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Electronic Supplementary Information (ESI)

One-pot synthesis of fluorescent 2,4-dialkenylindoles by rhodium-catalyzed dual C-H functionalization

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General Information and Procedure

1. General information

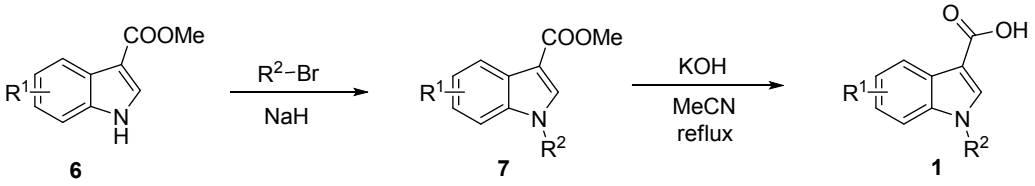
All commercial materials were used as received unless otherwise noted. Substutited Indoles were purchased from Energe® and $[Cp^*RhCl_2]_2$ from J&K®. $AgSbF_6$ from Strem®, acrylic esters and stryenes were purchased without any further purification. Starting materials **1b-1h** were synthesized according to literature procedures with some modification. ^1H NMR spectra were recorded at 400 MHz and 500 MHz NMR spectrometers using TMS as an internal standard, ^{13}C NMR spectra were recorded at 100 MHz and 125 MHz NMR spectrometers using TMS as an internal standard, and were fully decoupled by broad band proton decoupling. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonances (br). High-resolution mass spectra (HRMS) were recorded on an GCT Premier Mass spectrometer (WATERS, USA) using EI-TOF spectra were recorded using a HP6890 gas chromatograph with a HP5973 mass spectrometric detector equipped with an electron ionization source and a single-stage quadrupole. UV-Vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Flash column chromatography was performed employing 300-400 mesh silica gel. All reactions were carried out in oven-dried Schlenk tubes under a N_2 atmosphere. CH_2Cl_2 dried by distillation over CaH_2.

Luminescence spectra were recorded on fluorescence spectrophotometer at room temperature (25 °C) using the same solutions (CH_2Cl_2) as those for the UV-Vis determination. The fluorescence quantum yield gives the efficiency of the fluorescence process, and the popular method to calculate it is to compare the fluorescence intensities (integrated areas) of a standard sample and the unknown one using the following equation.[1] Here Φ_s is the luminescence quantum yield of the unknown sample, Φ_{std} is the luminescence quantum yield of the standard substance, D is the wavelength-integrated area of the emission spectrum, and A is the absorbance value at the excitation wavelength. The n_s and n_{std} terms represent the refractive

indices of the corresponding solvents (pure solvents were assumed). We use norharmane in its 0.1 M H_2SO_4 aqua solution as a standard sample (Φ_{std} = 0.58, n_{std} = 1.33),[2] and thiazole-containing compounds were dissolved in methanol (n_s = 1.42).

$$\Phi_s = \Phi_{std}\left(\frac{D_s}{D_{std}}\right)\left(\frac{A_{std}}{A_s}\right)\left(\frac{n_s}{n_{std}}\right)^2 \qquad \text{Eq. (1)}$$

2. General procedure for the preparation of indole-3-carboxylic acids

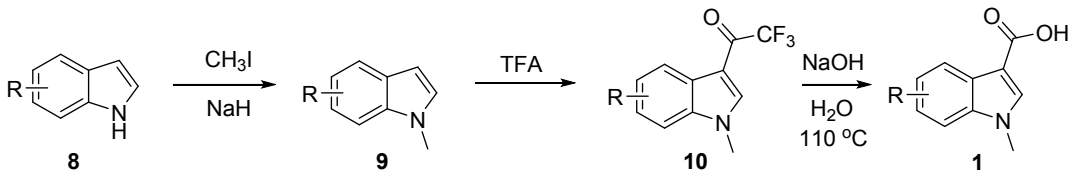


All *N*-alkyled indole-3-carboxylic acids were prepared according to literature procedures:

N-alkylation of methyl indole-3-carboxylates were done according to the literature procedure.[3] To a solution of methyl indole-3-carboxylate **6** (10 mmol) in THF (30 mL) at 0 °C was added NaH (0.60 g, 60 % dispersion in mineral oil, 15 mmol). the heterogeneous mixture was stirred at 0 °C for 15 minutes and 1 h at room temperature. The mixture was then cooled to 0 °C, treated with bromoalkane (14 mmol), and allow to warm to room temperature. After 30 minutes, the reaction mixture was cooled to 0 °C, quenched with saturated NH_4Cl (40 mL), and extracted with ether (3 x 50 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 5:1) to provide indole **7** as a colorless oil.

A 50 mL round bottom flask was charged with *N*-alkyled indole-3-carboxylic acid **7** (5.0 mmol), KOH (5.0 equiv), acetonitrile (30 mL), and a magnetic stirring bar. The reaction mixture was refluxed for 4 h and then cooled to room temperature. and H_2O (10 mL) was added. The layers were separated, and the organic layer was extracted with 1 M aqueous NaOH (10 mL). The combined aqueous phases were acidified to pH 1 with 12 M aqueous HCl, then the solution has been turned into suspension. the solid were filtered from this suspension. The solid was dried to afford the

corresponding product **1**.



All the 1-methylindole-3-carboxylic acids were prepared according to literature procedures:

Methylation of indoles were done according to the literature procedure.[4] To a solution of indole (10 mmol) in THF (30 mL) at 0 °C was added NaH (0.60 g, 60 % dispersion in mineral oil, 15 mmol). the heterogeneous mixture was stirred at 0 °C for 15 minutes and 1 h at room temperature. The mixture was then cooled to 0 °C, treated with iodomethane (14 mmol), and allow to warm to room temperature. After 30 minutes, the reaction mixture was cooled to 0 °C, quenched with saturated NH_4Cl (40 mL), and extracted with ether (3 x 50 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 10:1) to provide indole **9** as a colorless oil.

Typical procedure for synthesis of trifluoromethyl indol-3-yl ketones **9**.[5] Indoles **7**(0.2 mmol) and trifluoroacetic acid (3 equiv) were refluxed in a 100 °C oil bath in 2 mL of DCE in an air atmosphere, and the progress of the reaction was monitored by TLC. After completion of the reaction, as determined by TLC, the reaction mixture was cooled to room temperature. Water (2 x 5 mL) was added, the product was extracted with ethyl acetate (20 mL), the organic layers were washed with saturated brine, and the solvent was removed on a rotary evaporator. The product was purified by silica gel chromatography (petroleum ether/EtOAc 5/1) to afford the corresponding products **10**.

A 100 mL round bottom flask was charged with 2,2,2-trifluoro-1-(1-methylindol-3-yl)ethan-1-one (1.135 g, 5.0 mmol), NaOH (5 M, 30.0 mL), methanol (10 mL), and a magnetic stirring bar. The reaction mixture was refluxed for 12 h and then cooled to room temperature, and H_2O (10 mL) was added. The layers were separated, and the

organic layer was extracted with 1 M aqueous NaOH (10 mL). The combined aqueous phases were acidified to pH 1 with 12 M aqueous HCl, then the solution has been turned into suspension. the solid were filtered from this suspension. The solid was dried to afford the corresponding product **1**.

Reference

[1] J. N. Demasa and G. A.Crosby, *J. Phys. Chem.,* 1971, **75**, 991.

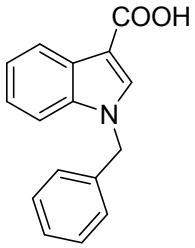
[2] A. Pardo, D. Reyman, J.M.L. Poyato and F. Medina, *J. Lumin.,* 1992, **51**, 269.

[3] S. A. Everett, M. A. Naylor, M. R. L. Stratford, K. B. Patel, E. Ford, A. Mortensen, A. C. Ferguson, B. Vojnovic and P. Wardmana, *J. Chem. Soc., Perkin Trans. 2* 2001, 1989.

[4] E. M. Ferreira and B. M. Stoltz, *J. Am. Chem. Soc.,* 2003, **125**, 9578.

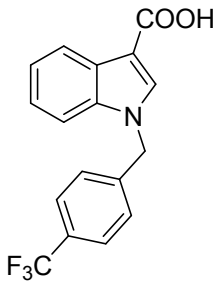
[5] S. Yao, Z. Ren, Y. Wang, Z. Guan, *J. Org. Chem.,* 2016, **81**, 4226.

3. Analytical data for starting indole-3-carboxylic acids



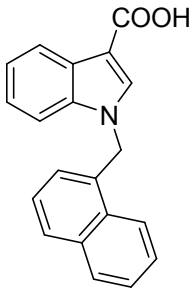
1-benzyl-1H-indole-3-carboxylic acid(1b)

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.058(s, 1H), 8.235(s, 1H), 8.028-8.050(m, 1H), 7.521-7.543 (m, 1H), 7.310-7.346 (m, 2H), 7.247-7.284 (m, 3H), 7.178-7.199 (m, 2H), 5.500(s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 165.571, 137.174, 136.258, 135.496, 128.636, 127.624, 127.269, 126.625, 122.314, 121.372, 120.859, 111.082, 106.852, 49.489. **HRMS** (EI-TOF) calcd for $C_{16}H_{13}NO_2$ (M^+): 251.0946, found: 251.0949.



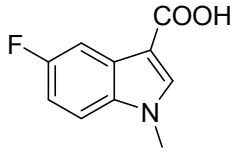
1-(4-(trifluoromethyl)benzyl)-1H-indole-3-carboxylic acid (1c)

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.165(s, 1H), 8.320(s, 1H), 8.086(dd, J_1 = 3.2 Hz, J_2 = 10.4 Hz, 1H), 7.706(d, J = 8.0 Hz, 2H), 7.518(dd, J_1 = 2.8 Hz, J_2 = 6.0 Hz, 1H), 7.454(d, J = 8.4 Hz, 2H), 7.215(dd, J_1 = 2.8 Hz, J_2 = 6.0 Hz, 2H), 5.651(s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 165.554, 142.008, 136.222, 135.634, 128.371, 128.043, 127.189, 126.639, 125.574-125.456 (dd, $J_{C\text{-}F}$ = 3.5 Hz), 122.749, 122.500, 121.502, 120.967, 110.948, 107.229, 48.930. **HRMS** (ESI-TOF) calcd for $C_{17}H_{12}F_3NO_2$ ([M-H^+]): 318.0742, found: 318.0739.



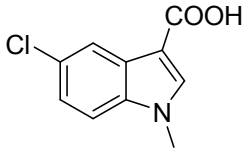
1-(naphthalen-1-ylmethyl)-1H-indole-3-carboxylic acid (1d)

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.089(s, 1H), 8.317(s, 1H), 7.841- 7.888(m, 5H), 7.485-7.508 (m, 3H), 7.417(d, J = 8.4Hz, 1H), 7.186 (dd, J_1 = 3.2 Hz, J_2 = 6.0 Hz, 2H), 5.674(s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 165.610,136.321, 135.615, 134.703, 132.753, 132.326, 128.393, 127.676, 127.562, 126.687, 126.445, 126.140, 125.996, 125.949, 125.349, 122.357, 121.407, 120.908, 111.119, 106.937, 49.751. **HRMS** (ESI-TOF) calcd for $C_{20}H_{15}NO_2$ ([M+H$^+$]): 302.1181, found: 302.1181.



5-fluoro-1-methyl-1H-indole-3-carboxylic acid (1e)

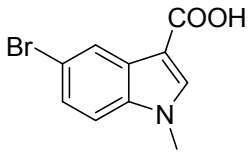
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.079(s, 1H), 8.113(s, 1H), 7.679(dd, J_1 = 2.4 Hz, J_2 = 10.0 Hz, 1H), 7.558 (dd, J_1 = 4.4Hz, J_2 = 8.8 Hz, 1H), 7.091-7.143(m, 1H), 3.864(s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 165.327, 159.535, 157.207, 137.495, 133.701, 127.013, 126.900 (d, $J_{C\text{-}F}$ = 11.3 Hz), 112.581, 112.324 (d, $J_{C\text{-}F}$ = 25.7 Hz), 110.457, 110.191 (d, $J_{C\text{-}F}$ = 26.6 Hz), 106.218, 105.535, 105.290 (d, $J_{C\text{-}F}$ = 24.5 Hz), 33.244. **HRMS** (EI-TOF) calcd for $C_{10}H_8FNO_2$ (M$^+$): 206.0739, found: 206.0743.



5-chloro-1-methyl-1H-indole-3-carboxylic acid (1f)

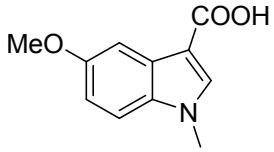
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.186(s, 1H), 8.119(s, 1H), 7.993(s, 1H), 7.569(dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 7.273(d, J = 8.8 Hz, 1H), 3.861(s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 165.213, 137.378, 135.530, 127.451, 126.186,

122.144, 119.703, 112.419, 105.884, 33.187. **HRMS** (EI-TOF) calcd for $C_{10}H_8ClNO_2$ (M^+): 209.0244, found: 209.0250.



5-bromo-1-methyl-1H-indole-3-carboxylic acid (1g)

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.216(s, 1H), 8.143(s, 1H), 8.103(s, 1H), 7.532(d, J = 8.4 Hz, 1H), 7.389(dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), , 3.857(s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 165.198, 137.226, 135.784, 128.047, 124.689, 122.739, 114.239, 112.886, 105.791, 33.182. **HRMS** (EI-TOF) calcd for $C_{10}H_8BrNO_2$ (M^+): 252.9738, found: 252.9748.

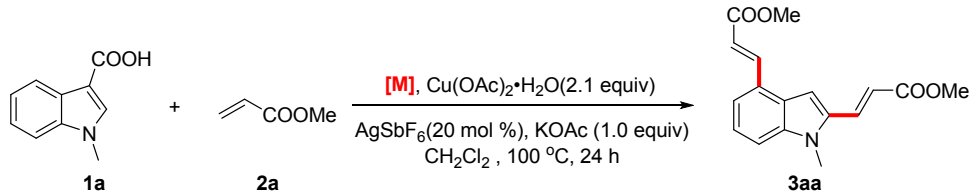


5-methoxy-1-methyl-1H-indole-3-carboxylic acid (1h)

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.918(s, 1H), 8.479(s, 1H), 7.702(s, 1H), 7.560(d, J = 8.4Hz, 1H), 7.032(d, J = 7.6Hz, 1H), 3.938(s, 3H), 3.839(s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 173.205, 156.936, 140.284, 132.173, 127.267, 113.685, 112.439, 107.402, 103.172, 55.346, 33.787. **HRMS** (ESI-TOF) calcd for $C_{11}H_{11}NO_3$ ([M+H$^+$]): 206.0817, found: 206.0828.

4. Optimization of reaction conditions with acrylates

Screening of Catalyst

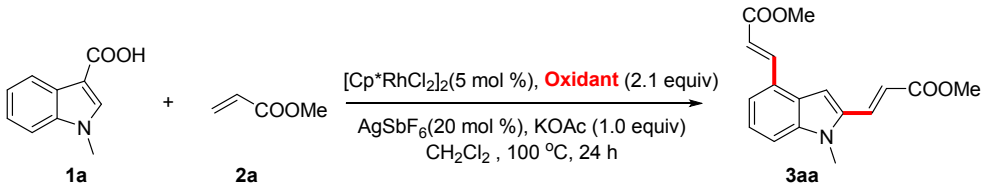


Entry[a]	[M]	Yield (%)[b]
1	--	N.R.

2	$[Cp^*RhCl_2]_2$	97
3	$RhCl_3$	5
4	$Rh(OAc)_2$	trace
5	Ru(p-cyeme)Cl_2	trace
6[c]	$[Cp^*Co(CO)]I_2$	N.R.

[a]Reactions conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), $Cu(OAc)_2•H_2O$ (0.21 mmol), $AgSbF_6$ (0.02 mmol), CH_2Cl_2 (2.0 mL), 24 h, N_2, 100 °C. [b]Isolated yield of **3aa** by flash column chromatography. [c]10 mol % $[Cp^*Co(CO)]I_2$ was used as catalyst. Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl.

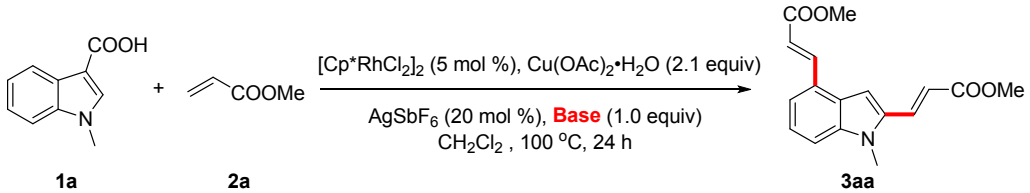
Screening of Oxidant



Entry[a]	Oxidant	Yield (%)[b]
1	$Cu(OAc)_2$	67
2	$Cu(OAc)_2·H_2O$	97
3[c]	$Cu(OAc)_2·H_2O$	42
4	$Cu_2(OH)_2CO_3$	85
5[d]	AgOAc	21
6[d]	Ag_2CO_3	trace

[a]Reactions conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), oxidant (0.21 mmol), $AgSbF_6$ (0.02 mmol), CH_2Cl_2 (2.0 mL), 24 h, N_2, 100 °C. [b]Isolated yield of **3aa** by flash column chromatography. [c]20 mol % of $Cu(OAc)_2·H_2O$ was used under air atmosphere. [d]3.0 equiv oxidant was used. Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl.

Screening of Base

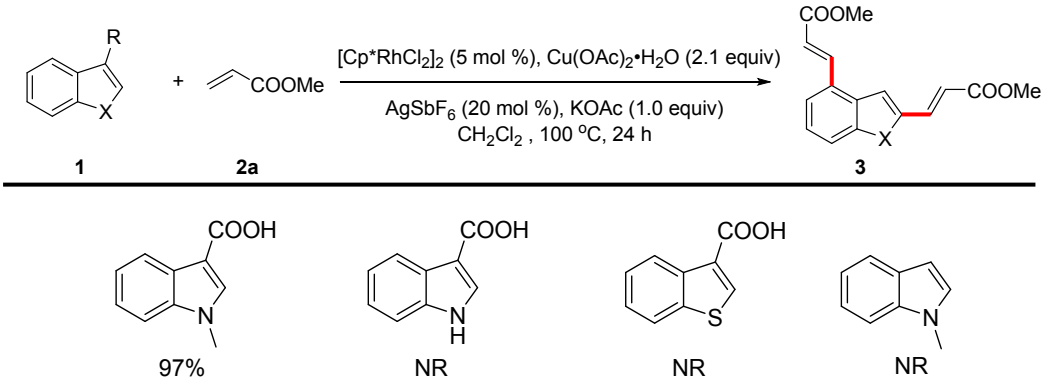


Entry[a]	Base	Yield (%)[b]
1	NaOAc	26
2	KOAc	97
3	Na_2CO_3	trace

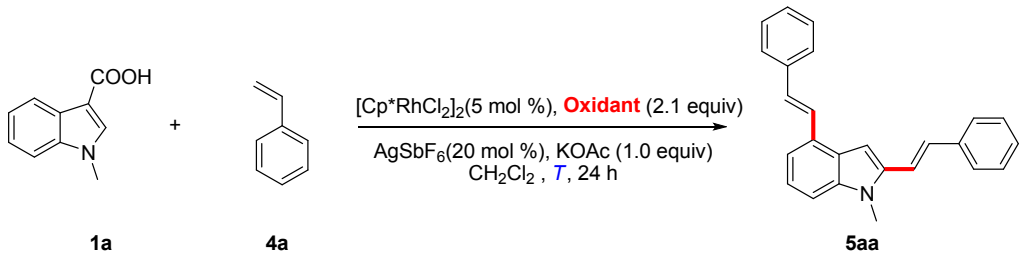
4	K_2CO_3	89
5	K_3PO_4	85
6	K_2HPO_4	90

[a]Reactions conditions: **1a** (0.1 mmol), **4a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), oxidant (0.21 mmol), $AgSbF_6$ (0.02 mmol), CH_2Cl_2 (2.0 mL), 24 h, N_2, 100 °C. [b]Isolated yield of **3aa** by flash column chromatography. Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl.

Screening of Substrates



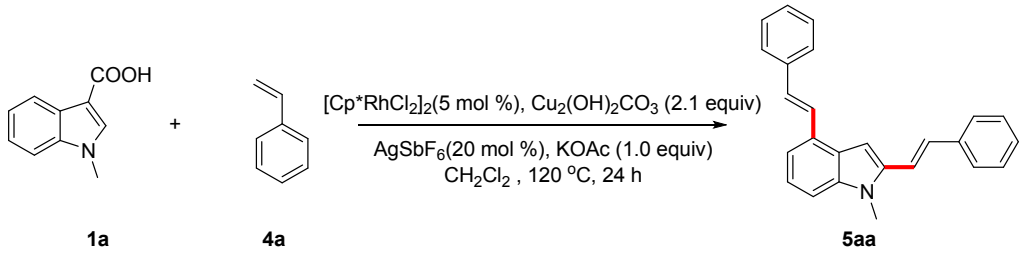
5. Optimization of reaction conditions with styrenes



Entry[a]	Oxidant	T (°C)	Yield (%)[b]
1	$Cu(OAc)_2 \cdot H_2O$	100	32
2	$Cu(OAc)_2 \cdot H_2O$	120	56
3	$Cu_2(OH)_2CO_3$	120	77
4	$Cu_2(OH)_2CO_3$	130	43
5	Ag_2CO_3	120	trace

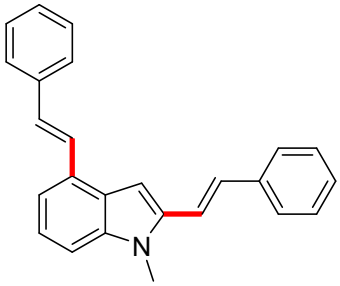
[a]Reactions conditions: **1a** (0.1 mmol), **4a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), Oxidant (0.21 mmol), $AgSbF_6$ (0.02 mmol), CH_2Cl_2 (2.0 mL), 24 h, N_2, T. [b]Isolated yield of **5aa** by flash column chromatography. Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl.

6. Control Experiment



1a **4a** **5aa**

GC-MS



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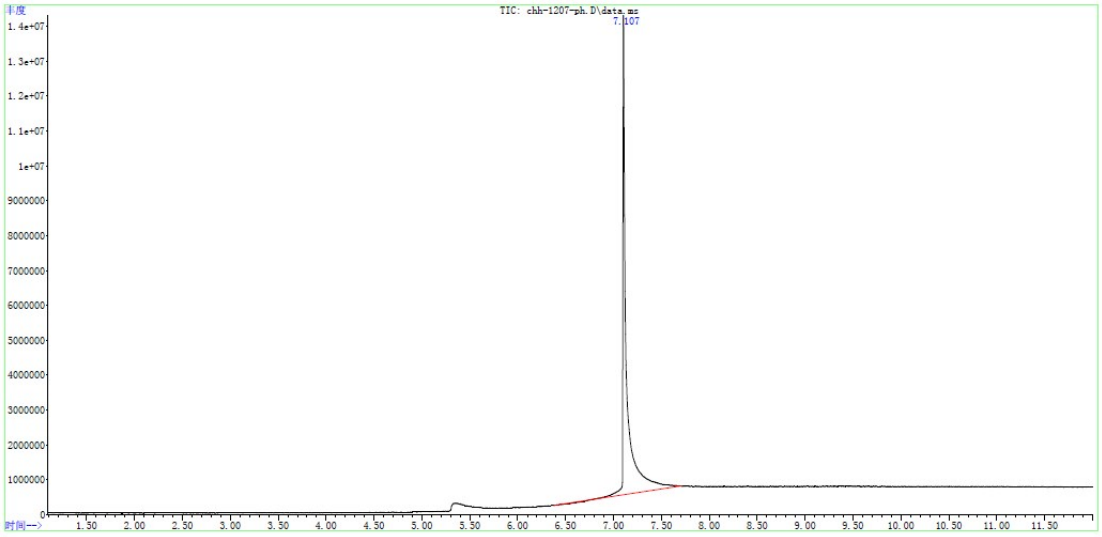
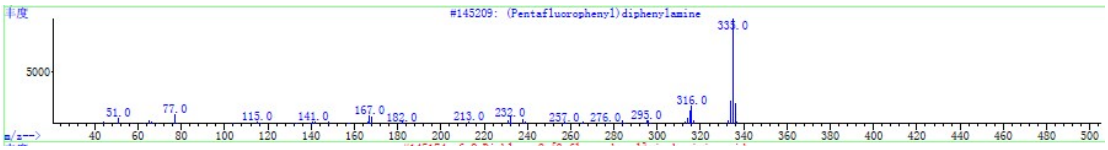
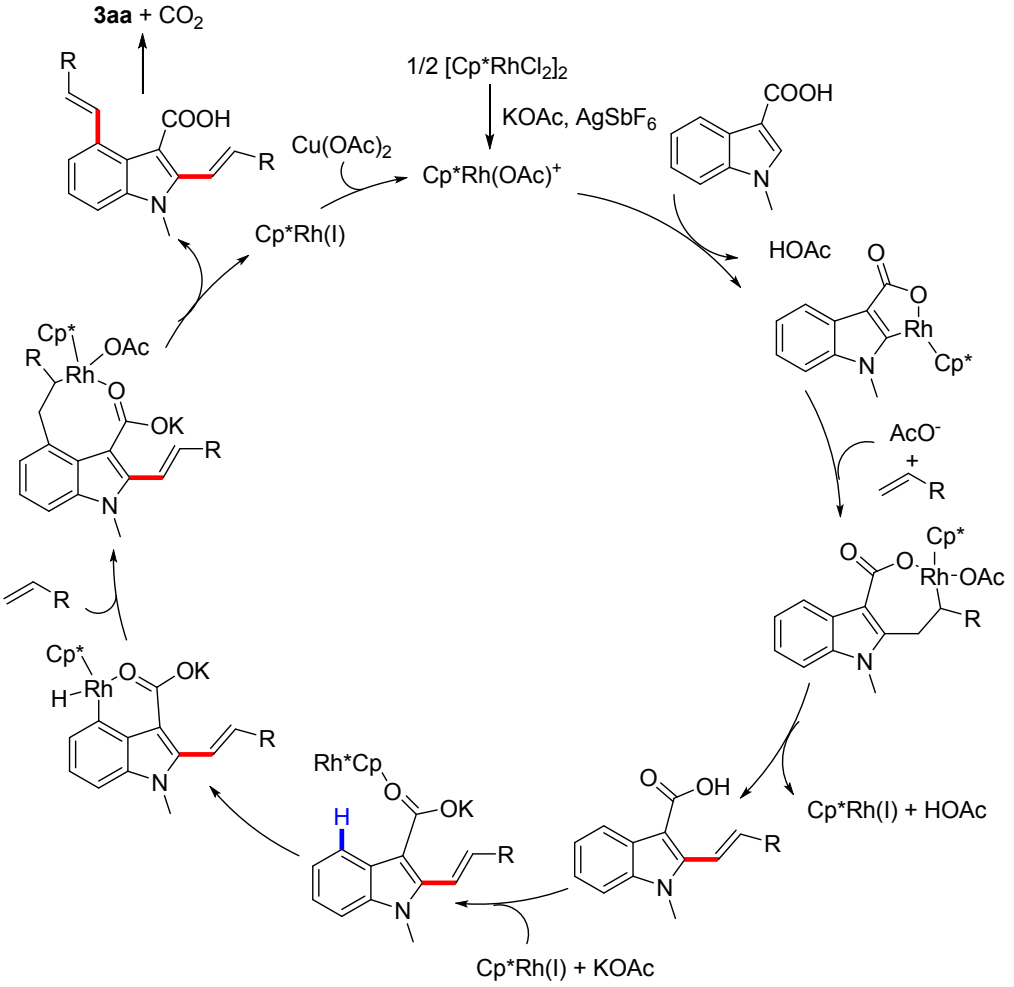




7. Plausible Mechanism for This Reaction



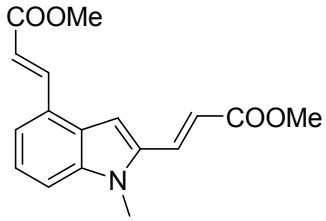
8. General procedure for rhodium-catalyzed indoles C-H bond dialkenylation.

General procedure for rhodium-catalyzed indoles C-H bond dialkenylation with acrylates: A mixture of indole-3-carboxylic acid (**1**, 0.1 mmol), acrylate (**2**, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (41.9 mg, 2.1 equiv), $AgSbF_6$ (6.9 mg, 20 mol %), KOAc (9.8 mg, 1.0 equiv) and dichloromethane (2.0 mL) added to a 25 mL sealed tube. The tube was stirred at 100 °C for 24 h under N_2 atmosphere. Then, the reaction mixture was cooled to room temperature. H_2O (10.0 mL) was added to the reaction tube. The mixture was extracted with ethyl acetate (3 x 15 mL), and the organic phase was dried over Na_2SO_4 and was concentrated in vacuo.

Then the mixture was subjected to column chromatography on silica gel (hexane/ethyl acetate = 5:1) to give the desired product (**3**).

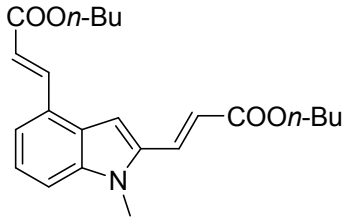
General procedure for rhodium-catalyzed indoles C-H bond divinylation with styrenes: A mixture of indole-3-carboxylic acid (**1**, 0.1 mmol), styrene (**2**, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $Cu_2(OH)_2CO_3$ (46.4 mg, 2.1 equiv), $AgSbF_6$ (6.9 mg, 20 mol %), KOAc (9.8 mg, 1.0 equiv) and dichloromethane (2.0 mL) added to a 25 mL sealed tube. The tube was stirred at 120 °C for 24 h under N_2 atmosphere. Then, the reaction mixture was cooled to room temperature. H_2O (10.0 mL) was added to the reaction tube. The mixture was extracted with ethyl acetate (3 x 15 mL), and the organic phase was dried over Na_2SO_4 and was concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the desired product (**5**).

9. Analytic Data of Products



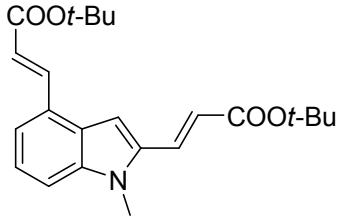
(2E,2'E)-dimethyl 3,3'-(1-methyl-1H-indole-2,4-diyl)diacrylate (3aa)

R_f 0.51 (hexane/EtOAc = 5/1). Yellow-green solid. Isolated yield: 29.0 mg, 97%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.042(d, *J* = 16 Hz, 1H), 7.761-7.805(m, 1H), 7.323-7.359(m, 2H), 7.259(dd, J_1 = 4.0 Hz, J_2 = 7.2 Hz, 1H), 7.204(s, 1H), 6.531-6.619(m, 2H), 3.839(d, *J*= 3.2 Hz, 6H), 3.812(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.760, 167.268, 143.032, 139.410, 136.065, 132.255, 127.075, 126.521, 123.462, 121.054, 119.032, 118.334, 111.659, 101.923, 51.904, 51.738, 30.222. **HRMS** (ESI-TOF) calcd for $C_{17}H_{17}NO_4$ ($[M+H^+]$): 300.1236, found: 300.1238.



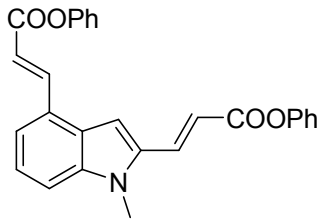
(2E,2'E)-dibutyl 3,3'-(1-methyl-1H-indole-2,4-diyl)diacrylate (3ab)

R_f 0.45 (hexane/EtOAc = 5/1). Yellow-green solid. Isolated yield: 28.7 mg, 75%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.039(d, J = 16.0 Hz, 1H), 7.897(d, J = 15.6 Hz, 1H), 7.356 (dd, J_1 = 3.2 Hz, J_2 = 7.6 Hz, 2H), 7.264 (dd, J_1 = 7.2 Hz, J_2 = 8.0 Hz, 1H), 7.233 (s, 1H), 6.595 (dd, J_1 = 11.6 Hz, J_2 = 16 Hz, 2H), 4.226-4.268 (m, 4H), 3.846 (s, 3H), 1.680-1.767(m, 4H), 1.415-1.508 (m, 4H), 0.935-1.008(m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.461, 166.977, 142.866, 139.438, 136.178, 132.043, 127.210, 126.466, 123.416, 121.229, 119.588, 118.877, 111.569, 101.977, 64.670, 64.469, 30.827, 30.794, 30.794, 19.259, 19.238, 13.806, 13.801. **HRMS** (ESI-TOF) calcd for $C_{23}H_{29}NO_4$ ([M+H$^+$]): 384.2175, found: 384.2179.



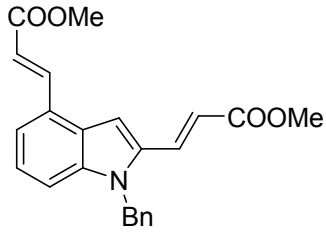
(2E,2'E)-tert-butyl 3,3'-(1-methyl-1H-indole-2,4-diyl)diacrylate (3ac)

R_f 0.46 (hexane/EtOAc = 5/1). Yellow-green solid. Isolated yield: 31.7 mg, 83%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.925-7.978(m, 1H), 7.713(d, J = 16 Hz, 1H),7.318-7.359(m, 2H), 7.243(dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H), 7.197(s, 1H), 6.489-6.565(m, 2H), 3.781-3.827(m, 6H), 1.572(s, 9H), 1.560(s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.742, 166.225, 141.953, 139.348, 136.252, 131.158, 127.342, 126.439, 123.229, 121.474, 121.062, 120.758, 111.278, 101.708, 80.863, 80.471, 30.189, 28.284, 28.234, 28.142. **HRMS** (ESI-TOF) calcd for $C_{23}H_{29}NO_4$ ([M+H$^+$]): 384.2175, found: 384.2179.



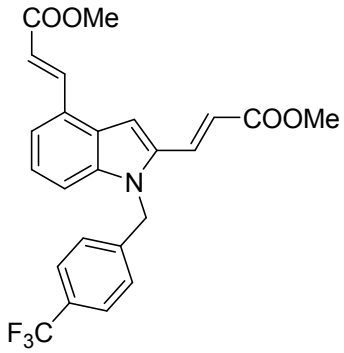
(2E,2'E)-diphenyl 3,3'-(1-methyl-1H-indole-2,4-diyl)diacrylate (3ad)

R_f 0.42 (hexane/EtOAc = 5/1). Yellow-green solid. Isolated yield: 39.0 mg, 92%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.164 (d, *J* = 16.4 Hz, 1H), 7.889 (d, *J* = 16.0 Hz, 1H), 7.316-7.377 (m, 6H), 7.283 (s, 1H), 7.246 (t, *J* = 8.0 Hz, 1H), 7.158-7.202 (m, 2H), 7.101-7.149 (m, 4H), 6.721 (t, *J* = 16.4 Hz, 2H), 3.796 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.732, 165.272, 150.930, 150.808, 144.755, 139.690, 136.065, 133.771, 129.578, 129.502, 129.409, 127.078, 126.597, 125.889, 125.792, 123.831, 121.844, 121.743, 121.614, 121.526, 118.534, 117.959, 112.194, 102.704, 30.302. **HRMS** (ESI-TOF) calcd for $C_{27}H_{21}NO_4$ ([M+H$^+$]): 424.1549, found: 424.1538.



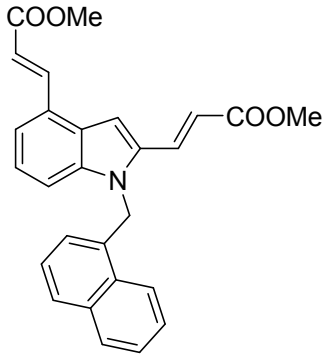
(2E,2'E)-dimethyl 3,3'-(1-benzyl-1H-indole-2,4-diyl)diacrylate (3ba)

R_f 0.38 (hexane/EtOAc = 5/1). Yellow-green solid. Isolated yield: 28.1 mg, 75%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.086 (d, *J* = 16.0 Hz, 1H), 7.731 (d, *J* = 15.6 Hz, 1H), 7.373 (d, *J* = 7.2 Hz, 1H), 7.279-7.305 (m, 3H), 7.193-7.260 (m, 3H), 6.993 (d, *J* = 6.4 Hz, 2H), 6.628 (d, *J* = 16.0 Hz, 1H), 6.546 (d, *J* = 15.6 Hz, 1H), 5.467 (s, 2H), 3.850 (s, 3H), 3.781(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.727, 167.086, 142.945, 139.206, 136.775, 136.050, 132.102, 128.995, 127.801, 127.279, 126.782, 125.913, 123.778, 121.256, 119.554, 118.521, 112.073, 102.419, 51.850, 51.762, 46.953. **HRMS** (EI-TOF) calcd for $C_{27}H_{23}NO_4$ (M^+): 375.1471, found: 375.1476.



(2E,2'E)-dimethyl-3,3'-(1-(4-(trifluoromethyl)benzyl)-1H-indole-2,4-diyl) Diacrylate (3ca)

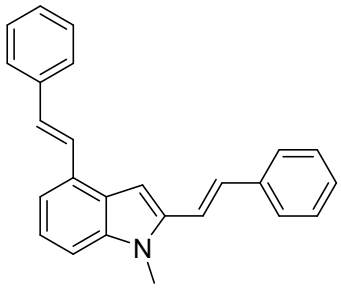
R_f 0.38 (hexane/EtOAc = 5/1). Yellow solid. Isolated yield: 31.9 mg, 72%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.093(d, *J* = 16.0 Hz, 1H), 7.680(d, *J* = 15.6 Hz, 1H), 7.343 (d, *J* = 8.0 Hz, 2H), 7.402 (dd, J_1 = 3.2 Hz, J_2 = 4.8 Hz, 1H), 7.338 (s, 1H), 7.261-7.235 (m, 2H), 7.089 (d, *J* = 8.0 Hz, 2H), 6.639(d, *J* = 16.0 Hz, 1H), 6.556(d, *J* = 16.0 Hz, 1H), 5.531 (s, 2H), 3.858 (s, 3H), 3.789 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.659, 166.998, 142.697, 140.759, 139.058, 135.839, 131.629, 127.479, 126.874, 126.199, 126.168, 126.107, 126.063, 126.029, 125.994, 125.222, 124.063, 124.370, 119.884, 118.768, 111.716, 102.806, 51.922, 51.797, 29.727. **HRMS** (ESI-TOF) calcd for $C_{24}H_{20}F_3NO_4$ ([M+H$^+$]): 444.1423, found: 444.1410.



(2E,2'E)-dimethyl 3,3'-(1-(naphthalen-1-ylmethyl)-1H-indole-2,4-diyl) diacrylate (3da)

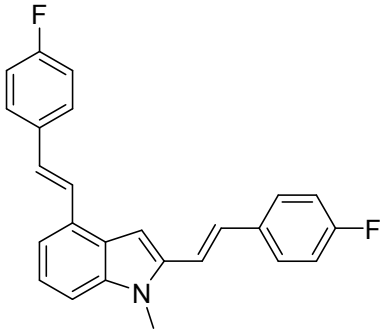
R_f 0.36 (hexane/EtOAc = 5/1). Yellow-green solid. Isolated yield: 30.6 mg, 72%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.111 (d, *J* = 16.4 Hz, 1H), 7.753-7.793(m, 3H), 7.666-7.689 (m, 1H), 7.422-7.444 (m, 1H), 7.384 (d, *J* = 7.2 Hz, 1H), 7.312-7.346 (m, 3H), 7.204-7.252 (m, 1H), 7.178 (dd, J_1 = 6.0 Hz, J_2 = 8.4 Hz, 1H), 6.649 (d, *J* = 16.0 Hz,

1H), 6.557 (d, *J* = 16.0 Hz, 1H), 5.617 (s, 2H), 3.857 (s, 3H), 3.754(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.749, 167.059, 142.966, 139.301, 136.132, 134.256, 133.354, 132.840, 132.110, 128.985, 127.864, 127.727, 127.310, 126.852, 126.490, 126.161, 124.639, 123.833, 121.301, 119.621, 118.543, 112.125, 102.566, 51.834, 51.775, 47.189. **HRMS** (EI-TOF) calcd for $C_{27}H_{23}NO_4$ (M^+): 425.1627, found: 425.1628.



1-methyl-2,4-distyryl-1H-indole (5aa)

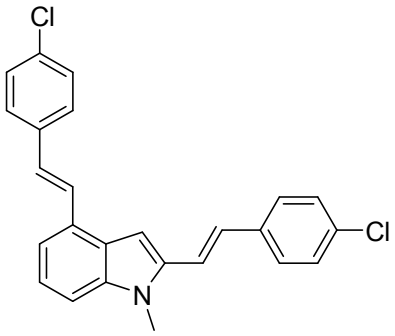
R_f 0.52 (hexane/EtOAc = 20/1). Red solid. Isolated yield: 25.8 mg, 77%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.510 (d, *J* = 5.6 Hz, 2H), 7.435-7.475(m, 3H), 7.253-7.3410 (m, 5H), 7.218 (d, *J* = 10.0 Hz, 1H), 7.180 (d, *J* = 7.2 Hz, 2H), 7.085-7.130 (m, 3H), 7.052 (d, *J* = 16.0 Hz, 1H), 7.003(s, 1H), 3.671 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.814, 138.750, 138.073, 137.162, 131.226, 129.349, 129.204, 128.741, 127.985, 127.429, 127.241, 126.608, 126.564, 126.542, 122.050, 117.612, 116.922, 108.587, 97.767, 30.070. **HRMS** (EI-TOF) calcd for $C_{25}H_{21}N$ (M^+): 335.1674, found: 335.1674.



2,4-bis(4-fluorostyryl)-1-methyl-1H-indole (5ab)

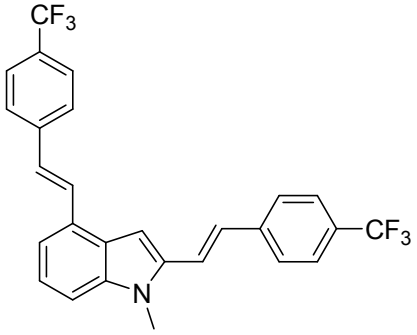
R_f 0.50 (hexane/EtOAc = 20/1). Brown solid. Isolated yield: 26.3 mg, 71%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.535-7.570 (m, 2H), 7.485-7.520 (m, 2H), 7.440 (d, *J* = 16.0

Hz, 1H), 7.331 (dd, J_1 = 3.2 Hz, J_2 = 5.6 Hz, 1H), 7.183-7.245 (m, 4H), 7.052-7.091 (m, 6H), 3.806 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.764, 163.484, 161.300, 161.026, 138.702, 138.664, 134.211, 134.171, 133.309, 133.289, 130.034, 129.175, 128.064, 127.979, 127.895, 126.970, 126.950, 126.466, 122.057, 117.570, 116.647, 116.637, 115.931, 115.711, 115.504, 108.580, 97.591, 30.077. **HRMS** (EI-TOF) calcd for $C_{25}H_{19}F_2N$ (M^+): 371.1486, found: 371.1490.



2,4-bis(4-chlorostyryl)-1-methyl-1H-indole(5ac)

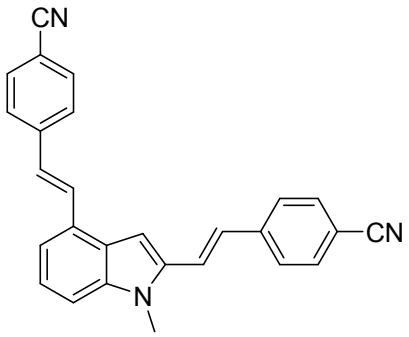
R_f 0.43 (hexane/EtOAc = 20/1). Orange solid. Isolated yield: 33.4 mg, 83%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.525(d, J = 2.0 Hz, 2H), 7.506-7.516(m, 1H), 7.448-7.475 (m, 1H), 7.331-7.358 (m, 5H), 7.254 (d, J = 1.6 Hz, 1H), 7.211-7.227 (m, 3H), 7.167 (d, J = 6.8 Hz, 2H), 7.084 (s, 1H), 3.820 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.778, 138.536, 136.487, 135.571, 135.551, 132.907, 129.877, 129.008, 128.838, 127.899, 127.741, 127.642, 126.477, 122.192, 117.800, 117.361, 108.809, 97.910, 30.107. **HRMS** (EI-TOF) calcd for $C_{25}H_{19}Cl_2N$ (M^+): 403.0895, found: 403.0890.



1-methyl-2,4-bis(4-(trifluoromethyl)styryl)-1H-indole (5ad)

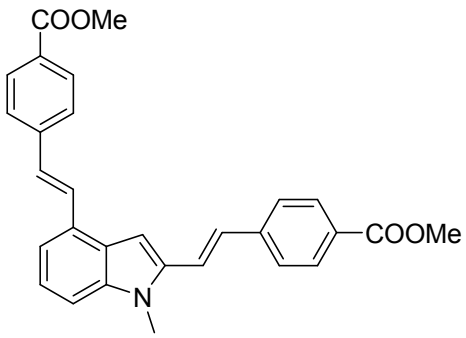
R_f 0.46 (hexane/EtOAc = 20/1). Brown solid. Isolated yield: 37.6 mg, 67%. **^{1}H NMR**

(400 MHz, $CDCl_3$): δ 7.644-7.678 (m, 2H), 7.622 (s, 6H), 7.594 (d, J = 8.8 Hz, 1H), 7.367-7.387 (m, 1H), 7.272-7.320 (m, 1H), 7.218-7.255 (m, 4H), 7.139 (s, 1H), 3.828 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.391, 140.439, 138.904, 138.258, 129.546, 128.866, 128.822, 127.717, 126.535, 125.842, 125.807, 125.770, 125.731, 125.673, 125.651, 125.565, 122.460, 119.140, 118.235, 109.291, 98.444, 30.219, 30.134, 29.741, 29.697. **HRMS** (EI-TOF) calcd for $C_{27}H_{19}F_6N$ (M^+): 471.1422, found: 471.1426.



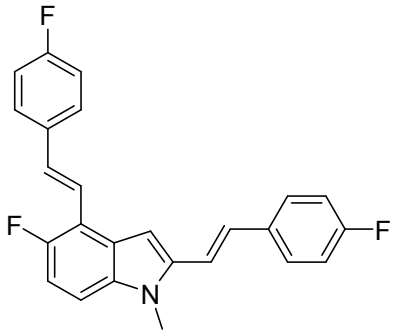
4,4'-(1E,1'E)-2,2'-(1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl)dibenzonitrile (5ae)

R_f 0.32 (hexane/EtOAc = 5/1). Brown solid. Isolated yield: 24.3 mg, 63%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.600 (m, 6H), 7.536-7.557 (m, 2H), 7.321 (d, J = 7.2 Hz, 1H), 7.242-7.259 (m, 3H), 7.189-7.233 (m, 3H), 7.094 (s, 1H), 3.802 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.392, 141.385, 139.304, 138.054, 132.639, 132.523, 130.687, 129.068, 128.602, 127.398, 126.835, 126.808, 126.546, 122.750, 120.184, 119.161, 118.589, 110.900, 110.339, 109.702, 98.888, 29.724. **HRMS** (ESI-TOF) calcd for $C_{27}H_{19}N_3$ ([M+H^+]): 386.1657, found: 386.1667.



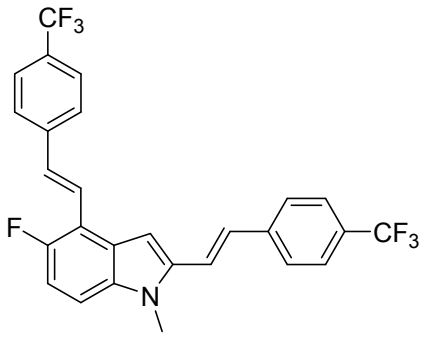
Dimethyl 4,4'-(1E,1'E)-2,2'-(1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl) Dibenzoate(5af)

R_f 0.33 (hexane/EtOAc = 5/1). Brown solid. Isolated yield: 33.9 mg, 75%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.037 (d, *J* = 8.4 Hz, 4H), 7.606-7.646 (m, 5H), 7.384 (d, *J* = 7.2 Hz, 2H), 7.283-7.330 (m, 4H), 7.247-7.265 (m, 1H), 3.925 (s, 6H), 3.817 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.019, 167.798, 136.487, 142.557, 137.225, 130.948, 130.212, 130.109, 130.035, 129.968, 129.540, 129.418, 129.150, 128.884, 128.587, 128.037, 126.964, 126.636, 126.255, 121.742, 111.703, 109.354, 99.510, 52.129, 52.085, 33.065. **HRMS** (ESI-TOF) calcd for $C_{29}H_{25}NO_4$ ([M+H$^+$]): 452.1862, found: 452.1872.



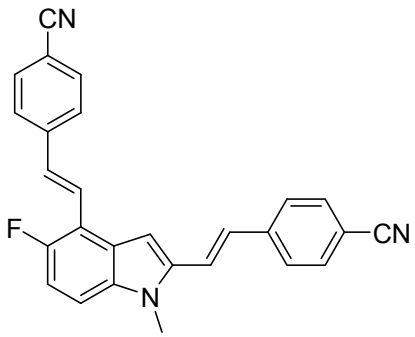
5-fluoro-2,4-bis(4-fluorostyryl)-1-methyl-1H-indole (5eb)

R_f 0.43 (hexane/EtOAc = 20/1). Brown solid. Isolated yield: 23.0 mg, 59%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.544-7.579 (m, 2H), 7.481-7.516 (m, 2H), 7.402 (s, 2H), 7.192 (d, *J* = 16.0 Hz, 1H),, 7.050-7.110 (m, 7H), 6.995 (d, *J* = 6.8 Hz, 1H), 6.930-6.959 (m, 1H), 3.775 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.845, 163.612, 161.382, 161.159, 157.315, 154.935, 139.914, 135.008, 134.374, 134.347, 133.140, 133.110, 131.237, 131.165, 130.941, 130.553, 130.497, 128.864, 128.136, 128.056, 128.033, 127.954, 126.467, 126.412, 121.044, 121.017, 120.999, 116.389, 116.360, 115.954, 115.743, 115.721, 115.608, 114.992, 110.582, 110.317, 108.910, 108.807, 98.332, 98.280, 30.086 **HRMS** (EI-TOF) calcd for $C_{25}H_{18}F_3N$ (M^+): 389.1391, found: 389.1391.



5-fluoro-1-methyl-2,4-bis(4-(trifluoromethyl)styryl)-1H-indole (5ed)

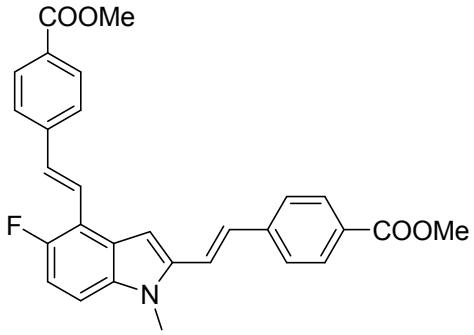
R_f 0.36 (hexane/EtOAc = 20/1). Brown solid. Isolated yield: 22.5 mg, 46%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.694 (d, *J* = 8.0 Hz, 2H), 7.603-7.635 (m, 6H), 7.547-7.576 (m, 1H), 7.446-7.526 (m, 1H),, 7.243-7.258 (m, 2H), 7.162-7.185 (m, 1H), 7.029-7.152 (m, 1H), 6.979-7.007 (m, 1H), 3.835 (s, 3H), 3.835 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.658, 155.260, 147.625, 147.099, 141.580, 140.246, 139.479, 135.215, 130.949, 129.967, 129.874, 129.608, 129.557, 129.409, 129.087, 126.610, 126.581, 126.481, 126.426, 125.829, 125.795, 125.762, 125.654, 125.617, 125.577, 125.491, 124.488, 123.995, 123.615, 122.775, 119.092, 118.897, 114.834, 114.706, 110.826, 109.712, 109.614, 99.134, 99.073, 29.371. **HRMS** (EI-TOF) calcd for $C_{27}H_{18}F_7N$ (M^+): 489.1327, found: 489.1334.



4,4'-(1E,1'E)-2,2'-(5-fluoro-1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl)dibenzonitrile (5ee)

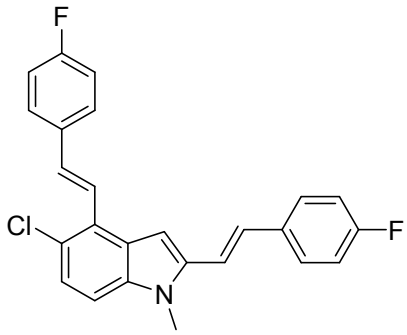
R_f 0.30 (hexane/EtOAc = 5/1). Brown solid. Isolated yield: 16.5 mg, 41%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.666-7.686 (m, 6H), 7.506-7.516(m, 1H), 7.448-7.475 (m, 1H), 7.331-7.358 (m, 5H), 7.254 (d, *J* = 1.6 Hz, 1H), 7.211-7.227 (m, 3H), 7.167 (d, *J* = 6.8 Hz, 2H), 7.084 (s, 1H), 3.820 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.591,

141.196, 139.263, 135.343, 132.655, 132.519, 132.313, 132.018, 130.944, 130.577, 130.499, 129.901, 129.590, 128.855, 126.877, 124.778, 124.755, 119.919, 119.113, 118.869, 111.432, 111.152, 111.093, 99.521, 99.465, 29.719. **HRMS** (EI-TOF) calcd for $C_{27}H_{18}FN_3$ (M^+): 403.1485, found: 403.1486.



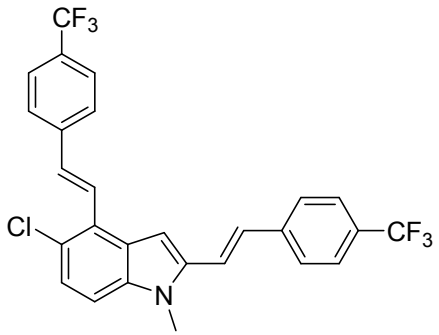
Dimethyl 4,4'-(1E,1'E)-2,2'-(5-fluoro-1-methyl-1H-indole-2,4-diyl) bis(ethene-2,1-diyl)dibenzoate (5ef)

R_f 0.28 (hexane/EtOAc = 5/1). Brown solid. Isolated yield: 26.3 mg, 56%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.044 (d, J = 7.2 Hz, 4H), 7.915 (d, J = 1.6 Hz,1H), 7.620-7.662 (m, 2H), 7.578-7.599 (m, 2H), 7.444-7.494 (m, 1H), 7.301-7.334 (m, 1H), 7.250-7.261 (m, 2H), 7.119-7.148 (m, 2H), 3.925 (d, J = 7.2 Hz, 6H), 3.894 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.985, 166.783, 141.243, 141.301 (d, $J_{C\text{-}F}$ = 120.08 Hz), 139.091, 135.216, 131.273 (d, $J_{C\text{-}F}$ = 33.2 Hz), 130.471, 130.156, 130.039, 129.973, 129.804, 129.301, 128.954, 126.332 (d, $J_{C\text{-}F}$ = 11.2 Hz), 123.642, 118.832, 113.042 (d, $J_{C\text{-}F}$ = 105.2 Hz), 111.169, 111.077, 111.024, 109.618 (d, $J_{C\text{-}F}$ = 46.4 Hz), 108.352, 108.099, 99.204, 99.149, 52.182, 52.121, 34.320. **HRMS** (ESI-TOF) calcd for $C_{29}H_{24}FNO_4$ ([M+H^+]): 470.1768, found: 470.1774.



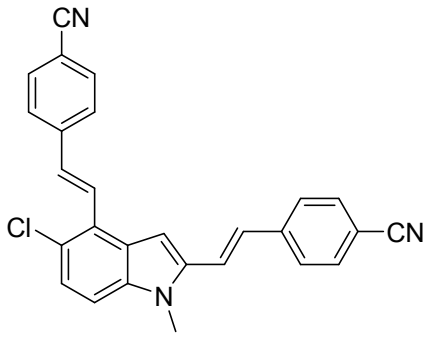
5-chloro-2,4-bis(4-fluorostyryl)-1-methyl-1H-indole(5fb)

R_f 0.43 (hexane/EtOAc = 20/1). Yellow-green solid. Isolated yield: 18.6 mg, 46%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.543-7.578 (m, 2H), 7.458-7.502 (m, 2H), 7.256-7.297 (m, 1H), 7.175-7.238 (m, 1H), 7.095-7.171 (m, 2H), 7.035-7.078 (m, 5H), 6.982-7.026 (m, 2H), 3.749 (s, 3H), 3.749 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.800 (d, J_{C-F} = 44.8 Hz), 161.332 (d, J_{C-F} = 46.4 Hz), 138.379 (d, J_{C-F} = 102.8 Hz), 134.009 (d, J_{C-F} = 17.2 Hz), 133.069 (d, J_{C-F} = 16.4 Hz), 132.083, 130.620, 128.173 (d, J_{C-F} = 34.4 Hz), 128.035 (d, J_{C-F} = 29.2 Hz), 126.765 (d, J_{C-F} = 94 Hz), 125.410 (d, J_{C-F} = 34.4 Hz), 125.331, 123.085, 116.228 (d, J_{C-F} = 9.2 Hz), 115.956, 115.870, 115.774, 115.739, 115.668, 115.560, 109.368, 98.826, 30.079. **HRMS** (EI-TOF) calcd for $C_{25}H_{18}ClF_2N$ (M^+): 405.1096, found: 405.1095.



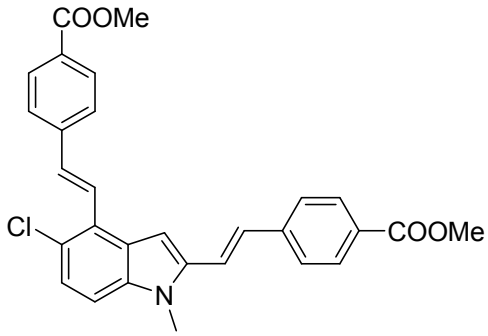
5-chloro-1-methyl-2,4-bis(4-(trifluoromethyl)styryl)-1H-indole (5fd)

R_f 0.34 (hexane/EtOAc = 20/1). Brown solid. Isolated yield: 30.3 mg, 60%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.668-7.730 (m, 3H), 7.594-7.647 (m, 6H), 7.346 (d, J = 16.4 Hz, 1H), 7.224-7.252 (m, 3H),, 7.162(d, J = 8.4 Hz, 1H), 7.110 (s, 1H), 3.821 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.110, 141.219, 140.199, 139.186, 137.340, 131.823, 130.133, 129.906, 129.627, 129.578, 129.313, 128.311, 128.008, 126.750, 126.611, 126.537, 126.048, 125.824, 125.788, 125.731, 125.696, 125.656, 125.616, 125.479, 124.495, 123.567, 122.909, 122.777, 118.754, 109.977, 99.599, 29.737. **HRMS** (EI-TOF) calcd for $C_{27}H_{18}ClF_6N$ (M^+): 505.1032, found: 505.1036.



4,4'-(1E,1'E)-2,2'-(5-chloro-1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl) Dibenzonitrile(5fe)

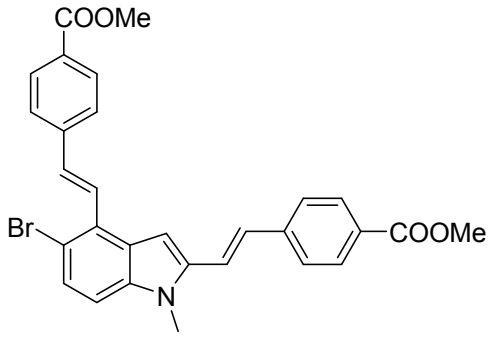
R_f 0.38 (hexane/EtOAc = 5/1). Brown solid. Isolated yield: 20.2 mg, 48%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.757 (d, *J* = 16.4 Hz, 1H), 7.656-7.713(m, 5H), 7.610(d, *J* = 8.4 Hz, 2H), 7.334(d, *J* = 16.4 Hz, 1H), 7.250-7.291 (m, 3H),, 7.196-7.235 (m, 2H), 7.130(s, 1H), 3.856 (s, 3H), 3.856 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.213, 141.130, 138.974, 137.496, 132.652, 132.556, 131.465, 129.698, 129.171, 127.053, 126.876, 126.563, 126.423, 126.390, 123.899, 119.805, 119.050, 111.136, 110.849, 110.359, 100.005, 29.727. **HRMS** (EI-TOF) calcd for $C_{27}H_{18}ClN_3$ ([M+H$^+$]): 420.1268, found: 420.1269.



Dimethyl 4,4'-(1E,1'E)-2,2'-(5-chloro-1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl)dibenzoate (5ff)

R_f 0.28 (hexane/EtOAc = 5/1). Brown solid. Isolated yield: 25.2 mg, 52%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.027-8.072 (m, 4H), 7.741 (d, *J* = 16.4 Hz,1H), 7.665 (d, *J* = 8.4 Hz, 2H), 7.578 (d, *J* = 8.4 Hz, 2H), 7.361 (d, *J* = 8.4 Hz, 1H), 7.217-7.260 (m, 3H), 7.127-7.165 (m, 2H), 7.117-7.125 (m, 1H), 3.935 (d, *J* = 4.2 Hz, 6H), 3.823 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.948, 166.766, 142.251, 141.184, 139.331,

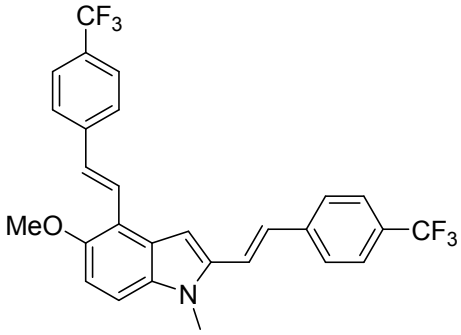
137.370, 132.237, 130.559, 130.158, 130.074, 129.336, 129.079, 128.036, 126.492, 126.355, 126.062, 123.537, 118.711, 109.947, 99.699, 52.188 52.147, 30.181. **HRMS** (ESI-TOF) calcd for $C_{29}H_{24}ClNO_4$ ([M+H$^+$]): 486.1472, found: 486.1480.



dimethyl 4,4'-(1E,1'E)-2,2'-(5-bromo-1-methyl-1H-indole-2,4-diyl)bis-

-(ethene-2,1-diyl)dibenzoate (5gf)

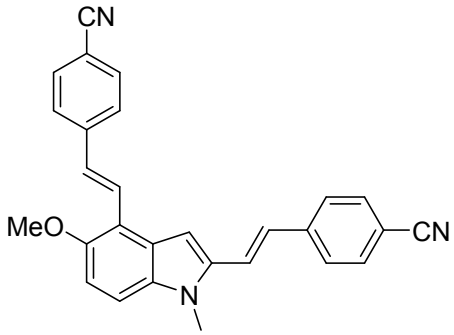
R_f 0.28 (hexane/EtOAc = 5/1). Brown solid. Isolated yield: 27.5 mg, 52%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.056 (dd, J_1 = 8.4 Hz, J_2 = 11.6 Hz, 4H), 7.661-7.702 (m, 3H), 7.584 (d, J = 8.4 Hz, 2H), 7.404 (d, J = 8.4 Hz, 1H), 7.273-7.332 (m, 2H), 7.255 (d, J = 4.4 Hz, 2H), 7.095-7.125 (m, 1H), 3.938 (d, J = 5.6 Hz, 6H), 3.835 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.946, 166.779, 142.147, 141.180, 139.154, 137.833, 132.387, 130.613, 130.539, 130.154, 130.096, 129.343, 129.110, 128.612, 127.722, 126.971, 126.503, 126.388, 126.354, 125.279, 118.677, 116.138, 111.541, 110.247, 99.781, 52.196, 52.152, 29.727. **HRMS** (ESI-TOF) calcd for $C_{29}H_{24}BrNO_4$ ([M+H$^+$]): 530.0967, found: 530.1968.



5-methoxy-1-methyl-2,3-bis(4-(trifluoromethyl)styryl)-1H-indole(5hd)

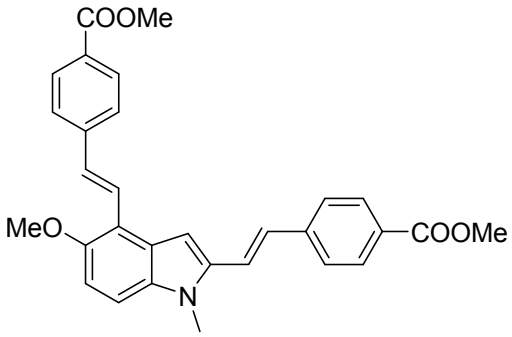
R_f 0.36 (hexane/EtOAc = 20/1). Brown solid. Isolated yield: 22.5 mg, 45%. **^{1}H NMR**

(400 MHz, $CDCl_3$): δ 7.771 (d, *J* = 16.8 Hz, 1H), 7.695 (d, *J* = 8.0 Hz, 2H), 7.605-7.625 (m, 6H), 7.459-7.501 (m, 1H),, 7.245-7.255 (m, 2H), 7.201-7.224 (m, 1H), 7.134 (s, 1H), 6.962 (d, *J* = 8.8 Hz, 1H), 3.946 (s, 3H), 3.822 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.627, 142.366, 140.463, 139.069, 134.566, 130.941, 129.469, 128.954, 126.835, 16.531, 126.435, 126.240, 125.785, 125.752, 125.716, 125.548, 125.503, 119.188, 116.417, 109.623. 108.928, 88.972, 57.234, 29.720. **HRMS** (EI-TOF) calcd for $C_{28}H_{21}F_6NO$ (M^+): 501.1527, found: 501.1534.



4,4'-(1E,1'E)-2,2'-(5-methoxy-1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl) Dibenzonitrile(5he)

R_f 0.26 (hexane/EtOAc = 5/1). Brown solid. Isolated yield: 22.0 mg, 53%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.798 (d, *J* = 16.4 Hz,1H), 7.646-7.682 (m, 5H), 7.294-7.646 (m, 2H),, 7.450 (d, *J* = 16.4 Hz, 1H), 7.249-7.260 (m, 2H), 7.226-7.236 (m, 1H), 7.135 (s, 1H), 6.974 (d, *J* = 8.8 Hz, 1H), 3.953 (s, 3H), 3.833 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.924, 143.421, 141.405, 138.841, 134.641, 132.615, 132.422, 129.026, 128.975, 127.409, 126.840, 126.793, 126.718, 120.206, 129.341, 118.953, 116.041, 110.842, 110.104, 109.884, 108.894, 99.369, 57.111, 29.728. **HRMS** (ESI-TOF) calcd for $C_{28}H_{21}N_3O$ ([M+H^+]): 416.1763, found: 416.1770.

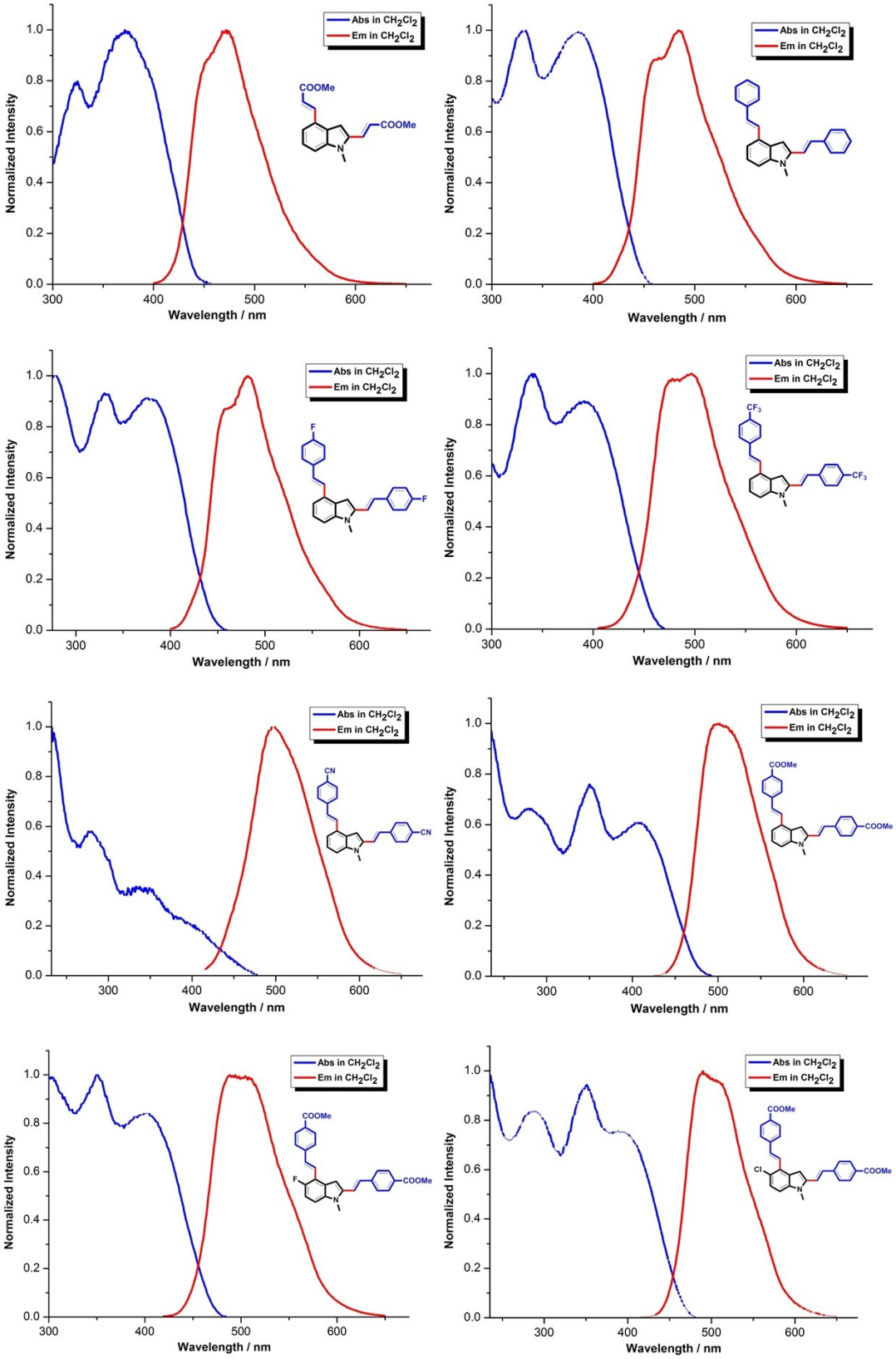


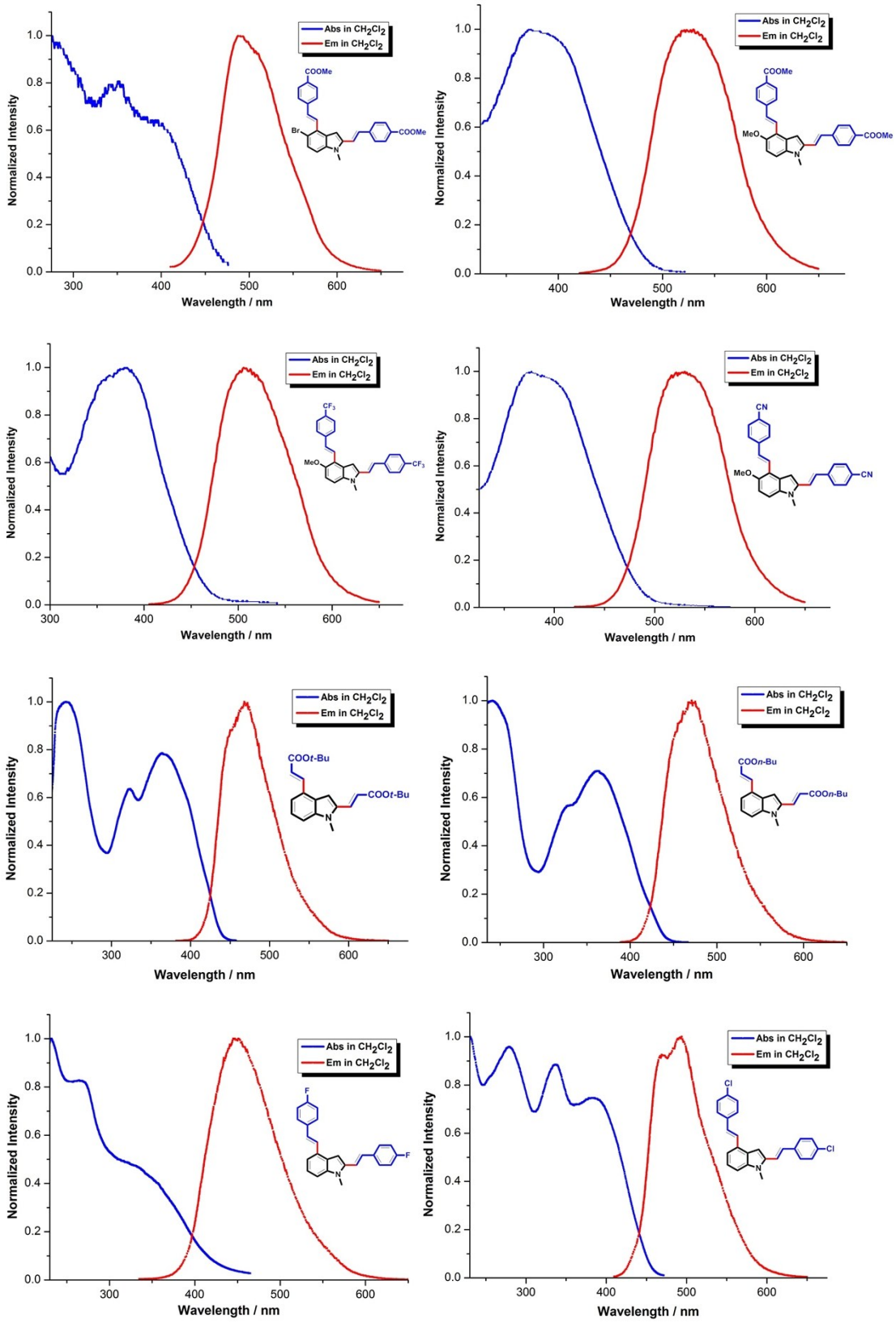
Dimethyl 4,4'-(1E,1'E)-2,2'-(5-methoxy-1-methyl-1H-indole-2,4-diyl)bis-

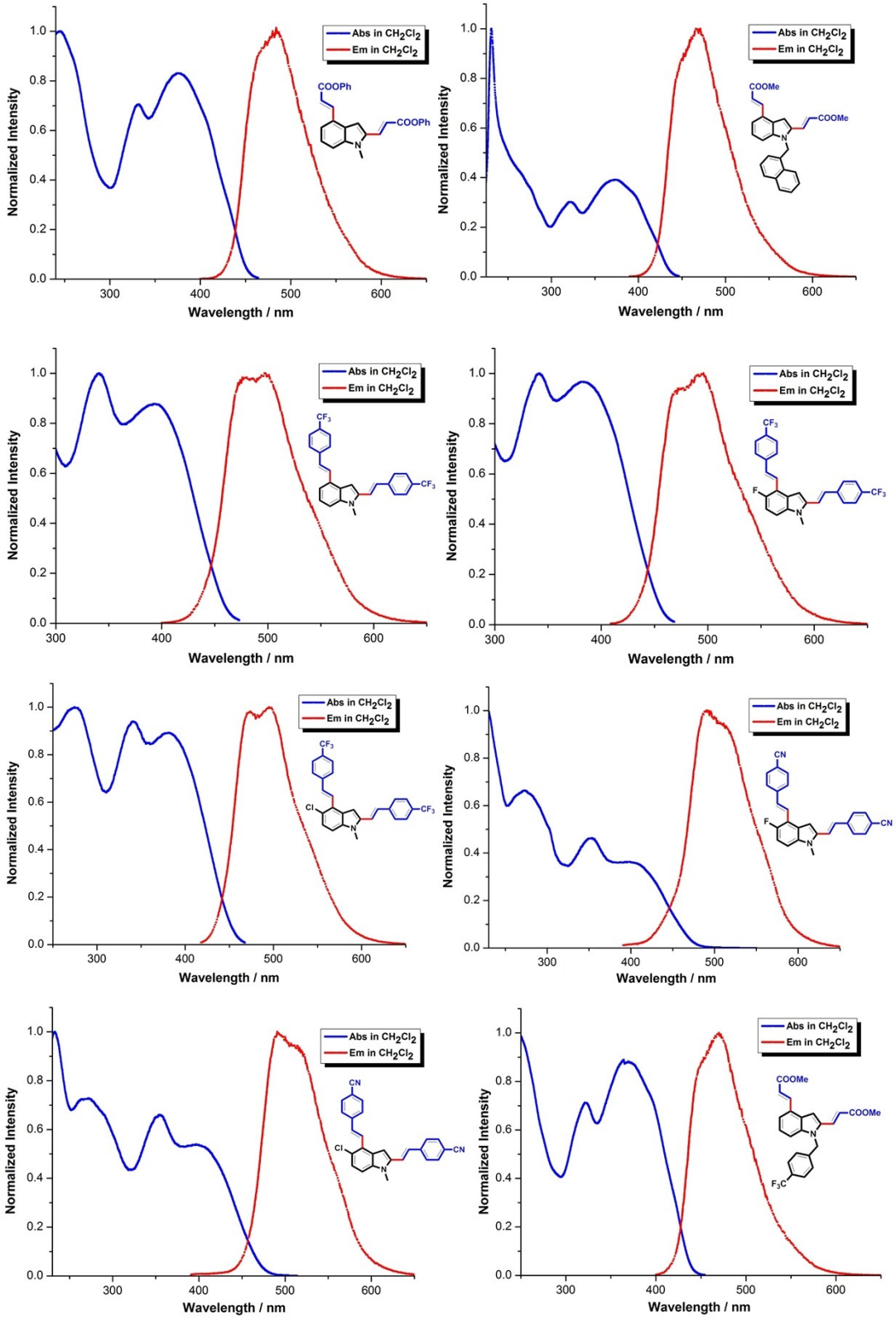
-(ethene-2,1-diyl)dibenzoate(5hf)

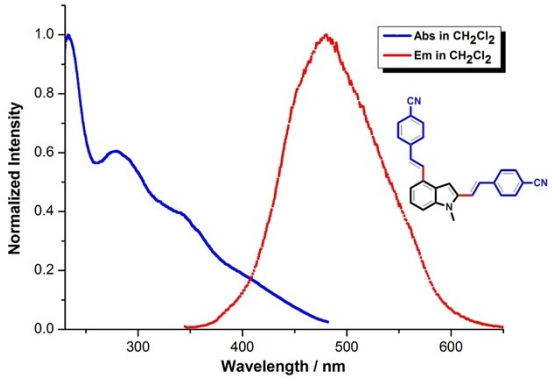
R_f 0.26 (hexane/EtOAc = 5/1). Red solid. Isolated yield: 29.9 mg, 62%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.038 (d, *J* = 8.0 Hz, 4H), 7.798(d, *J* = 16.4 Hz, 1H), 7.656 (d, *J* = 8.0 Hz, 2H), 7.581 (d, *J* = 8.4 Hz, 2H), 7.462-7.534 (m, 1H), 7.252 (d, *J* = 5.2 Hz, 2H), 7.187 (d, *J* = 8.8 Hz, 1H), 7.137 (s, 1H), 6.940 (d, *J* = 8.8 Hz, 1H), 3.928-3.937 (m, 9H), 3.798 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.113, 166.819, 152.670, 143.464, 141.459, 139.203, 134.581, 130.124, 129.976, 129.847, 129.108, 128.308, 126.864, 126.308, 126.276, 126.183, 119.145, 116.492, 109.604, 108.856, 99.075, 57.221, 52.160, 52.065, 29.723. **HRMS** (ESI-TOF) calcd for $C_{30}H_{27}NO_5$ ([M+H$^+$]): 482.1967, found: 482.1965.

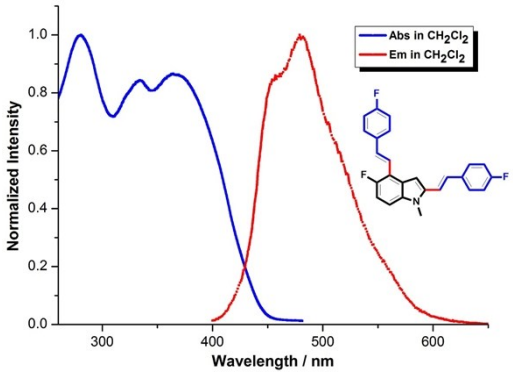
10. Photophysical spectra of 2,3-dialkenylindoles in CH_2Cl_2

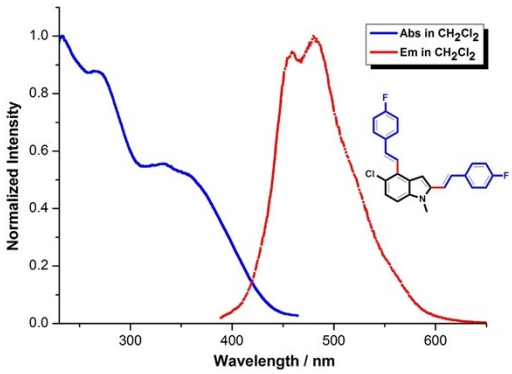


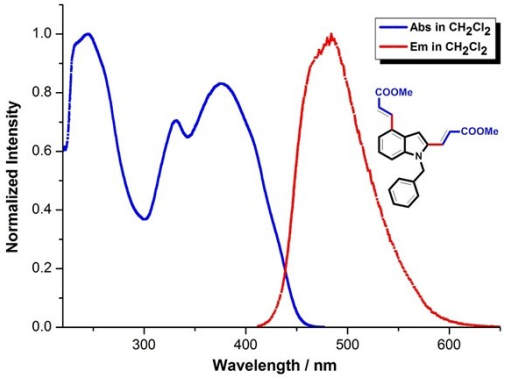

Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
COOMe
Br
COOMe
Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
COOMe
MeO
COOMe
Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
CF_3
MeO
CF_3
Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
CN
MeO
CN
Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
COO*t*-Bu
COO*t*-Bu
Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
COO*n*-Bu
COO*n*-Bu
Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
F
F
Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
Cl
Cl


Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
COOPh
COOMe
CF_3
CN
Cl
F
F_3C


Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
CN
CN

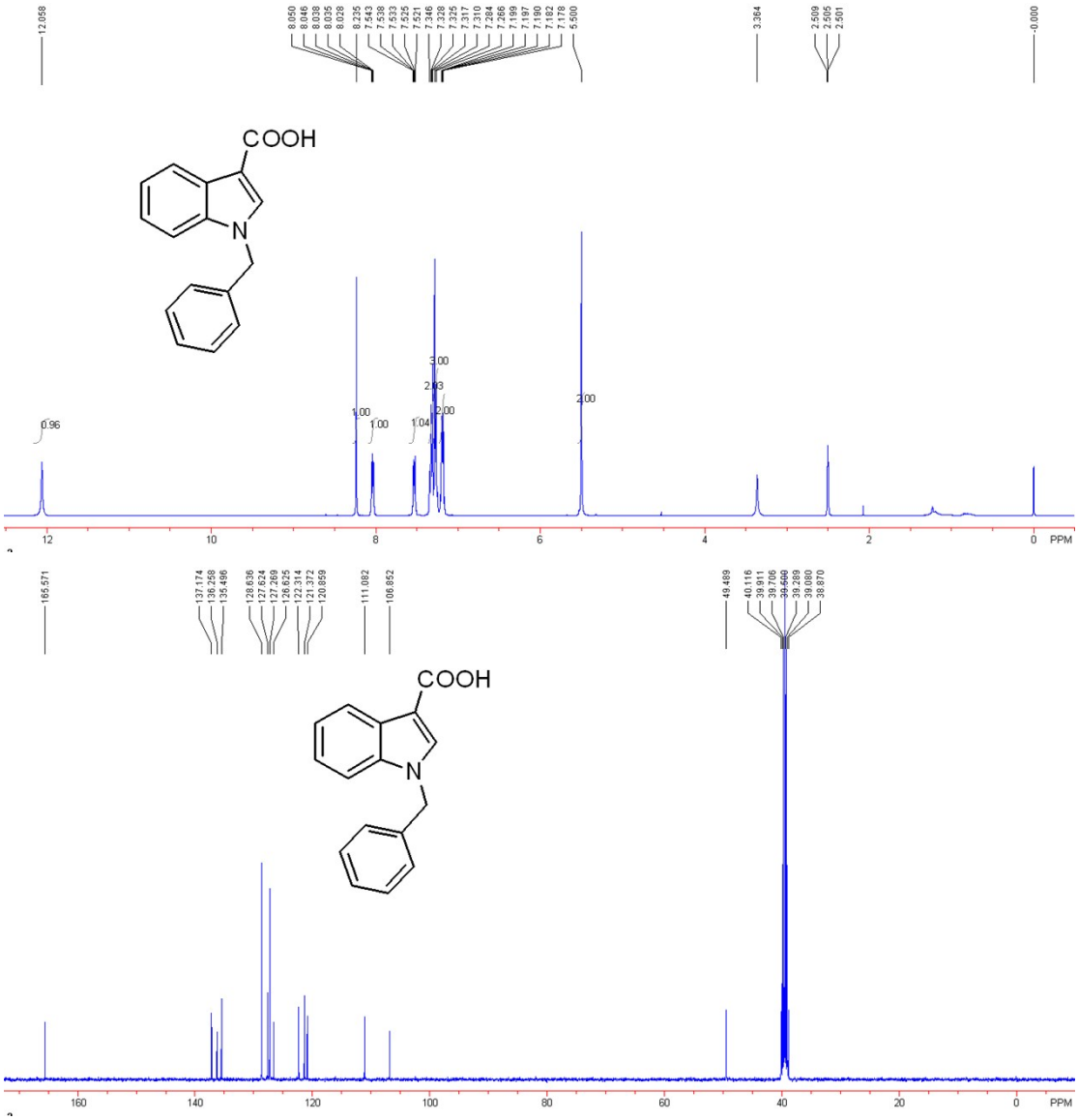

Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
F
F
F


Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
F
Cl
F

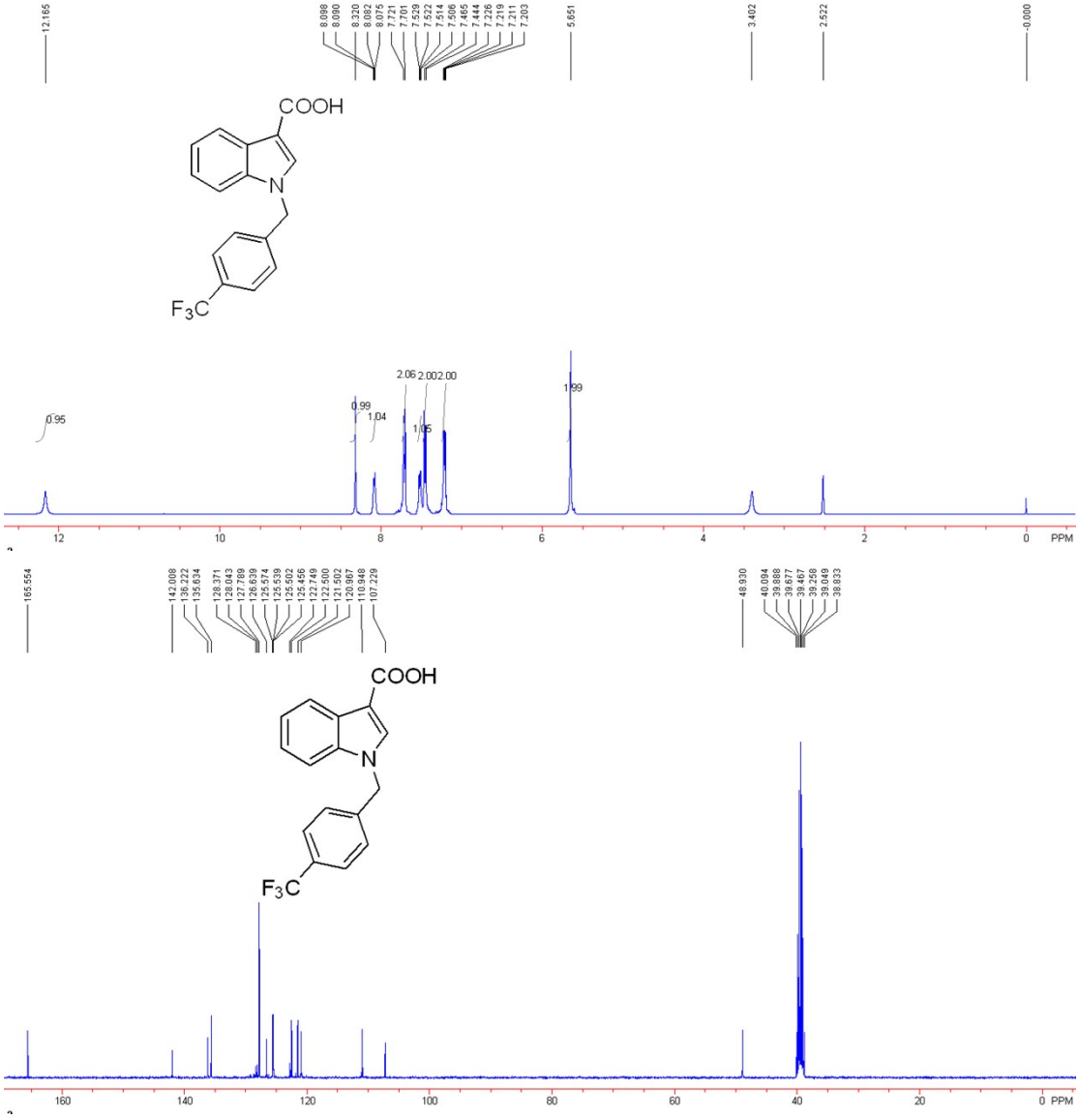

Abs in CH_2Cl_2
Em in CH_2Cl_2
Normalized Intensity
Wavelength / nm
COOMe
COOMe

11. Copies of ^{1}H and ^{13}C NMR Spectra

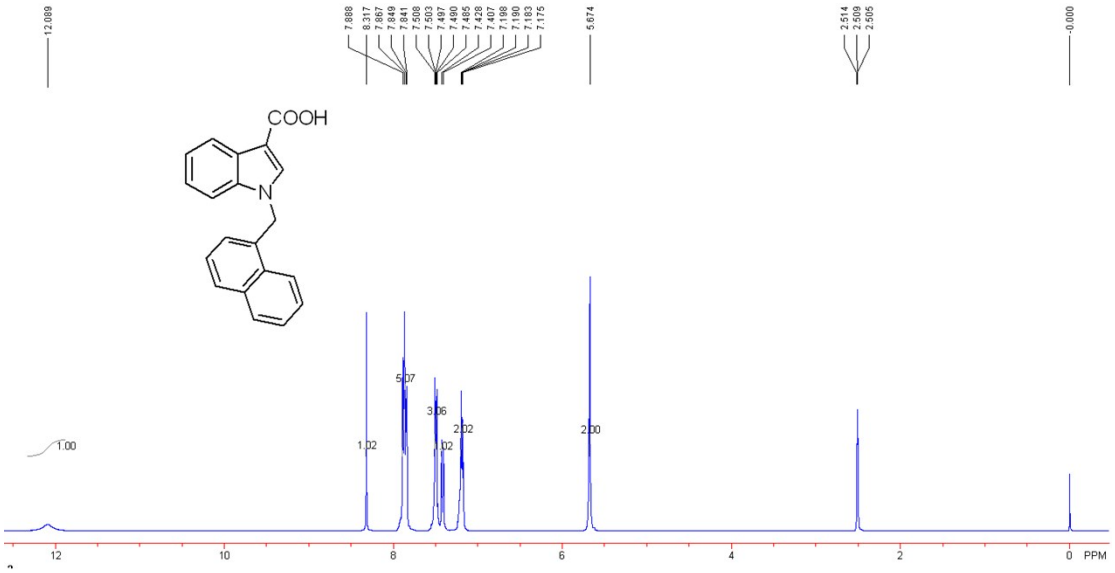
1-benzyl-1H-indole-3-carboxylic acid (1b)

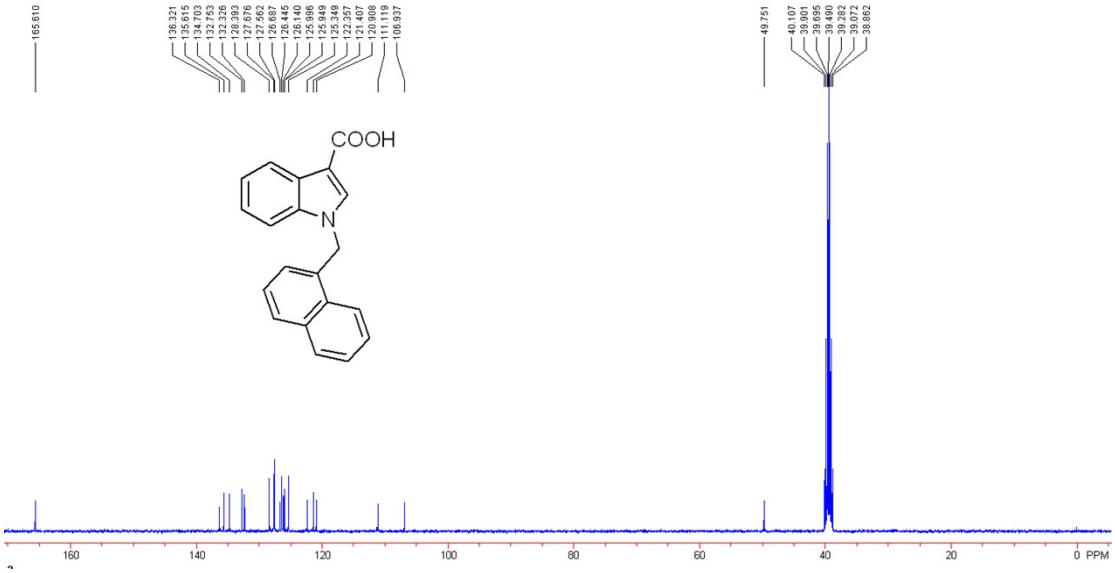


1-(4-(trifluoromethyl)benzyl)-1H-indole-3-carboxylic acid (1c)

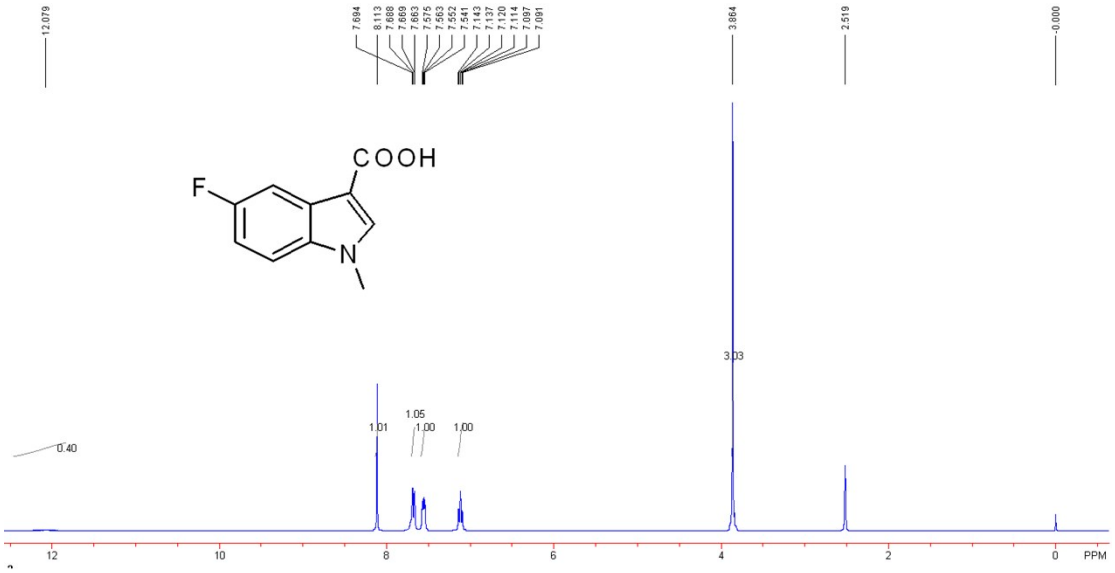


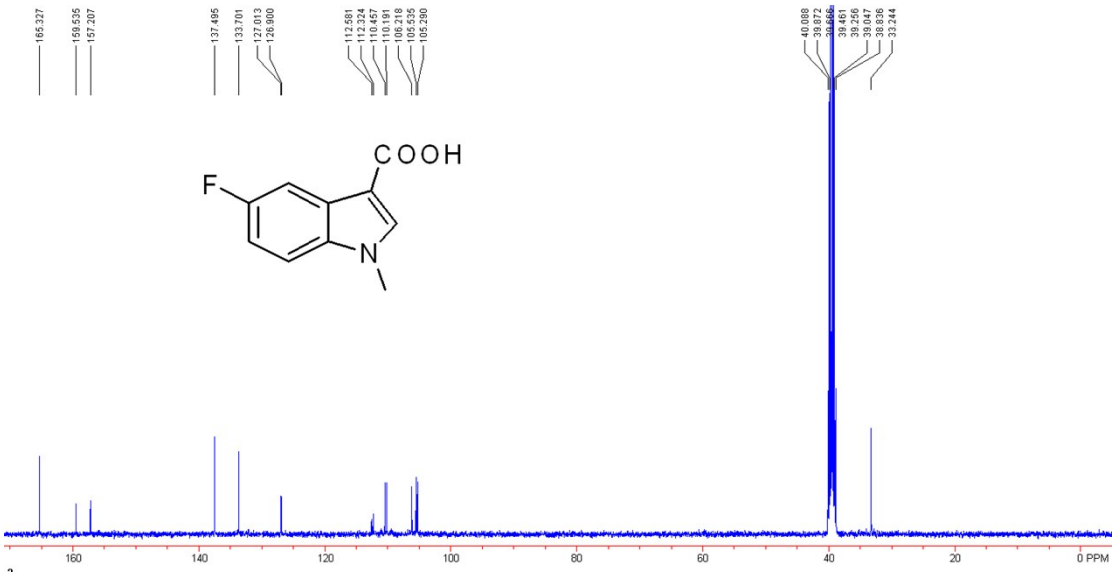
1-(naphthalen-1-ylmethyl)-1H-indole-3-carboxylic acid (1d)



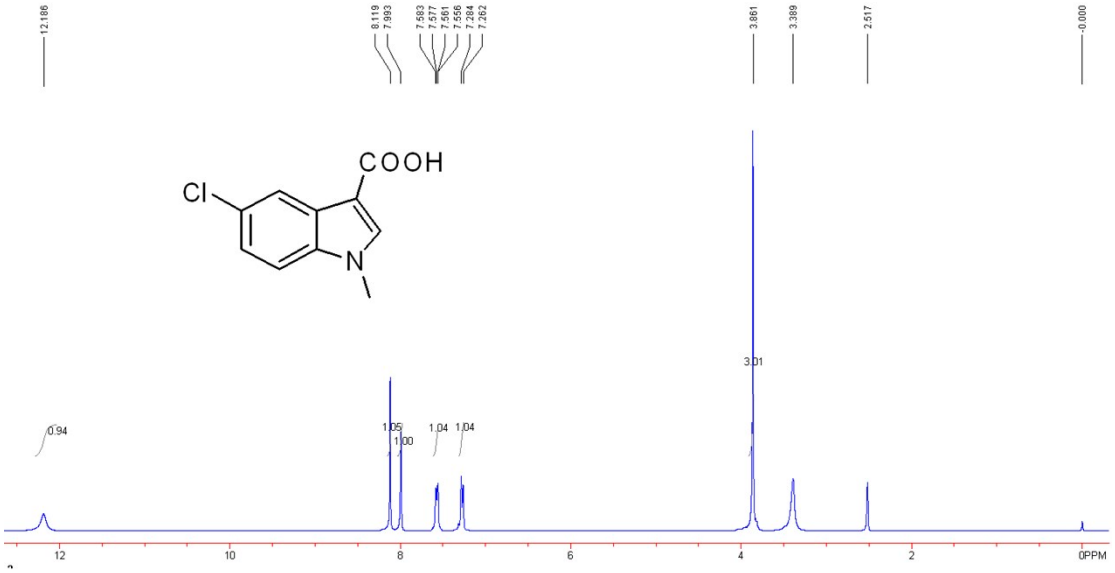


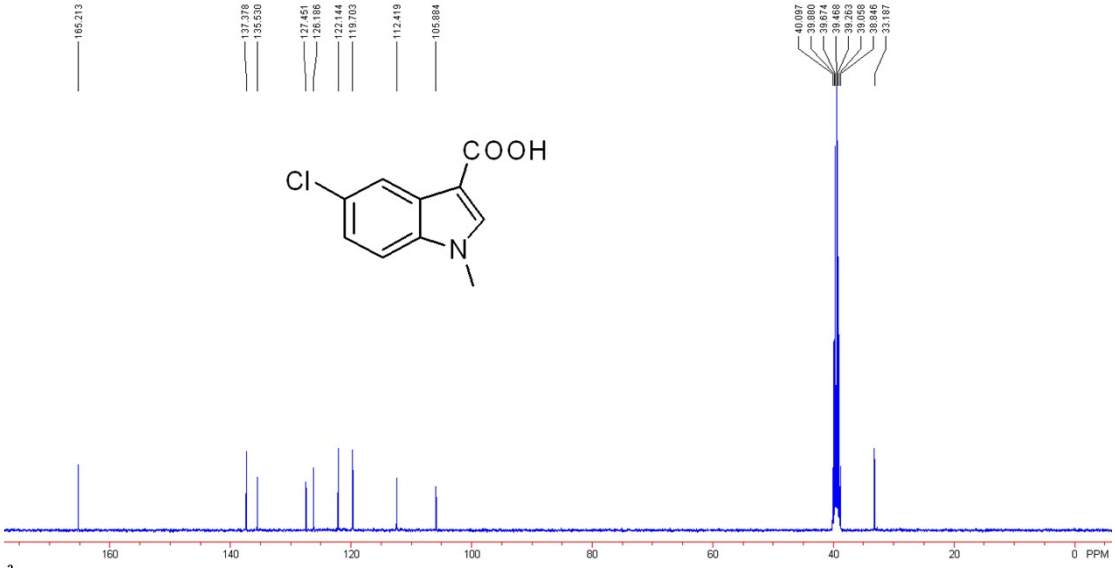
5-fluoro-1-methyl-1H-indole-3-carboxylic acid (1e)



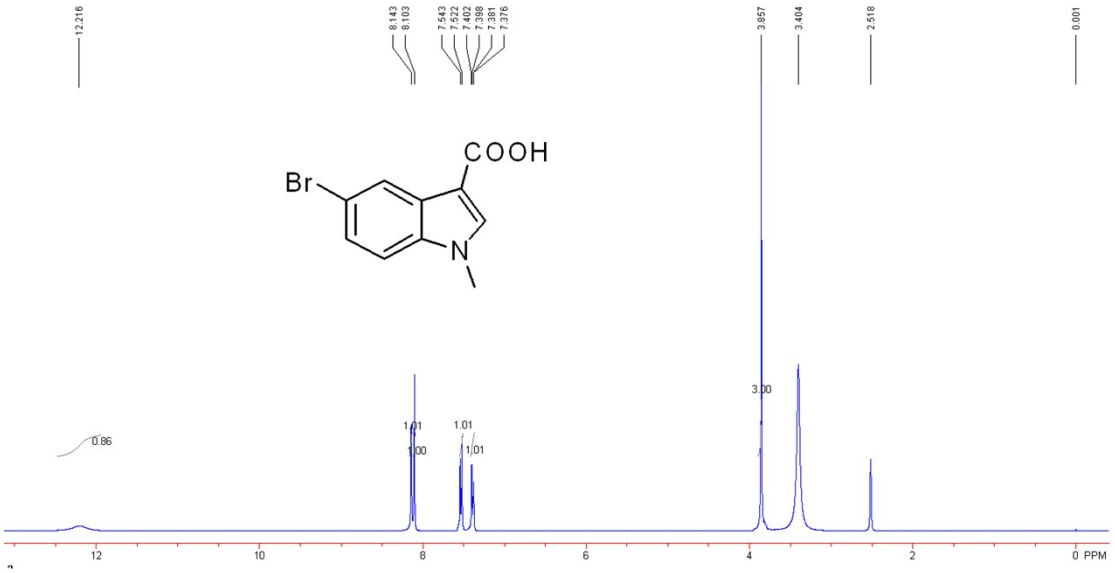


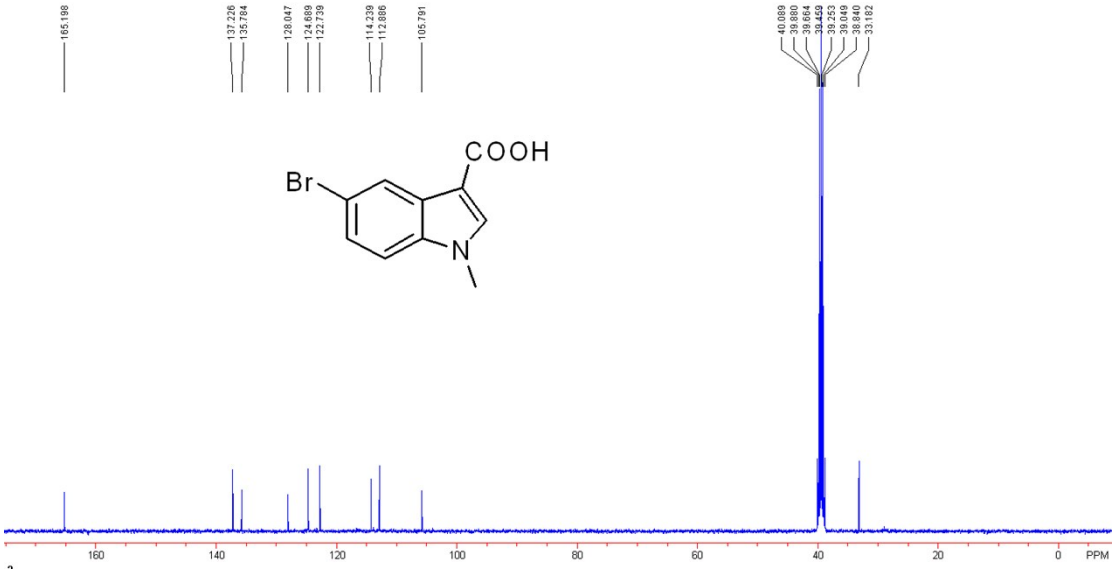
5-chloro-1-methyl-1H-indole-3-carboxylic acid (1f)



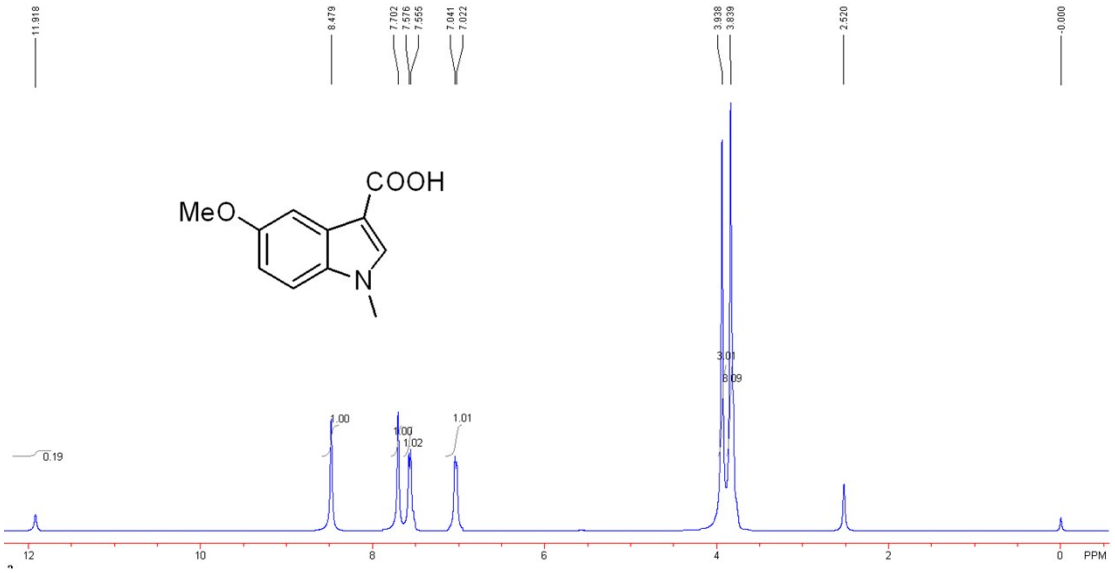


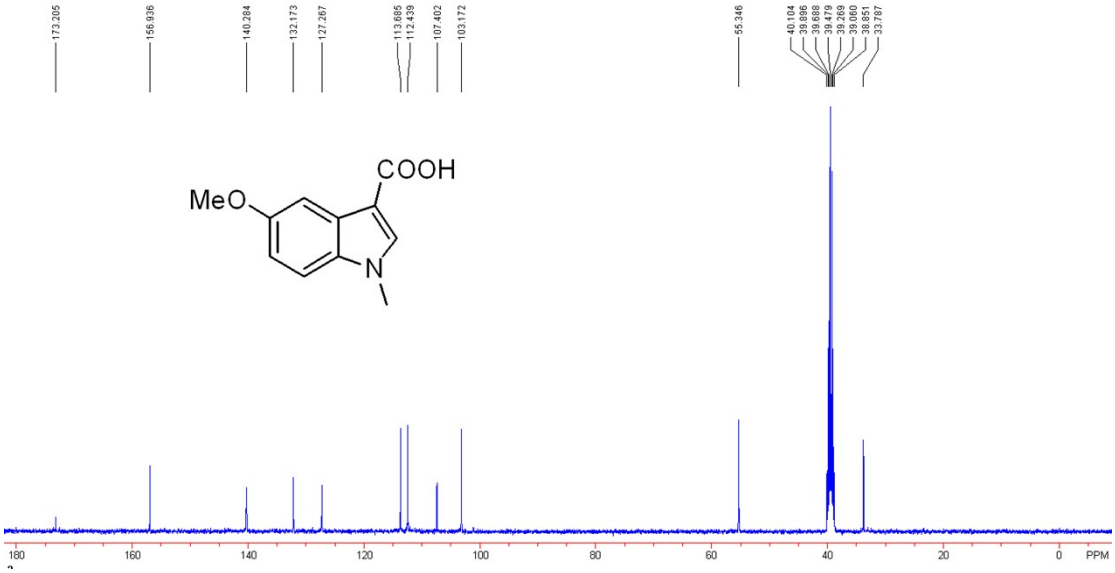
5-bromo-1-methyl-1H-indole-3-carboxylic acid (1g)



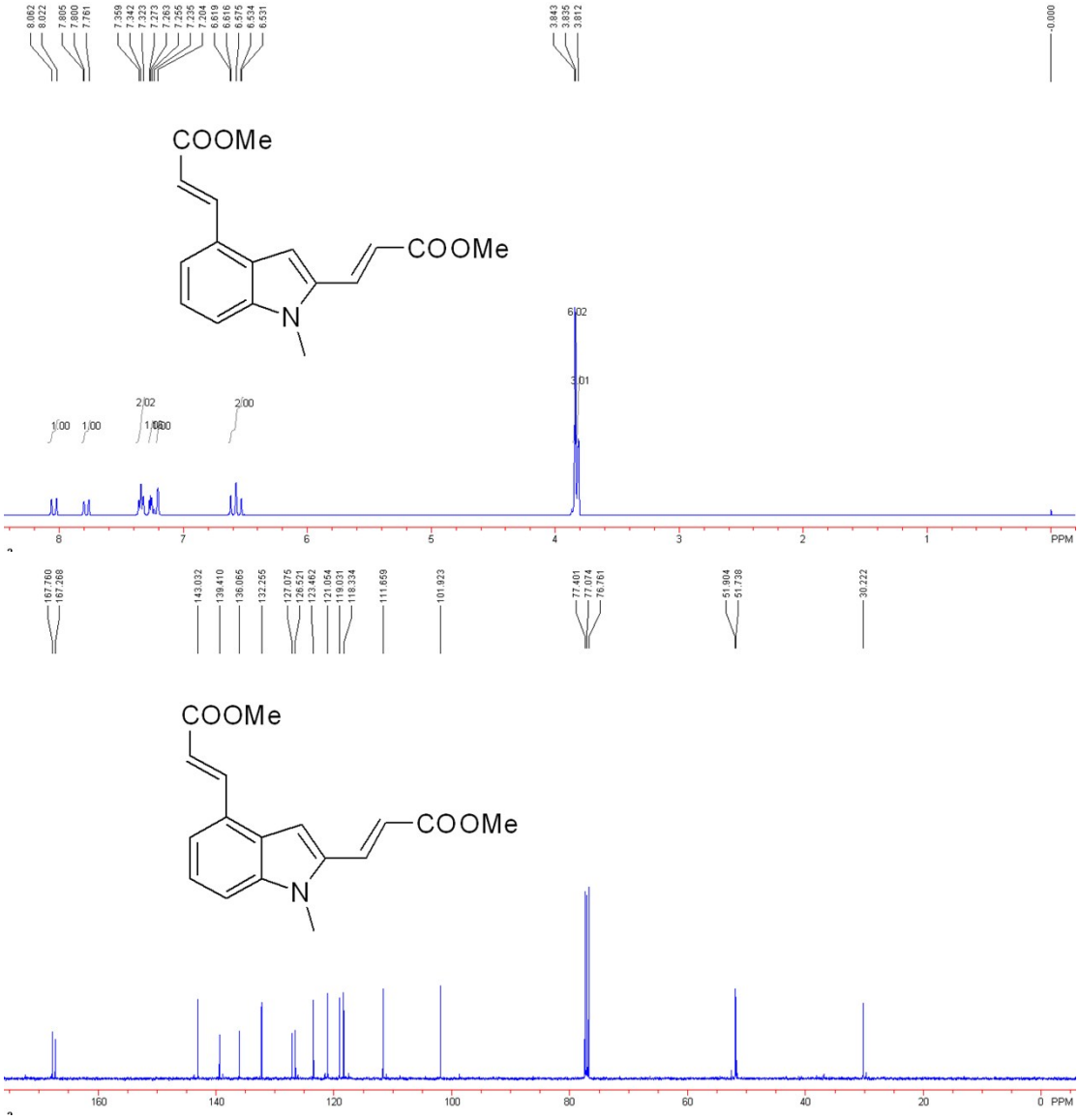


5-methoxy-1-methyl-1H-indole-3-carboxylic acid (1h)

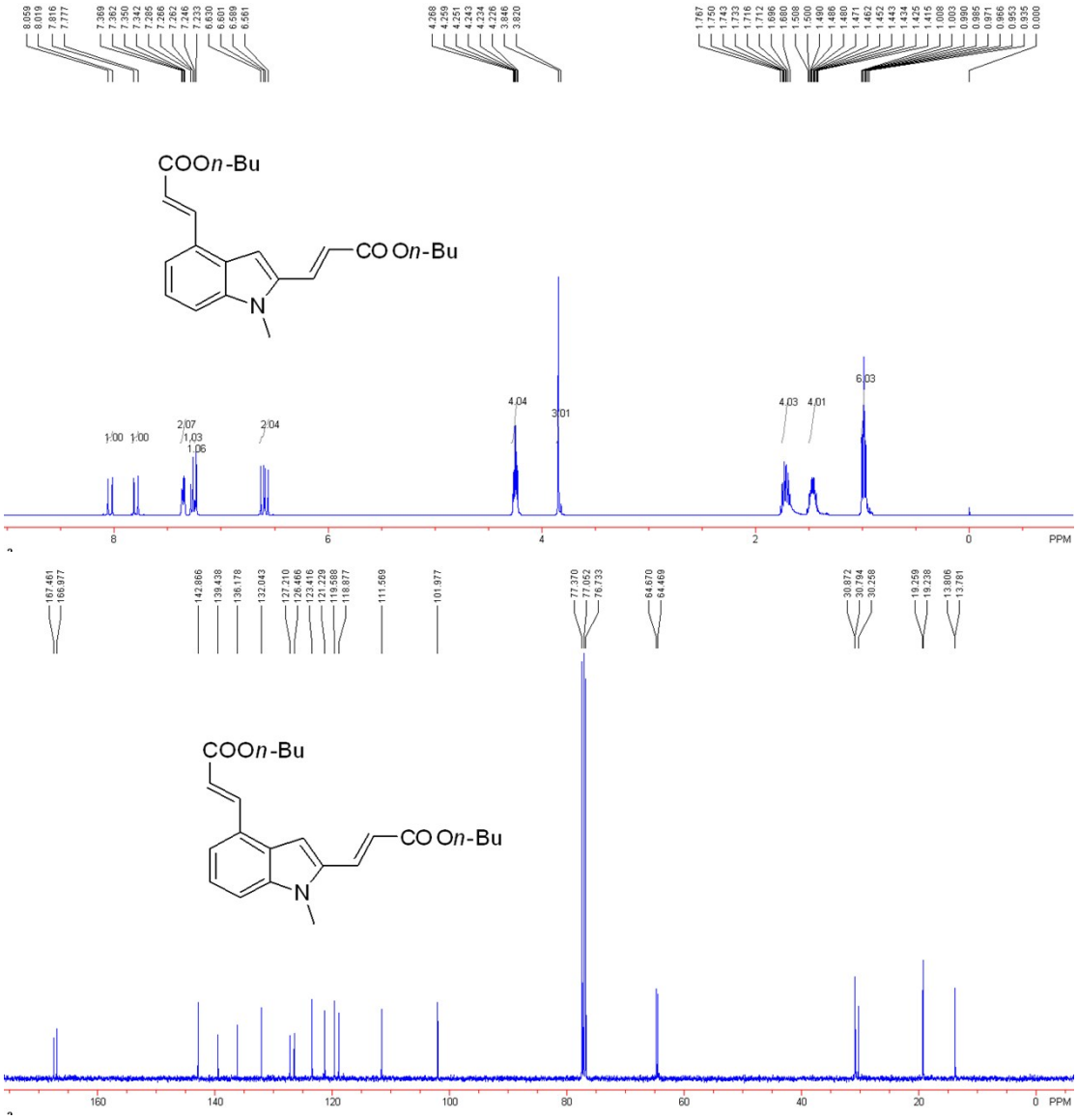




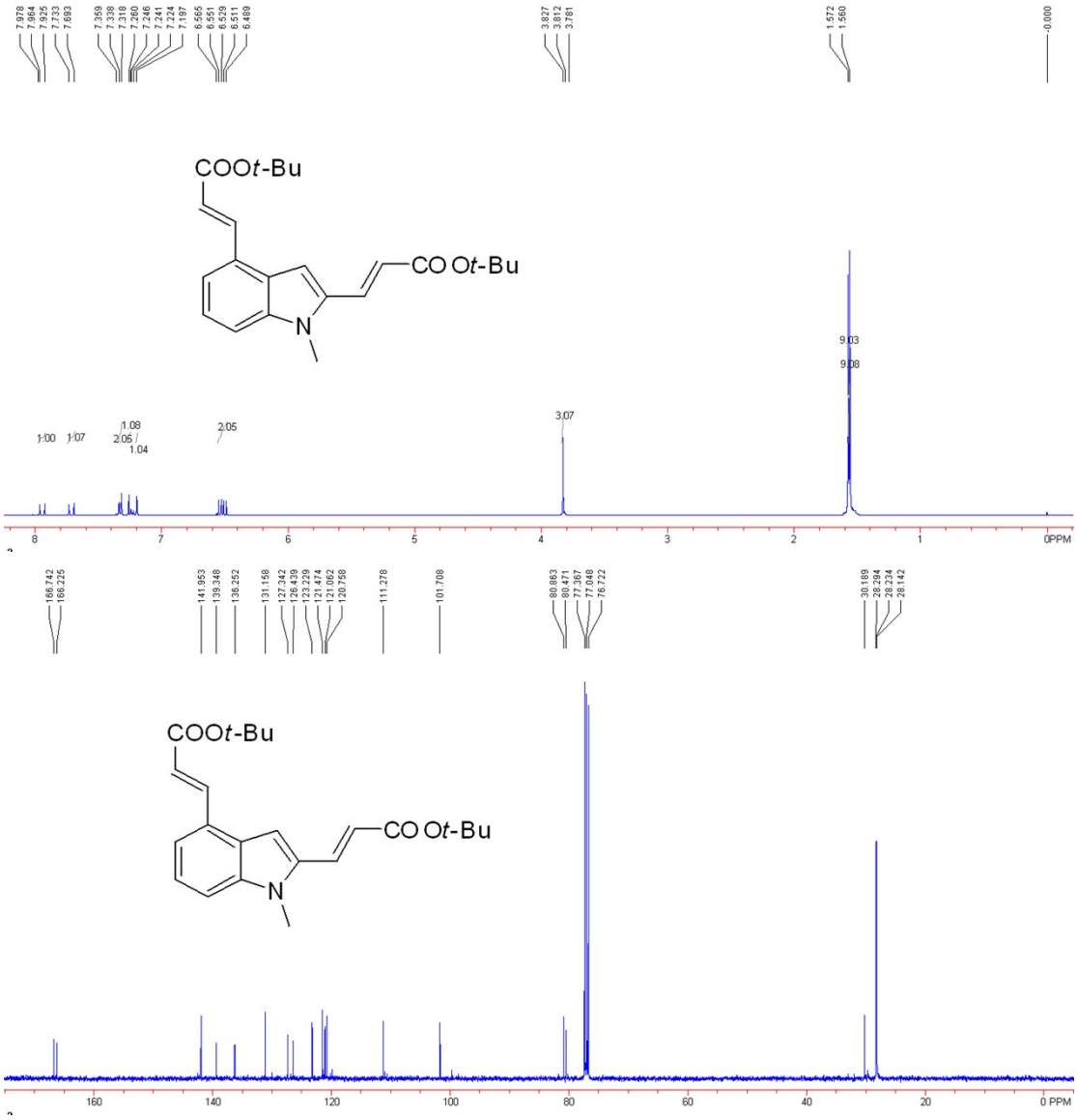
(2E,2'E)-dimethyl 3,3'-(1-methyl-1H-indole-2,4-diyl)diacrylate (3aa)



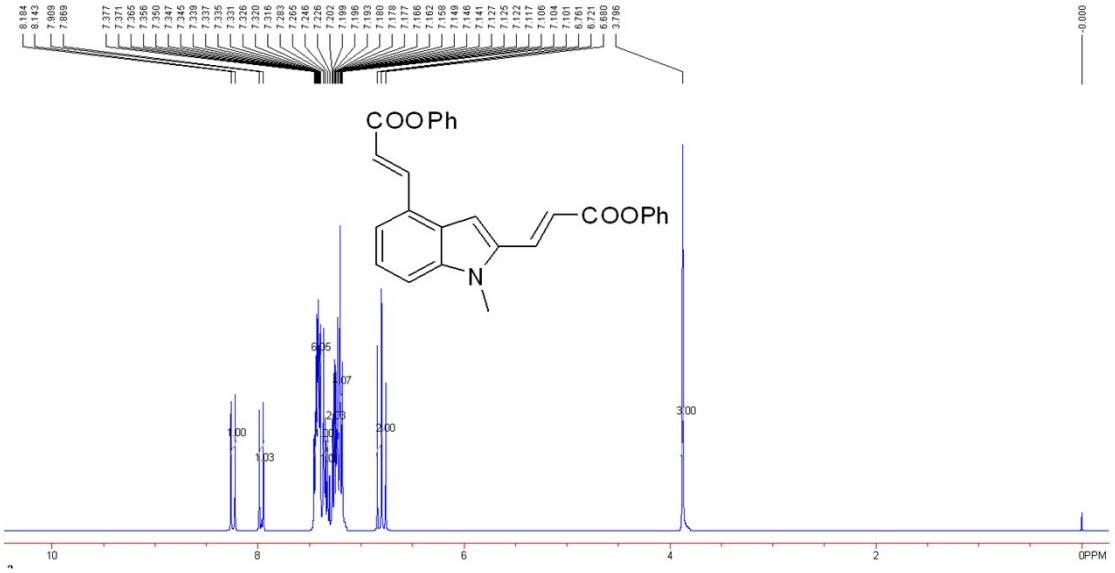
(2E,2'E)-dibutyl 3,3'-(1-methyl-1H-indole-2,4-diyl)diacrylate (3ab)

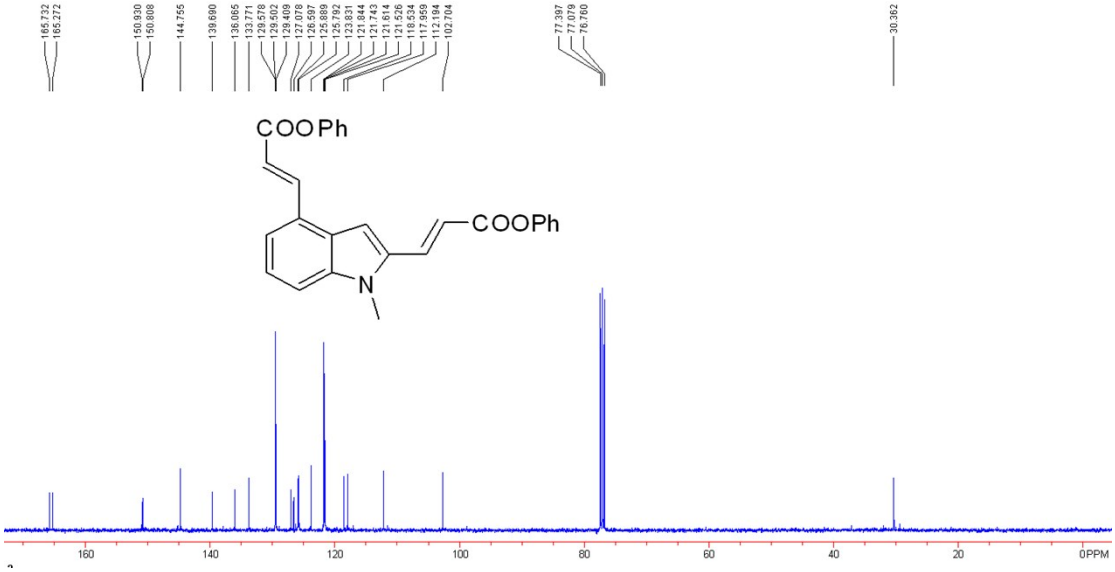


(2E,2'E)-tert-butyl 3,3'-(1-methyl-1H-indole-2,4-diyl)diacrylate (3ac)

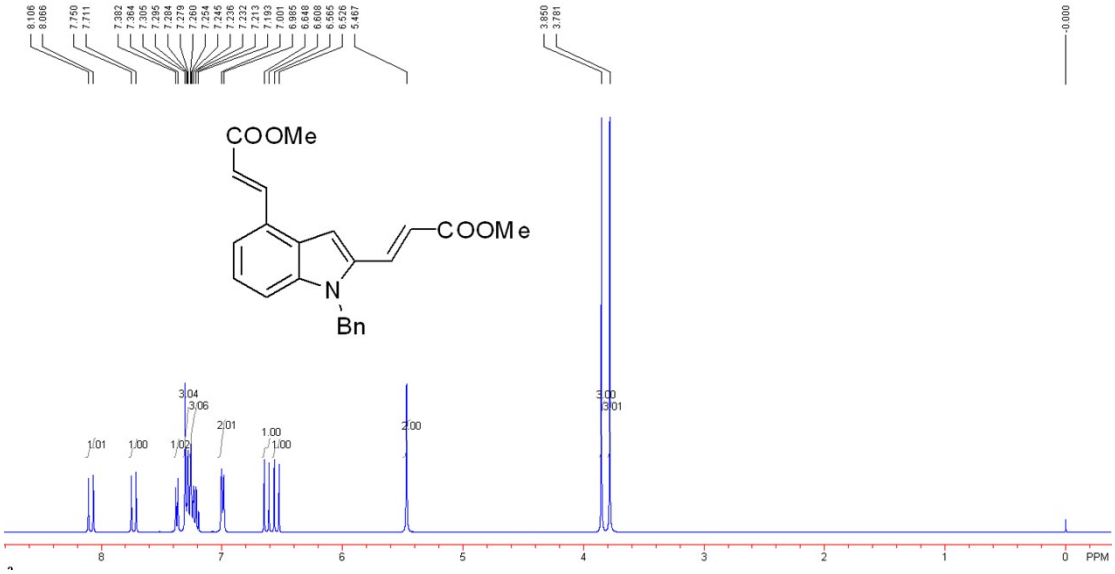


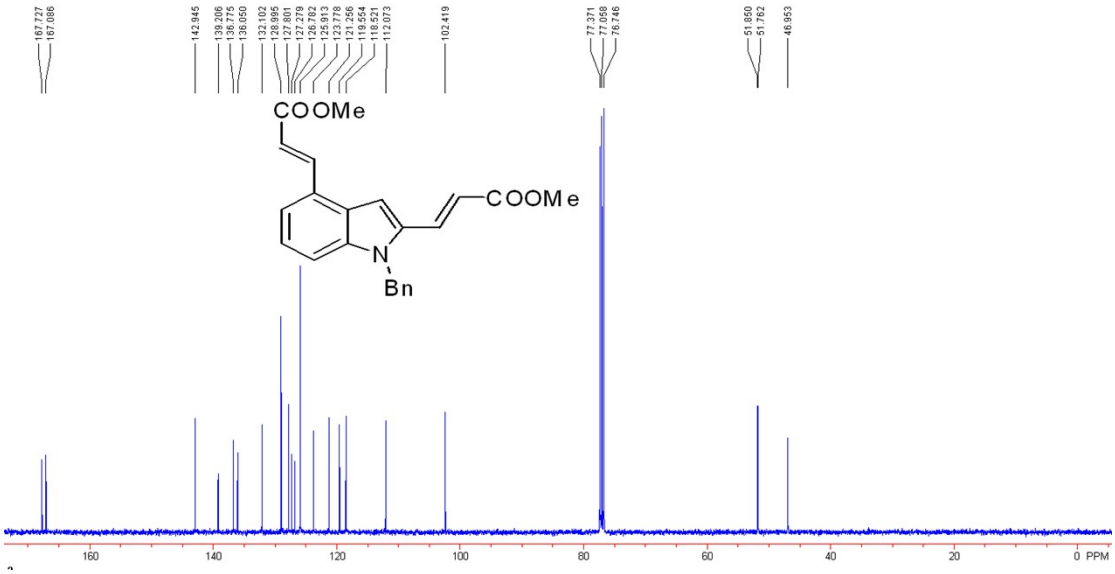
(2E,2'E)-diphenyl 3,3'-(1-methyl-1H-indole-2,4-diyl)diacrylate (3ad)



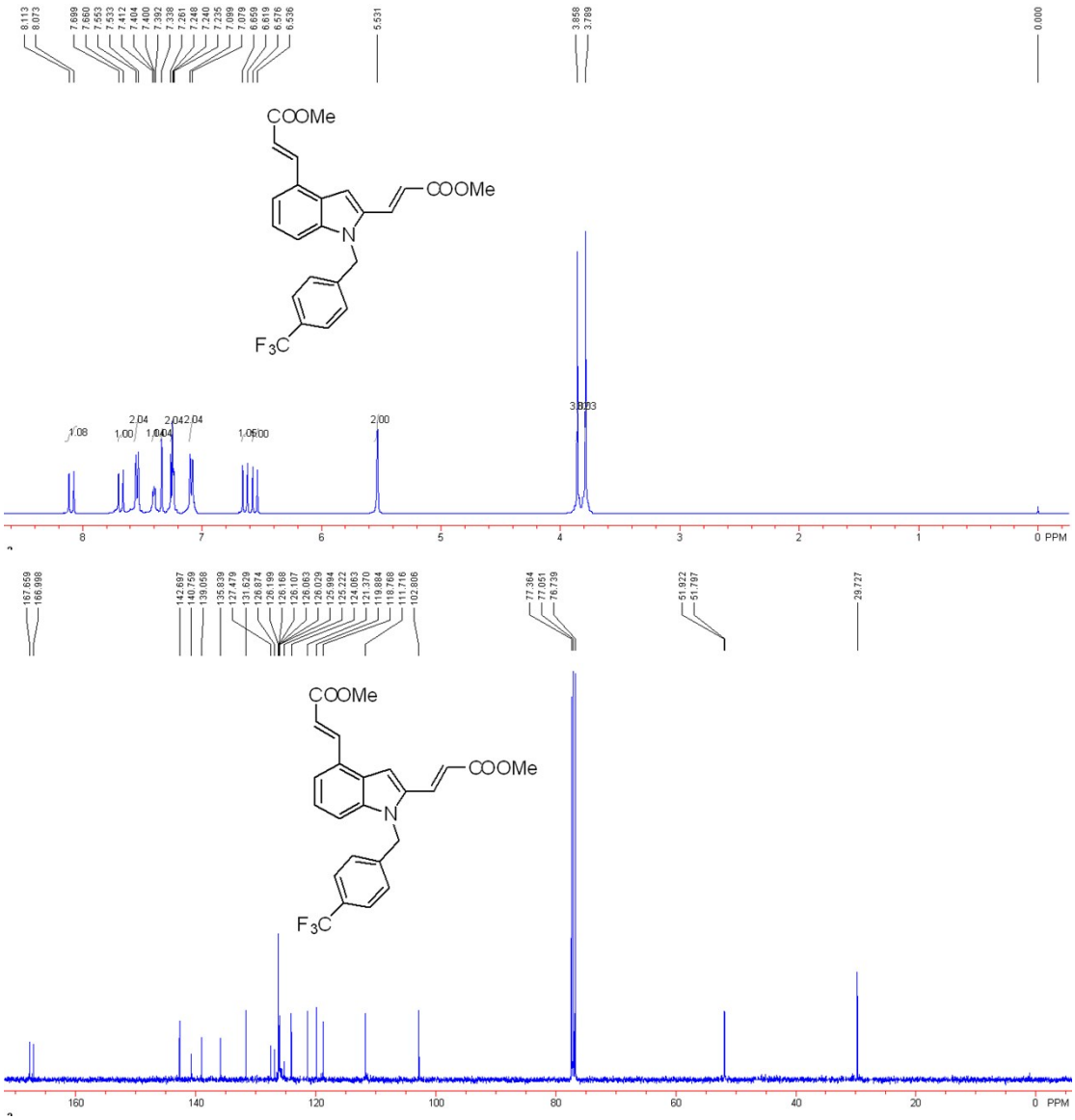


(2E,2'E)-dimethyl 3,3'-(1-benzyl-1H-indole-2,4-diyl)diacrylate (3ba)

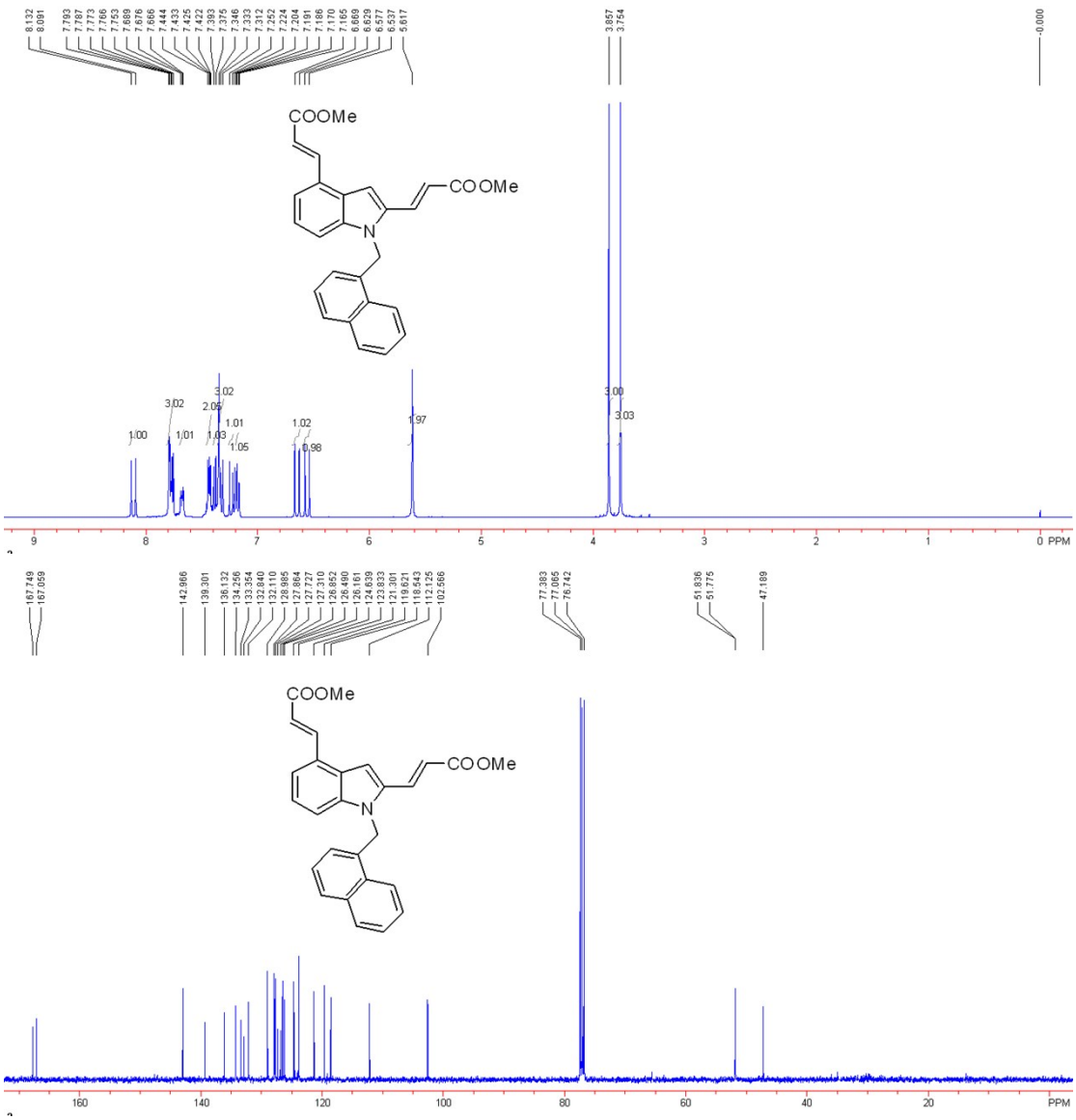




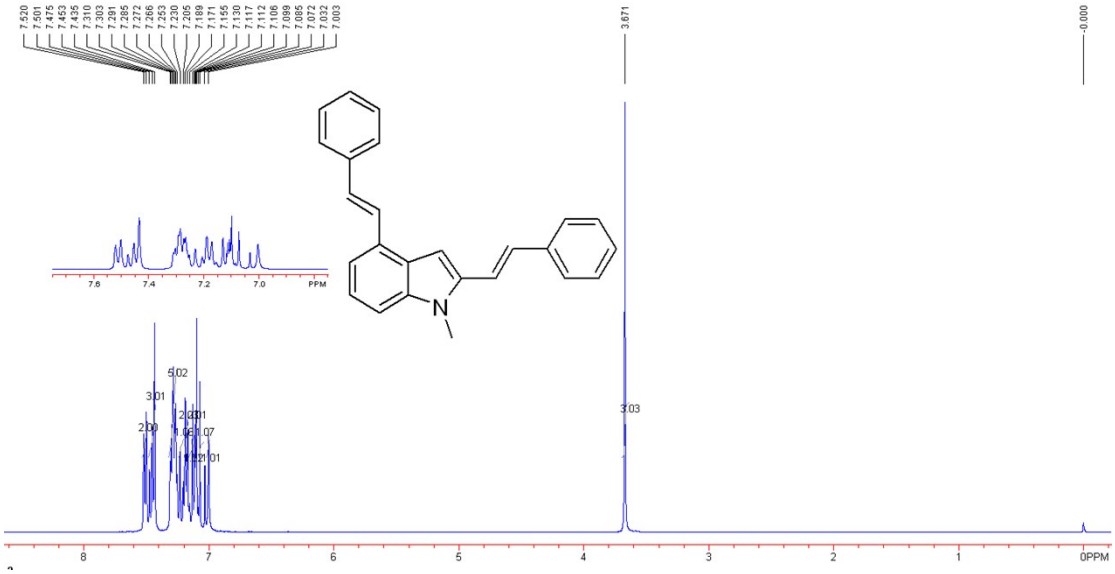
(2E,2'E)-dimethyl-3,3'-(1-(4-(trifluoromethyl)benzyl)-1H-indole-2,4-diyl) Diacrylate(3ca)

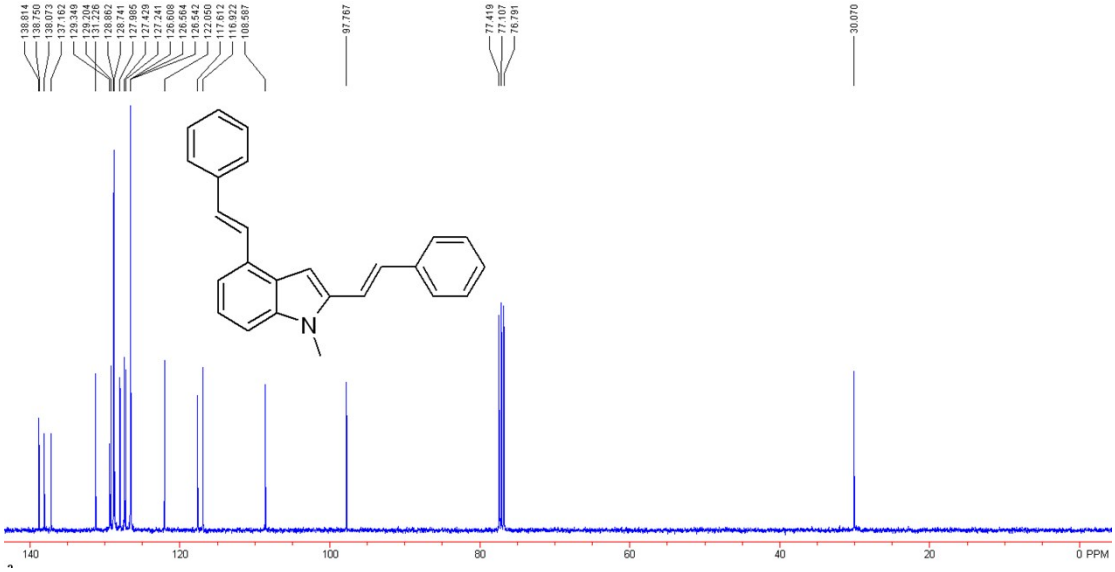


(2E,2'E)-dimethyl 3,3'-(1-(naphthalen-1-ylmethyl)-1H-indole-2,4-diyl) diacrylate(3da)

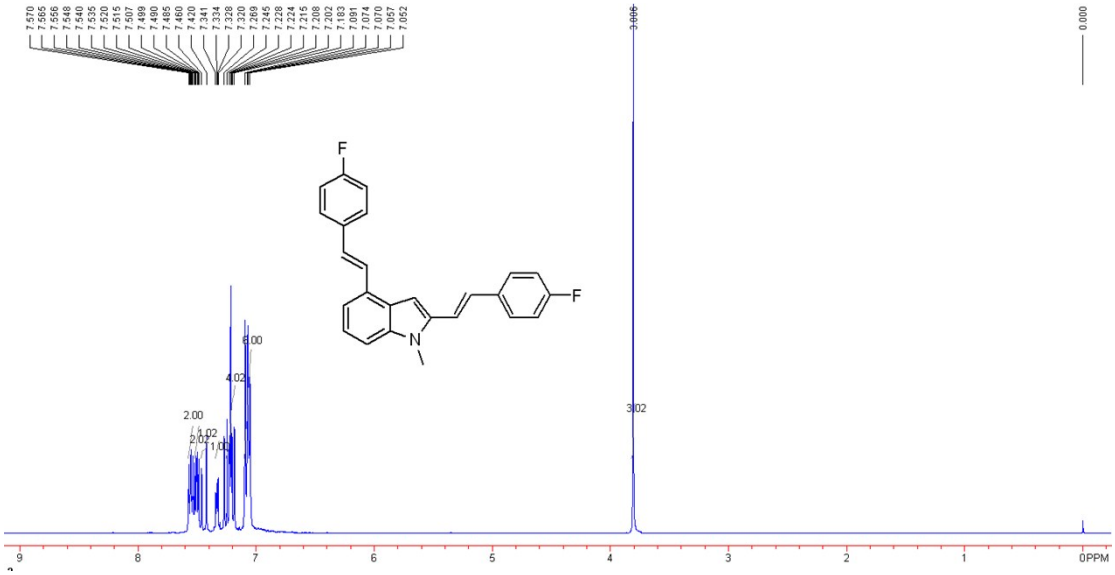


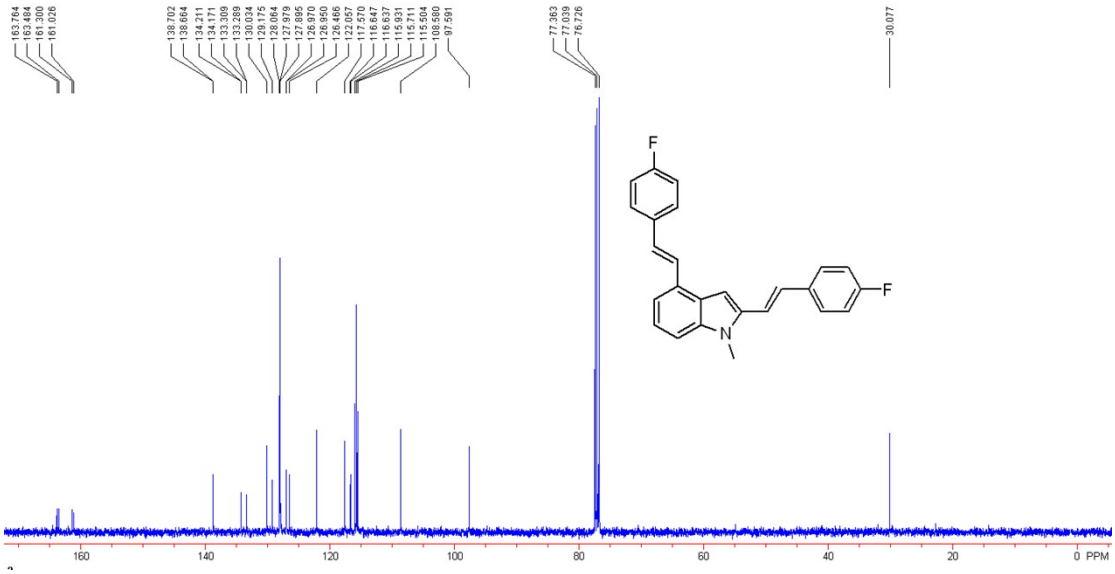
1-methyl-2,4-distyryl-1H-indole(5aa)



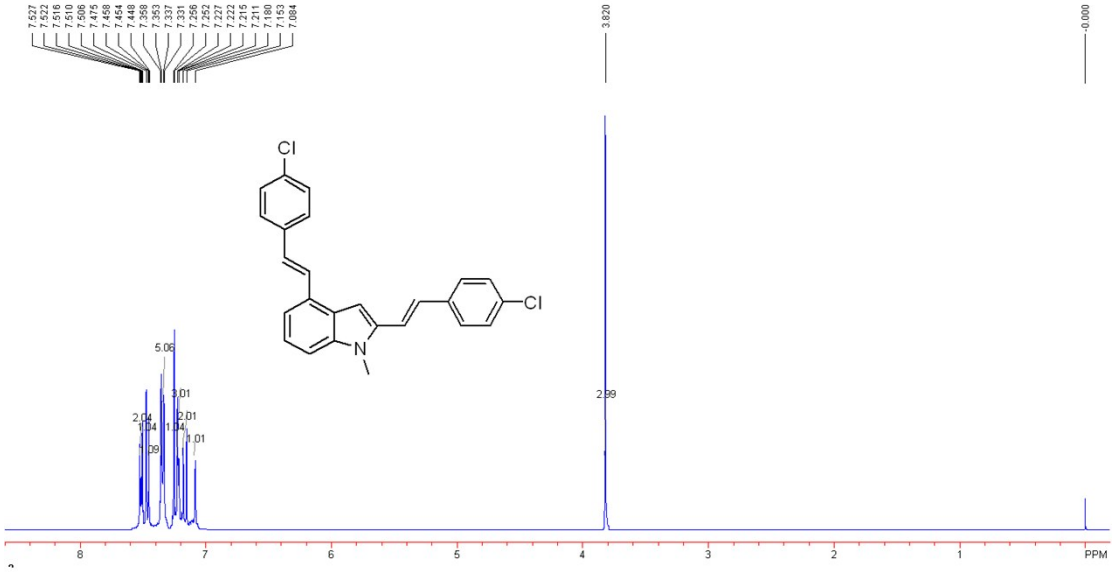


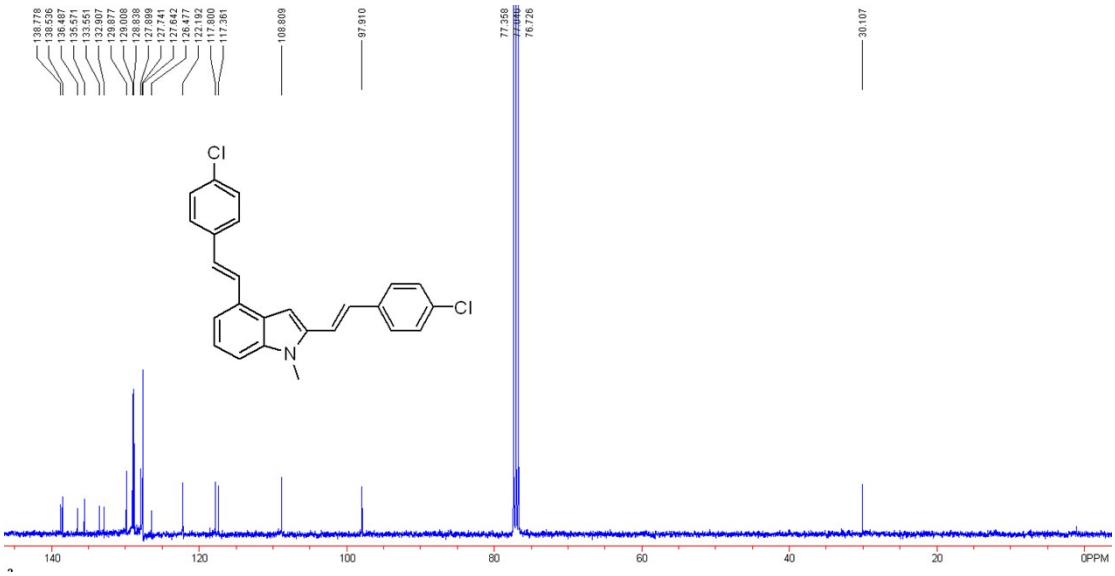
2,4-bis(4-fluorostyryl)-1-methyl-1H-indole (5ab)



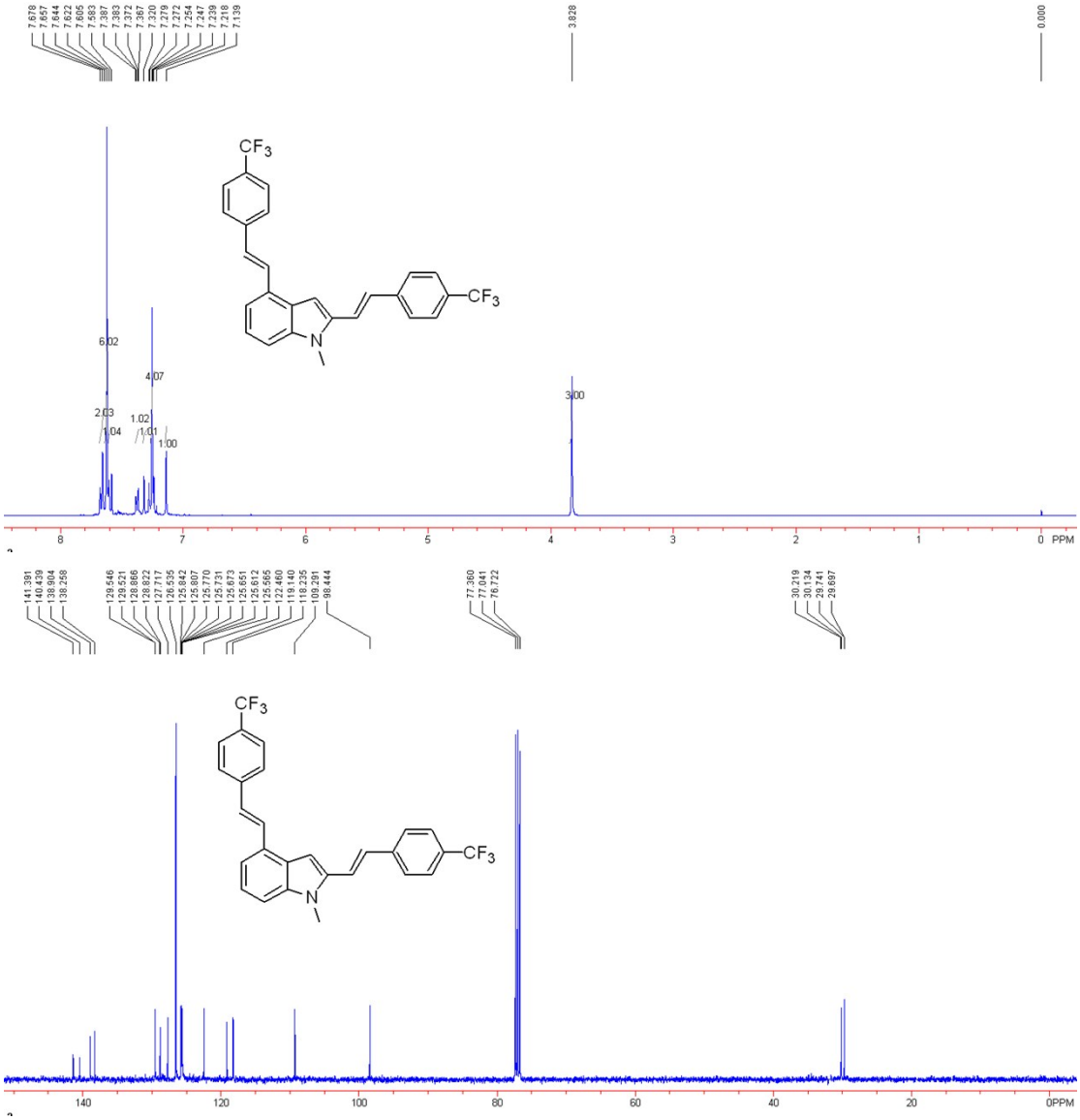


2,4-bis(4-chlorostyryl)-1-methyl-1H-indole (5ac)

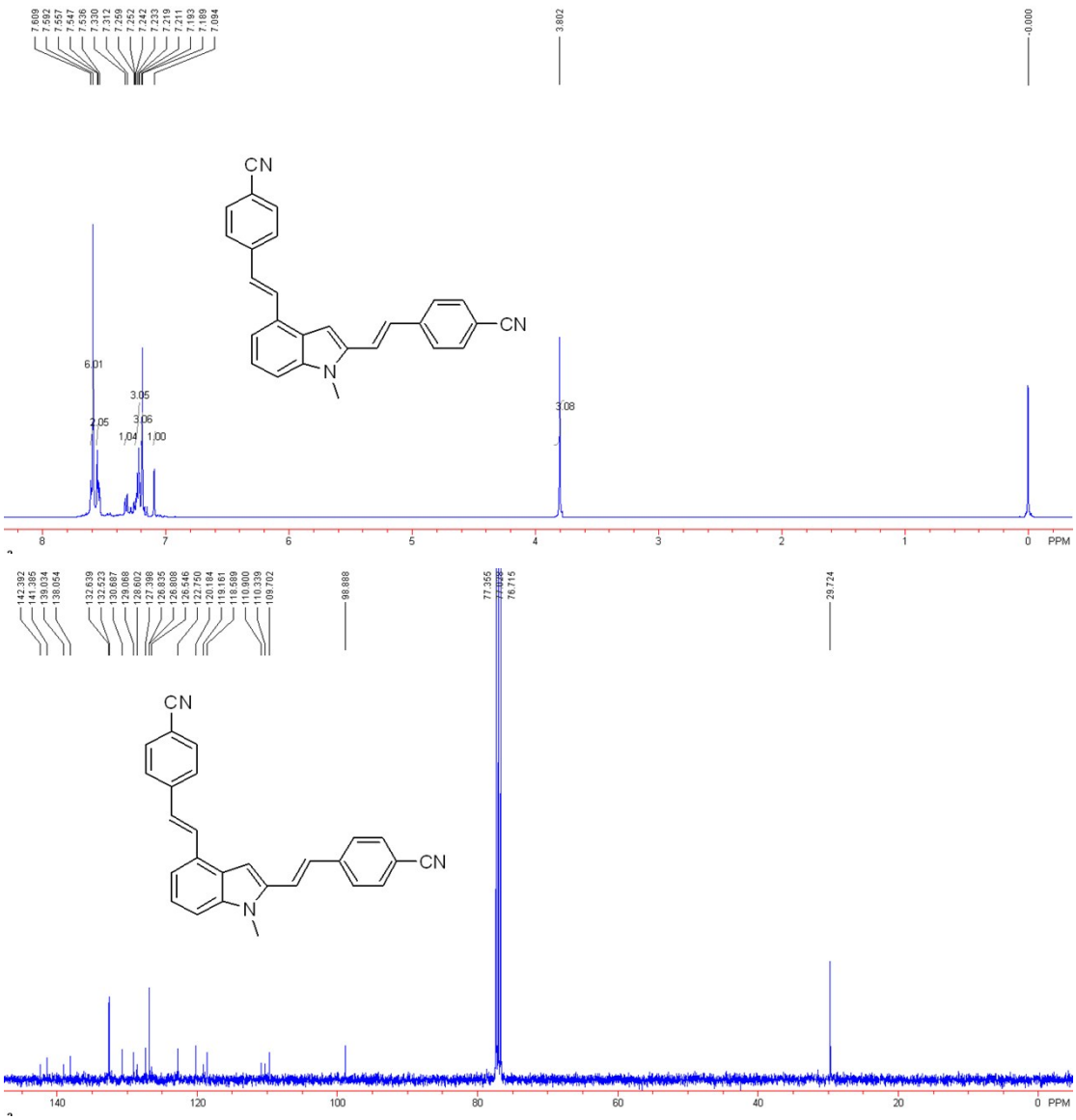




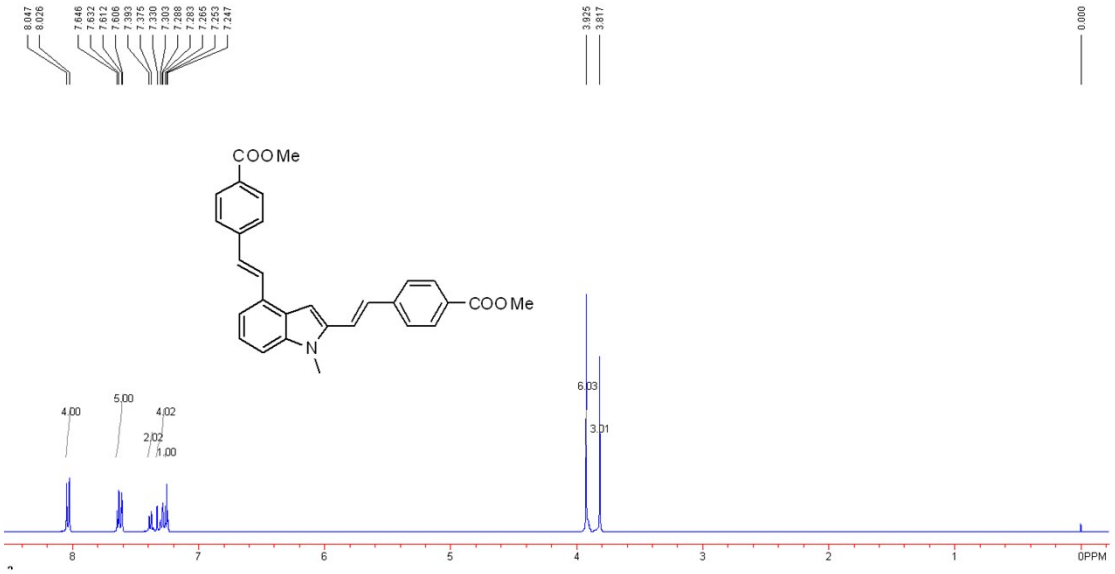
1-methyl-2,4-bis(4-(trifluoromethyl)styryl)-1H-indole (5ad)

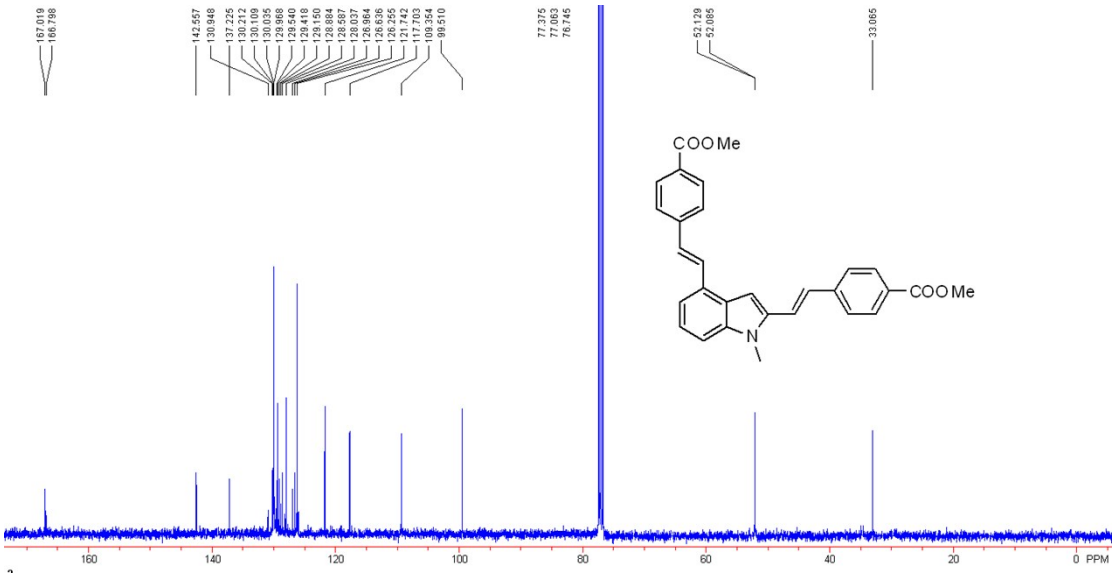


4,4'-(1E,1'E)-2,2'-(1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl)dibenzonitrile (5ae)

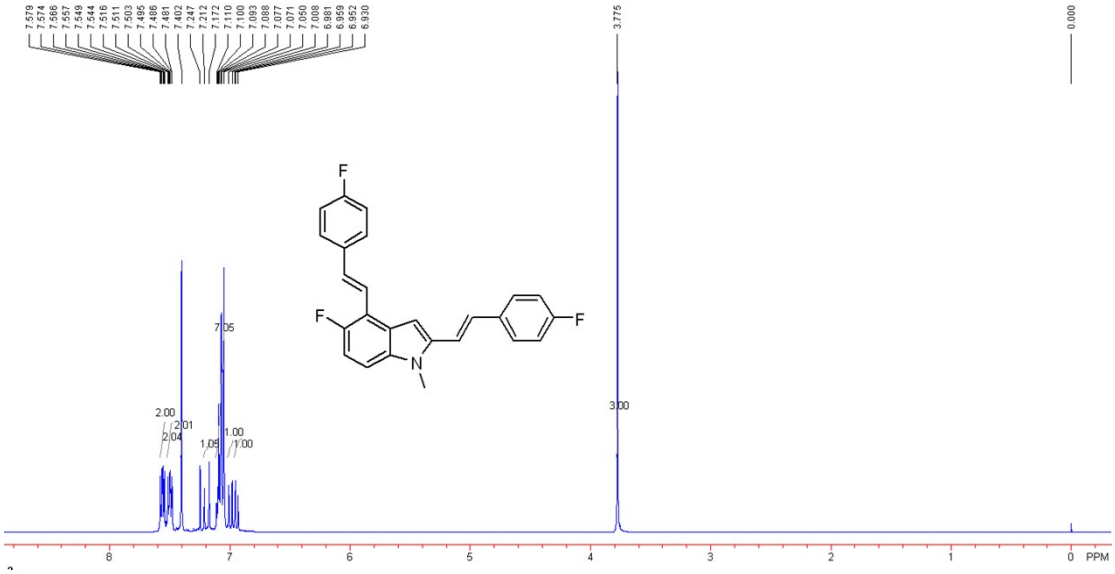


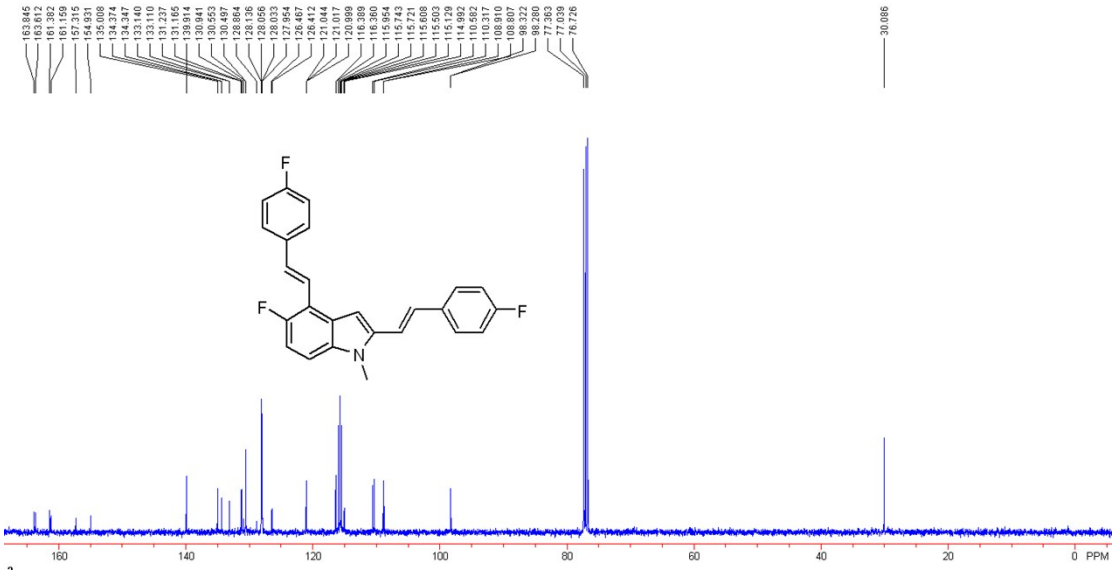
Dimethyl 4,4'-(1E,1'E)-2,2'-(1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl) dibenzoate (5af)



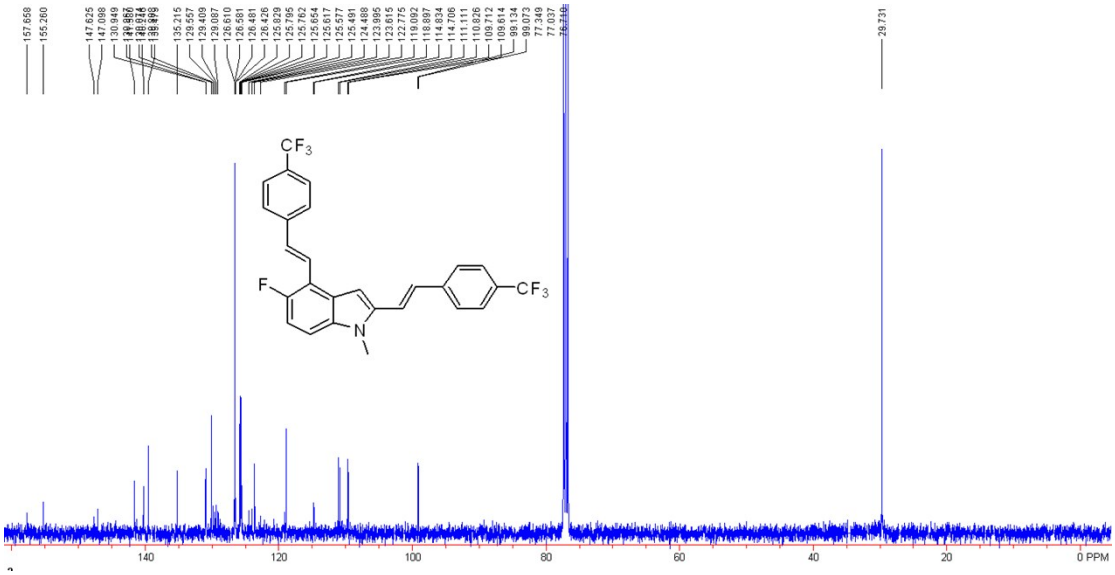


5-fluoro-2,4-bis(4-fluorostyryl)-1-methyl-1H-indole (5eb)

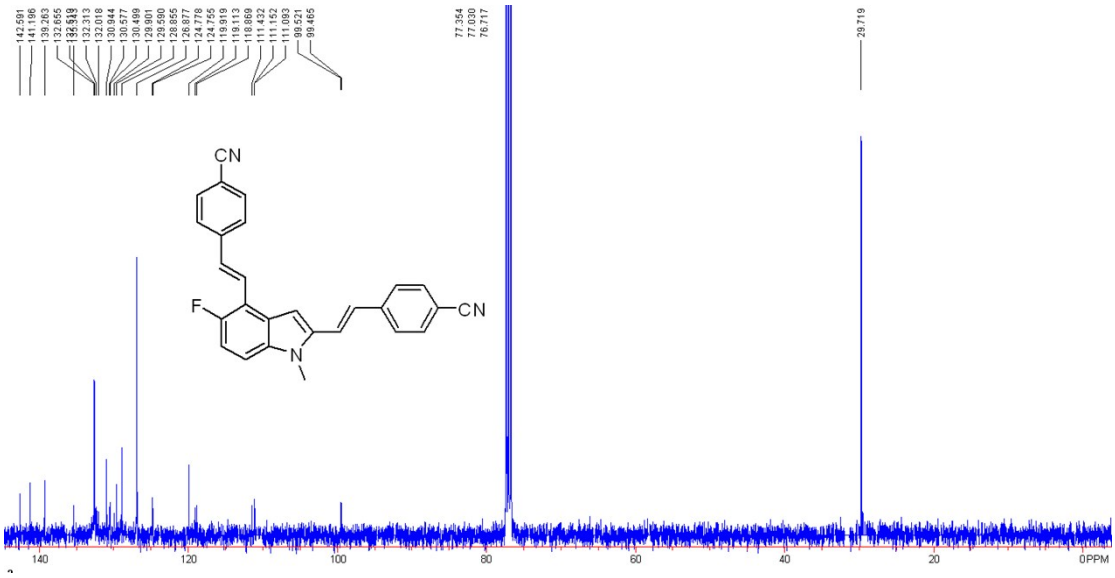




5-fluoro-1-methyl-2,4-bis(4-(trifluoromethyl)styryl)-1H-indole (5ed)

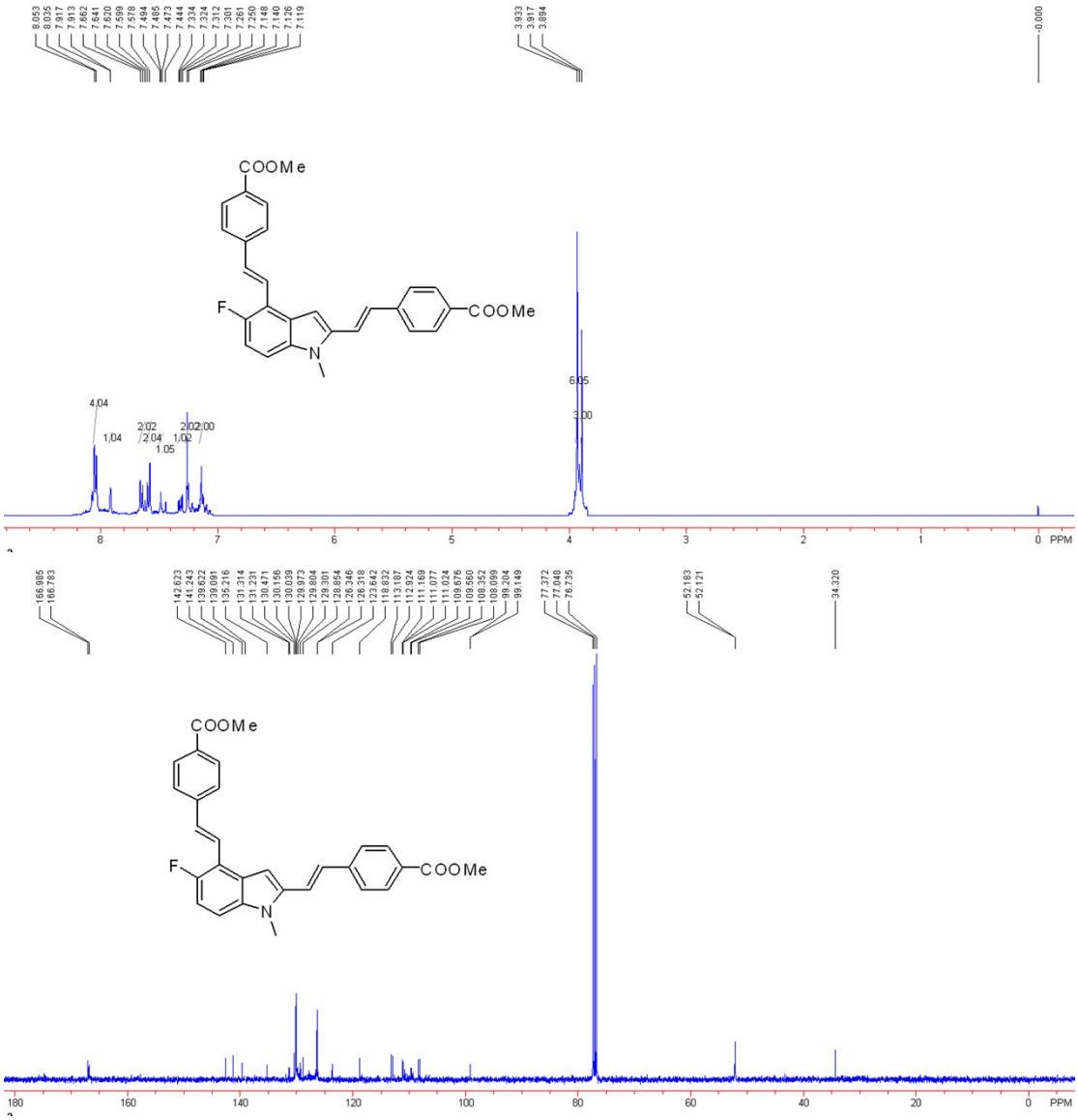


4,4'-(1E,1'E)-2,2'-(5-fluoro-1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl) Dibenzonitrile (5ee)

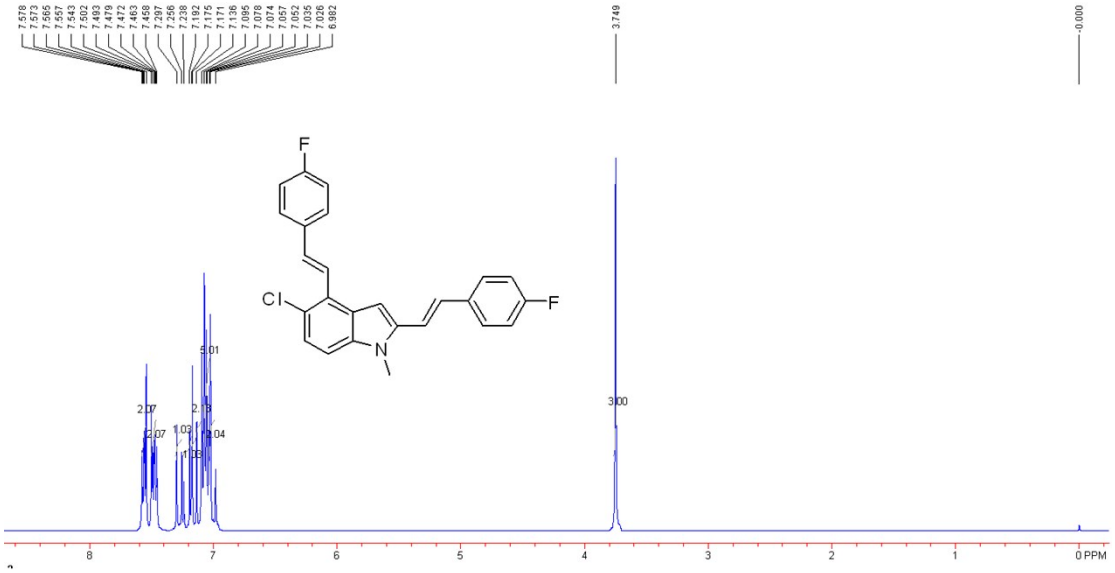


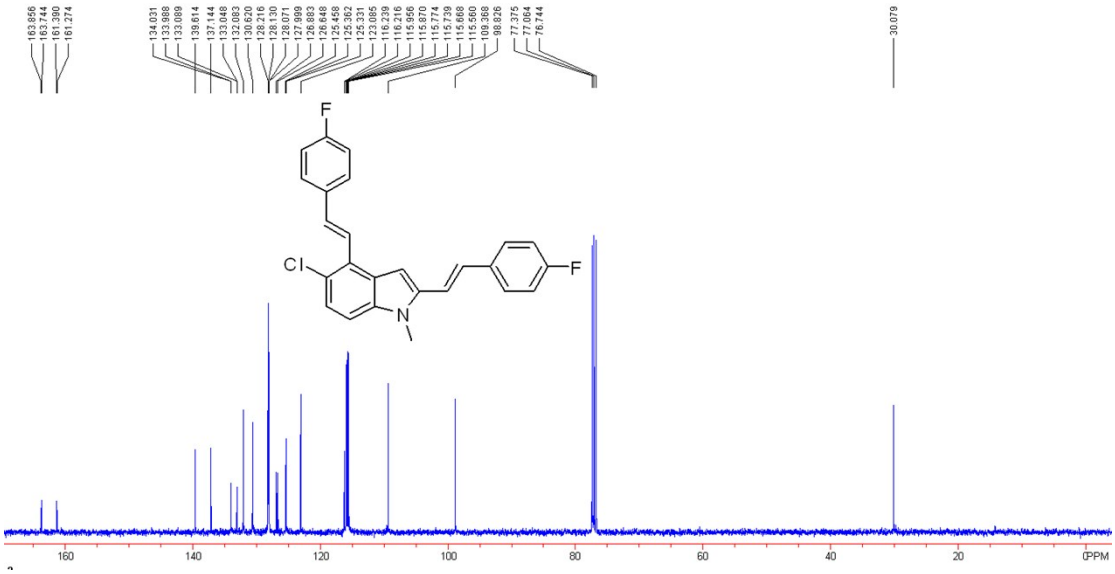
Dimethyl 4,4'-(1E,1'E)-2,2'-(5-fluoro-1-methyl-1H-indole-2,4-diyl)bis-

-(ethene-2,1-diyl)dibenzoate (5ef)

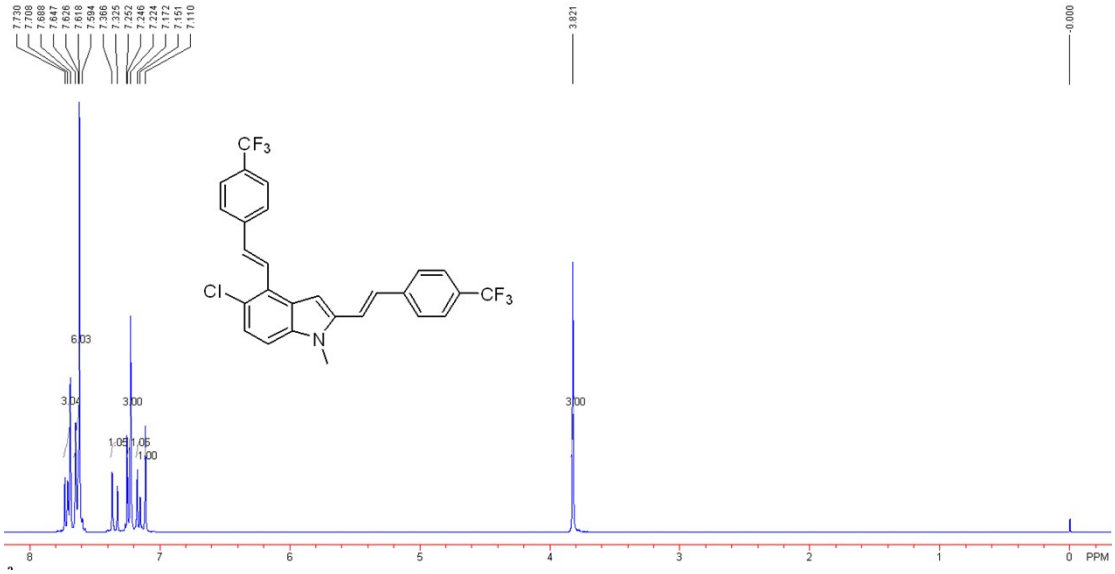


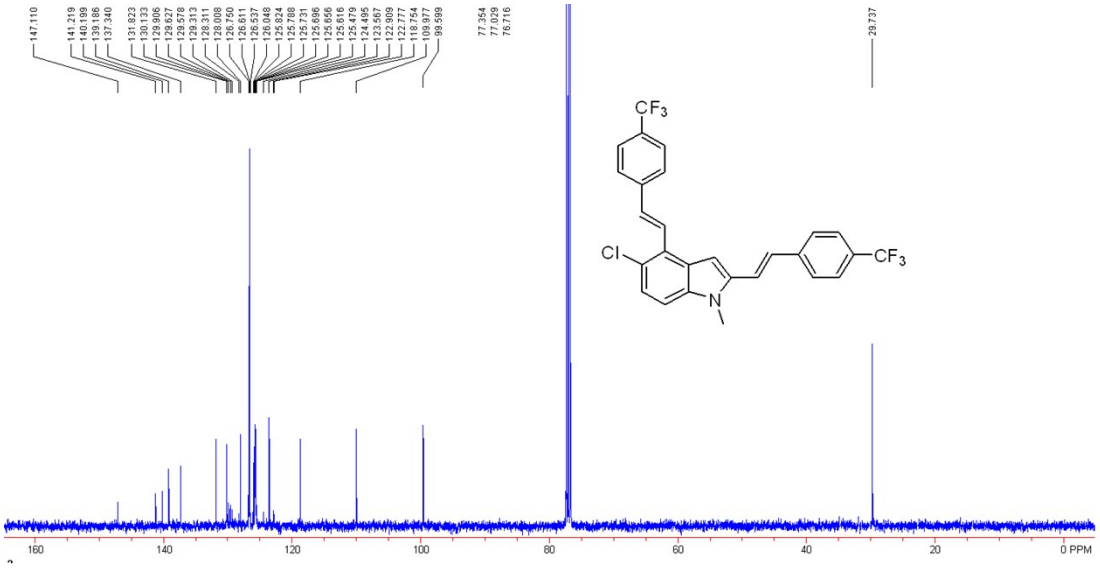
5-chloro-2,4-bis(4-fluorostyryl)-1-methyl-1H-indole (5fb)



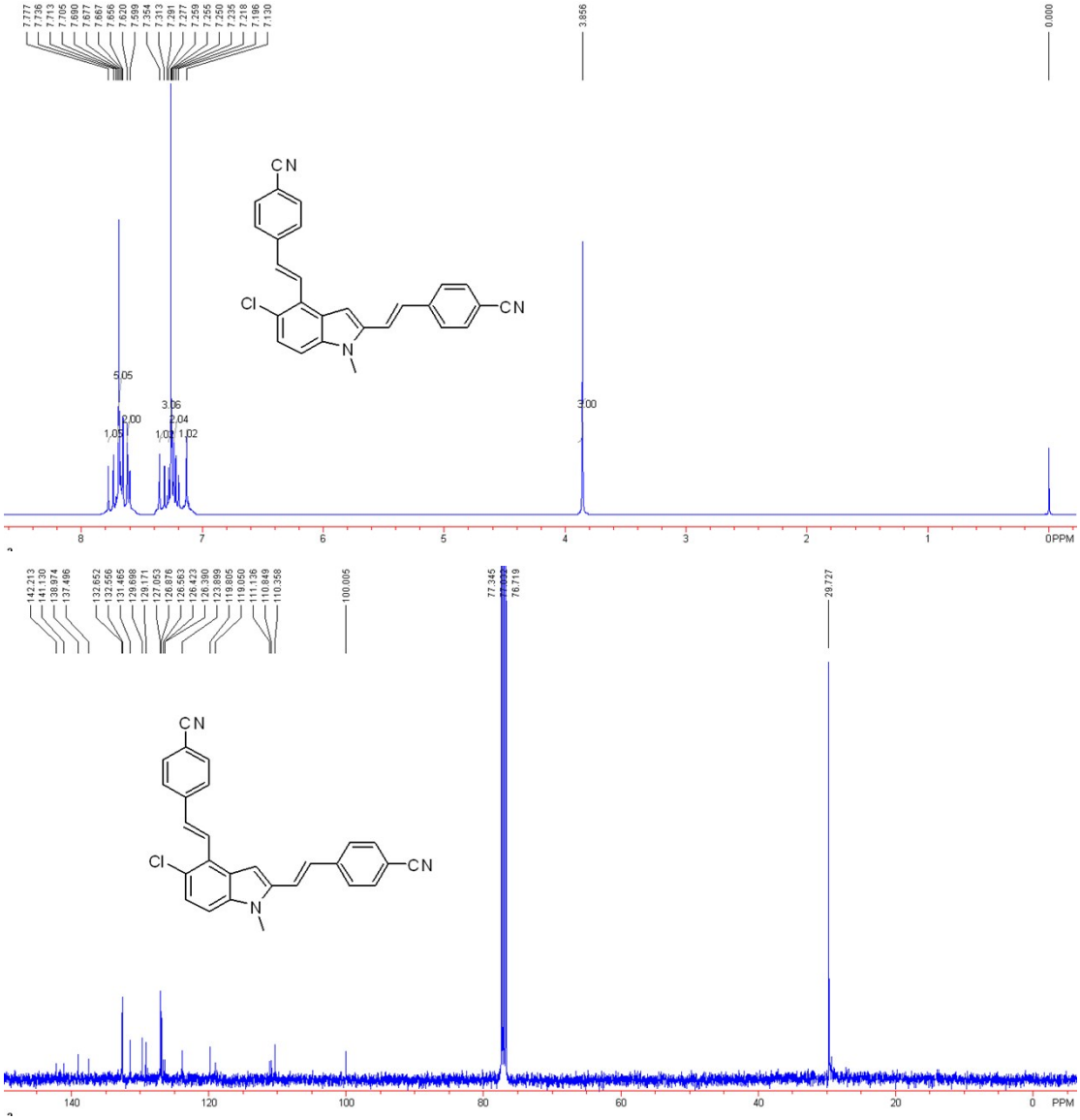


5-chloro-1-methyl-2,4-bis(4-(trifluoromethyl)styryl)-1H-indole (5fd)



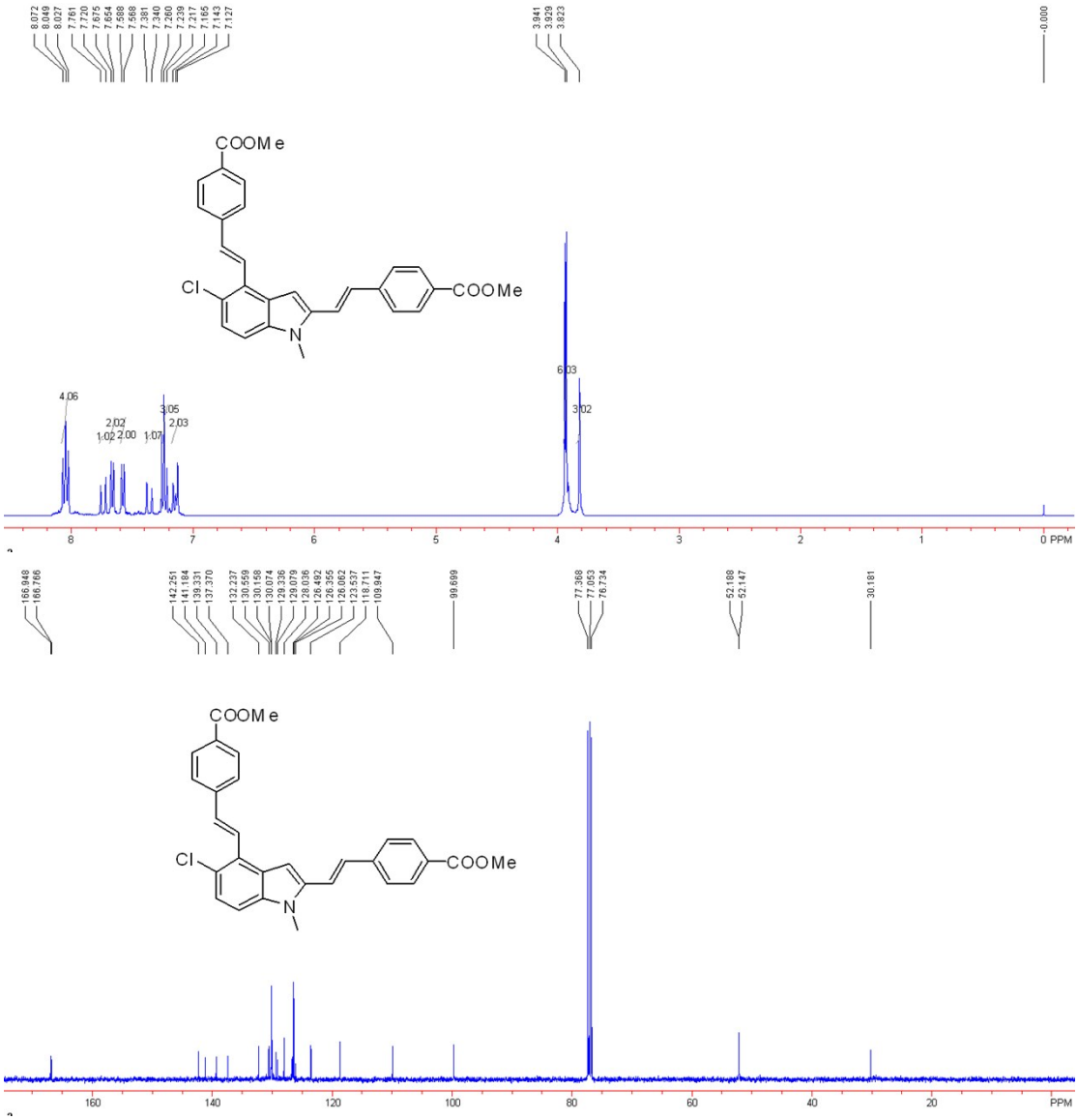


4,4'-(1E,1'E)-2,2'-(5-chloro-1-methyl-1H-indole-2,4-diyl)bis(ethene-2,1-diyl) Dibenzonitrile (5fe)



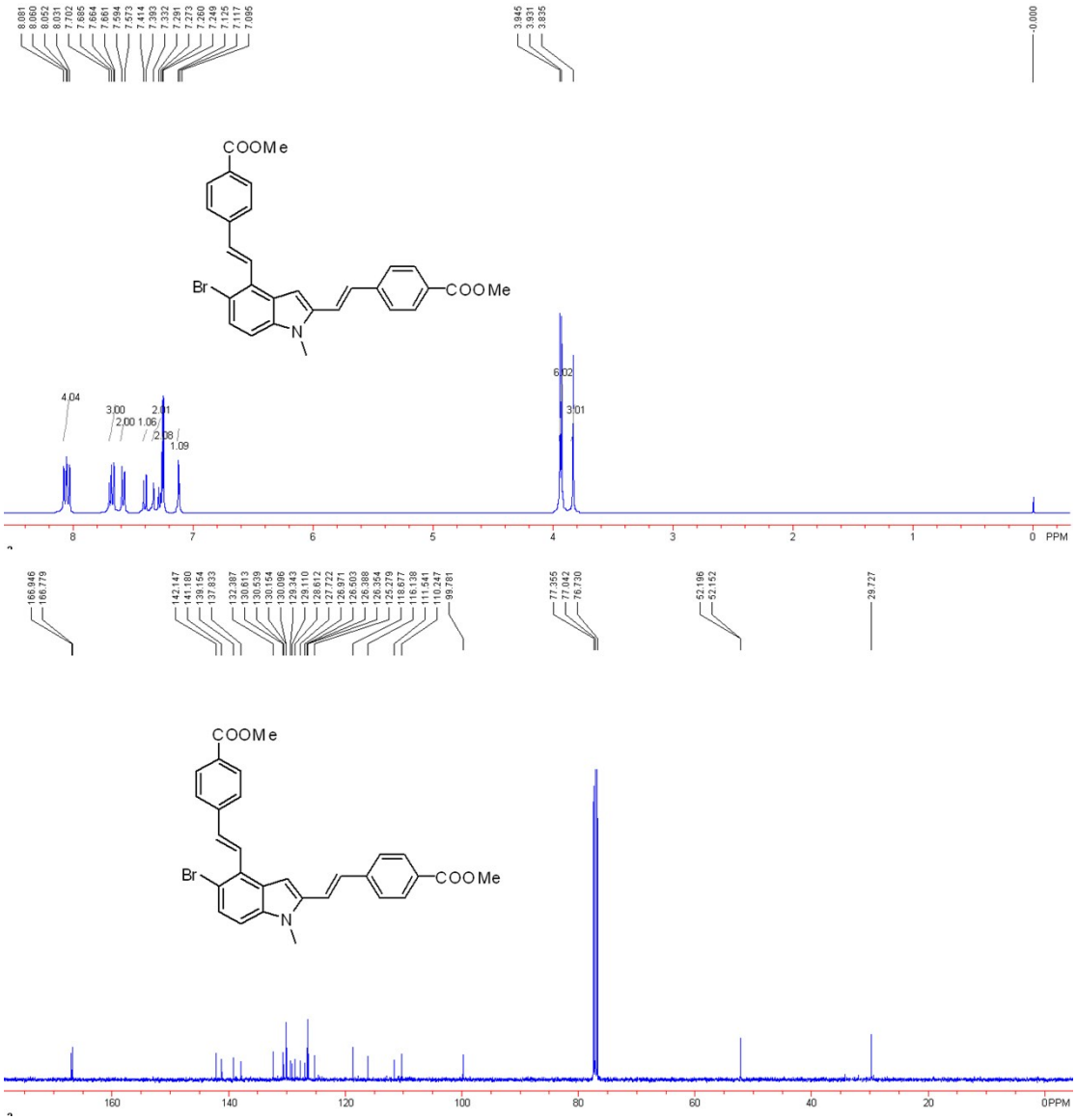
dimethyl 4,4'-(1E,1'E)-2,2'-(5-chloro-1-methyl-1H-indole-2,4-diyl)bis-

-(ethene-2,1-diyl)dibenzoate (5ff)

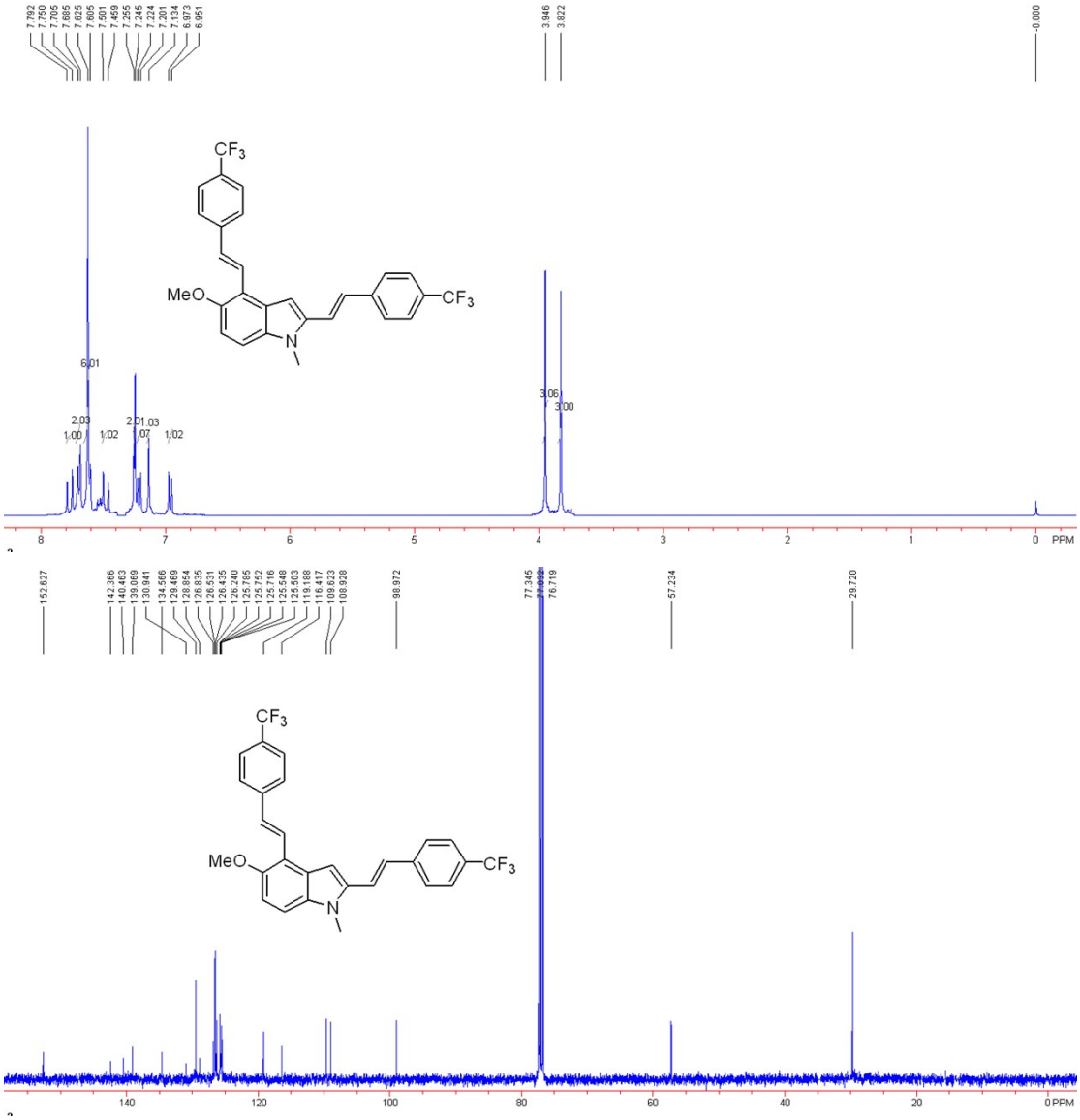


Dimethyl 4,4'-(1E,1'E)-2,2'-(5-bromo-1-methyl-1H-indole-2,4-diyl)bis-

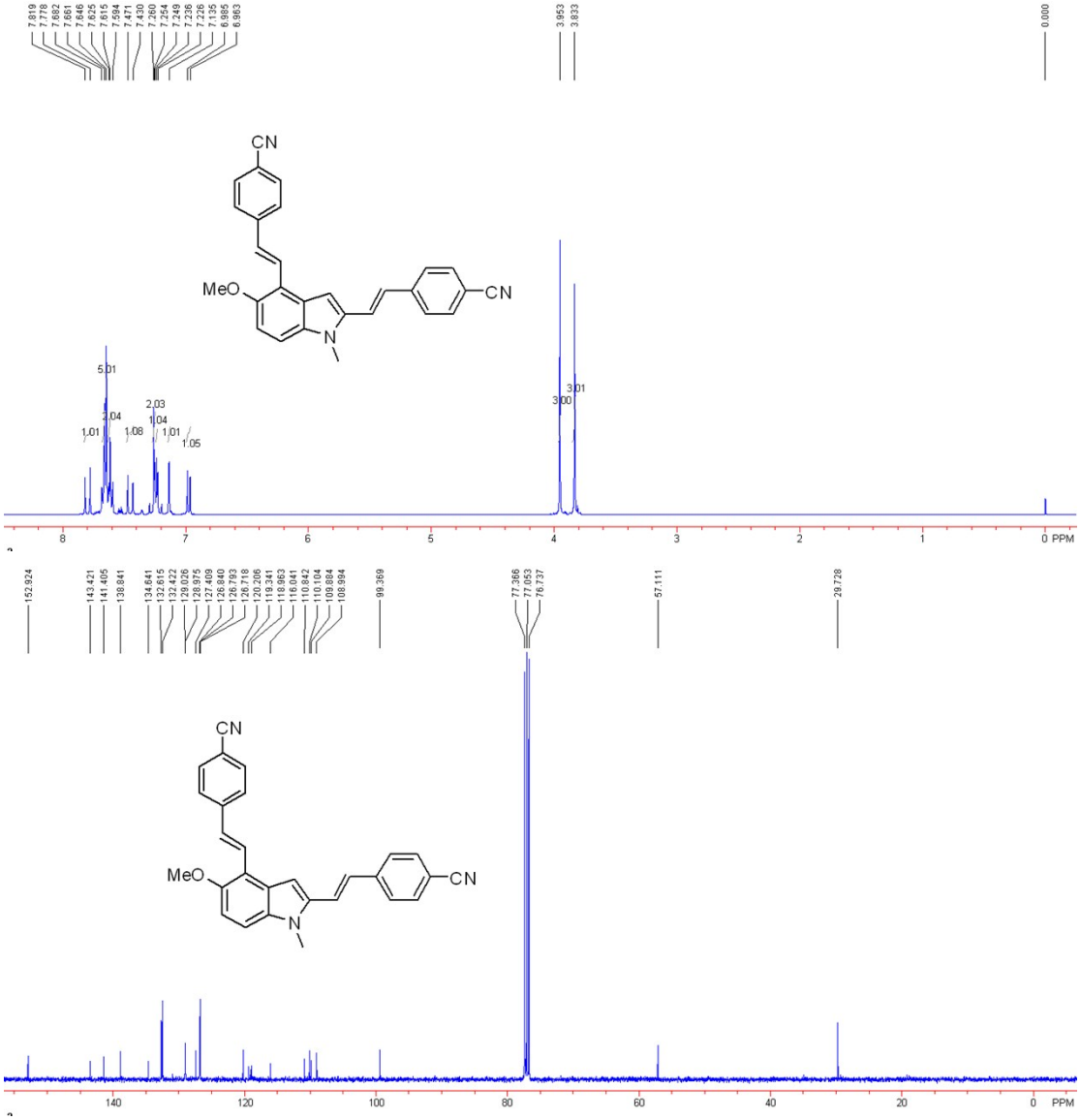
-(ethene-2,1-diyl)dibenzoate (5gf)



5-methoxy-1-methyl-2,3-bis(4-(trifluoromethyl)styryl)-1H-indole (5hd)

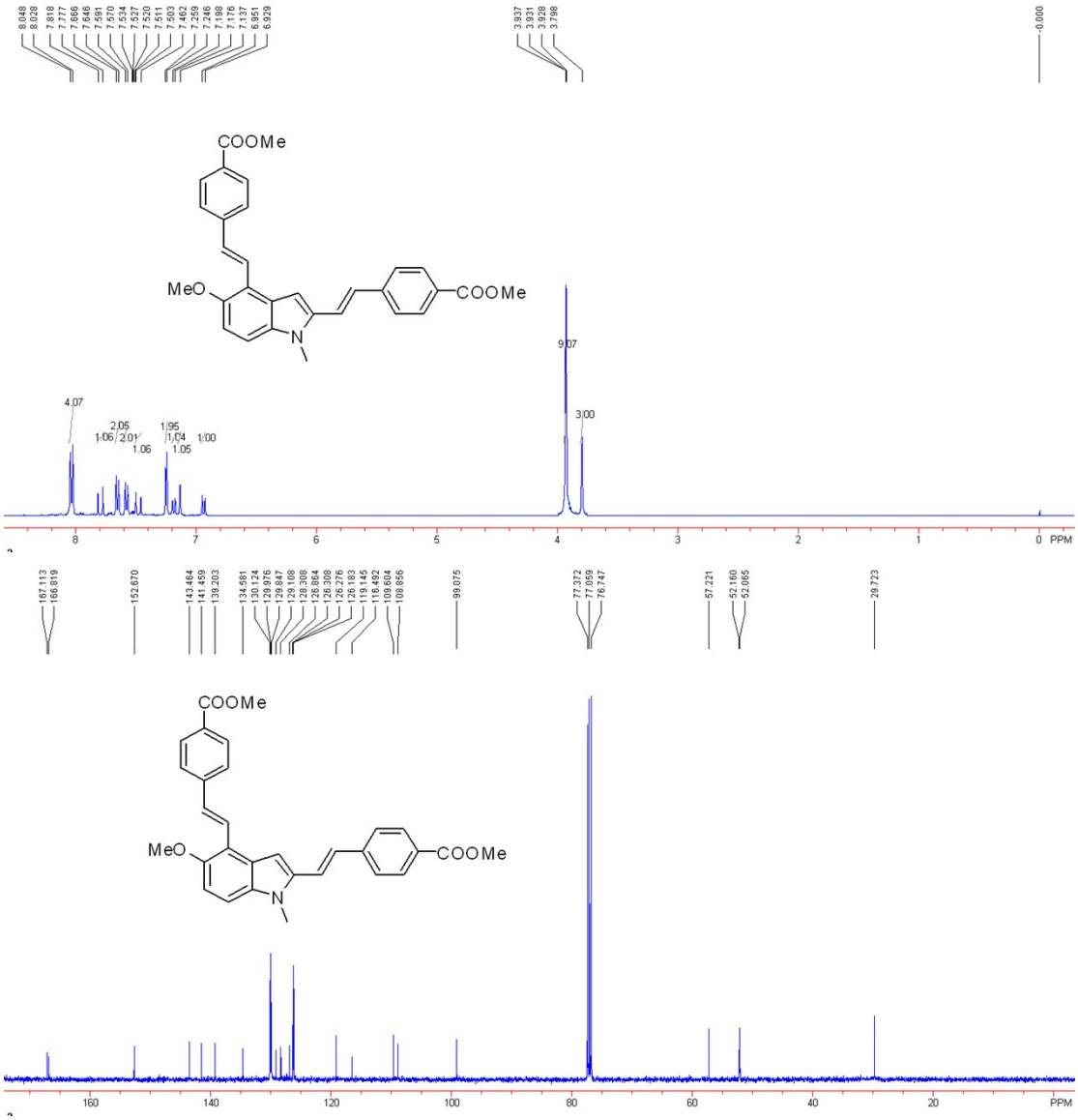


4,4'-(1E,1'E)-2,2'-(5-methoxy-1-methyl-1H-indole-2,3-diyl)bis(ethene-2,1-diyl) dibenzonitrile (5he)



Dimethyl 4,4'-(1E,1'E)-2,2'-(5-methoxy-1-methyl-1H-indole-2,4-diyl)bis-

-(ethene-2,1-diyl)dibenzoate (5hf)



12. Crystal Structures of 3aa