Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Chemodivergent synthesis of functionalized methanodibenzo[*b*,*f*][1,5]diazocin-13-ylmethanones and tetrahydroquinolines *via* solvent-dependent AB_2 and A_2B_2 multicomponent annulation reactions

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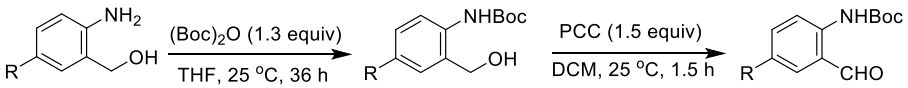
1. General Information

Commercially available reagents were used without further purification and the reaction solvents (THF, MeCN, DCM etc.) were purified using standard procedures. The reactions were monitored by thin-layer chromatography visualized by UV detection or using *p*-anisaldehyde or 2,4-DNP stains or molecular iodine. Flash column chromatography was performed with silica gel (230-400 mesh). Melting points were recorded on a melting point apparatus in capillaries and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at room temperature on a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Chemical shifts (δ) are expressed in ppm using TMS as internal standard, and coupling constants (*J*) are given in hertz. Infrared (IR) spectra were obtained using an Agilent Cary 630 FTIR spectrometer with a diamond ATR accessory for solid and liquid samples, requiring no sample preparation, and the major frequencies were reported in cm^{-1}. Elemental analyses were determined at the CAI de Microanálisis Elemental, Universidad Complutense, by using a Leco 932 CHNS combustion microanalyzer.

2. General Procedure for the Synthesis of *tert*-Butyl (2-Formylphenyl)carbamates 7.[1]



S1a-c **S2a-c**

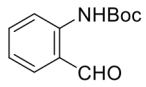
7a: R = H (95%)
7b: R = Cl (93%)
7c: R = Br (92%)

To a solution of 2-aminobenzyl alcohols **S1a-c** (20 mmol) in dry THF (66 mL) was added $(Boc)_2O$ (26 mmol, 1.3 equiv), and the reaction mixture was stirred at room temperature for 36 h. After completion, the reaction mixture was diluted with ethyl acetate, washed with water, dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether-ethyl acetate mixture as eluent (90:10, v/v).

[1] Y.-T. Lee, Y.-J. Jang, S.-E. Syu, S.-C. Chou, C.-J. Lee and W. Lin, Preparation of functional benzofurans and indoles via chemoselective intramolecular Wittig reactions, *Chem. Commun.,* 2012, **48**, 8135.

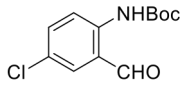
To a stirred solution of compounds **S2a-c** obtained in the previous step in DCM (60 mL) was added PCC (1.5 equiv), and stirring was continued at 25 ^{o}C for 1.5 hours. After complete conversion, the reaction mixture was filtered over celite and washed with DCM (3 x 40 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether-ethyl acetate mixture as eluent (95:5, v/v) to provide *tert*-butyl (2-formylphenyl)carbamates **7a-c** in excellent overall yields.

***tert*-Butyl (2-formylphenyl)carbamate (7a).**[1] Colourless solid; Yield: 95% (4.203 g); mp: 61-62 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (s, 9H), 7.14 (td, *J* = 7.8, 1.2 Hz, 1H), 7.58 (td, *J* = 7.8, 1.2 Hz, 1H), 7.63 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.46 (d, *J* = 8.4, 1H), 9.90 (s, 1H), 10.40 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 28.3, 80.9, 118.2, 121.2, 121.5, 135.9, 136.1, 141.8, 152.9, 195.0.



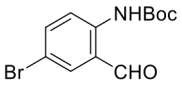
7a

***tert*-Butyl (4-chloro-2-formylphenyl)carbamate (7b).**[2] Colourless solid; Yield: 93% (4.744 g); mp: 106-108 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (s, 9H), 7.53 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 8.46 (d, *J* = 9.0 Hz, 1H), 9.84 (s, 1H), 10.30 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.2, 81.3, 120.0, 122.1, 126.5, 134.9, 135.7, 140.3, 152.7, 193.8.



7b

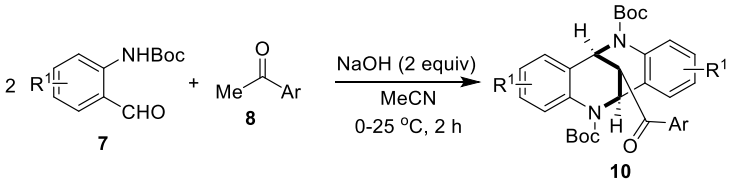
***tert*-Butyl (4-bromo-2-formylphenyl)carbamate (7c).**[3] Colourless solid; Yield: 92% (5.520 g); mp: 110-112 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (s, 9H), 7.65 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 8.40 (d, *J* = 9.0 Hz, 1H), 9.83 (s, 1H), 10.30 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 28.2, 81.4, 113.4, 120.3, 122.5, 138.0, 138.5, 140.8, 152.6, 193.7.



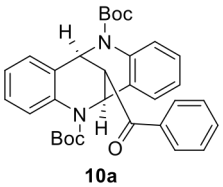
7c

[2] K. E. Frank and J. Aubé, Cyclizations of substituted benzylidene-3-alkenylamines: Synthesis of the tricyclic core of the martinellines, *J. Org. Chem*., 2000, **65**, 655.
[3] P. T. Lansbury, H. Han, C.-G. Cho, W. Zhen and J. D. Harper, US006054114A, 2000.

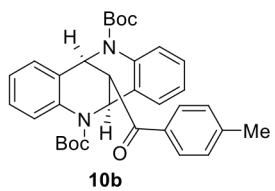
3. General Procedure for the Synthesis of Methanodibenzo[*b,f*][1,5]diazocin-13-ylmethanones 10.



To a stirred solution of aryl methyl ketones **8** (0.55 mmol) in MeCN (3.0 mL) was added *tert*-butyl (2-formylphenyl)carbamates **7** (1.0 mmol) followed by NaOH (2.0 mmol) at 0 °C, and stirring was continued for 2 hours at 25 °C. After completion of the reaction, the mixture was diluted with water, extracted with ethyl acetate (3 x 10 mL), washed with water, and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether-ethyl acetate mixture as eluent (95:5 to 90:10, v/v) to obtain methanodibenzo[*b,f*][1,5]diazocin-13-yl)methanones **10**.


10a

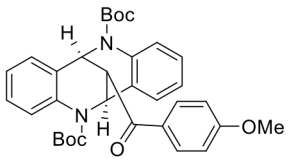
(±) Di-*tert*-butyl 13-benzoyl-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10a). Pale yellow solid; Yield: 89% (234 mg); mp: 205-208 °C. IR (neat): 2978.9, 2940.5, 1701.8, 1489.5, 1367.2, 1309.8, 1145.5, 1010.2 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.17 (s, 9H), 1.56 (s, 9H), 3.95 (dd, *J* = 3.3, 1.5 Hz, 1H), 6.07 (s, 1H), 6.28 (d, *J* = 2.4 Hz, 1H), 6.90-6.97 (m, 2H), 7.02 (td, *J* = 8.7, 1.5 Hz, 1H), 7.10 (td, *J* = 8.7, 1.5 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.38-7.46 (m, 3H), 7.53-7.64 (m, 2H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.90 (dd, *J* = 8.4, 1.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.9, 28.5, 45.1, 50.1, 52.2, 81.6, 82.3, 122.0, 122.8, 123.5, 123.6, 125.8, 126.6, 127.8, 128.4, 128.6, 129.0, 129.3, 129.4, 133.6, 135.7, 136.3, 137.3, 151.9, 152.4, 196.7. Anal Calcd for $C_{32}H_{34}N_2O_5$: C, 72.98; H, 6.51; N, 5.32. Found: C, 73.02; H, 6.54; N, 5.26.


10b

(±) Di-*tert*-butyl 13-(4-methylbenzoyl)-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10b). Colourless solid; Yield: 87% (235 mg); mp: 218-220 °C. IR (neat): 2977.8, 2896.3, 1702.9, 1606.5, 1488.4, 1366.2, 1312.2, 1155.4 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 9H), 1.62 (s,

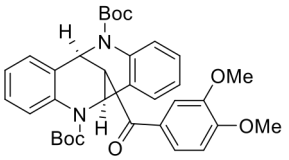
9H), 2.44 (s, 3H), 4.00 (dd, *J* = 3.0, 1.5 Hz, 1H), 6.12 (s, 1H), 6.34 (s, 1H), 6.98-7.03 (m, 2H), 7.09 (td, *J* = 8.7, 1.5 Hz, 1H), 7.16 (td, *J* = 8.7, 1.5 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.36 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.46 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.69 (brs, 1H), 7.86 (d, *J* = 8.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 21.7, 27.9, 28.5, 45.0, 50.1, 52.3, 81.5, 82.3, 122.1, 122.8, 123.5, 123.6, 125.9, 126.6, 127.7, 128.5, 129.2, 129.4, 129.6, 133.3, 136.4, 137.3, 144.4, 152.2, 152.4, 196.4. Anal Calcd for $C_{33}H_{36}N_2O_5$: C, 73.31; H, 6.71; N, 5.18. Found: C, 73.19; H, 6.69; N, 5.05. *One aromatic carbon is merged with others.

(±) Di-*tert*-butyl 13-(4-methoxybenzoyl)-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10c). Colourless solid; Yield: 73% (203 mg); mp: 178-180 ^{o}C. IR (neat): 2983.4, 2906.5, 1705.1, 1612.7, 1467.5, 1381.2, 1309.2, 1145.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (s, 9H), 1.62 (s, 9H), 3.89 (s, 3H), 3.96-3.89 (m, 1H), 6.10 (s, 1H), 6.33 (s, 1H), 6.96-7.03 (m, 4H), 7.08 (td, *J* = 8.4, 1.5 Hz, 1H), 7.16 (td, *J* = 8.4, 1.5 Hz, 1H), 7.36 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.46 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.68 (brs, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.0, 28.5, 44.8, 50.2, 52.4, 55.6, 81.5, 82.2, 114.1, 122.2, 122.8, 123.5, 123.6, 126.1, 126.7, 127.7, 128.5, 128.8, 129.2, 129.4, 130.6, 136.4, 137.3, 152.1, 152.4, 163.8, 195.2. Anal Calcd for $C_{33}H_{36}N_2O_6$: C, 71.20; H, 6.52; N, 5.03. Found: C, 69.92; H, 6.63; N, 5.14.



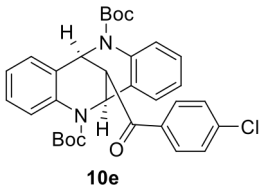
10c

(±) Di-*tert*-butyl 13-(3,4-dimethoxybenzoyl)-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10d). Colourless solid; Yield: 77% (226 mg); mp: 145-147 ^{o}C. IR (neat): 2976.3, 2935.0, 1700.5, 1513.0, 1460.9, 1366.2, 1313.6, 1268.2, 1157.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 9H), 1.56 (s, 9H), 3.80 (s, 3H), 3.90-3.93 (m, 4H), 6.04 (s, 1H), 6.27 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.91-6.96 (m, 2H), 7.02 (td, *J* = 9.3, 1.5 Hz, 1H), 7.10 (td, *J* = 8.7, 1.5 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.38-7.41 (m, 2H), 7.57-7.64 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.0, 28.5, 44.7, 50.3, 52.6, 56.0, 56.2, 81.5, 82.3, 110.2, 110.4, 122.2, 122.8, 122.9, 123.5, 123.6, 126.1, 126.7, 127.7, 128.6, 128.9, 129.2, 129.4, 136.4, 137. 3, 149.4, 152.1, 152.4, 153.6, 195.4. Anal Calcd for $C_{34}H_{38}N_2O_7$: C, 69.61; H, 6.53; N, 4.77. Found: C, 69.43; H, 6.49; N, 4.70.



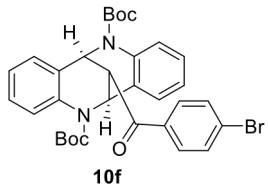
10d

(±) Di-*tert*-butyl 13-(4-chlorobenzoyl)-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10e). Colourless solid; Yield: 90% (252 mg); mp: 230-232 ^{o}C. IR (neat): 2978.4, 2929.4, 1697.0, 1488.6, 1366.5, 1311.9, 1153.5 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (s, 9H), 1.69 (s, 9H), 3.98 (s, 1H), 6.12 (s, 1H), 6.32 (s, 1H), 6.98-7.04 (m, 2H), 7.09 (t, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.45-7.50 (m, 3H), 7.66 (brs, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 28.0, 28.5, 45.3, 50.0, 52.1, 81.8, 82.4, 122.3, 122.9, 123.6, 123.8, 125.7, 126.4, 127.8, 128.7, 129.2, 129.4, 129.8, 134.1, 136.3, 137.3, 140.0, 152.0, 152.4, 195.7. Anal Calcd for $C_{32}H_{33}ClN_2O_5$: C, 68.50; H, 5.93; N, 4.99. Found: C, 68.34; H, 5.70; N, 4.73. *One aromatic carbon is merged with others.



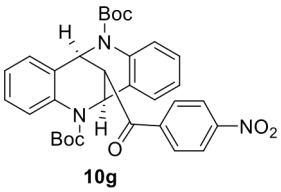
10e

(±) Di-*tert*-butyl 13-(4-bromobenzoyl)-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10f). Colourless solid; Yield: 87% (263 mg); mp: 224-226 ^{o}C. IR (neat): 2978.0, 2887.5, 1699.5, 1488.2, 1366.1, 1311.6, 1154.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (s, 9H), 1.62 (s, 9H), 3.96 (dd, *J* = 3.3, 1.5 Hz, 1H), 6.10 (s, 1H), 6.31 (d, *J* = 2.1 Hz, 1H), 6.98-7.04 (m, 2H), 7.09 (td, *J* = 8.4, 1.8 Hz, 1H), 7.17 (td, *J* = 8.4, 1.8 Hz, 1H), 7.35 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 (dd, *J* = 7.5. 1.5 Hz, 1H), 7.65 (m, 3H), 7.82 (d, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.0, 28.5, 45.2, 50.0, 52.0, 81.8, 82.4, 122.2, 122.9, 123.6, 123.8, 125.7, 126.3, 127.9, 128.6, 128.7, 129.2, 129.4, 129.8, 132.2, 134.5, 136.3, 137.2, 152.3, 152.4, 195.9. Anal Calcd for $C_{32}H_{33}BrN_2O_5$: C, 63.47; H, 5.49; N, 4.63. Found: C, 63.36; H, 5.51; N, 4.41.



10f

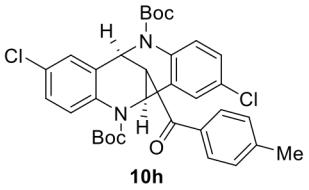
(±) Di-*tert*-butyl 13-(4-nitrobenzoyl)-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10g). Colourless solid; Yield: 81% (232 mg); mp: 218-220 ^{o}C. IR (neat): 2979.1, 2929.4, 1700.2, 1602.7, 1526.1, 1485.9, 1365.2, 1155.0, 1010.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 9H), 1.56 (s, 9H), 3.98 (s, 1H), 6.26 (s, 1H), 6.34 (s, 1H), 6.92-6.99 (m, 2H), 7.03 (t, *J* = 8.1 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.53 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 8.7 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 28.1, 28.5, 45.9, 49.9, 51.7, 82.1, 82.6, 122.5, 123.0, 123.7, 124.0, 124.1, 125.4, 126.0, 128.0, 128.7, 129.3, 129.4, 136.2, 137.2, 140.3, 150.5, 152.2,



10g

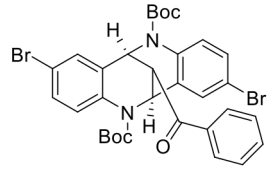
152.4, 195.8. Anal Calcd for $C_{32}H_{33}N_3O_7$: C, 67.24; H, 5.82; N, 7.35. Found: C, 67.01; H, 5.66; N, 7.04. *One aromatic carbon is merged with others.

(±) Di-*tert*-butyl 2,8-dichloro-13-(4-methylbenzoyl)-6,12-methanodibenzo[*b,f*][1,5] diazocine-5,11(6*H*,12*H*)-dicarboxylate (10h). Colourless solid; Yield: 87% (264 mg); mp: 226-228 °C. IR (neat): 3055.5, 2983.4, 2928.7, 1706.0, 1484.3, 1368.9, 1315.0, 1265.8, 1155.2 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 9H), 1.63 (s, 9H), 2.45 (s, 3H), 3.95 (s, 1H), 6.04 (s, 1H), 6.26 (s, 1H), 7.07 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.15 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.30-7.34 (m, 3H), 7.42 (s, 1H), 7.68 (brs, 1H), 7.82-7.92 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 27.9, 28.5, 44.5, 49.8, 51.9, 82.3, 83.0, 123.7, 124.2, 127.3, 127.9, 128.0, 128.4, 128.5, 128.6, 128.8, 128.9, 129.0, 129.7, 132.9, 134.9, 135.8, 144.8, 151.7, 152.1, 195.8. Anal Calcd for $C_{33}H_{34}Cl_2N_2O_5$: C, 65.03; H, 5.62; N, 4.60. Found: C, 64.76; H, 5.51; N, 4.49.



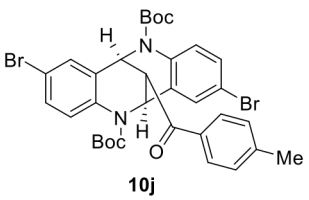
10h

(±) Di-*tert*-butyl 13-benzoyl-2,8-dibromo-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10i). Colourless solid; Yield: 88% (301 mg); mp: 217-219 °C. IR (neat): 2978.3, 2935.0, 1693.3, 1480.8, 1365.6, 1312.8, 1147.1, 1008.2 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 9H), 1.63 (s, 9H), 3.97 (s, 1H), 6.05 (s, 1H), 6.27 (s, 1H), 7.22 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.29 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.50-7.55 (m, 2H), 7.58 (d, *J* = 2.1 Hz, 1H), 7.62-7.67 (m, 2H), 7.81 (d, *J* = 9.3 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 27.9, 28.5, 44.5, 49.7, 51.7, 82.4, 83.1, 116.2, 116.4, 124.0, 124.5, 127.6, 128.1, 128.3, 129.1, 131.0, 131.7, 131.9, 132.0, 133.9, 135.3, 136.3, 151.5, 152.0, 196.2. Anal Calcd for $C_{32}H_{32}Br_2N_2O_5$: C, 56.16; H, 4.71; N, 4.09. Found: C, 55.85; H, 4.62; N, 4.00. *One aromatic carbon is merged with others.



10i

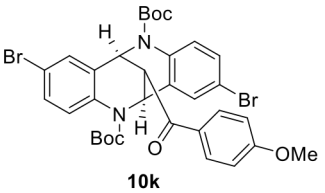
(±) Di-*tert*-butyl 2,8-dibromo-13-(4-methylbenzoyl)-6,12-methanodibenzo[*b,f*][1,5] diazocine-5,11(6*H*,12*H*)-dicarboxylate (10j). Colourless solid; Yield: 84% (293 mg); mp: 223-225 °C. IR (neat): 2977.7, 2935.0, 1707.7, 1606.5, 1480.5, 1365.3, 1312.6, 1153.1, 1008.2 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 9H), 1.63 (s, 9H), 2.44 (s, 3H), 3.94 (dd, *J* = 3.3, 1.5 Hz, 1H),



10j

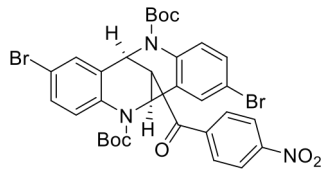
6.03 (s, 1H), 6.25 (s, 1H), 7.21 (dd, J = 9.0, 2.4 Hz, 1H), 7.26-7.32 (m, 3H), 7.45 (d, J = 2.4 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 7.62 (brs, 1H), 7.79-7.84 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 27.9, 28.5, 44.4, 49.7, 51.8, 82.4, 83.1, 116.1, 116.4, 124.0, 124.5, 127.7, 128.2, 128.4, 129.7, 130.9, 131.7, 131.8, 132.0, 132.9, 135.4, 136.3, 144.8, 151.6, 152.0, 195.8. Anal Calcd for $C_{33}H_{34}Br_2N_2O_5$: C, 56.75; H, 4.91; N, 4.01. Found: C, 56.50; H, 4.72; N, 3.82.

(±) Di-*tert*-butyl 2,8-dibromo-13-(4-methoxybenzoyl)-6,12-methanodibenzo[*b,f*][1,5] diazocine-5,11(6*H*,12*H*)-dicarboxylate (10k). Colourless solid; Yield: 74% (264 mg); mp: 222-224 ^{o}C. IR (neat): 2977.2, 2925.1, 1699.7, 1608.0, 1480.1, 1365.1, 1311.6, 1260.6, 1149.1, 1009.7 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (s, 9H), 1.63 (s, 9H), 3.90 (s, 3H), 3.90 (s, 1H), 6.01 (s, 1H), 6.25 (s, 1H), 6.98 (d, J = 9.0 Hz, 2H), 7.20 (dd, J = 9.0, 2.4 Hz, 1H), 7.29 (dd, J = 9.0, 2.4 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.57 (dd, J = 2.4 Hz, 1H), 7.60 (s, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 9.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.9, 28.5, 44.2, 49.8, 51.9, 55.6, 82.3, 83.1, 114.2, 116.1, 116.4, 124.1, 124.5, 127.9, 128.2, 128.4, 130.6, 130.8, 131.7, 131.8, 132.0, 135.4, 136.3, 151.7, 152.0, 164.1, 194.6. Anal Calcd for $C_{33}H_{34}Br_2N_2O_6$: C, 55.48; H, 4.80; N, 3.92. Found: C, 55.12; H, 4.72; N, 3.79.



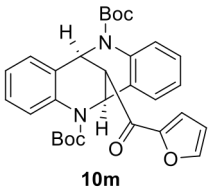
10k

(±) Di-*tert*-butyl 2,8-dibromo-13-(4-nitrobenzoyl)-6,12-methanodibenzo[*b,f*][1,5] diazocine-5,11(6*H*,12*H*)-dicarboxylate (10l). Colourless solid; Yield: 91% (332 mg); mp: 247-249 ^{o}C. IR (neat): 2979.3, 2929.4, 1700.6, 1528.8, 1480.6, 1363.6, 1314.7, 1151.9, 1008.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H), 1.63 (s, 9H), 3.99 (dd, J = 3.3, 1.8 Hz, 1H), 6.07 (s, 1H), 6.26 (s, 1H), 7.23 (dd, J = 9.0, 2.4 Hz, 1H), 7.30 (dd, J = 9.0, 2.4 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.48-7.51 (m, 1H), 7.57 (d, J = 2.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 9.0 Hz, 2H), 8.36 (d, J = 9.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.0, 28.4, 45.3, 49.5, 51.2, 82.9, 83.4, 116.4, 116.8, 124.2, 124.4, 124.7, 127.2, 127.6, 129.3, 131.1, 131.8, 131.9, 132.0, 135.2, 136.2, 139.9, 150.6, 151.9, 152.0, 195.3. Anal Calcd for $C_{32}H_{31}Br_2N_3O_7$: C, 52.69; H, 4.28; N, 5.76. Found: C, 52.33; H, 4.31; N, 5.59.



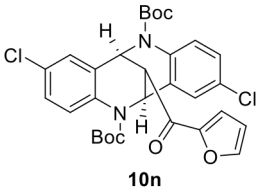
10l

(±) Di-*tert*-butyl 13-(furan-2-carbonyl)-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10m). Brown solid; Yield: 95% (245 mg); mp: 167-169 ^{o}C. IR (neat): 2978.4, 2932.4, 1703.7, 1571.4, 1487.9, 1366.1, 1314.6, 1248.3, 1158.5, 1011.2 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 9H), 1.62 (s, 9H), 3.86 (dd, *J* = 3.6, 1.5 Hz, 1H), 6.10 (s, 1H), 6.48 (s, 1H), 6.60 (dd, *J* = 3.3, 1.5 Hz, 1H), 6.98-7.03 (m, 2H) 7.08 (td, *J* = 8.7, 1.8 Hz, 1H), 7.16 (td, *J* = 8.7, 1.5 Hz, 1H), 7.24-7.26 (m, 1H), 7.39 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.64-7.70 (m, 2H), 7.82 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 28.1, 28.5, 45.9, 49.6, 51.6, 81.6, 82.2, 112.7, 117.2, 122.4, 122.9, 123.5, 123.7, 125.9, 126.7, 127.7, 128.5, 129.2, 129.4, 136.6, 137.3, 146.2, 152.3, 152.4, 185.7. Anal Calcd for $C_{30}H_{32}N_2O_6$: C, 69.75; H, 6.24; N, 5.42. Found: C, 69.47; H, 6.17; N, 5.31. *One aromatic carbon is merged with others.



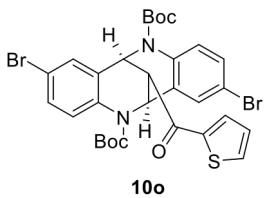
10m

(±) Di-*tert*-butyl 2,8-dichloro-13-(furan-2-carbonyl)-6,12-methanodibenzo[*b,f*][1,5] diazocine-5,11(6*H*,12*H*)-dicarboxylate (10n). Colourless solid; Yield: 92% (270 mg); mp: 173-175 ^{o}C. IR (neat): 2982.7, 2928.1, 1708.6, 1569.7, 1484.8, 1369.3, 1314.1, 1265.6, 1155.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 9H), 1.62 (s, 9H), 3.82 (dd, *J* = 3.3, 1.5 Hz, 1H), 6.02 (s, 1H), 6.43 (s, 1H), 6.62 (dd, *J* = 3.6, 1.5 Hz, 1H), 7.06 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.14 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.26 (d, *J* = 4.5 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.59-7.70 (m, 2H), 7.82 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 28.0, 28.4, 45.3, 49.2, 51.2, 82.4, 83.0, 112.9, 117.5, 124.0, 124.3, 127.3, 127.9, 128.0, 128.5, 128.6, 128.7, 128.8, 129.0, 135.1, 135.7, 146.4, 152.0, 152.2, 185.1. Anal Calcd for $C_{30}H_{30}ClN_2O_6$: C, 61.54; H, 5.17; N, 4.78. Found: C, 61.31; H, 5.03; N, 4.64. *One aromatic carbon is merged with others.



10n

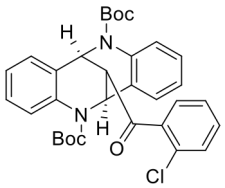
(±) Di-*tert*-butyl 2,8-dibromo-13-(thiophene-2-carbonyl)-6,12-methanodibenzo [*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10o). Colourless solid; Yield: 93% (321 mg); mp: 180-182 ^{o}C. IR (neat): 2979.2, 2918.7, 1708.9, 1663.5, 1482.6, 1413.8, 1367.8, 1313.2, 1278.6, 1154.8 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 9H), 1.63 (s, 9H), 3.83 (t, *J* = 1.8 Hz, 1H), 6.01 (s, 1H), 6.32 (s, 1H), 7.20-7.24 (m, 2H), 7.29 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.60 (brs, 1H), 7.72



10o

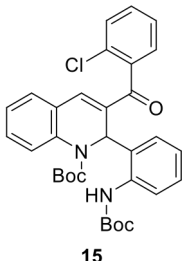
(d, J = 4.8 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.83 (d, J = 3.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 28.0, 28.5, 45.6, 49.7, 52.1, 82.5, 83.2, 116.2, 116.4, 124.3, 124.6, 127.6, 128.1, 128.4, 130.9, 131.7, 131.8, 132.0, 132.3, 134.5, 135.4, 136.2, 142.4, 152.0, 188.9. Anal Calcd for $C_{30}H_{30}BrN_2O_5S$: C, 52.19; H, 4.38; N, 4.06. Found: C, 51.91; H, 4.21; N, 4.13. *One aromatic carbon is merged with others.

(±) Di-*tert*-butyl 13-(2-chlorobenzoyl)-6,12-methanodibenzo[*b,f*][1,5]diazocine-5,11(6*H*,12*H*)-dicarboxylate (10q). Colourless solid; Yield: 27% (75 mg); mp: 162-164 ^{o}C. IR (neat): 3043.4, 2989.7, 2935.9, 1701.2, 1477.3, 1354.2, 1322.3, 1278.9, 1156.2 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (s, 9H), 1.62 (s, 9H), 4.03 (dd, J = 3.3, 2.4 Hz, 1H), 6.17 (s, 1H), 6.26 (d, J = 2.4 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 7.00 (d, J = 7.2 Hz, 1H), 7.07-7.18 (m, 2H), 7.29-7.31 (m, 2H), 7.38 (d, J = 7.8 Hz, 1H), 7.42-7.46 (m, 3H), 7.79-7.89 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3, 28.5, 48.0, 50.0, 50.5, 82.0, 82.2, 121.7, 122.6, 123.4, 123.5, 124.6, 126.5, 127.3, 128.2, 128.5, 129.4, 129.7, 130.0, 130.3, 130.8, 132.2, 136.6, 137.0, 137.6, 152.4, 152.5, 199.5. Anal Calcd for $C_{32}H_{33}ClN_2O_5$: C, 68.50; H, 5.93; N, 4.99. Found: C, 68.73; H, 5.99; N, 4.81.



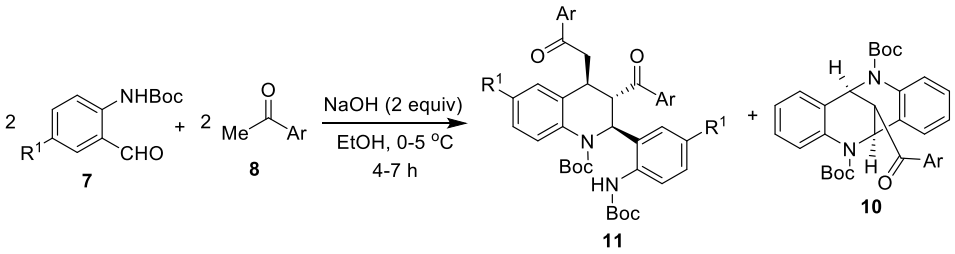
10q

(±) *tert*-Butyl 2-(2-((*tert*-butoxycarbonyl)amino)phenyl)-3-(2-chlorobenzoyl) quinoline-1(2*H*)-carboxylate (15). Colourless solid; Yield: 62% (173 mg); mp: 201-204 ^{o}C. IR (neat): 3295.8, 3074.1, 2979.2, 1725.6, 1678.1, 1539.5, 1455.2, 1368.3, 1249.2, 1162.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (s, 9H), 1.58 (s, 9H), 6.73 (t, J = 7.8 Hz, 1H), 6.86 (dd, J = 7.8, 1.2 Hz, 1H), 6.90 (s, 1H), 7.10 (t, J = 7.5 Hz, 1H), 7.16-7.27 (m, 4H), 7.30-7.46 (m, 5H), 8.07 (d, J = 8.1 Hz, 1H), 8.98 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 28.3, 28.5, 49.0, 79.8, 83.2, 121.4, 122.5, 124.6, 125.6, 125.8, 126.7, 127.3, 128.7, 128.9, 129.0, 130.1, 131.0, 131.1, 131.2, 136.3, 136.6, 137.0, 137.9, 139.4, 153.7, 153.8, 192.9. Anal Calcd for $C_{32}H_{33}ClN_2O_5$: C, 68.50; H, 5.93; N, 4.99. Found: C, 68.19; H, 5.80; N, 4.91. *One aromatic carbon is merged with others.



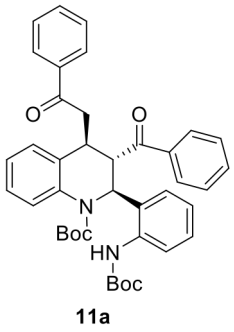
15

4. General Procedure for the Synthesis of 2,3,4-Trisubstituted 1,2,3,4-Tetrahydroquinolines 11.



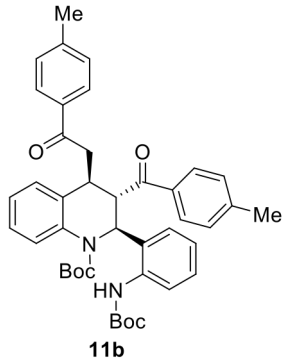
To a stirred solution of aryl methyl ketones **8** (1.0 mmol) in EtOH (3.0 mL) was added *tert*-butyl (2-formylphenyl)carbamates **7** (1.0 mmol) followed by NaOH (2.0 mmol) at 0 °C, and stirring was continued for 4-7 hours at 0-5 °C. After completion, water was added to the reaction mixture, and extracted with ethyl acetate (3 x 10 mL), washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether-ethyl acetate mixture as eluent (90:10 to 85:15, v/v) to obtain the products **11** as major product and **10** as minor product.

(±) *tert*-Butyl 3-benzoyl-2-(2-((*tert*-butoxycarbonyl)amino)phenyl)-4-(2-oxo-2-phenylethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11a). Colourless solid; Yield: 76% (246 mg); mp: 162-164 °C. IR (neat): 3354.7, 3036.9, 2974.4, 2933.7, 1721.3, 1674.2, 1590.7, 1447.2, 1337.9, 1156.5, 1050.7 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 9H), 1.36 (s, 9H), 3.17 (dd, *J* = 17.7, 2.4 Hz, 1H), 3.36 (dd, *J* = 17.7, 8.7 Hz, 1H), 3.80 (td, *J* = 8.7, 2.4 Hz, 1H), 4.13 (td, *J* = 11.1, 9.3 Hz, 1H), 5.59 (d, *J* = 9.3 Hz, 1H), 6.86-6.90 (m, 3H), 7.03 (t, *J* = 7.5 Hz, 2H), 7.11-7.21 (m, 3H), 7.31-7.51 (m, 9H), 7.81 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.2, 28.3, 35.6, 37.6, 56.9, 57.0, 79.8, 82.0, 123.7, 124.2, 124.4, 124.8, 125.8, 126.7, 127.2, 127.9, 128.0, 128.5, 128.6, 128.7, 133.1, 133.3, 133.6, 134.7, 135.7, 136.6, 136.9, 137.9, 153.2, 153.9, 197.6, 201.1. Anal Calcd for $C_{40}H_{42}N_2O_6$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.11; H, 6.47; N, 4.51.



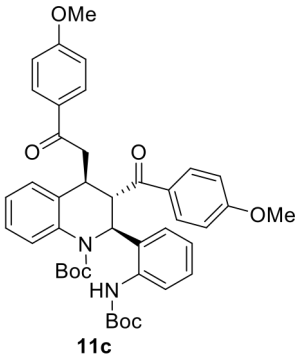
11a

(±) *tert*-Butyl 2-(2-((*tert*-butoxycarbonyl)amino)phenyl)-3-(4-methylbenzoyl)-4-(2-oxo-2-(*p*-tolyl)ethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11b). Colourless solid; Yield: 84% (284 mg); mp: 176-178 ^{o}C. IR (neat): 3364.3, 3063.9, 2990.6, 1677.8, 1613.8, 1474.8, 1371.9, 1296.8, 1255.0, 1194.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (s, 9H), 1.44 (s, 9H), 2.28 (s, 3H), 2.40 (s, 3H), 3.16 (dd, *J* = 17.4, 3.0 Hz, 1H), 3.37 (dd, *J* = 17.4, 8.7 Hz, 1H), 3.93 (t, *J* = 9.0 Hz, 1H), 4.13 (dd, *J* = 11.1, 8.7 Hz, 1H), 5.68 (d, *J* = 9.0 Hz, 1H), 6.91-7.02 (m, 5H), 7.05-7.13 (m, 3H), 7.21-7.26 (m, 2H), 7.40-7.54 (m, 5H), 7.78 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 21.6, 21.7, 28.3, 35.8, 37.6, 56.7, 57.3, 79.7, 81.9, 123.6, 124.2, 124.4, 124.8, 125.7, 126.7, 127.2, 127.8, 128.2, 128.7, 129.2, 129.3, 133.1, 134.2, 134.5, 135.0, 135.7, 137.9, 144.1, 144.6, 153.3, 153.9, 197.2, 200.6. Anal Calcd for $C_{42}H_{46}N_2O_6$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.53; H, 6.85; N, 4.05. *One aliphatic carbon is merged with others.



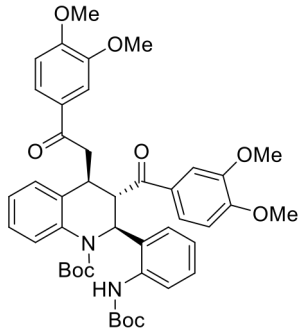
11b

(±) *tert*-Butyl 2-(2-((*tert*-butoxycarbonyl)amino)phenyl)-3-(4-methoxybenzoyl)-4-(2-(4-methoxyphenyl)-2-oxoethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11c). Colourless solid; Yield: 56% (197 mg); mp: 140-142 ^{o}C. IR (neat): 3257.6, 2985.1, 2840.4, 1669.4, 1574.9, 1508.1, 1374.7, 1255.4, 1143.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (s, 9H), 1.44 (s, 9H), 3.16 (dd, *J* = 17.4, 3.0 Hz, 1H), 3.34 (dd, *J* = 17.4, 8.4 Hz, 1H), 3.76 (s, 3H), 3.85-3.96 (m, 4H), 4.06-4.13 (m, 1H), 5.66 (d, *J* = 9.3 Hz, 1H), 6.67 (d, *J* = 9.0 Hz, 2H), 6.89-7.00 (m, 5H), 7.07-7.14 (m, 2H), 7.23-7.26 (m, 1H), 7.44-7.55 (m, 5H), 7.88 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.2, 28.3, 35.9, 37.3, 55.4, 55.5, 56.5, 57.4, 79.7, 81.9, 113.7, 113.8, 123.6, 124.2, 124.4, 124.7, 125.7, 126.6, 127.2, 127.8, 129.7, 130.1, 130.3, 131.0, 133.3, 135.1, 135.6, 137.9, 153.3, 153.9, 163.6, 163.9, 196.1, 199.2. Anal Calcd for $C_{42}H_{46}N_2O_8$: C, 71.37; H, 6.56; N, 3.96. Found: C, 70.99; H, 6.53; N, 3.71.



11c

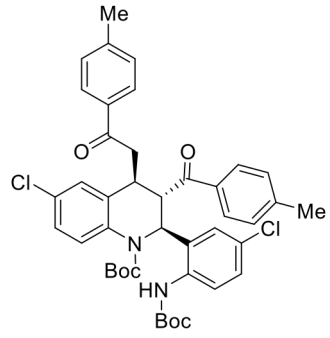
(±) *tert*-Butyl 2-(2-((tert-butoxycarbonyl)amino)phenyl)-3-(3,4-dimethoxybenzoyl)-4-(2-(3,4-dimethoxyphenyl)-2-oxoethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11d).



11d

Colourless solid; Yield: 47% (180 mg); mp: 162-164 ^{o}C. IR (neat): 3265.3, 2997.1, 2843.4, 1675.2, 1544.9, 1493.2, 1367.7, 1245.5, 1134.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (s, 9H), 1.42 (s, 9H), 3.20 (dd, *J* = 17.4, 3.0 Hz, 1H), 3.35 (dd, *J* = 17.4, 8.4 Hz, 1H), 3.72 (s, 3H), 3.84 (s, 3H), 3.92-3.97 (m, 7H), 4.15 (dd, *J* = 11.1, 9.0 Hz, 1H), 5.67 (d, *J* = 9.0 Hz, 1H), 6.61 (d, *J* = 8.7 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 6.89-6.97 (m, 3H), 7.02-7.15 (m, 5H), 7.23-7.27 (m, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.52-7.57 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 28.3, 35.9, 37.2, 55.7, 56.0, 56.1, 56.4, 79.7, 81.9, 110.0, 110.2, 110.6, 122.6, 123.6, 123.8, 124.5, 124.8, 125.7, 126.7, 127.3, 127.9, 129.8, 130.1, 133.3, 135.0, 135.8, 137.8, 148.7, 149.0, 153.4, 153.5, 153.8, 154.0, 196.3, 199.2. Anal Calcd for $C_{44}H_{50}N_2O_{10}$: C, 68.91; H, 6.57; N, 3.65. Found: C, 68.59; H, 6.40; N, 3.59. *Three aromatic carbons and one aliphatic carbon are merged with others.

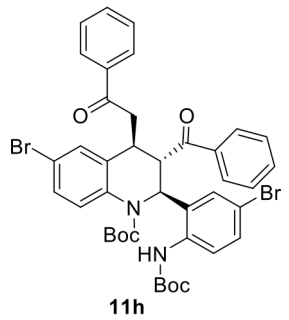
(±) *tert*-Butyl 2-(2-((*tert*-butoxycarbonyl)amino)-5-chlorophenyl)-6-chloro-3-(4-methylbenzoyl)-4-(2-oxo-2-(*p*-tolyl)ethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11g).



11g

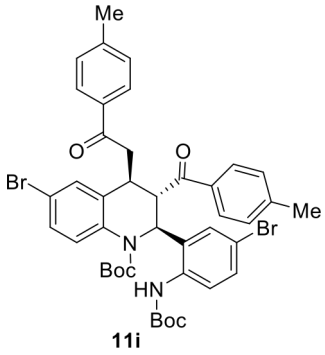
Colourless solid; Yield: 76% (283 mg); mp: 194-196 ^{o}C. IR (neat): 3362.0, 2980.2, 2931.9, 1726.6, 1683.1, 1606.8, 1486.8, 1368.7, 1285.6, 1160.6 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (s, 9H), 1.46 (s, 9H), 2.29 (s, 3H), 2.40 (s, 3H), 3.15 (dd, *J* = 18.0, 3.0 Hz, 1H), 3.34 (dd, *J* = 18.0, 8.4 Hz, 1H), 3.84 (t, *J* = 8.4 Hz, 1H), 4.04 (t, *J* = 10.2 Hz, 1H), 5.62 (d, *J* = 9.6 Hz, 1H), 6.92 (s, 2H), 7.03-7.07 (m, 3H), 7.21-7.26 (m, 3H), 7.35 (brs, 1H), 7.42-7.50 (m, 4H), 7.73 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 21.6, 21.7, 28.2, 28.3, 35.9, 37.2, 56.0, 57.2, 80.2, 82.6, 124.7, 125.1, 126.9, 127.0, 128.0, 128.1, 128.7, 129.2, 129.3, 130.3, 133.9, 134.2, 134.3, 134.6, 136.2, 136.7, 144.3, 145.1, 153.1, 153.5, 196.5, 199.8. Anal Calcd for $C_{42}H_{44}Cl_2N_2O_6$: C, 67.83; H, 5.96; N, 3.77. Found: C, 67.51; H, 6.02; N, 3.64. *Two aromatic carbons are merged with others.

(±) *tert*-Butyl 3-benzoyl-6-bromo-2-(5-bromo-2-((*tert*-butoxycarbonyl)amino)phenyl)-4-(2-oxo-2-phenylethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11h). Colourless solid; Yield: 79% (318 mg); mp: 188-190 ^{o}C. IR (neat): 3369.0, 3074.1, 2979.0, 1678.3, 1588.8, 1508.1, 1369.1, 1327.3, 1249.5, 1154.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 9H), 1.46 (s, 9H), 3.23 (dd, *J* = 18.0, 3.3 Hz, 1H), 3.40 (dd, *J* = 18.0, 8.1 Hz, 1H), 3.86 (t, *J* = 8.1 Hz, 1H), 4.11 (t, *J* = 10.5 Hz, 1H), 5.59 (d, *J* = 9.9 Hz, 1H), 7.06 (d, *J* = 2.1 Hz, 2H), 7.17-7.27 (m, 3H), 7.37-7.46 (m, 7H), 7.51-7.59 (m, 3H), 7.84 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$)*: δ 28.2, 28.3, 35.7, 37.2, 56.1, 57.2, 80.3, 82.7, 116.7, 118.2, 125.5, 127.3, 127.6, 128.0, 128.5, 128.6, 128.7, 129.8, 130.0, 131.0, 133.5, 134.0, 134.7, 134.9, 136.3, 136.7, 138.8, 152.9, 153.5, 197.0, 200.4. Anal Calcd for $C_{40}H_{40}Br_2N_2O_6$: C, 59.71; H, 5.01; N, 3.48. Found: C, 59.41; H, 4.89; N, 3.33. *One aromatic carbon is merged with others.



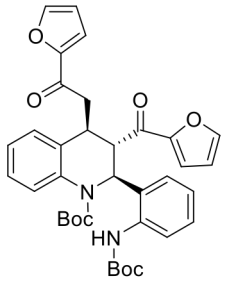
11h

(±) *tert*-Butyl 6-bromo-2-(5-bromo-2-((*tert*-butoxycarbonyl)amino)phenyl)-3-(4-methylbenzoyl)-4-(2-oxo-2-(p-tolyl)ethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11i). Colourless solid; Yield: 81% (337 mg); mp: 154-156 ^{o}C. IR (neat): 3360.0, 2977.7, 2930.4, 1679.7, 1487.1, 1328.3, 1236.5, 1160.7 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (s, 9H), 1.46 (s, 9H), 2.29 (s, 3H), 2.40 (s, 3H), 3.15 (dd, *J* = 19.7, 2.7 Hz, 1H), 3.34 (dd, *J* = 19.7, 8.4 Hz, 1H), 3.83 (t, *J* = 7.8 Hz, 1H), 4.03 (t, *J* = 10.2 Hz, 1H), 5.60 (d, *J* = 9.6 Hz, 1H), 7.01-7.07 (m, 4H), 7.16-7.25 (m, 4H), 7.39-7.46 (m, 5H), 7.72 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 21.7, 28.2, 28.3, 35.9, 37.2, 56.0, 57.3, 80.3, 82.6, 116.8, 118.1, 125.3, 127.2, 127.6, 128.1, 128.7, 129.3, 129.8, 129.9, 131.0, 133.9, 134.3, 134.8, 136.7, 137.0, 144.3, 145.1, 153.0, 153.4, 196.5, 199.8. Anal Calcd for $C_{42}H_{44}Br_2N_2O_6$: C, 60.59; H, 5.33; N, 3.36. Found: C, 60.34; H, 5.36; N, 3.20. *Two aromatic carbons are merged with others.



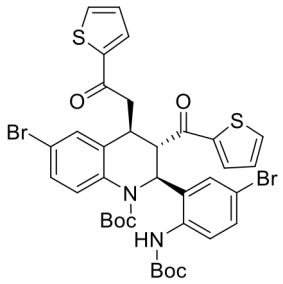
11i

(±) *tert*-Butyl 2-(2-((*tert*-butoxycarbonyl)amino)phenyl)-3-(furan-2-carbonyl)-4-(2-(furan-2-yl)-2-oxoethyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11j). Colourless solid; Yield: 63% (197 mg); mp: 196-198 ^{o}C. IR (neat): 3363.0, 2978.0, 2923.9, 1679.5, 1503.6, 1371.9, 1328.9, 1124.1, 1158.8 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (s, 9H), 1.47 (s, 9H), 3.13-3.34 (m, 2H), 3.85-3.88 (m, 2H), 5.66 (d, *J* = 8.7 Hz, 1H), 6.30 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.54 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.68 (d, *J* = 3.3 Hz, 1H), 6.90-6.96 (m, 2H), 7.08-7.18 (m, 3H), 7.24 (d, *J* = 3.3Hz, 1H), 7.27-7.30 (m, 1H), 7.42-7.46 (m, 2H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.2, 28.3, 34.9, 37.4, 57.5, 57.7, 79.9, 82.0, 112.4, 122.6, 117.5, 120.3, 124.1, 124.3, 124.5, 124.9, 125.7, 126.9, 127.4, 127.9, 133.5, 134.2, 135.6, 137.8, 146.5, 147.9, 152.2, 152.3, 153.5, 153.8, 186.7, 187.9. Anal Calcd for $C_{36}H_{38}N_2O_8$: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.69; H, 5.97; N, 4.36.



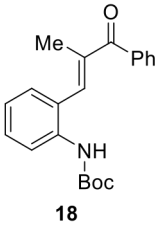
11j

(±) *tert*-Butyl 6-bromo-2-(5-bromo-2-((*tert*-butoxycarbonyl)amino)phenyl)-4-(2-oxo-2-(thiophen-2-yl)ethyl)-3-(thiophene-2-carbonyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11k). Colourless solid; Yield: 59% (240 mg); mp: 120-122 ^{o}C. IR (neat): 3384.8, 2979.9, 2931.6, 1723.9, 1662.2, 1503.8, 1485.1, 1414.0, 1336.4, 1239.4, 1159.6 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (s, 9H), 1.47 (s, 9H), 3.32-3. 39 (m, 2H), 3.78-3.86 (m, 2H), 5.55-5.58 (m, 1H), 6.90 (t, *J* = 4.2 Hz, 1H), 7.04 (d, *J* = 2.1 Hz, 1H), 7.11-7.15 (m, 2H), 7.20-7.24 (m, 2H), 7.36-7.45 (m, 3H), 7.58 (d, *J* = 4.5 Hz, 1H), 7.65 (d, *J* = 4.5 Hz, 1H); 7.71 (d, *J* = 3.9 Hz, 1H).^{13}C NMR (75 MHz, $CDCl_3$)*: δ 28.2, 28.3, 35.7, 37.8, 57.3, 58.3, 80.4, 82.8, 117.1, 118.3, 125.8, 127.2, 127.8, 128.3, 128.5, 129.8, 130.1, 131.1, 132.2, 133.9, 134.3, 134.9, 135.1, 136.3, 136.6, 143.5, 143.9, 153.1, 153.4, 189.8, 192.0. Anal Calcd for $C_{36}H_{36}Br_2N_2O_6S_2$: C, 52.95; H, 4.44; N, 3.43. Found: C, 52.90; H, 4.37; N, 3.36. *One aromatic carbon is merged with others.



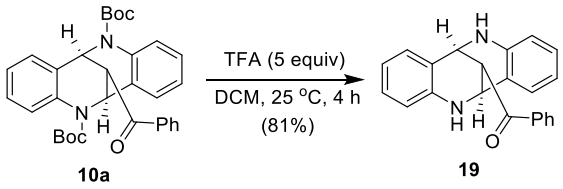
11k

***tert*-Butyl (*E*)-(2-(2-methyl-3-oxo-3-phenylprop-1-en-1-yl)phenyl)carbamate (18).** Colourless solid; Yield: 53% (221 mg); mp: 98-100 °C. IR (neat): 3325.2, 2979.9, 2929.5, 1727.8, 1645.3, 1515.4, 1449.5, 1367.7, 1267.3, 1157.8 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.49 (s, 9H), 2.10 (s, 3H), 6.22 (s, 1H), 7.06 (s, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.34 (td, *J* = 8.4, 1.5 Hz, 1H), 7.46-7.51 (m, 2H), 7.59 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.80 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.5, 28.3, 80.8, 121.3, 123.5, 126.4, 128.4, 129.2, 129.3, 129.6, 132.1, 136.0, 137.2, 138.0, 139.7, 152.7, 198.8. Anal Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.41; H, 6.82; N, 4.14.



18

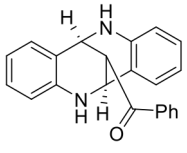
5. Deprotection of *N*-Boc Functionality of Methanodibenzo[*b*,*f*][1,5]diazocin-13-ylmethanone 10a.



10a 19

To a stirred solution compound **10a** (0.5 mmol) in DCM (10 mL) was added TFA (2.5 mmol) in 5 mL of DCM dropwise at 25 °C and stirring was continued for 4 h. After completion, the reaction mixture was added saturated $NaHCO_3$ solution and extracted with DCM (2 x 10 mL), washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by flash column chromatography eluting with petroleum ether-ethyl acetate mixture (80:20 v/v) to obtain compound **19**.

(±) Phenyl(5,6,11,12-tetrahydro-6,12-methanodibenzo[*b*,*f*][1,5]diazocin-13-yl)methanone (19). Colourless solid; Yield: 81% (132 mg); mp: 212-214 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 3.99 (t, *J* = 2.7 Hz, 1H), 4.35 (brs, 1H), 4.63 (brs, 1H), 4.70 (s, 1H), 4.75 (s, 1H), 6.43 (d, *J* = 8.1 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.68-6.78 (m, 2H), 6.95-7.08 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 43.9, 48.5, 51.4, 115.6, 116.0, 118.3, 119.0, 125.3, 125.7, 128.0, 128.2, 128.2, 128.8, 128.9,

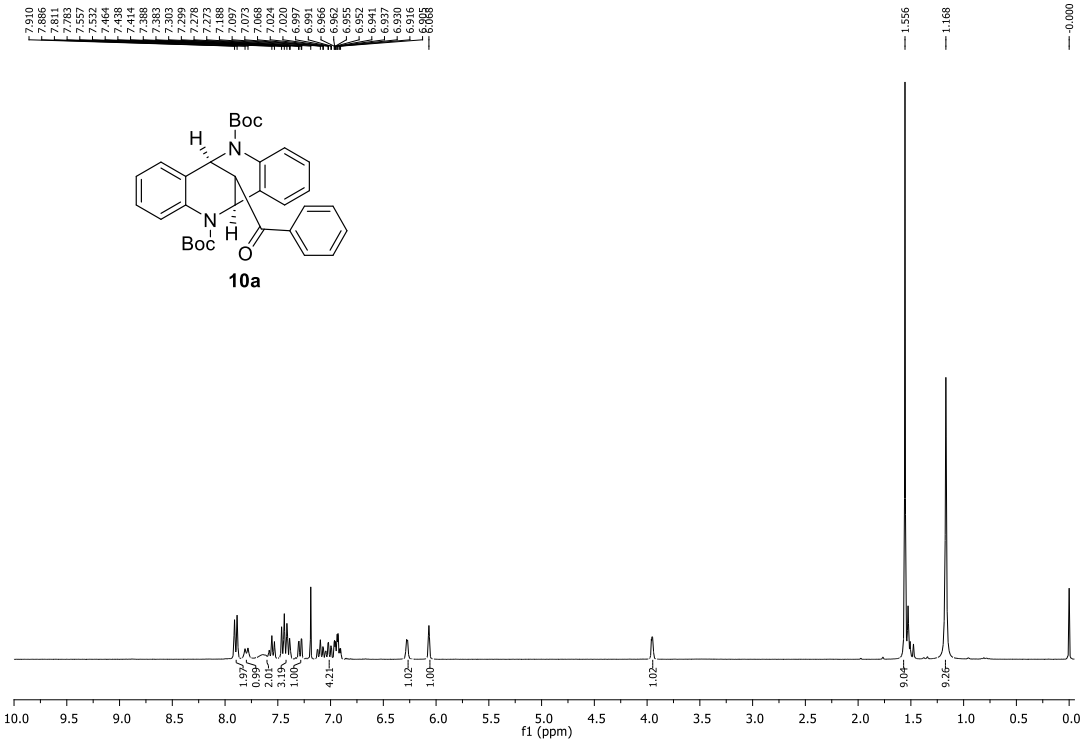


19

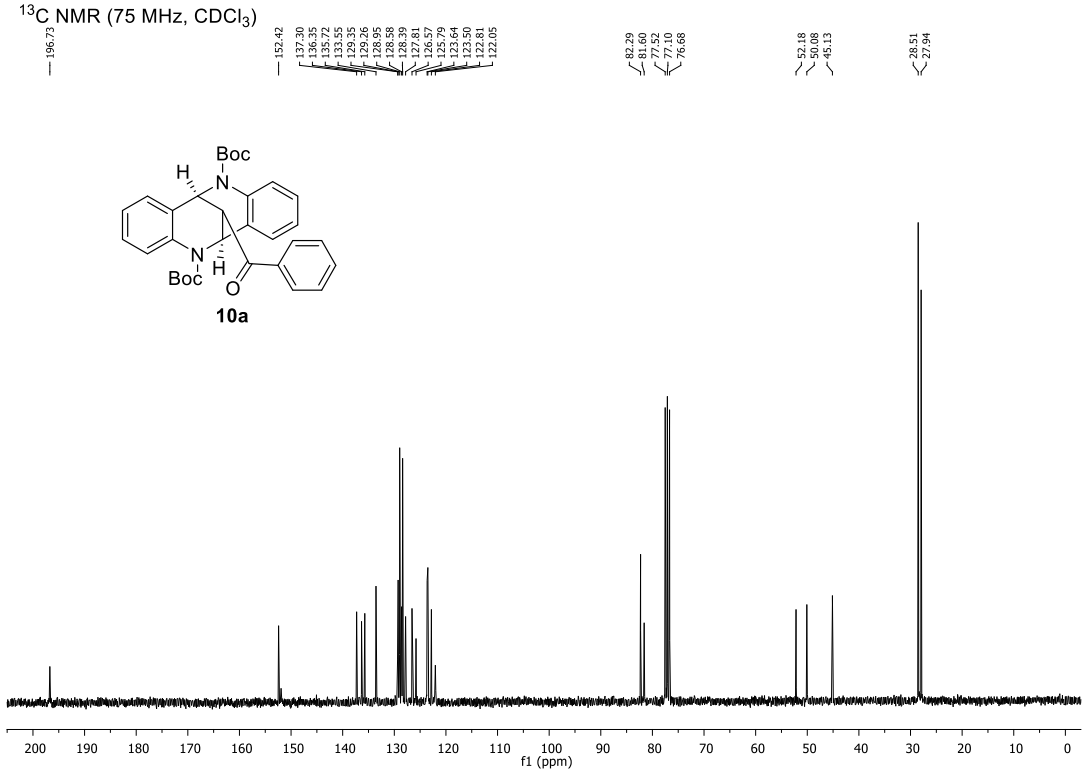
129.0, 132.9, 136.3, 141.6, 143.6, 198.4. Anal Calcd for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 80.63; H, 5.48; N, 8.57.

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

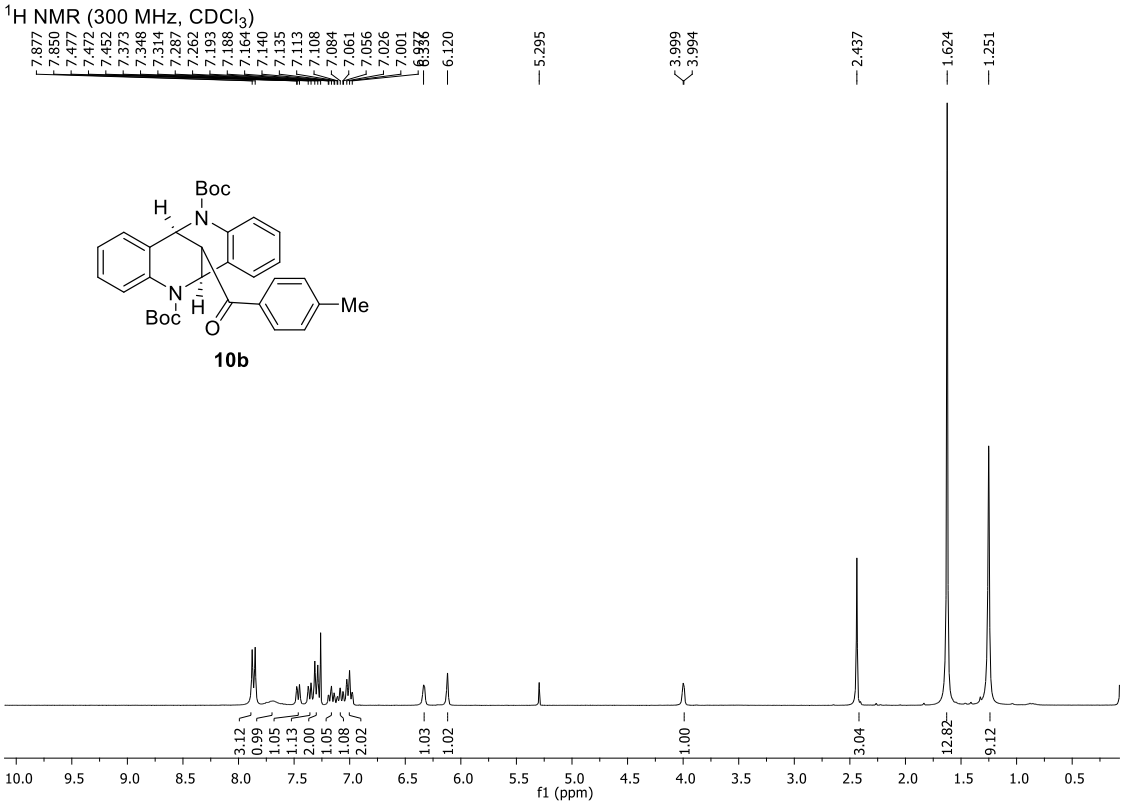
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

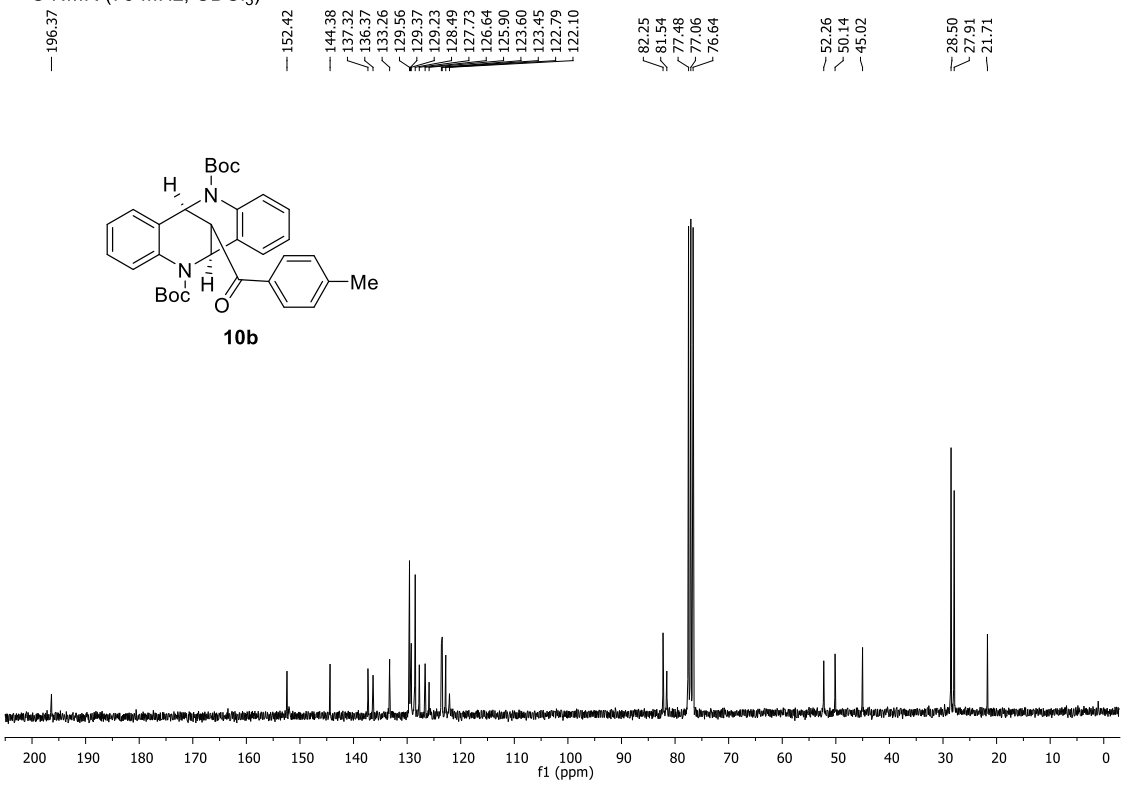


^{1}H NMR (300 MHz, $CDCl_3$)



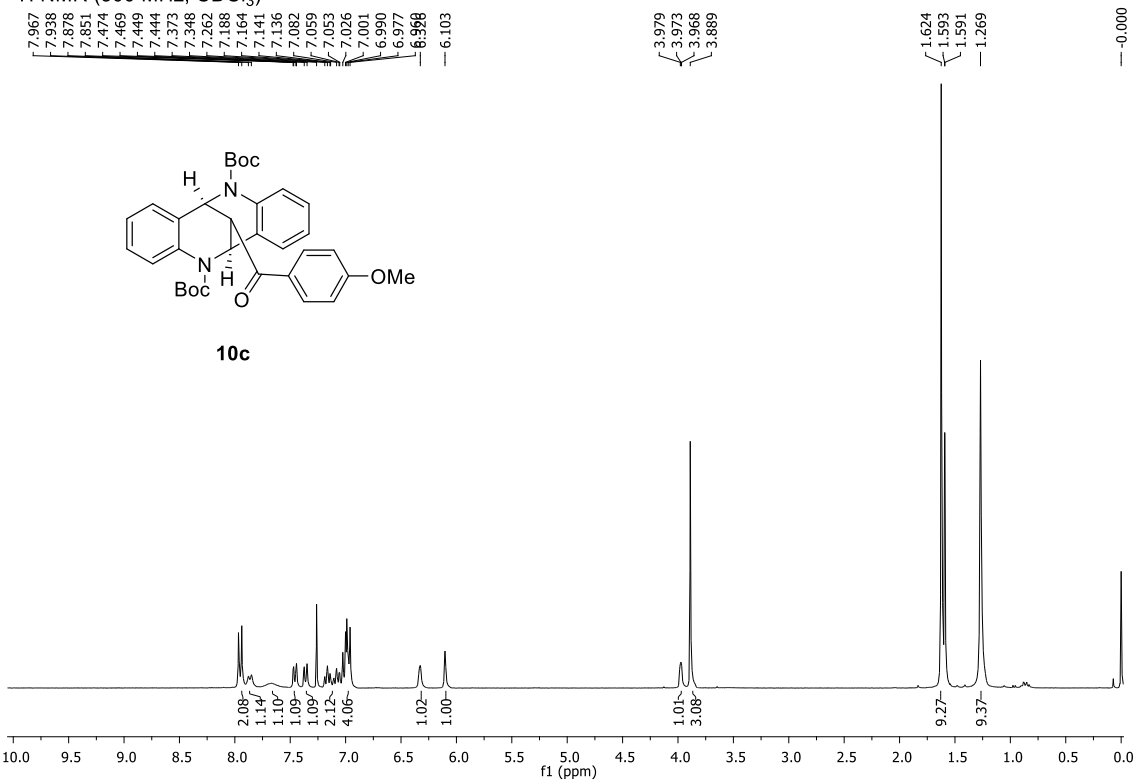
10b

^{13}C NMR (75 MHz, $CDCl_3$)



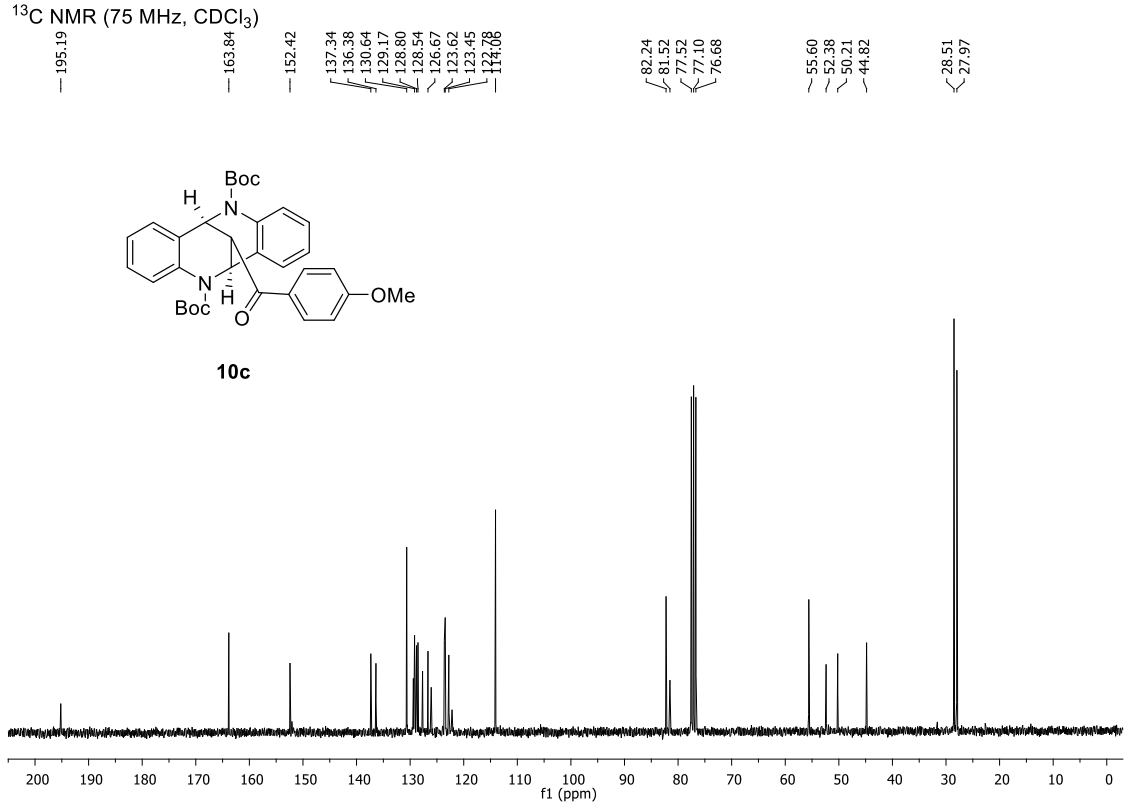
10b

^{1}H NMR (300 MHz, $CDCl_3$)



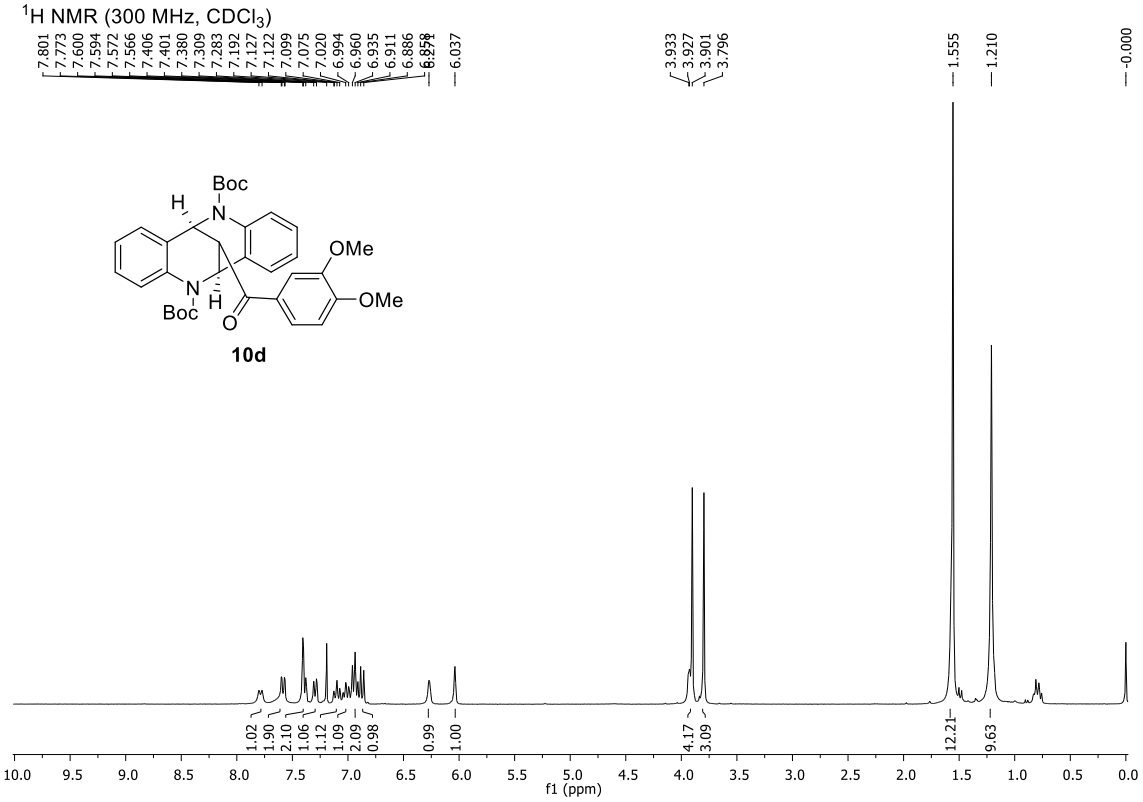
10c

^{13}C NMR (75 MHz, $CDCl_3$)



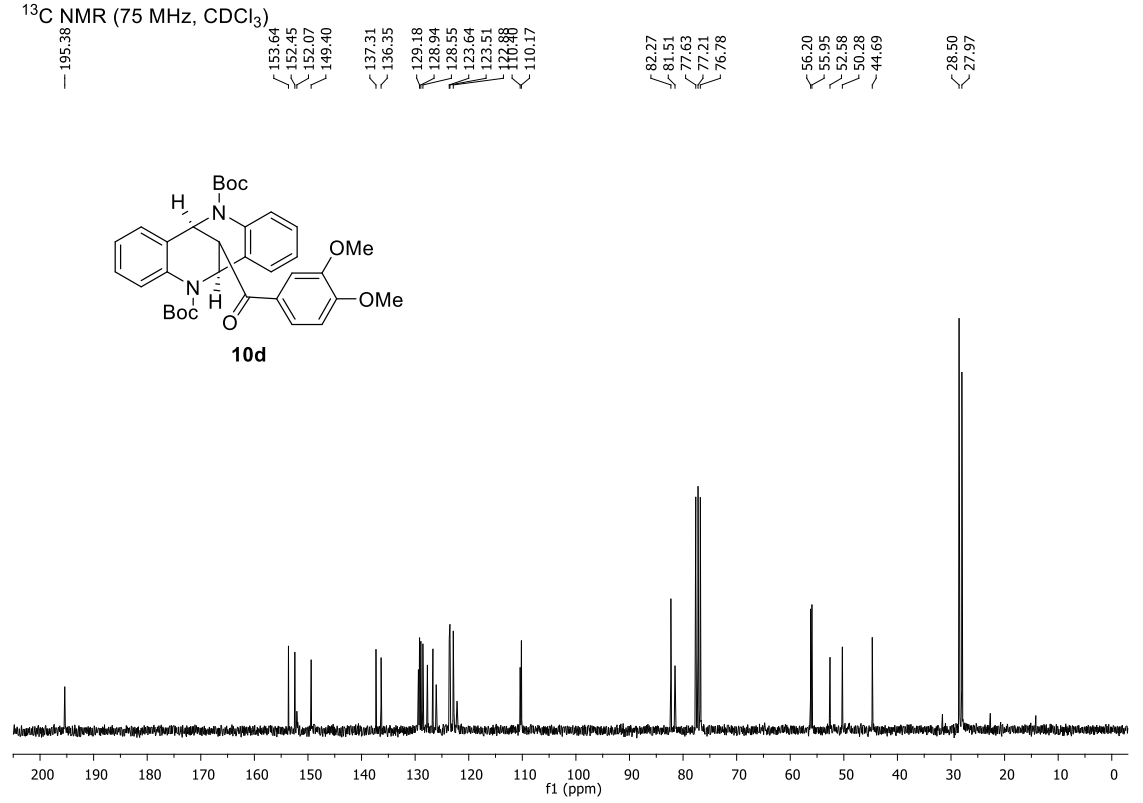
10c

^{1}H NMR (300 MHz, $CDCl_3$)



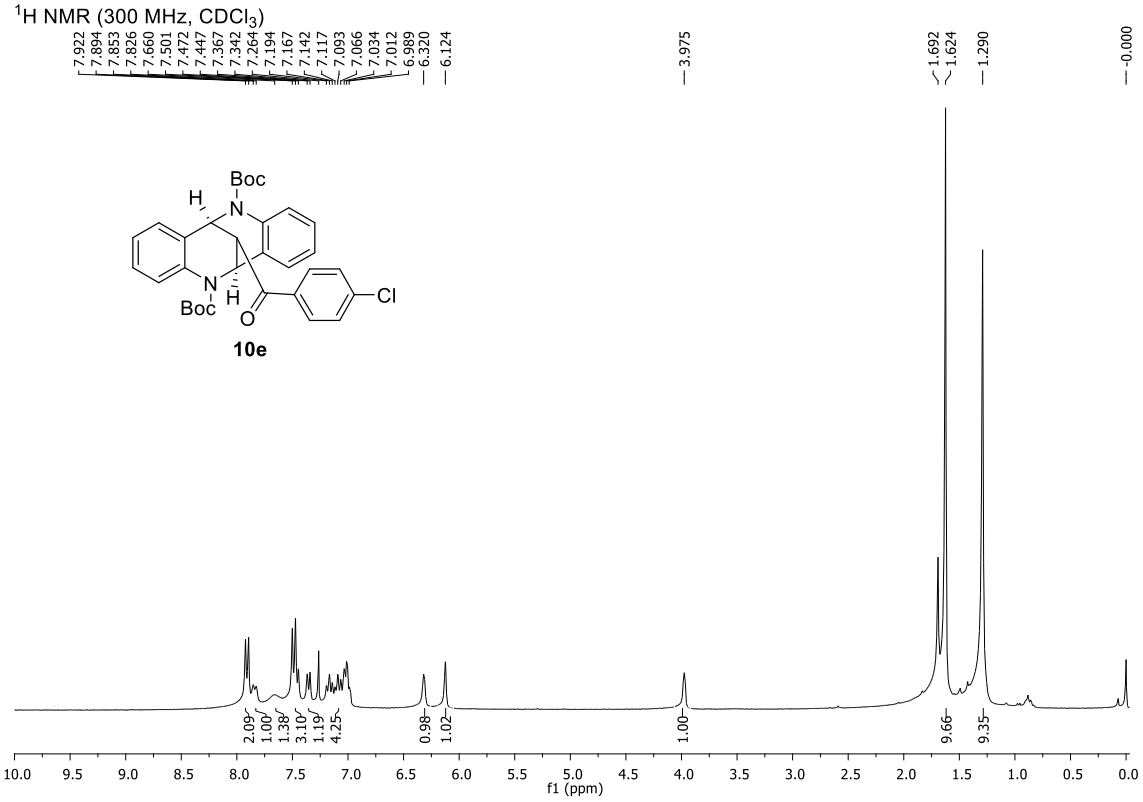
10d

^{13}C NMR (75 MHz, $CDCl_3$)



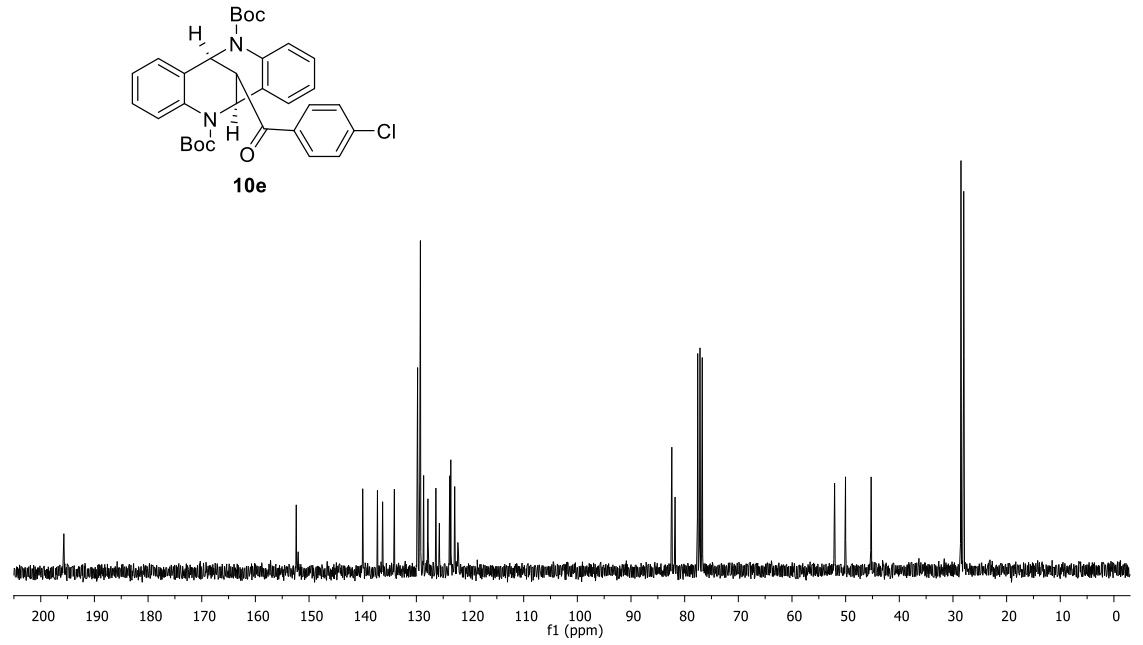
10d

^{1}H NMR (300 MHz, $CDCl_3$)



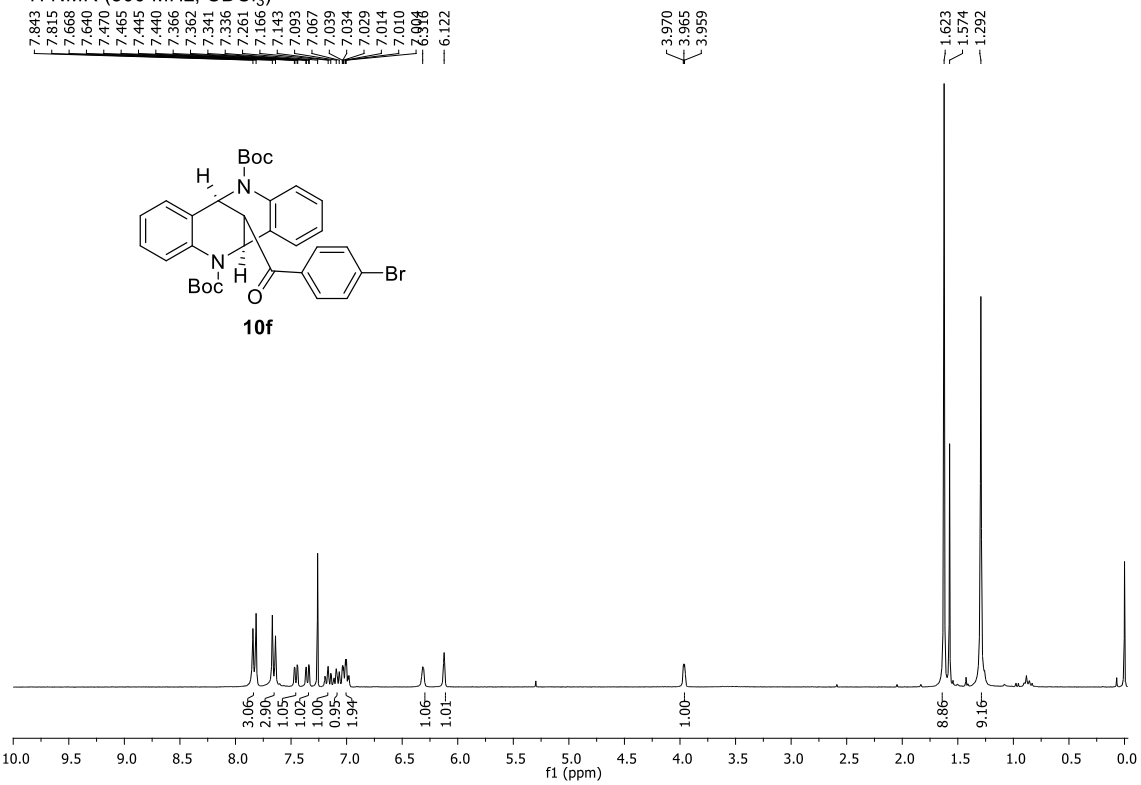
10e

^{13}C NMR (75 MHz, $CDCl_3$)



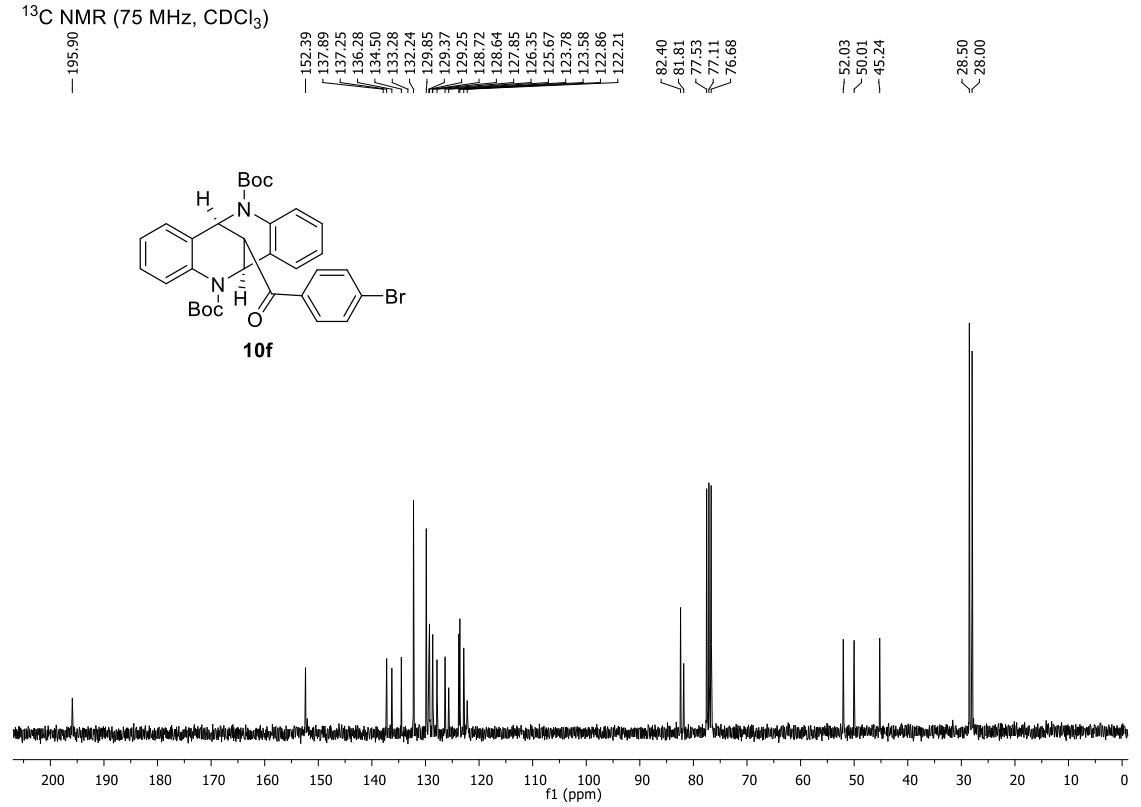
10e

^{1}H NMR (300 MHz, $CDCl_3$)



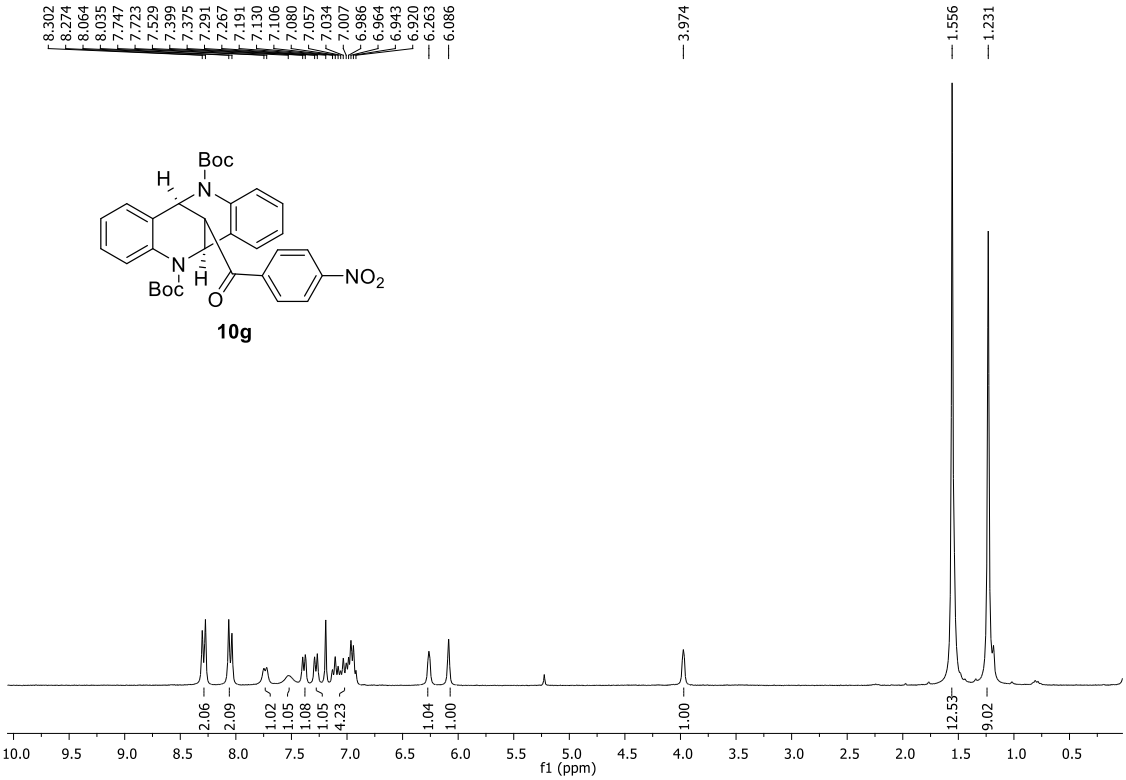
10f

^{13}C NMR (75 MHz, $CDCl_3$)



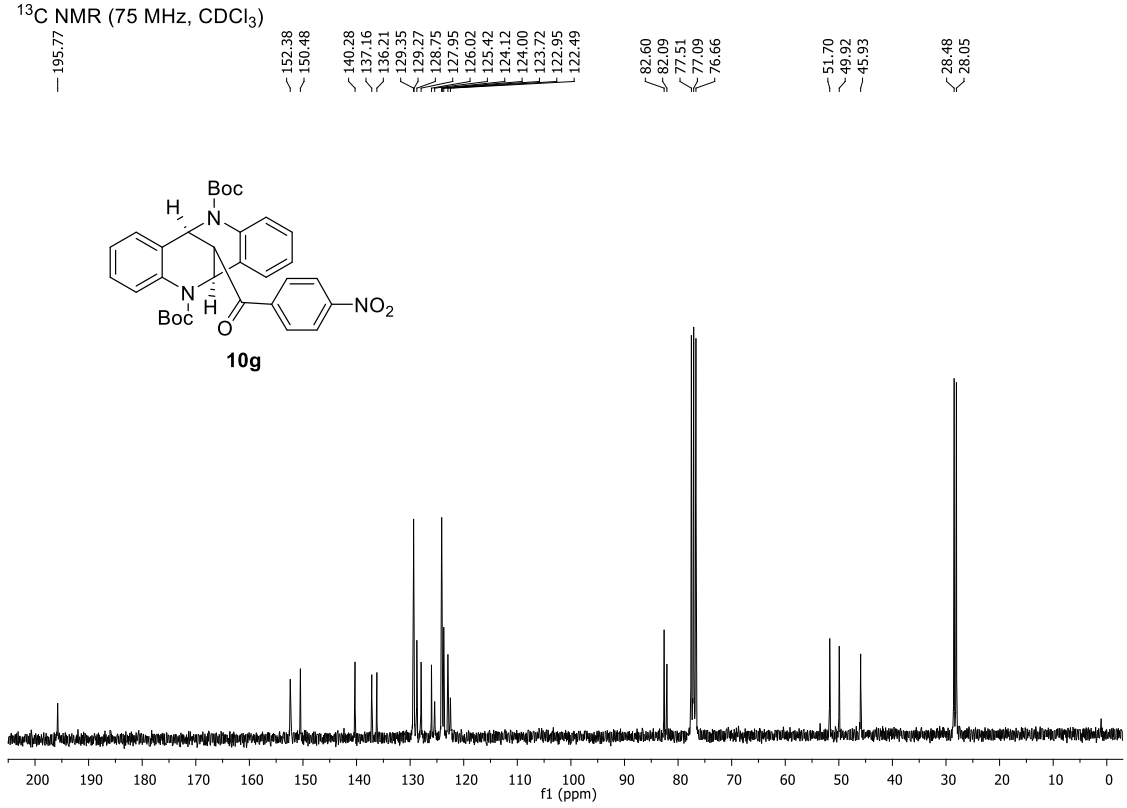
10f

^{1}H NMR (300 MHz, $CDCl_3$)



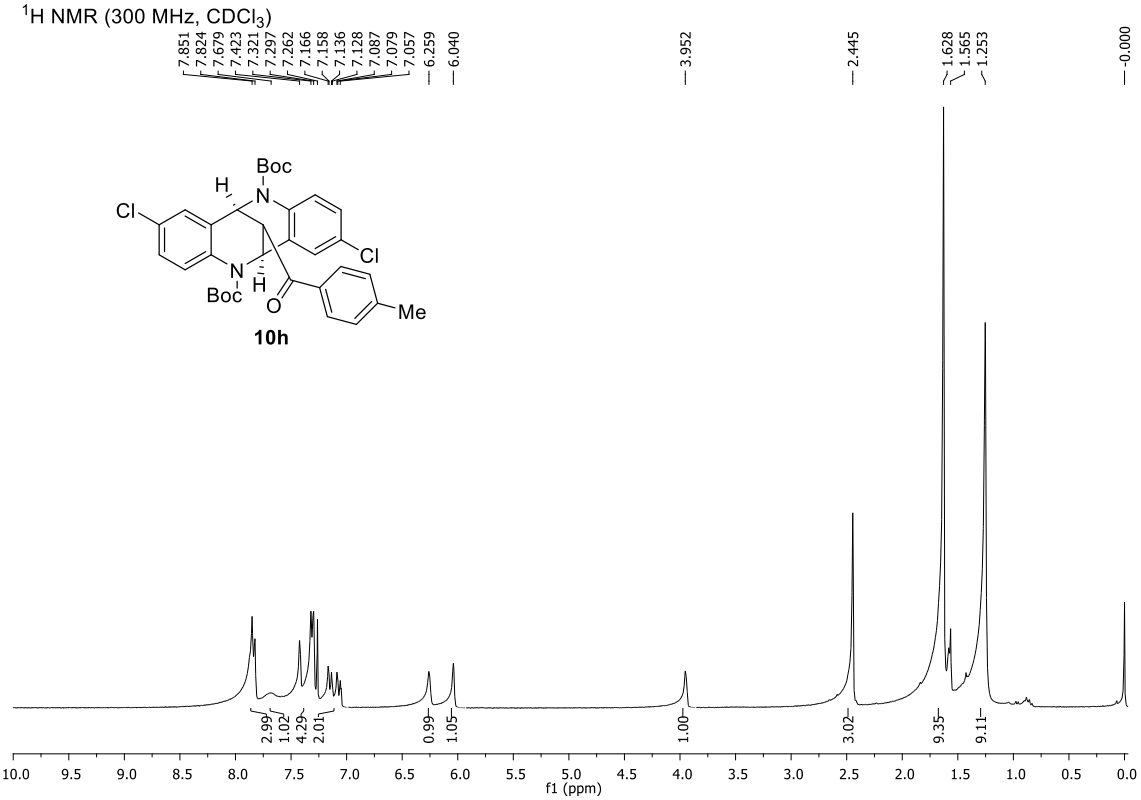
10g

^{13}C NMR (75 MHz, $CDCl_3$)

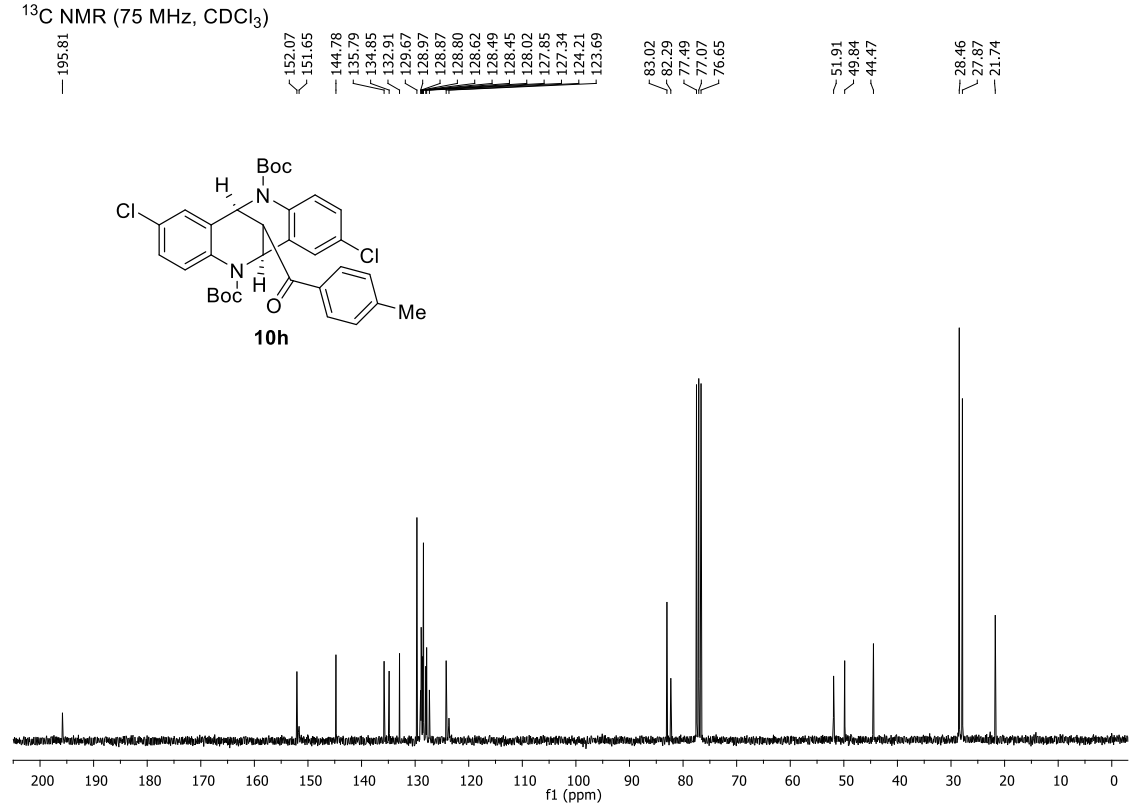


10g

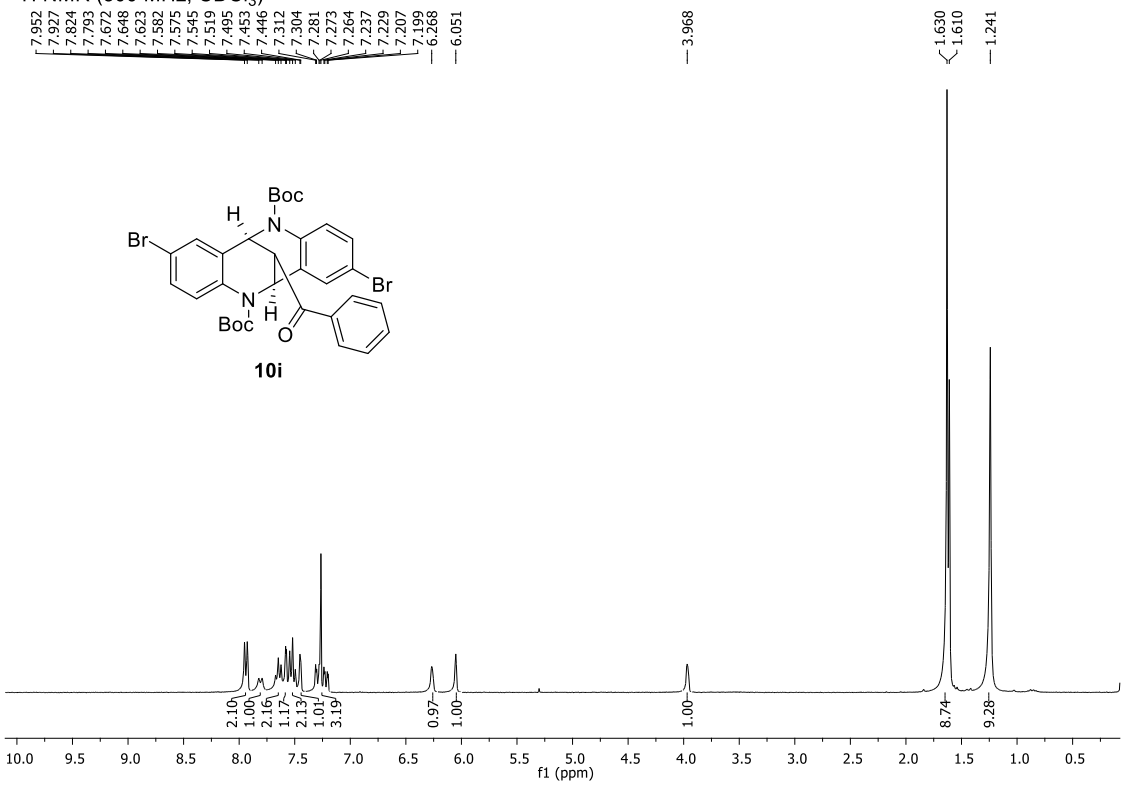
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

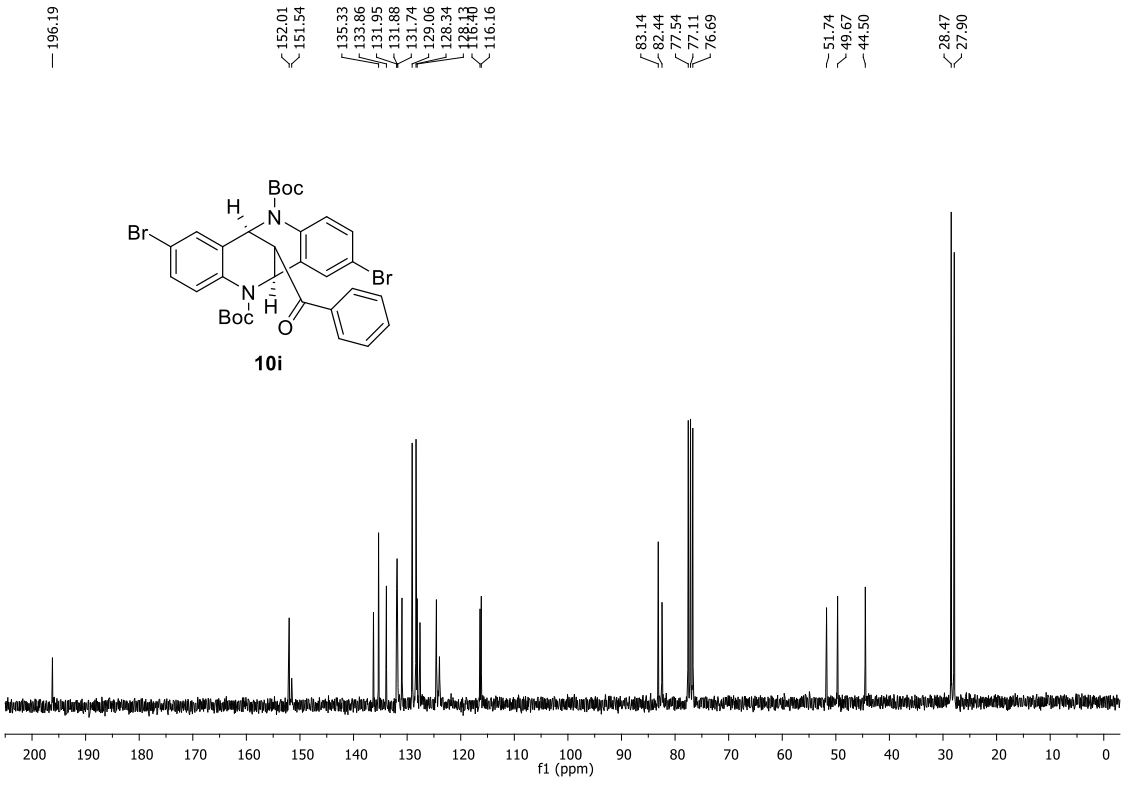


^{1}H NMR (300 MHz, $CDCl_3$)



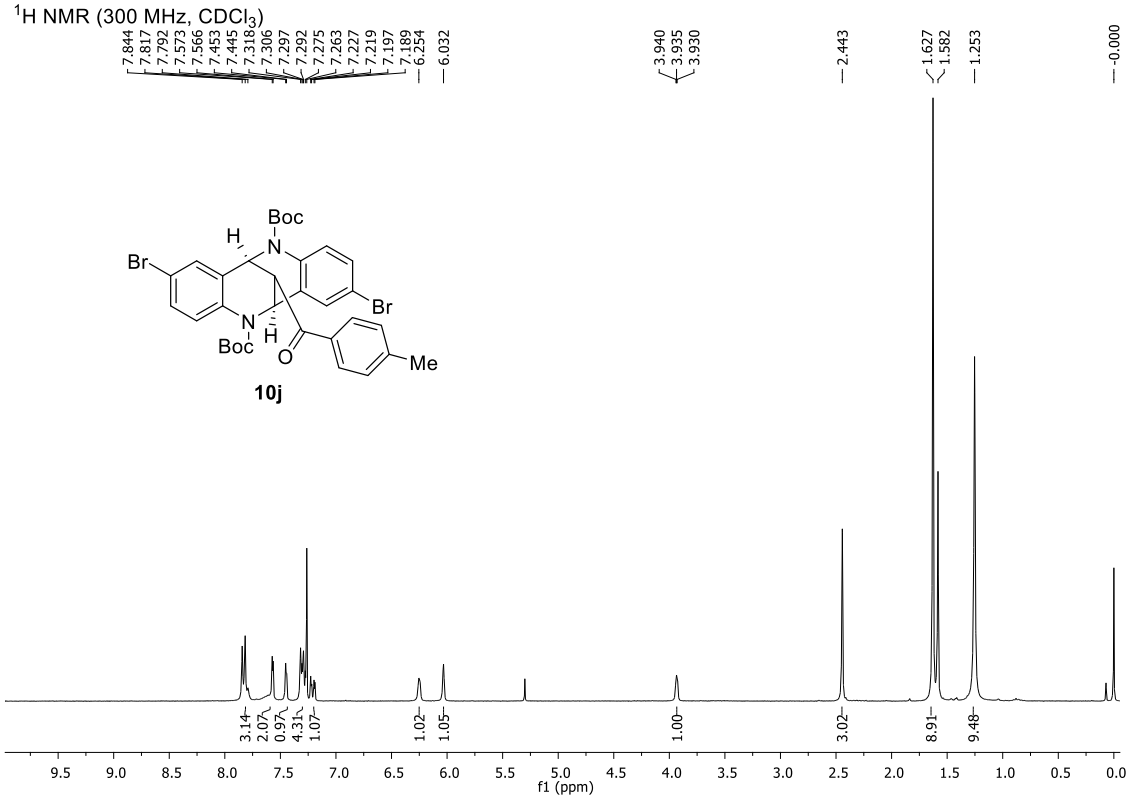
10i

^{13}C NMR (75 MHz, $CDCl_3$)

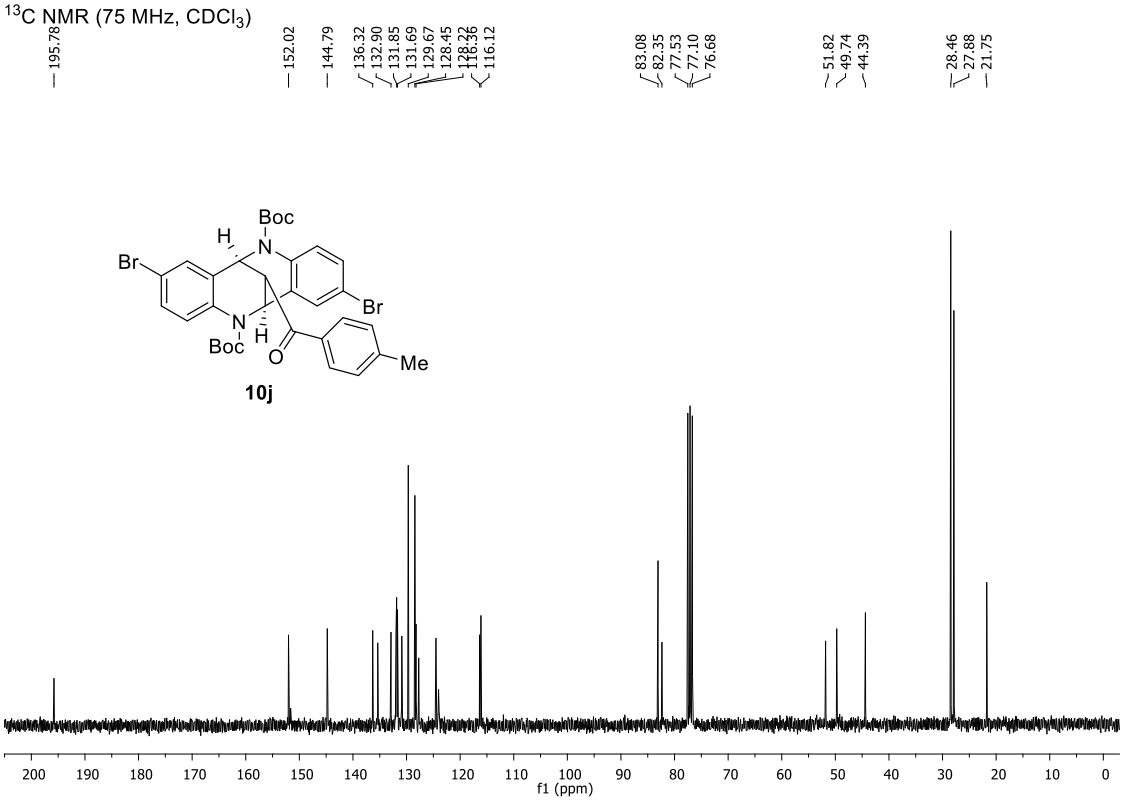


10i

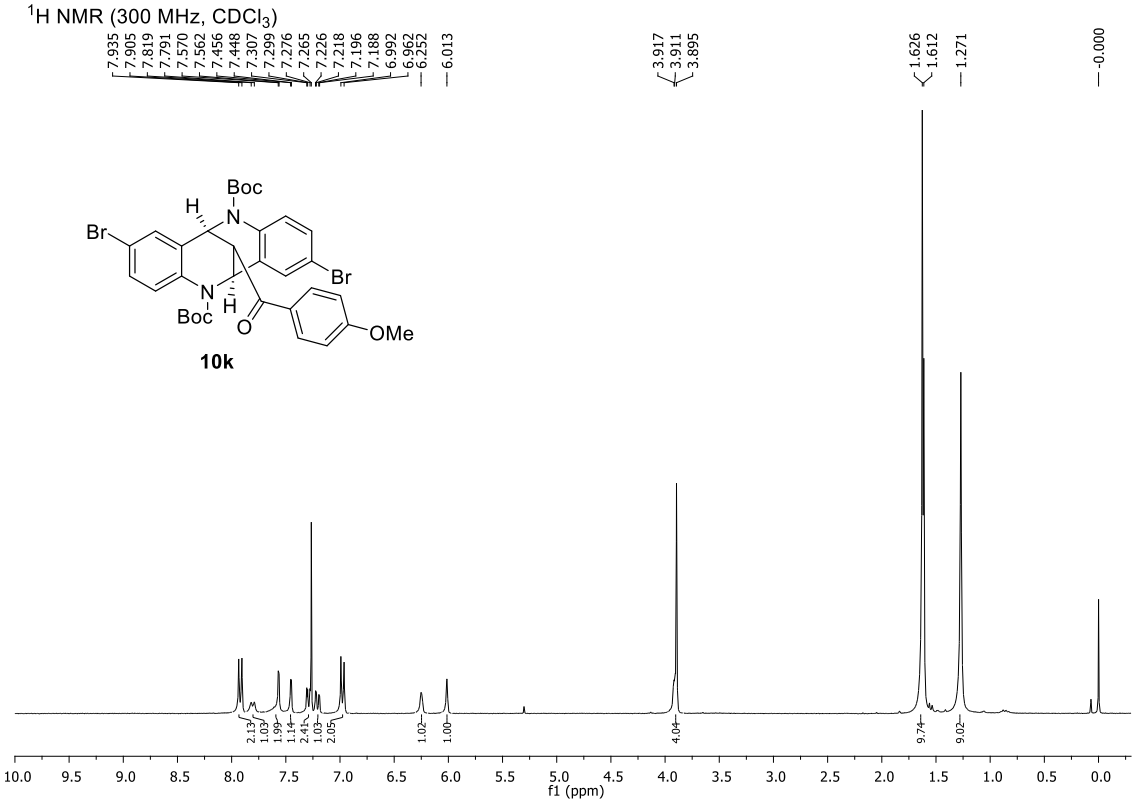
^{1}H NMR (300 MHz, $CDCl_3$)



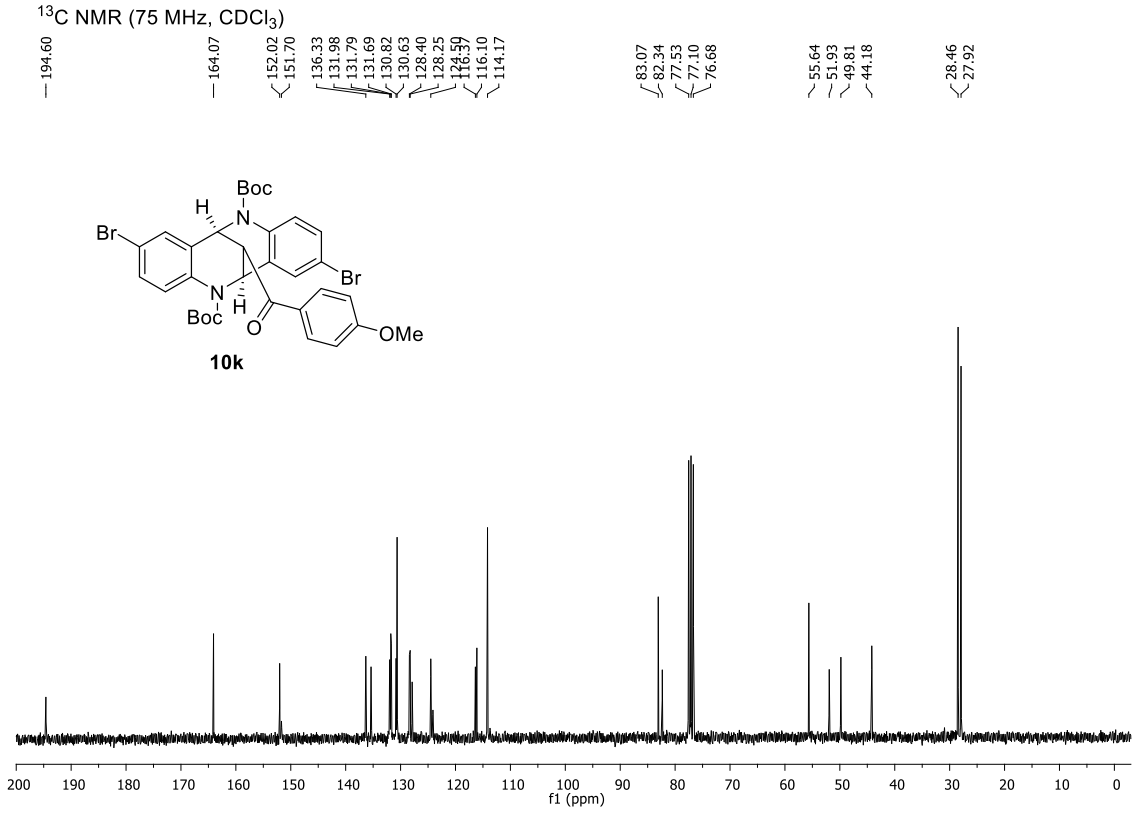
^{13}C NMR (75 MHz, $CDCl_3$)



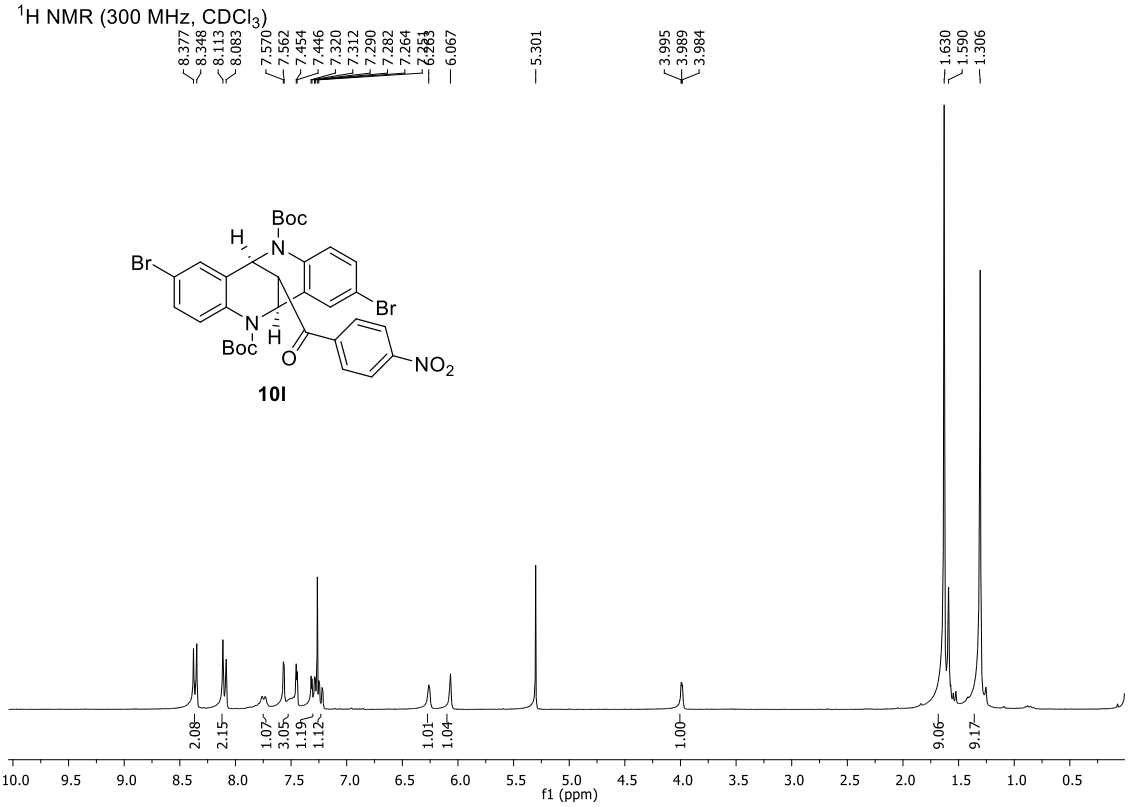
^{1}H NMR (300 MHz, $CDCl_3$)



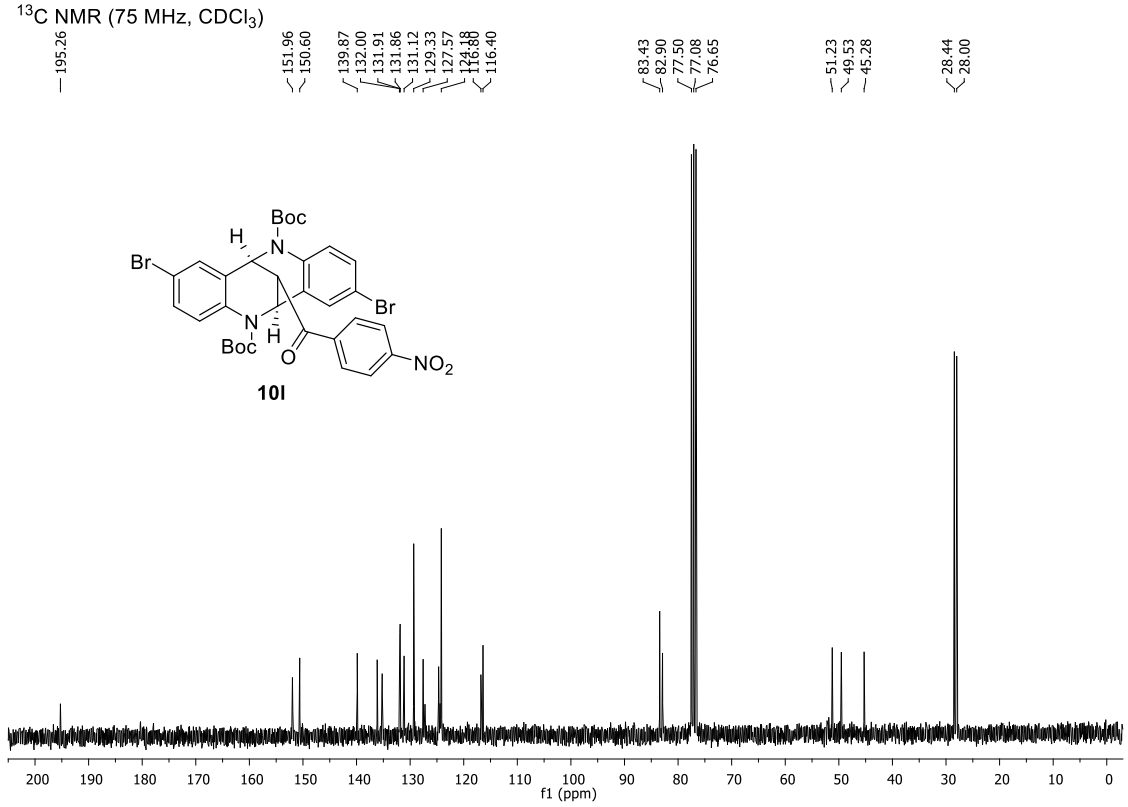
^{13}C NMR (75 MHz, $CDCl_3$)



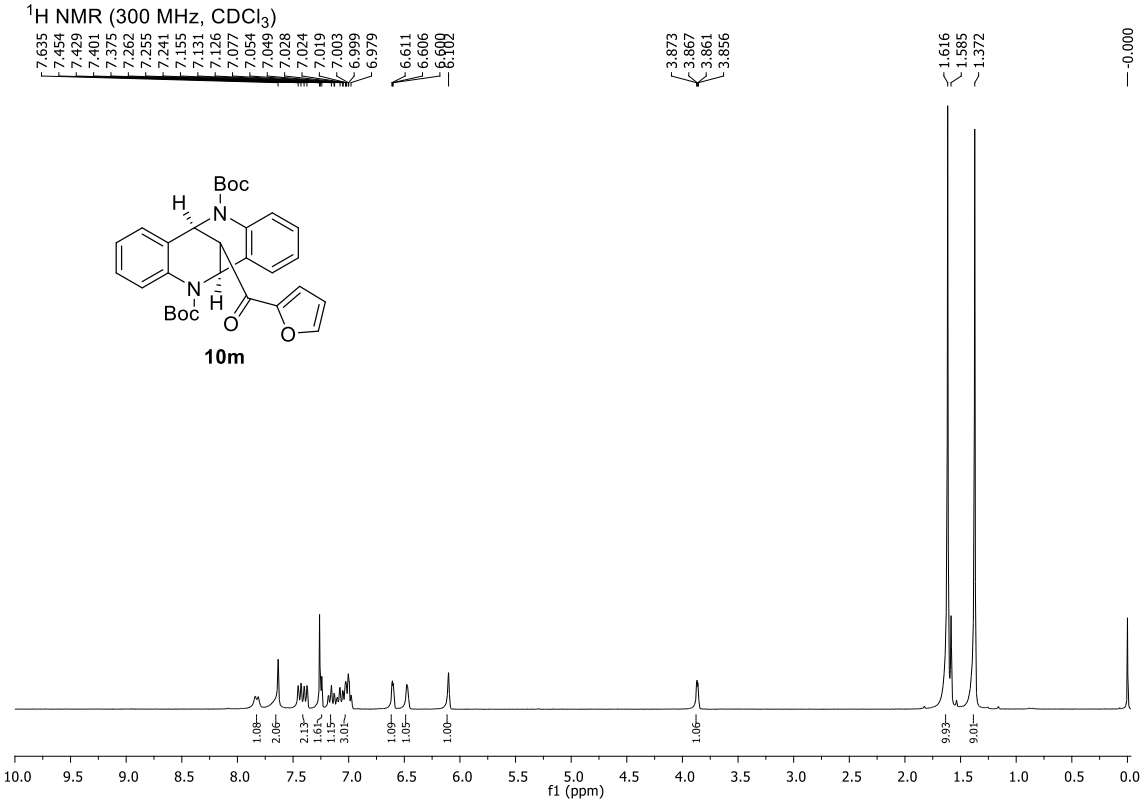
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

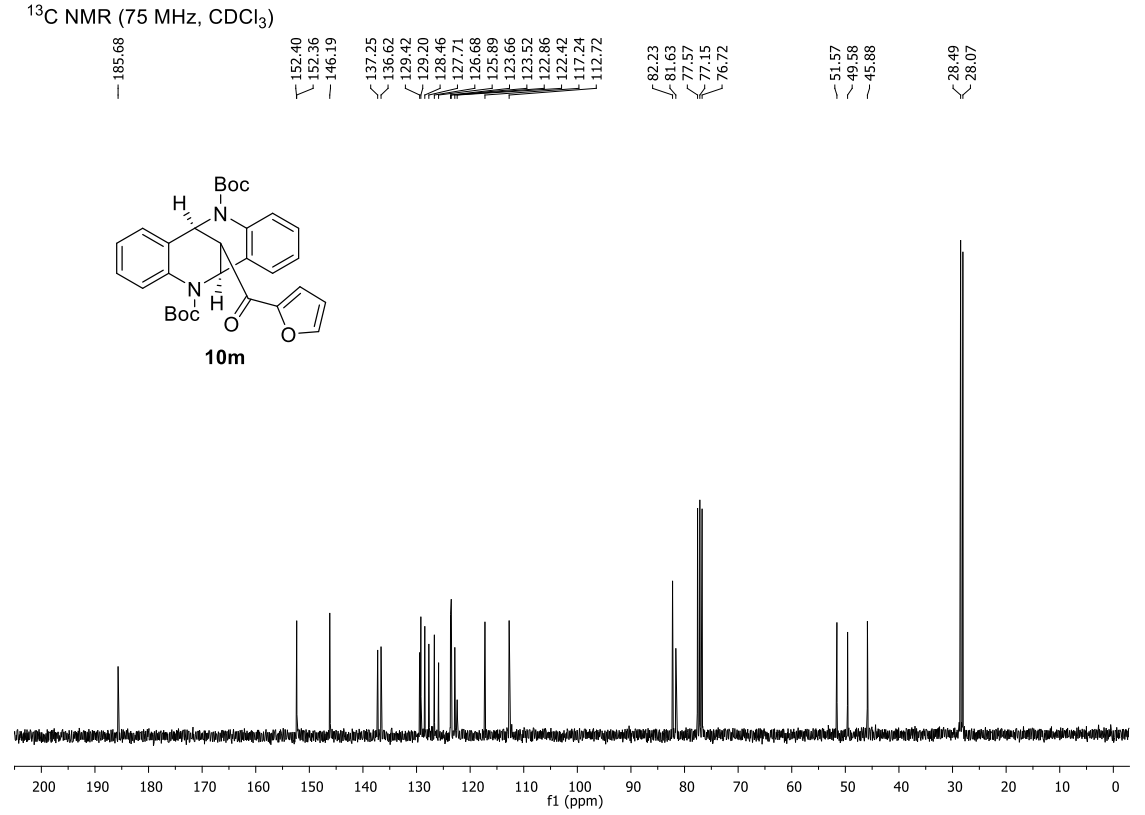


^{1}H NMR (300 MHz, $CDCl_3$)



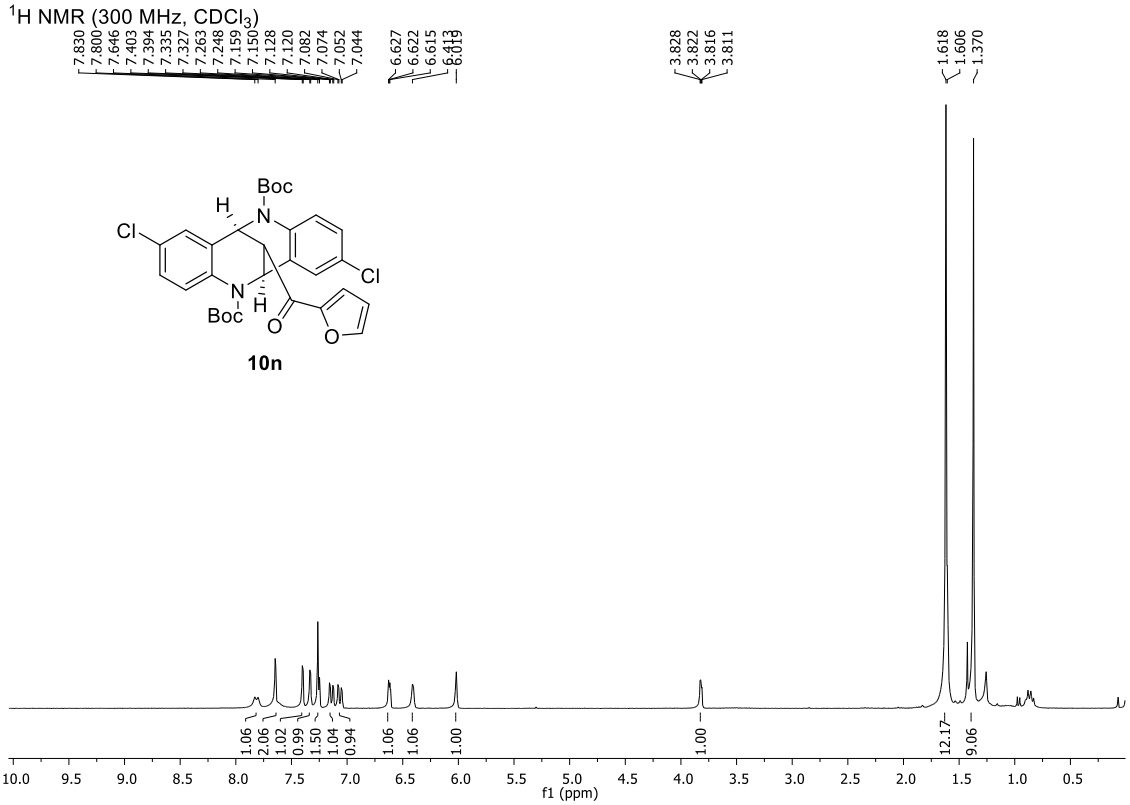
10m

^{13}C NMR (75 MHz, $CDCl_3$)

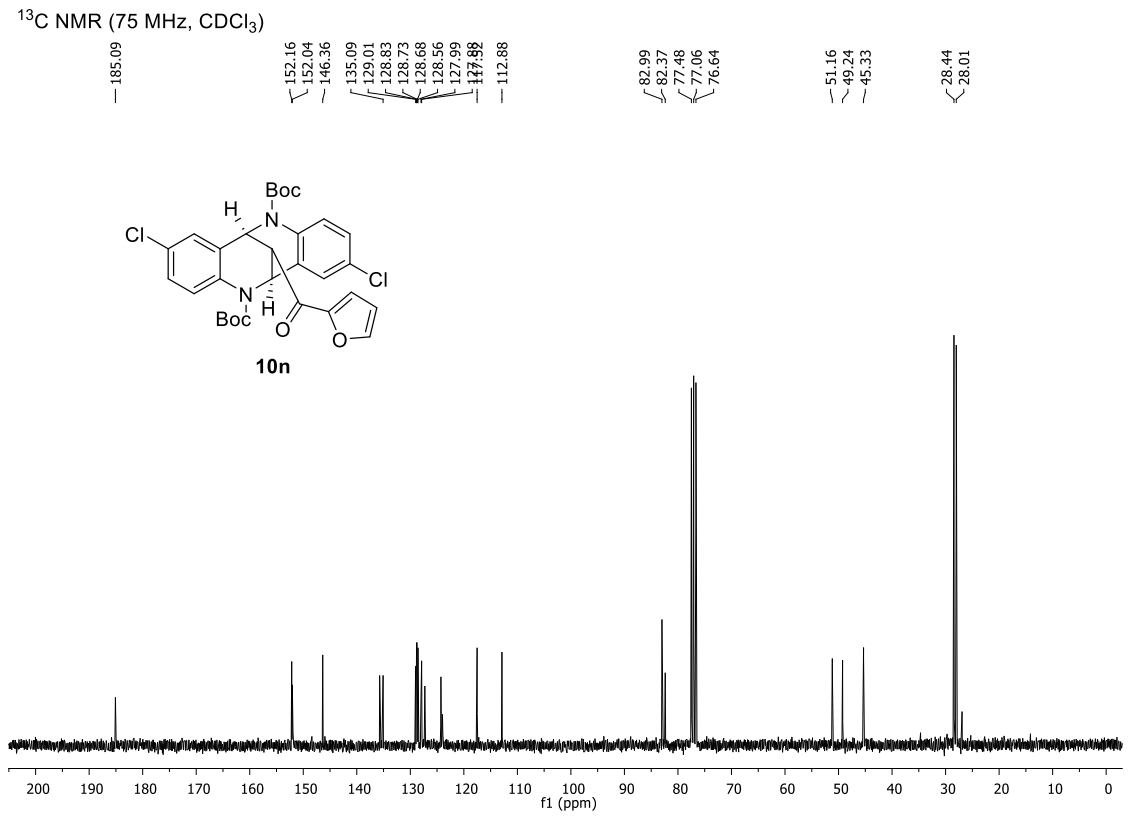


10m

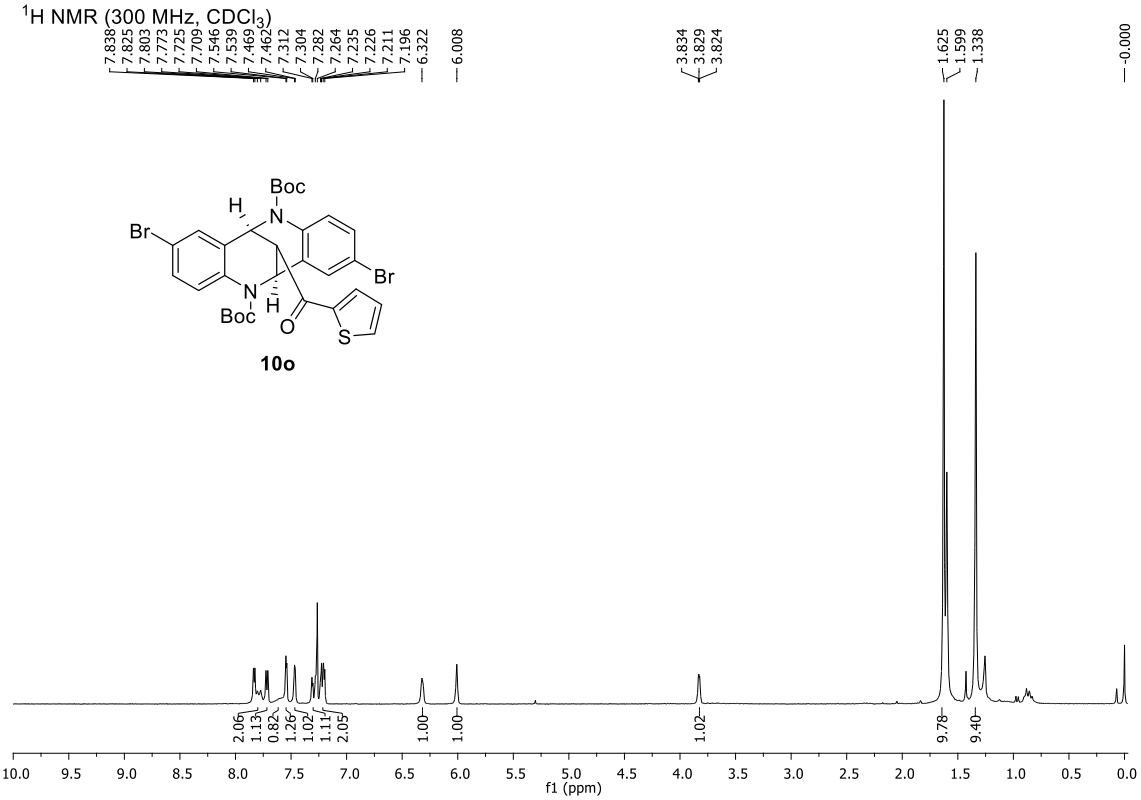
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

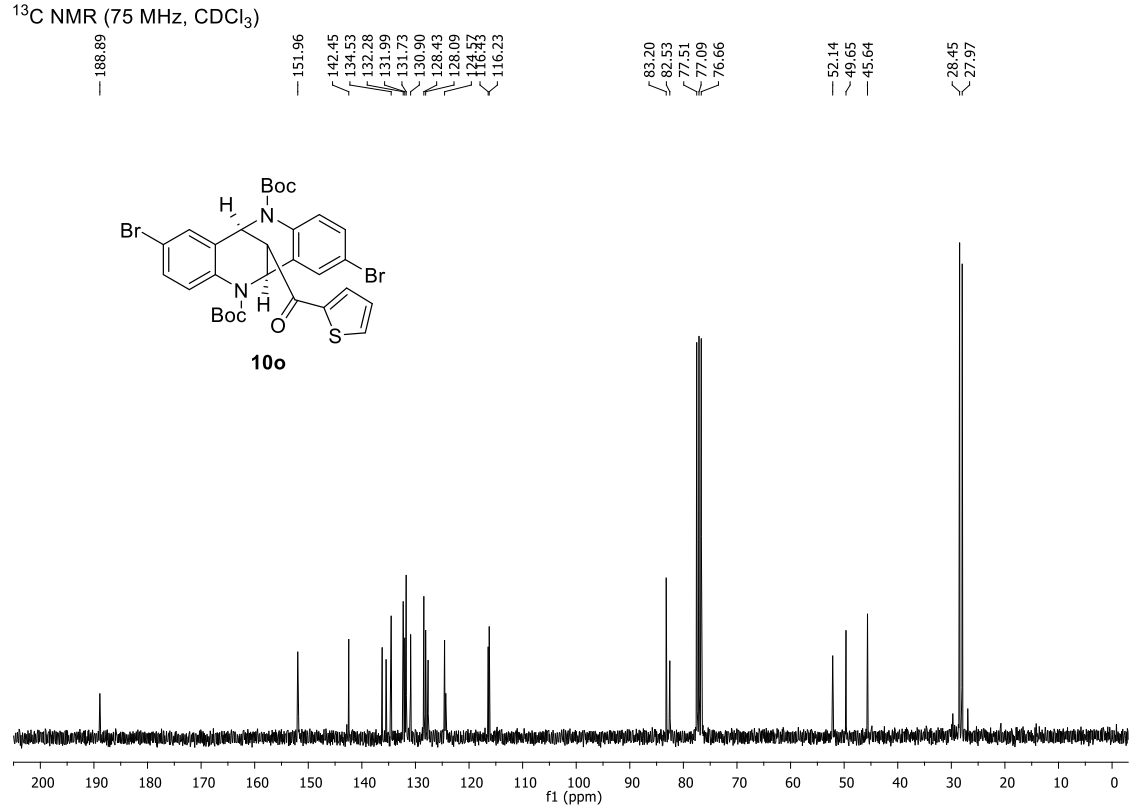


^{1}H NMR (300 MHz, $CDCl_3$)



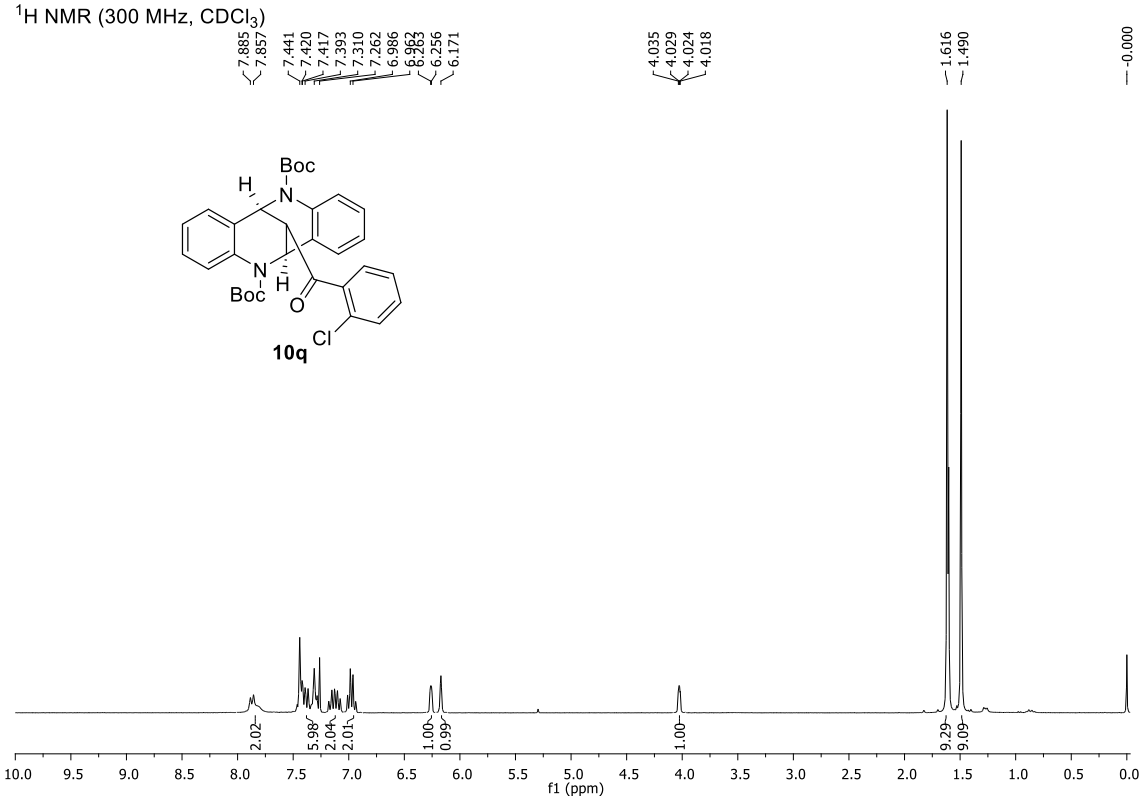
10o

^{13}C NMR (75 MHz, $CDCl_3$)

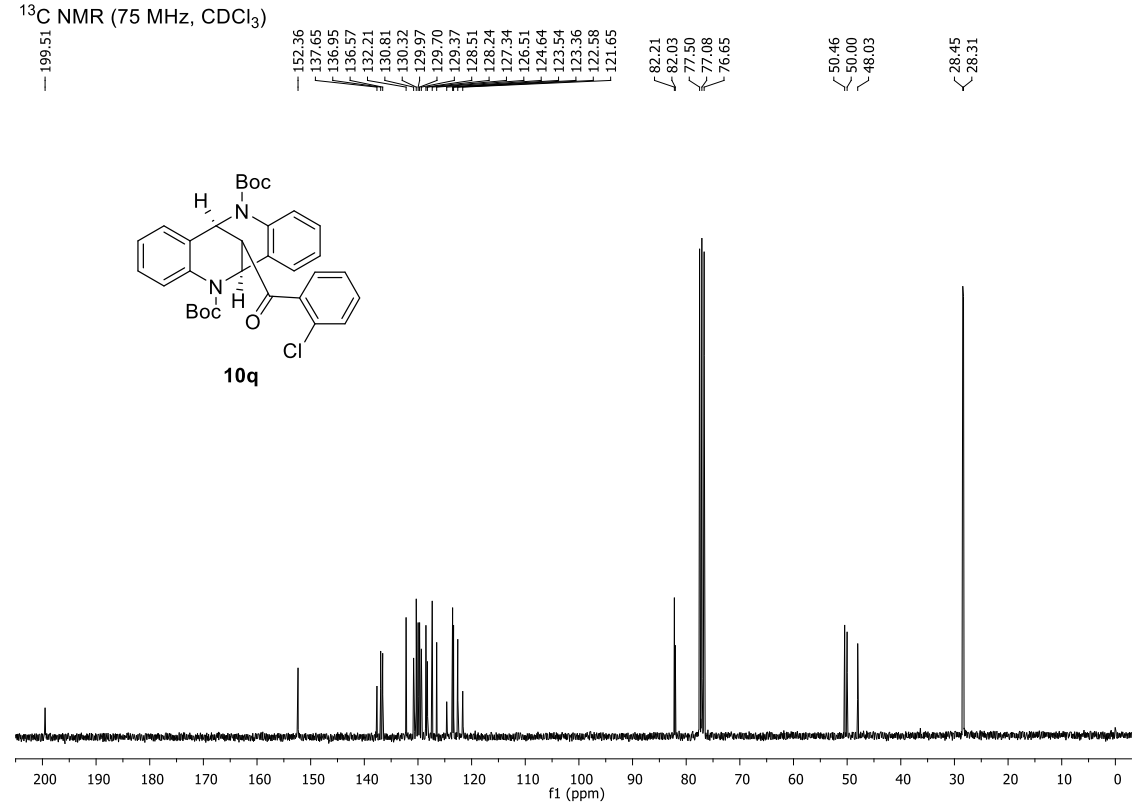


10o

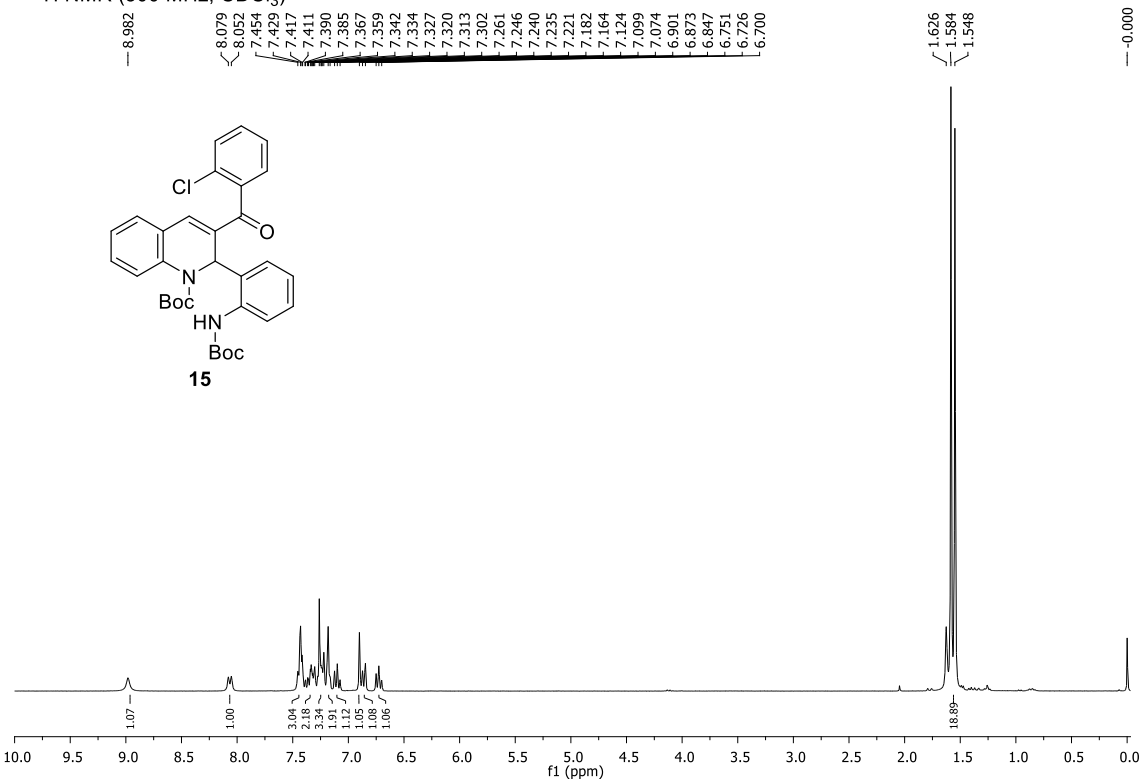
^{1}H NMR (300 MHz, $CDCl_3$)



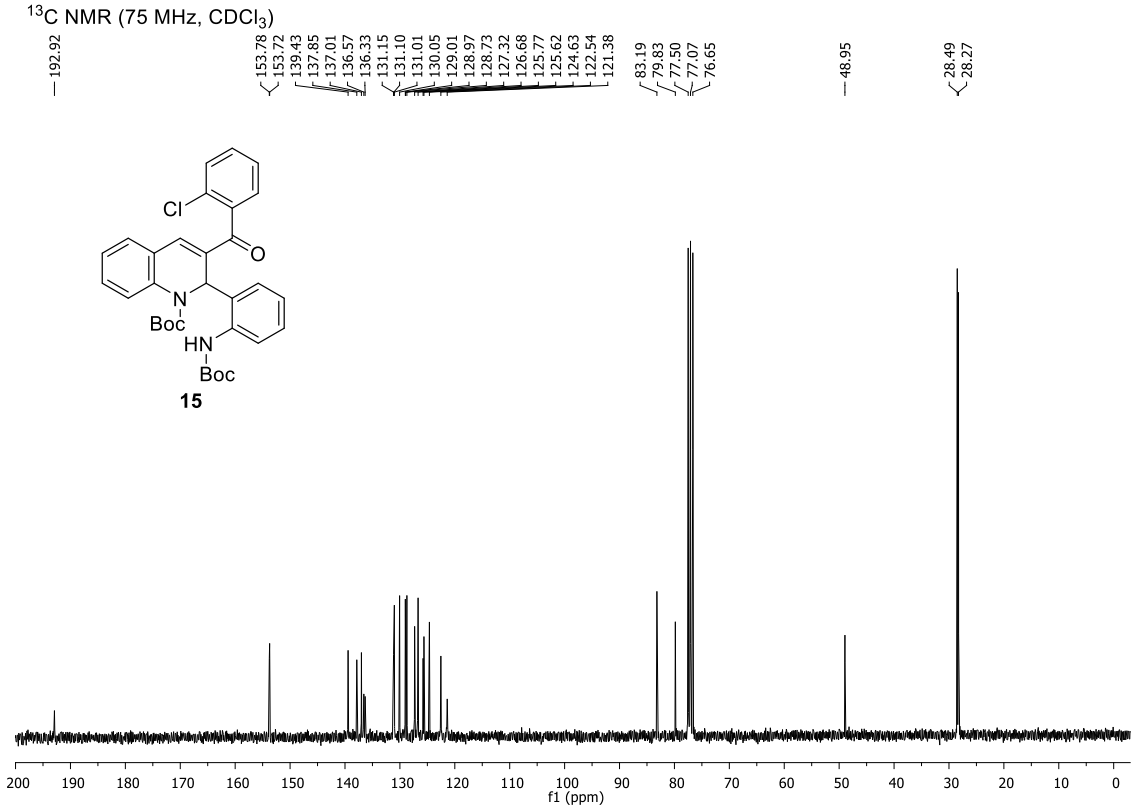
^{13}C NMR (75 MHz, $CDCl_3$)



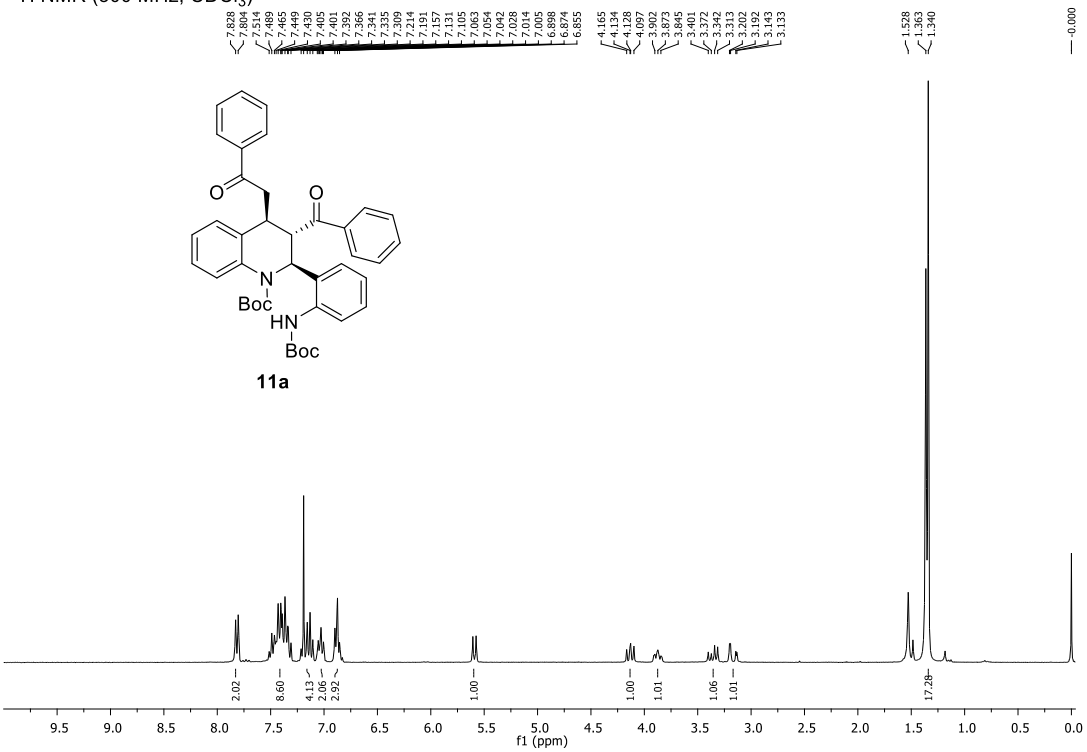
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

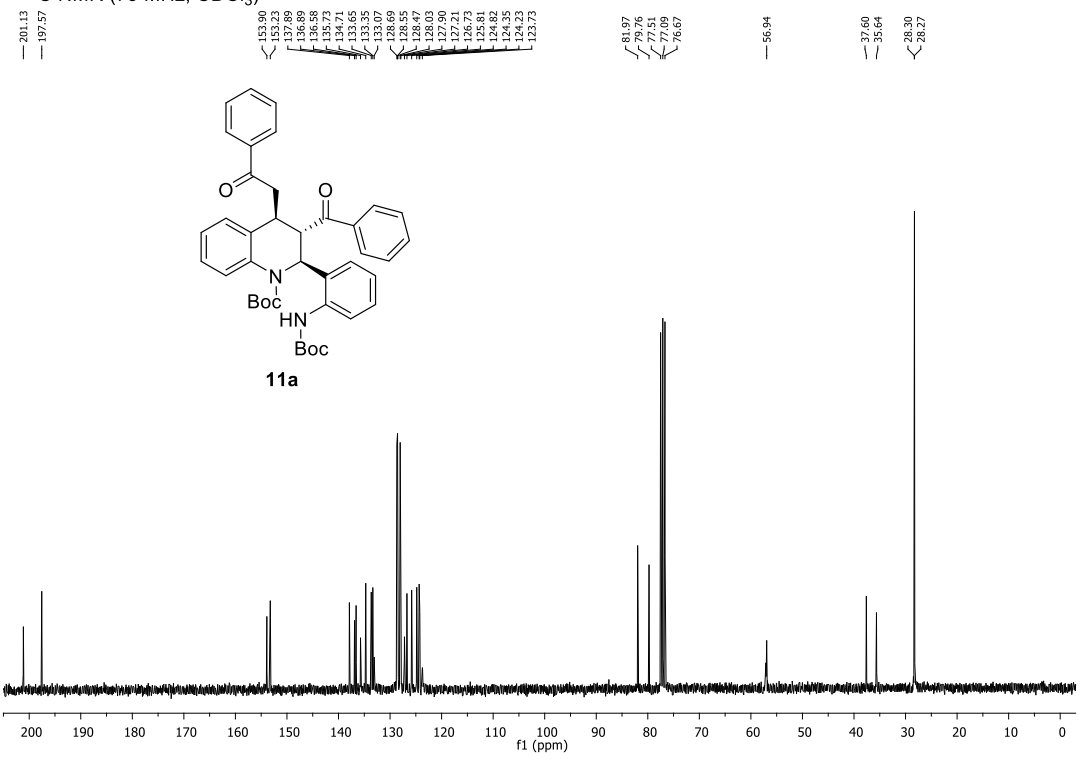


^{1}H NMR (300 MHz, $CDCl_3$)



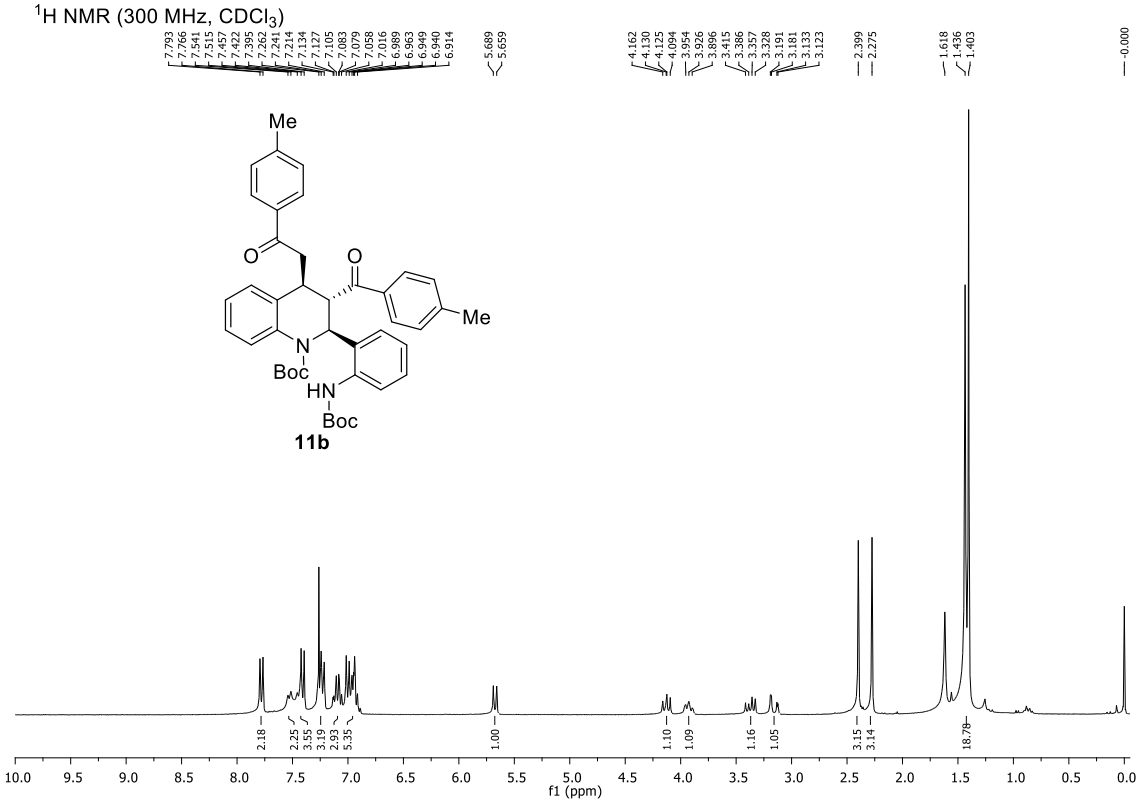
11a

^{13}C NMR (75 MHz, $CDCl_3$)

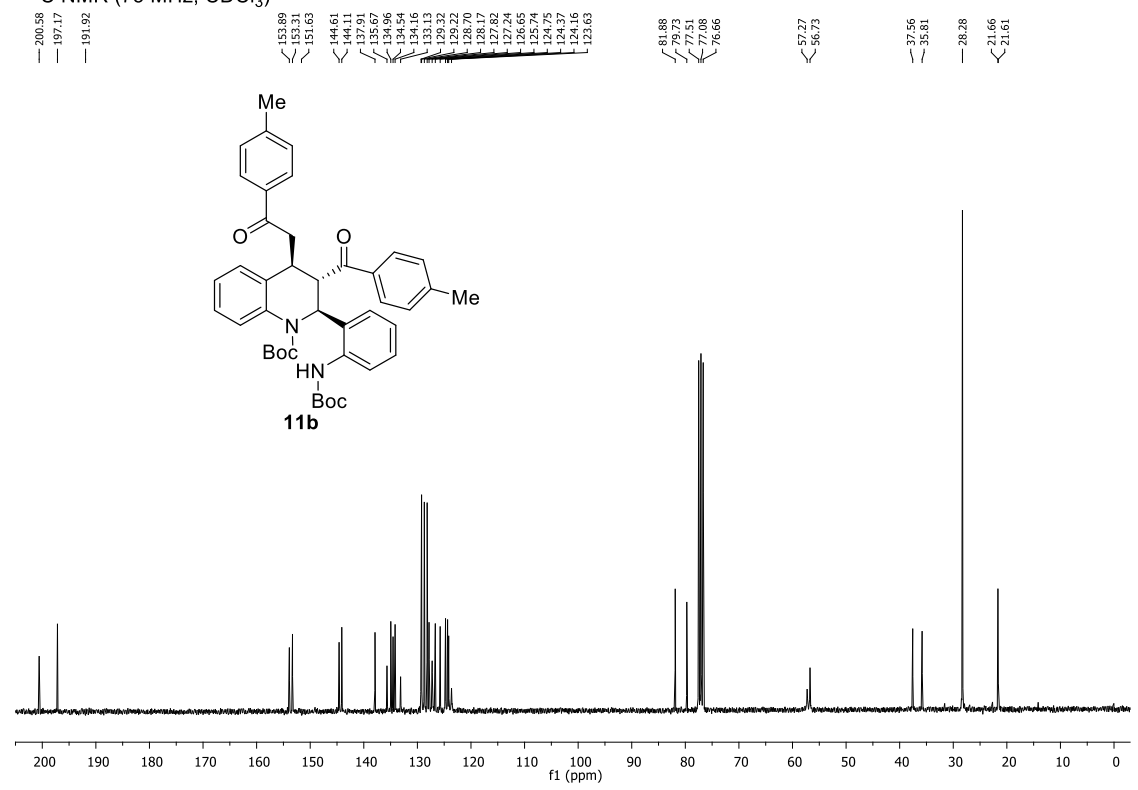


11a

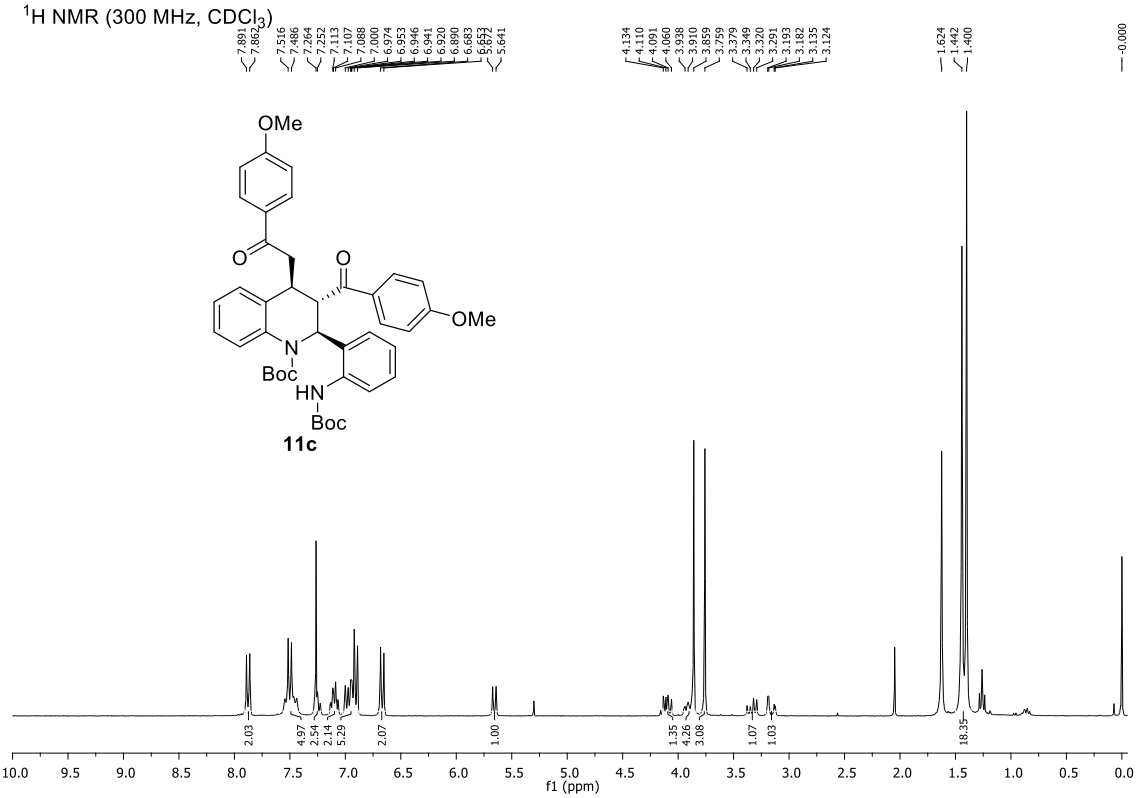
^{1}H NMR (300 MHz, $CDCl_3$)



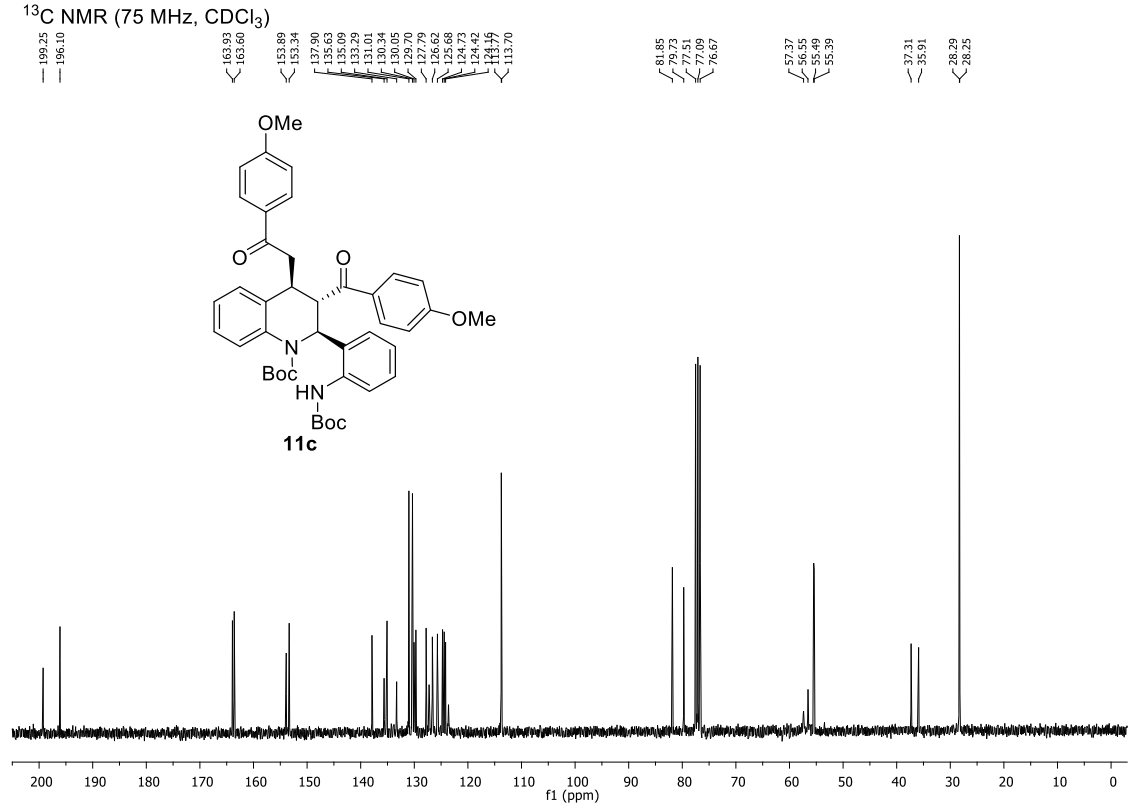
^{13}C NMR (75 MHz, $CDCl_3$)



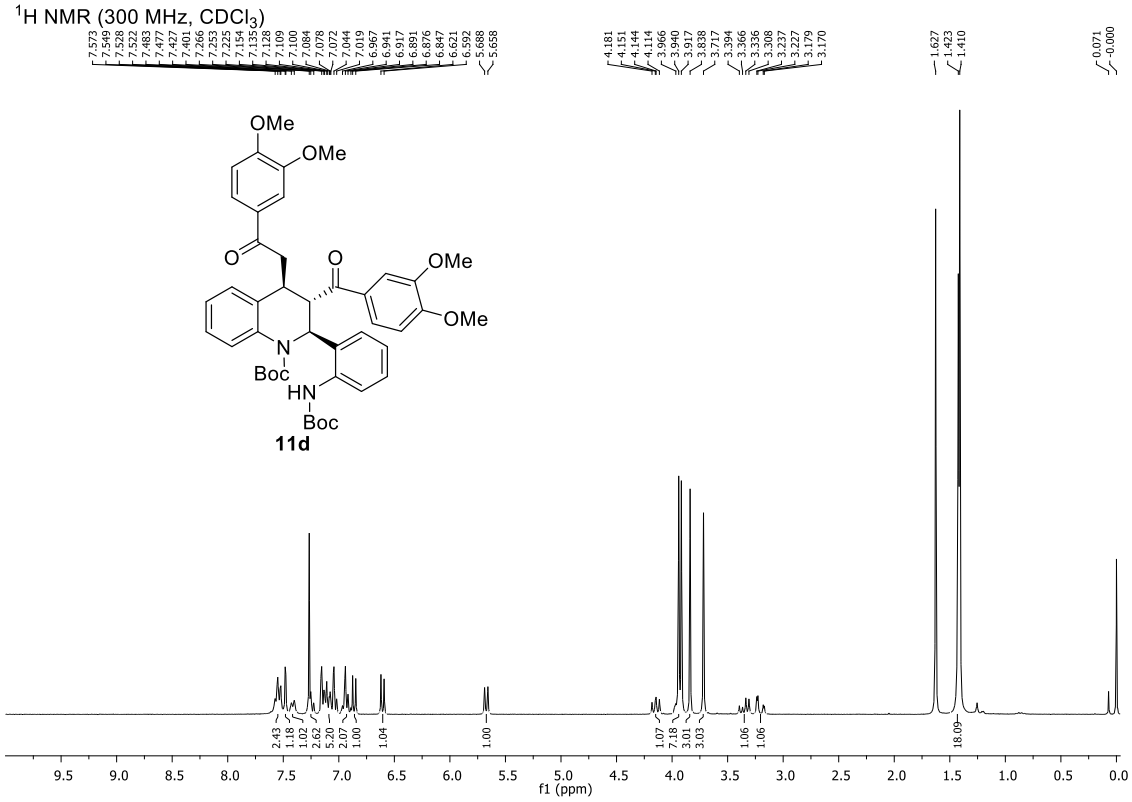
^{1}H NMR (300 MHz, $CDCl_3$)



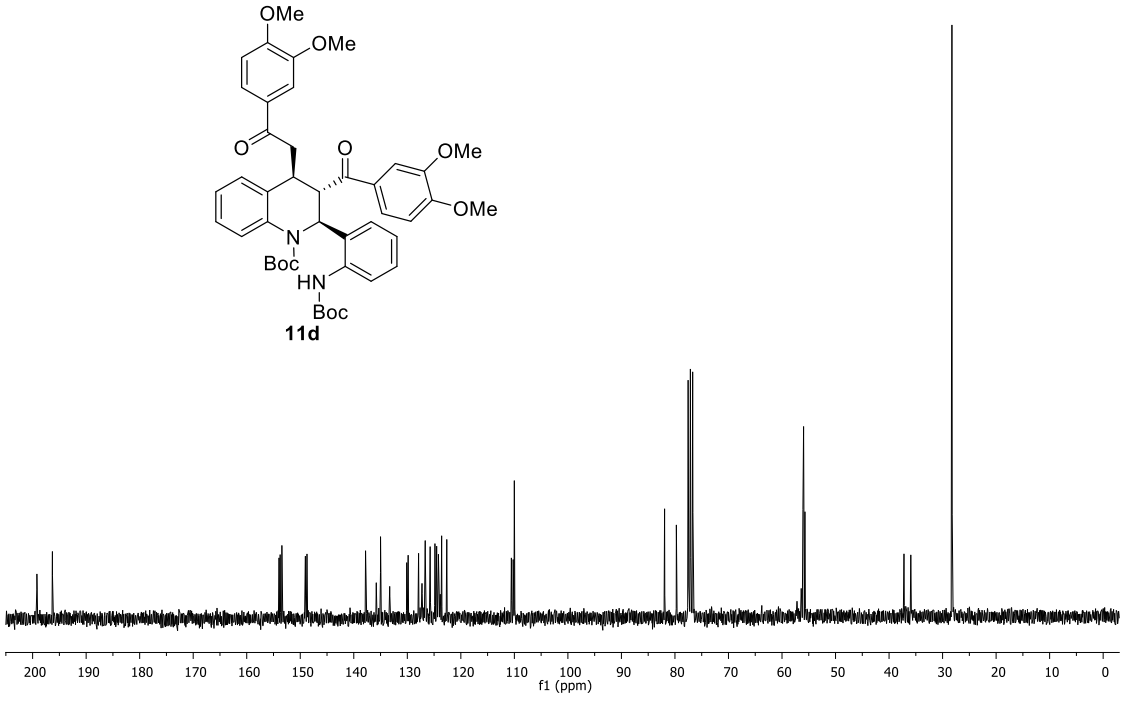
^{13}C NMR (75 MHz, $CDCl_3$)



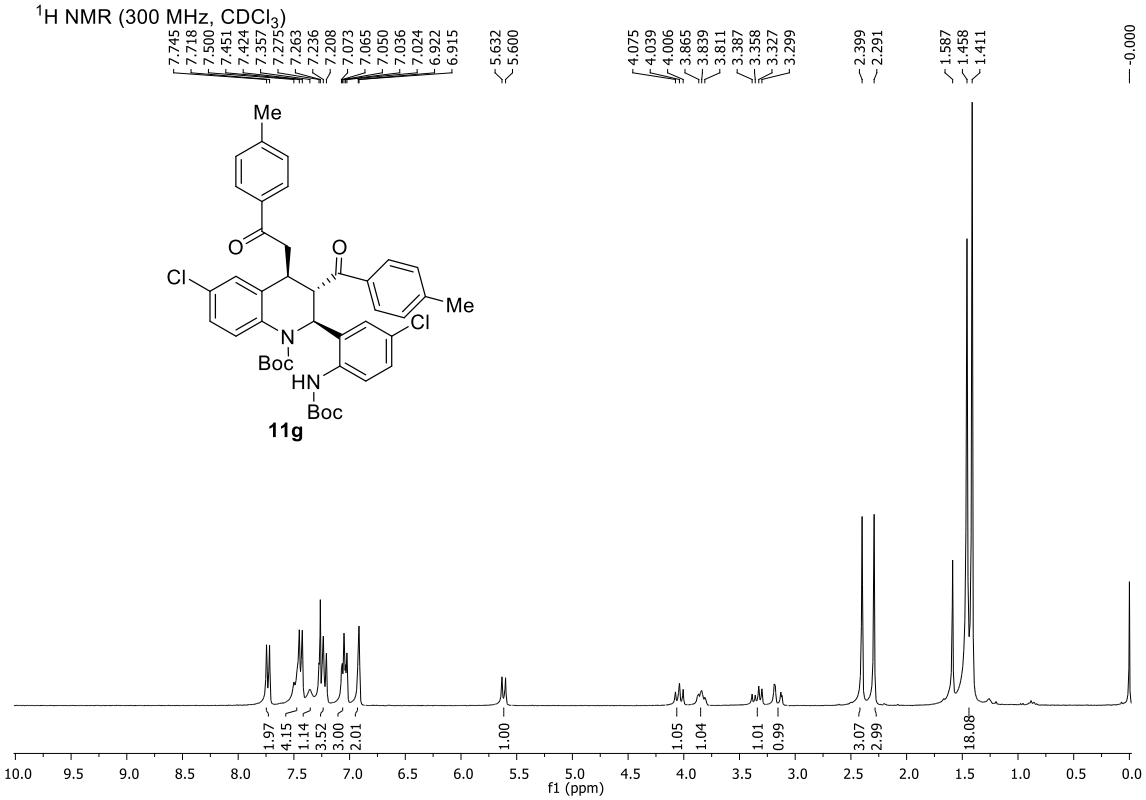
^{1}H NMR (300 MHz, $CDCl_3$)



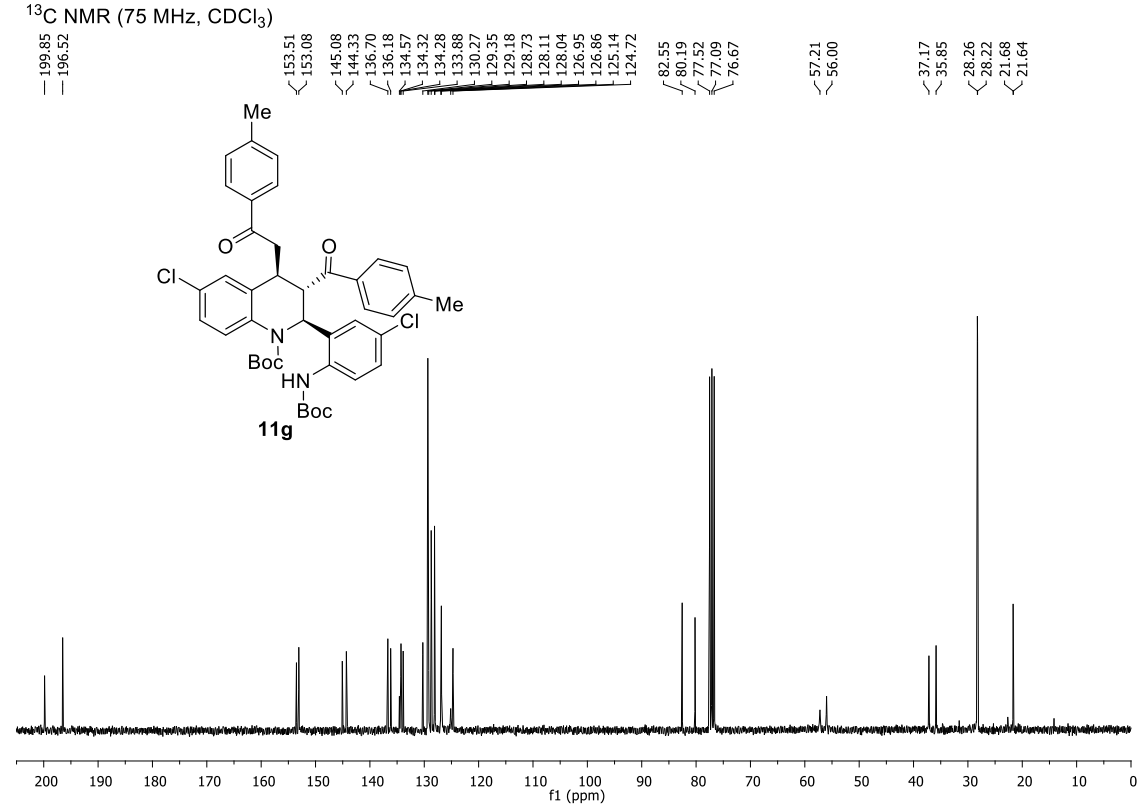
^{13}C NMR (75 MHz, $CDCl_3$)



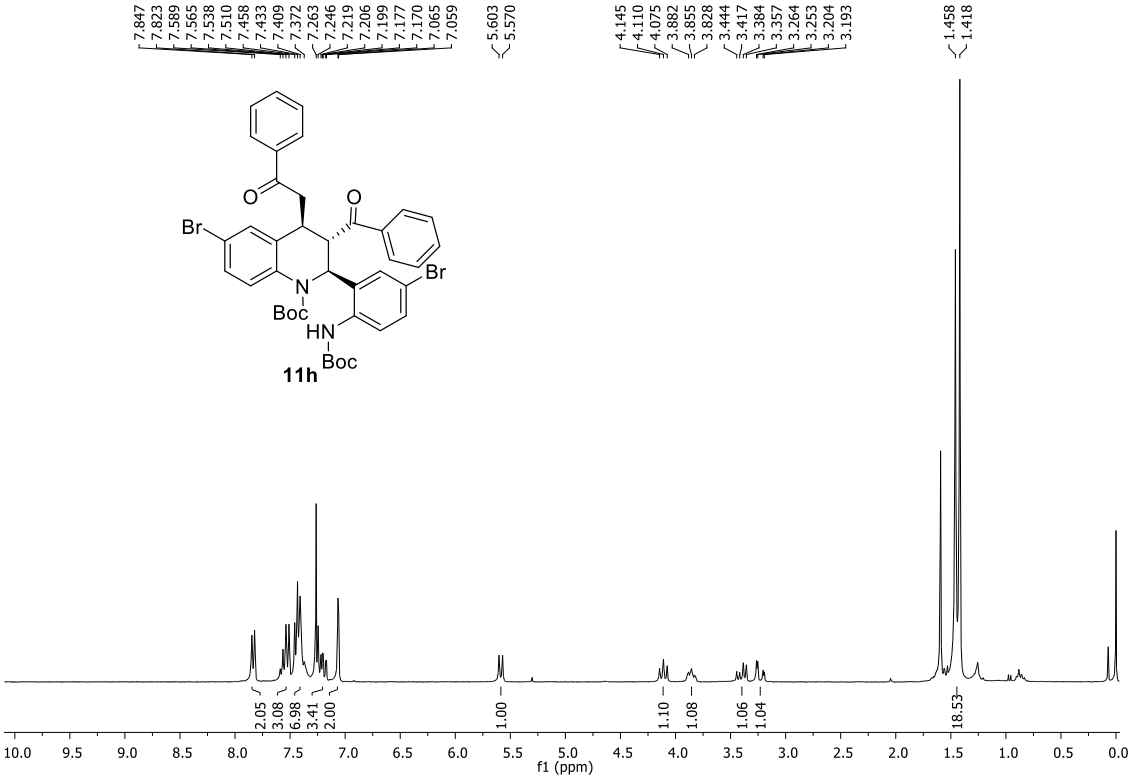
^{1}H NMR (300 MHz, $CDCl_3$)



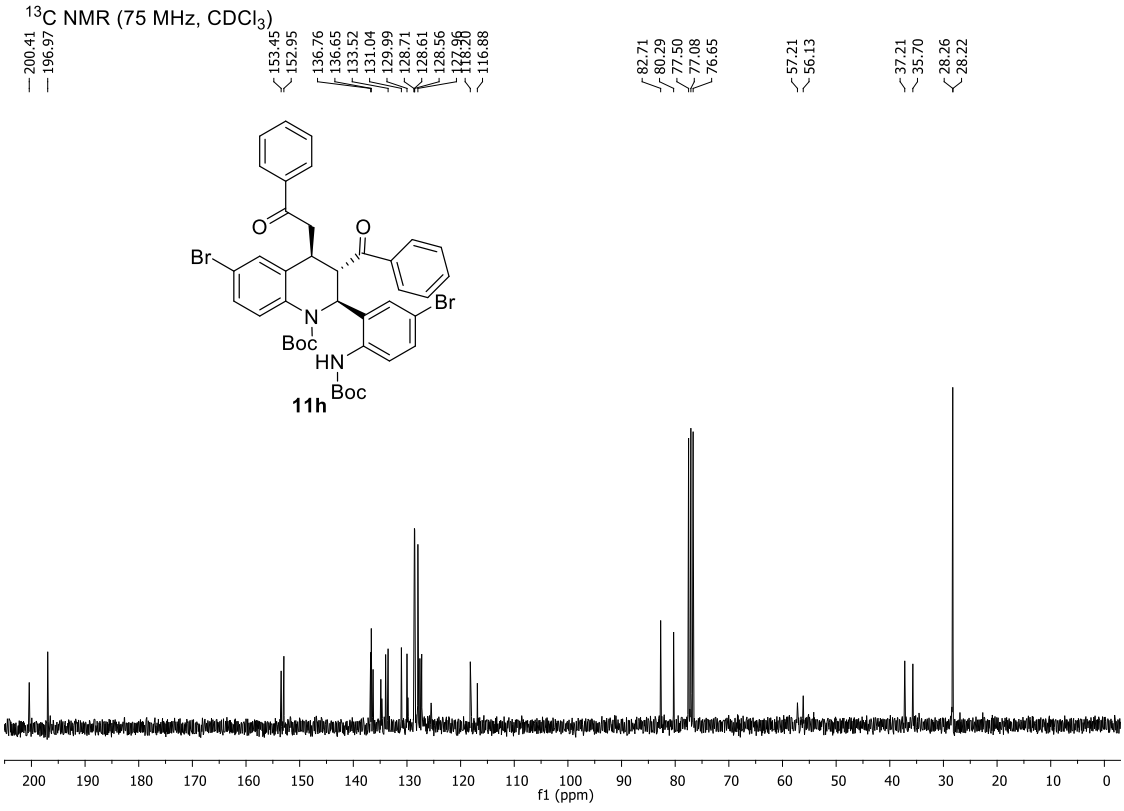
^{13}C NMR (75 MHz, $CDCl_3$)



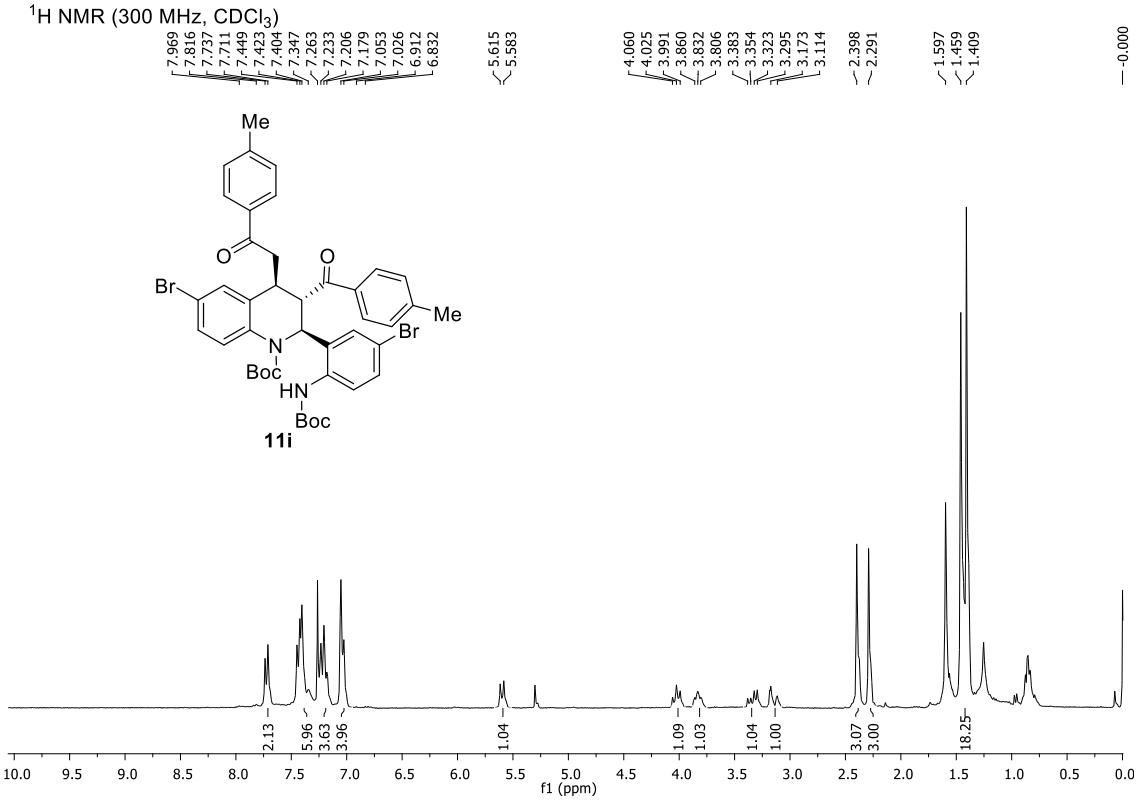
^{1}H NMR (300 MHz, $CDCl_3$)



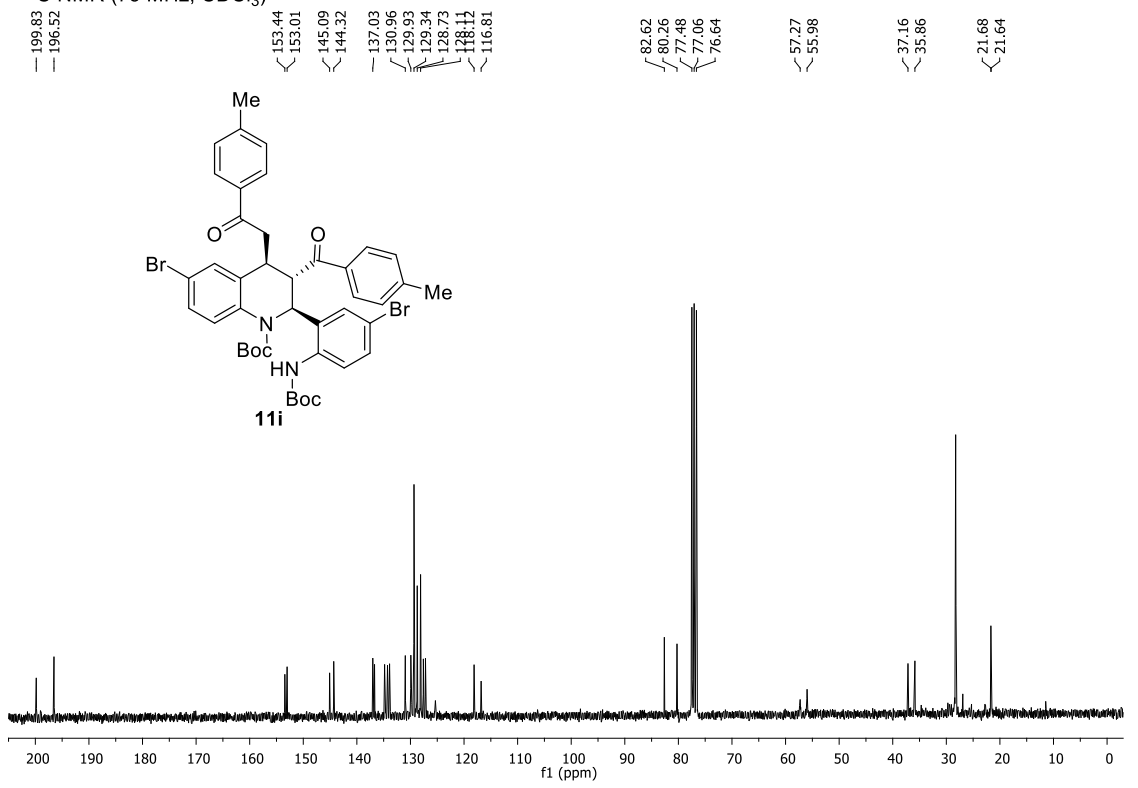
^{13}C NMR (75 MHz, $CDCl_3$)



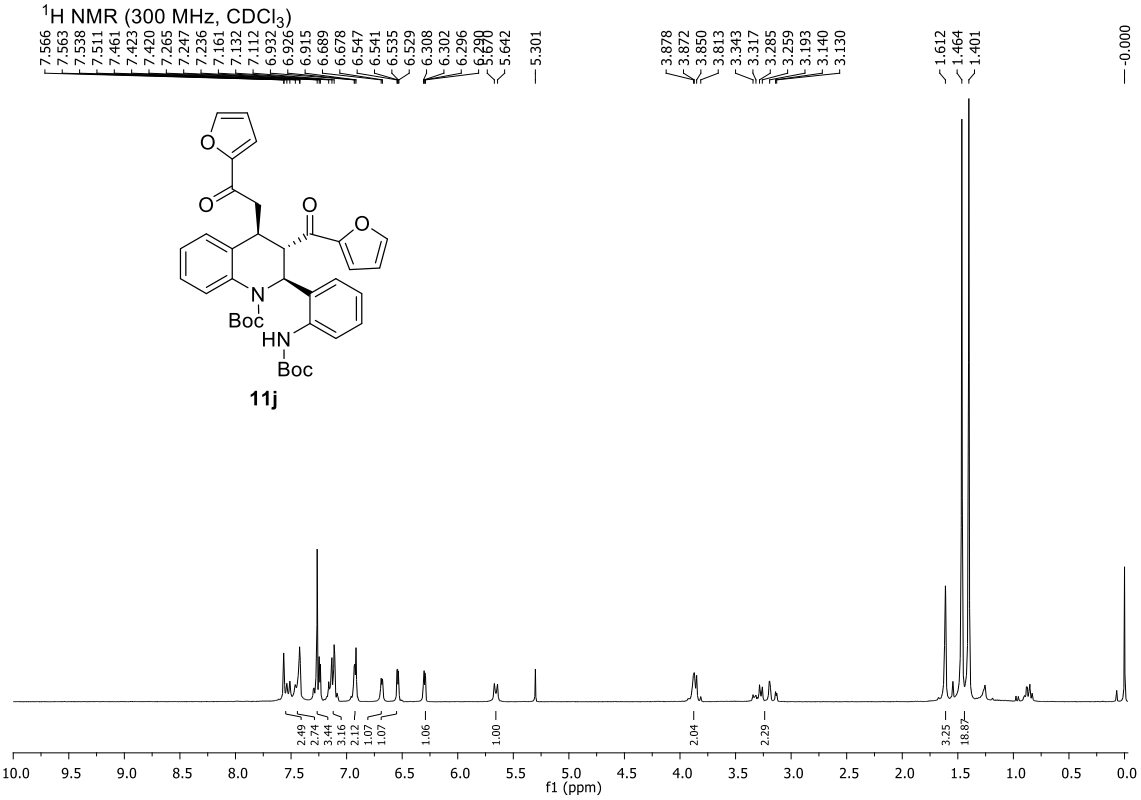
^{1}H NMR (300 MHz, $CDCl_3$)



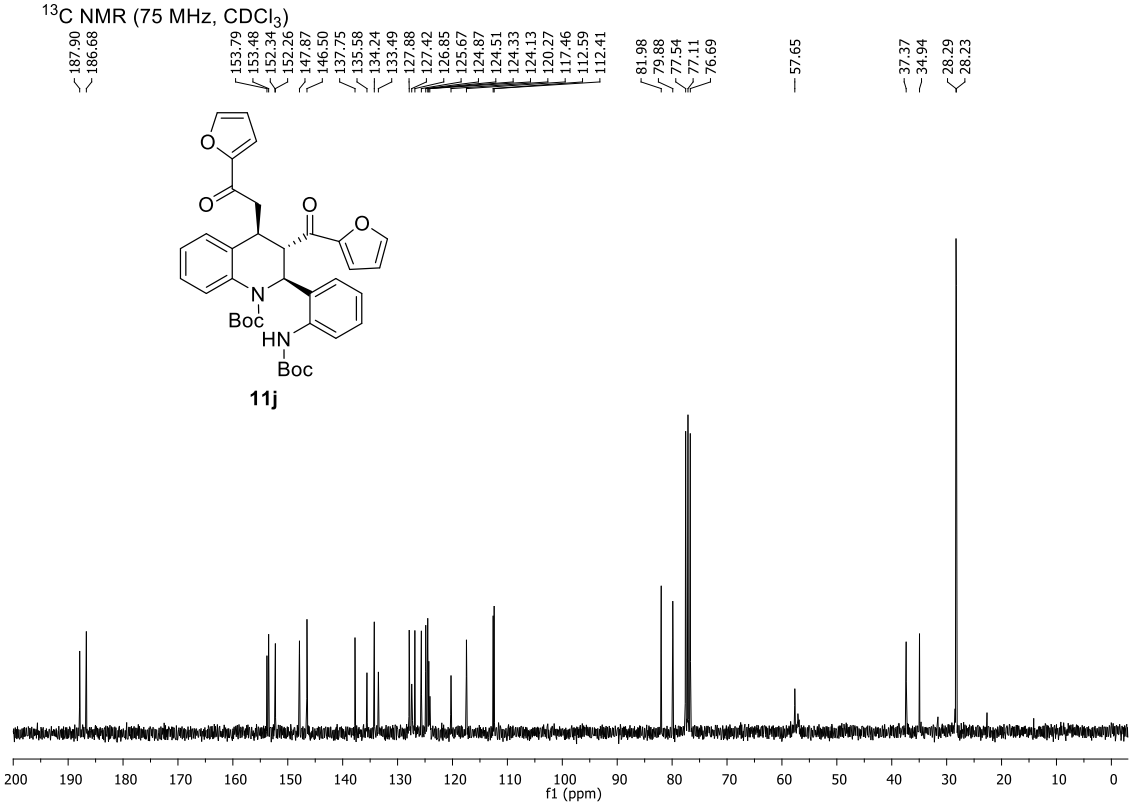
^{13}C NMR (75 MHz, $CDCl_3$)



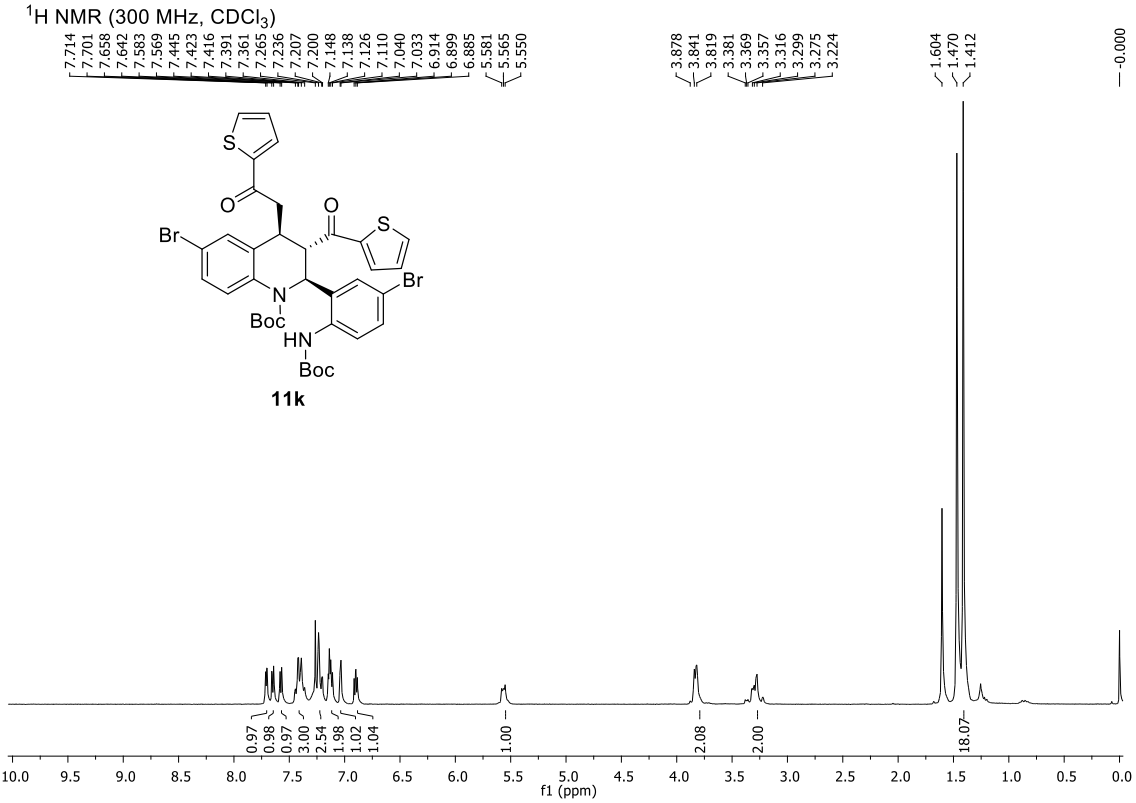
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

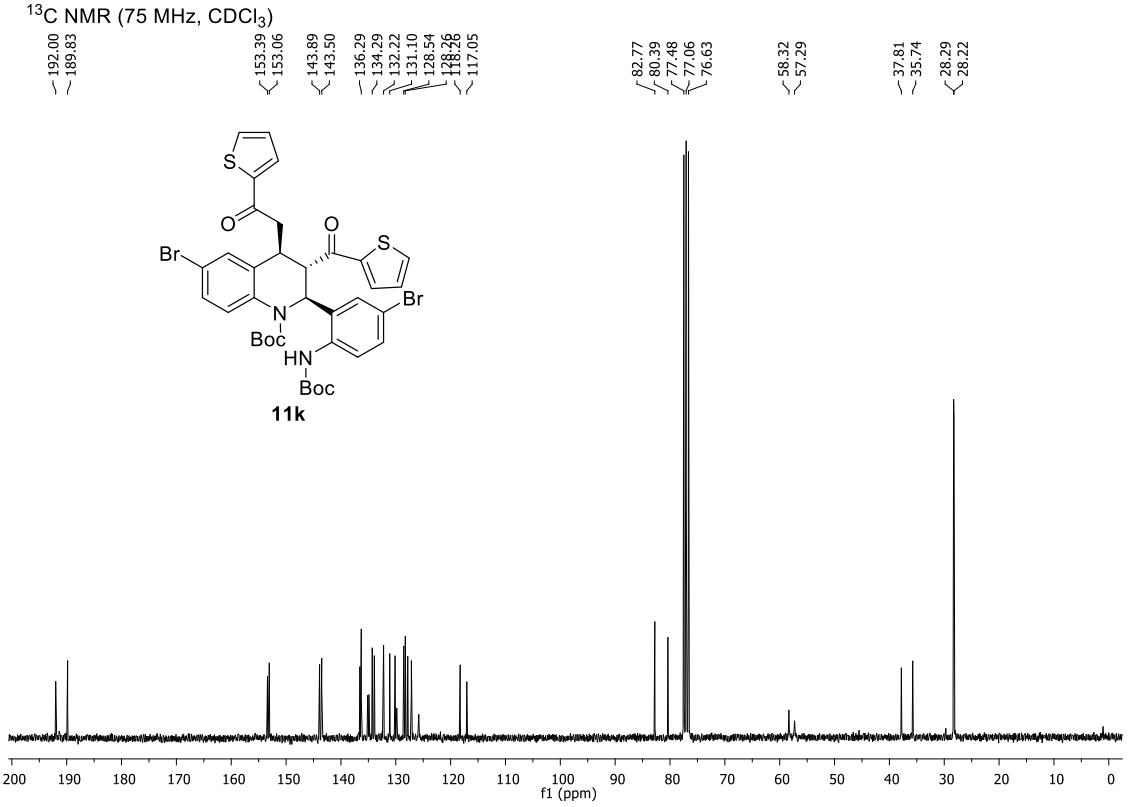


^{1}H NMR (300 MHz, $CDCl_3$)



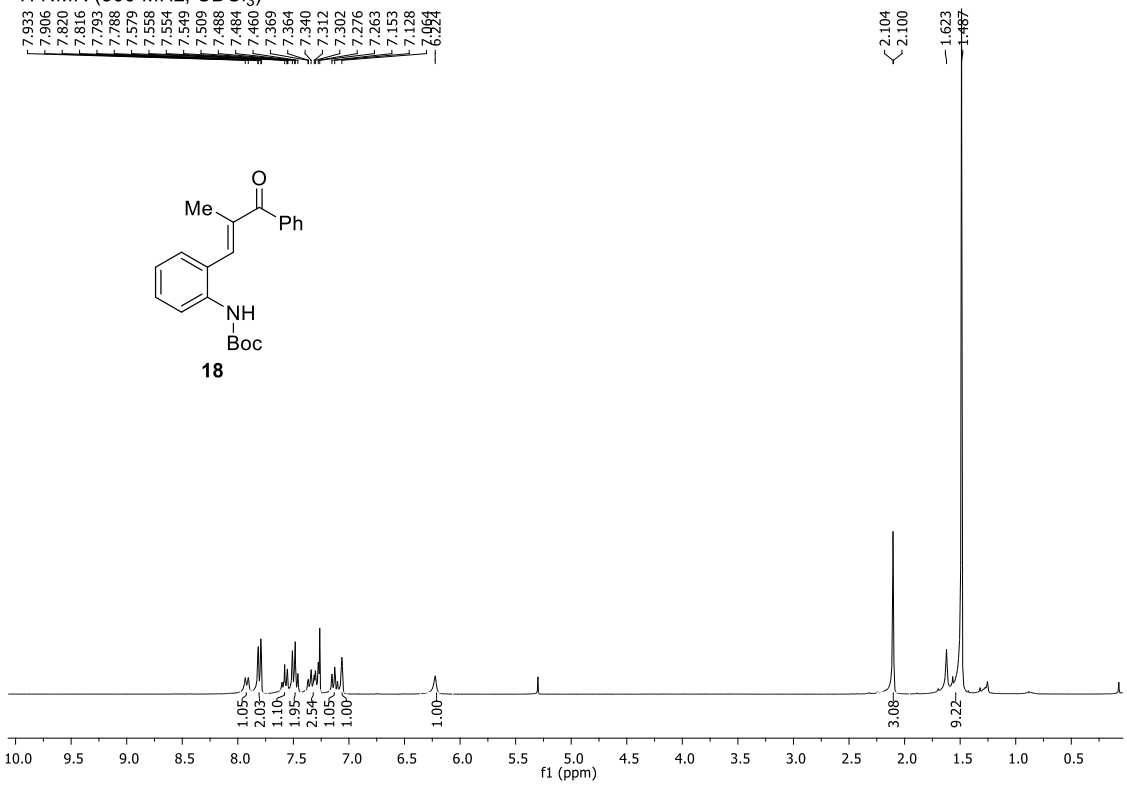
11k

^{13}C NMR (75 MHz, $CDCl_3$)



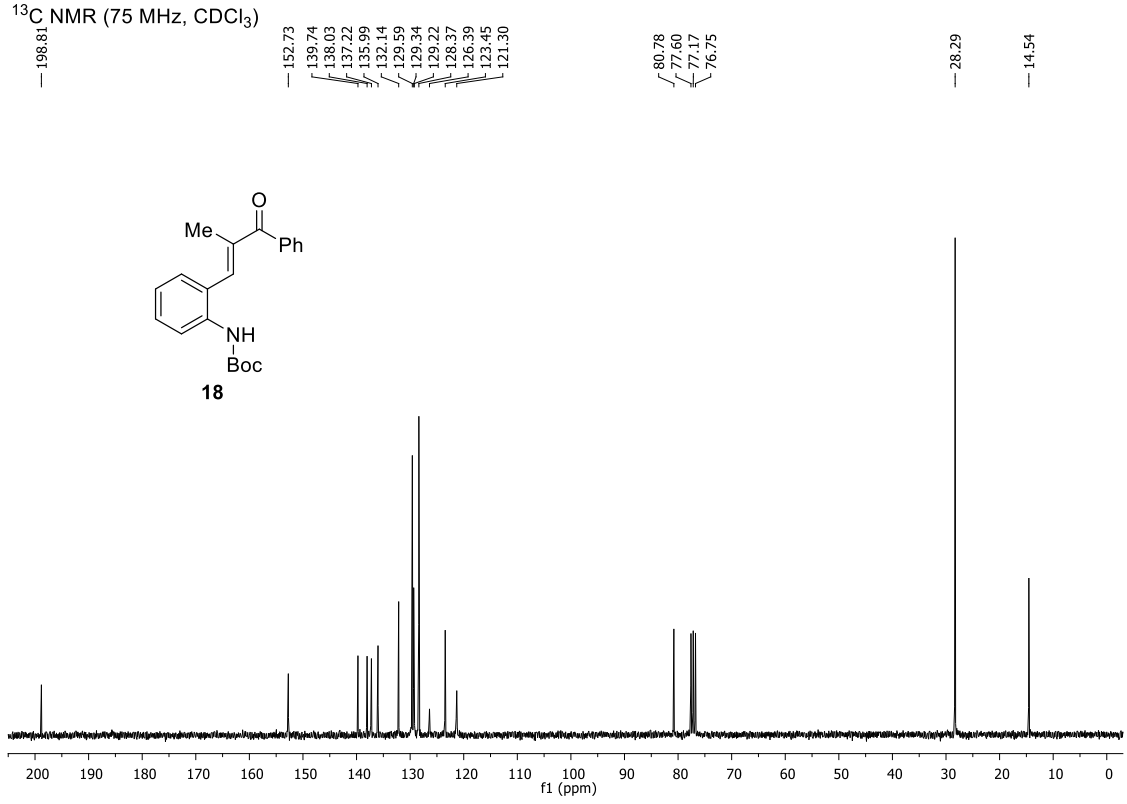
11k

^{1}H NMR (300 MHz, $CDCl_3$)



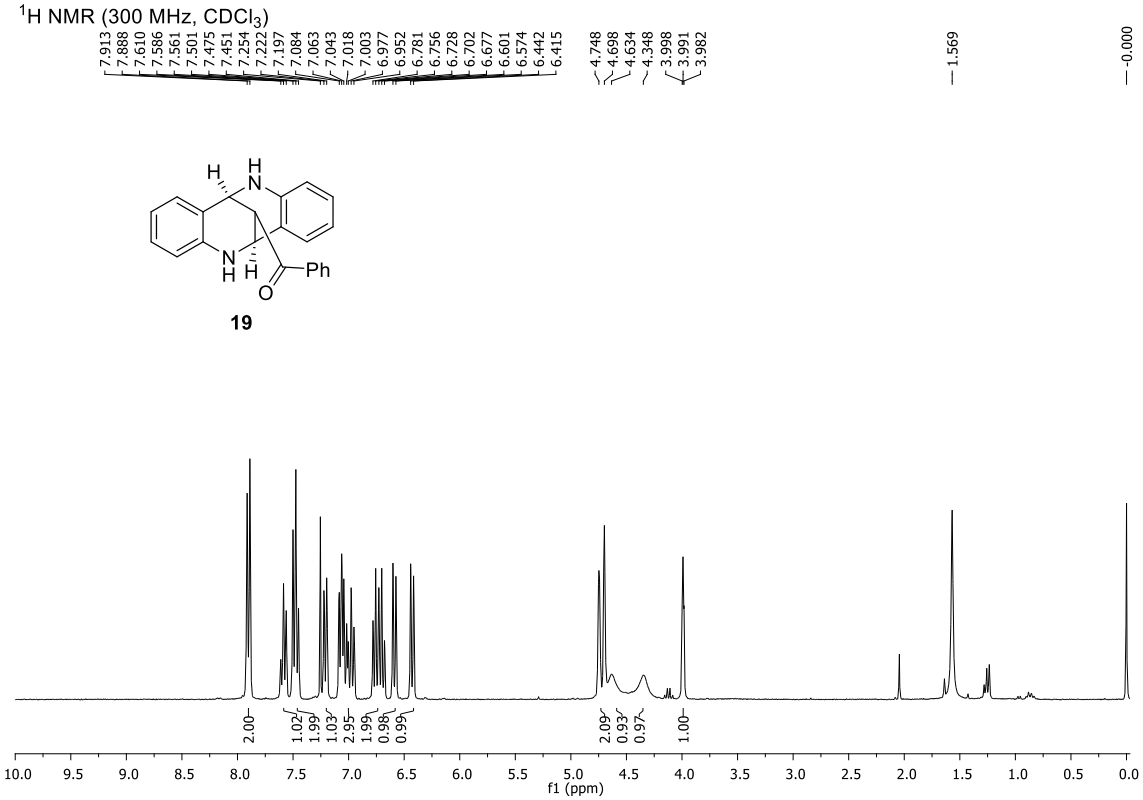
18

^{13}C NMR (75 MHz, $CDCl_3$)



18

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)