Substrate-controlled [4 + 1] and [3 + 2] annulations of ninhydrin-derived Morita−Baylis−Hillman carbonates to access polysubstituted furans and cyclopentenes

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Supporting Information

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1. General methods

NMR data were obtained for ^{1}H at 400 MHz, and for ^{13}C at 100 MHz, and ^{19}F at 376 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate/petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and ethyl acetate were distilled. THF was freshly distilled from sodium/benzophenone. Unless otherwise noted, experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes. The α-cyano-α,β-unsaturated ketones **1**[1], ninhydrin-derived MBH carbonates **2**[2] and 2-arylidene-1,3-indandiones **4**[3] were prepared according to the literature procedures.

(1) (a) K.-K. Wang, P. Wang, Q. Ouyang, W. Du and Y.-C. Chen, *Chem. Commun.*, **2016**, *52*, 11104. (b) P. K. Amancha, Y.-C. Lai, I.-C. Chen, H.-J. Liu and J.-L. Zhu, *Tetrahedron*, **2010**, *66*, 871; (c) W. Liu, J. Zhou, C. Zheng, X. Chen, H. Xiao, Y. Yang, Y. Guo and G. Zhao, *Tetrahedron*, **2011**, *67*, 1768. (d) K.-K. Wang, J. Jing, W.-W. Zhou, C. Wang, J.-W. Ye, R. Zhou, T.-T. Wang, Z.-Y. Wang, R. Chen, *J. Org. Chem.* **2023**, *88*, 5982.

(2) (a) Z. Lu, Y. Jia, X. Chen, P. Li, *J. Org. Chem.* **2022**, *87*, 3184. (b) K.-K. Wang, Y.-L. Li, J. Jing, R. Chen, N.-N. Zhao, Z.-H. Li, M.-Y. Wang, S.-K. Ji, *Org. Biomol. Chem.* **2022**, *20*, 6923. (c) X. Tang, Y. Wu, J. Jiang, H. Fang, W.-J. Zhou, W. Huang, G. Zhan, *Org. Lett.* **2021**, *23*, 8937. (d) K.-K. Wang, W. Zhou, J. Jia, J. Ye, M. Yuan, J. Yang, Y. Qi, R. Chen, *Molecules* **2023**, *28*, 6761; (d) K.-K. Wang, J.-W. Ye, J. Jia, Y.-F. Li, W.-W. Yao, L.-X. Li, S.-M. Zhao, Y. Xu, R. Chen, *Tetrahedron* **2024**, *150*, 133772.

(3) (a) F. Li, Z. Li, Y. Wang, Z. Zhou, *Synthesis* **2023**, *55*, 1427; (b) S. Mahajan, P. Chauhan, M. Blümel, R. Puttreddy, K. Rissanen, G. Raabe, D. Enders, *Synthesis* **2016**, *48*, 1131; (c) G. Zhan, M. L. Shi, Q. He, W. J. Lin, Q. Ouyang, W. Du, Y. C. Chen, *Angew. Chem., Int. Ed.* **2016**, *55*, 2147.

2. Optimization of reaction conditions

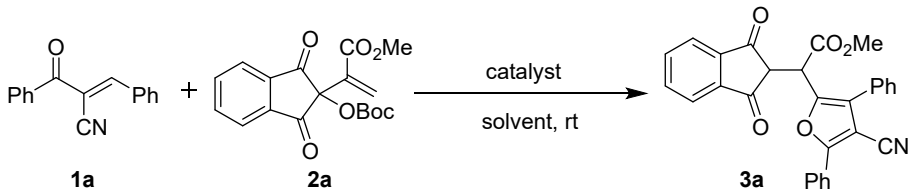


Table 1 Optimization of reaction conditions [a]

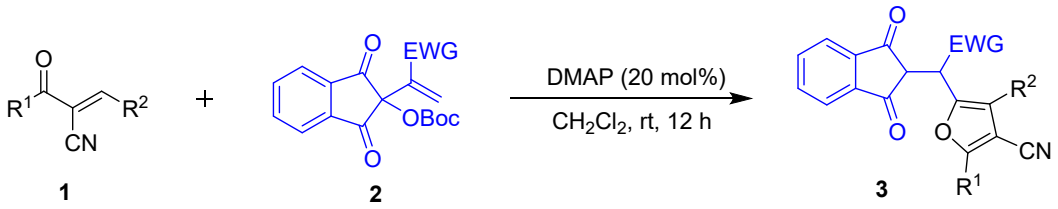
Entry	Catalyst	Solvent	Time	Yield of **3a** (%)[b]
1	DABCO	$CHCl_3$	24	62
2	Quinine	$CHCl_3$	24	56

3	DMAP	$CHCl_3$	12	81
4	PPh_3	$CHCl_3$	24	0
5	*n*-Bu_3P	$CHCl_3$	24	0
6	**DMAP**	**CH_2Cl_2**	**12**	**90**
7	DMAP	DCE	12	80
8	DMAP	EtOAc	24	71
9	DMAP	CH_3CN	24	66
10	DMAP	toluene	24	57
11	DMAP	THF	24	46
12	DMAP	dioxane	24	41
13	DMAP	Et_2O	24	35
14[c]	DMAP	CH_2Cl_2	24	72
15[d]	DMAP	CH_2Cl_2	12	87

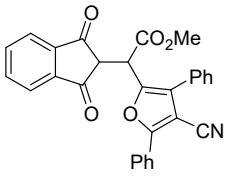
[a]Reaction conditions: **1a** (0.1 mmol), MBH carbonate **2a** (0.12 mmol), catalyst (20 mol%) and solvent (1.0 mL) at room temperature. [b]Isolated Yield. [c]10 mol% of catalyst. [d]at 40 °C.

At the outset, the α-cyano-chalcone **1a** and ninhydrin-derived MBH carbonate **2a** were chosen as the model substrates to optimize the reaction conditions. The results were summarized in Table 1. Gratifyingly, the model reaction could proceed smoothly in the presence of DABCO catalyst at room temperature, to furnish an unprecedented product **3a** with dense substitutions after 24 h in 62% yield via α-regioselective [4 + 1] annulation and rearrangement reaction (in Table 1, entry 1). Furthermore, the structure of **3a** was unambiguously established by the single-crystal X-ray diffraction analysis (in Table 2, CCDC 2311771).[14] Encouraged by this preliminary result, we screened the reaction in detail under a variety of conditions to further improve the yield of the α-regioselective [4 + 1] annulation reaction. The screening of catalysts revealed DMAP as the preferred one to produce polysubstituted furan **3a** in 81% yield (in Table 1, entries 2−5). Moreover, no desired product was detected when switching the tertiary amines to phosphine catalysts (in Table 1, entries 4−5). Subsequently, we further explored the effect of solvents for this reaction. The reaults indicated that CH_2Cl_2 was the most suitable solvent to give product **3a** in 90% yield (in Table 1, entry 6). Compared with other solvents, such as $CHCl_3$, DCE, EtOAc, CH_3CN, toluene, THF, dioxane and Et_2O, none of them revealed better effectiveness than CH_2Cl_2 in this reaction (in Table 1, entries 3 and 7-13). Nevertheless, when the catalyst loading was decreased to 10 mol %, the reaction provided to a lower yield (72% yield) even if further prolonging reaction time (in Table 1, entry 14). In addition, the reaction supplied the target product in slightly lower chemical yield (87% yield) when further increasing in the reaction temperature (in Table 1, entry 15). Thus, the optimal reaction conditions were determined as follows: using CH_2Cl_2 as the solvent and 0.2 equivalents DMAP as the catalyst at ambient temperature for 12 h (in Table 1, entry 6).

3. General procedure for [4 + 1] annulations of α-cyano-α,β-unsaturated ketones 1 with ninhydrin-derived MBH carbonates 2

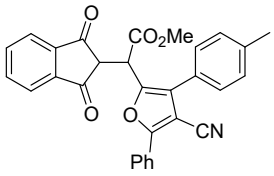


The α-cyano-α,β-unsaturated ketones **1** (0.1 mmol, 1.0 equiv), ninhydrin-derived MBH carbonates **2** (0.12 mmol, 1.2 equiv) and CH_2Cl_2 (1.0 mL) were added to a dry flask at room temperature, and then DMAP (20 mol%) was added to the above solution. This solution was stirred at room temperature for 12 h until the complete consumption of the starting materials monitored by TLC. After the removal of the solvent, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 to 2:1) to afford products **3**.



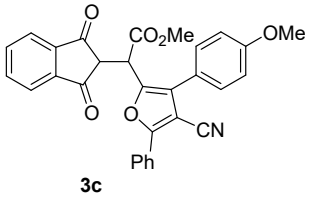
3a

3a, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (41.5 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 6.8 Hz, 1H), 7.85 – 7.83 (m, 4H), 7.52 – 7.49 (m, 4H), 7.45 – 7.40 (m, 4H), 4.80 (d, *J* = 4.4 Hz, 1H), 3.83 (d, *J* = 4.4 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 196.5, 169.2, 159.3, 144.4, 142.1, 141.8, 135.9, 135.8, 130.2, 129.2, 129.0, 128.9, 128.8, 127.7, 127.3, 125.4, 123.5, 123.4, 114.5, 93.7, 54.1, 53.2, 41.1 ppm. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{29}H_{20}NO_5$ 462.1336, found 462.1331.



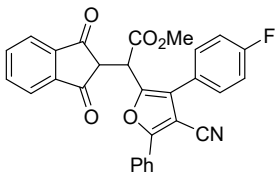
3b

3b, Purification by flash chromatography (PE/EA = 3:1) gave a faint yellow solid (42.3 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 1H), 7.97 – 7.80 (m, 1H), 7.84 – 7.80 (m, 4H), 7.42 – 7.39 (m, 5H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.80 (d, *J* = 4.0 Hz, 1H), 3.82 (d, *J* = 4.4 Hz, 1H), 3.70 (s, 3H), 2.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 196.5, 169.3, 159.1, 144.2, 142.1, 141.8, 138.8, 135.9, 135.8, 130.2, 129.9, 128.9, 128.6, 127.7, 127.3, 125.9, 125.4, 123.5, 123.3, 114.6, 93.7, 54.1, 53.2, 41.1, 21.3 ppm. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{30}H_{22}NO_5$ 476.1492, found 476.1486.



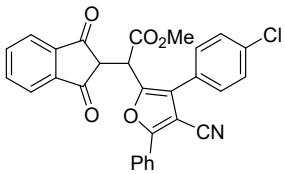
3c

3c, Purification by flash chromatography (PE/EA = 2:1) gave a yellow solid (41.7 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 6.4 Hz, 1H), 7.83 (d, *J* = 5.2 Hz, 4H), 7.46 – 7.39 (m, 5H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.78 (d, *J* = 4.0 Hz, 1H), 3.86 (s, 3H), 3.83 (d, *J* = 4.0 Hz, 1H), 3.71 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 196.6, 169.3, 160.0, 159.1, 144.0, 142.1, 141.9, 135.9, 135.8, 130.2, 130.0, 129.0, 127.8, 127.1, 125.4, 123.5, 123.4, 121.1, 114.7, 93.8, 55.4, 54.1, 53.2, 41.1 ppm. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{30}H_{22}NO_6$ 492.1442, found 492.1439.



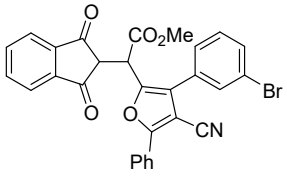
3d

3d, Purification by flash chromatography (PE/EA = 3:1) gave a faint yellow solid (41.2 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.81 (m, 4H), 7.51 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.40 (d, *J* = 5.6 Hz, 3H), 7.20 (t, *J* = 8.4 Hz, 2H), 4.73 (d, *J* = 4.4 Hz, 1H), 3.86 (d, *J* = 4.4 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 196.5, 169.1, 163.31 (d, *J* = 247.6 Hz), 159.3, 144.4, 142.0, 141.8, 136.0, 135.9, 130.8, 130.7, 130.4, 129.0, 127.6, 126.4, 125.4, 125.0 (d, *J* = 3.2 Hz), 123.6, 123.4, 116.3 (d, *J* = 21.7 Hz), 114.4, 93.7, 54.0, 53.3, 41.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.1 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{19}FNO_5$ 480.1242, found 480.1236.



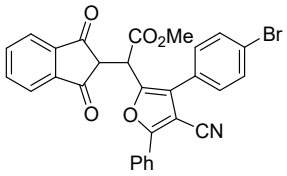
3e

3e, Purification by flash chromatography (PE/EA = 3:1) gave a faint yellow solid (43.6 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 6.8 Hz, 1H), 7.87 – 7.81 (m, 4H), 7.50 – 7.45 (m, 4H), 7.40 (d, *J* = 5.2 Hz, 3H), 4.73 (d, *J* = 4.0 Hz, 1H), 3.86 (d, *J* = 4.0 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.52, 196.46, 169.0, 159.4, 144.5, 142.0, 141.8, 136.0, 135.9, 135.1, 130.4, 130.1, 129.5, 129.0, 127.5, 127.4, 126.3, 125.4, 123.6, 123.4, 114.3, 93.5, 54.0, 53.3, 41.0 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{19}ClNO_5$ 496.0946, found 496.0942.



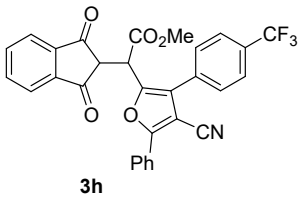
3f

3f, Purification by flash chromatography (PE/EA = 4:1) gave a yellow solid (46.9 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 1H), 7.98 (d, *J* = 6.8 Hz, 1H), 7.88 – 7.81 (m, 4H), 7.68 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.37 (m, 4H), 4.73 (d, *J* = 4.4 Hz, 1H), 3.87 (d, *J* = 4.4 Hz, 1H), 3.72 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 196.4, 168.9, 159.4, 144.7, 142.0, 141.8, 136.0, 135.9, 132.0, 131.7, 131.0, 130.7, 130.4, 129.0, 127.5, 127.4, 125.9, 125.4, 123.6, 123.4, 123.1, 114.1, 93.4, 54.0, 53.3, 41.0 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{19}BrNO_5$ 540.0441 (^{79}Br) and 542.0421 (^{81}Br), found 540.0437, 542.0416.



3g

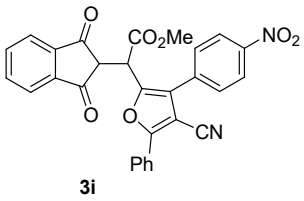
3g, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (45.8 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 6.8 Hz, 1H), 7.86 – 7.81 (m, 4H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 6.4 Hz, 5H), 4.73 (d, *J* = 4.0 Hz, 1H), 3.86 (d, *J* = 4.0 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.51, 196.45, 169.0, 159.5, 144.5, 142.0, 141.8, 136.0, 135.9, 132.5, 130.4, 129.0, 127.9, 127.5, 126.3, 125.4, 123.6, 123.4, 123.3, 114.3, 93.4, 54.0, 53.3, 41.0 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{19}BrNO_5$ 540.0441 (^{79}Br) and 542.0421 (^{81}Br), found 540.0436, 542.0417.



3h

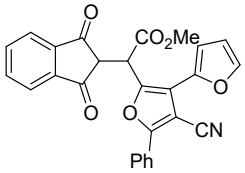
3h, Purification by flash chromatography (PE/EA = 3:1) gave a white solid (43.9 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.8 Hz, 1H), 7.98 (d, *J* = 6.4 Hz, 1H), 7.89 – 7.82 (m, 4H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 4.4 Hz, 3H), 4.73 (d, *J* = 4.4 Hz, 1H), 3.88 (d, *J* = 4.4 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 196.4, 168.8, 159.7, 144.9, 142.0, 141.8, 136.03, 135.97, 132.7, 131.0 (q, *J* = 32.6 Hz), 130.5, 129.2, 129.1, 127.4, 126.2 (q, *J* = 3.7 Hz), 126.1, 125.5,

123.9 (q, J = 271.9 Hz)123.6, 123.5, 114.1, 93.3, 54.0, 53.3, 41.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{19}F_3NO_5$ 530.1210, found 530.1207.



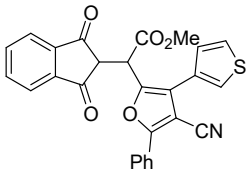
3i

3i, Purification by flash chromatography (PE/EA = 3:1) gave a white solid (43.0 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 7.6 Hz, 2H), 8.05 (d, J = 6.4 Hz, 1H), 7.98 (d, J = 6.4 Hz, 1H), 7.88 – 7.82 (m, 4H), 7.75 (d, J = 8.0 Hz, 2H), 7.42 (s, 3H), 4.72 (d, J = 3.2 Hz, 1H), 3.93 (d, J = 3.2 Hz, 1H), 3.72 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 196.2, 168.6, 159.9, 148.0, 145.3, 141.9, 141.8, 136.09, 136.07, 135.7, 130.7, 129.8, 129.1, 127.1, 125.5, 125.4, 124.4, 123.6, 123.5, 113.9, 93.1, 54.0, 53.4, 41.0 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{19}N_2O_7$ 507.1187, found 507.1180.



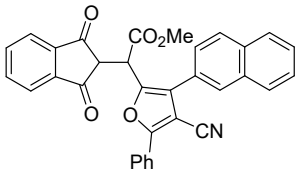
3j

3j, Purification by flash chromatography (PE/EA = 2:1) gave a yellow solid (35.2 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 6.4 Hz, 1H), 7.99 – 7.97 (m, 1H), 7.89 – 7.83 (m, 2H), 7.79 – 7.77 (m, 2H), 7.55 (s, 1H), 7.40 – 7.39 (m, 3H), 7.00 (d, J = 3.2 Hz, 1H), 6.54 (d, J = 0.8 Hz, 1H), 5.37 (d, J = 4.0 Hz, 1H), 3.83 (d, J = 4.0 Hz, 1H), 3.73 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 196.6, 169.3, 159.7, 144.1, 144.0, 142.9, 142.2, 141.8, 135.8, 135.7, 130.4, 129.0, 127.4, 125.5, 123.5, 123.4, 117.0, 114.5, 111.7, 109.0, 90.5, 54.2, 53.2, 42.3 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{18}NO_6$ 452.1129, found 452.1126.



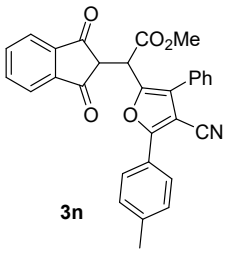
3k

3k, Purification by flash chromatography (PE/EA = 3:1) gave a faint yellow solid (37.8 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 1H), 7.98 – 7.96 (m, 1H), 7.87 – 7.83 (m, 4H), 7.61 (d, J = 1.6 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.43 – 7.36 (m, 4H), 4.85 (d, J = 4.0 Hz, 1H), 3.86 (d, J = 4.4 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.62, 196.58, 169.1, 159.2, 144.3, 142.0, 141.8, 135.9, 135.8, 130.3, 129.0, 128.9, 127.6, 127.3, 127.0, 125.4, 124.5, 123.5, 123.4, 122.4, 114.6, 93.3, 54.0, 53.2, 41.3 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{18}NO_5S$ 468.0900, found 468.0897.



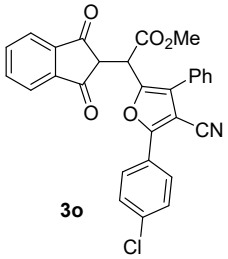
3l

3l, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (40.9 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 5H), 7.90 – 7.82 (m, 5H), 7.63 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 3.2 Hz, 2H), 7.44 – 7.41 (m, 3H), 4.87 (d, J = 4.0 Hz, 1H), 3.87 (d, J = 4.4 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 169.2, 159.4, 144.7, 142.1, 141.9, 135.9, 135.8, 133.4, 133.2, 130.3, 129.1, 129.0, 128.4, 128.3, 127.8, 127.7, 127.4, 126.9, 126.7, 126.4, 126.1, 125.5, 123.6, 123.4, 114.6, 93.8, 54.1, 53.3, 41.2 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{33}H_{22}NO_5$ 512.1492, found 512.1490.



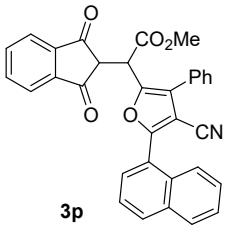
3n

3n, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (41.8 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 6.4 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.44 (m, 5H), 7.20 (d, *J* = 7.6 Hz, 2H), 4.79 (d, *J* = 4.0 Hz, 1H), 3.84 (d, *J* = 4.0 Hz, 1H), 3.69 (s, 3H), 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 196.6, 169.3, 159.6, 143.9, 142.0, 141.9, 140.7, 135.9, 135.8, 129.7, 129.2, 129.1, 128.81, 128.78, 127.2, 125.4, 125.0, 123.5, 123.4, 114.7, 92.9, 54.1, 53.2, 41.1, 21.5 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{30}H_{22}NO_5$ 476.1492, found 476.1488.



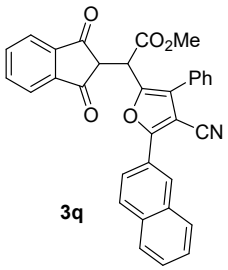
3o

3o, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (42.6 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 5.6 Hz, 1H), 7.97 (d, *J* = 5.2 Hz, 1H), 7.85 (d, *J* = 4.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 2.8 Hz, 4H), 7.45 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 4.80 (d, *J* = 3.6 Hz, 1H), 3.82 (d, *J* = 2.8 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 196.5, 169.1, 158.1, 144.7, 142.0, 141.8, 136.2, 136.0, 135.9, 129.32, 129.26, 129.0, 128.7, 127.5, 126.6, 126.2, 123.6, 123.4, 114.3, 94.0, 54.1, 53.3, 41.1 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{19}ClNO_5$ 496.0946, found 496.0941.



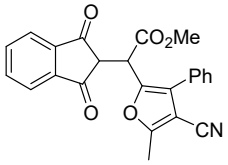
3p

3p, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (42.4 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.15 (m, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.90 – 7.85 (m, 2H), 7.81 – 7.73 (m, 3H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.54 – 7.49 (m, 5H), 7.44 (t, *J* = 7.2 Hz, 1H), 4.84 (d, *J* = 4.8 Hz, 1H), 3.85 (d, *J* = 5.2 Hz, 1H), 3.71 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 196.4, 169.2, 160.9, 145.3, 142.0, 141.8, 135.8, 135.7, 133.8, 131.4, 130.5, 129.2, 129.1, 128.9, 128.6, 127.4, 126.8, 126.5, 125.4, 125.1, 124.8, 123.5, 123.4, 114.0, 97.7, 54.0, 53.2, 41.5 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{33}H_{22}NO_5$ 512.1492, found 512.1489.



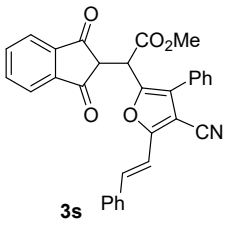
3q

3q, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (43.4 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.08 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 6.8 Hz, 1H), 7.93 – 7.79 (m, 6H), 7.57 – 7.51 (m, 6H), 7.46 (t, *J* = 6.8 Hz, 1H), 4.83 (d, *J* = 3.6 Hz, 1H), 3.89 (d, *J* = 3.6 Hz, 1H), 3.72 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 196.6, 169.3, 159.3, 144.5, 142.1, 141.9, 136.0, 135.9, 133.8, 132.9, 129.2, 129.0, 128.92, 128.87, 128.8, 127.8, 127.6, 127.5, 127.0, 125.4, 125.0, 123.6, 123.4, 122.1, 114.7, 93.9, 54.1, 53.3, 41.2 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{33}H_{22}NO_5$ 512.1492, found 512.1487.



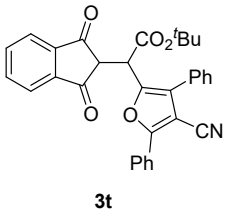
3r

3r, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (32.7 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.86 – 7.84 (m, 2H), 7.48 – 7.39 (m, 5H), 4.68 (d, *J* = 4.8 Hz, 1H), 3.75 (d, *J* = 4.8 Hz, 1H), 3.66 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 196.6, 169.3, 161.4, 143.8, 142.0, 141.8, 135.8, 129.3, 129.1, 128.60, 128.58, 125.3, 123.4, 123.3, 113.6, 96.6, 53.9, 53.1, 41.2, 13.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{18}NO_5$ 400.1179, found 400.1173.



3s

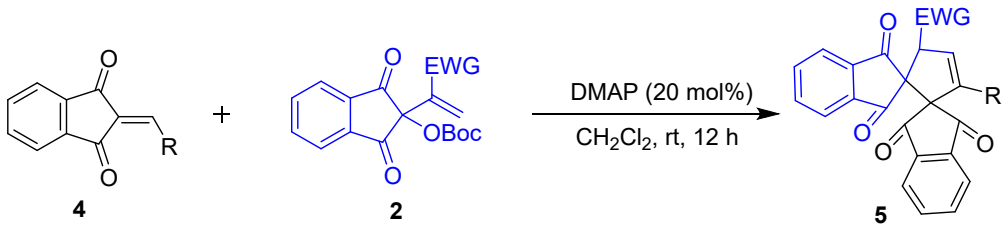
3s, Purification by flash chromatography (PE/EA = 4:1) gave a brown solid (40.9 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 6.8 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.49 – 7.41 (m, 7H), 7.39 – 7.30 (m, 3H), 7.00 (d, *J* = 16.4 Hz, 1H), 6.89 (d, *J* = 16.0 Hz, 1H), 4.76 (d, *J* = 4.8 Hz, 1H), 3.87 (d, *J* = 4.8 Hz, 1H), 3.72 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.62, 196.55, 169.2, 159.4, 144.5, 142.0, 141.9, 135.94, 135.91, 135.3, 133.9, 129.3, 129.2, 129.0, 128.9, 128.8, 128.6, 127.2, 126.7, 123.6, 123.3, 113.5, 112.5, 95.9, 54.0, 53.2, 41.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{22}NO_5$ 488.1492, found 488.1489.



3t

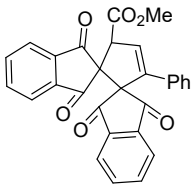
3t, Purification by flash chromatography (PE/EA = 3:1) gave a faint yellow solid (43.8 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 1H), 7.99 – 7.97 (m, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.85 – 7.83 (m, 2H), 7.55 – 7.49 (m, 4H), 7.46 – 7.39 (m, 4H), 4.72 (d, *J* = 3.6 Hz, 1H), 3.75 (d, *J* = 4.0 Hz, 1H), 1.34 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 196.7, 167.3, 159.1, 145.3, 142.2, 141.9, 135.8, 135.7, 130.1, 129.2, 129.0, 128.8, 128.7, 127.9, 127.0, 125.4, 123.5, 123.4, 114.7, 93.4, 83.6, 54.3, 42.1, 27.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{32}H_{26}NO_5$ 504.1805, found 504.1801.

4. General procedure for [3 + 2] annulations of 2-arylidene-1,3-indandiones 4 with ninhydrin-derived MBH carbonates 2



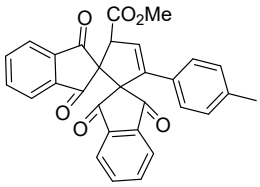
4 2 5

The 2-arylidene-1,3-indandiones **4** (0.1 mmol, 1.0 equiv), ninhydrin-derived MBH carbonates **2** (0.12 mmol, 1.2 equiv) and CH_2Cl_2 (1.0 mL) were added to a dry flask at room temperature, and then DMAP (20 mol%) was added to the above solution. This solution was stirred at room temperature for 12 h until the complete consumption of the starting materials monitored by TLC. After the removal of the solvent, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 to 3:1) to afford products **5**.



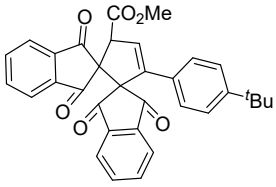
5a

5a, Purification by flash chromatography (PE/EA = 5:1) gave a faint yellow solid (33.3 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.79 (t, *J* = 7.2 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.16 – 7.10 (m, 3H), 6.98 (d, *J* = 6.8 Hz, 2H), 6.90 (s, 1H), 4.88 (s, 1H), 3.57 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 195.9, 195.1, 194.7, 170.2, 142.4, 141.4, 141.1, 140.5, 139.3, 136.7, 136.4, 136.1, 135.3, 133.2, 130.9, 128.5, 128.2, 126.3, 124.4, 123.9, 123.2, 122.9, 73.0, 68.7, 53.1, 52.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{19}O_6$ 463.1176, found 463.1172.



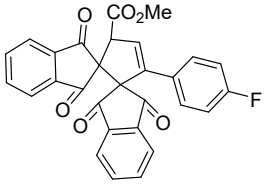
5b

5b, Purification by flash chromatography (PE/EA = 5:1) gave a faint yellow solid (32.4 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.84 (t, *J* = 7.2 Hz, 1H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.55 – 7.50 (m, 2H), 6.93 – 6.84 (m, 5H), 4.87 (s, 1H), 3.56 (s, 3H), 2.20 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 196.0, 195.1, 194.8, 170.3, 142.5, 141.4, 141.1, 140.5, 139.3, 138.1, 136.7, 136.4, 136.1, 135.3, 130.4, 130.0, 129.2, 126.2, 124.4, 123.9, 123.2, 122.9, 73.1, 68.7, 53.1, 52.4, 21.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{21}O_6$ 477.1333, found 477.1331.



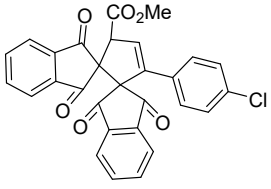
5c

5c, Purification by flash chromatography (PE/EA = 5:1) gave a faint yellow solid (36.3 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.79 (t, *J* = 7.2 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.92 – 6.88 (m, 3H), 4.86 (s, 1H), 3.56 (s, 3H), 1.19 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 196.0, 195.1, 194.7, 170.3, 151.3, 142.5, 141.4, 141.1, 140.5, 139.1, 136.7, 136.4, 136.0, 135.3, 130.2, 129.9, 125.9, 125.5, 124.4, 123.9, 123.2, 122.9, 72.9, 68.8, 53.1, 52.4, 34.5, 31.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{33}H_{27}O_6$ 519.1802, found 519.1799.



5d

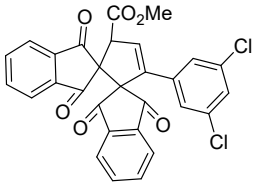
5d, Purification by flash chromatography (PE/EA = 5:1) gave a faint yellow solid (36.0 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.56 – 7.51 (m, 2H), 6.99 – 6.96 (m, 2H), 6.84 – 6.80 (m, 3H), 4.86 (s, 1H), 3.57 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 195.8, 195.1, 194.6, 170.1, 162.6 (d, *J* = 246.6 Hz), 142.4, 141.4, 141.2, 140.5, 138.3, 136.8, 136.5, 136.2, 135.4, 131.2, 129.5 (d, *J* = 3.4 Hz),128.3 (d, *J* = 8.1 Hz), 124.4, 123.9, 123.2, 123.0, 115.6 (d, *J* = 21.6 Hz), 73.1, 68.7, 53.1, 52.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{18}FO_6$ 481.1082, found 481.1080.



5e

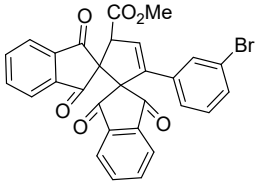
5e, Purification by flash chromatography (PE/EA = 5:1) gave a faint yellow solid (36.2 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.68 (t, *J* = 7.2

Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.93 – 6.89 (m, 3H), 4.86 (s, 1H), 3.57 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 195.7, 195.0, 194.5, 170.0, 142.3, 141.4, 141.1, 140.5, 138.2, 136.9, 136.5, 136.2, 135.4, 134.2, 131.8, 128.8, 127.7, 124.4, 123.9, 123.2, 123.0, 73.0, 68.7, 53.1, 52.4 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{18}ClO_6$ 497.0786, found 497.0783.



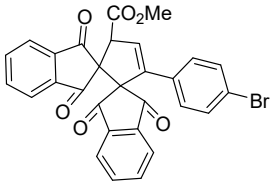
5f

5f, Purification by flash chromatography (PE/EA = 3:1) gave a faint yellow solid (37.6 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.87 (t, *J* = 7.2 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.15 (s, 1H), 6.93 (s, 1H), 6.88 (s, 2H), 4.86 (s, 1H), 3.58 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.50, 195.46, 194.8, 194.1, 169.7, 142.3, 141.3, 141.0, 140.4, 137.02, 136.95, 136.6, 136.4, 136.3, 135.5, 135.1, 134.1, 128.3, 125.0, 124.5, 123.9, 123.3, 123.0, 72.9, 68.7, 53.1, 52.5 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{17}Cl_2O_6$ 531.0397, found 531.0396.



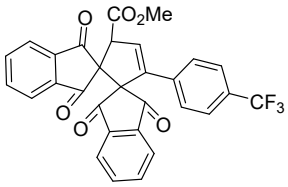
5g

5g, Purification by flash chromatography (PE/EA = 3:1) gave a faint yellow solid (37.3 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.86 (t, *J* = 7.2 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.32 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.88 (s, 1H), 3.58 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 195.7, 195.0, 194.4, 169.9, 142.3, 141.4, 141.1, 140.5, 138.0, 136.9, 136.5, 136.3, 135.4, 135.3, 132.6, 131.3, 130.0, 129.8, 124.7, 124.5, 123.9, 123.3, 123.0, 122.8, 72.9, 68.7, 53.1, 52.5 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{18}BrO_6$ 541.0281 (^{79}Br) and 543.0261 (^{81}Br), found 541.0279, 543.0257.



5h

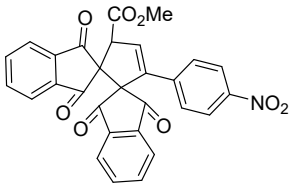
5h, Purification by flash chromatography (PE/EA = 5:1) gave a yellow solid (38.3 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.86 (t, *J* = 7.2 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.56 – 7.50 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.90 – 6.85 (m, 3H), 4.85 (s, 1H), 3.57 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 195.7, 195.0, 194.5, 170.0, 142.3, 141.3, 141.1, 140.5, 138.3, 136.9, 136.5, 136.2, 135.4, 132.2, 131.9, 131.7, 128.0, 124.4, 123.9, 123.2, 123.0, 122.4, 73.0, 68.7, 53.1, 52.5 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{18}BrO_6$ 541.0281 (^{79}Br) and 543.0261 (^{81}Br), found 541.0277, 543.0254.



5i

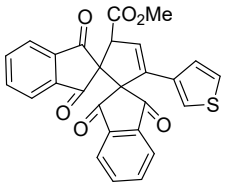
5i, Purification by flash chromatography (PE/EA = 5:1) gave a faint yellow solid (37.1 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.87 (t, *J* = 7.2 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.00 (s, 1H), 4.89 (s, 1H), 3.58 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 195.6, 194.9, 194.3, 169.8, 142.3, 141.3, 141.1, 140.5, 138.0, 136.8, 136.5, 136.3, 135.5, 133.5, 130.3 (q, *J* = 3.7 Hz), 126.7, 125.6 (q, *J* = 3.7 Hz), 124.5, 123.9, 123.7 (q, *J* =

235.5 Hz), 123.3, 123.0, 73.0, 68.8, 53.2, 52.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{18}F_3O_6$ 531.1050, found 531.1045.



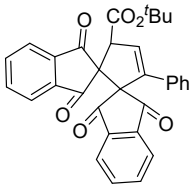
5j

5j, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (37.5 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.2 Hz, 1H), 8.02 – 7.97 (m, 3H), 7.90 (t, *J* = 7.2 Hz, 1H), 7.82 (t, *J* = 7.2 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.10 (s, 1H), 4.89 (s, 1H), 3.59 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 195.3, 194.7, 194.0, 169.5, 147.3, 142.2, 141.2, 141.0, 140.4, 139.7, 137.4, 137.1, 136.6, 136.5, 135.6, 135.3, 127.1, 124.6, 124.0, 123.9, 123.3, 123.0, 72.9, 68.8, 53.2, 52.6 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{18}NO_8$ 508.1027, found 508.1021.



5k

5k, Purification by flash chromatography (PE/EA = 3:1) gave a yellow solid (31.4 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 14.0, 7.2 Hz, 2H), 7.87 – 7.79 (m, 2H), 7.71 (t, *J* = 6.8 Hz, 1H), 7.64 – 7.59 (m, 3H), 7.15 (s, 1H), 7.05 (s, 1H), 6.87 (s, 1H), 6.52 (s, 1H), 4.86 (s, 1H), 3.56 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 195.9, 195.2, 194.7, 170.1, 142.5, 141.4, 141.3, 140.5, 136.8, 136.4, 136.2, 135.3, 134.24, 134.15, 129.8, 126.4, 126.1, 124.3, 123.9, 123.3, 123.0, 121.7, 72.7, 68.3, 53.1, 52.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{17}O_6S$ 469.0740, found 469.0733.

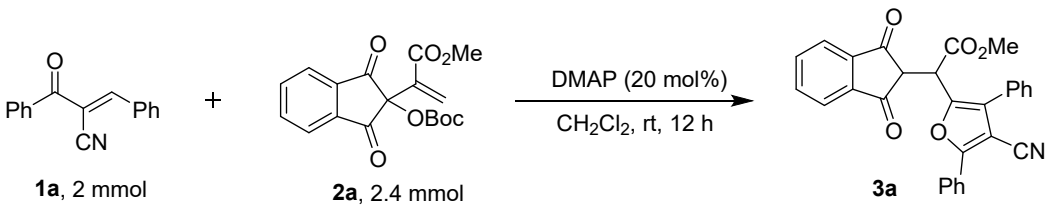


5j

5l, Purification by flash chromatography (PE/EA = 5:1) gave a faint yellow solid (34.8 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.69 – 7.62 (m, 2H), 7.58 – 7.52 (m, 2H), 7.12 – 7.11 (m, 3H), 6.99 (d, *J* = 7.2 Hz, 2H), 6.88 (s, 1H), 4.78 (s, 1H), 1.09 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 196.2, 195.0, 194.9, 168.2, 142.7, 141.4, 141.2, 140.7, 139.1, 136.7, 136.3, 136.0, 135.2, 133.4, 131.7, 128.5, 128.1, 126.4, 124.4, 123.7, 123.2, 122.9, 82.5, 73.2, 68.4, 53.9, 27.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{32}H_{25}O_6$ 505.1646, found 505.1642.

5. Gram scale reaction and synthetic transformation

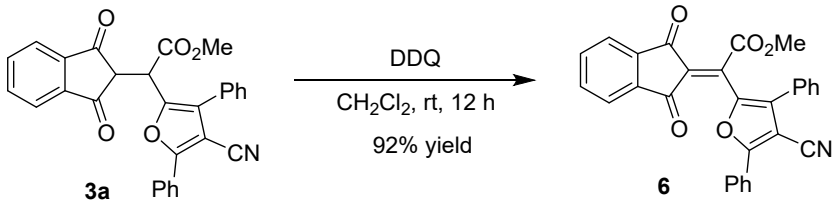
5.1 Gram scale reaction



The α-cyano-α,β-unsaturated ketone **1a** (0.466 g, 2 mmol) and ninhydrin-derived MBH carbonate **2a** (0.830 g, 2.4 mmol) and CH_2Cl_2 (15 mL) were added to a 50 mL dry flask at room temperature, then DMAP

(48.8 mg) was added to the above solution in one portion. The resulting solution of the reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated to give the crude product, which was directly purified by flash chromatography (PE /EA = 3:1) to provide the desired product **3a** as a white solid (0.821 g, 89% yield). The analytical data of the gram scale reaction of **3a** are consistent with those of the 0.1 mmol scale experiment.

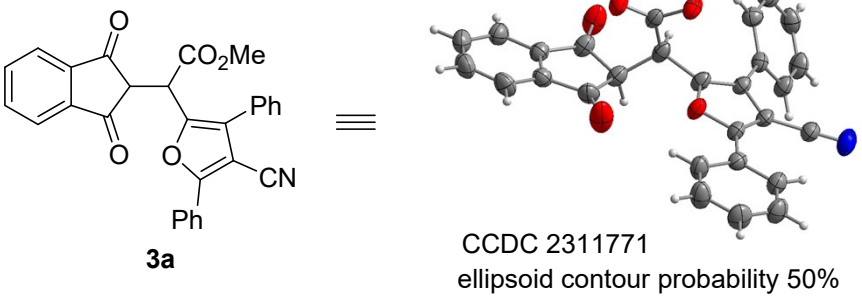
5.2 Synthetic transformation from 3a to 6



To a solution of compound **3a** (0.2 mmol, 92.2 mg) in CH_2Cl_2 (3 mL) was added the DDQ (0.22 mmol, 49.9 mg), then the mixture was then stirred at the room temperature for 12 h until the reaction was completed as monitored by TLC analysis. Evaporation of the solvent followed by a flash column chromatography on silica gel (PE /EA = 3:1) to give the product **6** (84.5 mg, 92% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.24 (m, 2H), 8.00 (d, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 6.8 Hz, 1H), 7.85 – 7.81 (m, 2H), 7.57 (d, *J* = 4.0 Hz, 3H), 7.48 (d, *J* = 3.6 Hz, 5H), 3.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 185.9, 164.6, 162.8, 142.4, 142.3, 140.6, 139.5, 135.9, 135.6, 132.8, 132.0, 129.9, 129.6, 129.4, 128.7, 128.3, 127.9, 127.1, 126.8, 123.6, 123.4, 113.4, 97.0, 52.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{18}NO_5$ 460.1179, found 460.1174.

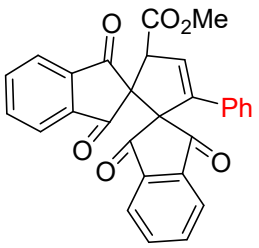
6. Crystal Structure and Data

Preparation of Single Crystal. Single crystal **3a** and **5a** was obtained by the layer-to-layer diffusion method. Products **3a** and **5a** were added to dichloromethane (1.0 mL) , and stratified with *n*-hexane after 3 days to obtain crystals suitable for single-crystal X-ray diffraction.

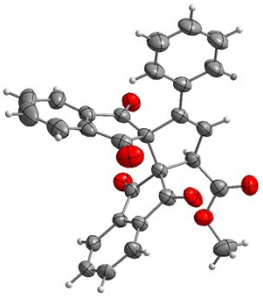


Identification code	**3a**
Empirical formula	$C_{29}H_{19}NO_5$
Formula weight	461.45

Temperature/K	296
Crystal system	triclinic
Space group	P-1
a/Å	9.9434(12)
b/Å	11.2111(13)
c/Å	11.3362(13)
α/°	100.833(2)
β/°	92.317(2)
γ/°	115.863(2)
Volume/Å^3	1106.1(2)
Z	2
ρ_{calc}g/cm^3	1.385
μ/mm^{-1}	0.095
F(000)	480
Crystal size/mm^3	0.23 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.484 to 55.272
Index ranges	−12 ≤ h ≤ 12, −14 ≤ k ≤ 14, −14 ≤ l ≤ 14
Reflections collected	6746
Independent reflections	4834 [R_{int} = 0.0193, R_{sigma} = 0.0369]
Data/restraints/parameters	4834/ 0 / 317
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0483, wR_2 = 0.1142
R indices (all data)	R_1 = 0.0753, wR_2 = 0.1305
Largest diff. peak and hole/ 1-sigma level	0.231 / − 0.312 / 0.059



5a

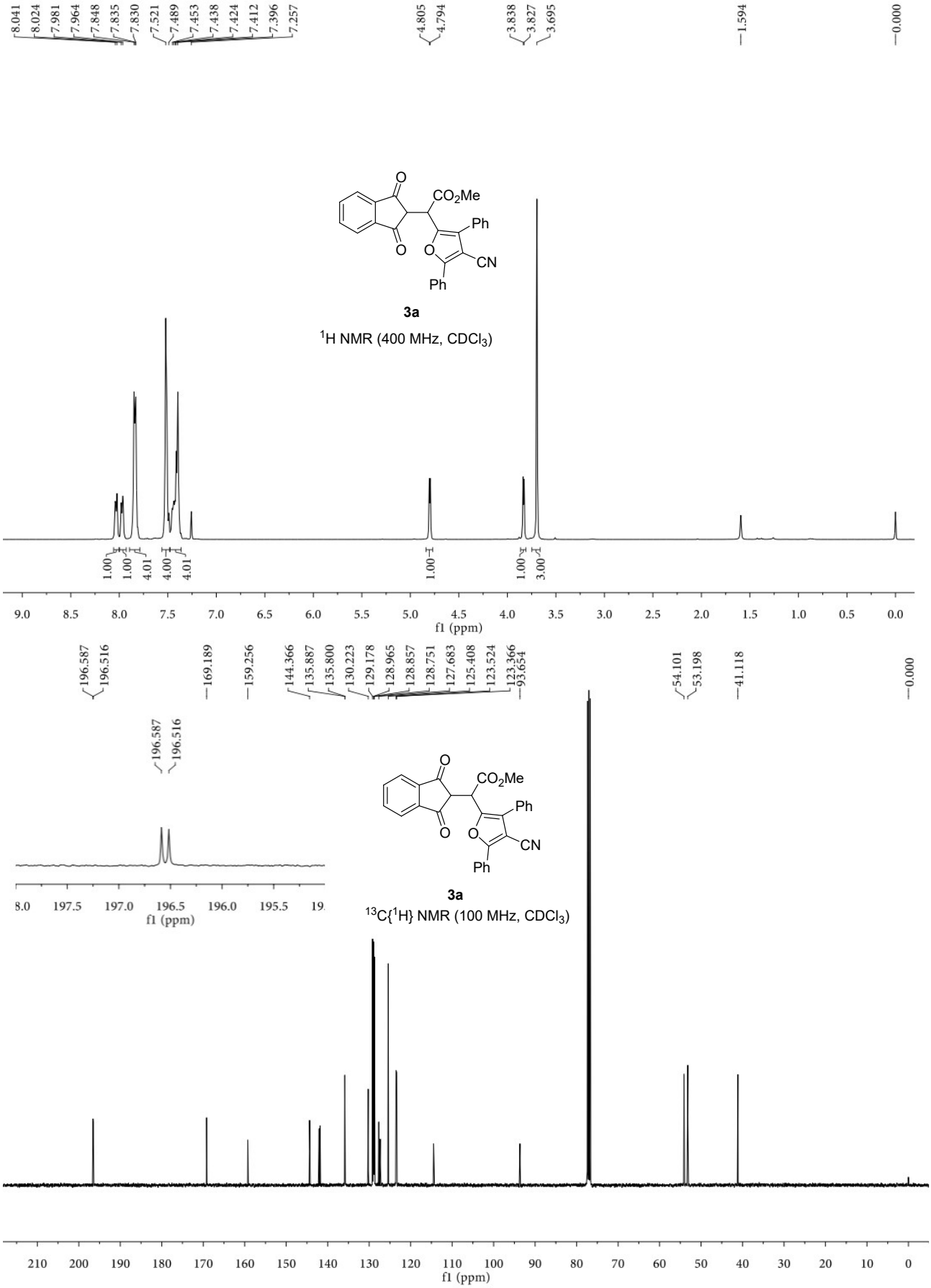


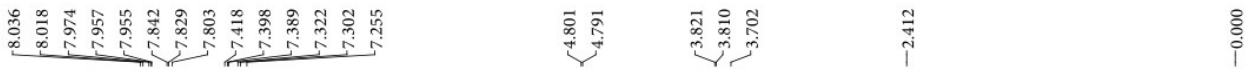
CCDC 2311772
ellipsoid contour probability 50%

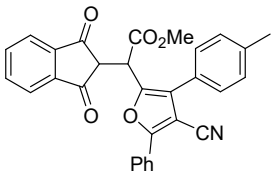
Identification code	**5a**
Empirical formula	$C_{29}H_{18}O_6$
Formula weight	462.43
Temperature/K	296.15
Crystal system	monoclinic
Space group	P1 2_1/c1
a/Å	8.5559(17)
b/Å	26.500(5)
c/Å	9.988(2)
α/°	90
β/°	99.097(4)
γ/°	90
Volume/Å^3	2236.1(8)
Z	4
ρ_{calc}g/cm^3	1.374
μ/mm^{-1}	0.097
F(000)	960.0
Crystal size/mm^3	0.26 × 0.22 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.074 to 55.094
Index ranges	$-10 \leq h \leq 10$, $-29 \leq k \leq 34$, $-12 \leq l \leq 12$
Reflections collected	13417
Independent reflections	5055 [R_{int} = 0.0441, R_{sigma} = 0.0608]

Data/restraints/parameters	5055/0/317
Goodness-of-fit on F^2	1.007
Final R indexes [I>=2σ (I)]	$R_1 = 0.0516$, $wR_2 = 0.1036$
R indices (all data)	$R_1 = 0.1089$, $wR_2 = 0.1245$
Largest diff. peak and hole/ 1-sigma level	0.161 / − 0.16 / 0.036

7. NMR spectra

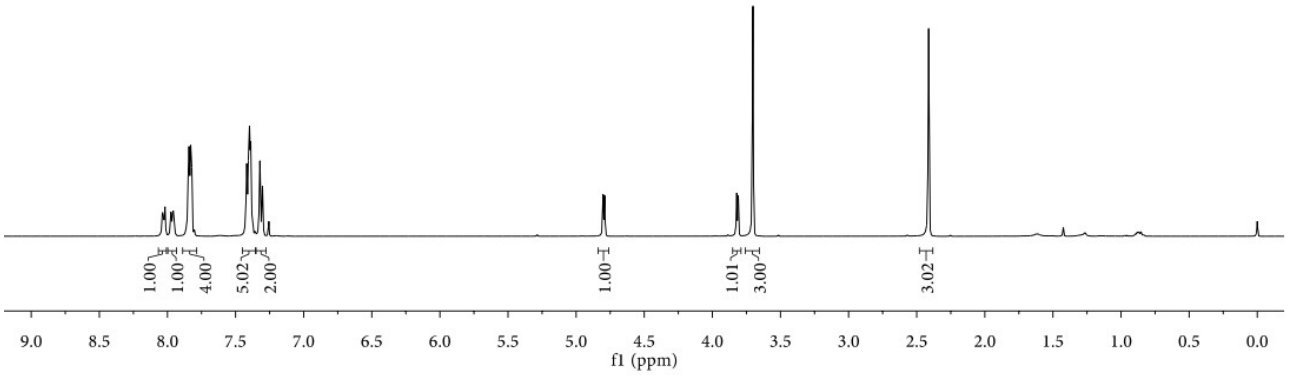


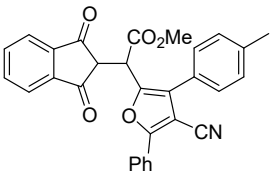




3b

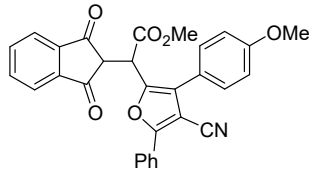
^{1}H NMR (400 MHz, $CDCl_3$)





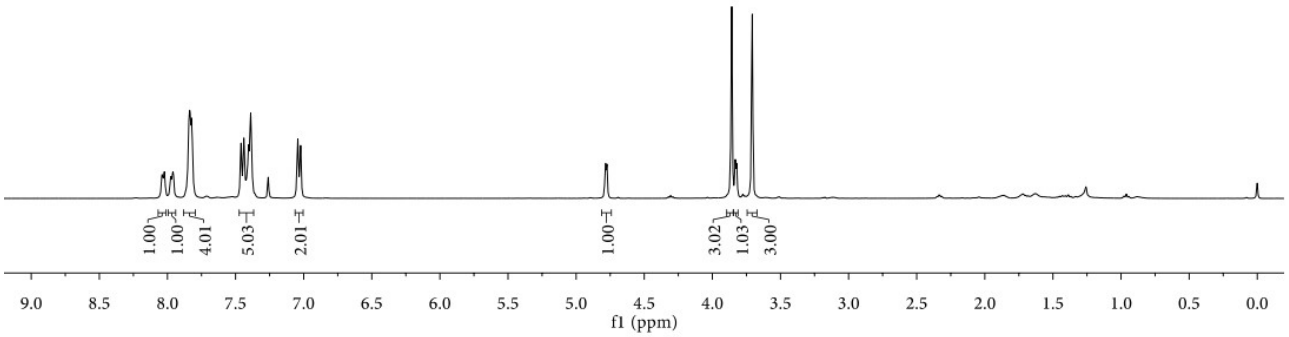
3b

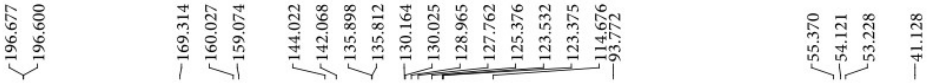
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

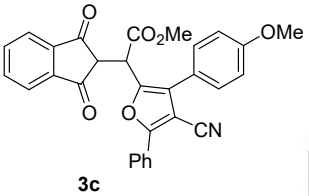


3c

^{1}H NMR (400 MHz, $CDCl_3$)

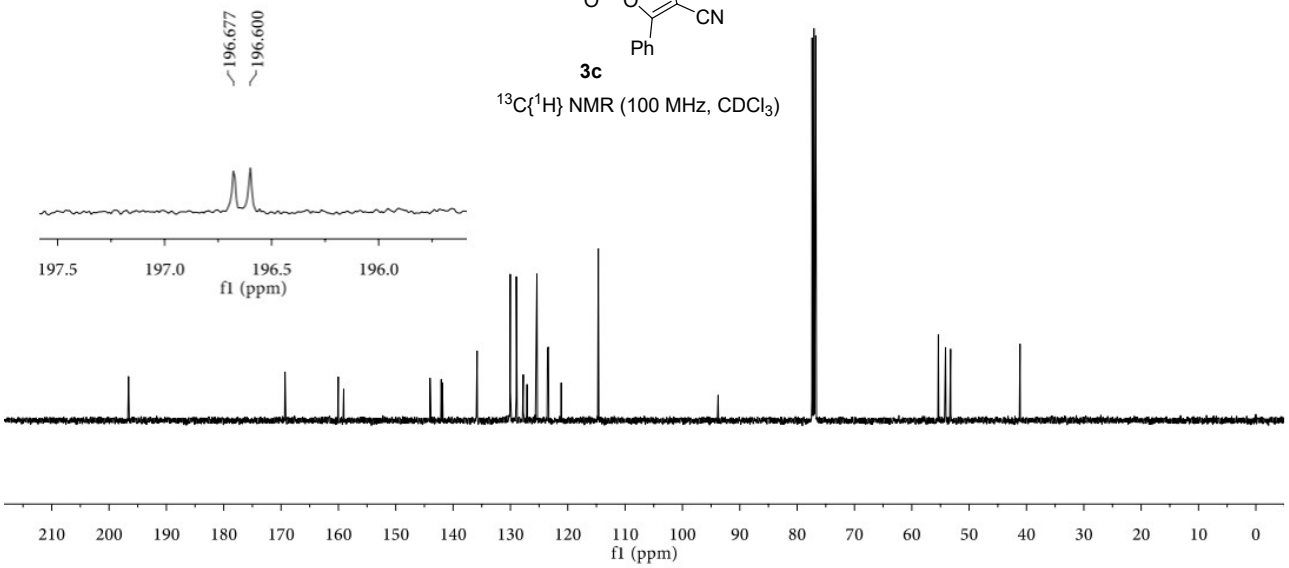


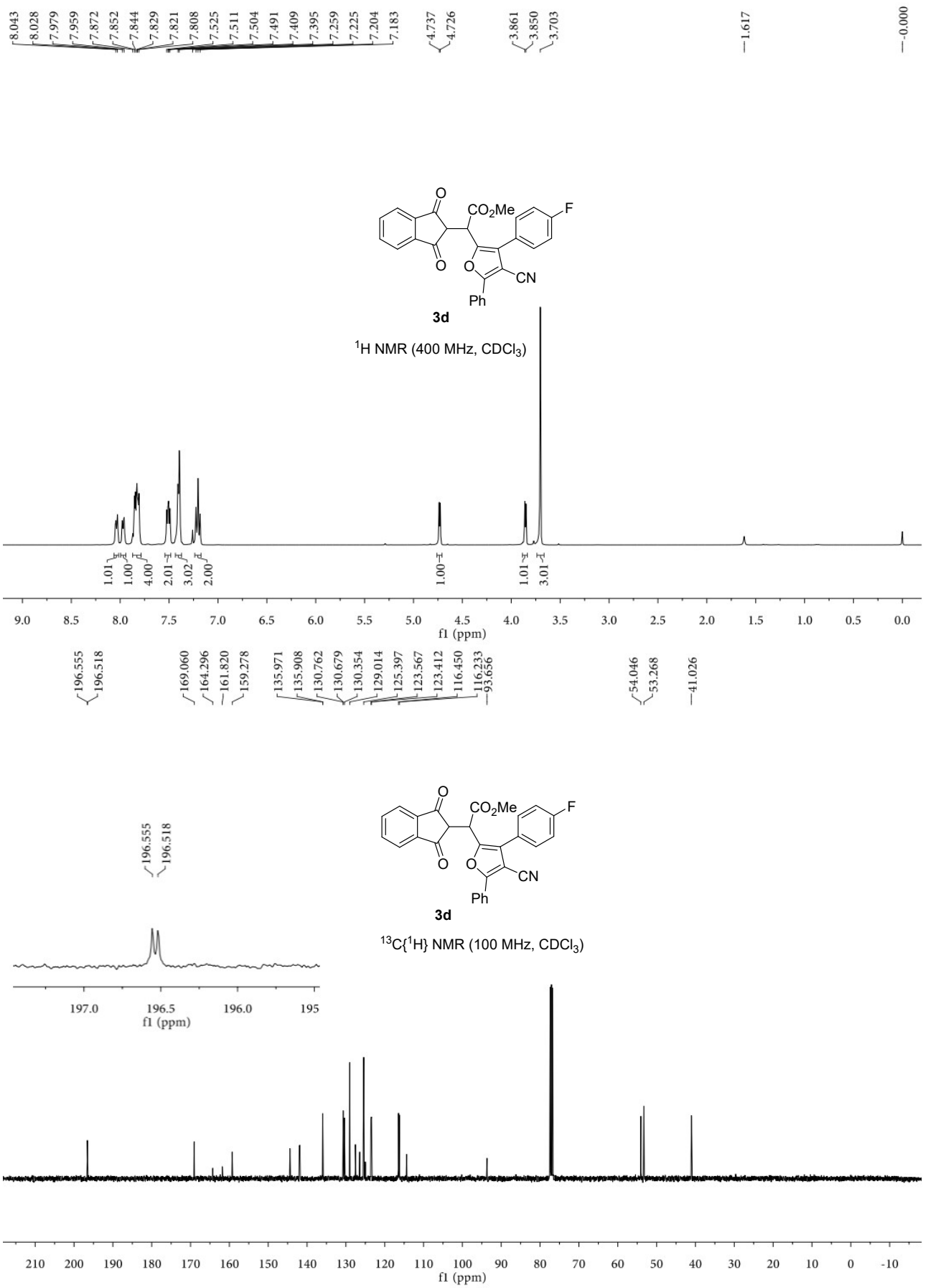




3c

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

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F
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O
CN
Ph
3d
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3.02
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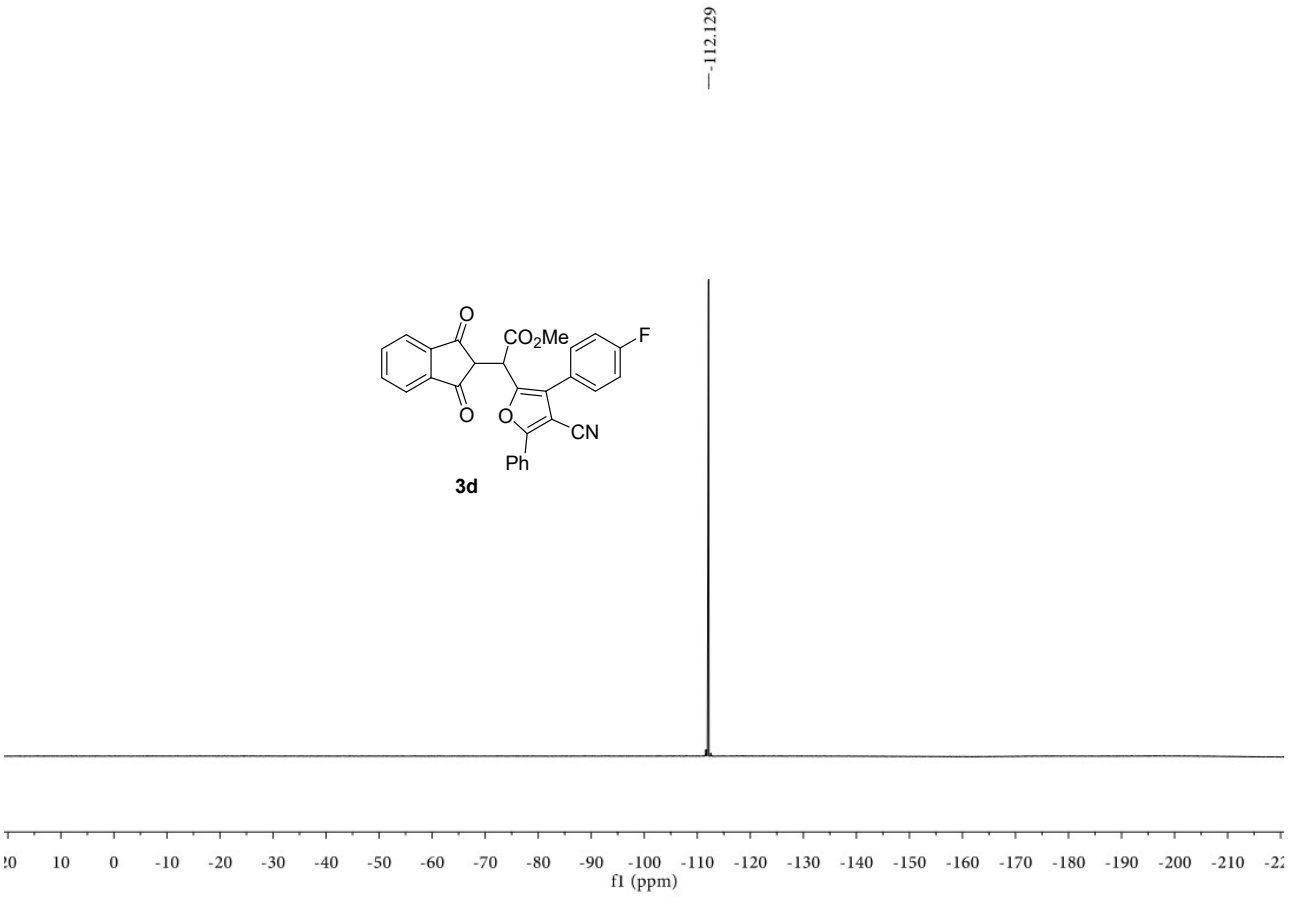
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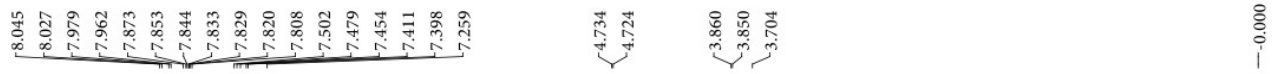
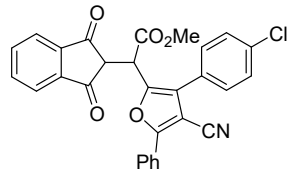
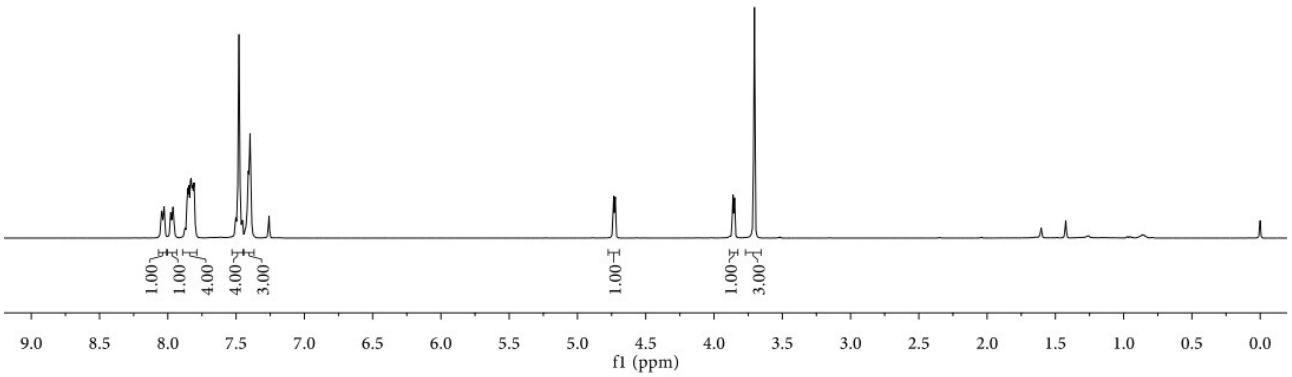
f1 (ppm)

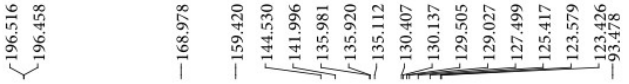


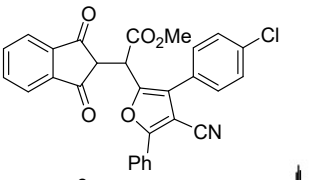


3e

^{1}H NMR (400 MHz, $CDCl_3$)

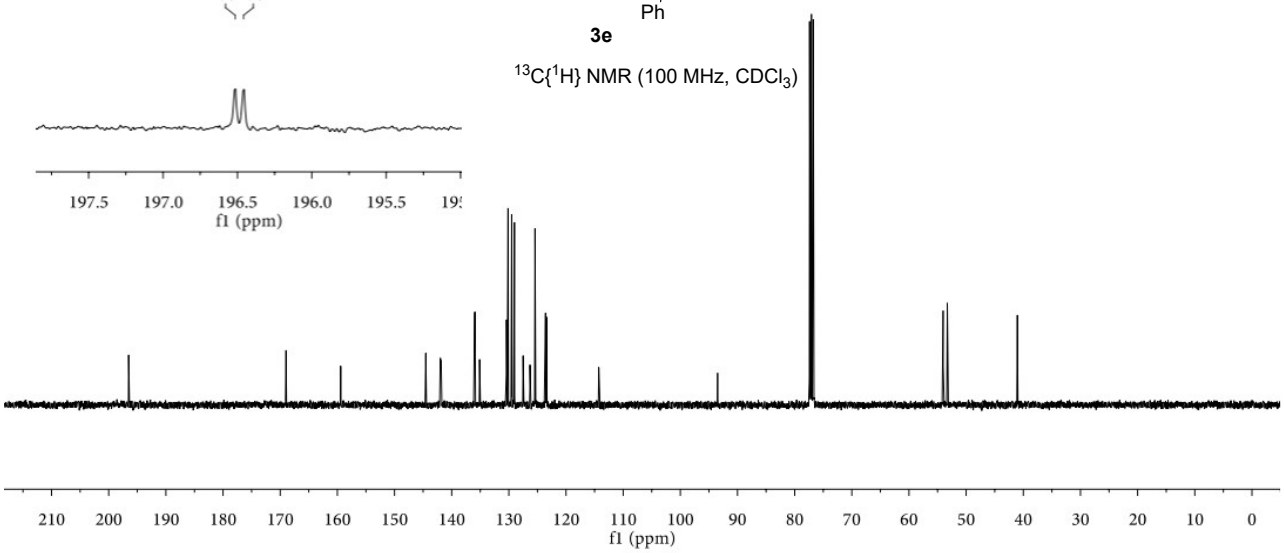


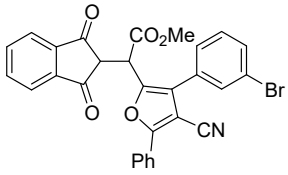




3e

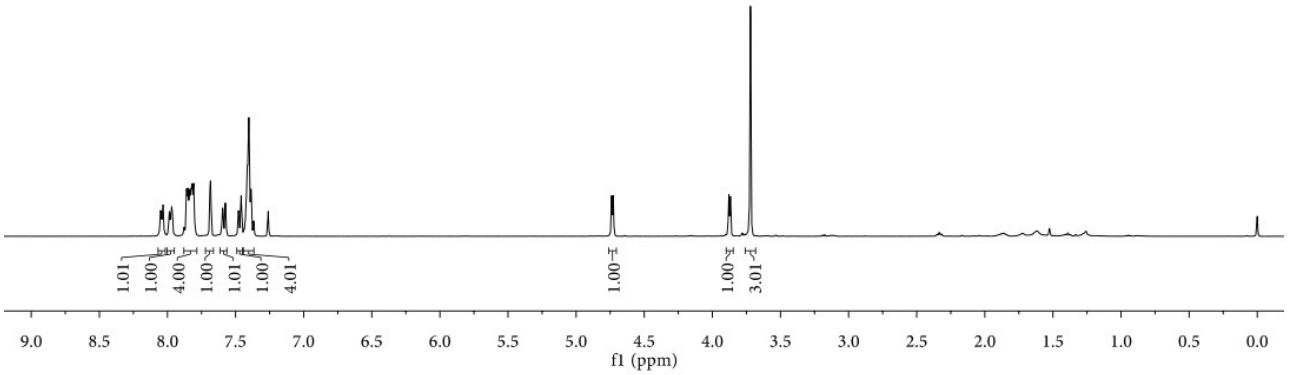
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

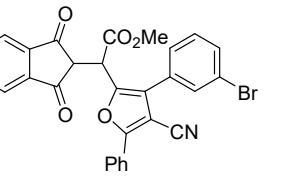




3f

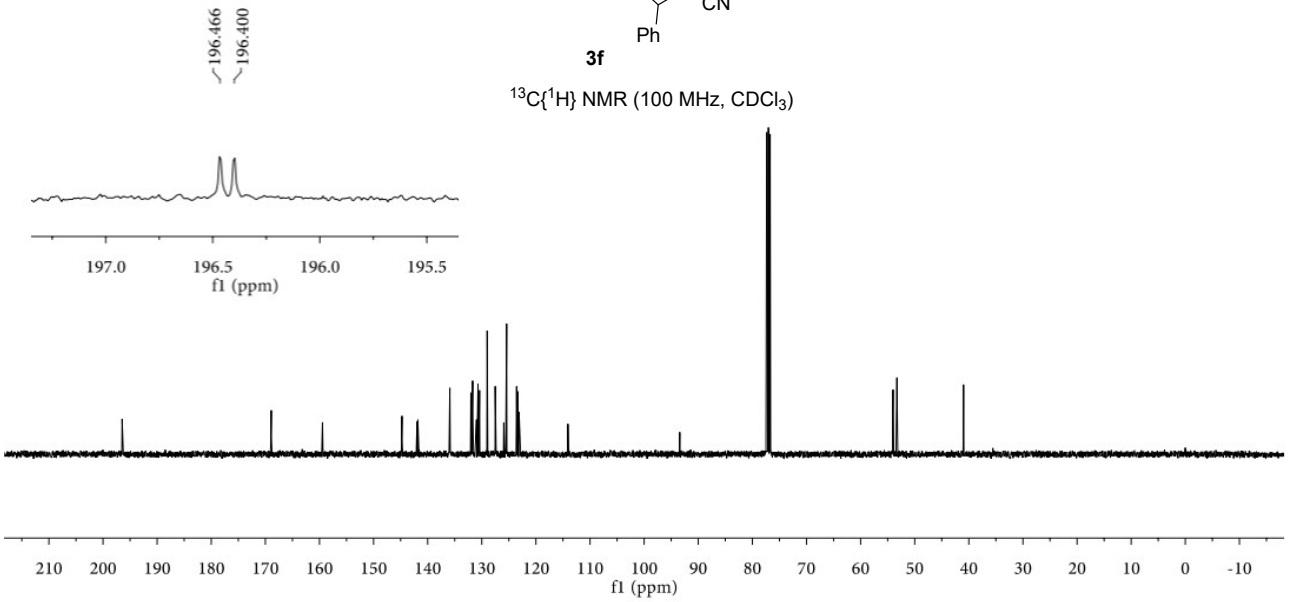
^{1}H NMR (400 MHz, $CDCl_3$)

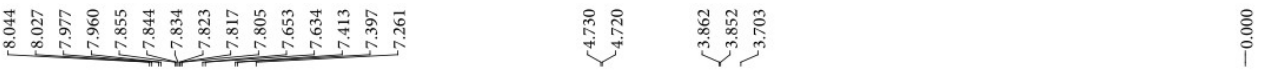


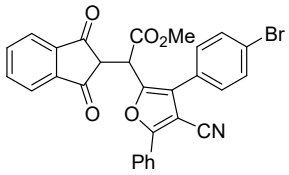


3f

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

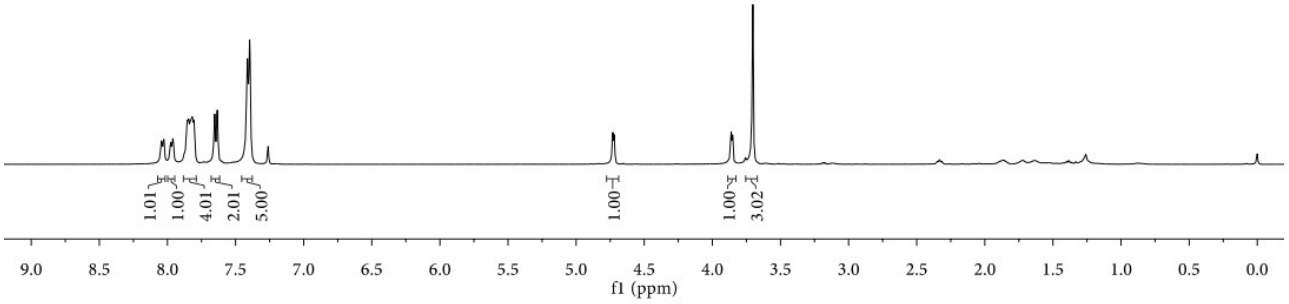


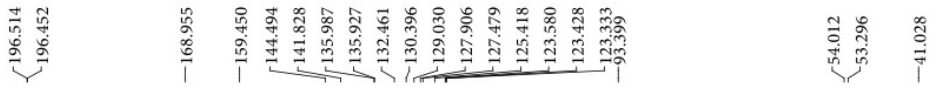


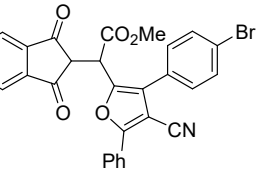


3g

^{1}H NMR (400 MHz, $CDCl_3$)

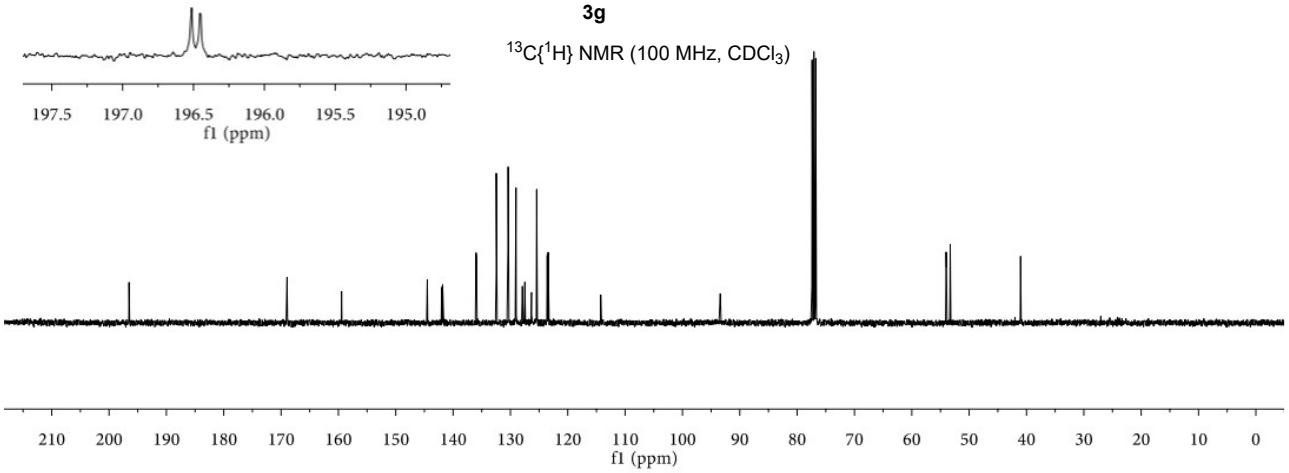


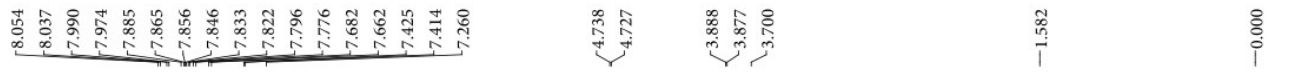


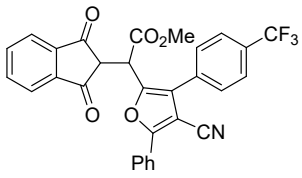


3g

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

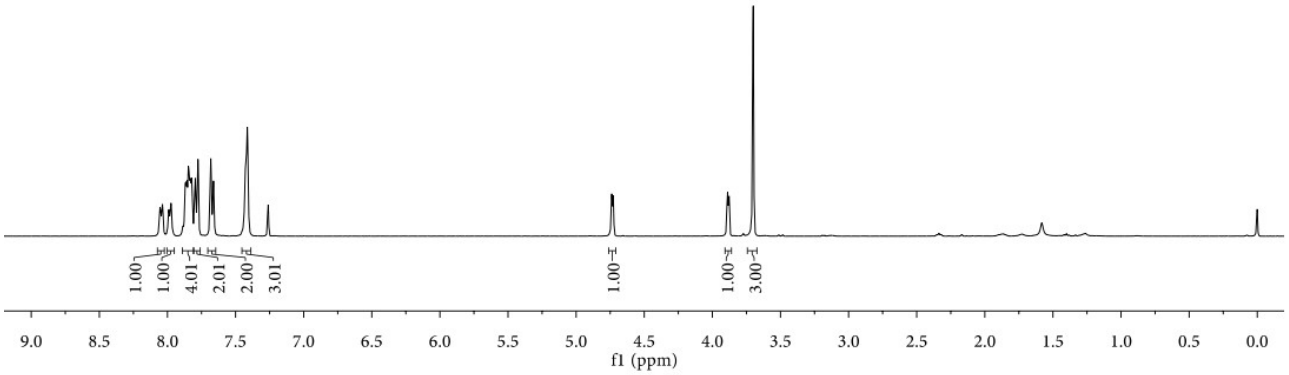


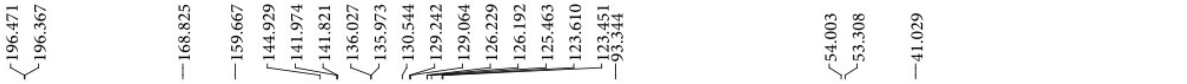


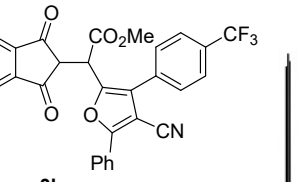


3h

^{1}H NMR (400 MHz, $CDCl_3$)

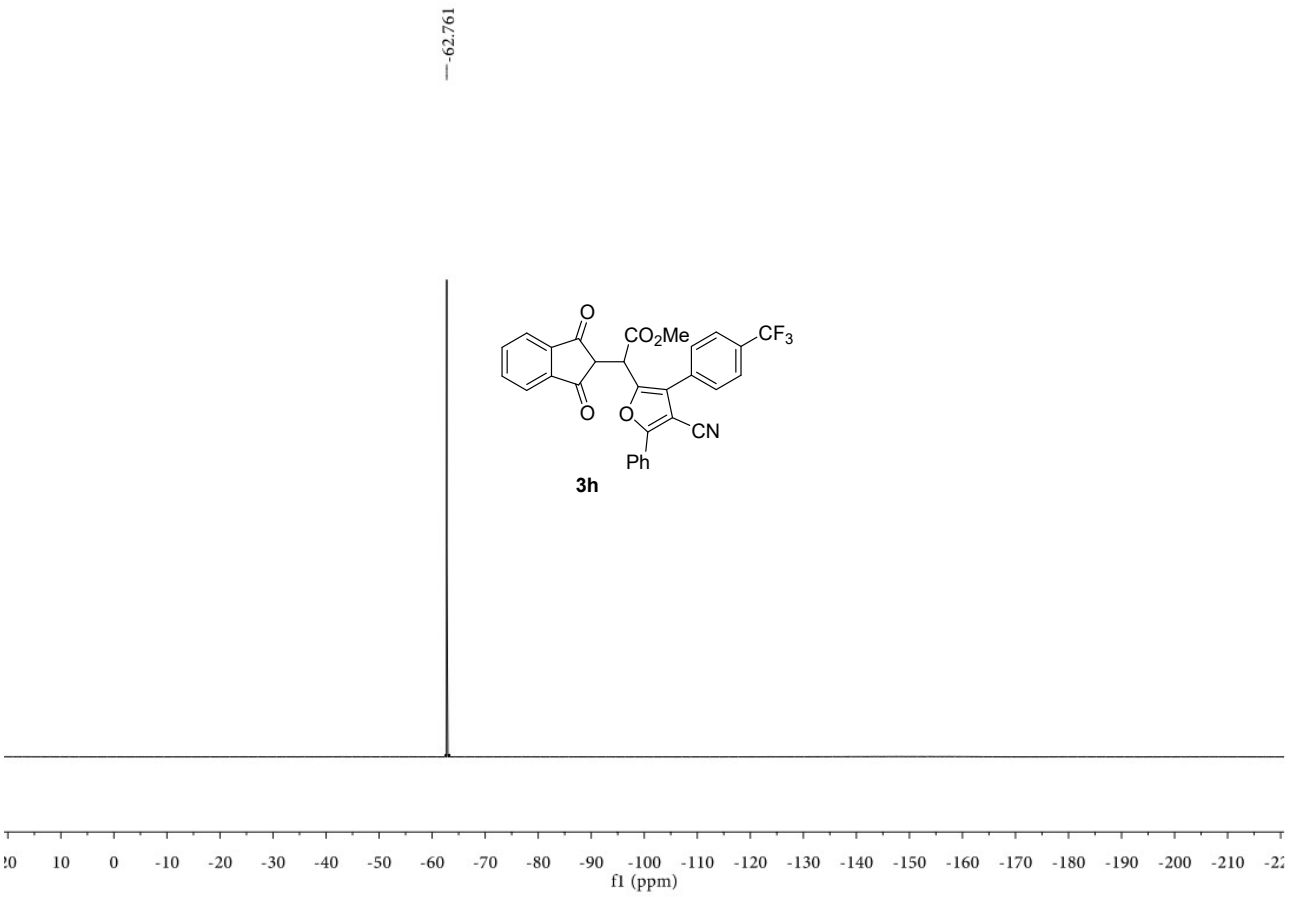


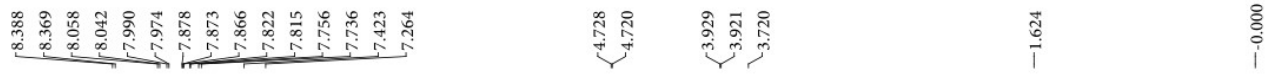


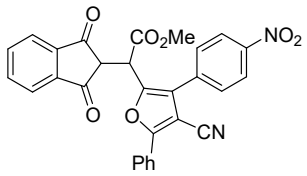


3h

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

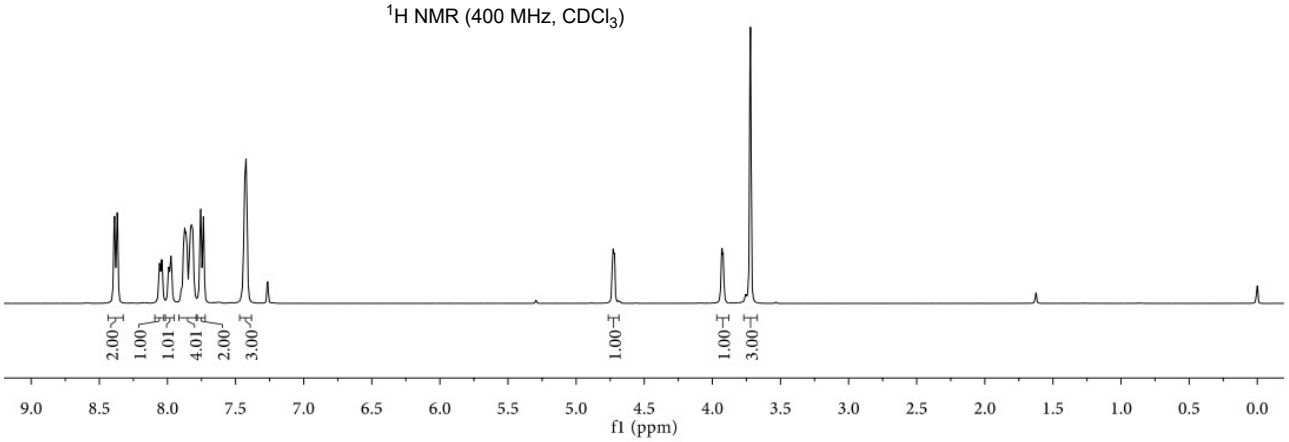

-62.761
O
CO2Me
CF3
O
O
CN
Ph
3h
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

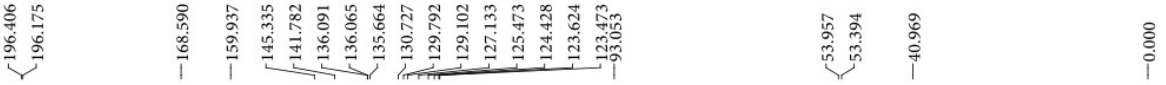


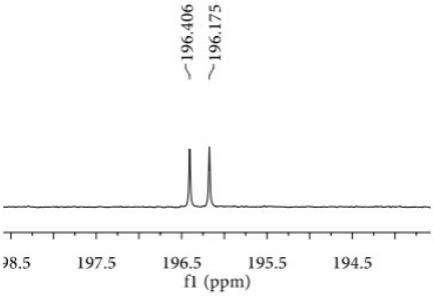


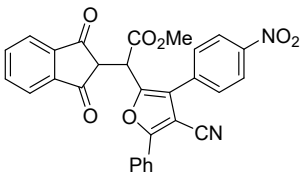
3i

^{1}H NMR (400 MHz, $CDCl_3$)



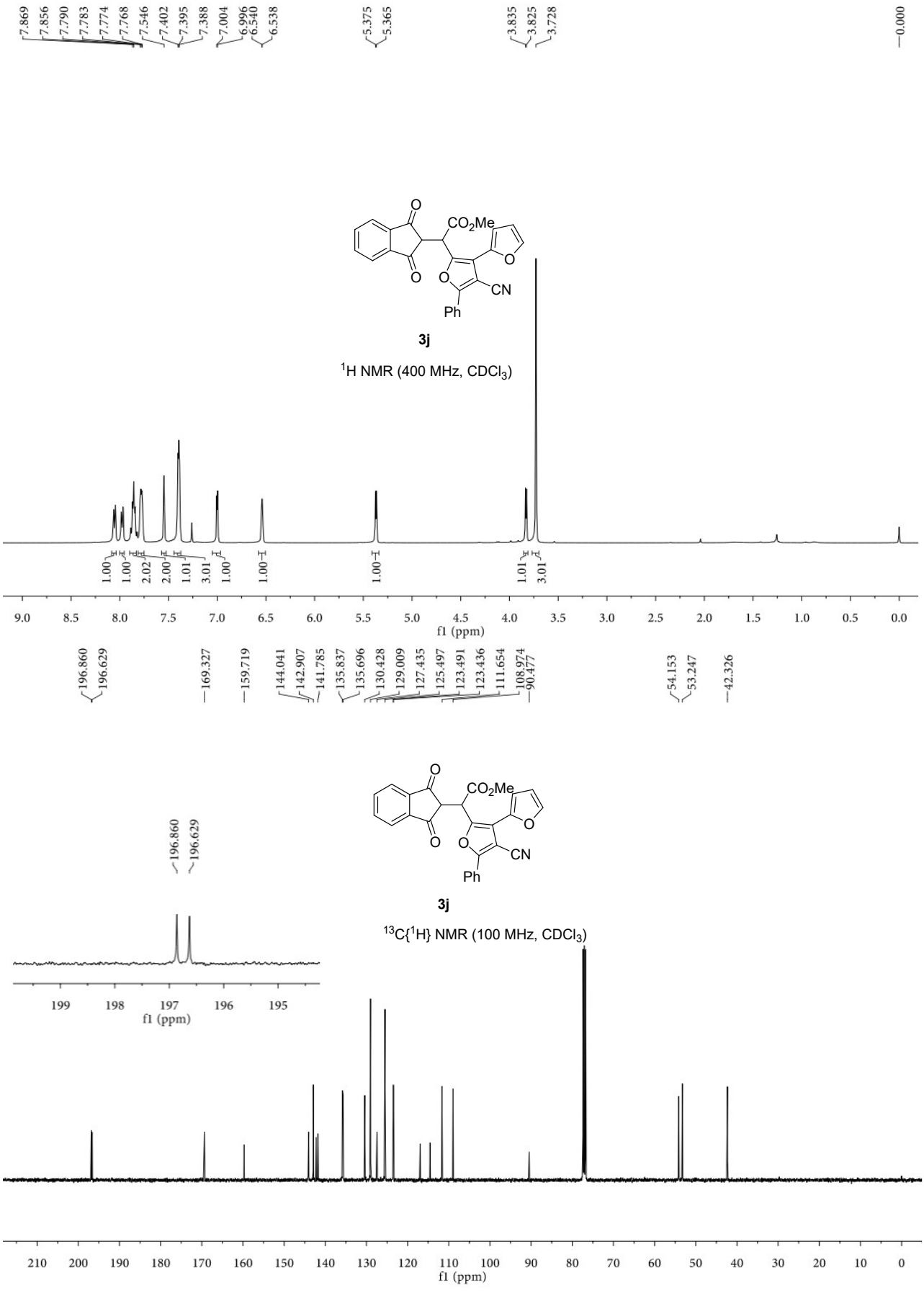


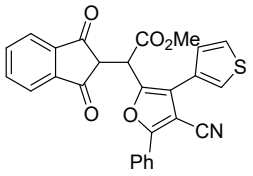




3i

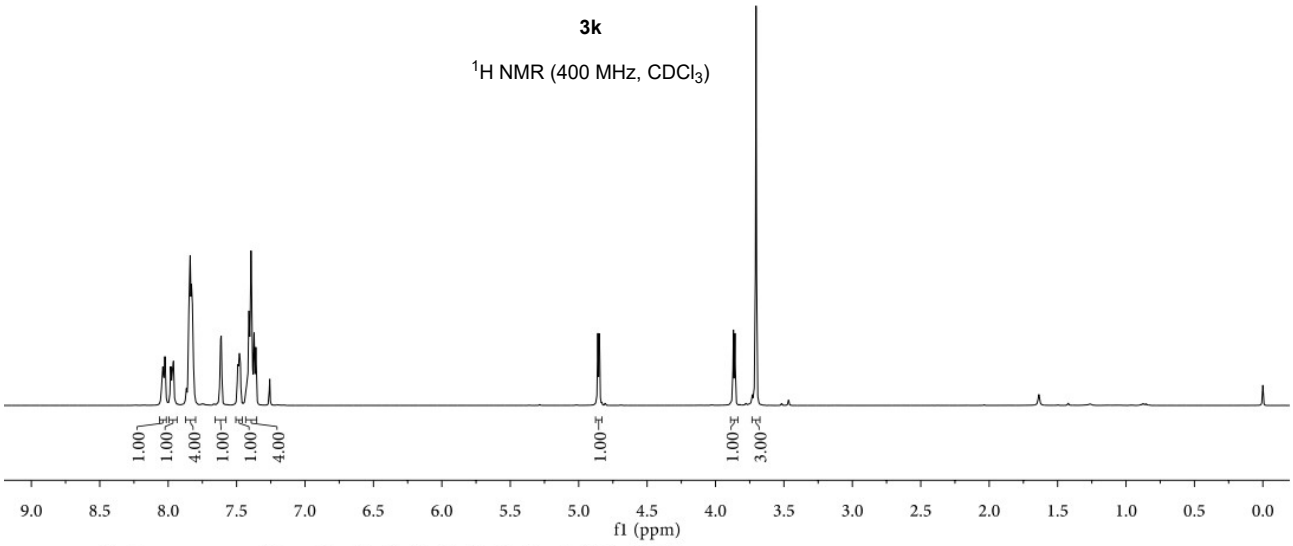
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

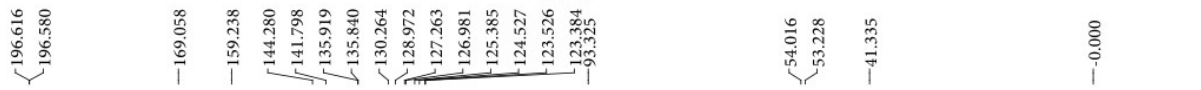

7.869
7.856
7.790
7.783
7.774
7.768
7.546
7.402
7.395
7.388
7.004
6.996
6.540
6.538
5.375
5.365
3.835
3.825
3.728
0.000
O
CO2Me
O
O
O
CN
Ph
3j
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.02
2.00
1.01
3.01
1.00
1.00
1.00
1.01
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
196.860
196.629
169.327
159.719
144.041
142.907
141.785
135.837
135.696
130.428
129.009
127.435
125.497
123.491
123.436
111.654
108.974
90.477
54.153
53.247
42.326
O
CO2Me
O
O
O
CN
Ph
3j
13C{1H} NMR (100 MHz, CDCl3)
196.860
196.629
199 198 197 196 195
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

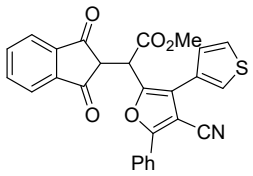


3k

^{1}H NMR (400 MHz, $CDCl_3$)

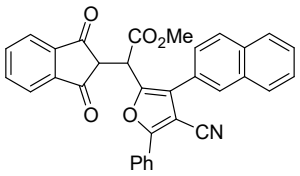






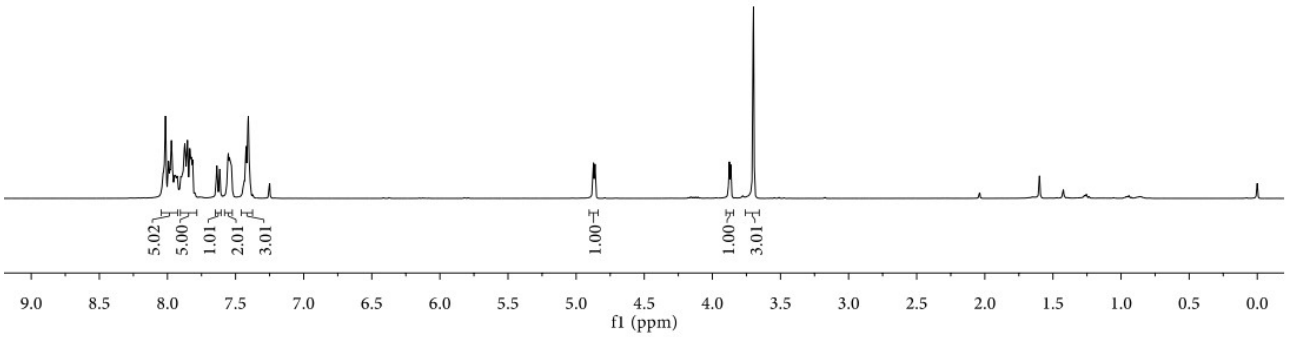
3k

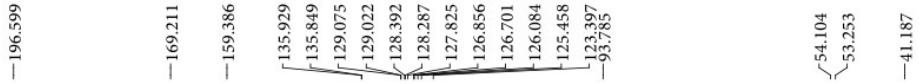
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

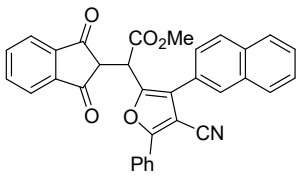


3l

^{1}H NMR (400 MHz, $CDCl_3$)

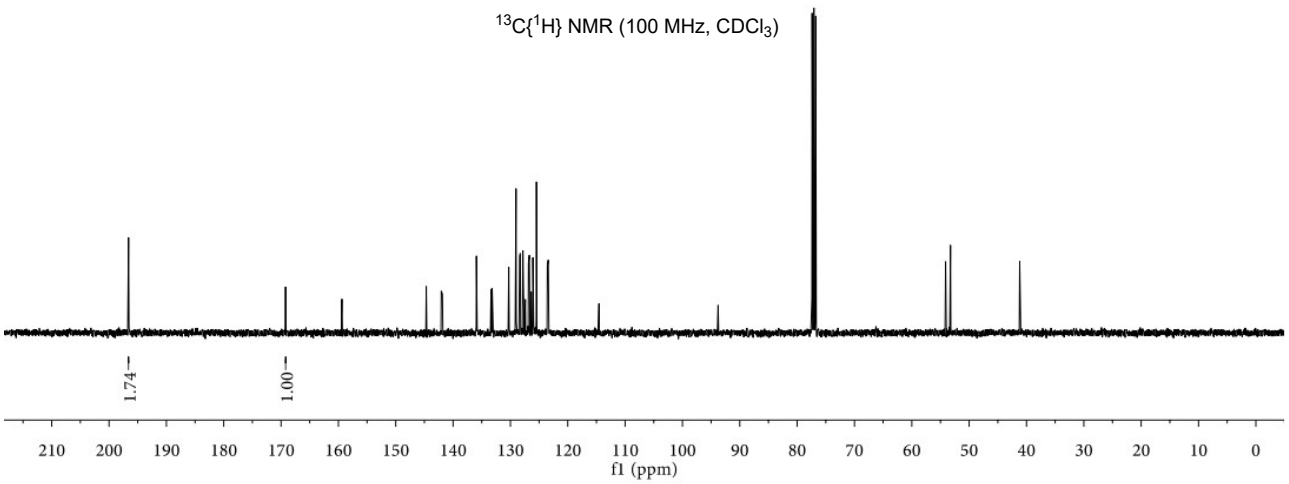


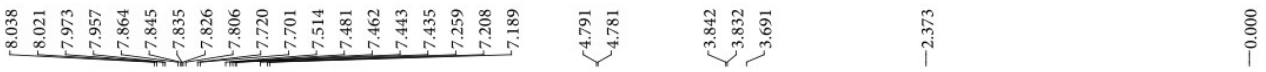


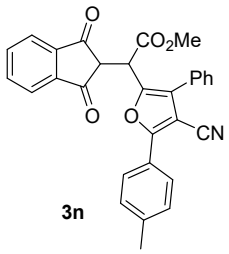


3l

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

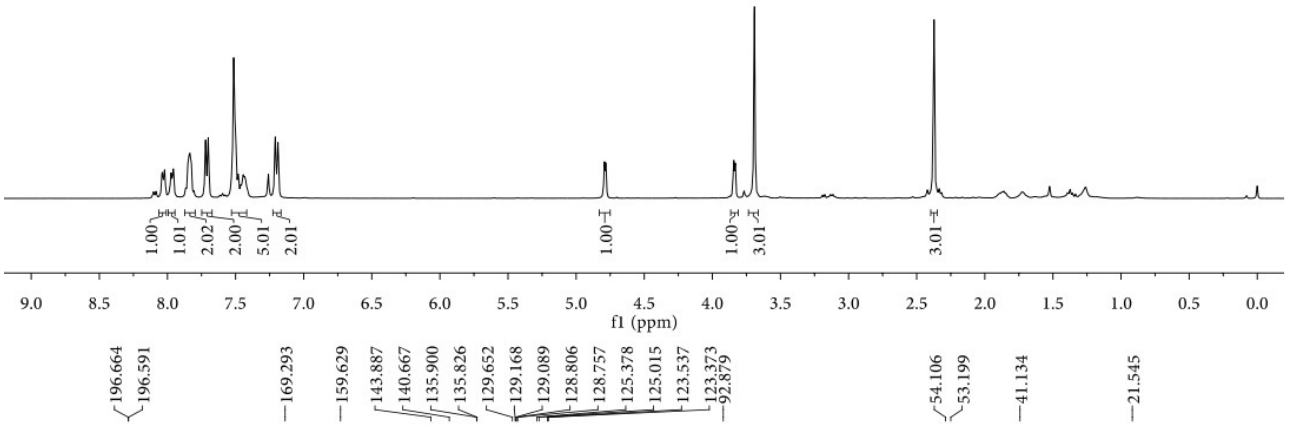


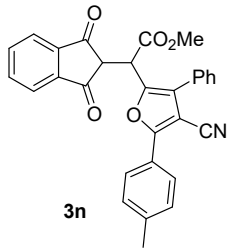




3n

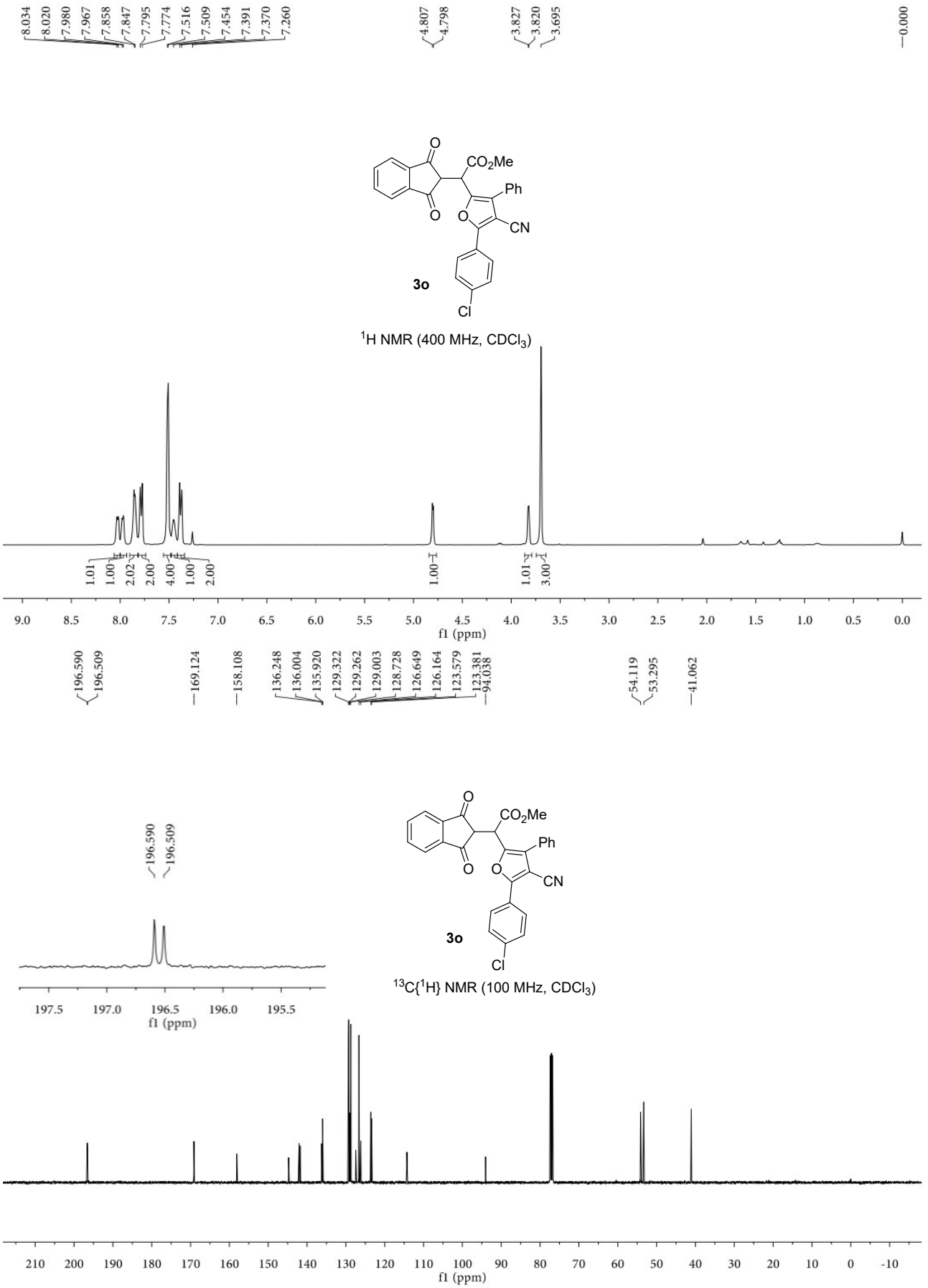
^{1}H NMR (400 MHz, $CDCl_3$)

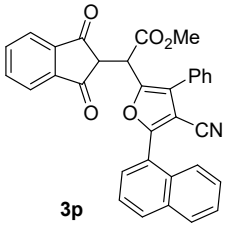




3n

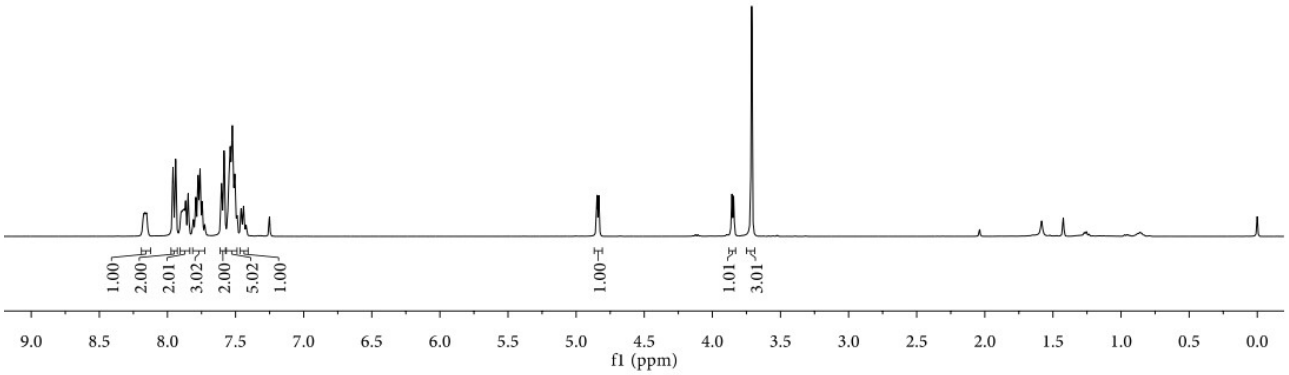
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

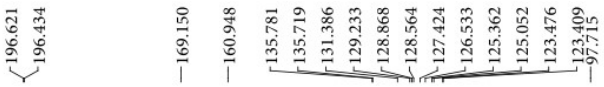

8.034
8.020
7.980
7.967
7.858
7.847
7.795
7.774
7.516
7.509
7.454
7.391
7.370
7.260
4.807
4.798
3.827
3.820
3.695
0.000
O
CO2Me
Ph
O
O
CN
3o
Cl
1H NMR (400 MHz, CDCl3)
1.01
1.00
2.02
2.00
4.00
1.00
2.00
1.00
1.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
196.590
196.509
169.124
158.108
136.248
136.004
135.920
129.322
129.262
129.003
128.728
126.649
126.164
123.579
123.381
94.038
54.119
53.295
41.062
O
CO2Me
Ph
O
O
CN
3o
Cl
13C{1H} NMR (100 MHz, CDCl3)
196.590
196.509
197.5 197.0 196.5 196.0 195.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

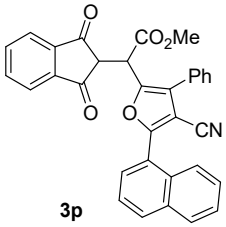


3p

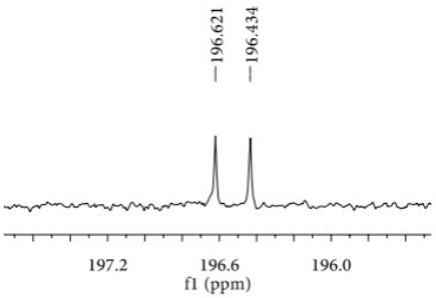
^{1}H NMR (400 MHz, $CDCl_3$)



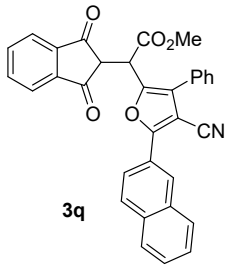




3p

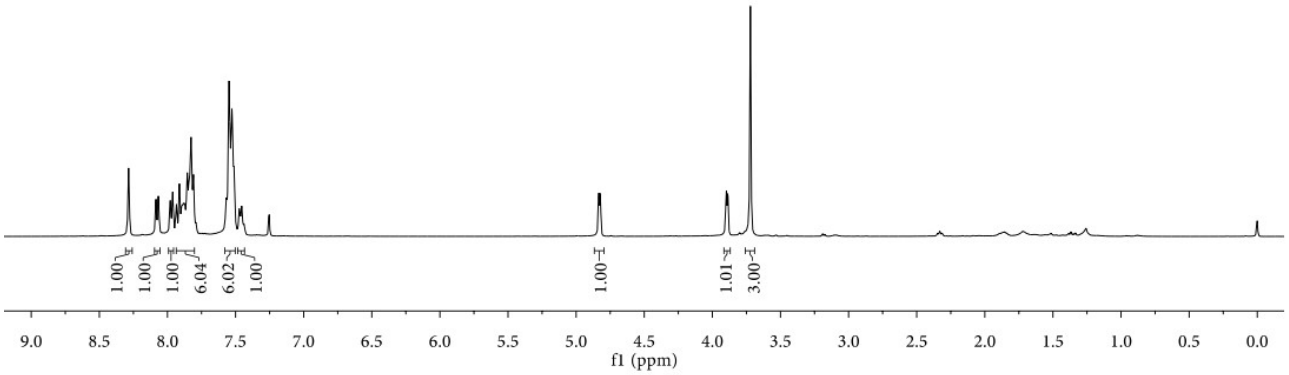


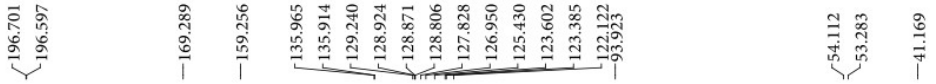
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

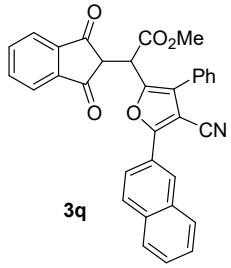


3q

^{1}H NMR (400 MHz, $CDCl_3$)

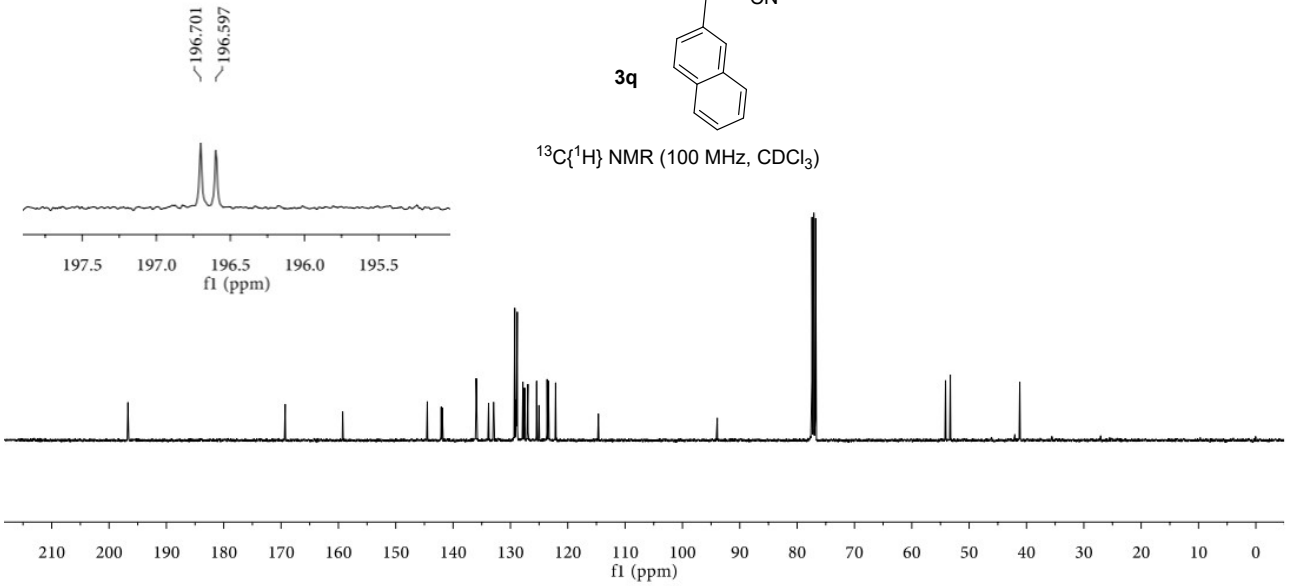


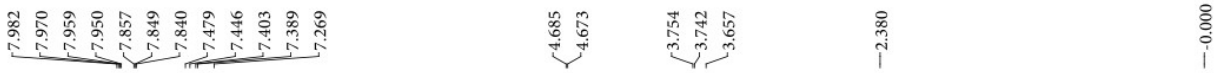


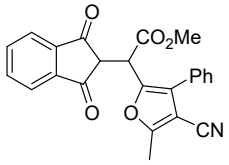


3q

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

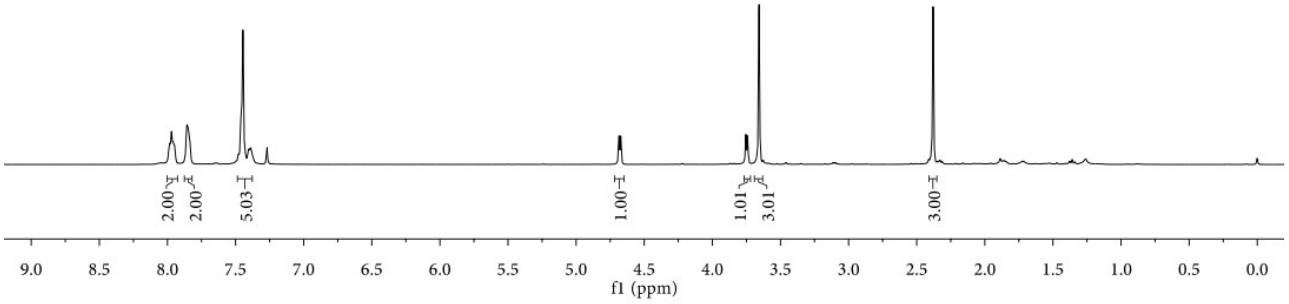


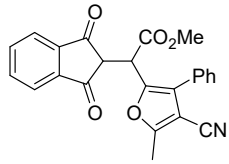




3r

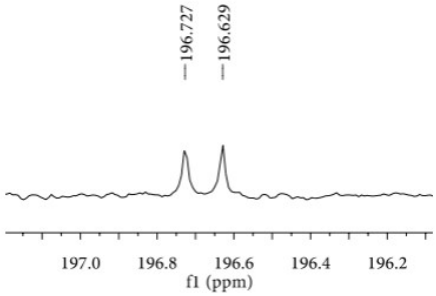
^{1}H NMR (400 MHz, $CDCl_3$)

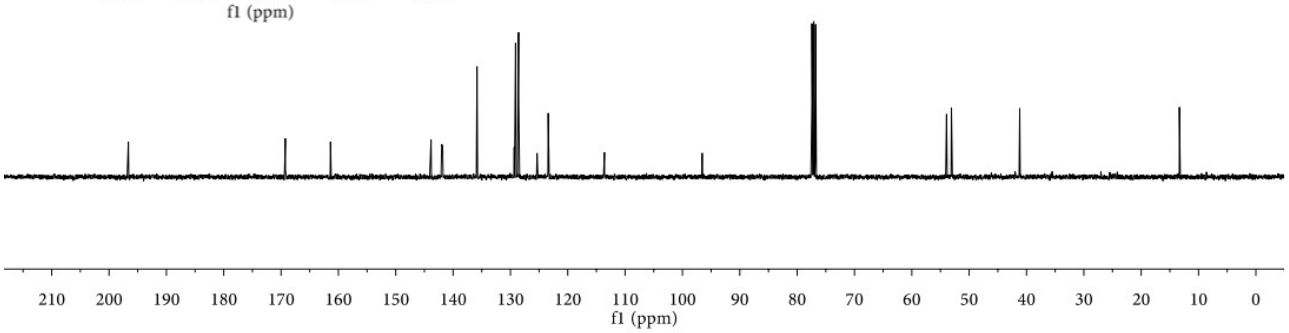


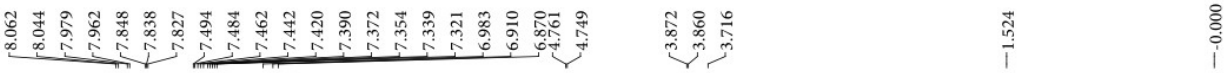


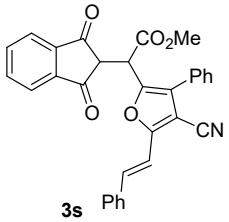
3r

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



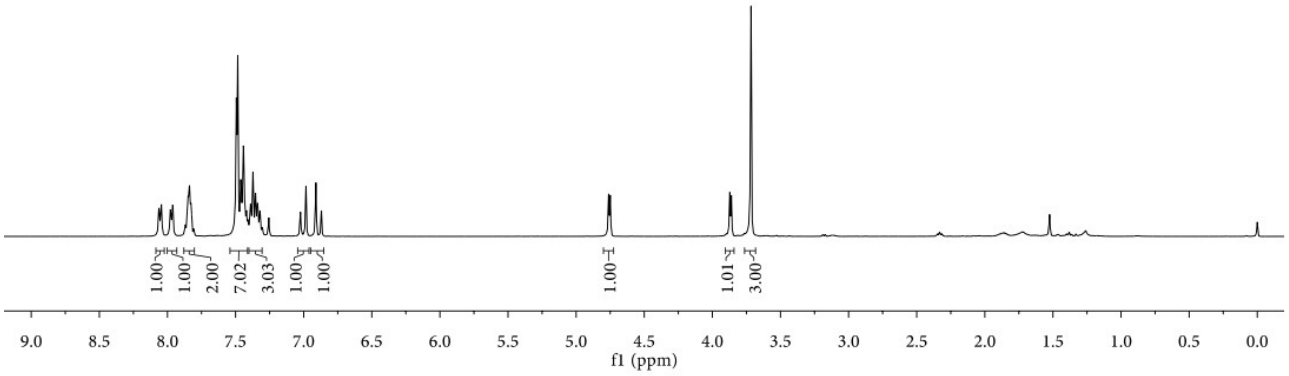


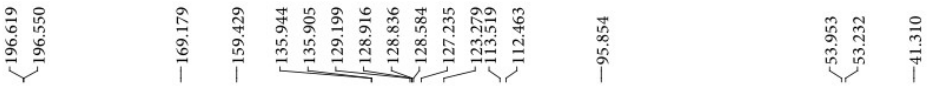


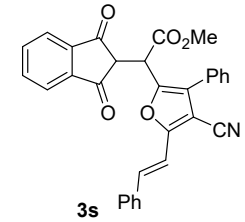


3s

^{1}H NMR (400 MHz, $CDCl_3$)

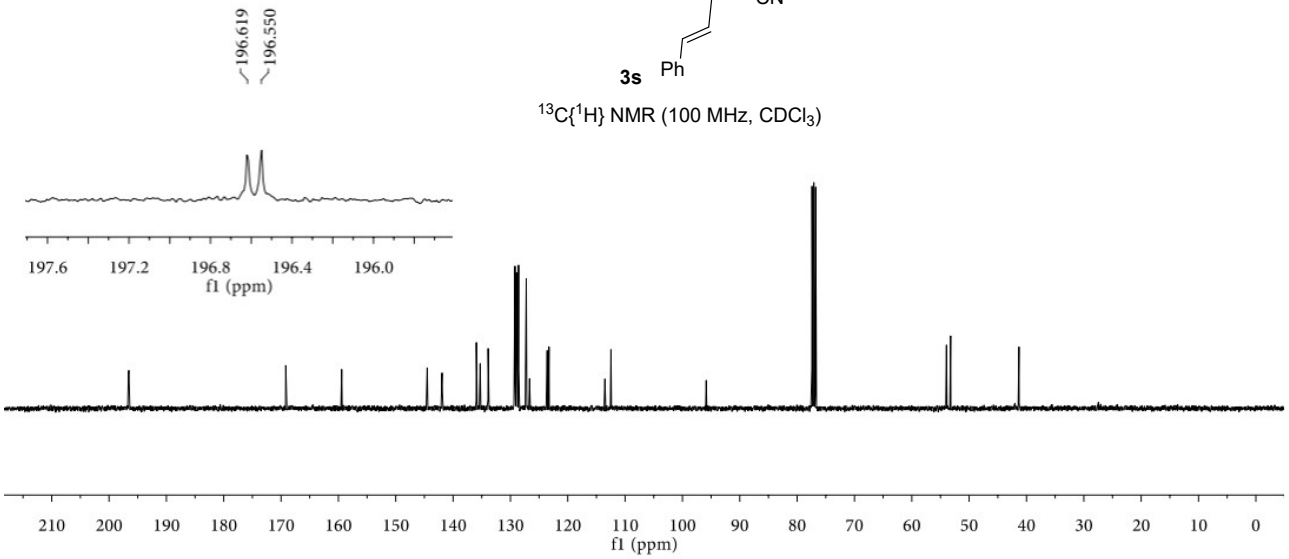


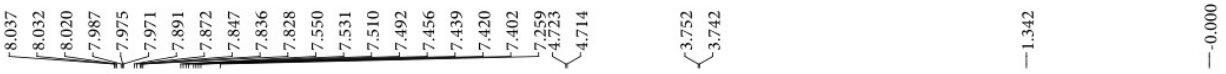


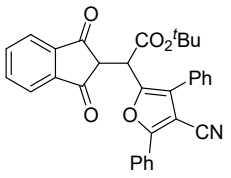


3s

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

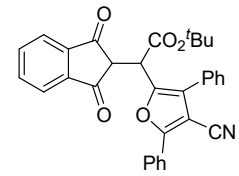






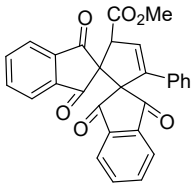
3t

^{1}H NMR (400 MHz, $CDCl_3$)



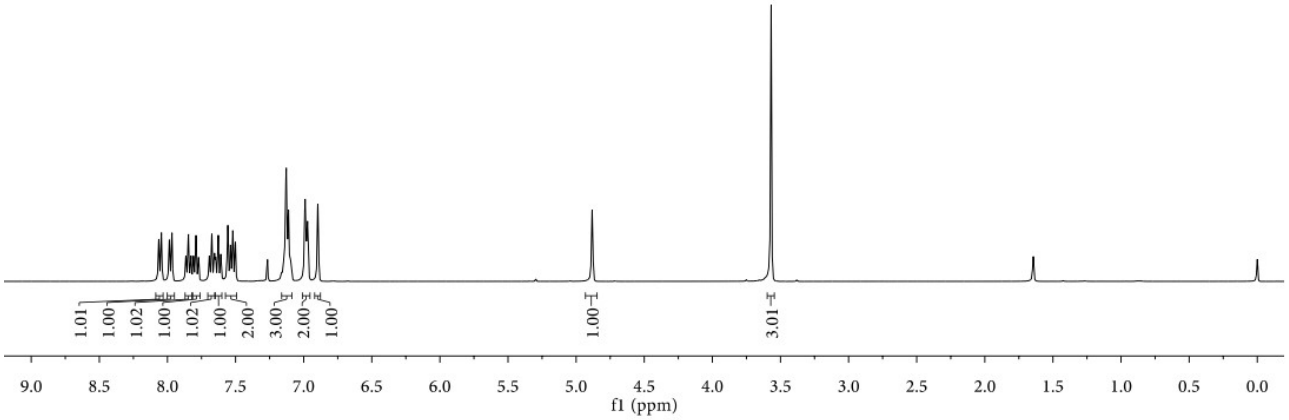
3t

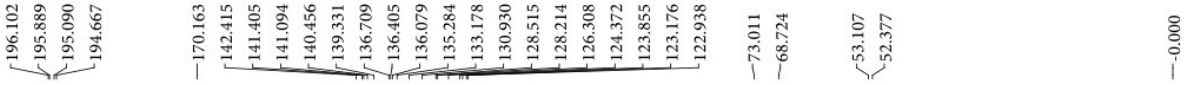
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

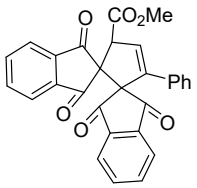


5a

^{1}H NMR (400 MHz, $CDCl_3$)

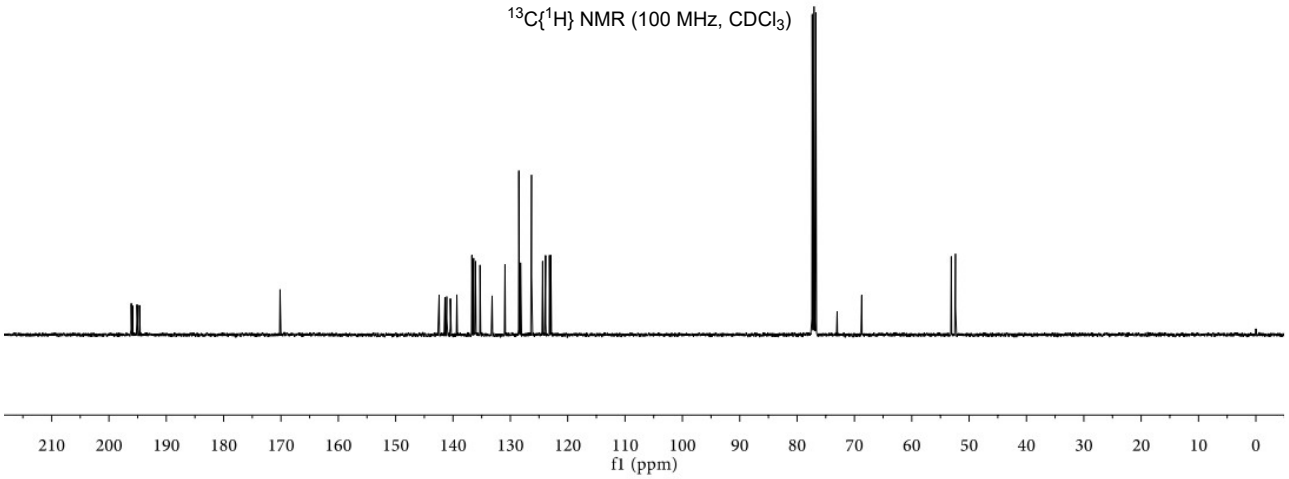


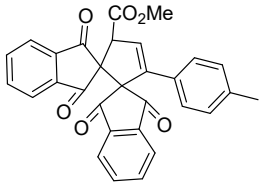




5a

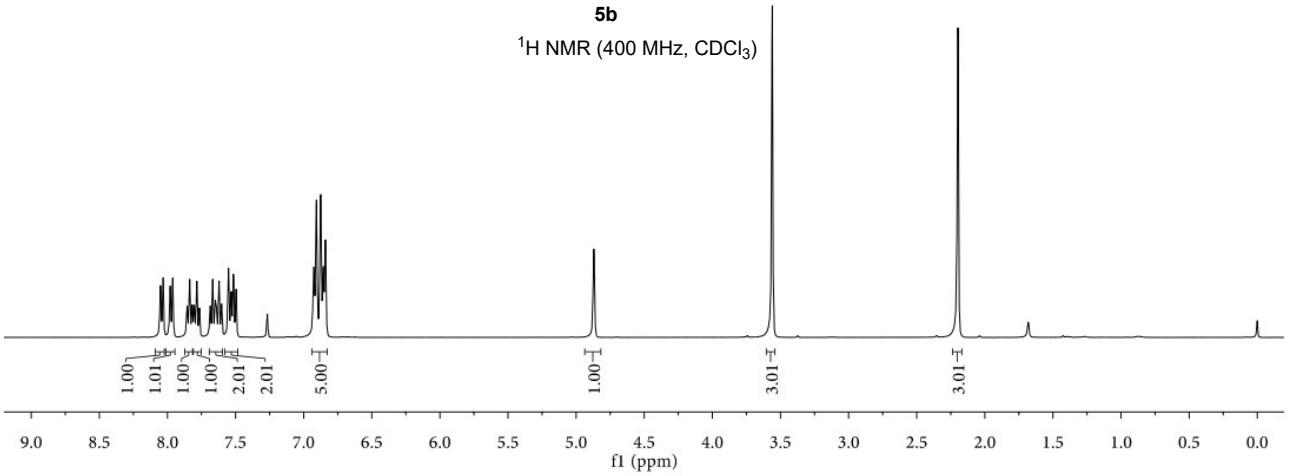
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

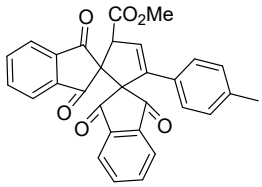




5b

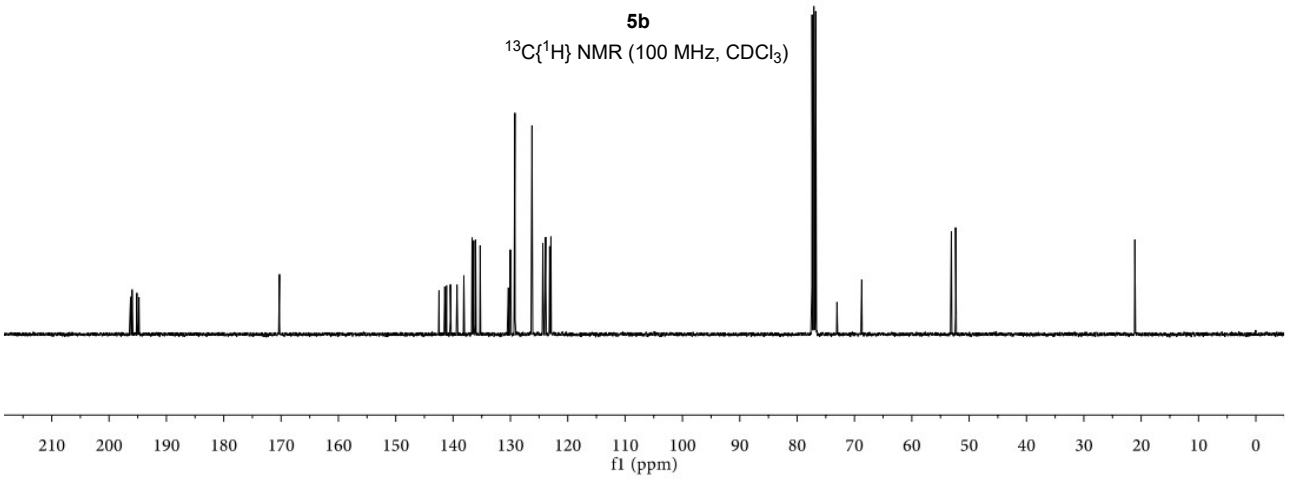
^{1}H NMR (400 MHz, $CDCl_3$)

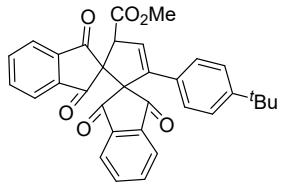




5b

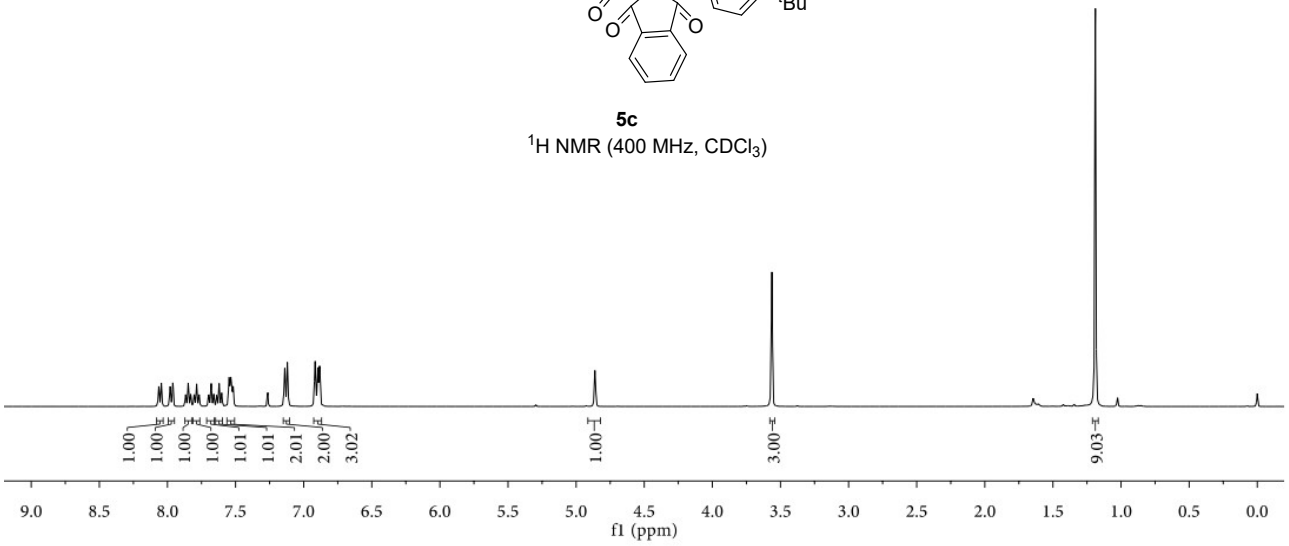
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

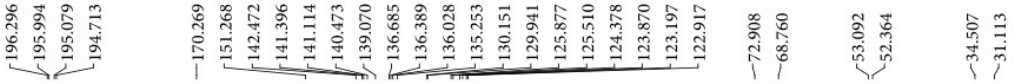


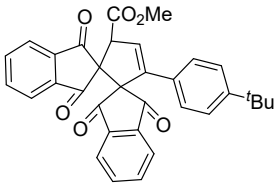


5c

^{1}H NMR (400 MHz, $CDCl_3$)

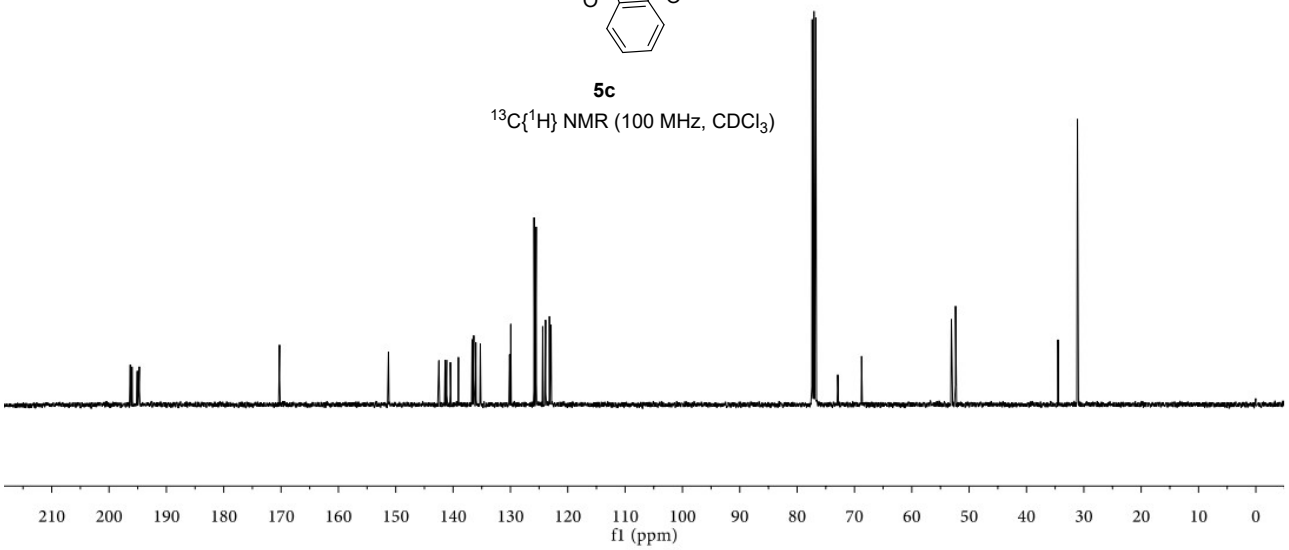


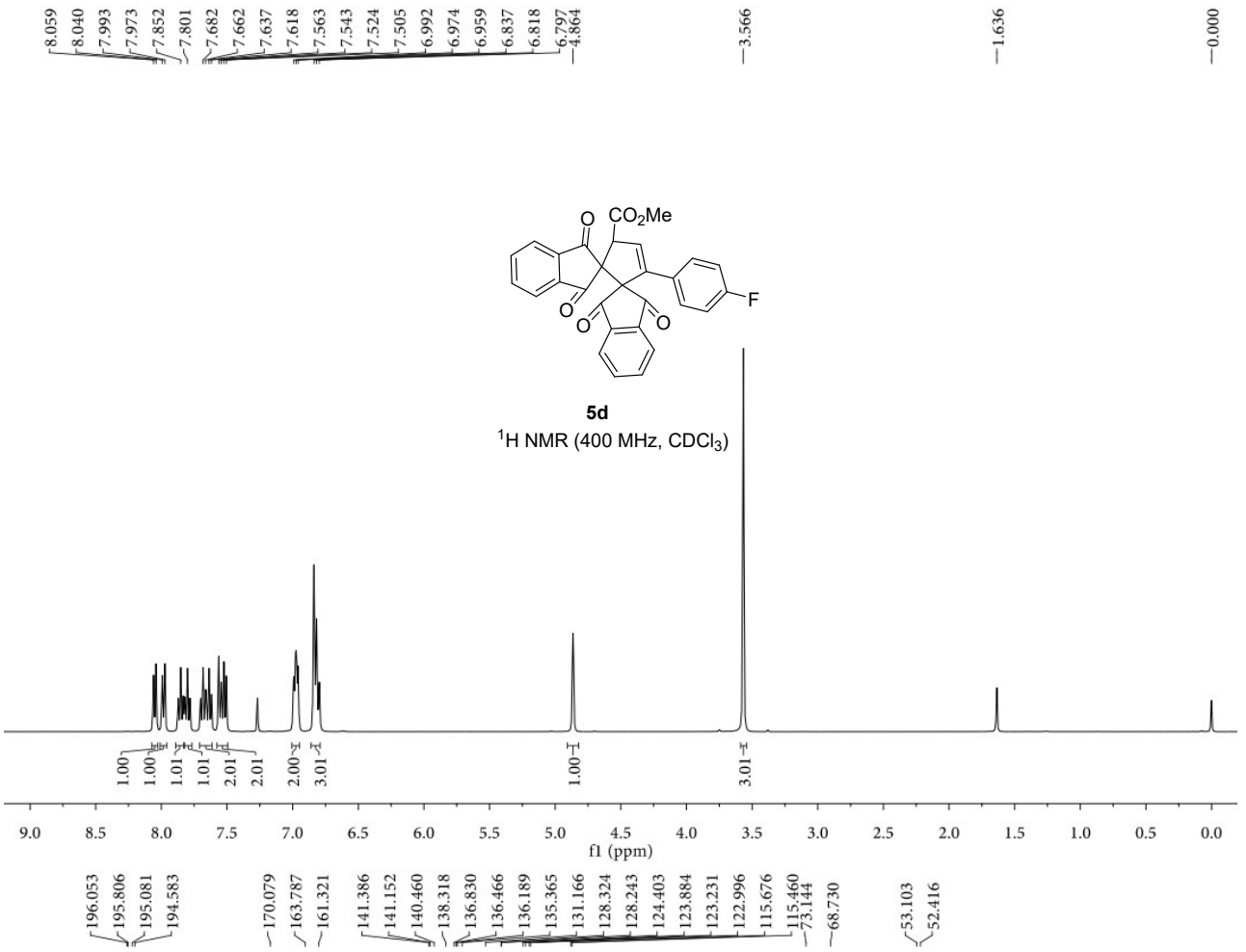




5c

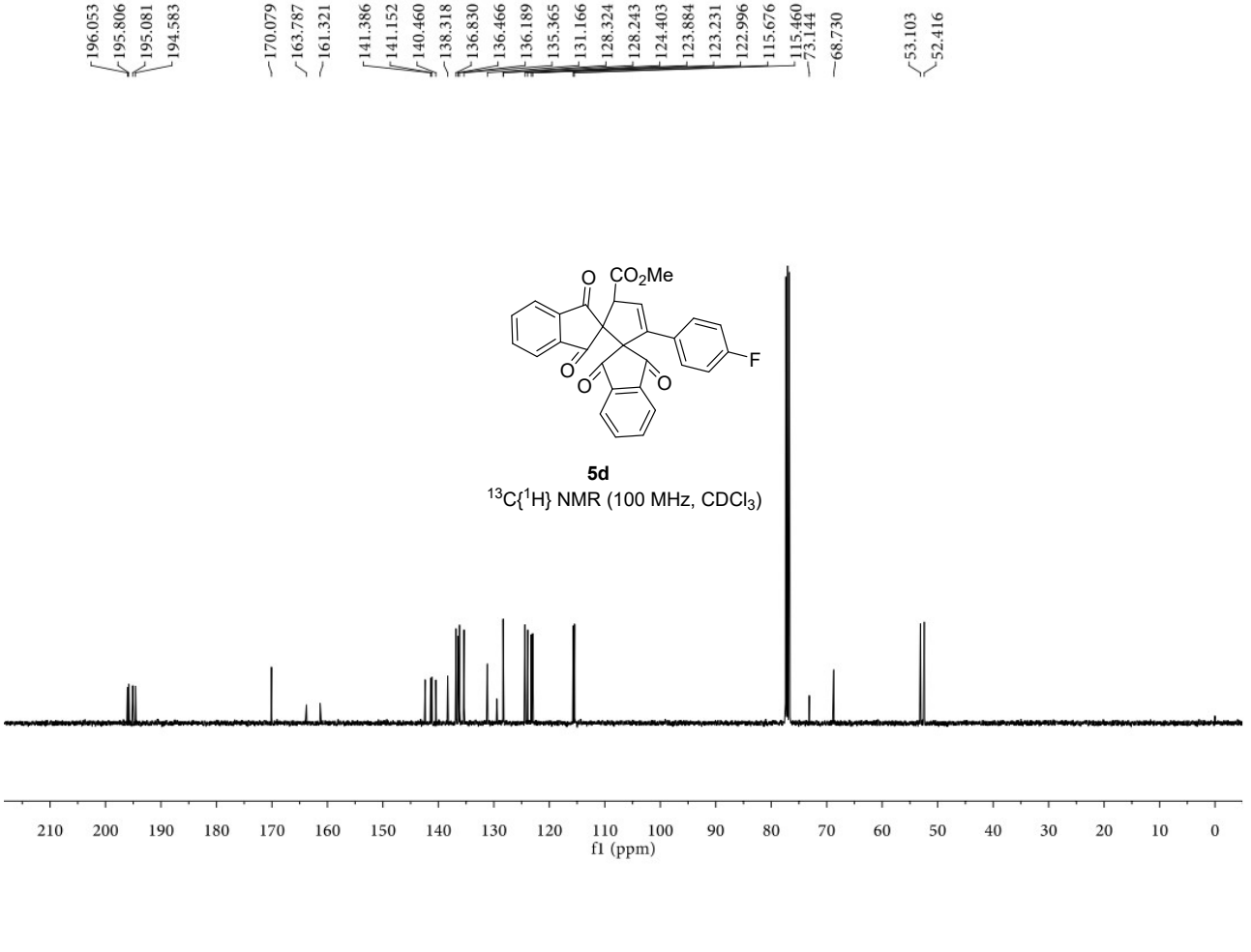
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)





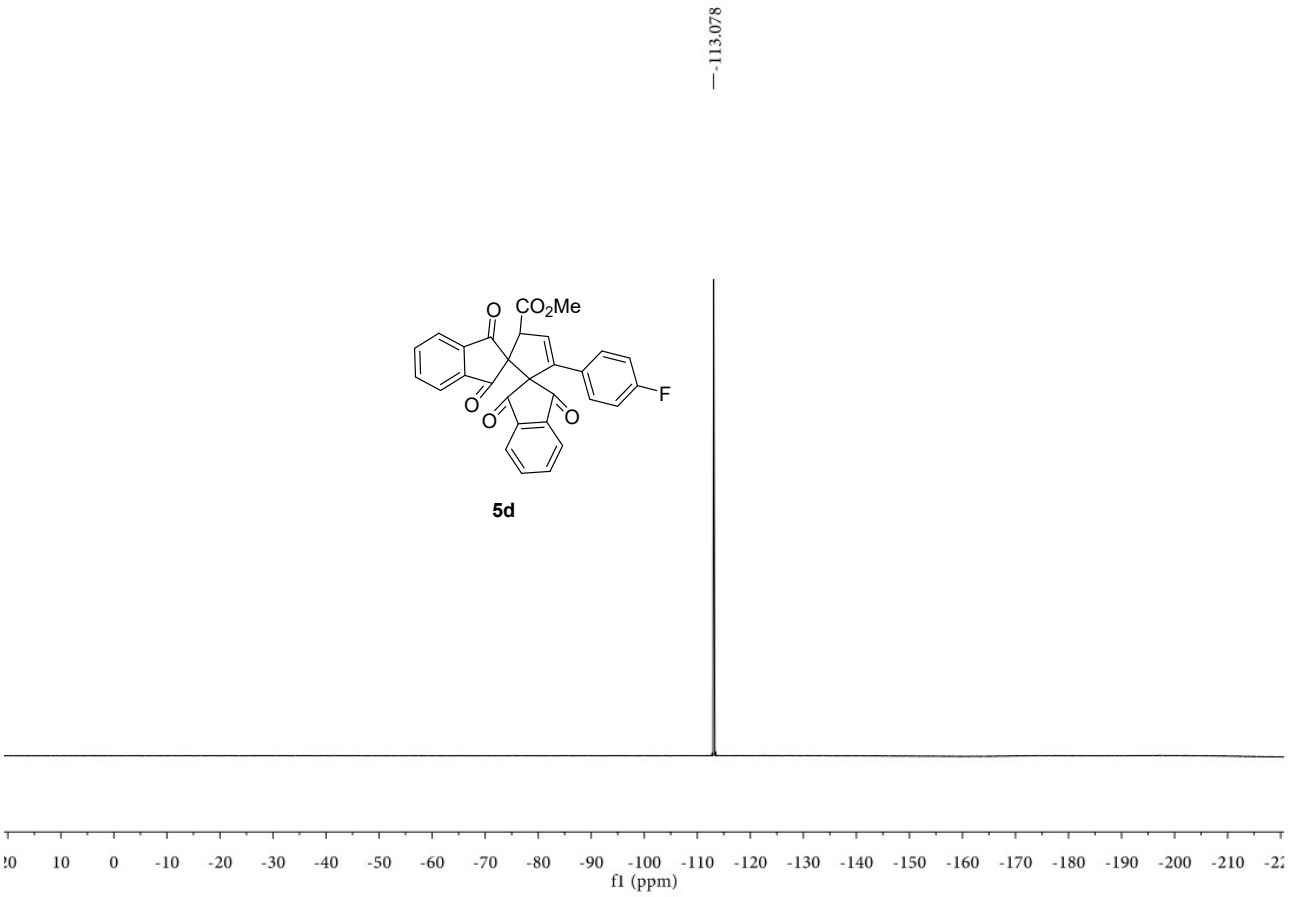
5d

^{1}H NMR (400 MHz, $CDCl_3$)



5d

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


-113.078
O
CO2Me
O
O
O
F
5d
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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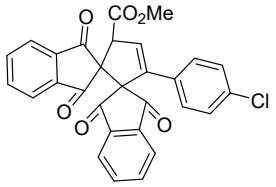
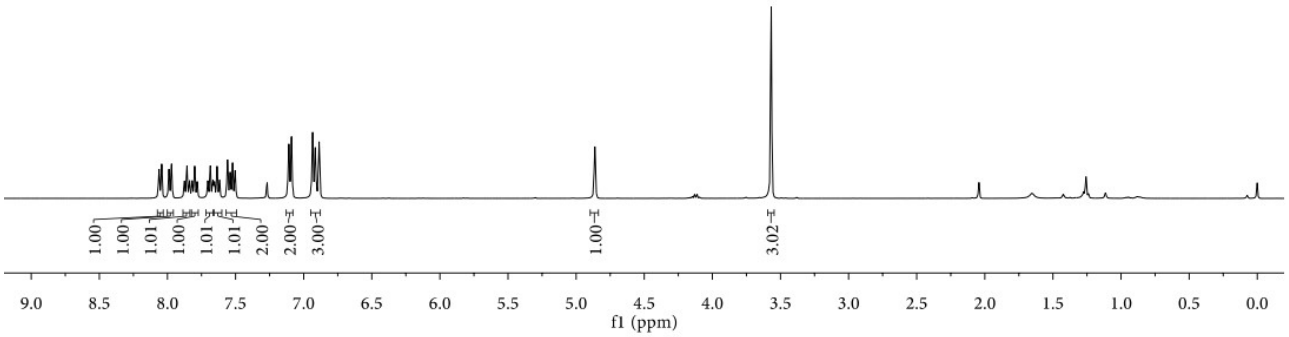
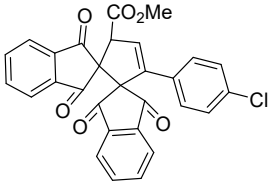
-160
-170
-180
-190
-200
-210
f1 (ppm)



5e

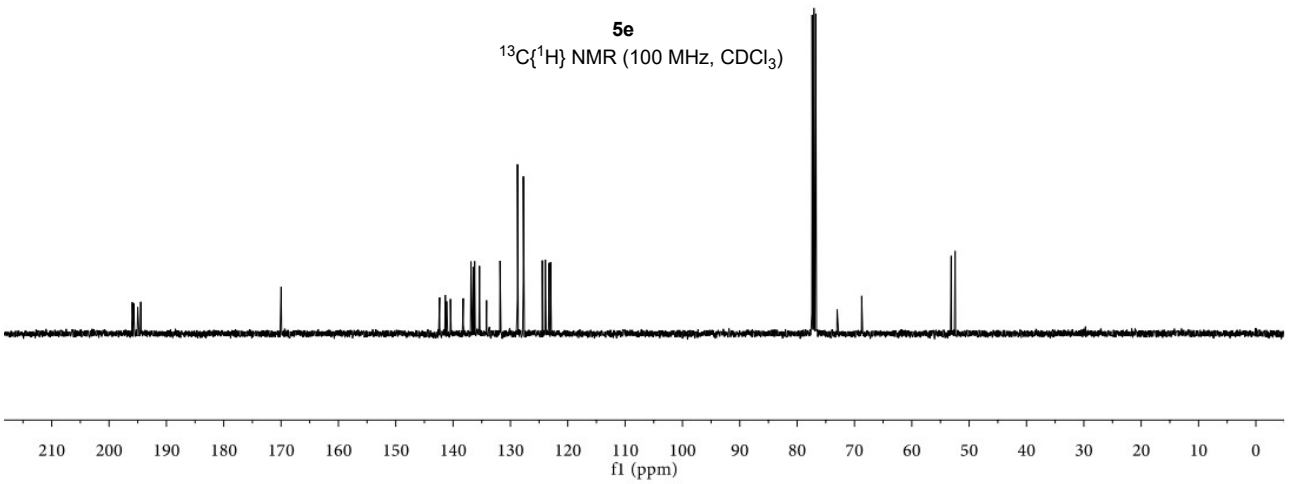
^{1}H NMR (400 MHz, $CDCl_3$)

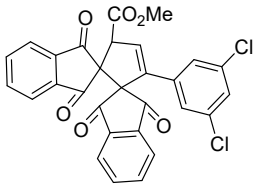




5e

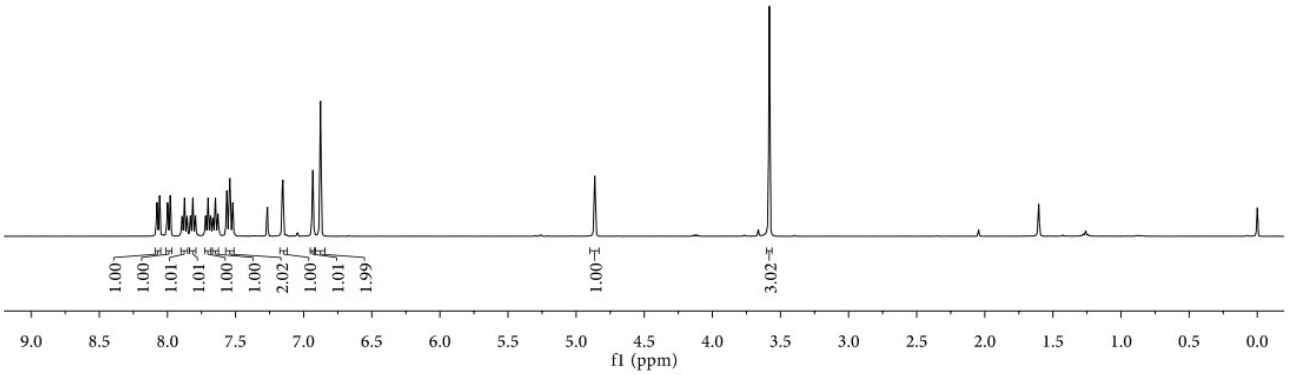
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

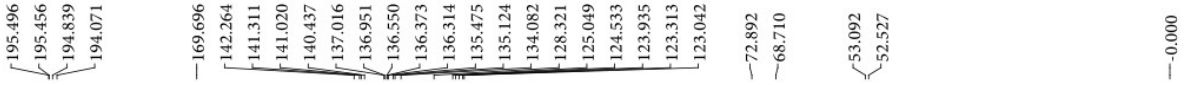


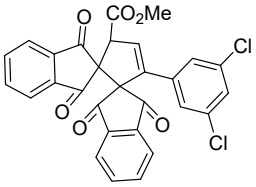


5f

^{1}H NMR (400 MHz, $CDCl_3$)

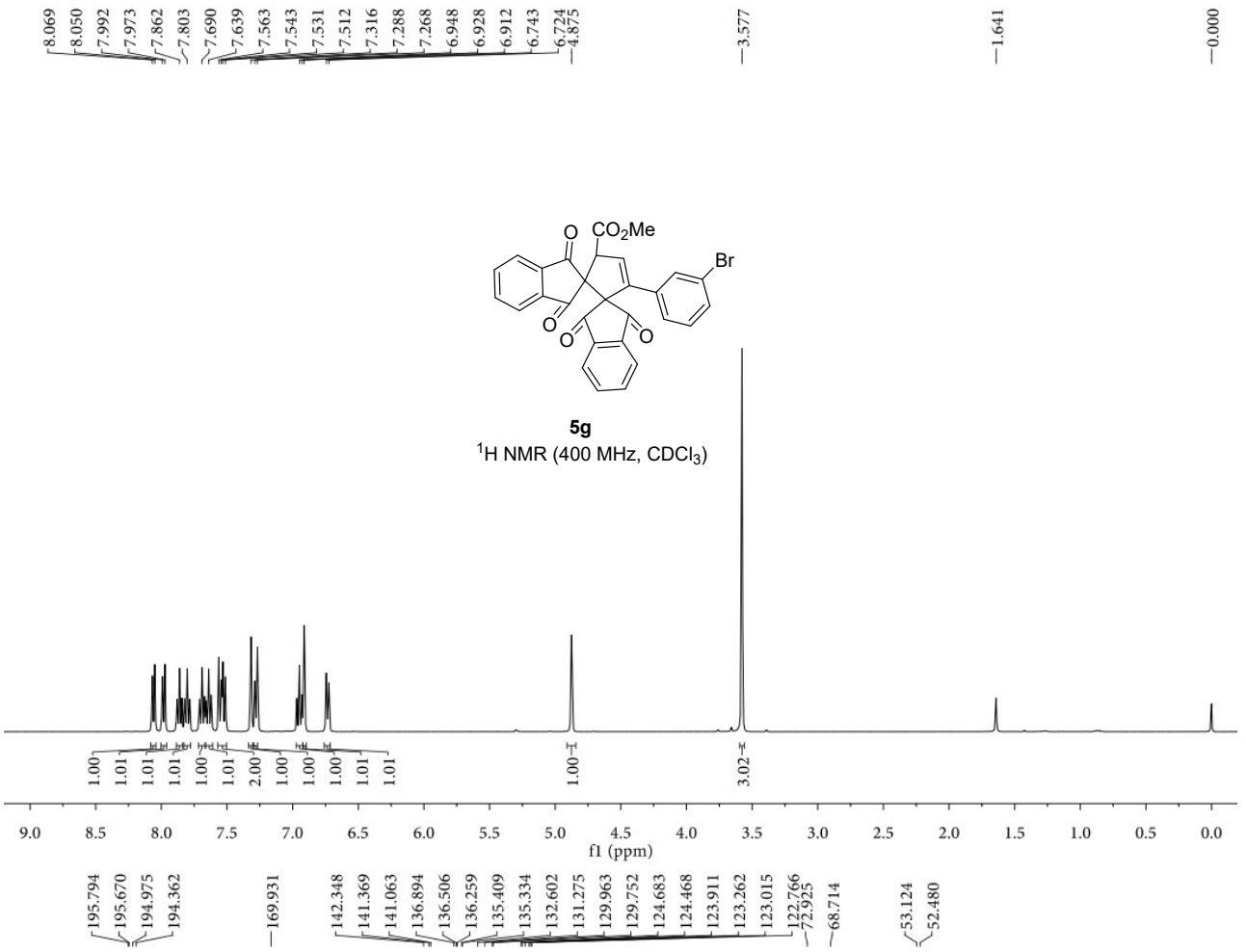






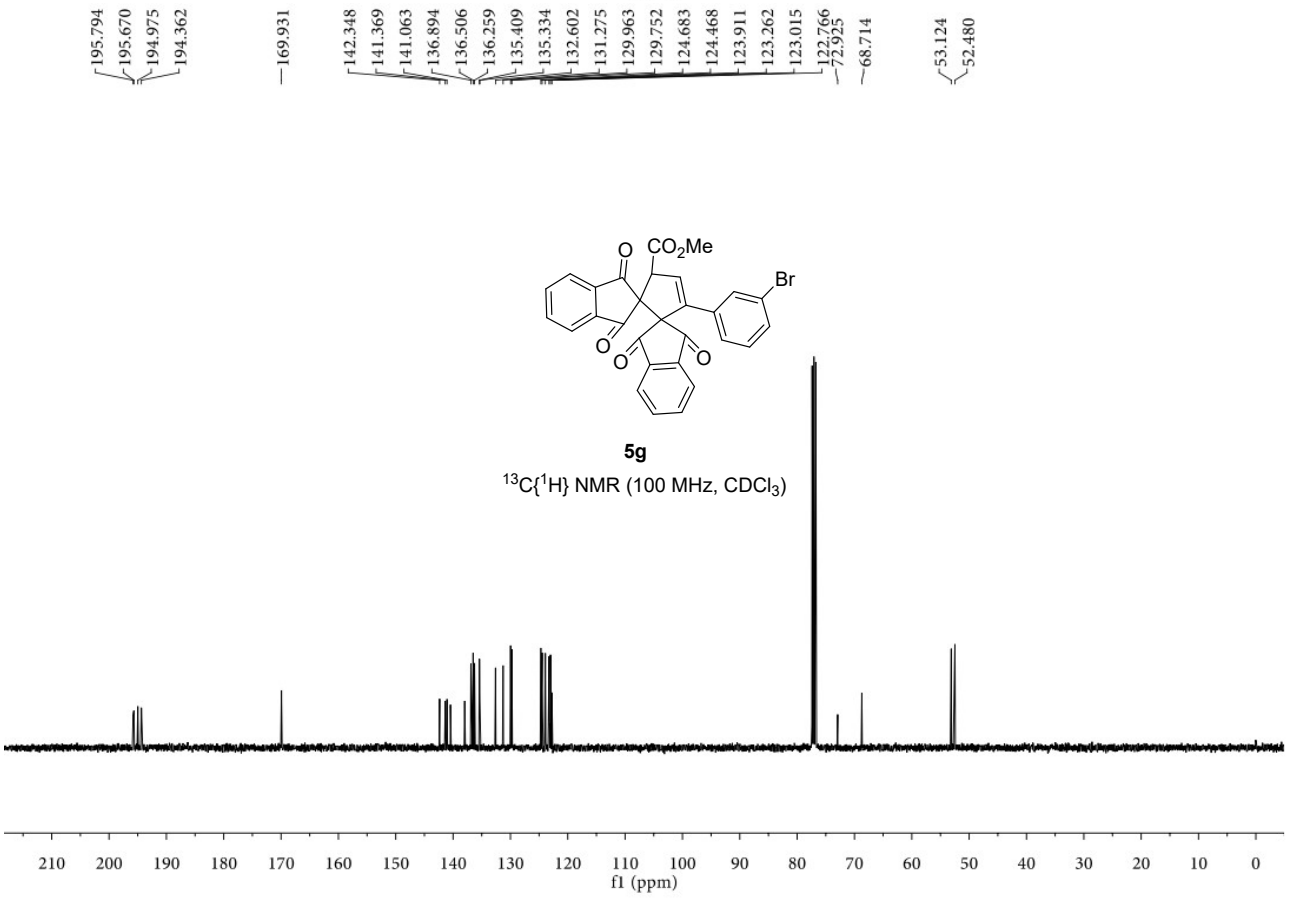
5f

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



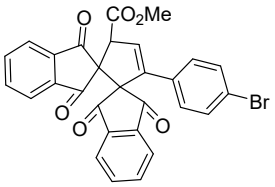
5g

^{1}H NMR (400 MHz, $CDCl_3$)



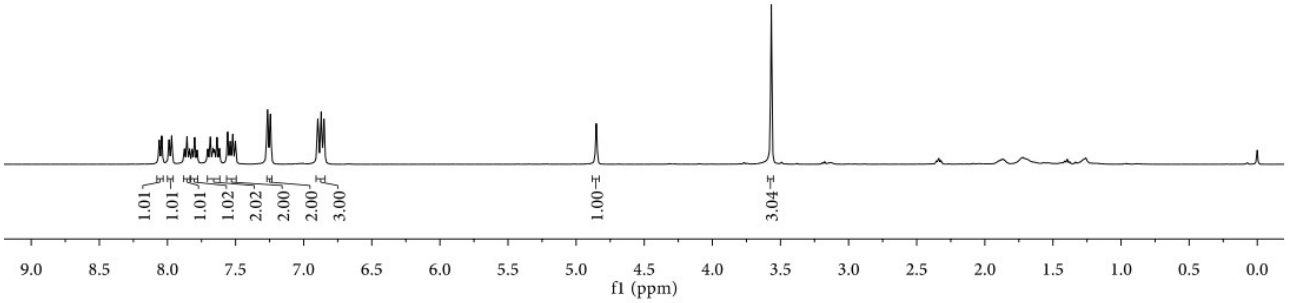
5g

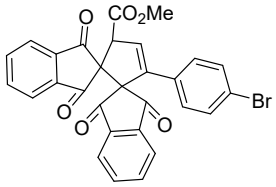
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



5h

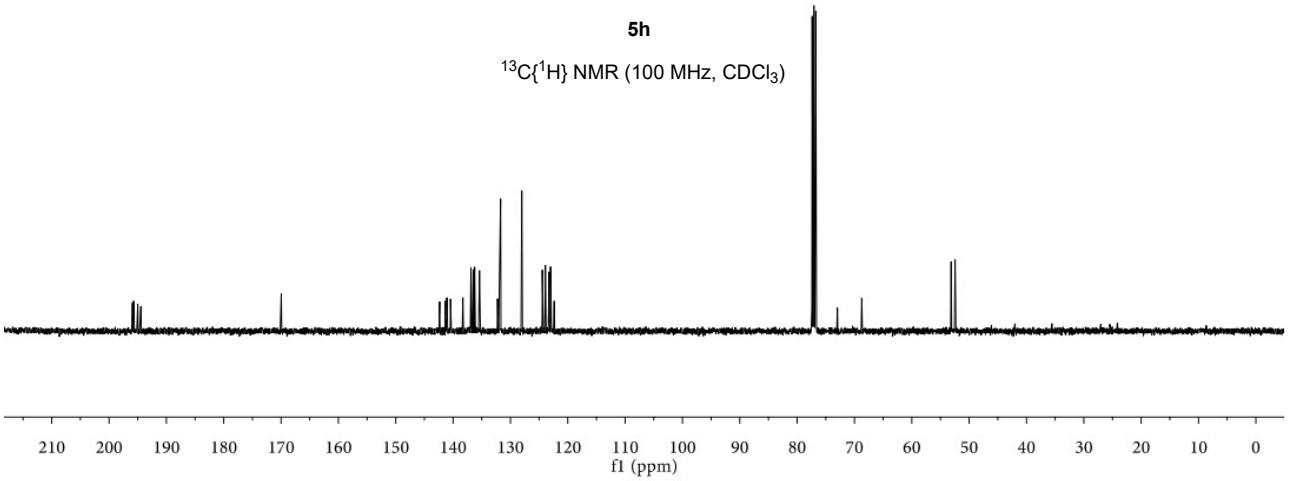
^{1}H NMR (400 MHz, $CDCl_3$)

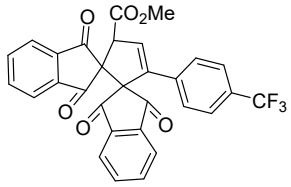




5h

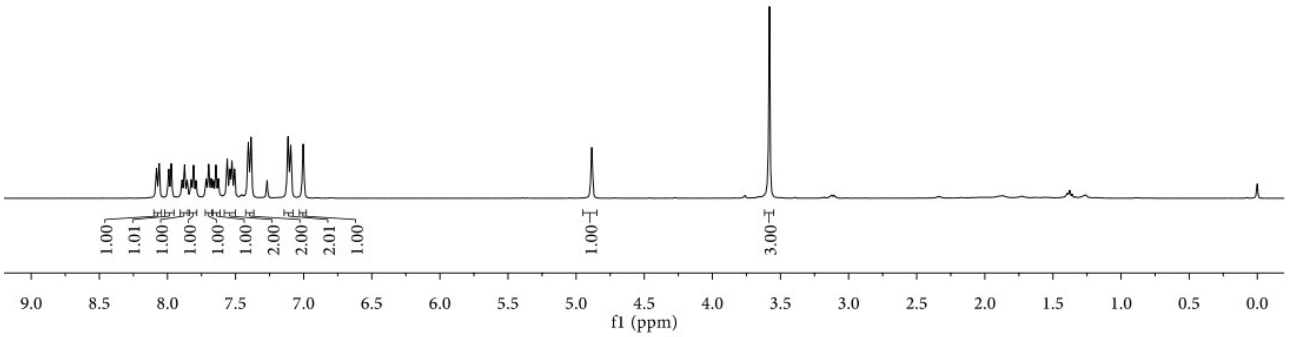
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

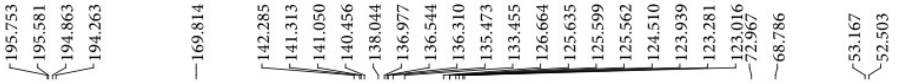


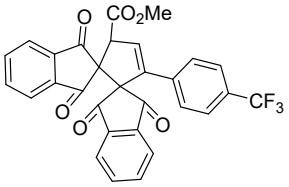


5i

^{1}H NMR (400 MHz, $CDCl_3$)

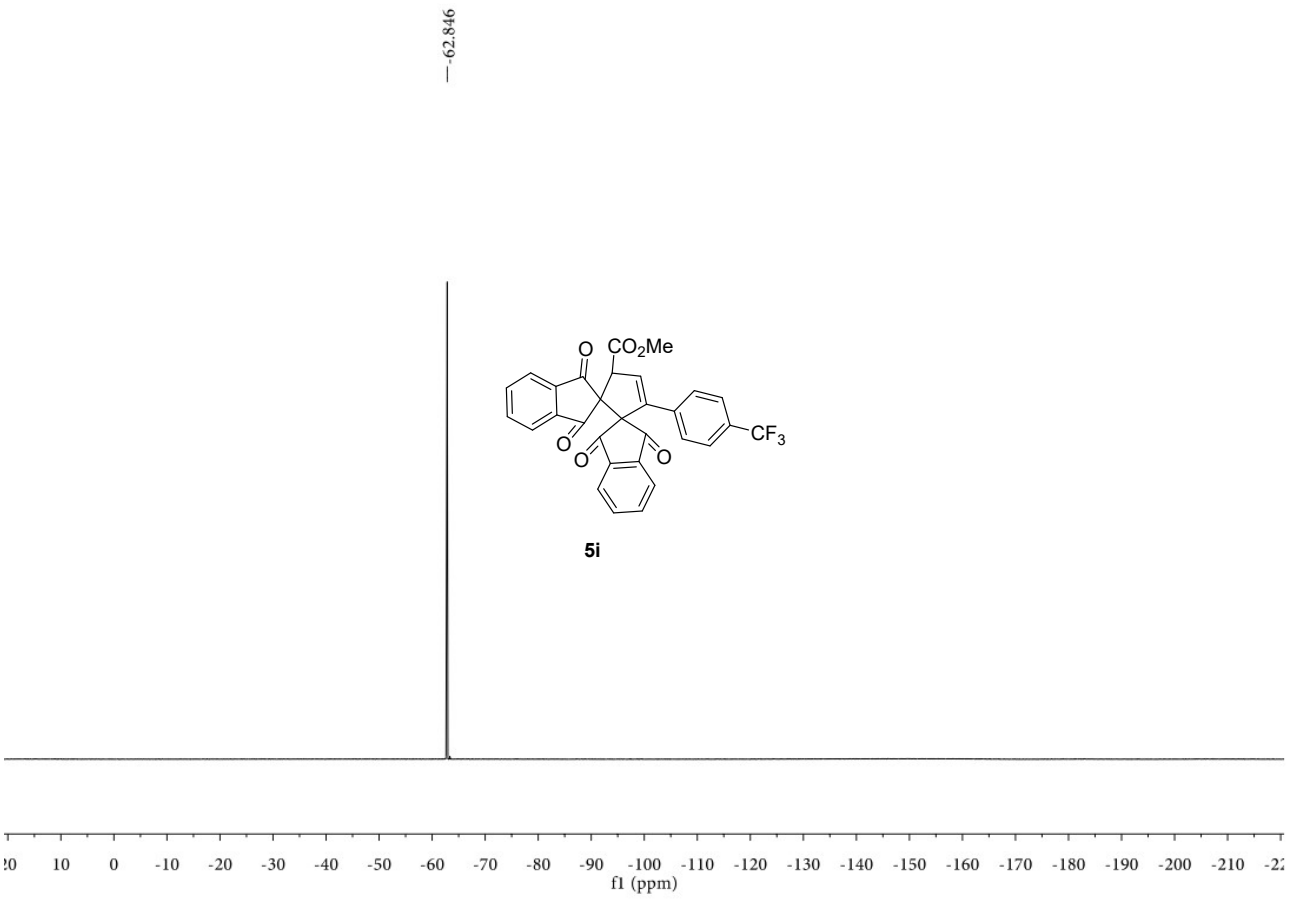


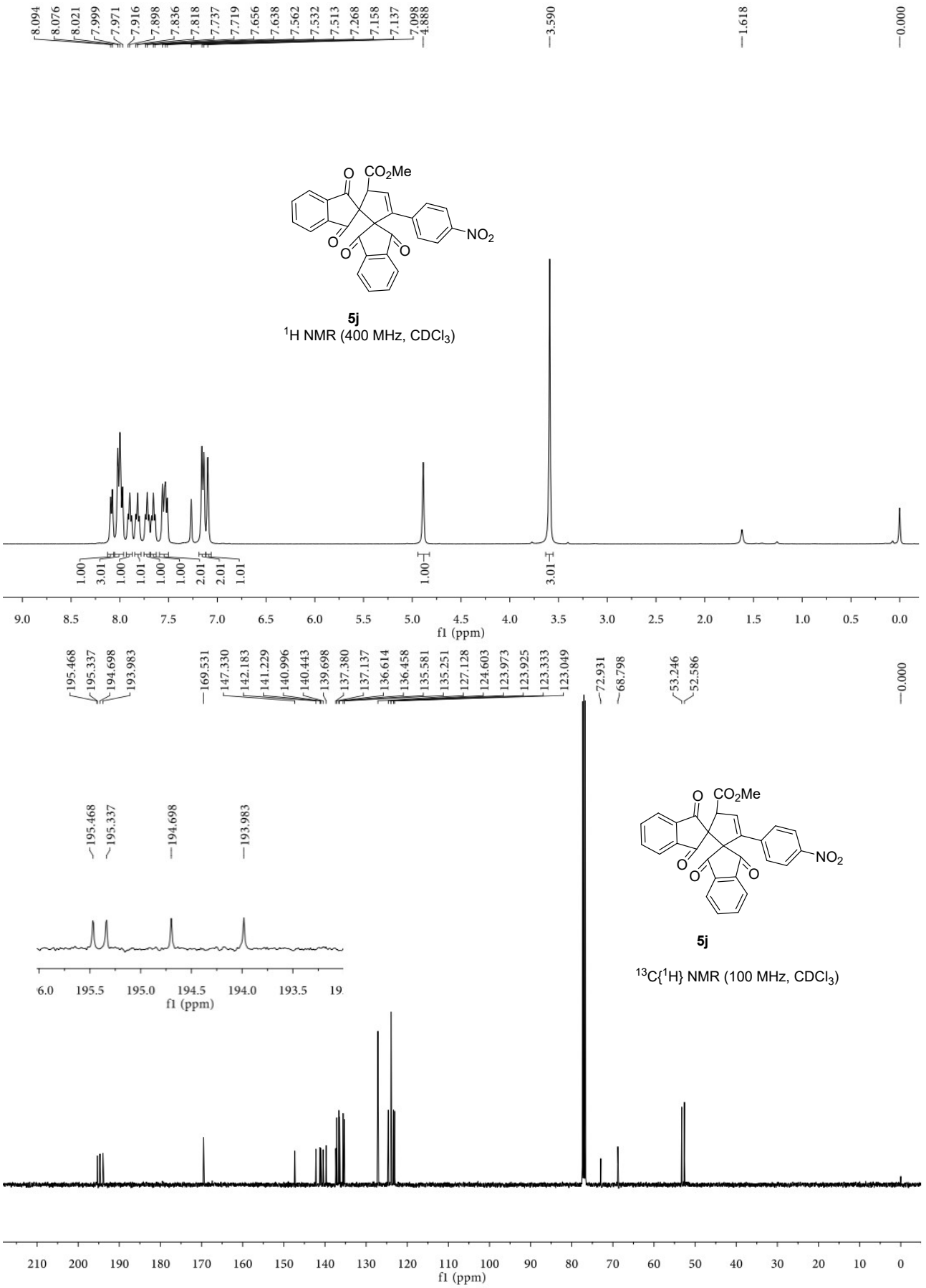


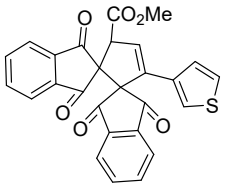


5i

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

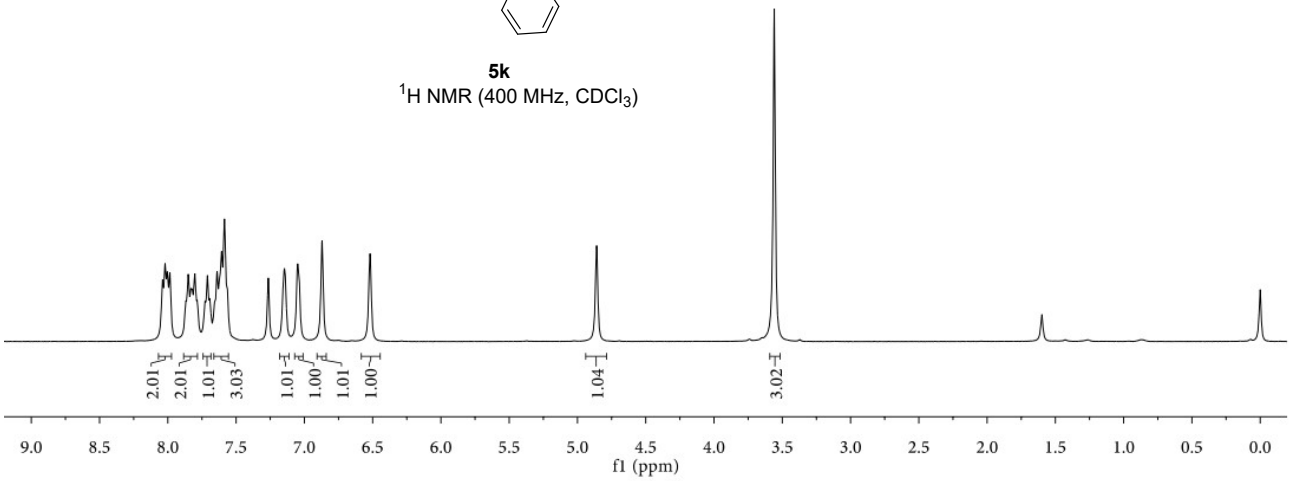

-62.846
O
CO2Me
O
O
O
CF3
5i
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

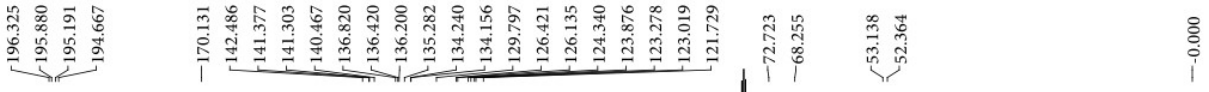

8.094
8.076
8.021
7.999
7.971
7.916
7.898
7.836
7.818
7.737
7.719
7.656
7.638
7.562
7.532
7.513
7.268
7.158
7.137
7.098
4.888
3.590
1.618
0.000
CO2Me
NO2
O
5j
1H NMR (400 MHz, CDCl3)
1.00
3.01
1.00
1.01
1.00
1.00
2.01
2.01
1.01
1.00
3.01
f1 (ppm)
195.468
195.337
194.698
193.983
169.531
147.330
142.183
141.229
140.996
140.443
139.698
137.380
137.137
136.614
136.458
135.581
135.251
127.128
124.603
123.973
123.925
123.333
123.049
72.931
68.798
53.246
52.586
0.000
5j
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

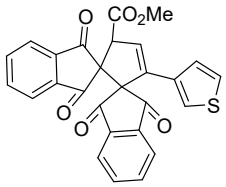


5k

^{1}H NMR (400 MHz, $CDCl_3$)

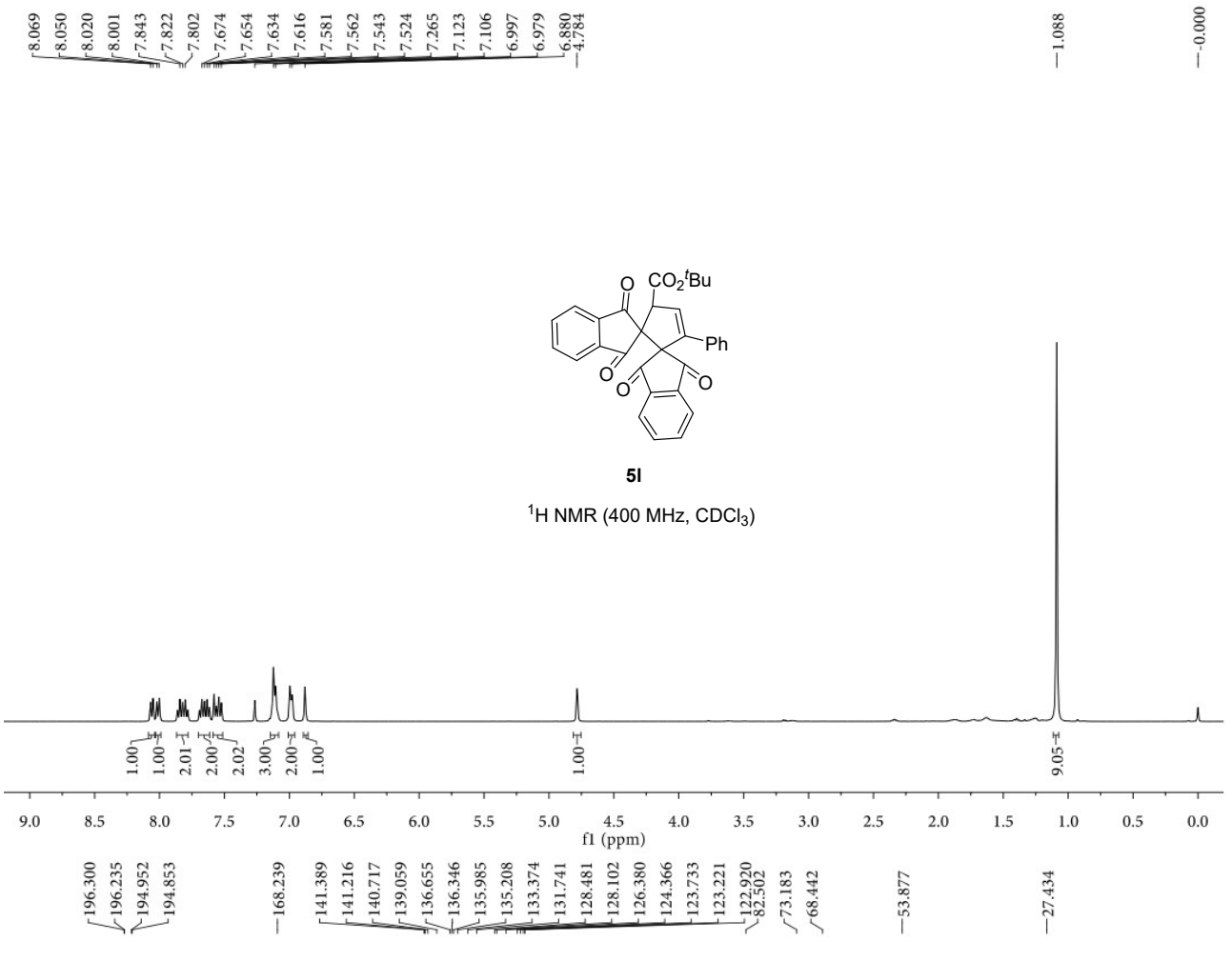


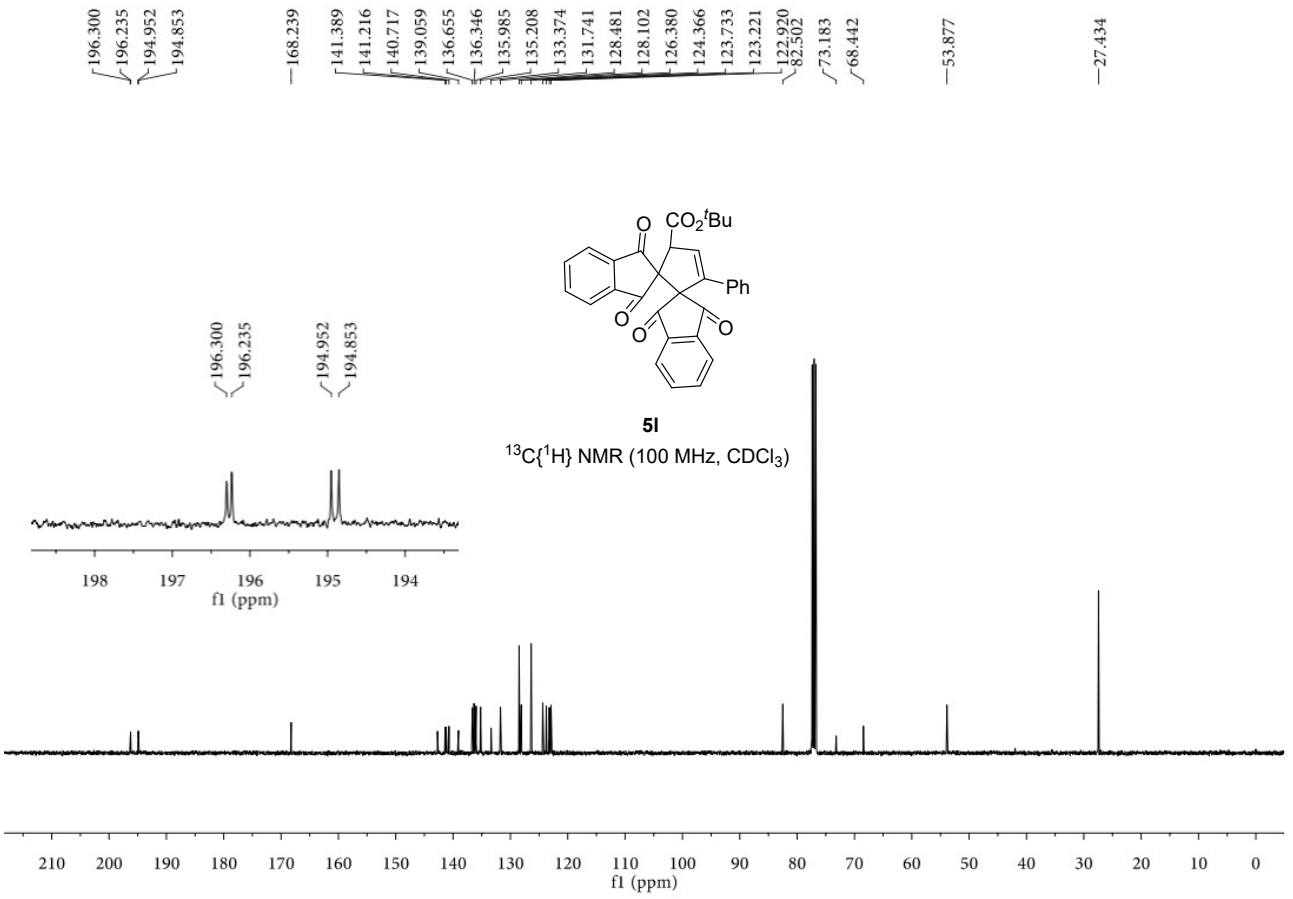


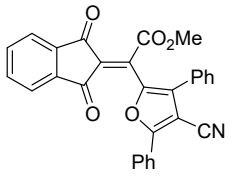


5k

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

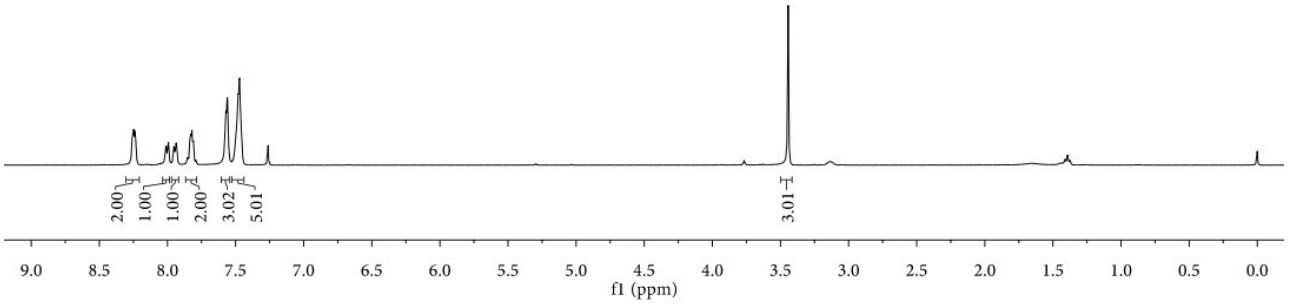

8.069
8.050
8.020
8.001
7.843
7.822
7.802
7.674
7.654
7.634
7.616
7.581
7.562
7.543
7.524
7.265
7.123
7.106
6.997
6.979
6.880
4.784
1.088
-0.000
O
CO2tBu
Ph
O
O
O
5l
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.01
2.00
2.02
3.00
2.00
1.00
1.00
9.05
f1 (ppm)

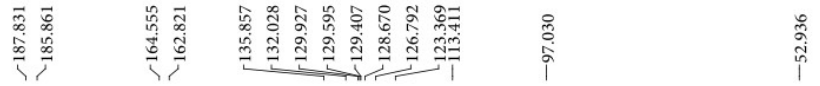

196.300
196.235
194.952
194.853
168.239
141.389
141.216
140.717
139.059
136.655
136.346
135.985
135.208
133.374
131.741
128.481
128.102
126.380
124.366
123.733
123.221
122.920
82.502
73.183
68.442
53.877
27.434
O
CO2tBu
Ph
O
O
O
196.300
196.235
194.952
194.853
198
197
196
195
194
f1 (ppm)
5l
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

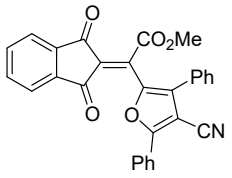


6

^{1}H NMR (400 MHz, $CDCl_3$)







6

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)