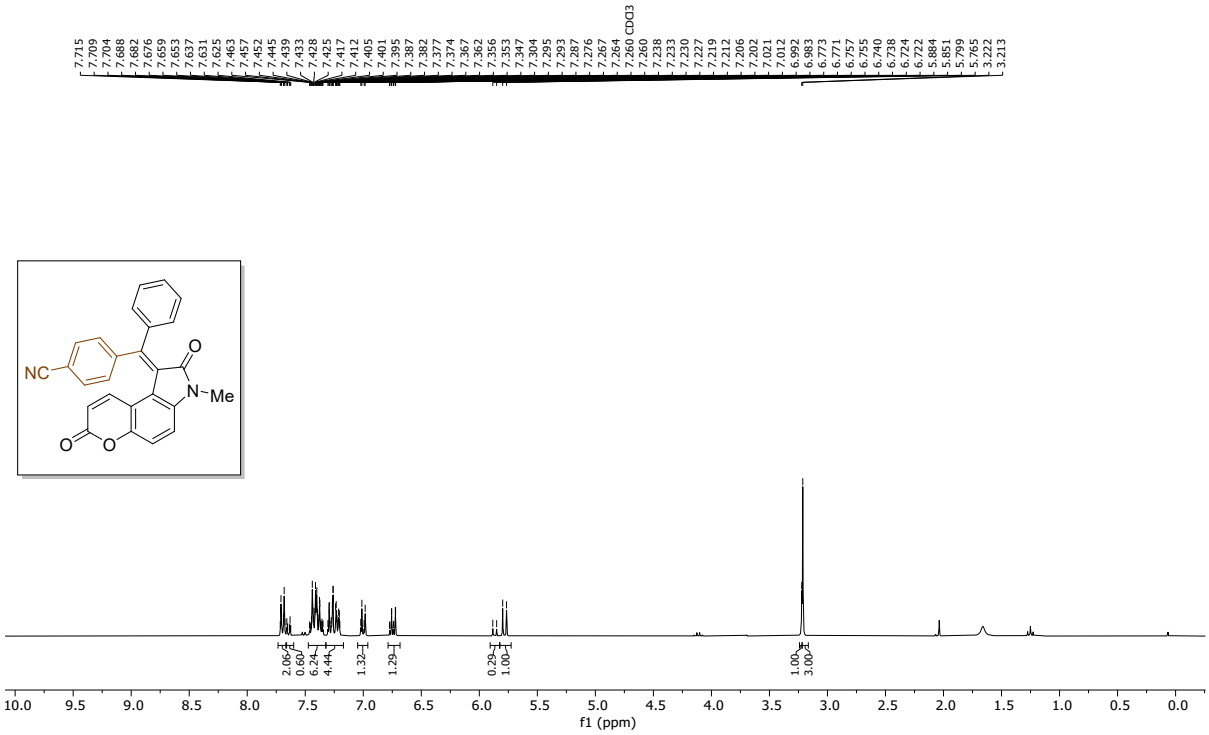


Figure S10. ^{1}H NMR (400 MHz) and ^{13}C NMR (75 MHz) spectra of compound (*E*)-4-((3-methyl-2,7-dioxo-2,3-dihydropyrano[3,2-*e*]indol-1(7*H*)-ylidene)(phenyl)methyl)benzonitrile (3j) in $CDCl_3$.



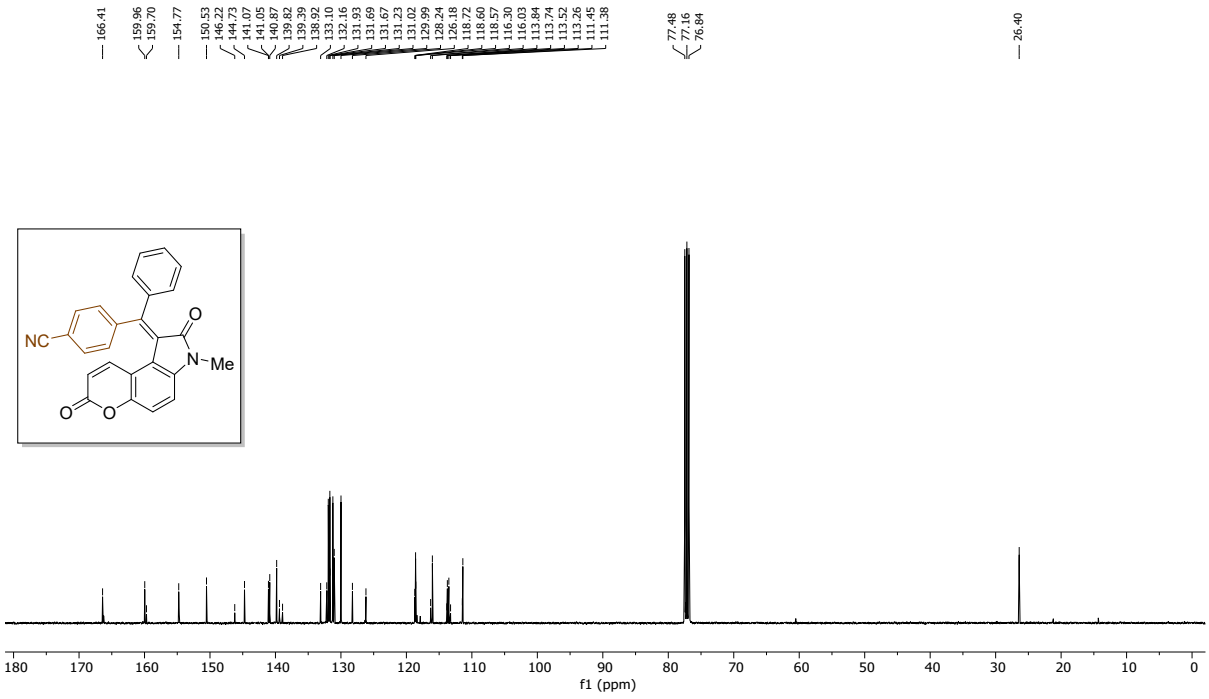
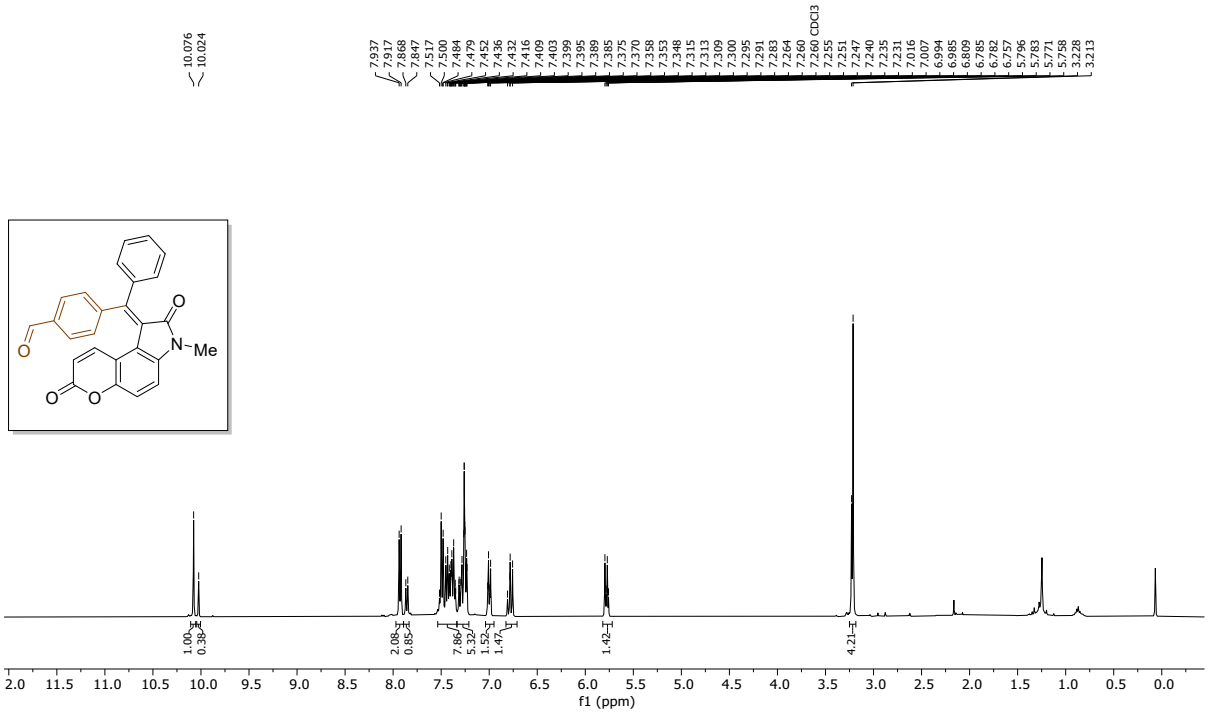


Figure S11. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-4-((3-methyl-2,7-dioxo-2,3-dihydropyrano[3,2-*e*]indol-1(7*H*)-ylidene)(phenyl)methyl)benzaldehyde (3k) in $CDCl_3$.



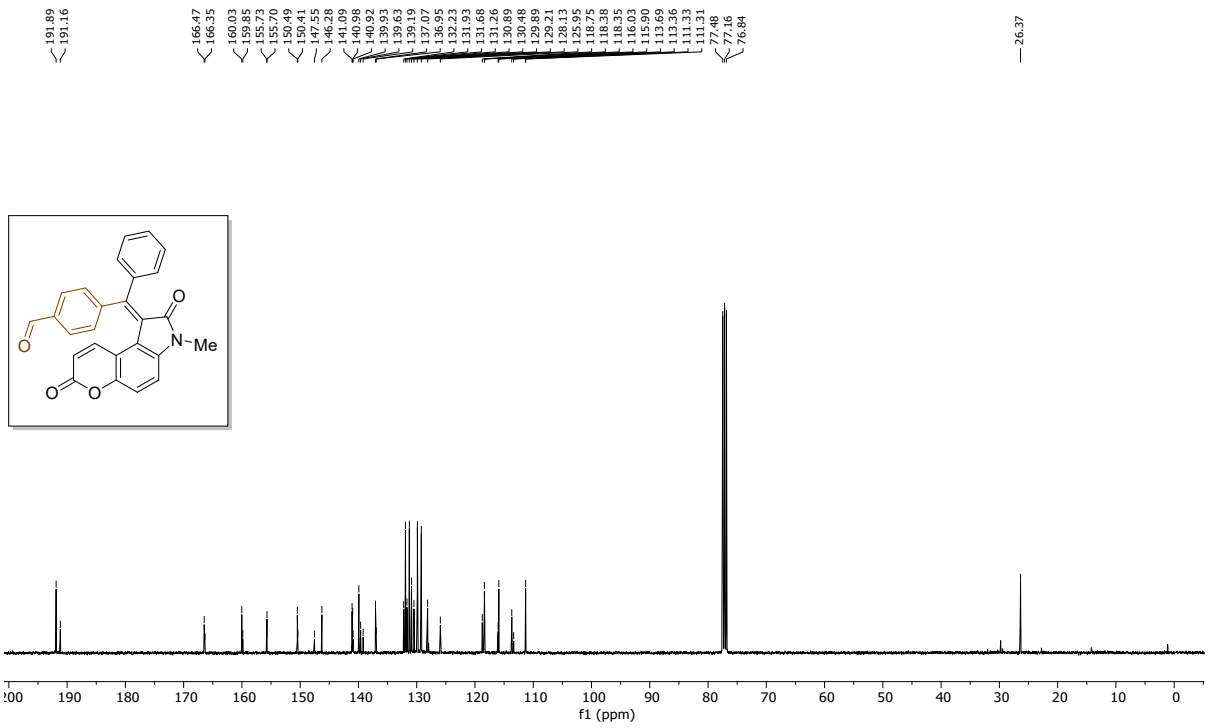
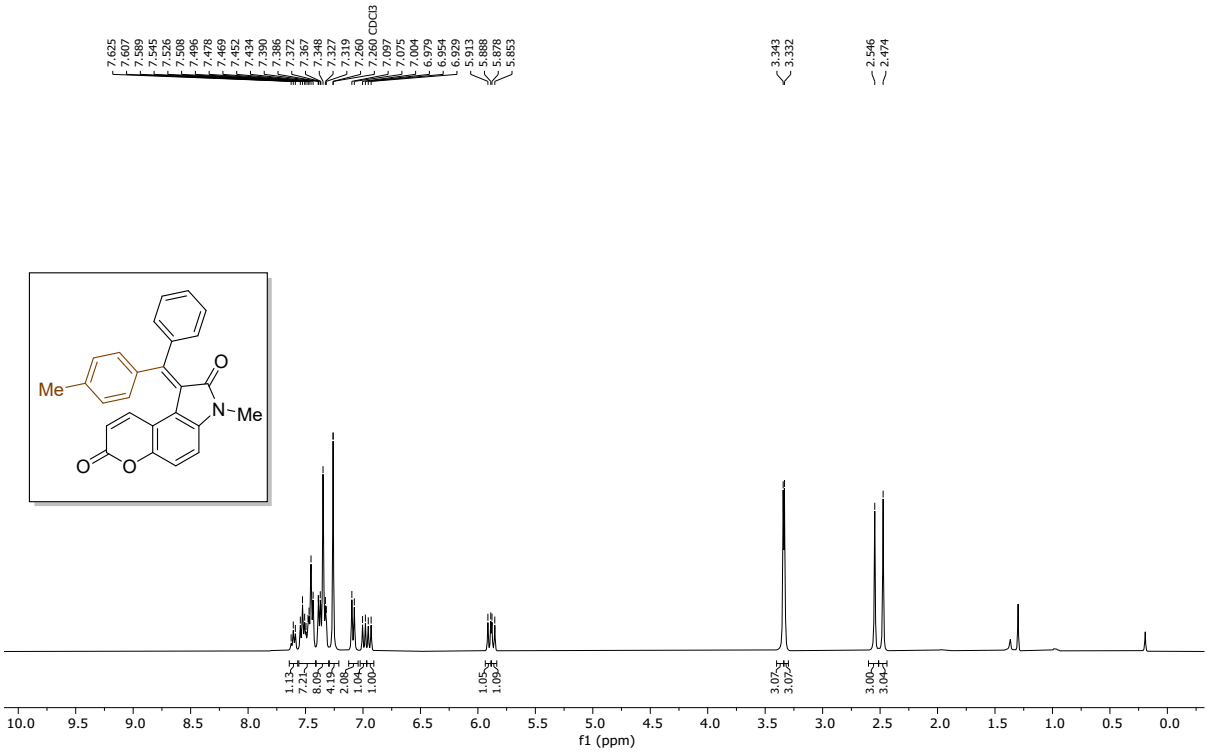


Figure S12. ^{1}H NMR (400 MHz) and ^{13}C NMR (75 MHz) spectra of compound (*E*)-3-methyl-1-(phenyl(p-tolyl)methylene)-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3l) in $CDCl_3$.



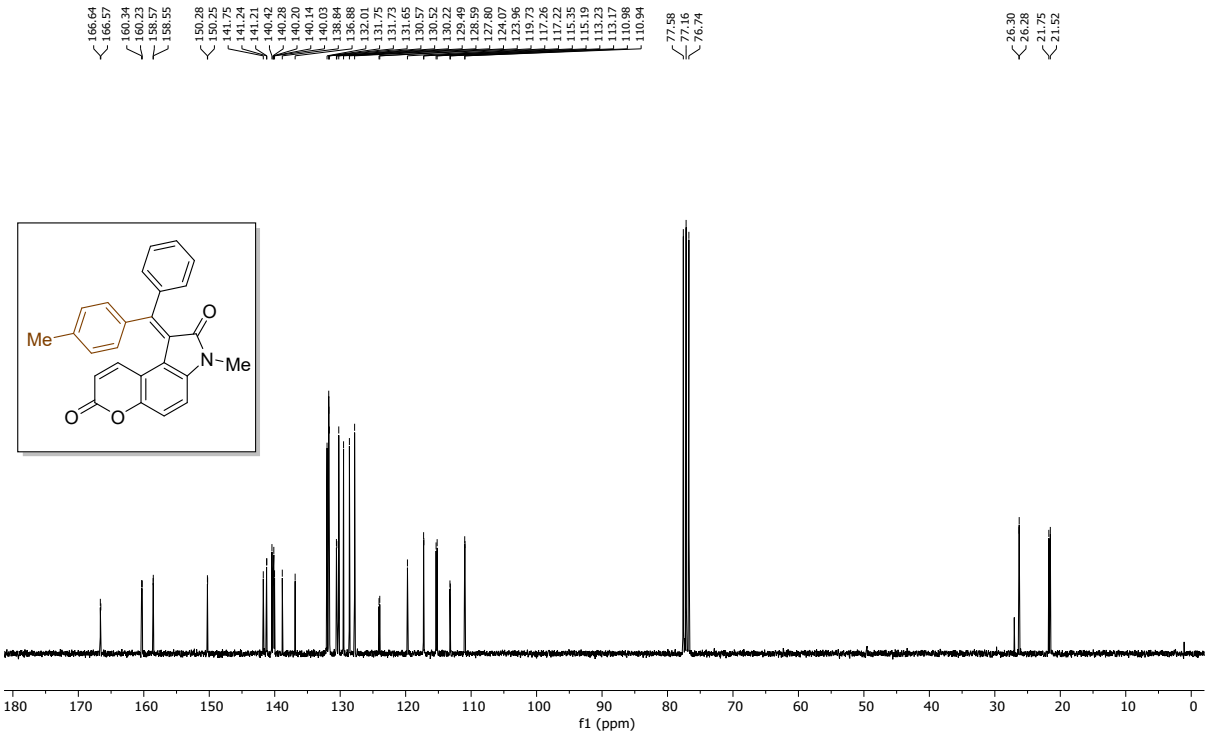
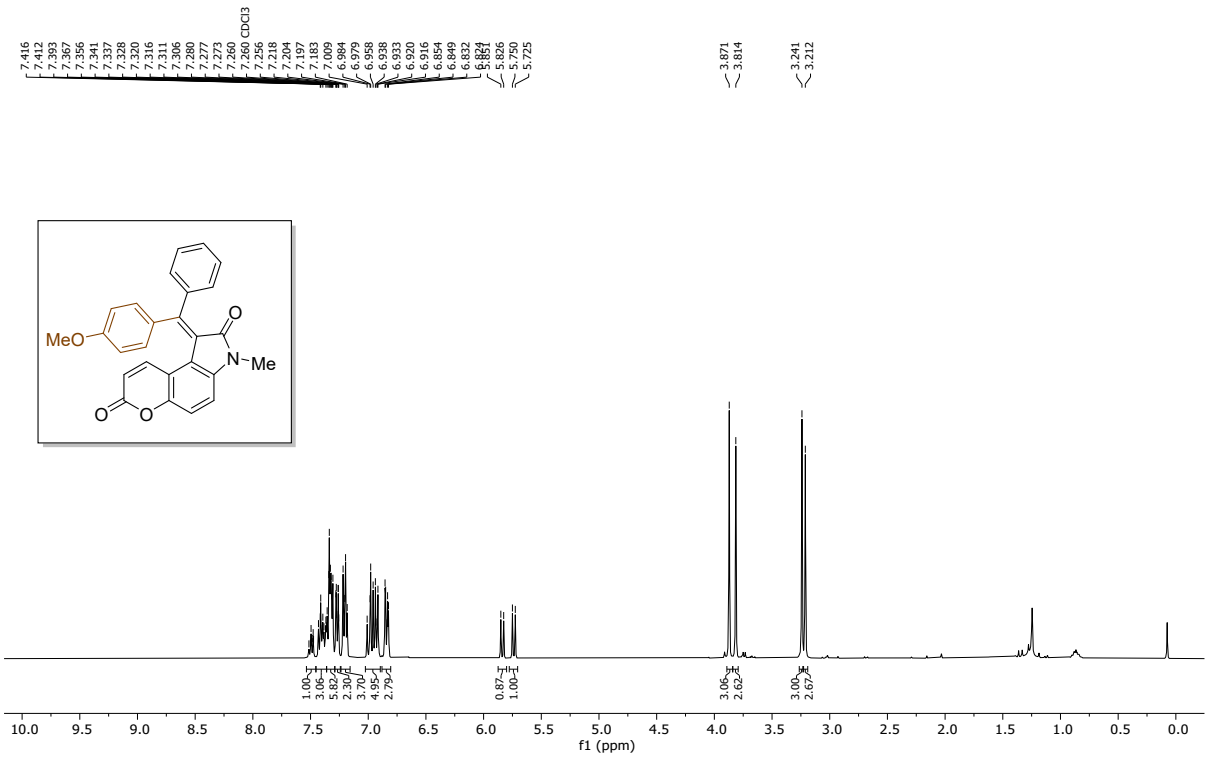


Figure S13. ^{1}H NMR (400 MHz) and ^{13}C NMR (75 MHz) spectra of compound (*E*)-1-((4-methoxyphenyl)(phenyl)methylene)-3-methyl-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3m) in $CDCl_3$.



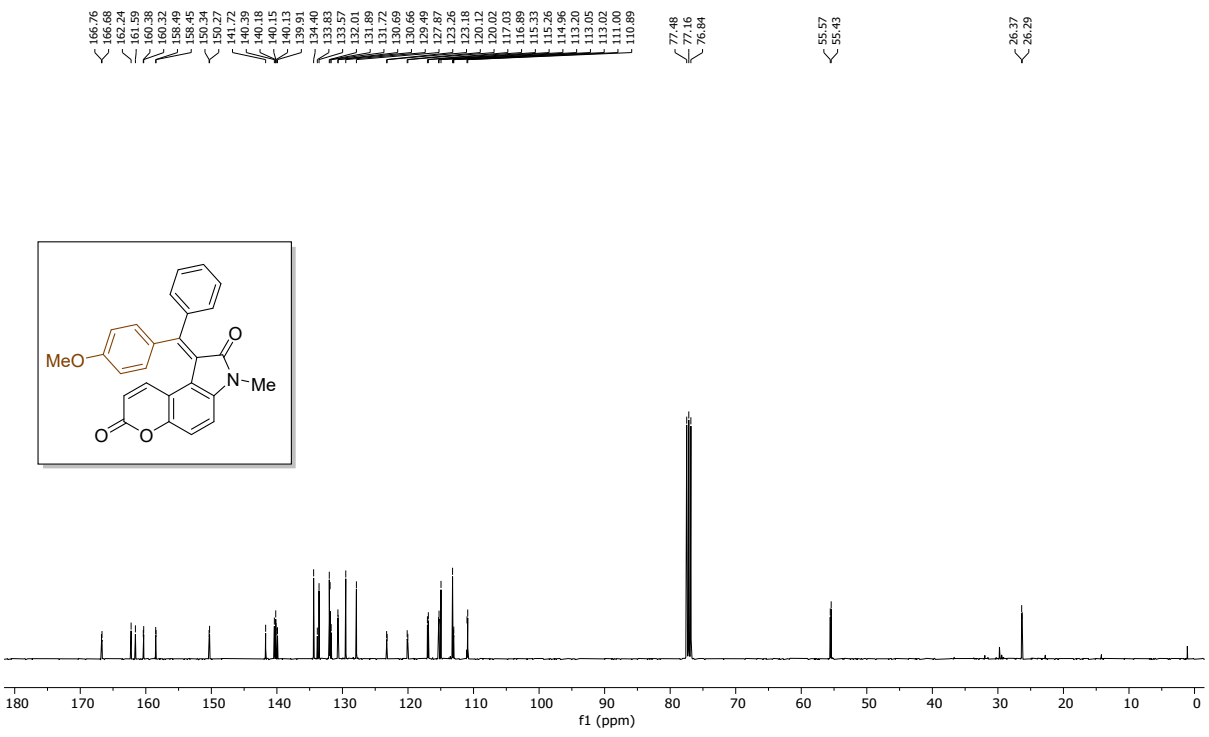
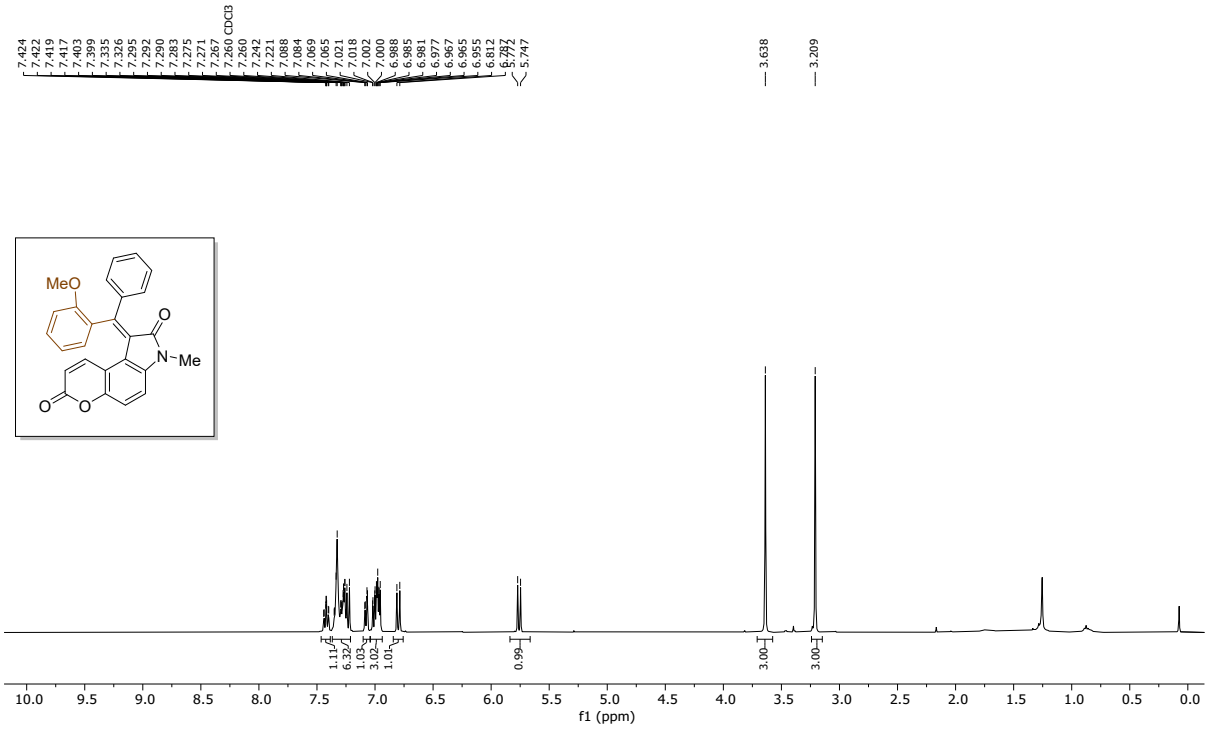


Figure S14. ^{1}H NMR (100 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-1-((2-methoxyphenyl)(phenyl)methylene)-3-methyl-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3n) in $CDCl_3$.



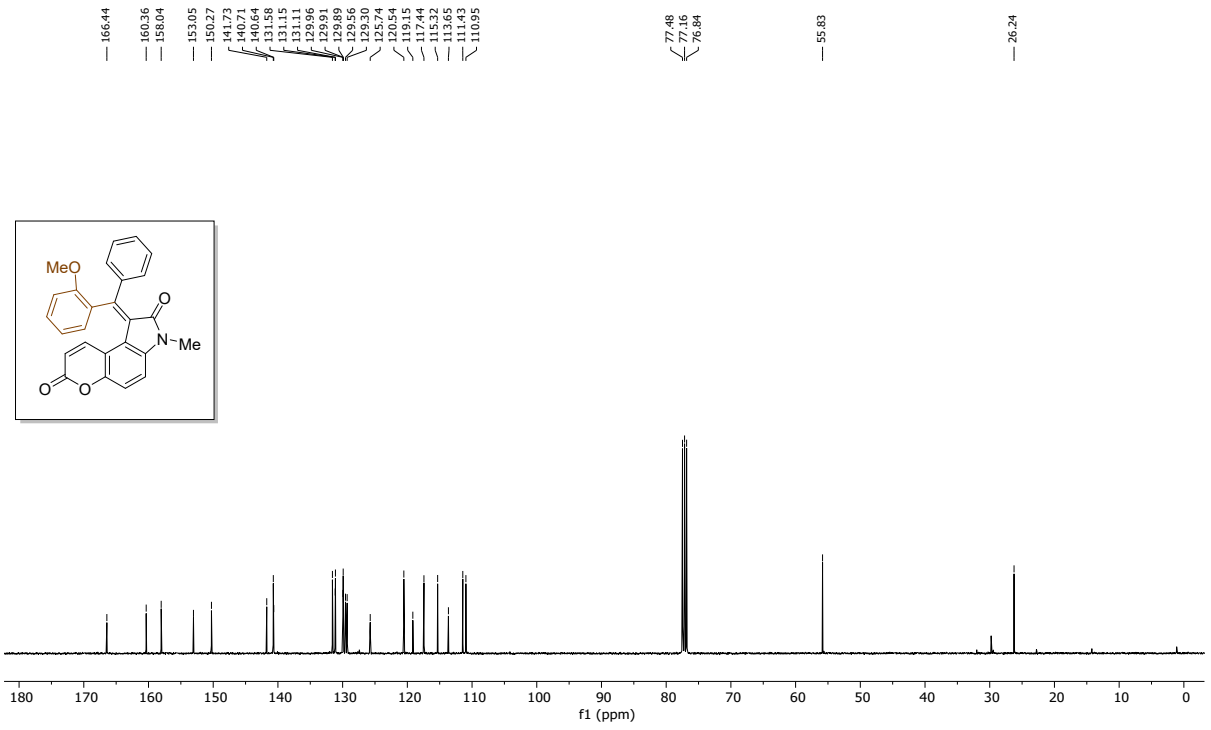


Figure S15. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra of compound (*E*)-1-((1H-indol-5-yl)(phenyl)methylene)-3-methyl-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3o) in $CDCl_3$.

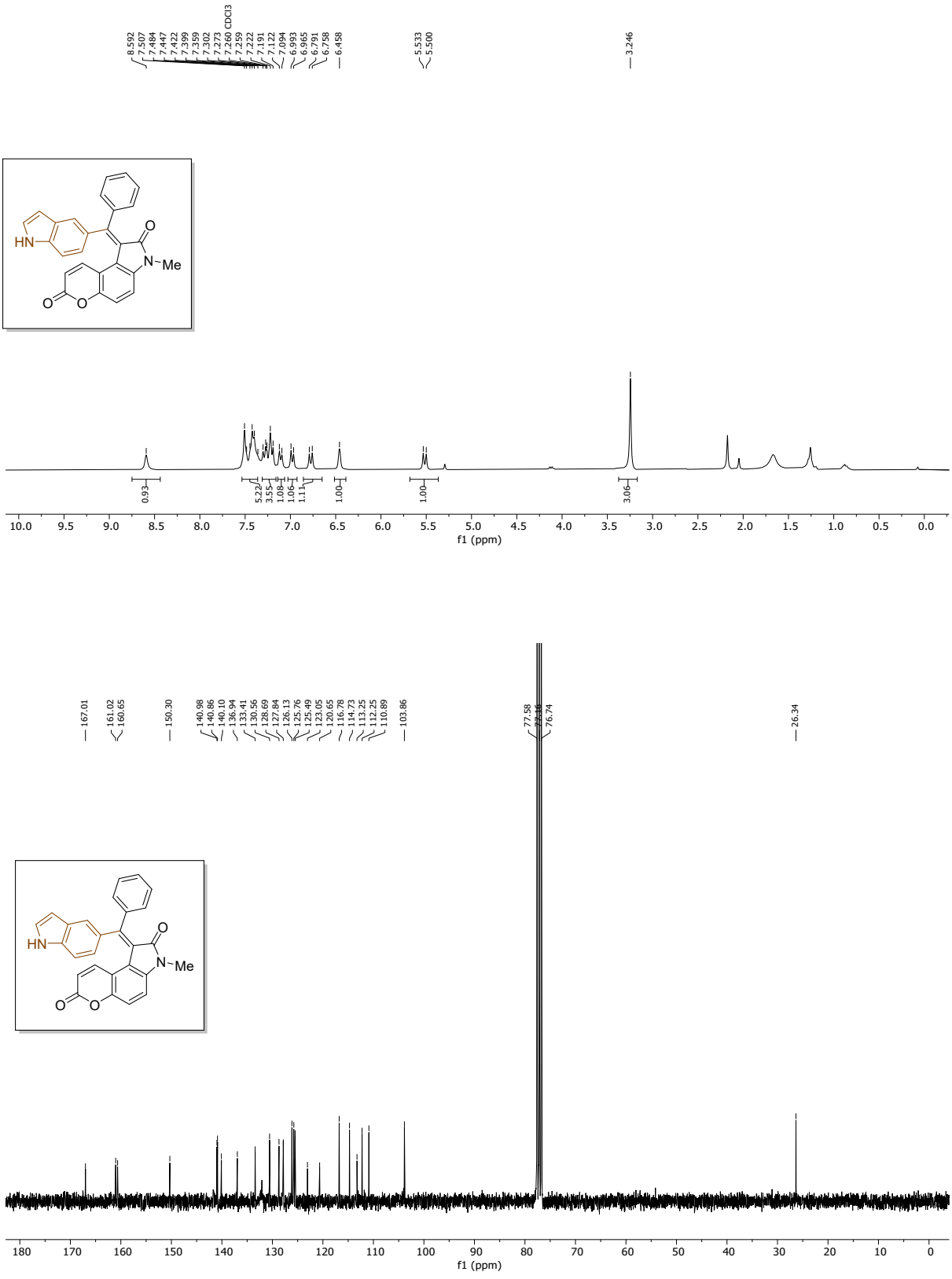
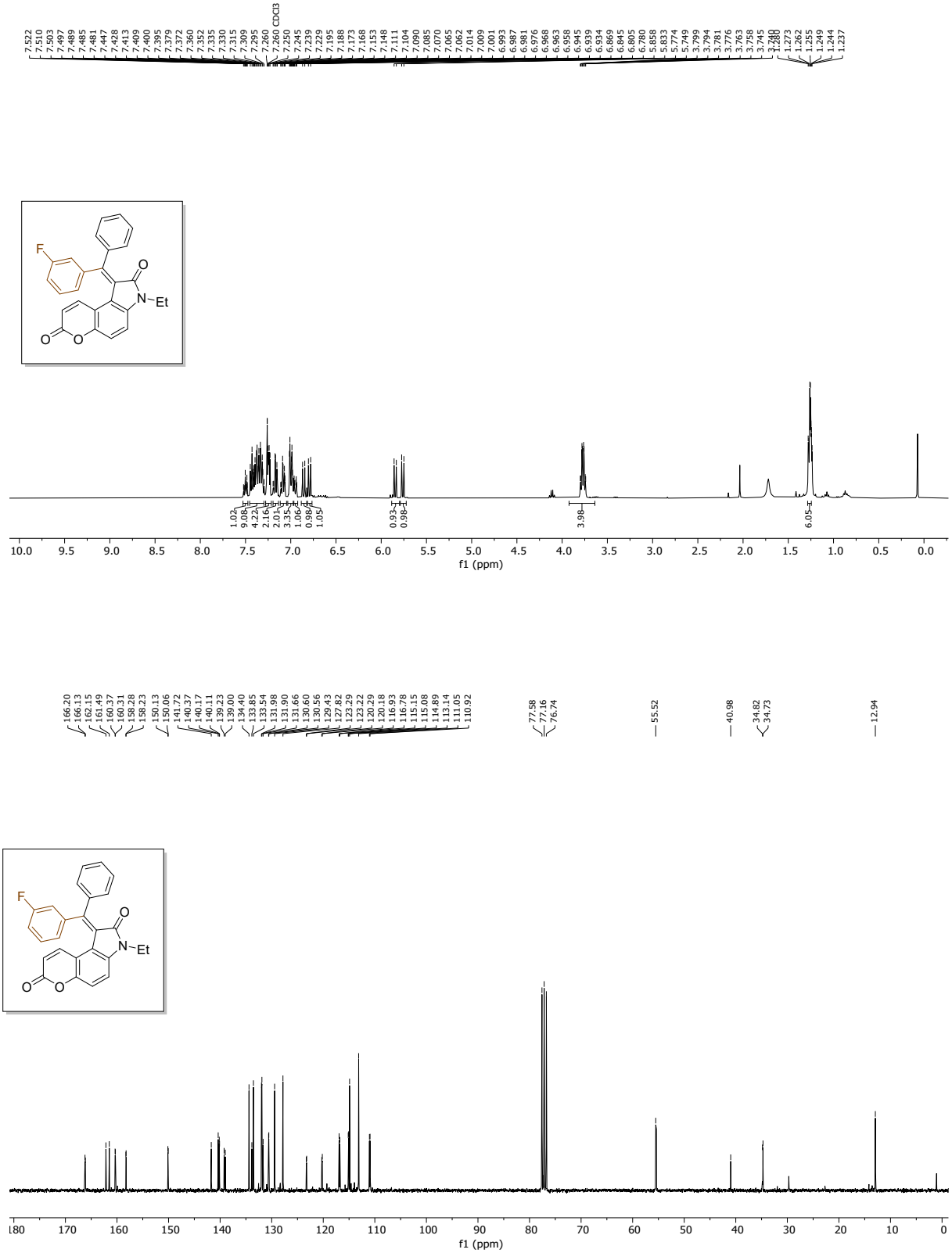
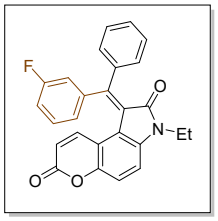


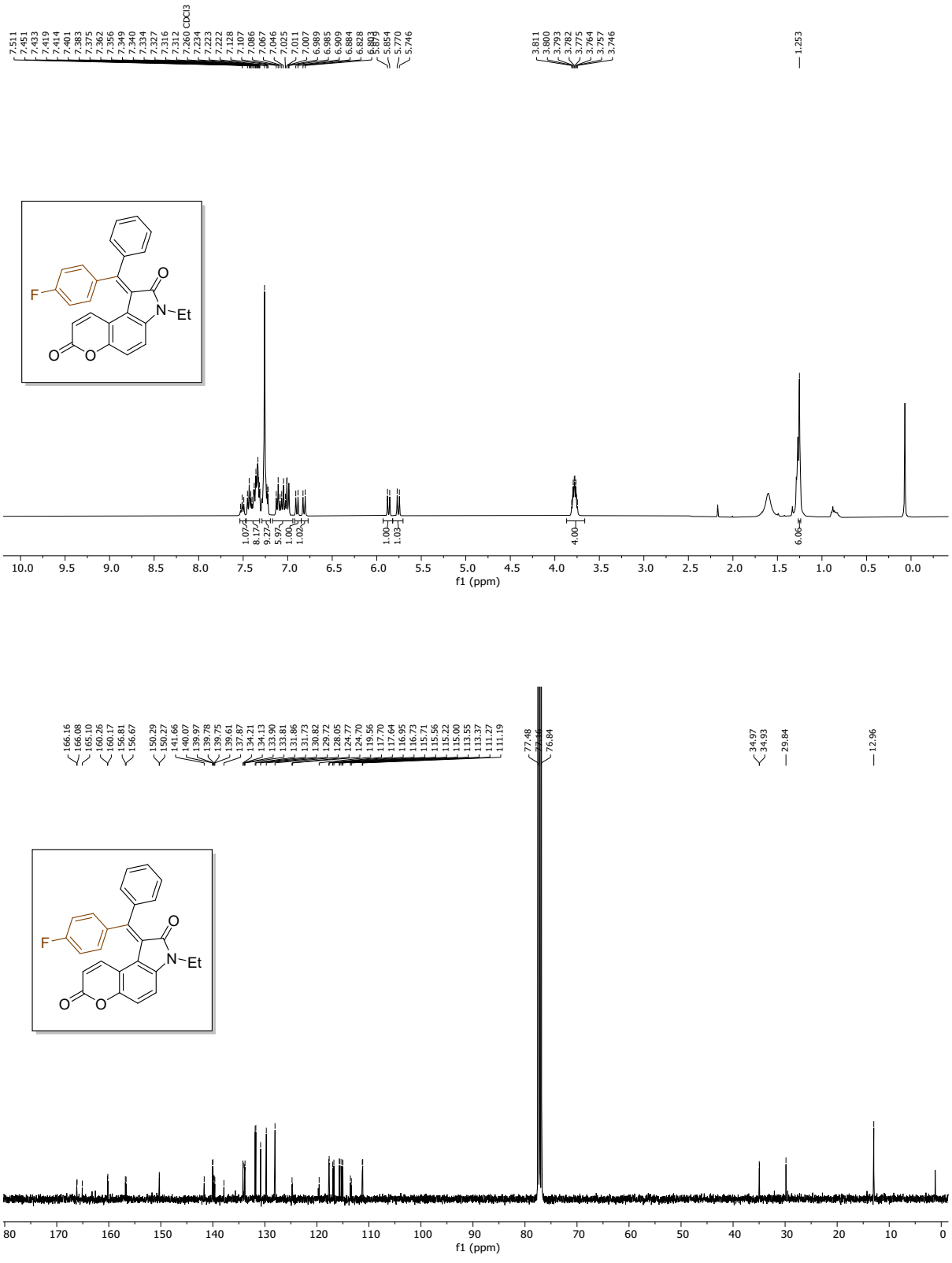
Figure S16. ^{1}H NMR (400 MHz), ^{13}C NMR (75 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-3-ethyl-1-((3-fluorophenyl)(phenyl)methylene)-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3p) in $CDCl_3$.




F
O
N
Et
O
O

-110.451
-113.443
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

Figure S17. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-3-ethyl-1-((4-fluorophenyl)(phenyl)methylene)-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3q) in $CDCl_3$.



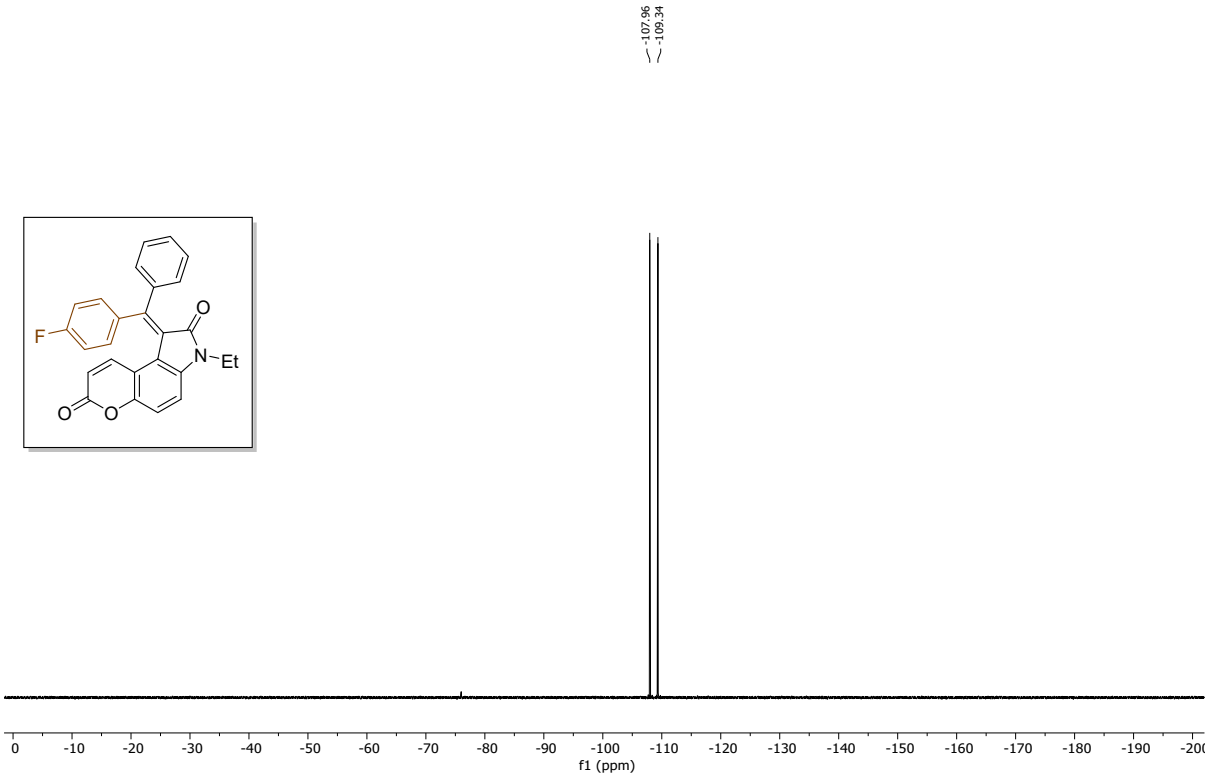
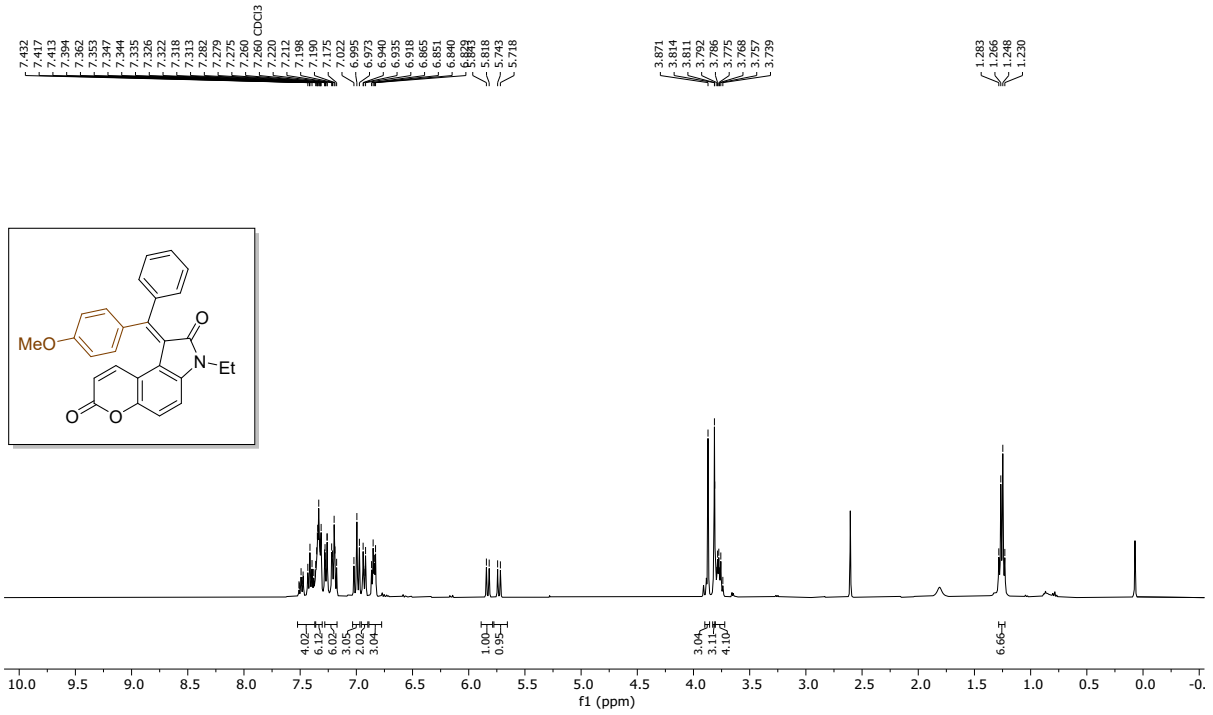

-107.96
-109.34
F
O
N
Et
O
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Figure S18. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra of compound (*E*)-3-ethyl-1-((4-methoxyphenyl)(phenyl)methylene)-1,3-dihydropyrano[3,2-*e*]indole-2,7-dione (3r) in $CDCl_3$.



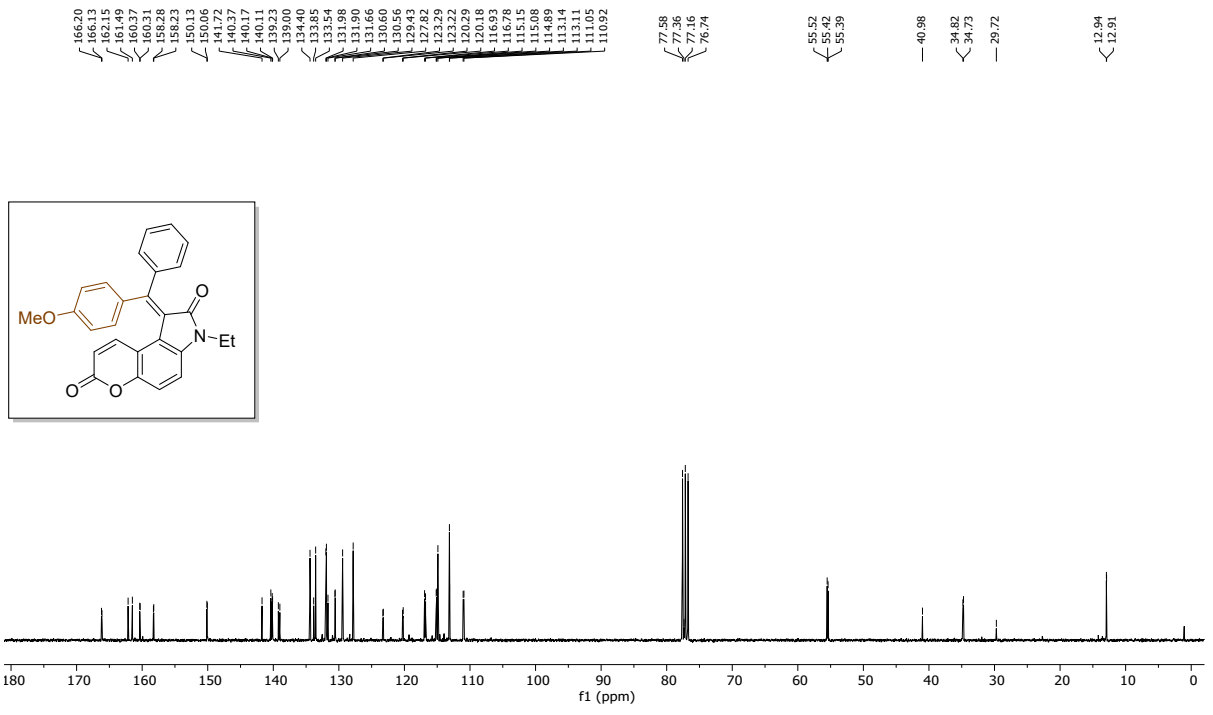
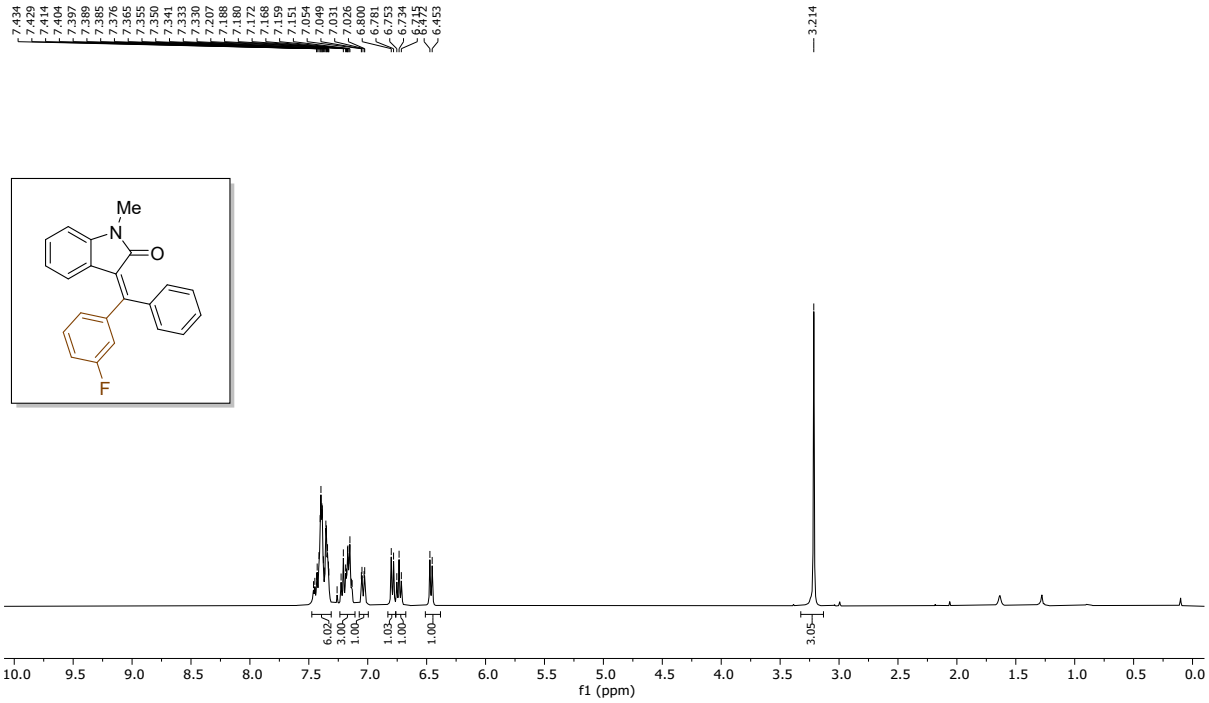
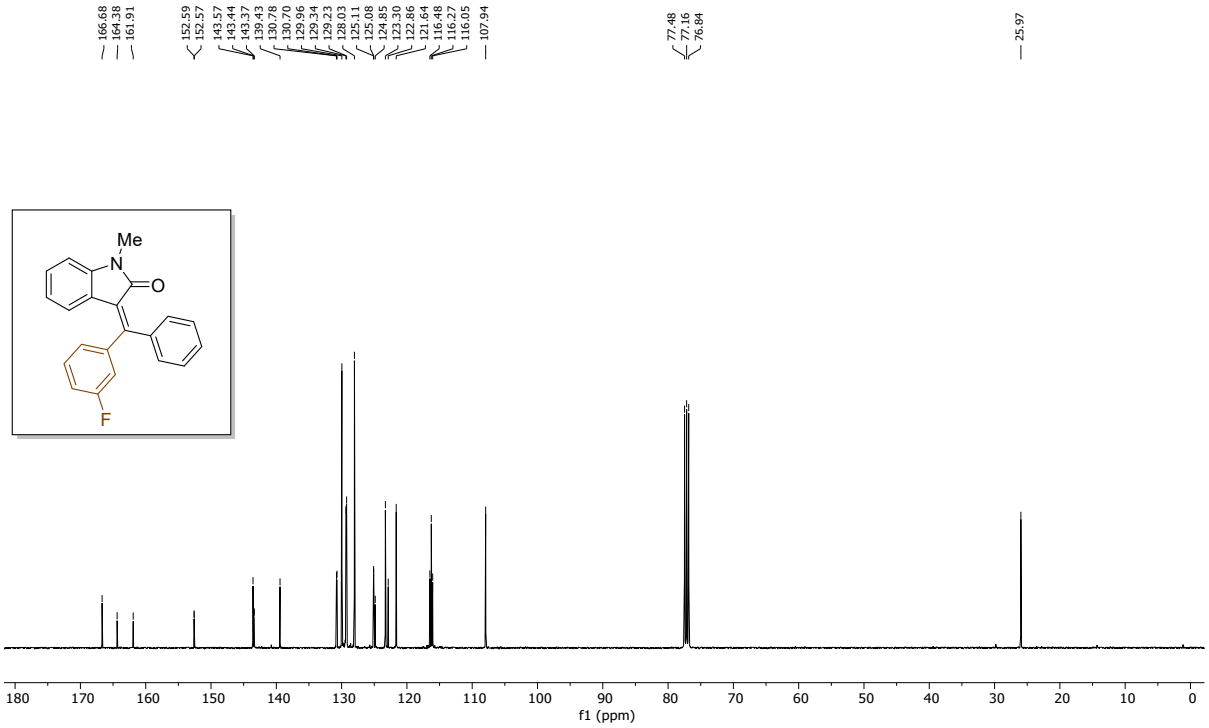


Figure S19. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-3-((3-fluorophenyl)(phenyl)methylene)-1-methylindolin-2-one (3s) in $CDCl_3$.





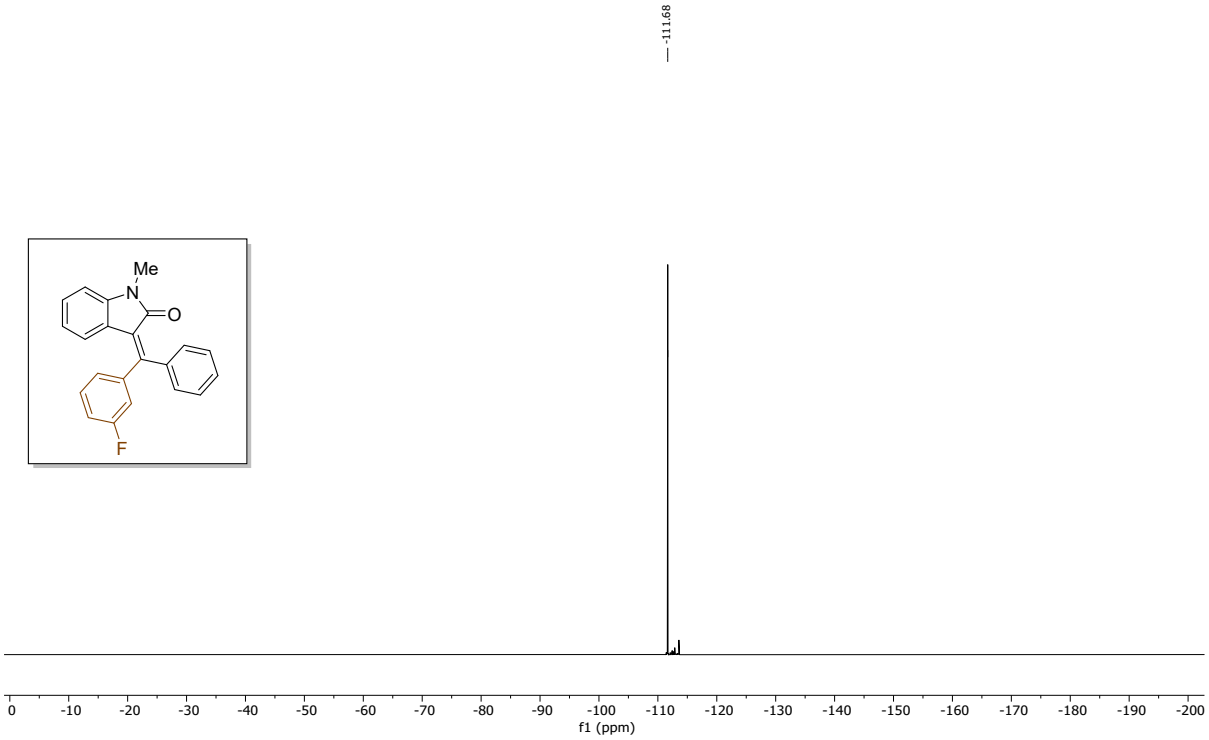
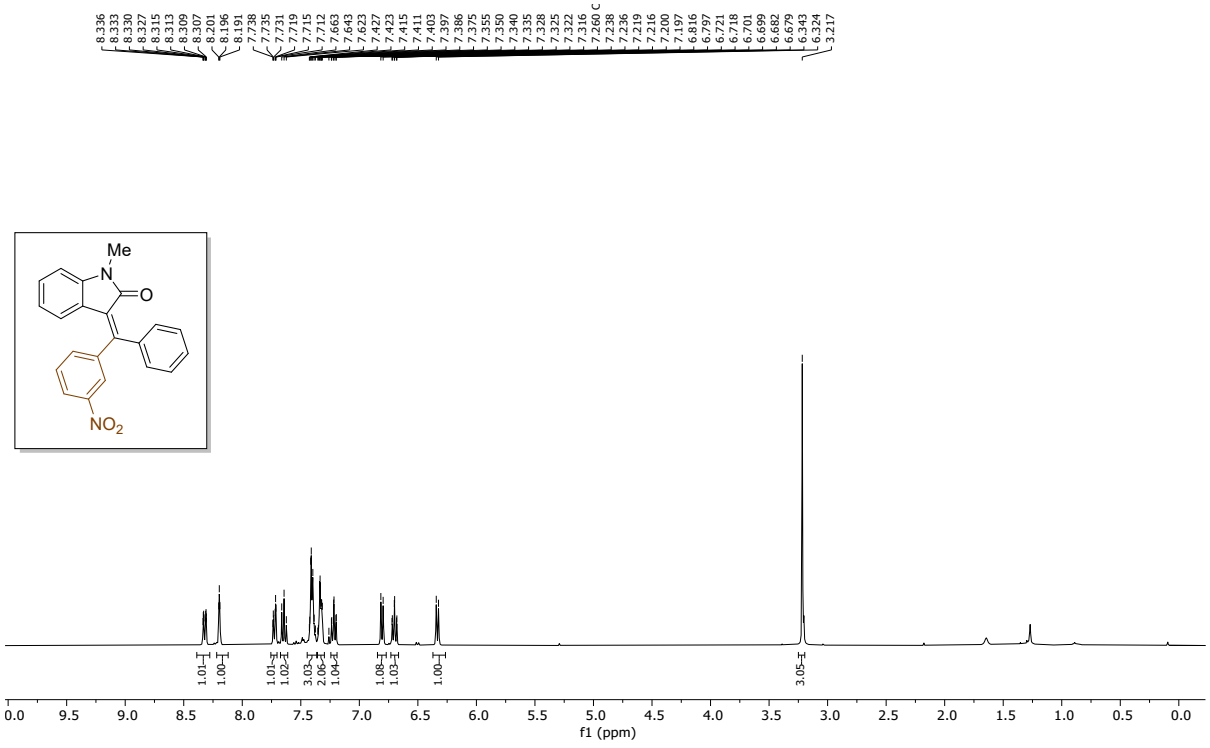

-111.68
Me
N
O
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

Figure S20. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra of compound (*E*)-1-methyl-3-((3-nitrophenyl)(phenyl)methylene)indolin-2-one (3t) in $CDCl_3$.



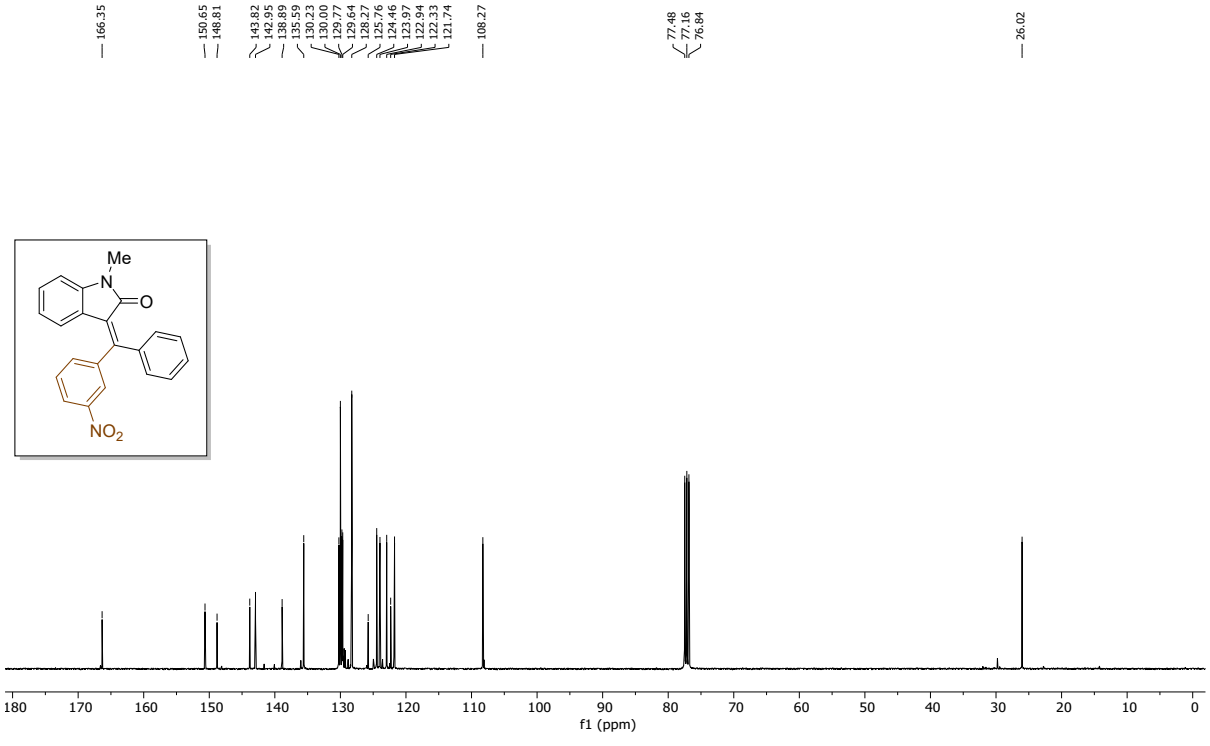
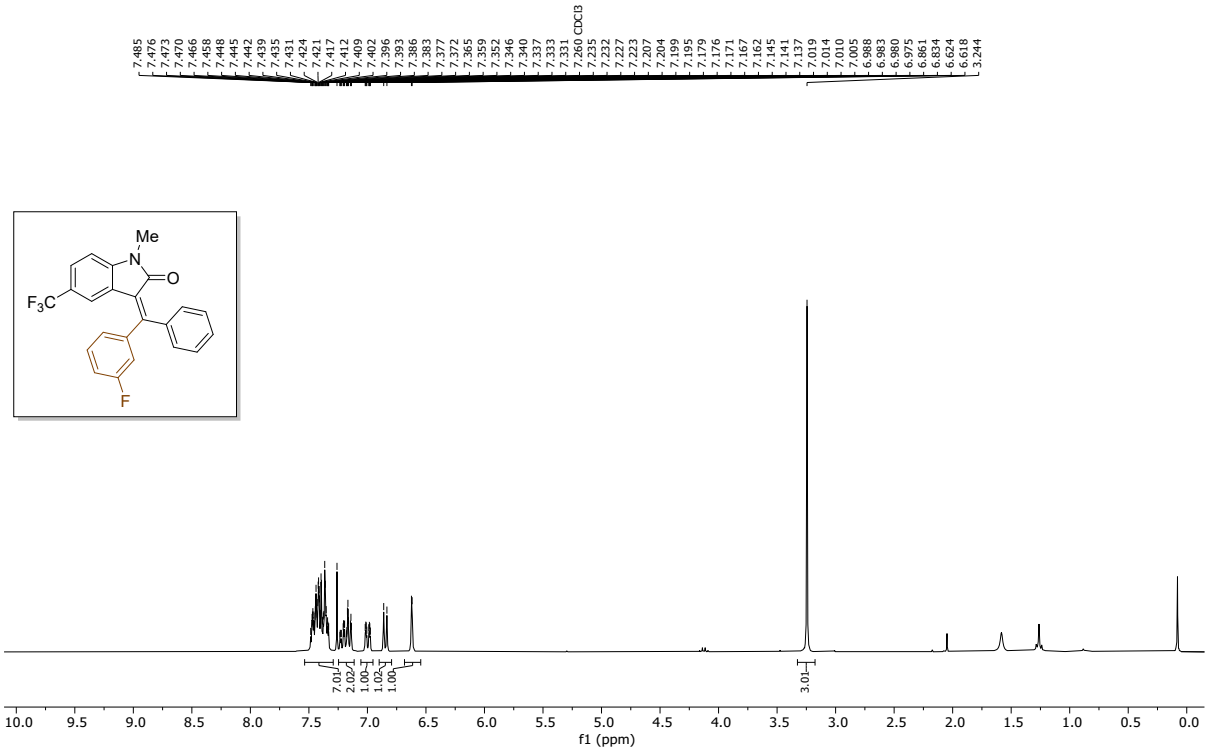
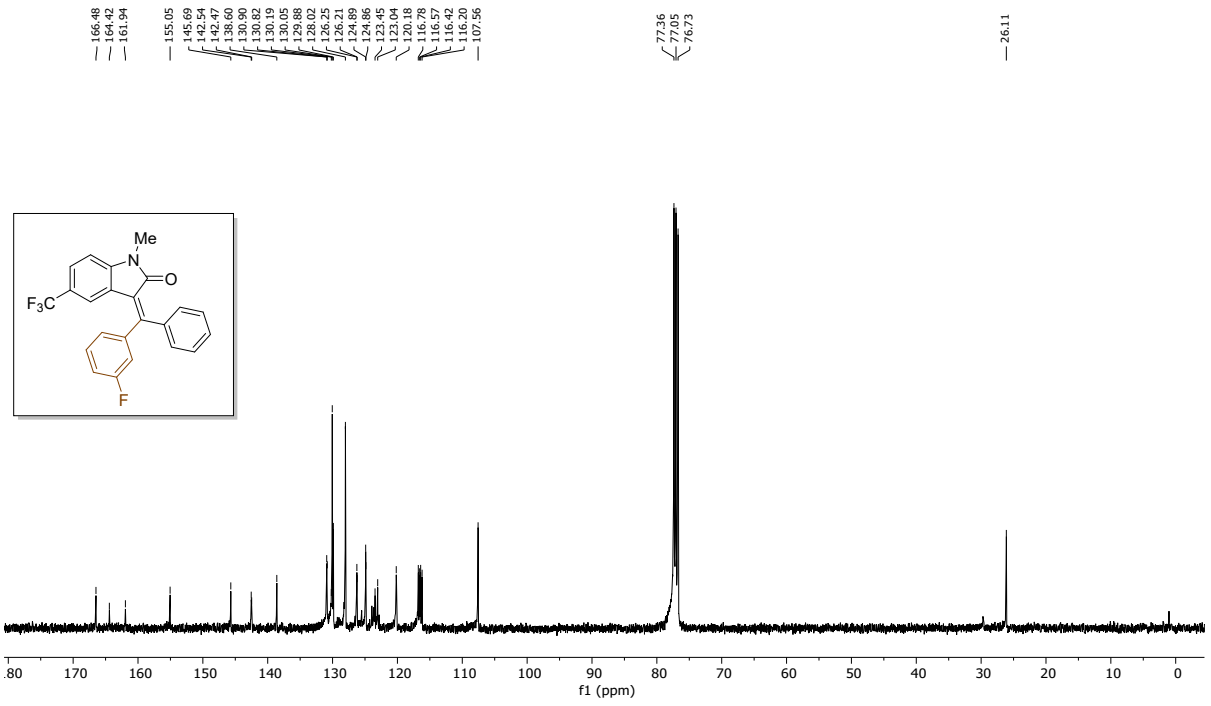


Figure S21. ^{1}H NMR (300 MHz), ^{13}C NMR (100 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-3-((3-fluorophenyl)(phenyl)methylene)-1-methyl-5-(trifluoromethyl)indolin-2-one (3u) in $CDCl_3$.





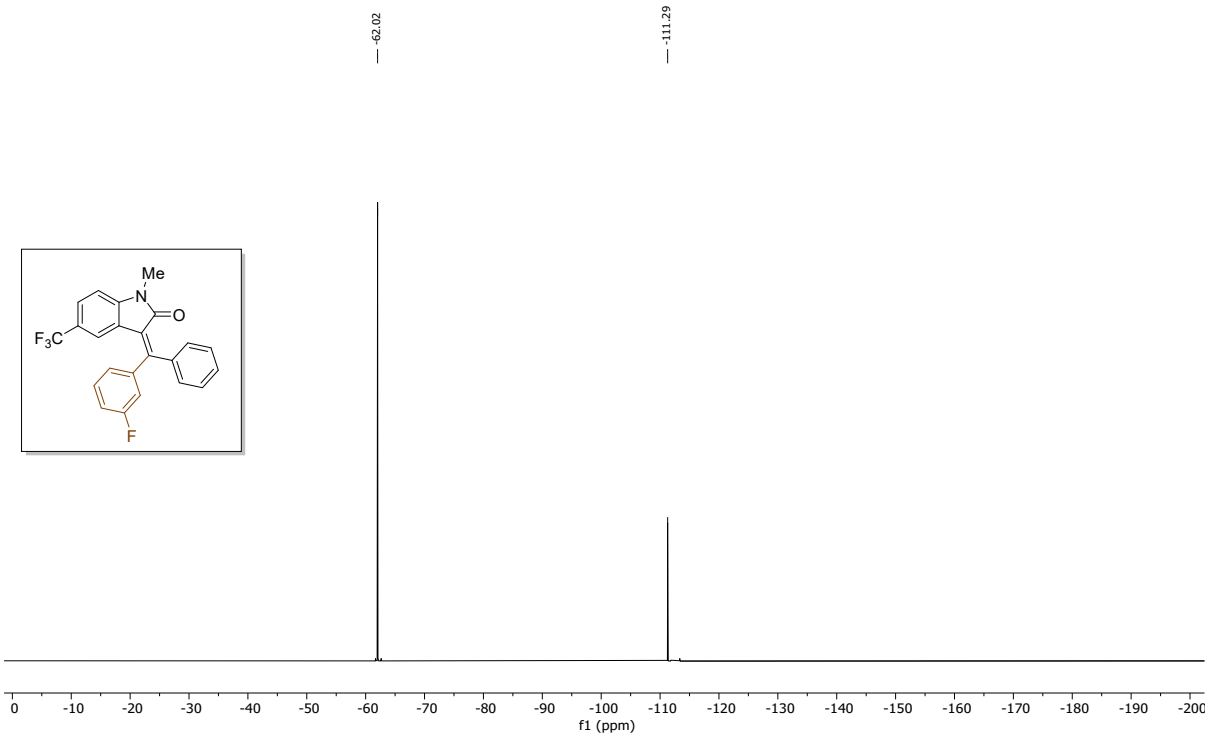
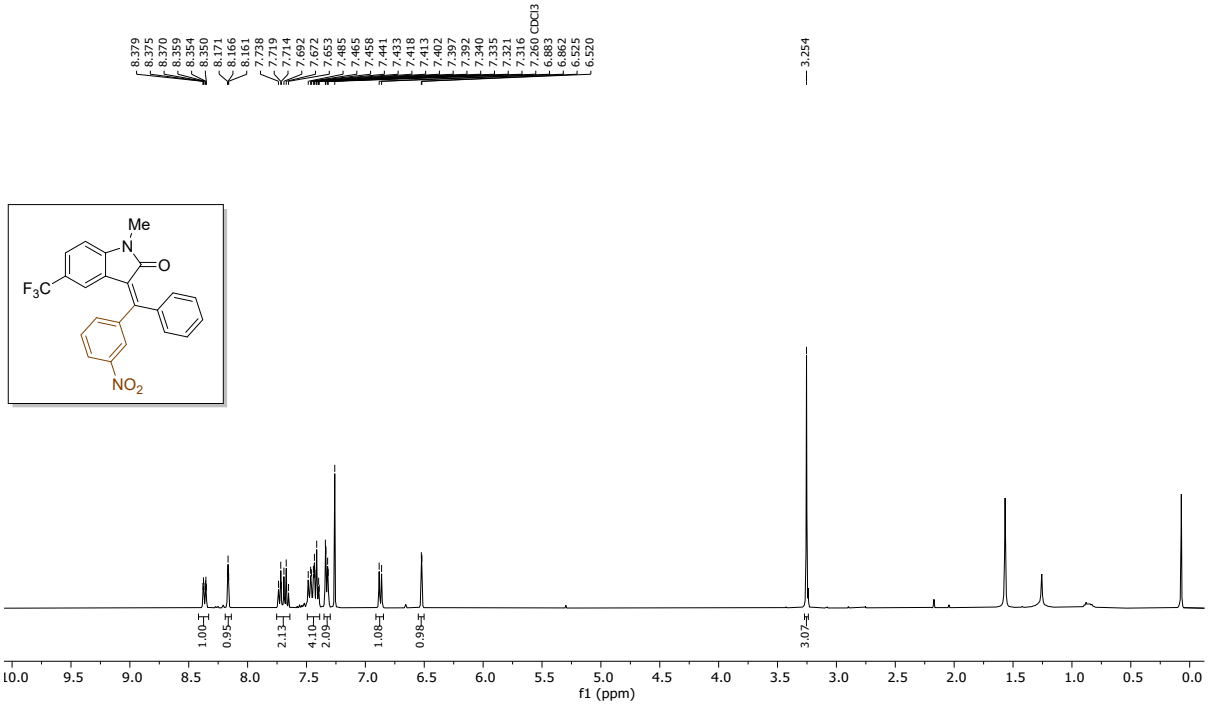
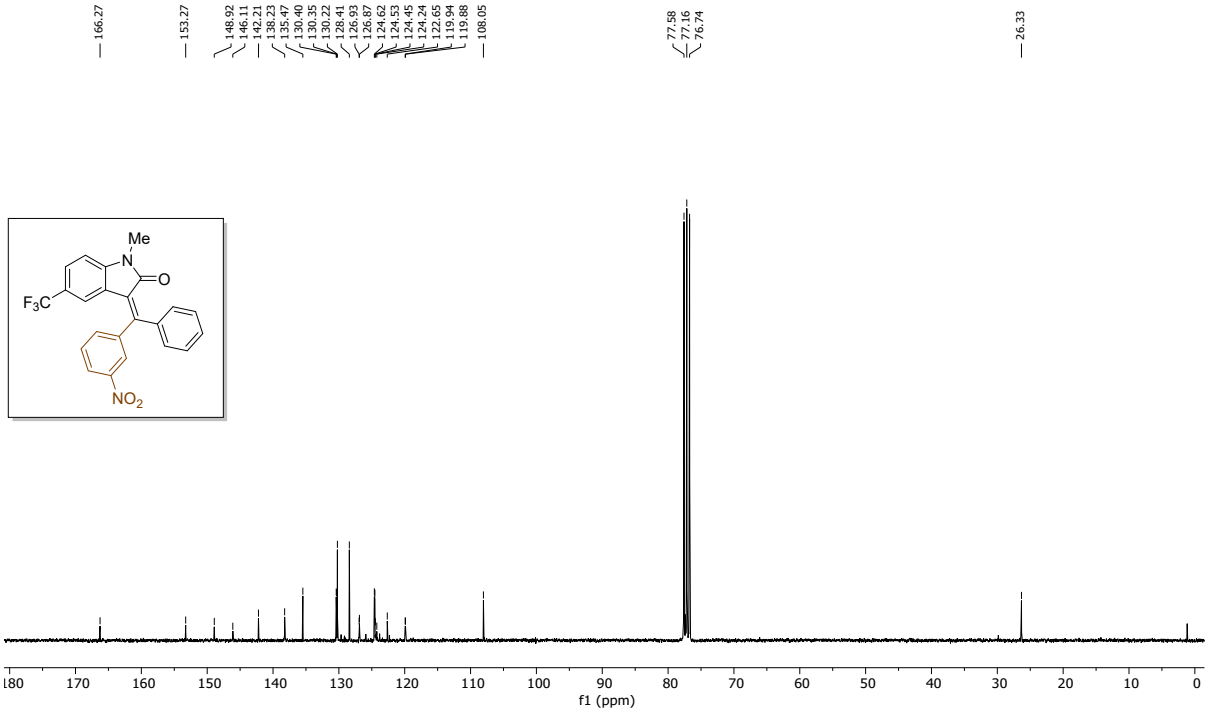

-62.02
-111.29
Me
N
O
F3C
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

Figure S22. ^{1}H NMR (400 MHz), ^{13}C NMR (75 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-1-methyl-3-((3-nitrophenyl)(phenyl)methylene)-5-(trifluoromethyl)indolin-2-one (3v) in $CDCl_3$.





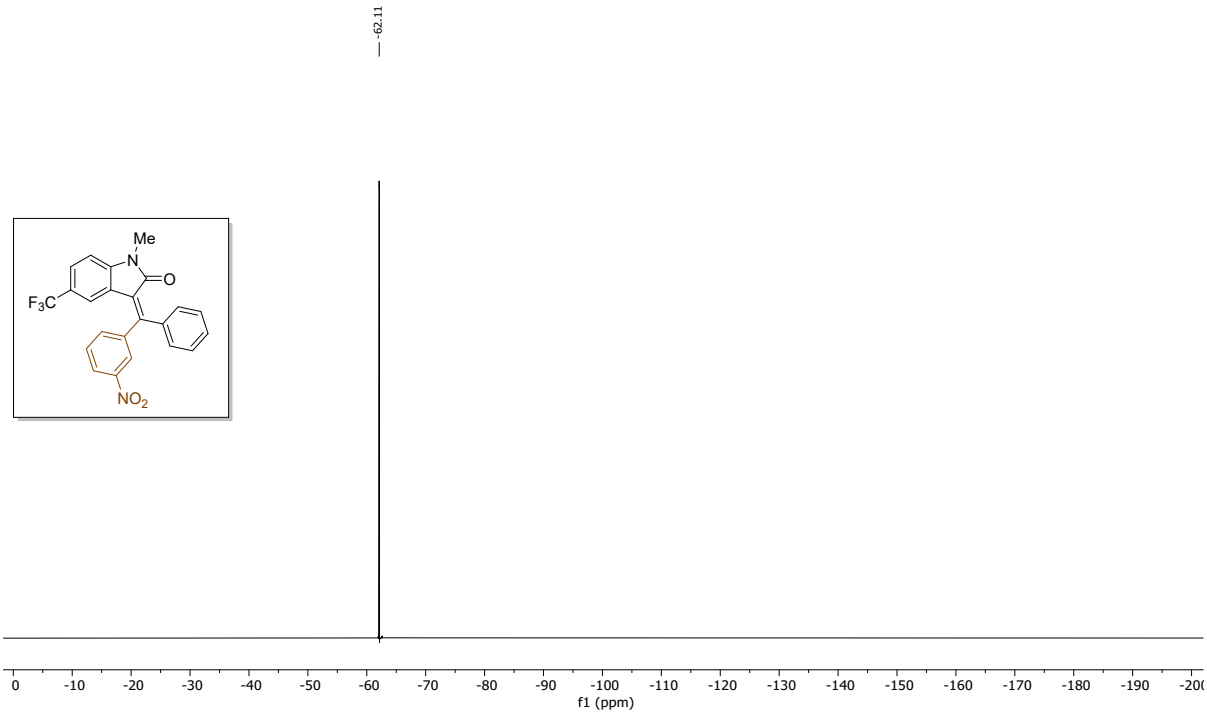
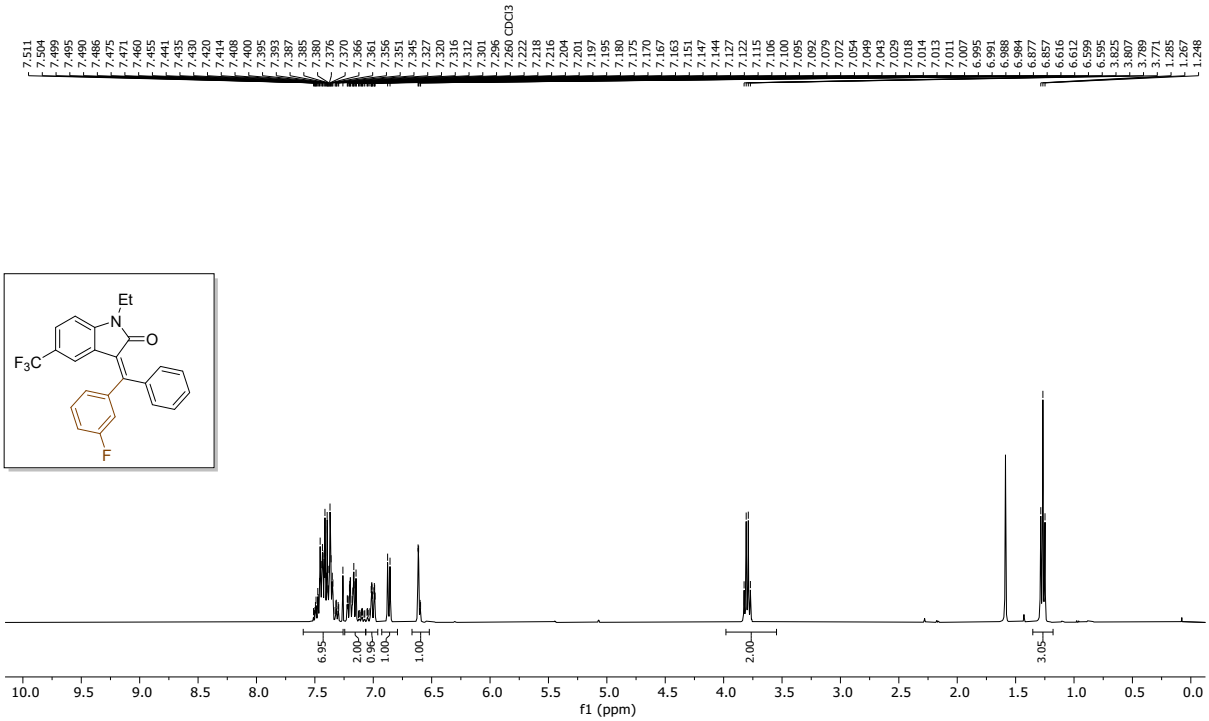
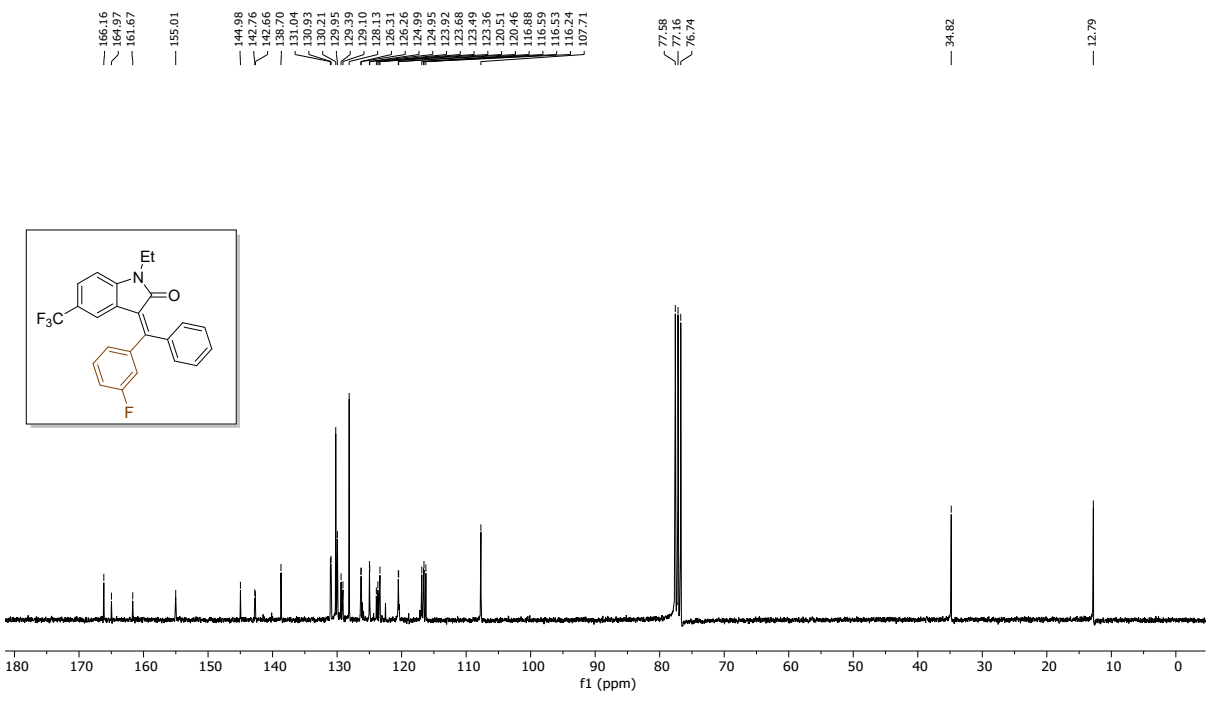

-62.11
Me
N
O
F3C
NO2
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Figure S23. ^{1}H NMR (400 MHz), ^{13}C NMR (75 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-1-ethyl-3-((3-fluorophenyl)(phenyl)methylene)-5-(trifluoromethyl)indolin-2-one (3w) in $CDCl_3$.





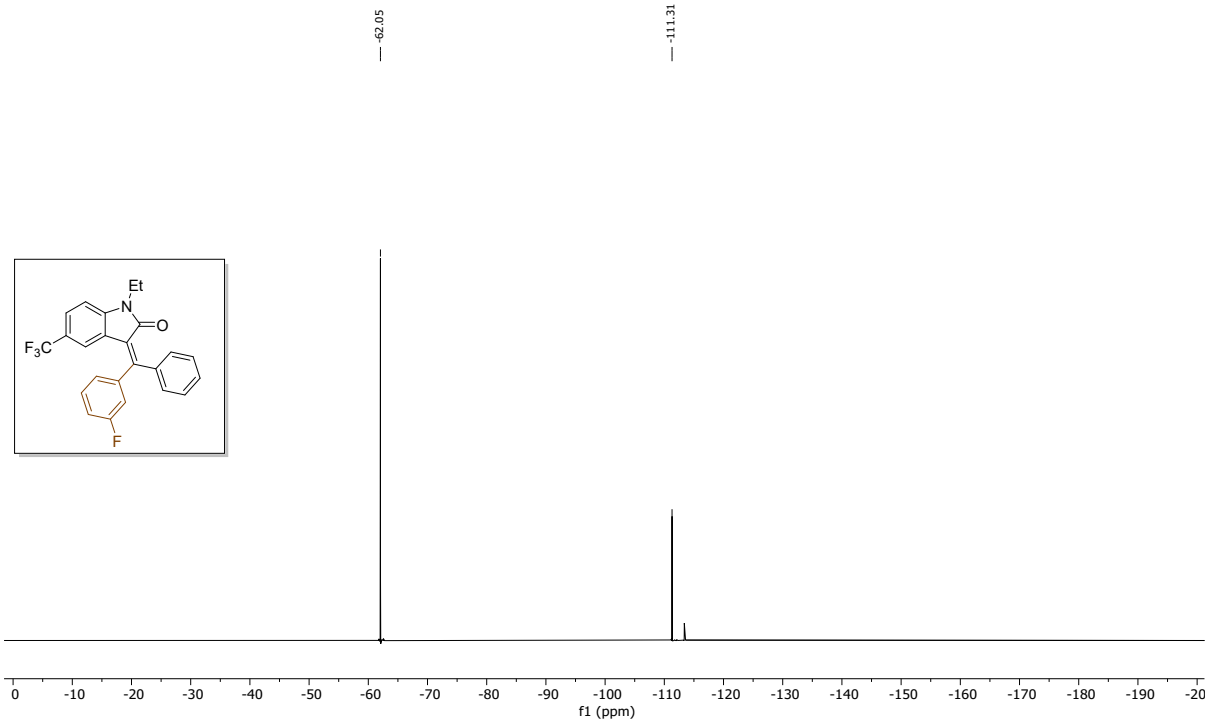
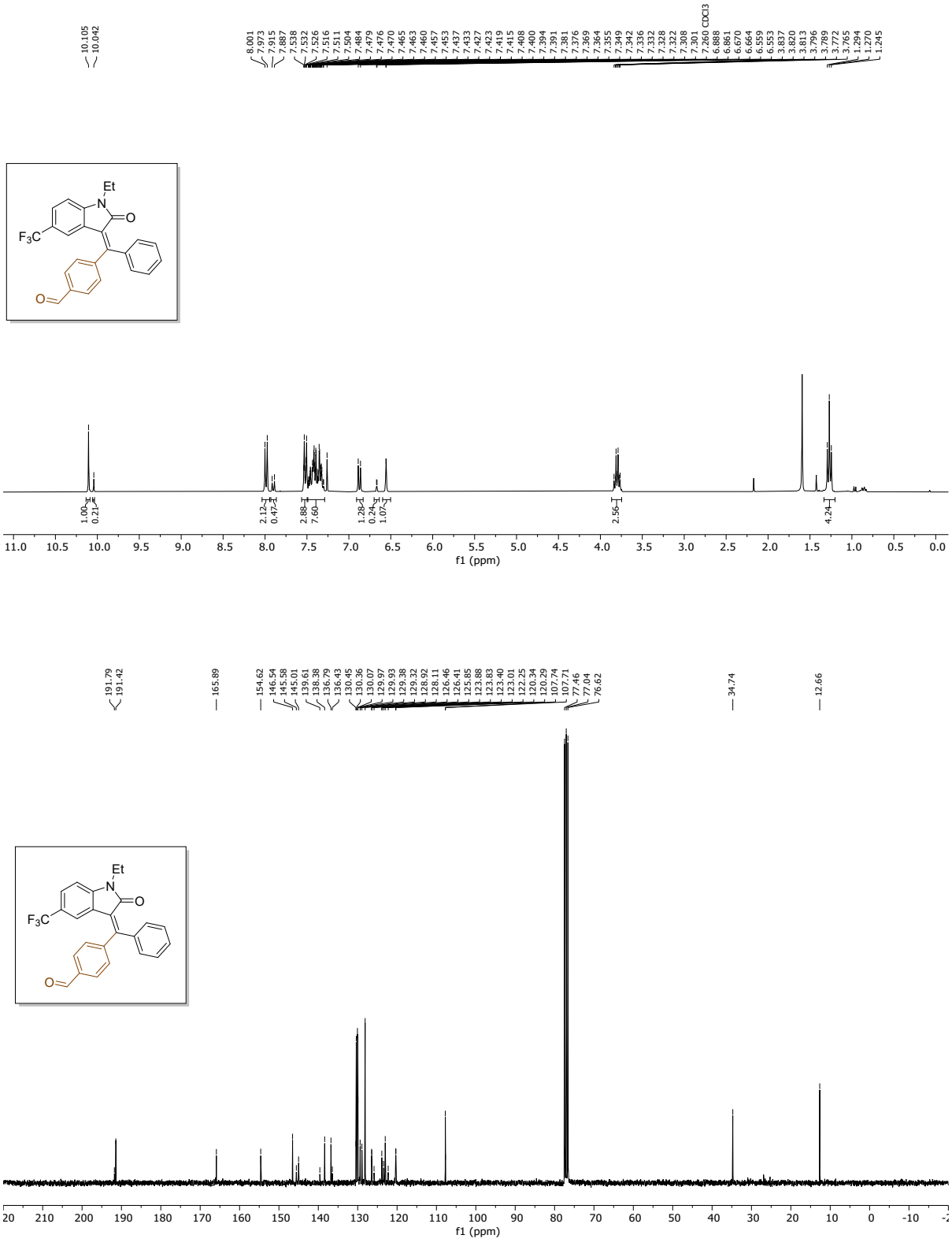

-62.05
-111.31
Et
N
O
F3C
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

Figure S24. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) and ^{19}F (282 MHz) spectra of compound (*E*)-4-((1-ethyl-2-oxo-5-(trifluoromethyl)indolin-3-ylidene)(phenyl)methyl)benzaldehyde (3x) in $CDCl_3$.



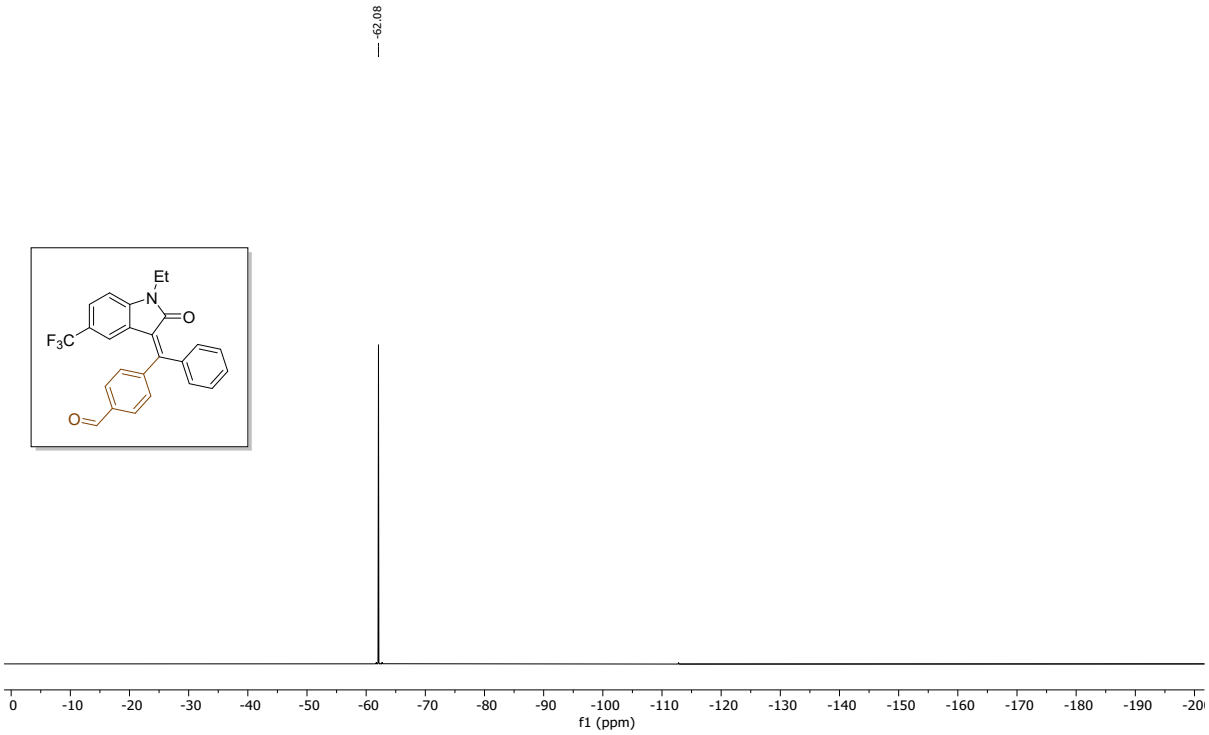
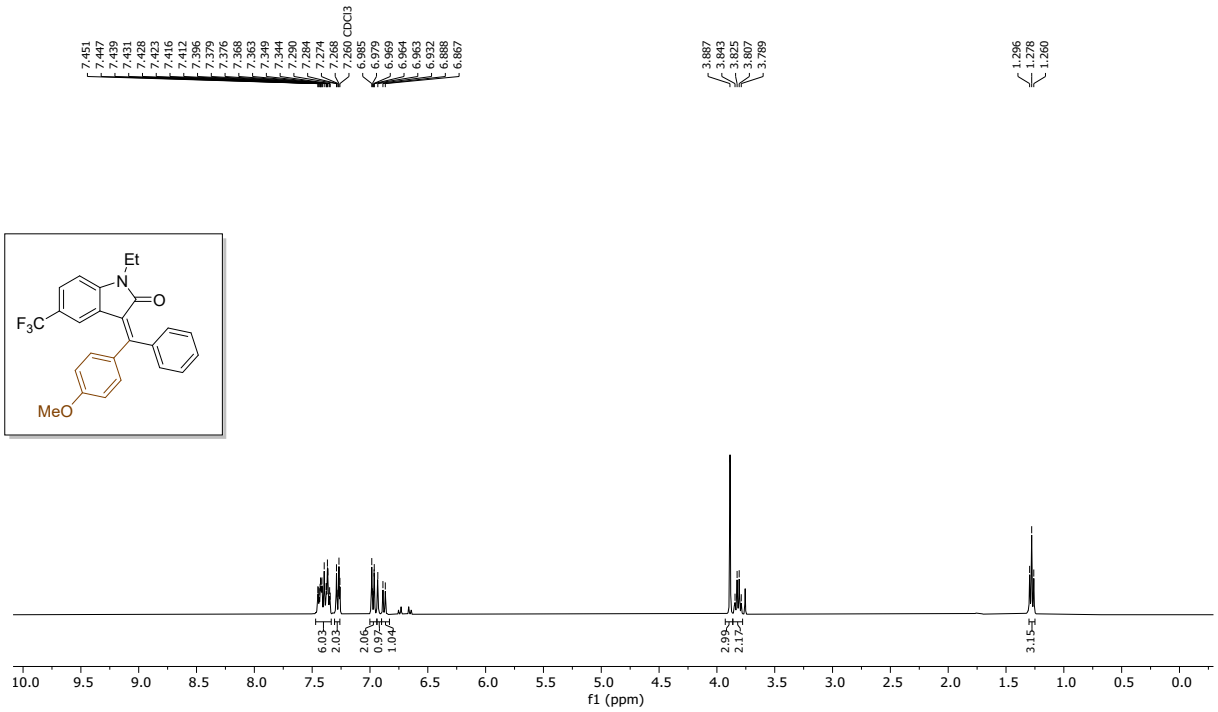
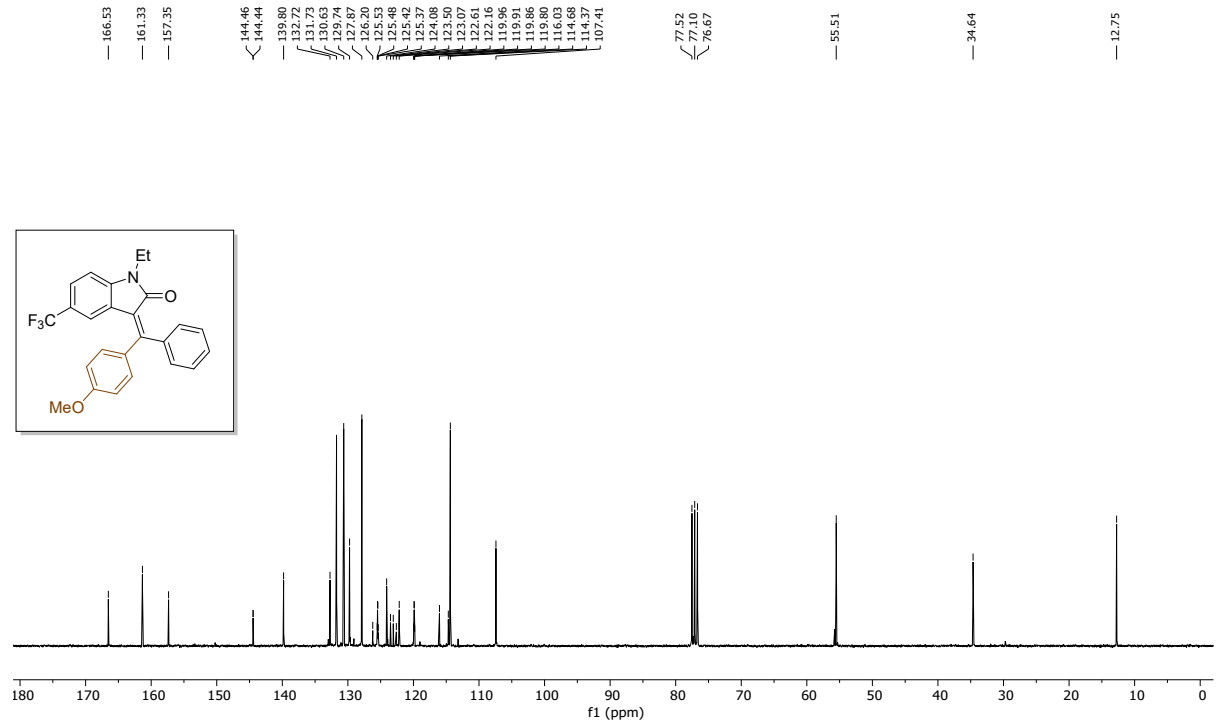
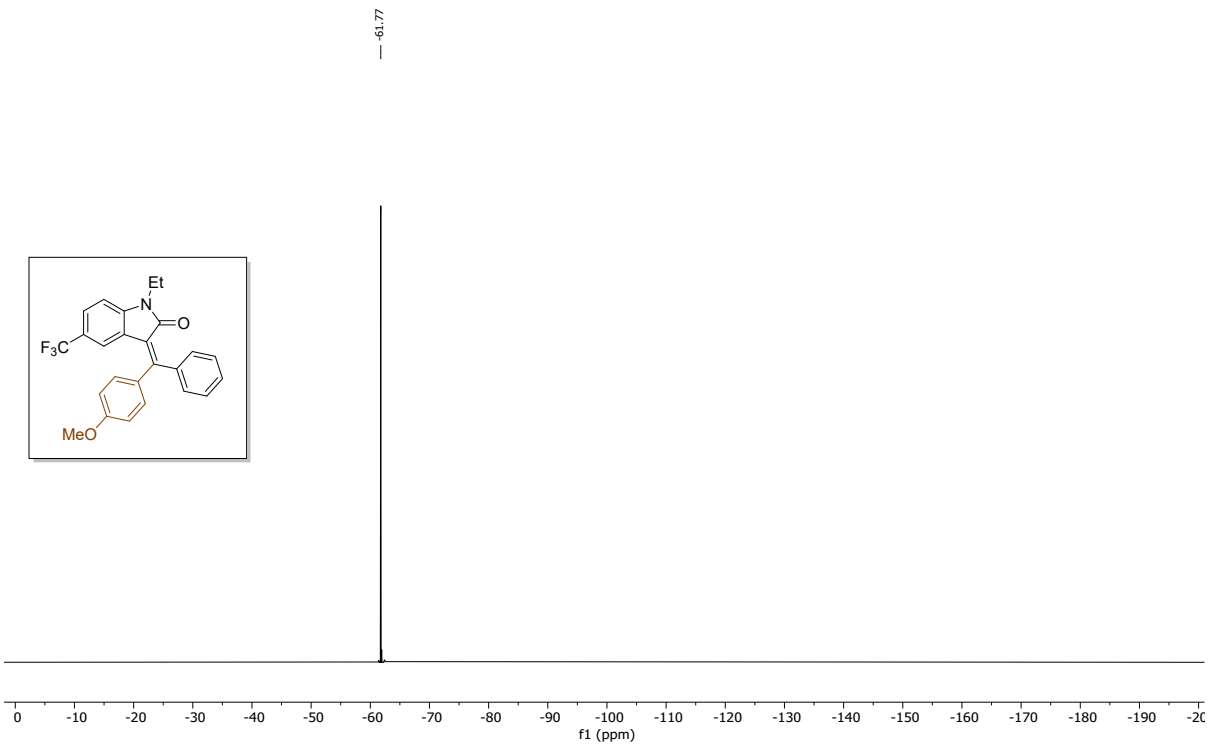

-62.08
Et
N
O
F3C
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Figure S25. ^{1}H NMR (400 MHz), ^{13}C NMR (75 MHz) and ^{19}F (282 MHz) spectra of compound (*E*)-1-ethyl-3-((4-methoxyphenyl)(phenyl)methylene)-5-(trifluoromethyl)indolin-2-one (3y) (3y) in $CDCl_3$.






-61.77
Et
N
O
F3C
MeO
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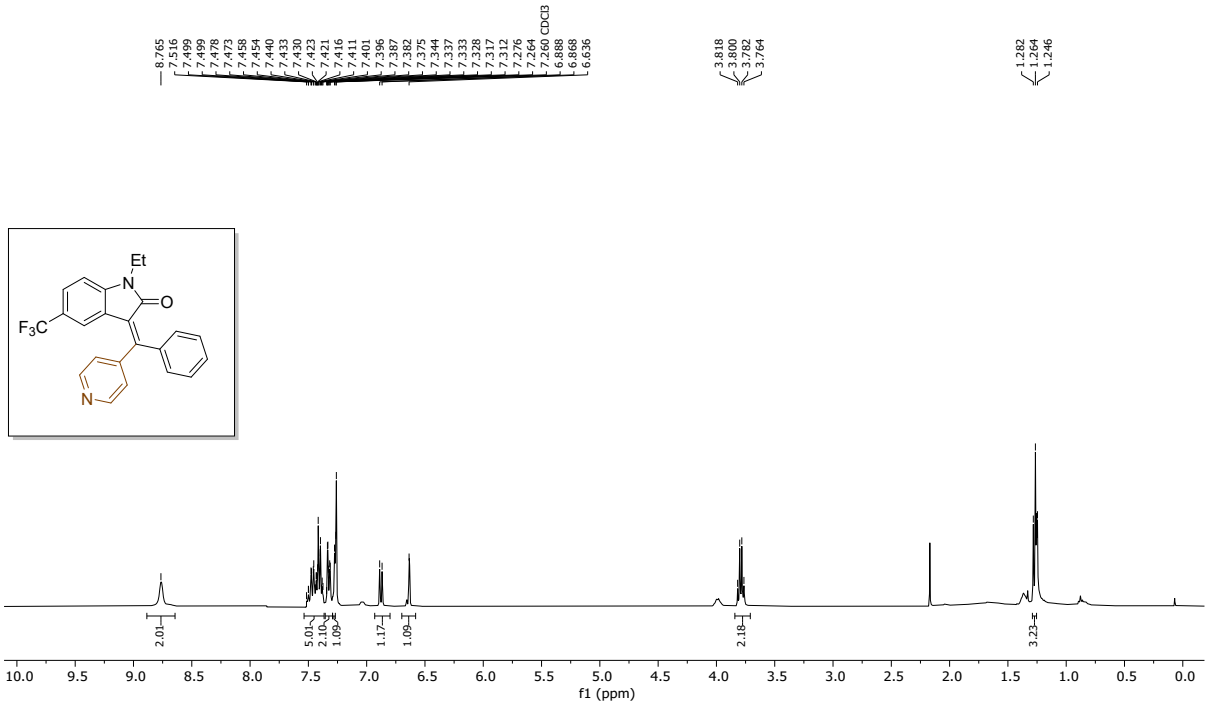
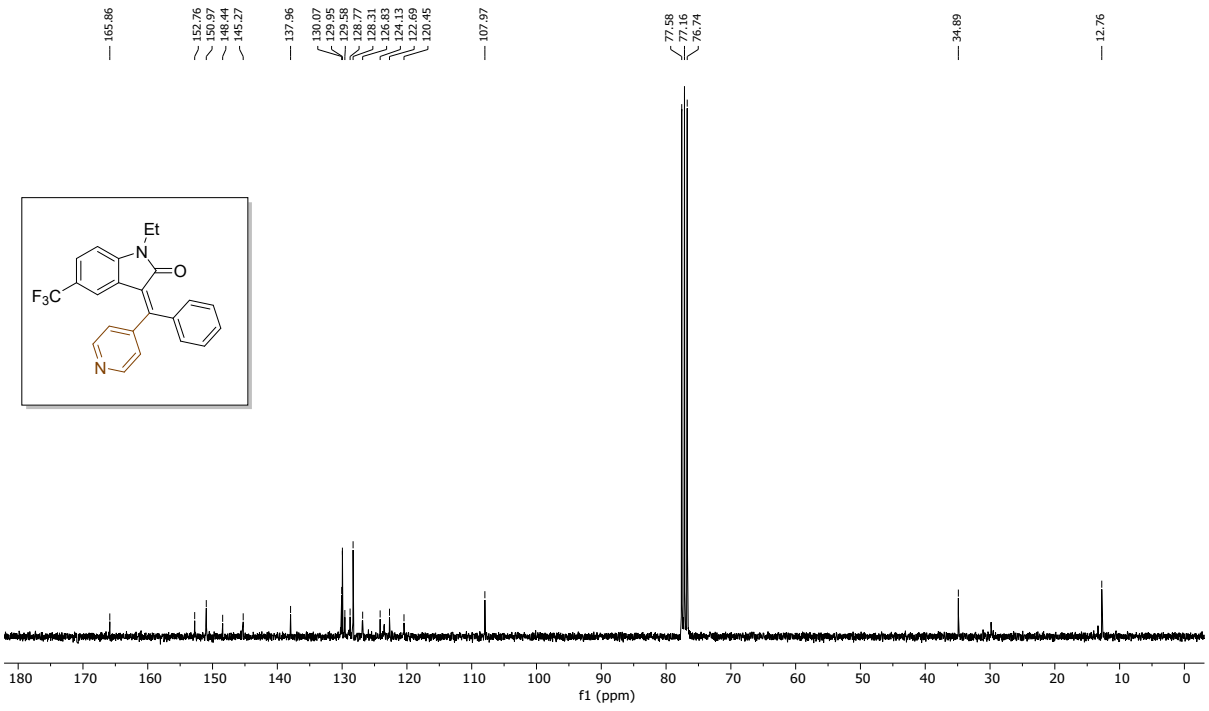
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Figure S26. ^{1}H NMR (400 MHz), ^{13}C NMR (75 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-1-ethyl-3-(phenyl(pyridin-4-yl)methylene)-5-(trifluoromethyl)indolin-2-one (3z) in $CDCl_3$.





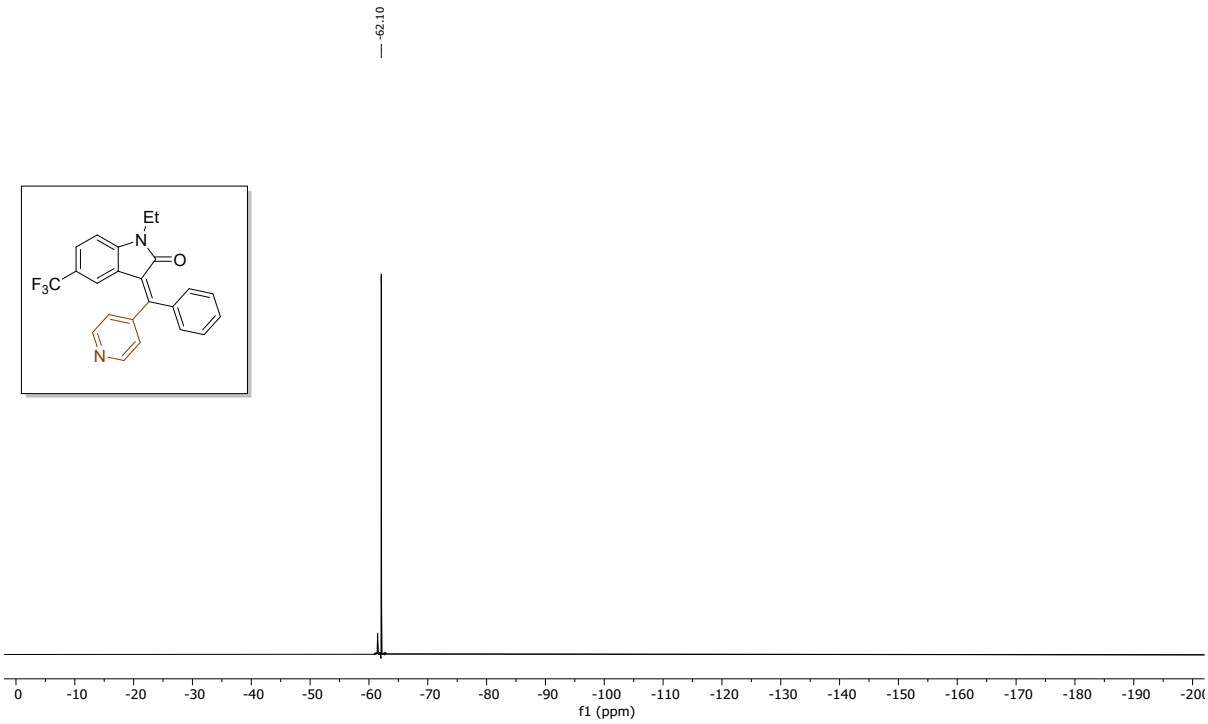
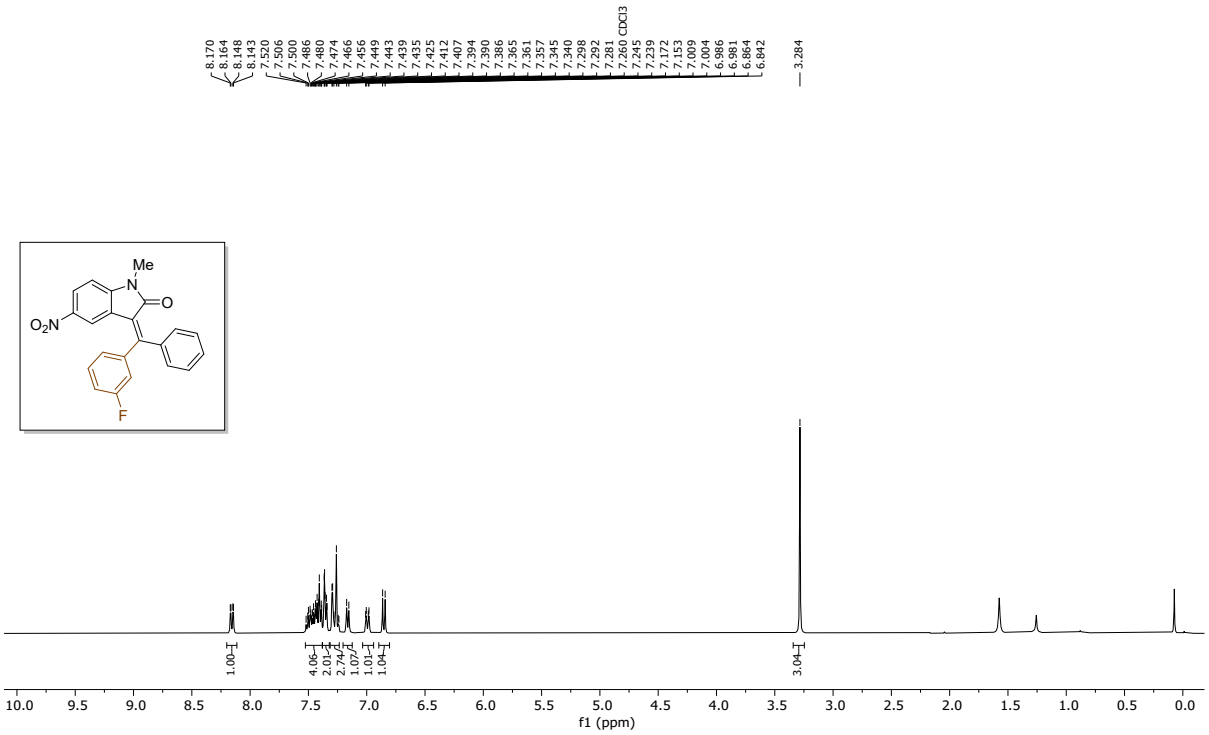
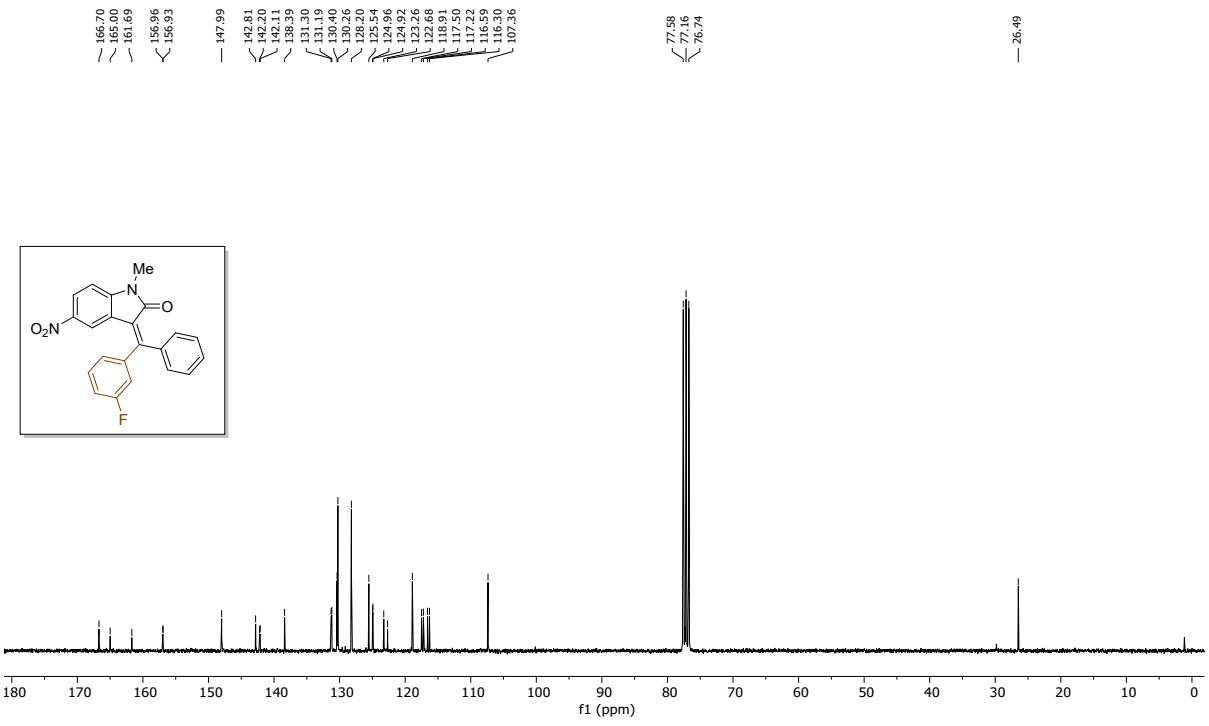

-62.10
Et
N
O
F3C
N
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Figure S27. ^{1}H NMR (400 MHz), ^{13}C NMR (75 MHz) and ^{19}F (377 MHz) spectra of compound (*E*)-3-((3-fluorophenyl)(phenyl)methylene)-1-methyl-5-nitroindolin-2-one (3aa) in $CDCl_3$.





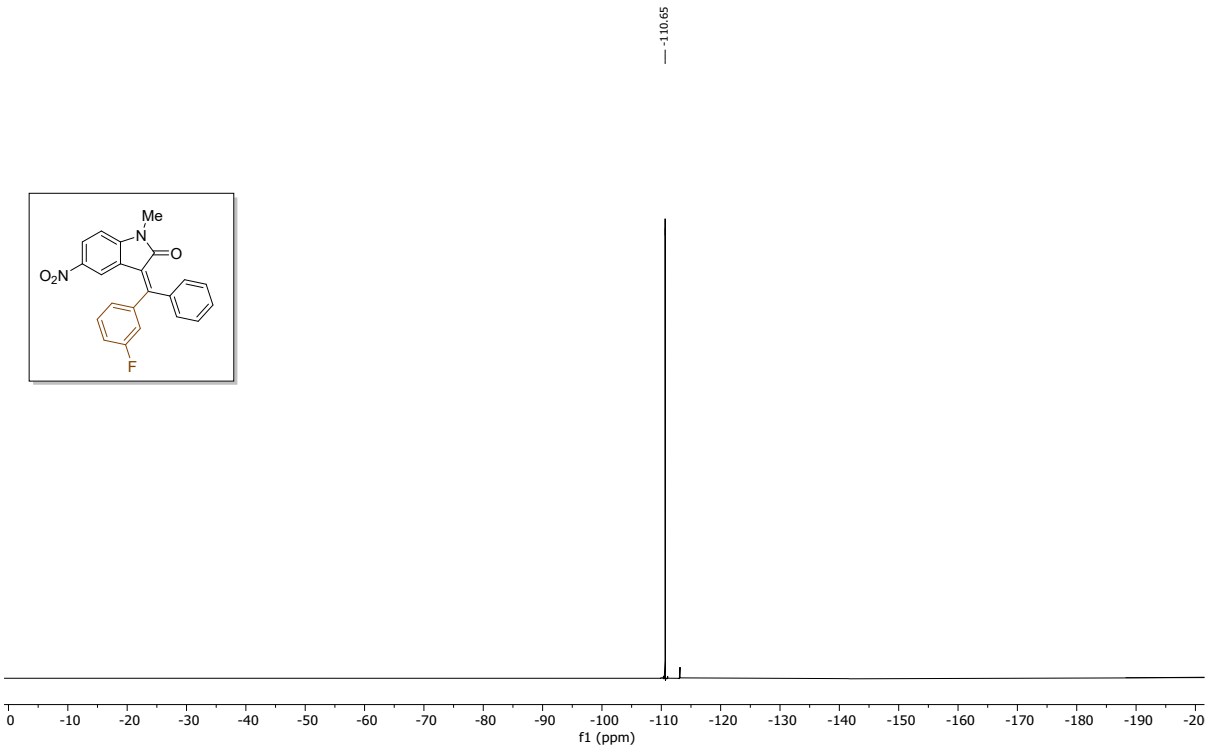
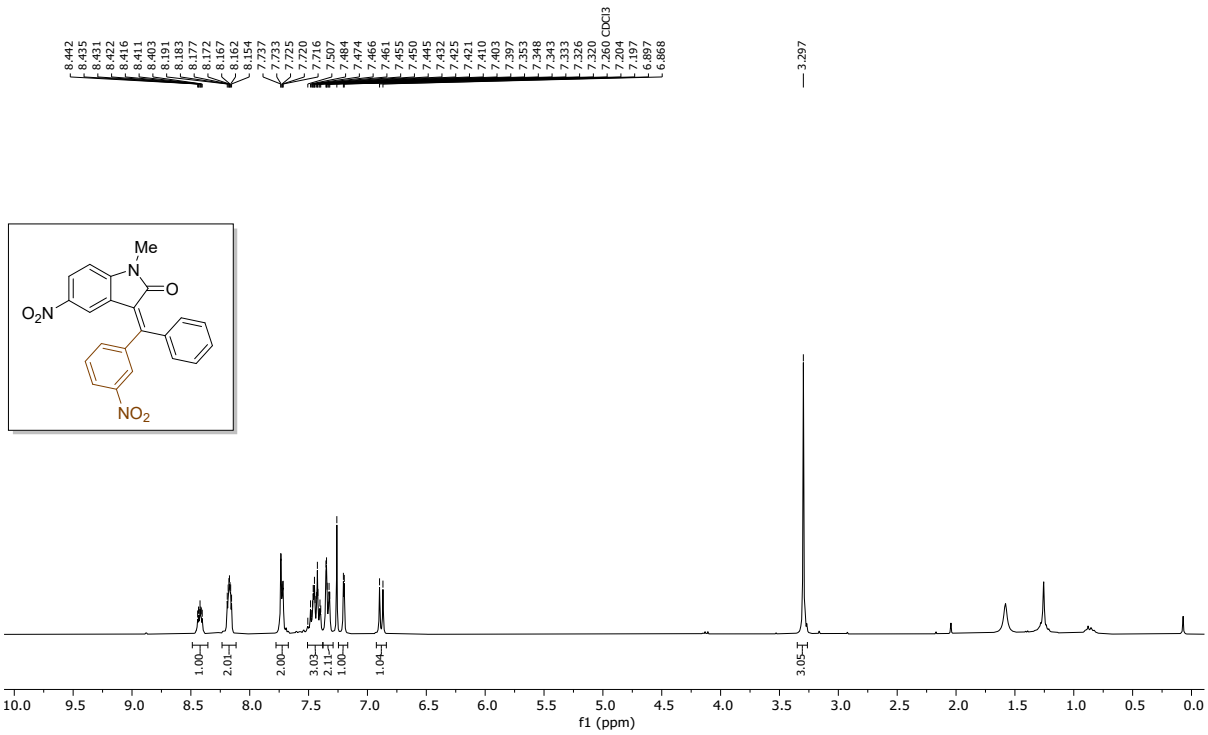

-110.65
Me
N
O
O2N
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

Figure S28. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra of compound (*E*)-1-methyl-5-nitro-3-((3-nitrophenyl)(phenyl)methylene)indolin-2-one (3ab) in $CDCl_3$.



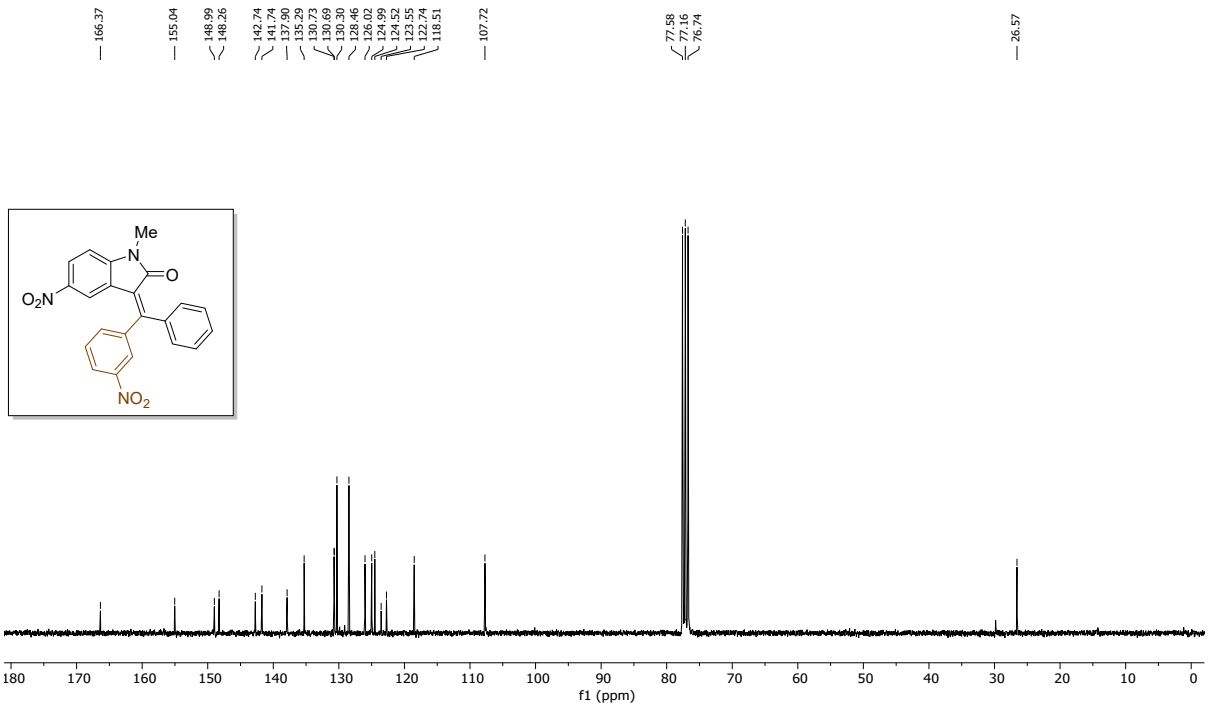
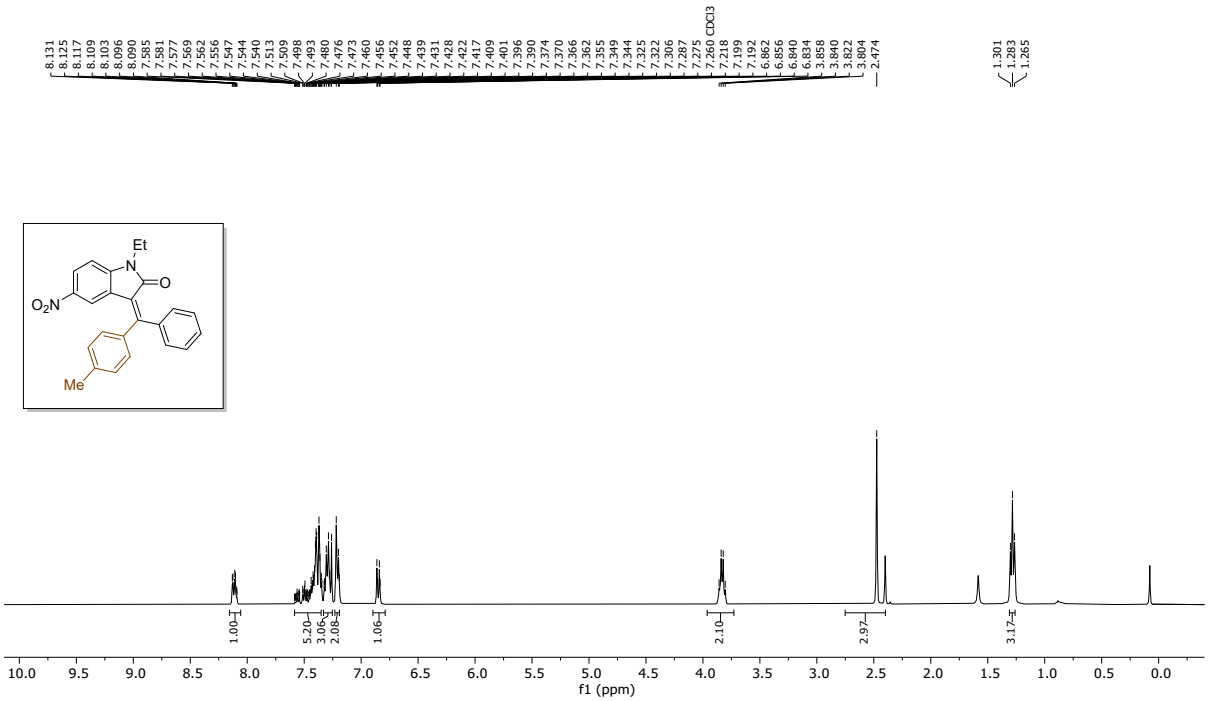


Figure S29. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-1-ethyl-5-nitro-3-(phenyl(p-tolyl)methylene)indolin-2-one (3ac) in $CDCl_3$.



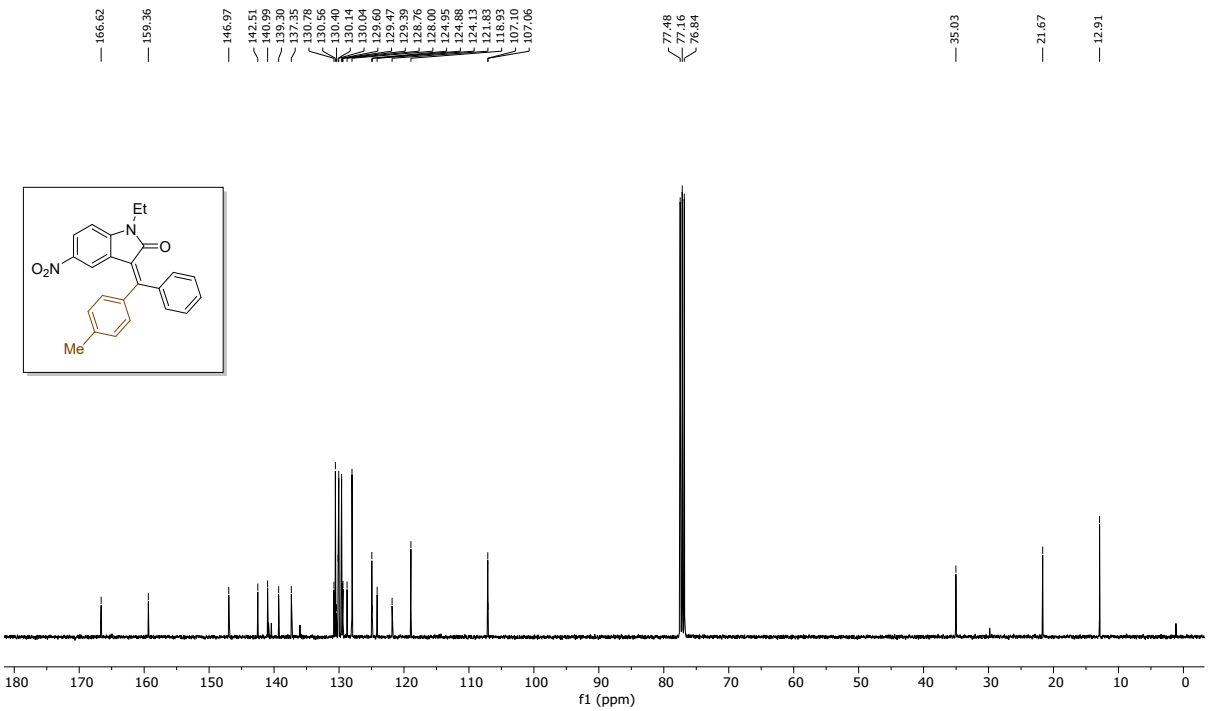
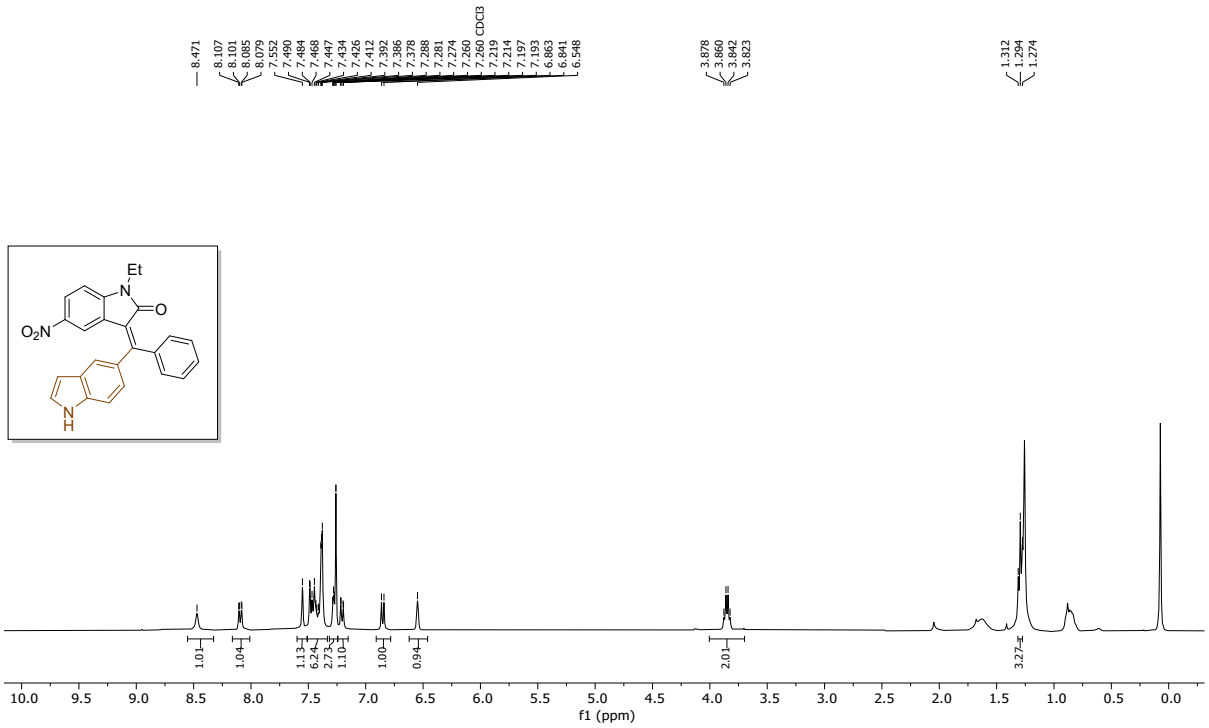


Figure S30. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of compound (*E*)-3-((1*H*-indol-5-yl)(phenyl)methylene)-1-ethyl-5-nitroindolin-2-one (3ad) in $CDCl_3$.



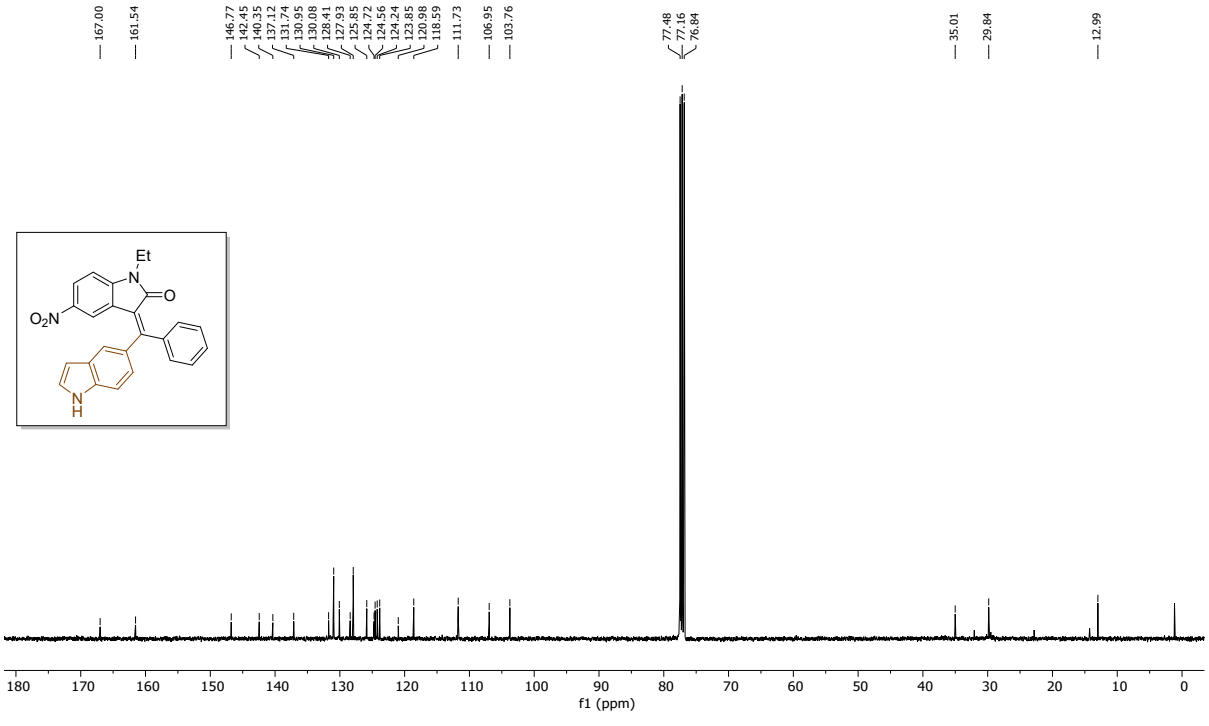
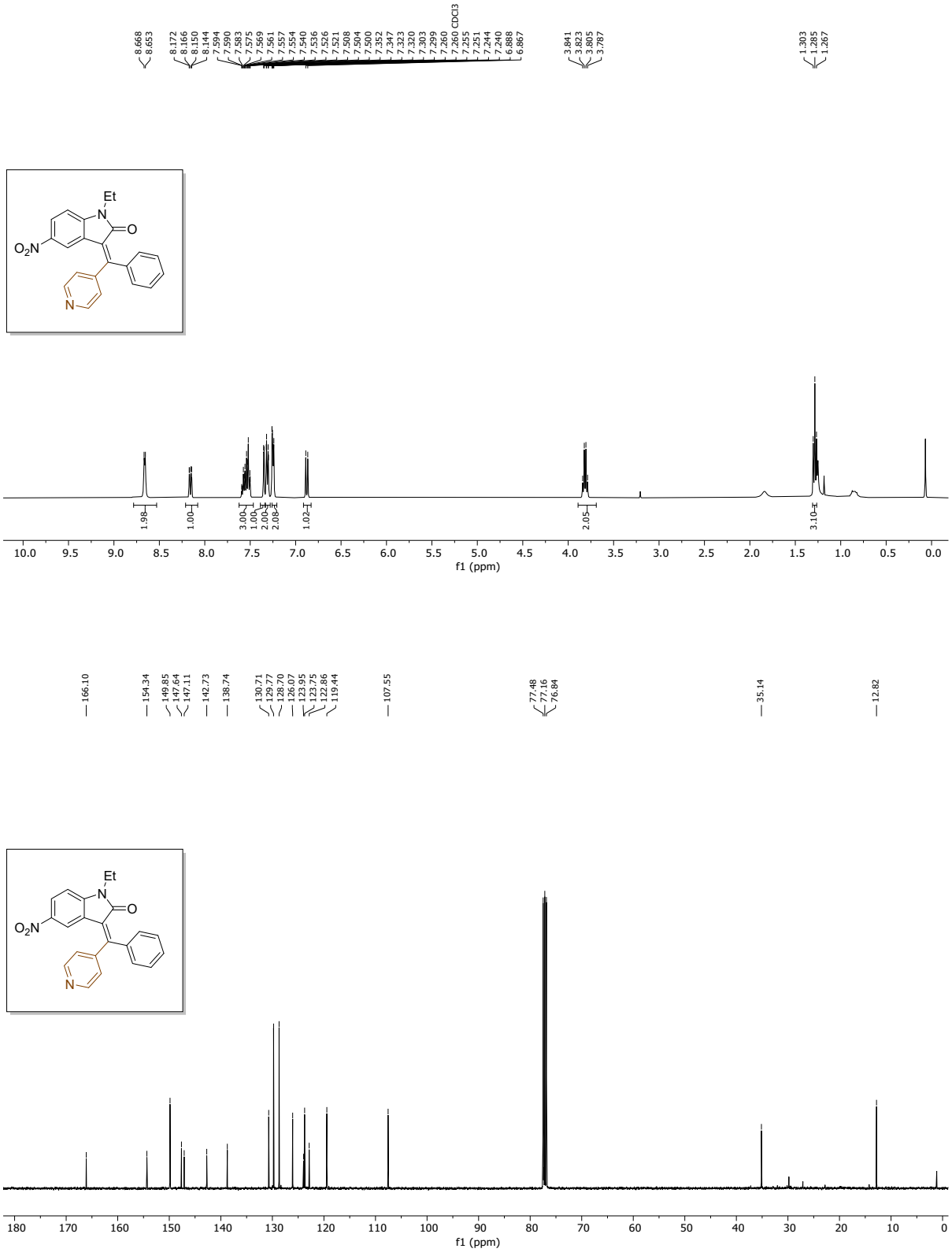
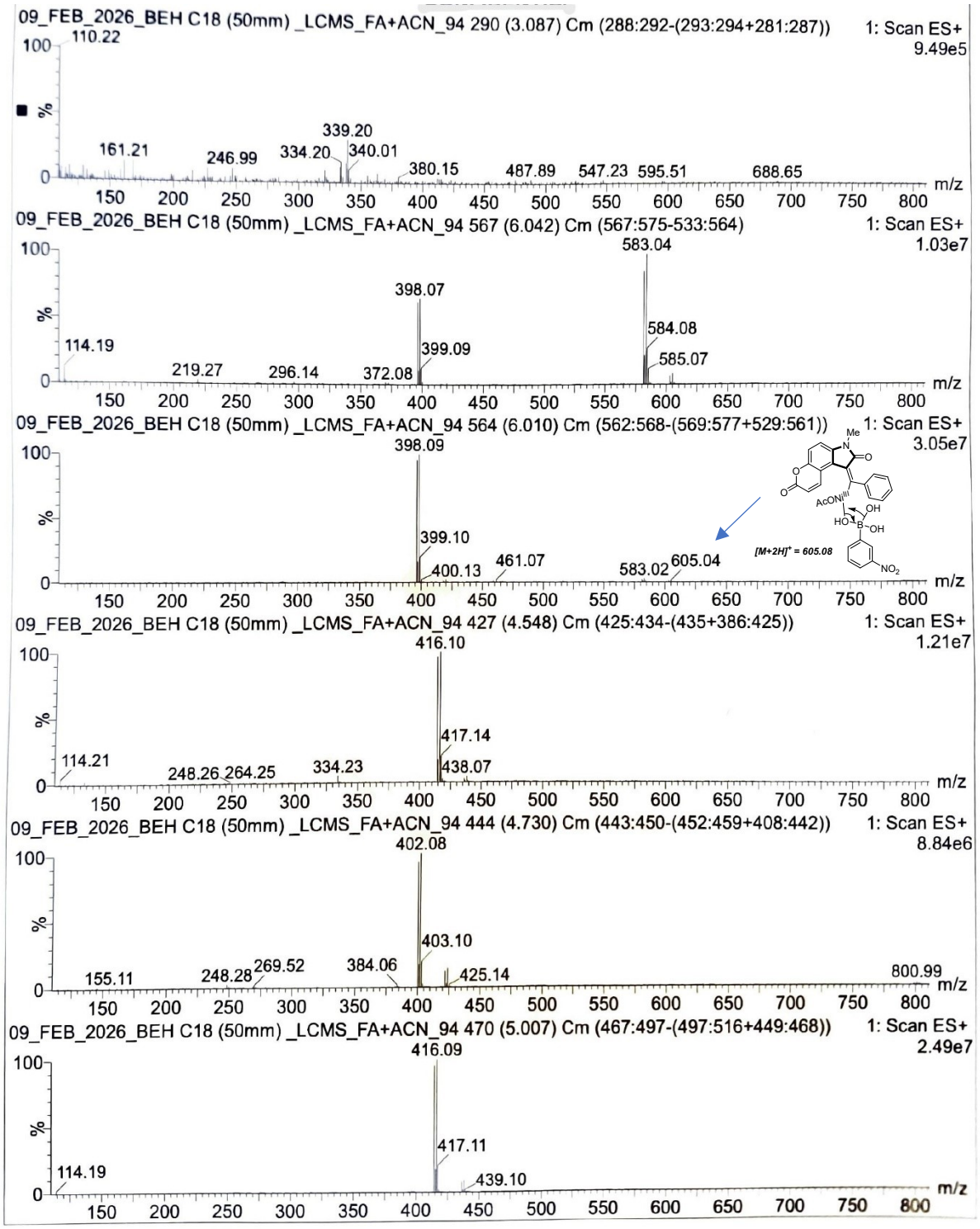


Figure S31. ^{1}H NMR (400 MHz) and ^{13}C NMR (75 MHz) spectra of compound (*E*)-1-ethyl-5-nitro-3-(phenyl(pyridin-4-yl)methylene)indolin-2-one (3ae) in $CDCl_3$.



7) LC-MS Spectra of intermediate C:



8) X-ray crystal structure of compound 3ab:

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of the purified product in hexane/ethyl acetate (1:1) at room temperature over 3-5 days. The X-ray single-crystal data for complex **3ab** has been collected at room temperature in a Bruker made APEX III diffractometer. At first, single crystals of the compound **3ab** have been isolated and then mounted on the glass fiber tip using commercial super glue. Mo−Kα radiation (λ = 0.71073 Å) from a sealed tube X-ray source has been used. The raw data have been integrated using the SAINT program and by utilizing SADABS, the absorption corrections were performed. The structures have been solved by SHELXL-2016/6, and full-matrix least-squares refinements on F^2 for all non-hydrogen atoms were performed by SHELXL-2016/6, with anisotropic displacement parameters. All the calculations and molecular graphics were done by SHELXL-2016/6, PLATON v1.15, WinGX system Ver-1.80, Mercury. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC), and the corresponding CCDC numbers are provided in the Supporting Information. ORTEP drawings were generated with 50% probability ellipsoids. All the crystallographic data and structural refinement parameters for the compound **3ab** has been mentioned.

Crystallographic data of compound (*E*)-1-methyl-5-nitro-3-((3-nitrophenyl)(phenyl)methylene)indolin-2-one (3ab):

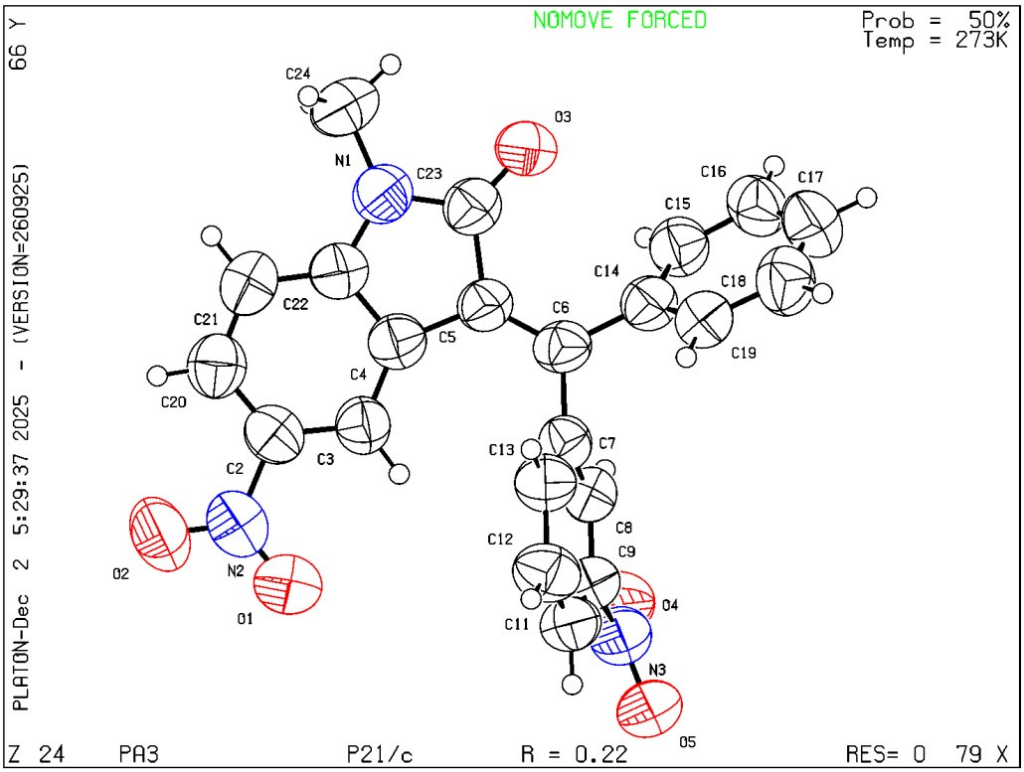
```
Bond precision:   C-C = 0.0104 A          Wavelength=0.71073

Cell:             a=9.3324(7)     b=21.7592(16)        c=9.8515(7)
                  alpha=90        beta=112.594(3)      gamma=90
Temperature:      273 K

                  Calculated                  Reported
Volume            1847.0(2)                   1847.0(2)
Space group       P 21/c                      P21/c
Hall group        -P 2ybc                     ?
Moiety formula    C22 H15 N3 O5               C22 H15 N3 O5
Sum formula       C22 H15 N3 O5               C22 H15 N3 O5
Mr                401.37                      401.37
Dx,g cm-3         1.443                       1.443
Z                 4                           4
Mu (mm-1)         0.105                       0.105
F000              832.0                       832.0
F000'             832.43
h,k,lmax          11,27,12                    11,27,12
Nref              4100                        4085
Tmin,Tmax                                     0.861,0.893
Tmin'

Correction method= # Reported T Limits: Tmin=0.861 Tmax=0.893
AbsCorr = MULTI-SCAN
```

Figure S32. Thermal ellipsoidal (50% ellipsoid probability) structure of compound 3ab (CCDC No. 2512397):



9) Computational details:

We performed full geometry optimizations for all molecules using the PBE0-D3 functional,[1,2] which incorporates dispersion corrections, along with the def2-TZVPP basis set.[3] We also accounted for solvent effects from 1,4-dioxane using the COSMO solvation model.[4] Subsequently, we carried out vibrational frequency calculations at the same level of theory. This allowed us to characterize each optimized structure: those with no imaginary frequencies were designated as minima, while those with one imaginary frequency were identified as transition states. All calculations were executed using the Gaussian 16 software package.[5]

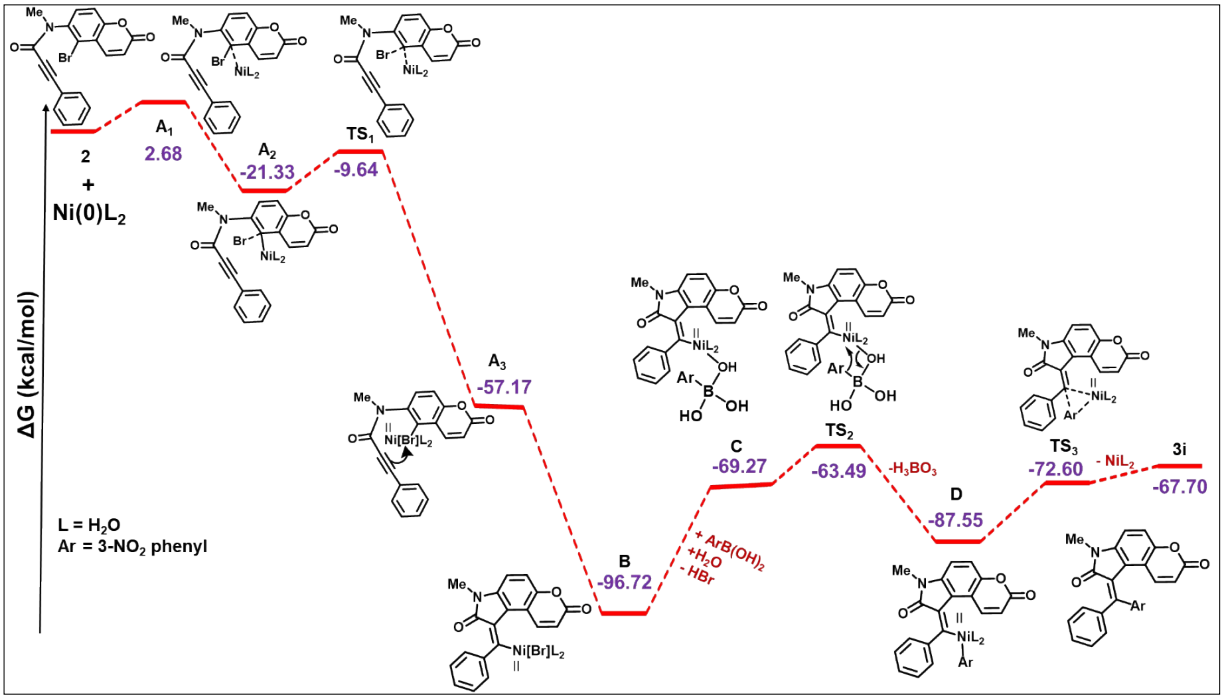
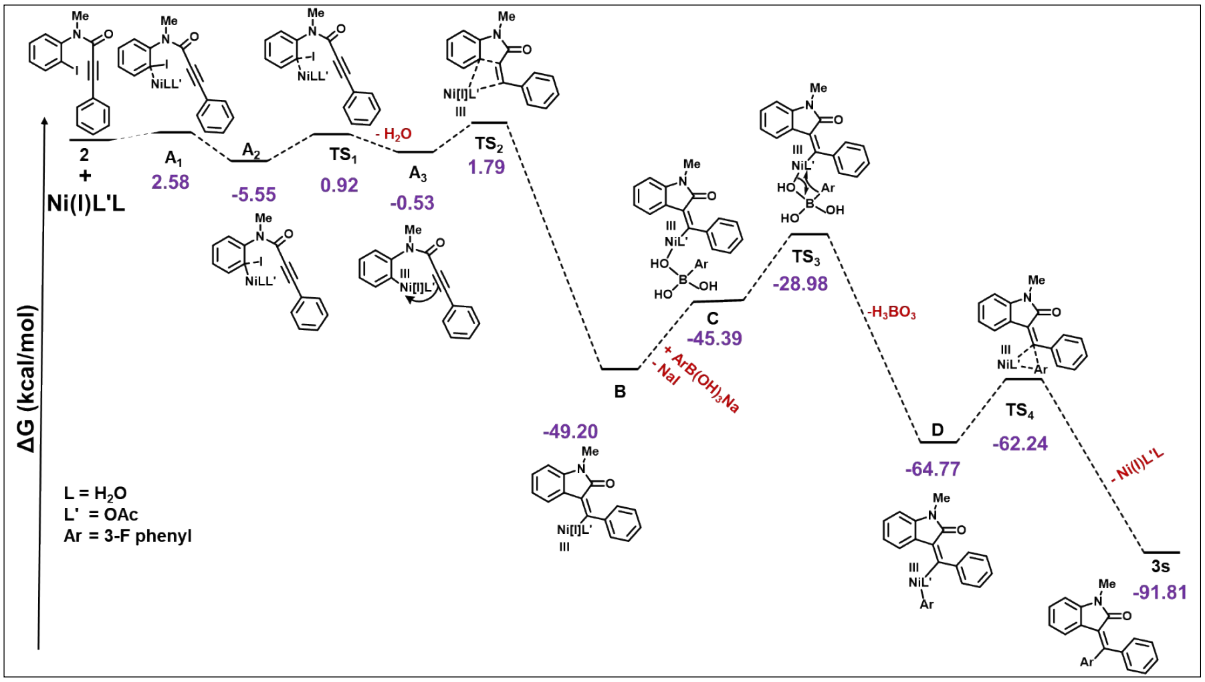


Figure S33. The free energy diagram for forming the coumarin-fused lactam derivative, 3i, through Ni^0/Ni^{II} process.

a)



b)

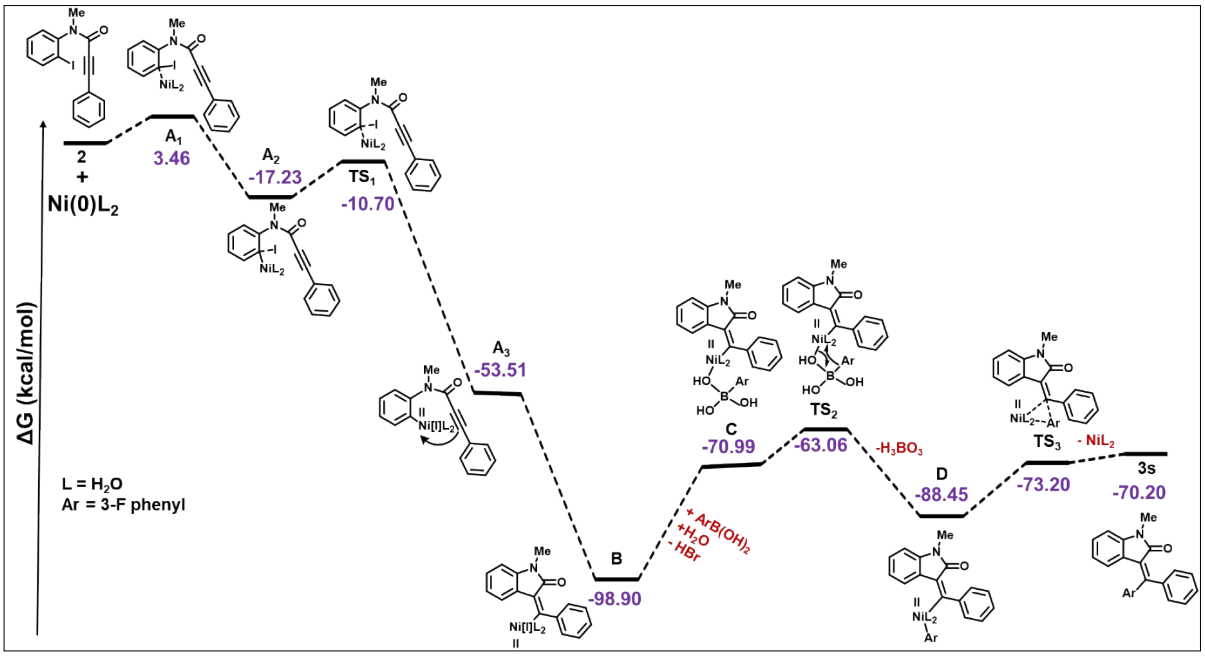
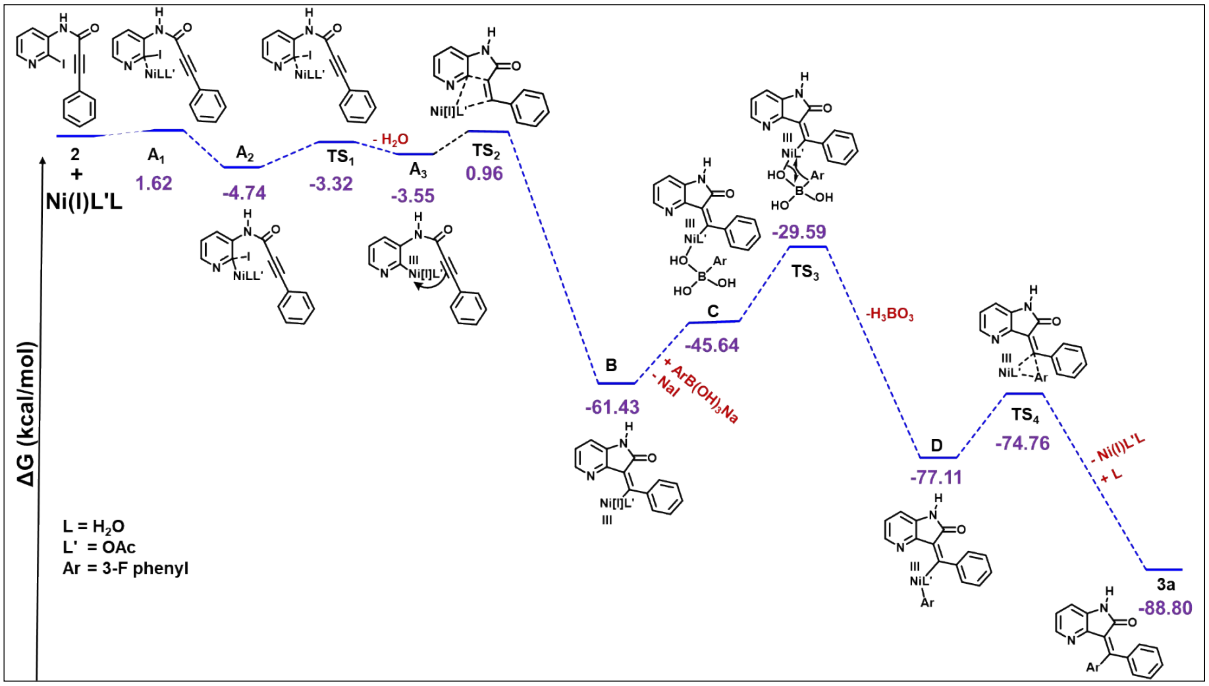


Figure S34. The free energy diagram for forming the benzene-fused lactam derivative, 3s, through a) Ni^{I}/Ni^{III} b) Ni^{0}/Ni^{II} process.

a)



b)

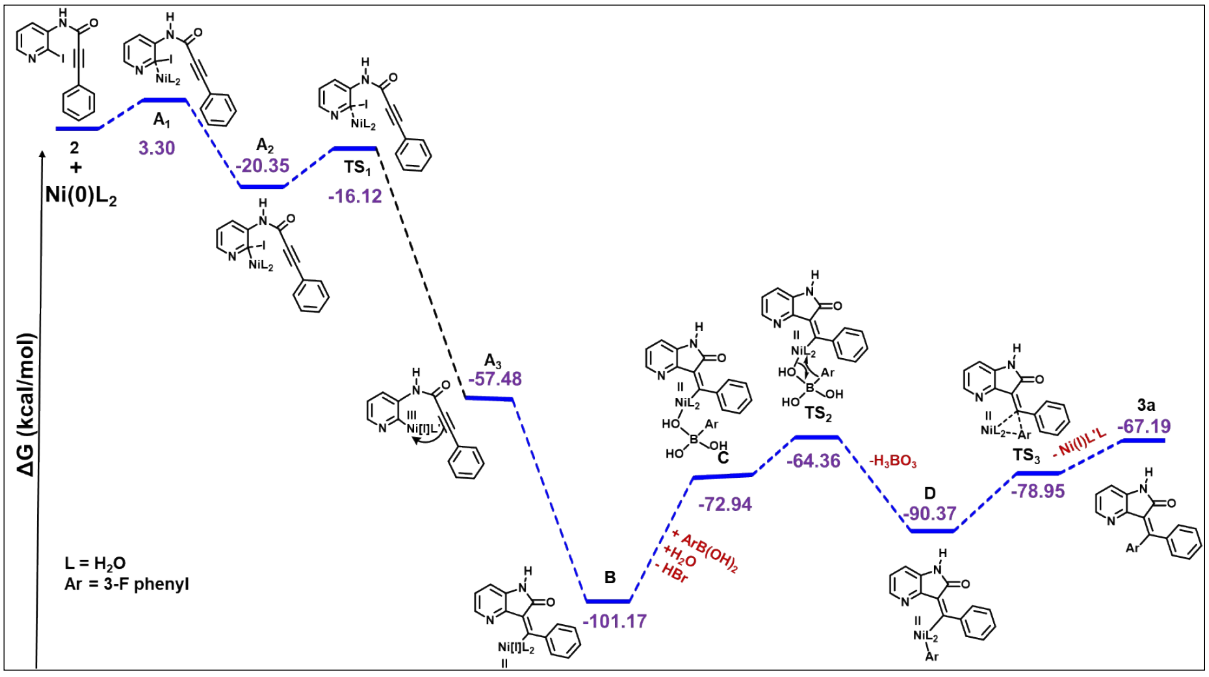


Figure S35. The free energy diagram for forming the pyridine-fused lactam derivative, 3a, through a) Ni^{I}/Ni^{III} b) Ni^{0}/Ni^{II} process.

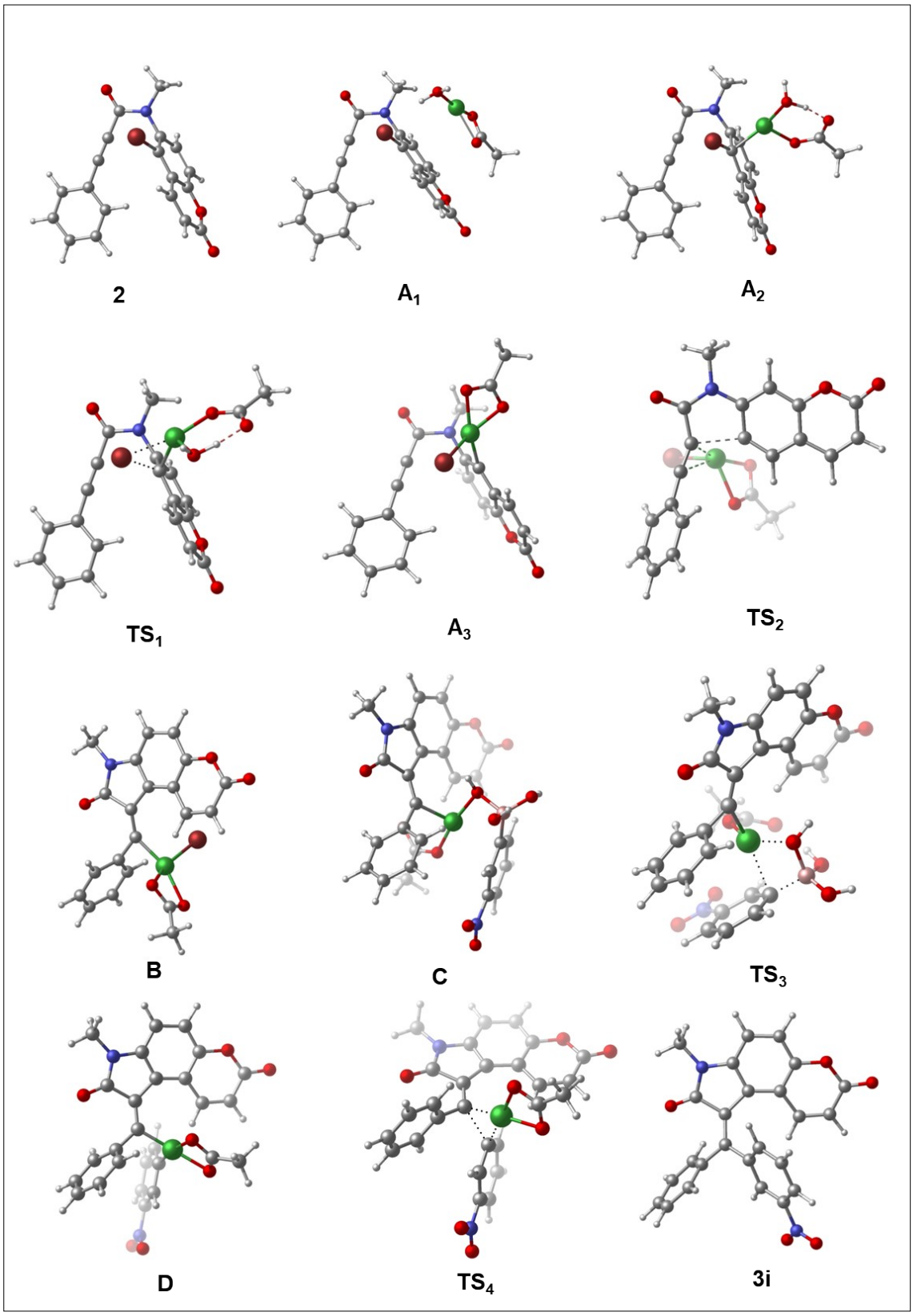


Figure S36. Optimized geometries of stationary points for forming the final product, coumarin-fused lactam derivative, 3i, along with regeneration of the active catalyst through Ni^{I}/Ni^{III} process. The distances are given in Å. [C: grey, O: red, H: white, Br: reddish brown, Ni: green, N: blue, B: pink].

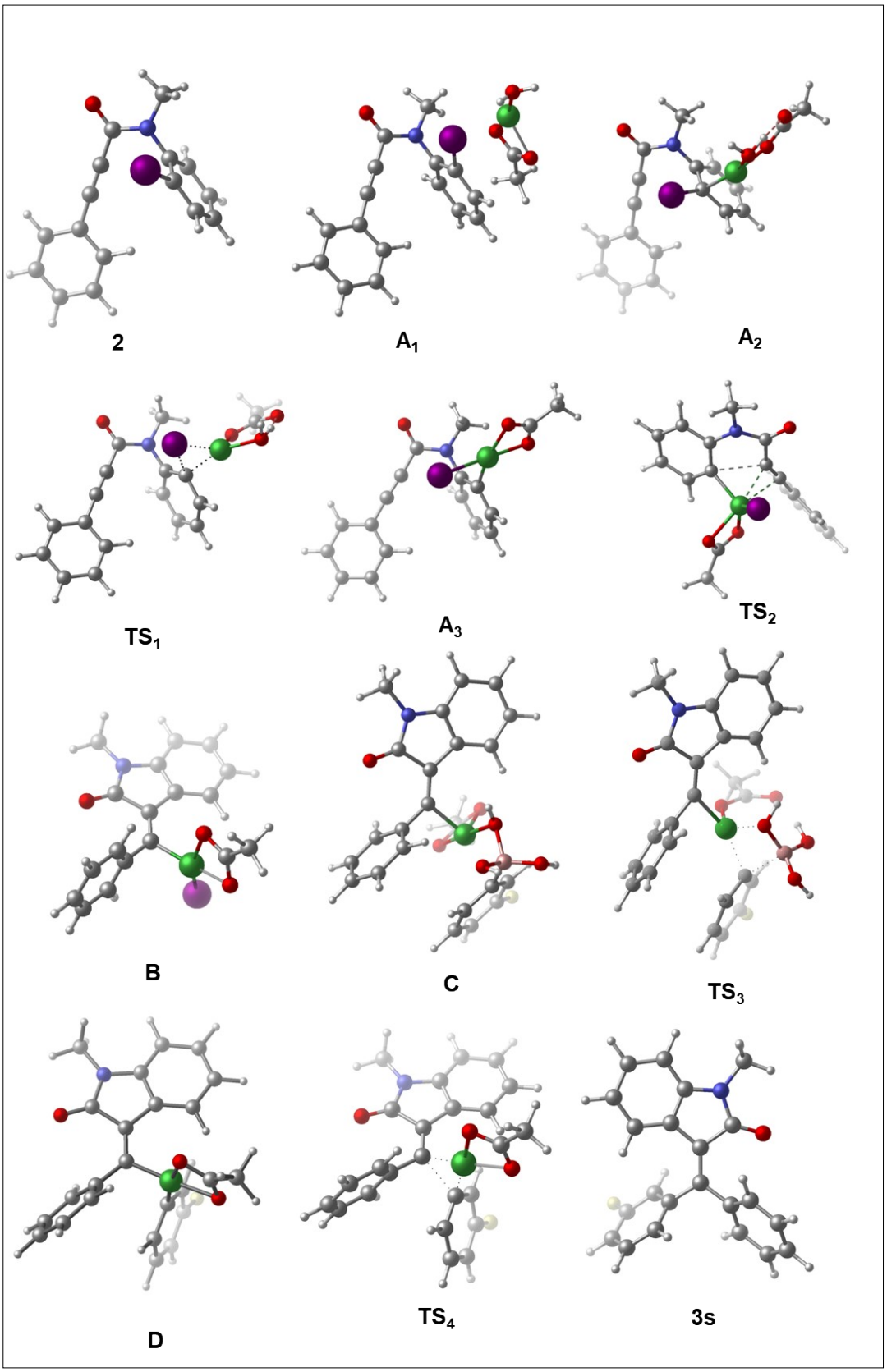


Figure S37. Optimized geometries of stationary points for forming the final product, benzene-fused lactam derivative, 3s, along with regeneration of the active catalyst through Ni^{I}/Ni^{III} process. The distances are given in Å. [C: grey, O: red, H: white, Br: reddish brown, Ni: green, N: blue, B: pink, F: yellow].

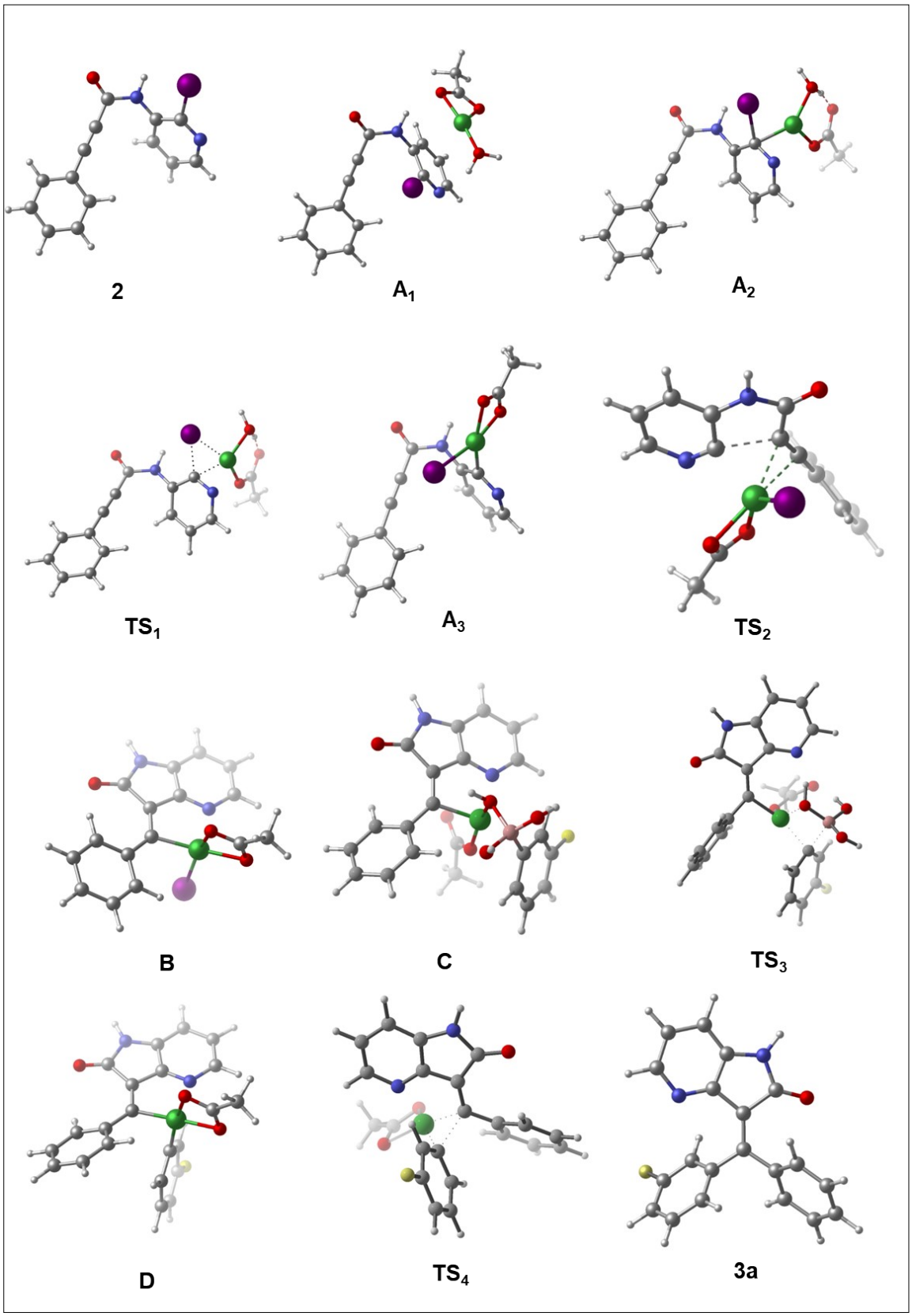


Figure S38. Optimized geometries of stationary points for forming the final product, pyridine-fused lactam derivative, 3a, along with regeneration of the active catalyst through Ni^{I}/Ni^{III} process. The distances are given in Å. [C: grey, O: red, H: white, Br: reddish brown, Ni: green, N: blue, B: pink, F: yellow].

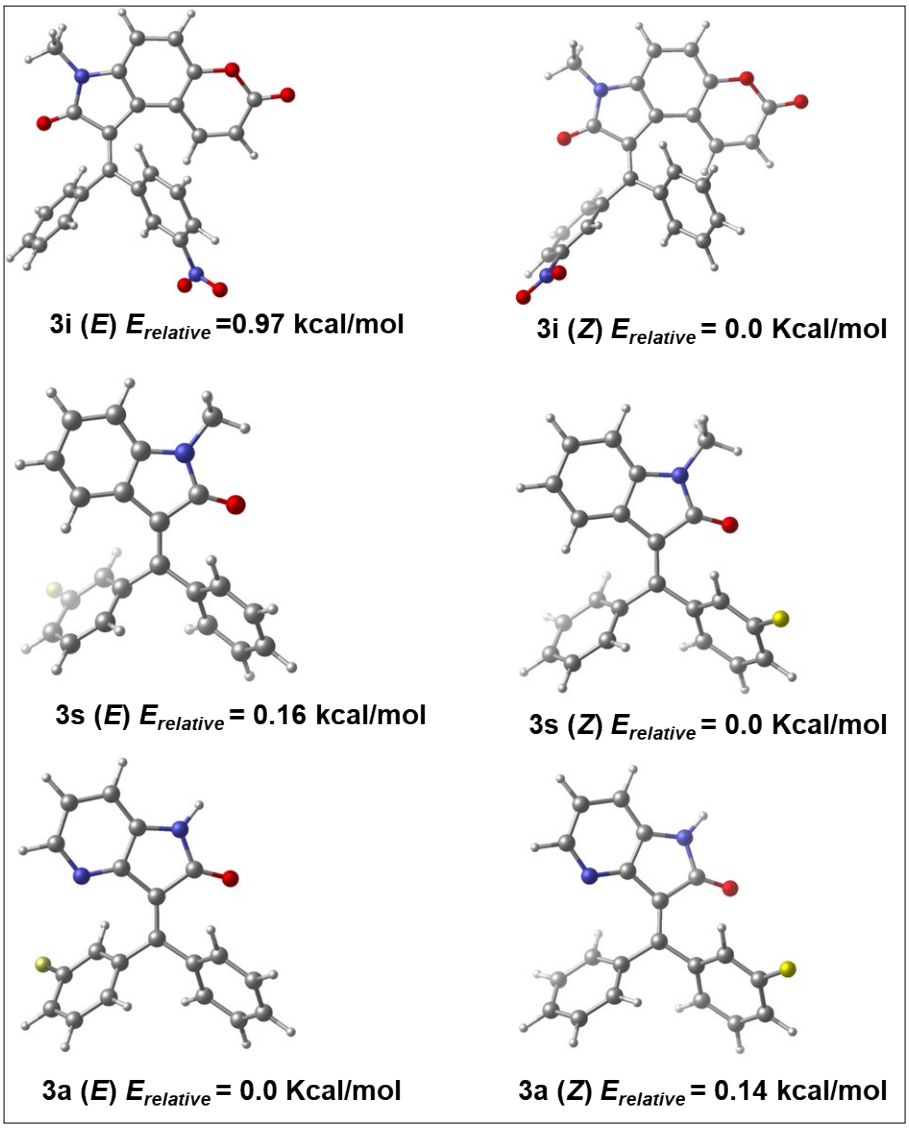


Figure S39. Optimized geometries and relative stabilities of coumarin-fused lactam derivative (3i), benzene-fused lactam derivative (3s) and pyridine-fused lactam derivative (3a).

10) EPR Analysis:

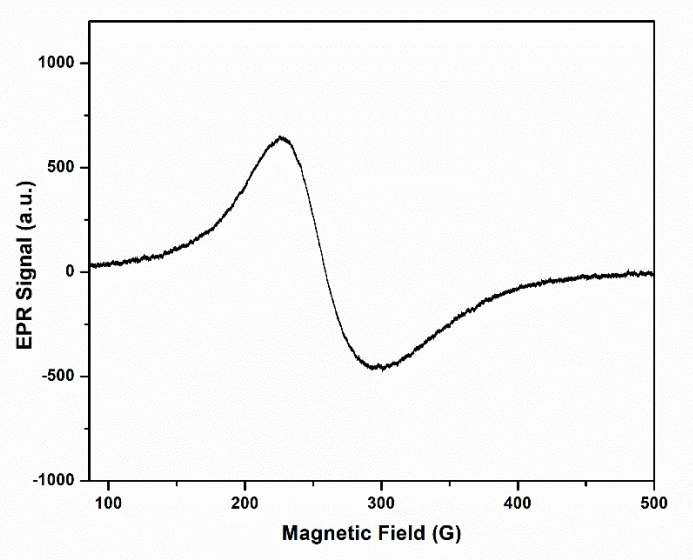


Figure S40. Experimental X-band continuous-wave EPR spectrum recorded from the reaction mixture. Frequency = 9.447 GHz, microwave power = 0.998 mW, T = 298 K, modulation amplitude = 4 G.

11) References:

1. C. Adamo and V. Barone, *J. Chem. Phys.*, **1999**, *110*, 6158.
2. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, **2010**, *132*, 154104.
3. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297.
4. A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, **1993**, *2*, 799.
5. M. J. Frisch *et al.*, *Gaussian 16*, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.