SUPPORTING INFORMATION

Diastereoselective Synthesis of Cycloheptannelated Indoles *via* Lewis-Acid-Catalyzed (4+3)-Cyclization of Donor–Acceptor Cyclopropanes

Bao Qiong Li,[†] Zong-Wang Qiu, [†] Ai-Jun Ma,[†] Jin-Bao, Peng,[†] Na Feng,[†] Ji-Yuan-Du,[‡] Han-Peng Pan,[†] Xiang-Zhi Zhang,*[,†] Xue-Tao Xu*[,†]

[†]School of Biotechnology and Health Sciences, Wuyi University, Jiangmen, Guangdong 529020, P. R. China

[‡]College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059, P. R. China

E-mail: wyuchemzxz126.com

Table of Contents

General

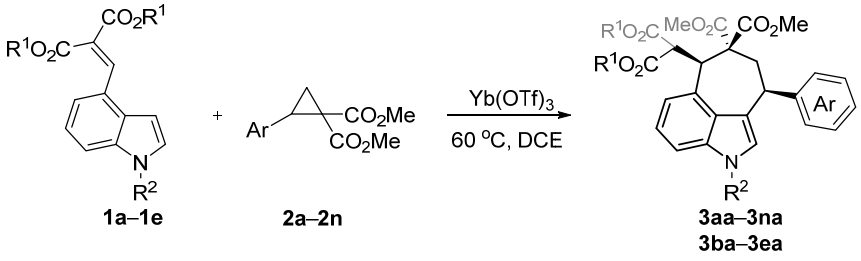
All moisture or oxygen-sensitive reactions were carried out under an argon atmosphere in oven or heat-dried flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: THF (Na), CH_2Cl_2 (CaH_2), toluene (Na), $CHCl_3$ (P_2O_5). All reactions were monitored by thin-layer chromatography (TLC) on silica gel F_{254} plates using UV light as visualizing agent (if applicable), and a solution of ammonium molybdate tetrahydrate (50 g/L) in EtOH followed by heating as developing agents. The products were purified by flash column chromatography on silica gel (200-300 meshes) from the Anhui Liangchen Silicon Material Company in China.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker AM 400 or 500 MHz instrument. Chemical shifts were denoted in ppm (δ) and calibrated by using residual undeuterated solvent ($CHCl_3$ (7.27 ppm) tetramethylsilane (0.00 ppm)) as internal reference for ^{1}H NMR and the deuterated solvent ($CDCl_3$ (77.00 ppm) as internal standard for ^{13}C NMR. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = double doublet, tq = triplet quartet, br = broad, m = multiplet. High-resolution mass spectral analysis (HRMS) data were measured on a Thermo Scientific™ Q Exactive™ UHMR (Ultra-High Mass Range) Hybrid Quadrupole-Orbitrap™ mass spectrometer. The IR spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer. The X-ray single-crystal determination was performed on an Agilent SuperNova single crystal X-ray diffractometer. The melting points were measured on a Kolfer melting point apparatus without calibration (Beijing Tech Instrument Co., LTD).

1. Preparation of Substrates

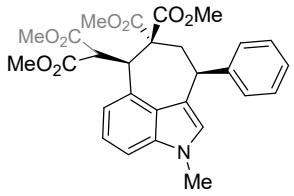
The indoles **1a**–**1e** were prepared according to the reported literature procedures.[1] The cyclopropanes **2a**–**2n** were prepared according to the reported literature procedures. [2]

2. General Procedure for the Synthesis of Products 3aa–3an and 3ba–3ea



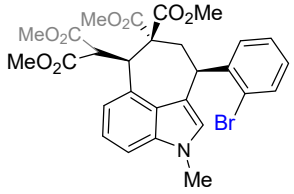
To a solution of indoles **1** (0.2 mmol) and D-A cyclopropanes **2** (0.24 mmol) in DCE (2.0 mL) was added $Yb(OTf)_3$ (0.02 mmol). The resulting mixture was stirred vigorously at 60 °C (oil bath) for the indicated time. The solvent was concentrated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate, giving the products **3**.

3. Spectroscopic Data for the Products 3aa–3an, 3ba–3ea, 4aa and 5aa



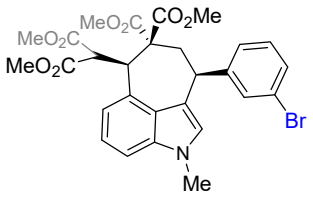
3aa
13:1 dr

3aa: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10: 1 – 3:1), giving the product **3aa**, (24 h, white foam, 96.3 mg, 95% yield, 13:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.37 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.20 (dd, *J* = 6.6, 1.6 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.24 (d, *J* = 1.4 Hz, 1H), 5.15 (dd, *J* = 4.6, 0.8 Hz, 1H), 4.14 (dd, *J* = 12.9, 3.3 Hz, 1H), 4.00 (d, *J* = 3.9 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.58 (s, 3H), 3.04 – 2.96 (m, 1H), 2.89 (s, 3H), 2.74 ppm (ddd, *J* = 14.6, 4.2, 1.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.9, 169.6, 169.5, 167.7, 146.8, 136.9, 130.8, 128.43, 128.40, 128.3, 126.5, 125.3, 121.4, 121.0, 117.3, 107.9, 60.6, 54.4, 53.0, 52.7, 52.4, 51.7, 47.9, 41.8, 37.0, 32.6 ppm. **IR**: $\bar{\upsilon}$ =2956, 1734, 1639, 1455, 1366, 1182, 1025, 703 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{30}NO_8$ 508.1966; found: 508.1969.



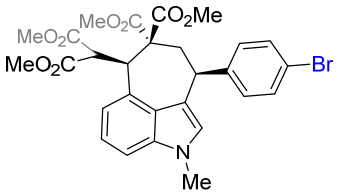
3ab
8.1:1 dr

3ab: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10: 1 – 3:1), giving the product the product **3ab** (60 h, white foam, 104.1 mg, 89% yield, 8.1:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ δ 7.70 – 7.50 (m, 2H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21 (dd, *J* = 6.5, 1.7 Hz, 1H), 7.13 (td, *J* = 7.8, 4.1 Hz, 3H), 6.22 (d, *J* = 1.5 Hz, 1H), 5.15 (d, *J* = 3.7 Hz, 1H), 4.84 – 4.70 (m, 1H), 3.98 (d, *J* = 4.5 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.69 (s, 3H), 3.58 (s, 3H), 2.95 – 2.85 (m, 4H), 2.73 ppm (ddd, *J* = 14.4, 4.2, 1.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.4, 167.7, 146.2, 137.0, 132.4, 130.8, 130.7, 128.1, 127.9, 127.8, 125.5, 124.0, 121.6, 121.1, 116.3, 108.0, 60.6, 54.5, 53.0, 52.7, 52.5, 51.7, 47.9, 40.0, 35.9, 32.7 ppm. **IR**: $\bar{\upsilon}$ = 3454, 2088, 1734, 1734, 1638, 1435, 1266, 1204, 742 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{29}BrNO_8$ 586.1071; found: 586.1086.



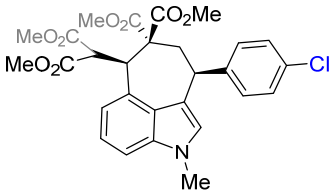
3ac
6.1:1 dr

3ac: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3ac** (24 h, white foam, 108.8 mg, 93% yield, 6.1:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (t, *J* = 1.6 Hz, 1H), 7.42 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.21 (dd, *J* = 6.3, 2.3 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.25 (d, *J* = 1.4 Hz, 1H), 5.16 (d, *J* = 3.6 Hz, 1H), 4.17 (dd, *J* = 12.6, 3.6 Hz, 1H), 3.99 (d, *J* = 4.1 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.63 (s, 3H), 3.59 (s, 3H), 3.01 – 2.91 (m, 1H), 2.90 (s, 3H), 2.72 ppm (ddd, *J* = 14.6, 4.4, 1.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 169.5, 167.7, 149.4, 137.0, 131.5, 130.7, 130.1, 129.7, 128.3, 127.2, 125.3, 122.4, 121.7, 121.2, 116.7, 108.0, 60.7, 54.4, 53.1, 52.7, 52.4, 51.7, 47.9, 41.5, 37.0, 32.7 ppm. **IR**: $\bar{\upsilon}$ = 3437, 2952, 2850, 1735, 1637, 1455, 1226, 745 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{29}BrNO_8$ 586.1071; found: 586.1084.



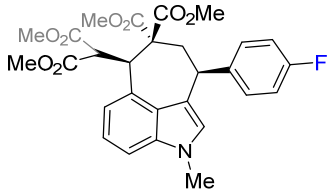
3ad
7.5:1 dr

3ad: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3ad** (15 h, white solid, 105.4 mg mg, 90% yield, 7.5:1 dr, mp 187–189 °C). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.20 (dd, *J* = 6.2, 1.7 Hz, 1H), 7.18 – 7.04 (m, 2H), 6.22 (s, 1H), 5.15 (d, *J* = 4.1 Hz, 1H), 4.16 (d, *J* = 9.5 Hz, 1H), 3.98 (d, *J* = 3.6 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.63 (s, 3H), 3.59 (s, 3H), 3.01 – 2.90 (m, 1H), 2.90 (d, *J* = 9.1 Hz, 3H), 2.71 ppm (dd, *J* = 14.6, 3.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 169.52, 169.47, 167.7, 146.0, 137.0, 131.6, 130.8, 130.3, 128.3, 125.4, 121.6, 121.2, 120.3, 116.9, 108.0, 60.7, 54.5, 53.1, 52.7, 52.4, 51.7, 47.9, 41.3, 37.0, 32.7 ppm. **IR**: $\bar{\upsilon}$ = 3442, 2922, 1735, 1605, 1485, 1455, 1226, 1198, 1011, 746 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{29}BrNO_8$ 586.1071; found: 586.1082.



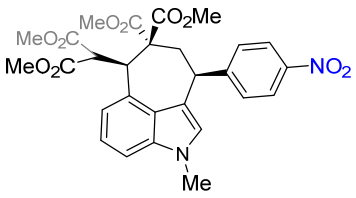
3ae
5.1:1 dr

3ae: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3ae** (15 h, white foam, 103.8 mg, 96% yield, 5.1:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 4H), 7.23 – 7.07 (m, 3H), 6.22 (d, J = 1.2 Hz, 1H), 5.15 (d, J = 3.9 Hz, 1H), 4.17 (dd, J = 12.6, 3.4 Hz, 1H), 3.98 (d, J = 4.0 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.63 (s, 3H), 3.59 (s, 3H), 3.07 – 2.90 (m, 1H), 2.89 (s, 3H), 2.75 – 2.64 ppm (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.6, 169.5, 167.7, 145.5, 137.0, 132.2, 130.8, 129.9, 128.6, 128.3, 125.4, 121.6, 121.2, 117.0, 108.0, 60.7, 54.5, 53.1, 52.7, 52.5, 51.8, 47.9, 41.2, 37.1, 32.7 ppm. **IR**: $\bar{\upsilon}$ = 3418, 2084, 1638 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{29}ClNO_8$ 542.1576; found: 542.1587.



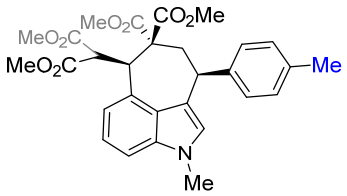
3af
6.8:1 dr

3af: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3af** (15 h, white foam, 95.5 mg, 91% yield, 6.8:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 2H), 7.20 (dd, J = 6.1, 2.3 Hz, 1H), 7.16 – 7.00 (m, 4H), 6.22 (d, J = 1.5 Hz, 1H), 5.15 (dd, J = 4.5, 0.9 Hz, 1H), 4.17 (dd, J = 12.6, 3.4 Hz, 1H), 3.99 (d, J = 4.2 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.63 (s, 3H), 3.58 (s, 3H), 2.96 (dd, J = 14.4, 13.1 Hz, 1H), 2.88 (s, 3H), 2.71 ppm (ddd, J = 14.6, 4.3, 1.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.5, 169.4, 167.7, 161.6 (d, $^1J_{F\text{-}C}$ = 244.3 Hz), 142.7, 142.6, 137.0, 130.7, 129.9, 129.80, 128.2, 125.3, 121.5, 121.1, 115.3, 115.1, 108.0, 60.7, 54.5, 53.0, 52.7, 52.4, 51.7, 47.9, 41.0, 37.3, 32.6 ppm. **IR**: $\bar{\upsilon}$ = 3444, 2953, 1735, 1637, 1434, 1222 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{29}FNO_8$ 526.1872; found: 526.1879.



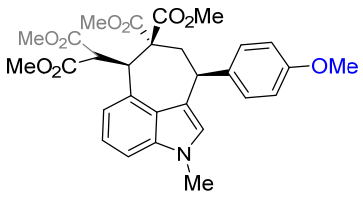
3ag
4.3:1 dr

3ag: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1 – 3:1), giving the product **3ag** (60 h, white foam, 72.8 mg, 66% yield, 4.3:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.34 – 7.10 (m, 3H), 6.19 (d, *J* = 1.1 Hz, 1H), 5.19 (d, *J* = 3.7 Hz, 1H), 4.39 (dd, *J* = 12.4, 3.8 Hz, 1H), 3.98 (d, *J* = 3.8 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.64 (s, 3H), 3.60 (s, 3H), 3.08 – 2.94 (m, 1H), 2.91 (s, 3H), 2.74 ppm (dd, *J* = 14.7, 3.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.6, 169.4, 169.3, 167.7, 154.6, 146.8, 136.9, 130.6, 129.4, 128.2, 125.3, 123.9, 121.8, 121.4, 116.0, 108.2, 60.6, 54.5, 53.2, 52.8, 52.5, 51.8, 47.9, 41.6, 36.7, 32.7 ppm. **IR**: $\bar{\upsilon}$ = 3443, 2954, 2089, 1638, 1251, 1436, 1227, 1077, 741 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{29}N_2O_{10}$ 553.1817; found: 553.1826.



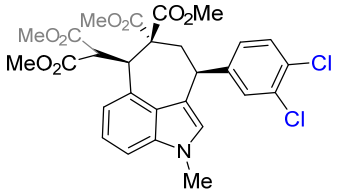
3ah
8.2:1 dr

3ah: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3ah** (11 h, white foam, 96.9 mg, 93% yield, 8.2:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.14 (m, 3H),, 7.12 – 7.08 (m, 2H), 6.25 (d, *J* = 1.4 Hz, 1H), 5.14 (d, *J* = 4.0 Hz, 1H), 4.18 – 4.07 (m, 1H), 4.00 (d, *J* = 4.3 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.63 (s, 3H), 3.57 (s, 3H), 3.04 – 2.92 (m, 1H), 2.88 (s, 3H), 2.72 (ddd, *J* = 14.7, 4.3, 1.3 Hz, 1H), 2.38 ppm (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.7, 169.5, 167.7, 143.9, 137.0, 136.0, 130.9, 129.1, 128.3, 128.2, 125.4, 121.4, 121.0, 117.5, 107.9, 60.7, 54.5, 53.0, 52.6, 52.3, 51.6, 47.9, 41.3, 37.2, 32.6, 21.0 ppm. **IR**: $\bar{\upsilon}$ = 3439, 2952, 1735, 1637, 1434, 1330, 1225, 743 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{32}NO_8$ 522.2122; found: 522.2126.



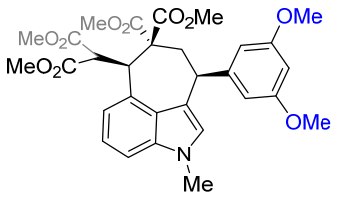
3ai
7.8:1 dr

3ai: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1 – 3:1), giving the product **3ai** (8 h, white foam, 91.6 mg, 87% yield, 7.8:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.19 (dd, *J* = 6.2, 2.2 Hz, 1H), 7.10 (dd, *J* = 7.2, 5.1 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.25 (d, *J* = 1.5 Hz, 1H), 5.17 – 5.10 (m, 1H), 4.16 – 4.04 (m, 1H), 4.00 (d, *J* = 4.2 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.69 (s, 3H), 3.64 (s, 3H), 3.58 (s, 3H), 3.01 – 2.90 (m, 1H), 2.88 (s, 3H), 2.71 ppm (ddd, *J* = 14.6, 4.2, 1.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.7, 169.5, 167.7, 158.3, 139.1, 137.0, 130.8, 129.3, 128.3, 125.4, 121.4, 121.0, 117.7, 113.8, 107.9, 60.7, 55.2, 54.5, 53.0, 52.7, 52.3, 51.7, 47.9, 40.9, 37.3, 32.6 ppm. **IR**: $\bar{\upsilon}$ = 3458, 2952, 1735, 1511, 1435, 1229 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{32}NO_9$ 538.2072; found: 538.2079.



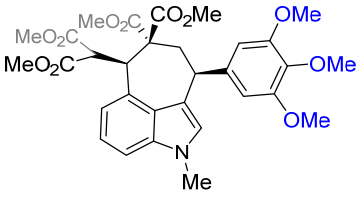
3aj
6.1:1 dr

3aj: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3aj** (24 h, white foam, 98.9 mg, 86% yield, 6.1:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.18 (m, 2H), 7.12 (dd, *J* = 6.9, 4.5 Hz, 2H), 6.25 (d, *J* = 1.3 Hz, 1H), 5.16 (d, *J* = 3.6 Hz, 1H), 4.29 – 4.14 (m, 1H), 3.97 (d, *J* = 3.9 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.63 (s, 3H), 3.60 (s, 3H), 3.01 – 2.90 (m, 1H), 2.90 (s, 3H), 2.80 – 2.64 ppm (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 169.4, 169.3, 167.6, 147.4, 137.0, 132.3, 130.6, 130.5, 130.4, 128.2, 128.0, 125.2, 121.7, 121.2, 116.3, 108.1, 60.6, 54.4, 53.1, 52.7, 52.5, 51.7, 47.8, 41.0, 36.9, 32.7 ppm. **IR**: $\bar{\upsilon}$ = 3458, 2953, 2088, 1734, 1641, 1463, 1227, 1029, 739 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{28}Cl_2NO_8$ 576.1186; found: 576.1204.



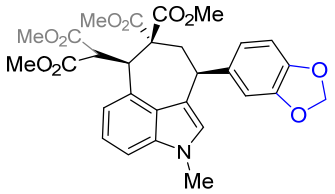
3ak
>20:1 dr

3ak: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1 – 3:1), giving the product (12 h, white foam, 97.6 mg, 86% yield, >20:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 5.4, 2.9 Hz, 1H), 7.14 – 7.05 (m, 2H), 6.60 (d, *J* = 2.2 Hz, 2H), 6.40 (t, *J* = 2.2 Hz, 1H), 6.35 (d, *J* = 1.3 Hz, 1H), 5.14 (d, *J* = 3.8 Hz, 1H), 4.20 – 4.08 (m, 1H), 4.01 (d, *J* = 3.9 Hz, 1H), 3.80 (s, 6H), 3.75 (s, 3H), 3.70 (s, 3H), 3.62 (s, 3H), 3.59 (s, 3H), 3.05 – 2.93 (m, 1H), 2.85 (s, 3H), 2.81 – 2.71 ppm (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 169.6, 169.5, 167.7, 160.7, 149.4, 136.9, 130.7, 128.3, 125.4, 121.5, 120.9, 116.8, 107.9, 106.7, 98.2, 60.7, 55.22, 55.20, 54.4, 53.0, 52.6, 52.3, 51.5, 47.9, 42.0, 36.9, 32.6 ppm. **IR**: $\bar{\upsilon}$ = 3439, 2956, 2922, 2089, 1732, 1638, 1457, 1431, 1203, 1154, 749 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{34}NO_{10}$ 568.2177; found: 568.2180.



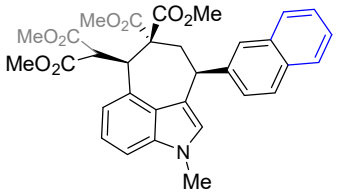
3al
13:1 dr

3al: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1 – 3:1), giving the product **3al** (24 h, white foam, 112.2 mg, 94% yield, 13:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 4.8, 3.5 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.68 (s, 2H), 6.35 (d, *J* = 1.1 Hz, 1H), 5.16 (d, *J* = 4.1 Hz, 1H), 4.26 – 4.15 (m, 1H), 4.04 (d, *J* = 3.1 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 6H), 3.76 (s, 3H), 3.72 (s, 3H), 3.62 (s, 3H), 3.62 (s, 3H), 3.05 – 2.93 (m, 1H), 2.85 (s, 3H), 2.76 ppm (dd, *J* = 14.6, 4.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.0, 169.7, 169.5, 167.8, 153.1, 142.9, 136.9, 136.5, 130.6, 128.5, 125.3, 121.5, 121.0, 117.1 108.0, 105.4, 60.9, 60.6, 56.1, 54.5, 53.1, 52.8, 52.5, 51.7, 47.9, 42.1, 37.1, 32.8 ppm. **IR**: $\bar{\upsilon}$ = 3450, 2953, 2064, 1733, 1952, 1459, 1227, 1127, 752 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{36}NO_{11}$ 598.2283; found: 598.2292.



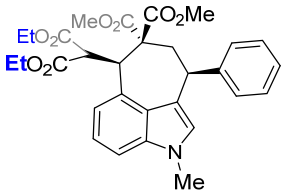
3am
8.8:1 dr

3am: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1 – 3:1), giving the product **3am** (8 h, white foam, 98.1 mg, 89% yield, 8.8:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.13 – 7.05 (m, 2H), 6.92 (d, *J* = 1.5 Hz, 1H), 6.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.31 (d, *J* = 1.4 Hz, 1H), 5.95 – 5.85 (m, 2H), 5.13 (d, *J* = 4.0 Hz, 1H), 4.11 (dd, *J* = 12.2, 3.7 Hz, 1H), 3.98 (d, *J* = 4.1 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.61 (s, 3H), 3.58 (s, 3H), 3.00 – 2.89 (m, 1H), 2.86 (s, 3H), 2.75 – 2.67 ppm (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 169.5, 169.4, 167.6, 147.6, 146.1, 140.8, 136.9, 130.7, 128.2, 125.2, 121.4, 121.2, 120.9, 108.7, 107.8, 100.7, 60.6, 54.4, 52.9, 52.5, 52.2, 51.5, 47.8, 41.4, 37.3, 32.5 ppm. **IR**: $\bar{\upsilon}$ = 3464, 1734, 1636, 1486, 1437, 1230, 1037, 738 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{30}NO_{10}$ 552.1864; found: 552.1869.



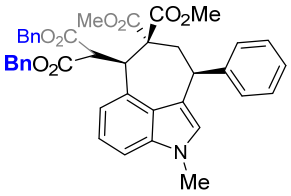
3an
6.3:1 dr

3an: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3an** (8 h, white foam, 110.3 mg, 99% yield, 6.3:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.76 (m, 4H), 7.58 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.54 – 7.40 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.12 (dd, *J* = 5.5, 4.2 Hz, 2H), 6.22 (d, *J* = 1.1 Hz, 1H), 5.19 (d, *J* = 4.3 Hz, 1H), 4.44 – 4.27 (m, 1H), 4.05 (d, *J* = 4.2 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.68 (s, 3H), 3.53 (s, 3H), 3.18 – 3.04 (m, 1H), 2.94 (s, 3H), 2.81 ppm (dd, *J* = 14.7, 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.7, 169.5, 167.7, 144.1, 137.0, 133.5, 132.5, 130.9, 128.5, 128.3, 127.7, 127.6, 126.9, 126.6, 126.0, 125.5, 121.5, 121.0, 117.2, 108.0, 60.8, 54.5, 53.0, 52.7, 52.4, 51.7, 48.0, 41.9, 36.9, 32.6 ppm. **IR**: $\bar{\upsilon}$ = 3477, 2953, 2094, 1734, 1634, 1456, 1434, 1227, 1079, 742 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{32}H_{32}NO_8$ 558.2122; found: 558.2130.



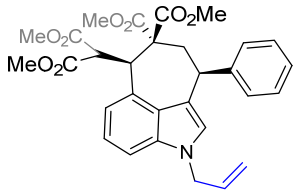
3ba
20:1 dr

3ba: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3ba** (36 h, white foam, 87.7 mg, 82% yield, 20:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.0 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.31 – 7.19 (m, 2H), 7.15 – 7.05 (m, 2H), 6.22 (d, J = 1.4 Hz, 1H), 5.18 (d, J = 3.7 Hz, 1H), 4.36 – 4.17 (m, 2H), 4.17 – 4.07 (m, 1H), 3.97 (d, J = 4.2 Hz, 1H), 3.68 (s, 3H), 3.64 (s, 3H), 3.56 (s, 3H), 3.47 – 3.29 (m, 1H), 3.25 – 3.12 (m, 1H), 3.07 – 2.92 (m, 1H), 2.82 – 2.62 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H), 0.62 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.7, 169.1, 167.5, 147.0, 137.0, 131.1, 128.5, 128.4, 128.1, 126.5, 125.7, 121.6, 121.0, 117.6, 107.8, 61.5, 61.0, 60.9, 54.8, 52.9, 52.3, 47.6, 41.9, 37.2, 32.6, 14.0, 13.0 ppm. **IR**: $\bar{\upsilon}$ = 3438, 2086, 1639, 1457, 702 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{34}NO_8$ 536.2279; found: 536.2286.



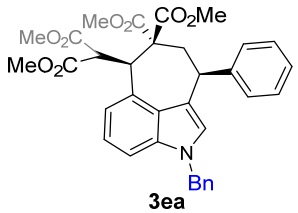
3ca
>20:1 dr

3ca: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3ca** (24 h, white foam, 110.1 mg, 76% yield, >20:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.03 (m, 17H), 6.76 (d, J = 7.2 Hz, 2H), 6.19 (s, 1H), 5.29 – 5.18 (m, 2H), 5.12 (d, J = 12.3 Hz, 1H), 4.40 (d, J = 12.2 Hz, 1H), 4.19 – 4.03 (m, 2H), 3.82 (d, J = 12.0 Hz, 1H), 3.63 (s, 3H), 3.55 (s, 3H), 3.50 (s, 3H), 3.01 – 2.84 (m, 1H), 2.68 ppm (dd, J = 14.3, 3.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 169.7, 168.9, 167.4, 146.7, 136.9, 135.3, 134.7, 131.0, 128.41, 128.38, 128.3, 128.22, 128.15, 128.1, 128.0, 126.4, 125.6, 121.7, 121.1, 117.5, 107.9, 67.4, 67.0, 60.7, 54.8, 52.8, 52.3, 47.7, 41.9, 37.4, 32.5 ppm. **IR**: $\bar{\upsilon}$ = 3442, 2958, 2087, 1730, 1637, 1455, 1227, 749, 699 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{40}H_{38}NO_8$ 660.2592; found: 660.2598.



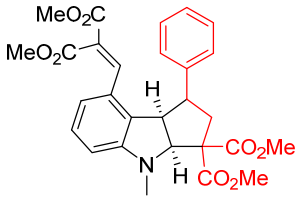
3da
9:1 dr

3da: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3da** (24 h, white foam, 102.3 mg, 96% yield, 9:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.33 (m, 4H), 7.27 (dd, *J* = 14.1, 6.9 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.10 (d, *J* = 3.7 Hz, 2H), 6.27 (s, 1H), 5.83 (ddt, *J* = 15.6, 10.5, 5.3 Hz, 1H), 5.15 (d, *J* = 4.2 Hz, 1H), 5.08 (d, *J* = 10.2 Hz, 1H), 4.94 (d, *J* = 16.1 Hz, 1H), 4.51 (d, *J* = 5.2 Hz, 2H), 4.15 (d, *J* = 9.7 Hz, 1H), 4.00 (d, *J* = 3.6 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.65 (s, 3H), 3.00 (t, *J* = 13.8 Hz, 1H), 2.86 (s, 3H), 2.74 ppm (dd, *J* = 14.7, 3.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.6, 169.5, 167.8, 146.8, 136.4, 133.4, 130.9, 128.5, 128.4, 127.2, 126.6, 125.7, 121.7, 121.1, 117.8, 116.8, 108.3, 60.8, 54.4, 53.0, 52.7, 52.3, 51.6, 48.6, 47.9, 41.9, 37.2 ppm. **IR**: $\bar{\upsilon}$ = 3439, 2087, 1640, 1434, 1223, 1196, 702 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{32}NO_8$ 534.2122; found: 534.2130.



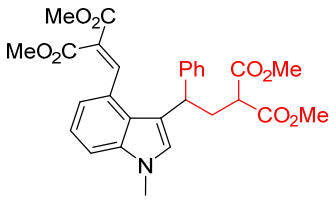
3ea
9:1 dr

3ea: Following the above *General Procedure*, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **3ea** (24 h, white foam, 107.2 mg, 92% yield, 9:1 *dr*). Spectroscopic data of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.15 (m, 6H), 7.05 (d, *J* = 4.4 Hz, 2H), 6.96 (d, *J* = 6.3 Hz, 2H), 6.36 (d, *J* = 1.1 Hz, 1H), 5.16 (d, *J* = 4.1 Hz, 1H), 5.10 (d, *J* = 2.4 Hz, 2H), 4.17 (d, *J* = 9.9 Hz, 1H), 4.01 (d, *J* = 3.7 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.01 (t, *J* = 13.8 Hz, 1H), 2.81 – 2.70 ppm (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 169.6, 169.5, 167.8, 146.8, 137.6, 136.6, 131.0, 128.5, 128.4, 127.8, 127.4, 126.6, 126.4, 125.9, 121.8, 121.3, 118.1, 108.5, 60.8, 54.5, 53.0, 52.7, 52.4, 51.6, 49.9, 47.9, 41.9, 37.3 ppm. **IR**: $\bar{\upsilon}$ = 3438, 2088, 1639, 1433, 1124, 701 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{34}H_{34}NO_8$ 584.2279; found: 584.2294.



4aa
5:1 dr

4aa: Following the above *General Procedure*, $AgSbF_6$ was the catalyst in this case, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the product **4aa** (48 h, white foam, 17.2 mg, 34% yield, 5:1 dr). Spectroscopic data of mixed isomers: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 5H, major + minor), 7.22 – 7.14 (m, 1H), 7.12 – 6.96 (m, 3H, major + minor), 6.83 (s, 1H), 6.79 – 6.71 (m, 1H), 6.57 – 6.39 (m, 3H, major + minor), 4.95 (d, J = 10.3 Hz, 1H, major), 4.68 (d, J = 7.9 Hz, 1H, minor), 4.41 (dd, J = 9.8, 8.1 Hz, 1H, minor), 4.01 (t, J = 10.1 Hz, 1H, major), 3.85 (s, 1H, minor), 3.84 (s, 1H, minor), 3.78 (s, 3H, major), 3.77 (s, 1H, minor), 3.73 (s, 3H, major), 3.72 (s, 3H, major), 3.70 (s, 1H, minor), 3.59 (s, 3H, major), 3.58 – 3.50 (m, 1H, major), 3.39 (ddd, J = 18.5, 10.1, 6.0 Hz, 1H, minor), 2.87 (s, 3H, major), 2.77 (dd, J = 13.3, 6.0 Hz, 1H, major), 2.72 (d, J = 4.4 Hz, 1H, minor), 2.40 (dd, J = 13.0, 5.9 Hz, 1H, minor), 2.12 ppm (t, J = 12.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0 (major), 171.5 (minor), 167.0 (major), 169.2 (minor), 167.0 (minor), 166.8 (major), 164.2 (minor), 163.9 (major), 155.3 (minor), 153.1 (major), 141.03 (major), 140.98 (major), 139.9 (minor), 138.2 (minor), 131.7 (major), 130.4 (minor), 129.9 (minor), 129.6 (major), 129.3 (minor), 128.69 (major), 128.65 (minor), 128.5 (major), 128.1 (major), 127.8 (major), 127.1 (minor), 126.7 (major), 125.1 (major), 123.7 (minor), 117.2 (major), 116.7 (minor), 110.2 (minor), 101.0 (major), 77.8 (minor), 77.6 (major), 65.9 (major), 64.4 (minor), 54.3 (major), 53.7 (major), 52.9 (minor), 52.8 (major), 52.4 (minor), 52.33 (major), 52.26 (major), 52.2 (minor), 52.1 (minor), 52.0 (major), 49.6 (major), 48.1 (minor), 44.5 (minor), 38.5 (minor), 38.4 (minor), 37.6 ppm (major). **IR**: $\bar{\upsilon}$ = 2951, 1732, 1631, 1442, 1247, 1075, 1005, 828, 701 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{29}NO_8Na$ 530.1785; found: 530.1776.

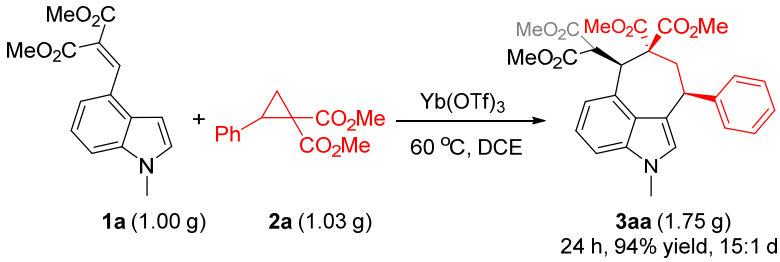


5aa

5aa: Following the above *General Procedure*, EtOAc was the solvent in this case, the reaction residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1 – 3:1), giving the product **5aa** (24 h, white foam, 29.9 mg, 59% yield) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.35 – 7.21 (m, 6H), 7.21 – 7.13 (m, 2H), 7.10 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 7.3 Hz, 1H), 4.35 (t, J = 7.7 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 3.51 (t, J = 7.3 Hz, 1H), 2.71 – 2.47 ppm (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 169.5, 166.8, 164.2, 143.9, 143.8, 137.4, 128.3, 128.1,

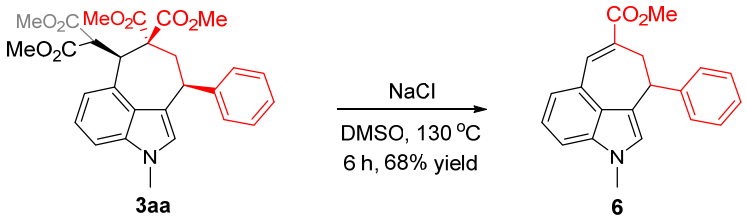
127.8, 126.7, 126.5, 126.4, 125.3, 121.4, 119.5, 116.8, 111.20, 52.4, 52.3, 52.2, 52.1, 50.1, 41.3, 36.8, 32.9 ppm. **IR**: $\bar{\upsilon}$ = 2938, 1730, 1437, 1221, 1069, 751 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{29}NO_8Na$ 530.1785; found: 530.1780.

4. General Procedure for the Gram-Scale reaction



To a solution of **1a** (1.00 g, 3.66 mmol) and **2a** (1.03 g, 4.39 mmol) in DCE (37.0 mL) was added $Yb(OTf)_3$ (226 mg, 3.66 mmol). The resulting mixture was stirred vigorously at 60 °C (oil bath) for 24 h, then the reaction mixture was quenched by H_2O, the resulting residue was extracted with DCM, the combined organic phases were washed with brine, then dried over Na_2SO_4, filtered and concentrated and the resulting residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1 – 3:1), giving the corresponding products **3aa** (1.75 g, 94% yield, 15:1 dr).

5. General Procedure for the Synthesis of 6

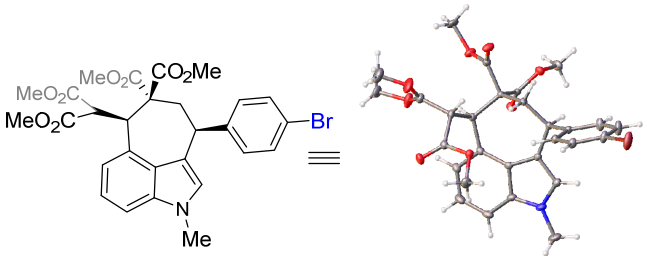


To a solution of **3aa** (50.7 mg, 0.1 mmol) in DMSO (1.0 mL) and H_2O (0.1 mL) was added NaCl (35.1mg, 0.60 mmol). The resulting mixture was stirred vigorously at 130 °C (oil bath) for 6 h, then the solution was diluted with saturated aqueous $NaHCO_3$ (2 mL) and extracted with EtOAc. Then the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (5:1) to give **6** in 68 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, J = 0.7 Hz, 1H), 7.39 – 7.14 (m, 8 H), 6.40 (s, 1H), 4.25 (d, J = 9.2 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.35 (dd, J = 14.6, 1.5 Hz, 1H), 3.09 ppm (dd, J = 14.5, 9.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 145.3, 140.4, 137.3, 129.8, 128.5, 128.3, 128.0, 127.1, 126.3, 126.1, 124.0, 121.6, 120.9, 110.6, 52.1, 43.0, 35.5, 32.7. **IR**: $\bar{\upsilon}$ = 2922, 1696, 1627, 14563, 1273, 1217, 746 cm^{-1}. **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{19}NO_2Na$ 340.1308; found: 340.1303.

6. Relative Configuration Assignment of 3ad by X-Ray Crystallographic Analysis

The single crystal of **3ad** which was used for the determination of its relative configurations via X-ray crystallography (see below), was recrystallized from ethyl acetate and petroleum ether. The intensity data were collected using graphite-monochromated Mo Kα radiation.

Crystal Structure of 3ad



3ad X-ray of **3ad**

(Displacement ellipsoids are drawn at the 20% probability level)

X-Ray Crystallographic Data of 3aa

CCDC number	1973911
Empirical formula	$C_{28}H_{28}BrNO_8$
Formula weight	586.42
Temperature/K	294.34(10)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	18.6120(12)
b/Å	14.5673(4)
c/Å	21.9115(7)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	5940.8(5)
Z	8
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	1.430
F(000)	2416.0
Crystal size/mm^3	0.35 × 0.31 × 0.28
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	6.72 to 52.04
Index ranges	-24 ≤ h ≤ 17, -11 ≤ k ≤ 19, -29 ≤ l ≤ 14
Reflections collected	18653

Independent reflections	5836 [R_{int} = 0.0621, R_{sigma} = 0.1008]
Data/restraints/parameters	5836/24/358
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0760, wR_2 = 0.2019
Final R indexes [all data]	R_1 = 0.1565, wR_2 = 0.2434
Largest diff. peak/hole / e $Å^{-3}$	0.63/-0.94

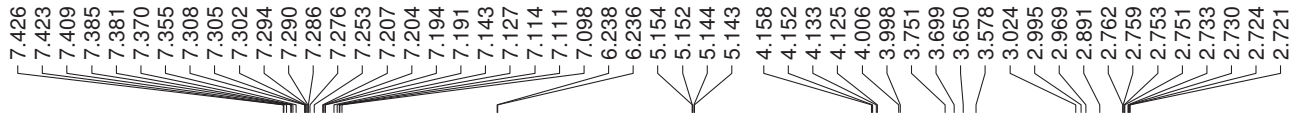
7. References

(1) Romanini, S.; Galletti, E.; Caruana, L.; Mazzanti, A.; Himo, F.; Santoro, S.; Fochi, M.; Bernardi, L. *Chem. - Eur. J.* **2015**, *21*, 17578.

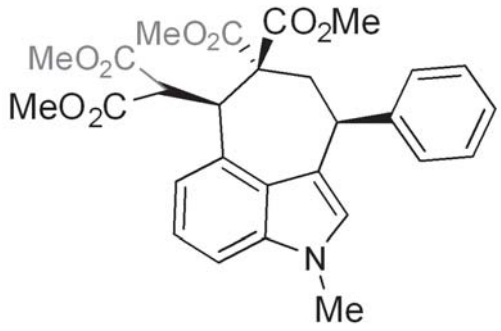
(2) Novikov, R. A.; Tarasova, A. V.; Korolev, V. A.; Timofeev, V. P.; Tomilov, Y. V. *Angew. Chem. Int. Ed.* **2014**, 53**,** 3187.

8. Copies of NMR Spectra

(Please see the next page!)



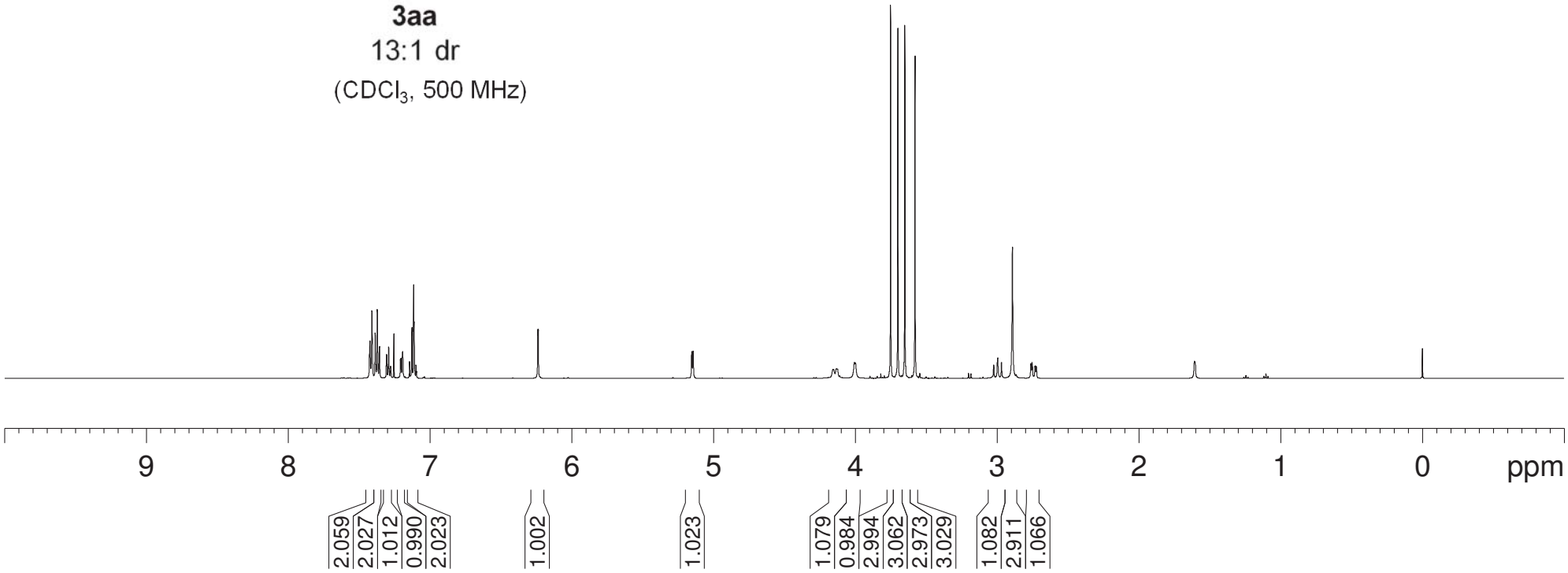
NAME zxz_150_H_20200104
EXPNO 10
PROCNO 1
Date_ 20200104
Time 13.13 h
INSTRUM Avance NEO 500
PROBHD Z119470_0332 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2768500 sec
RG 60
DW 50.000 usec
DE 10.79 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1
SFO1 500.1530884 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
SI 65536
SF 500.1500154 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



3aa

13:1 dr

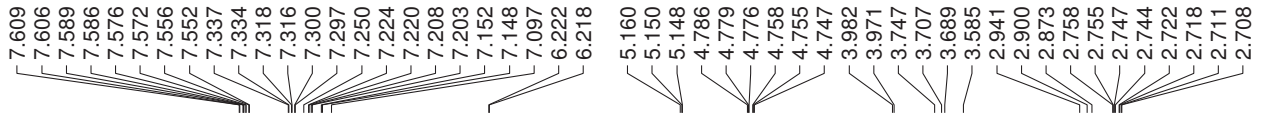
($CDCl_3$, 500 MHz)

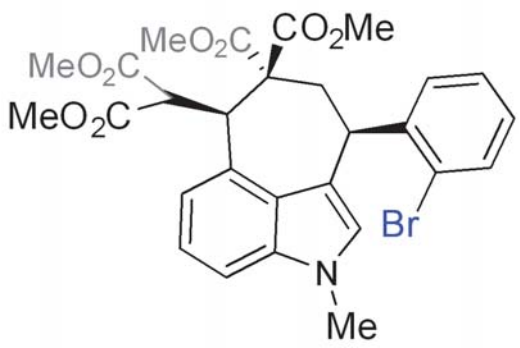


3aa

13:1 dr

($CDCl_3$, 126 MHz)



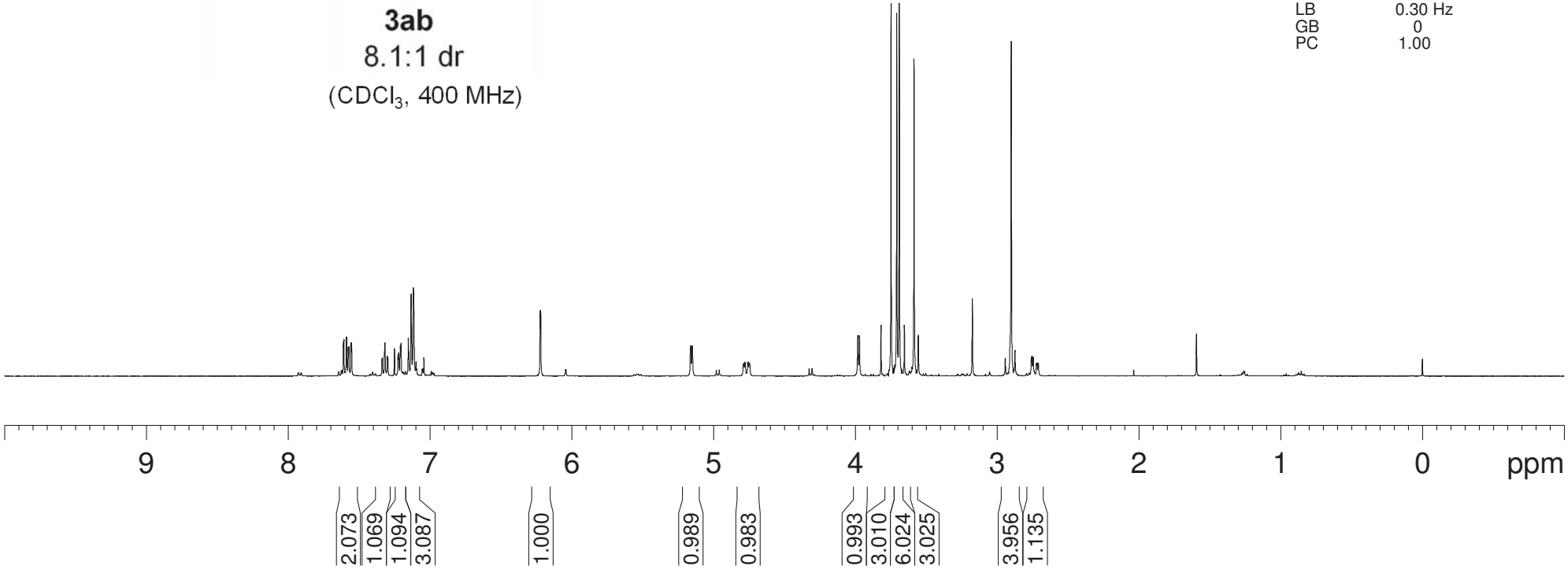


3ab

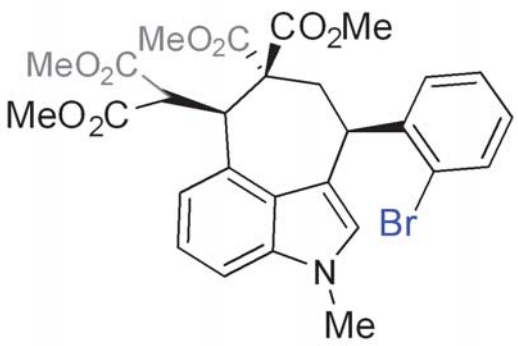
8.1:1 dr

($CDCl_3$, 400 MHz)

```
NAME      zxz-20180505-9-chun
EXPNO             10
PROCNO             1
Date_          20180520
Time             17.15
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 2
DS                 2
SWH           8012.820 Hz
FIDRES         0.122266 Hz
AQ           4.0894966 sec
RG               114
DW             62.400 usec
DE              6.50 usec
TE              298.8 K
D1          1.00000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1       400.1324710 MHz
NUC1              1H
P1              10.92 usec
SI              65536
SF         400.1300134 MHz
WDW               EM
SSB                0
LB              0.30 Hz
GB                 0
PC              1.00
```

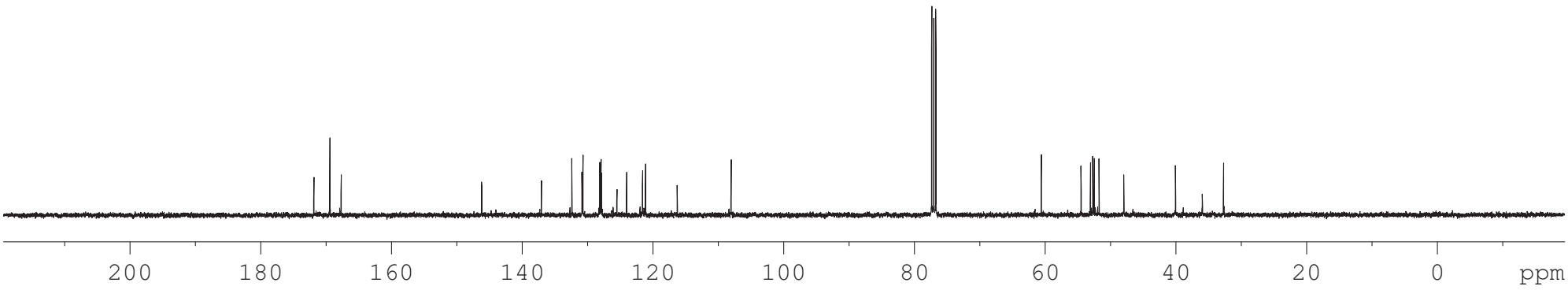


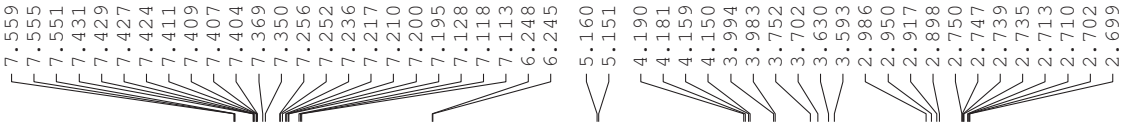
171.854
169.391
167.685
146.173
137.017
132.375
130.828
130.689
128.104
127.922
127.847
125.483
124.002
121.567
121.103
116.257
108.005
77.317
76.999
76.682
60.554
54.463
53.029
52.672
52.453
51.717
47.927
40.020
35.917
32.673

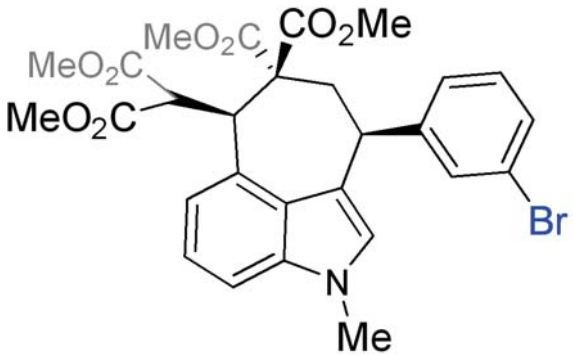


3ab
8.1:1 dr
($CDCl_3$, 101 MHz)

```
NAME        zxz-20180505-9-chun
EXPNO                    11
PROCNO                    1
Date_               20180520
Time                   17.21
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        100
DS                          2
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                       2050
DW                     20.800 usec
DE                      6.50 usec
TE                     299.5 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             100.6228298 MHz
NUC1                     13C
P1                     14.70 usec
SI                      32768
SF               100.6127755 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```





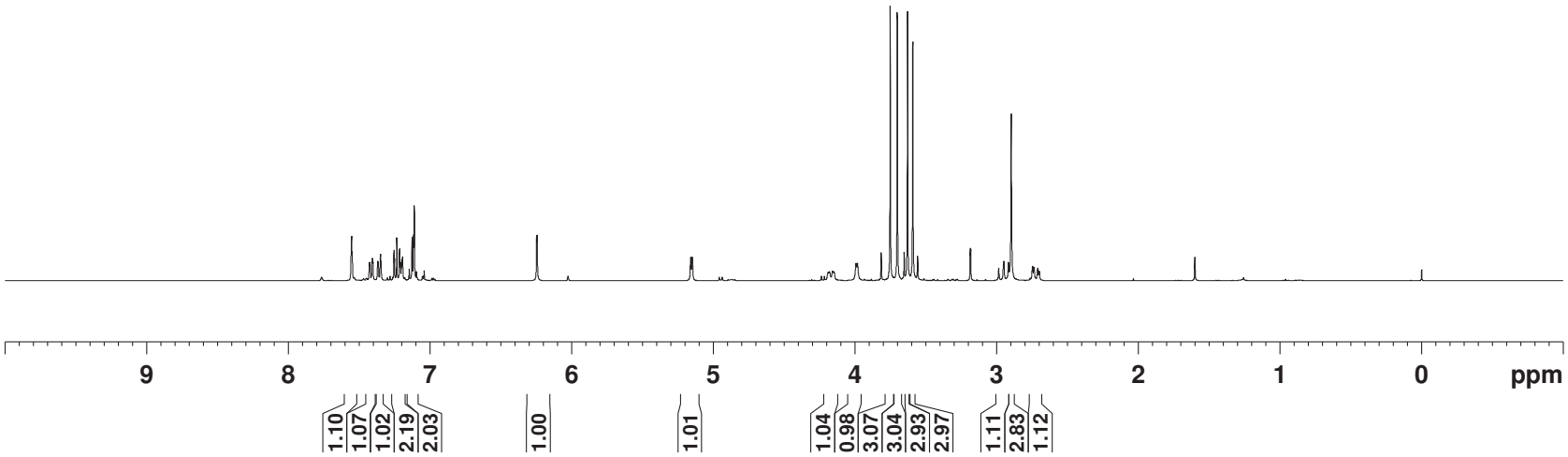


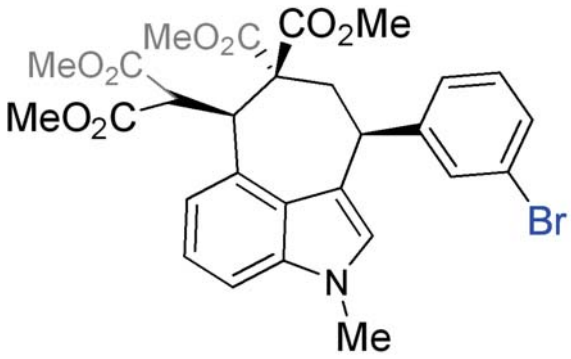
3ac

6.1:1 dr

($CDCl_3$, 400 MHz)

```
NAME      zxz-20180505-8-chun
EXPNO                  10
PROCNO                  1
Date_           20180520
Time                17.04
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      2
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894966 sec
RG                    101
DW                 62.400 usec
DE                  6.50 usec
TE                 298.7 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                  65536
SF           400.1300126 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



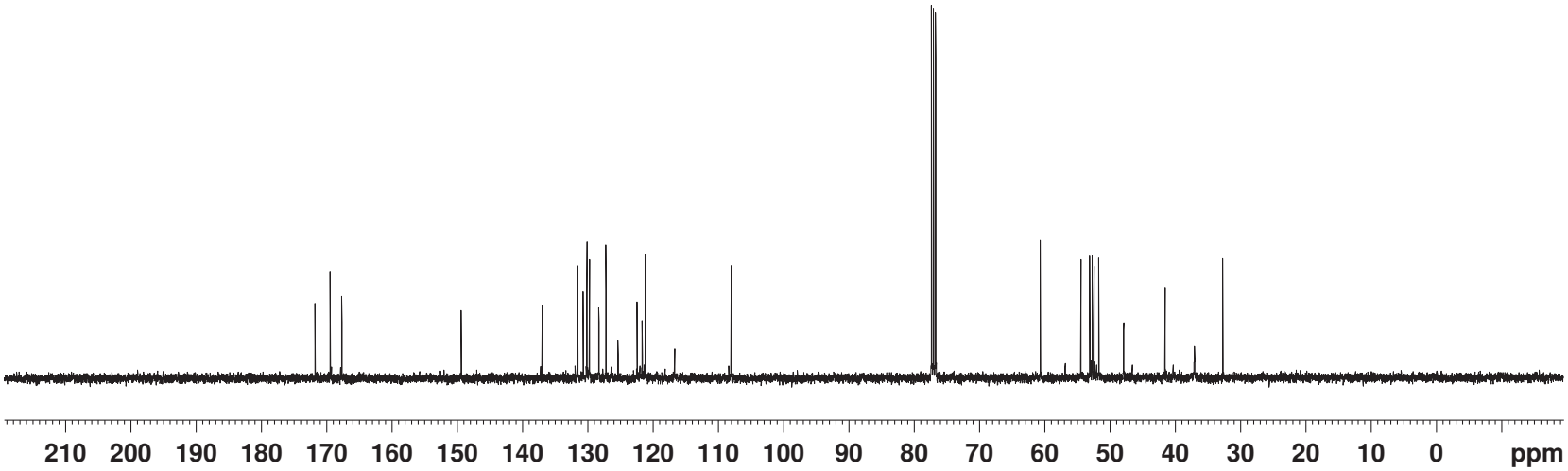


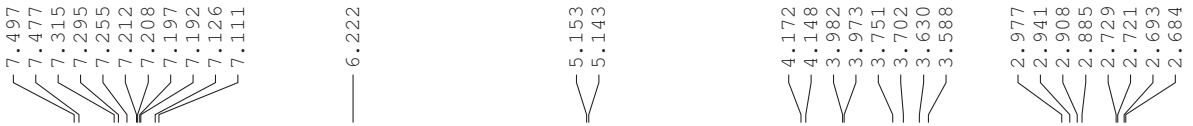
3ac

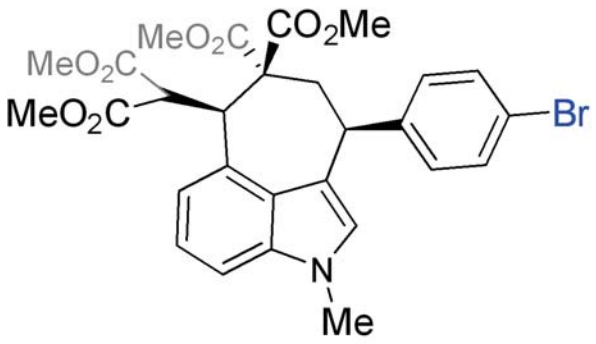
6.1:1 dr

($CDCl_3$, 101 MHz)

```
NAME        zxz-20180505-8-chun
EXPNO                        12
PROCNO                        1
Date_                  20180520
Time                      17.10
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         100
DS                           2
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         2050
DW                       20.800 usec
DE                        6.50 usec
TE                       299.5 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228298 MHz
NUC1                       13C
P1                       14.70 usec
SI                         32768
SF                 100.6127758 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```





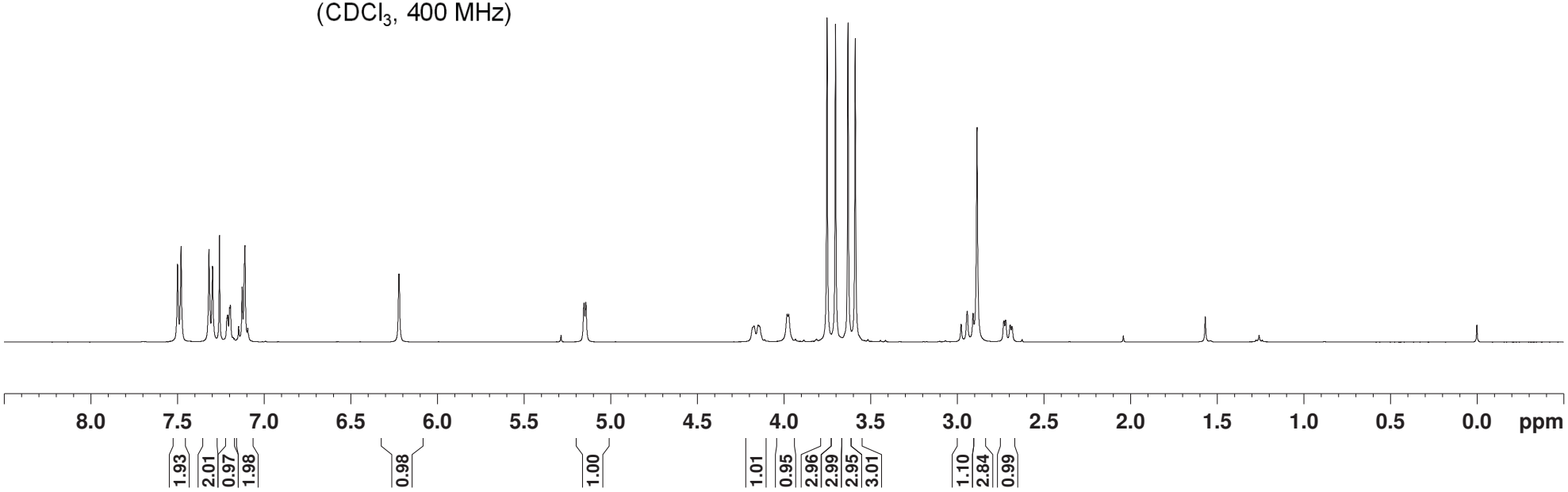


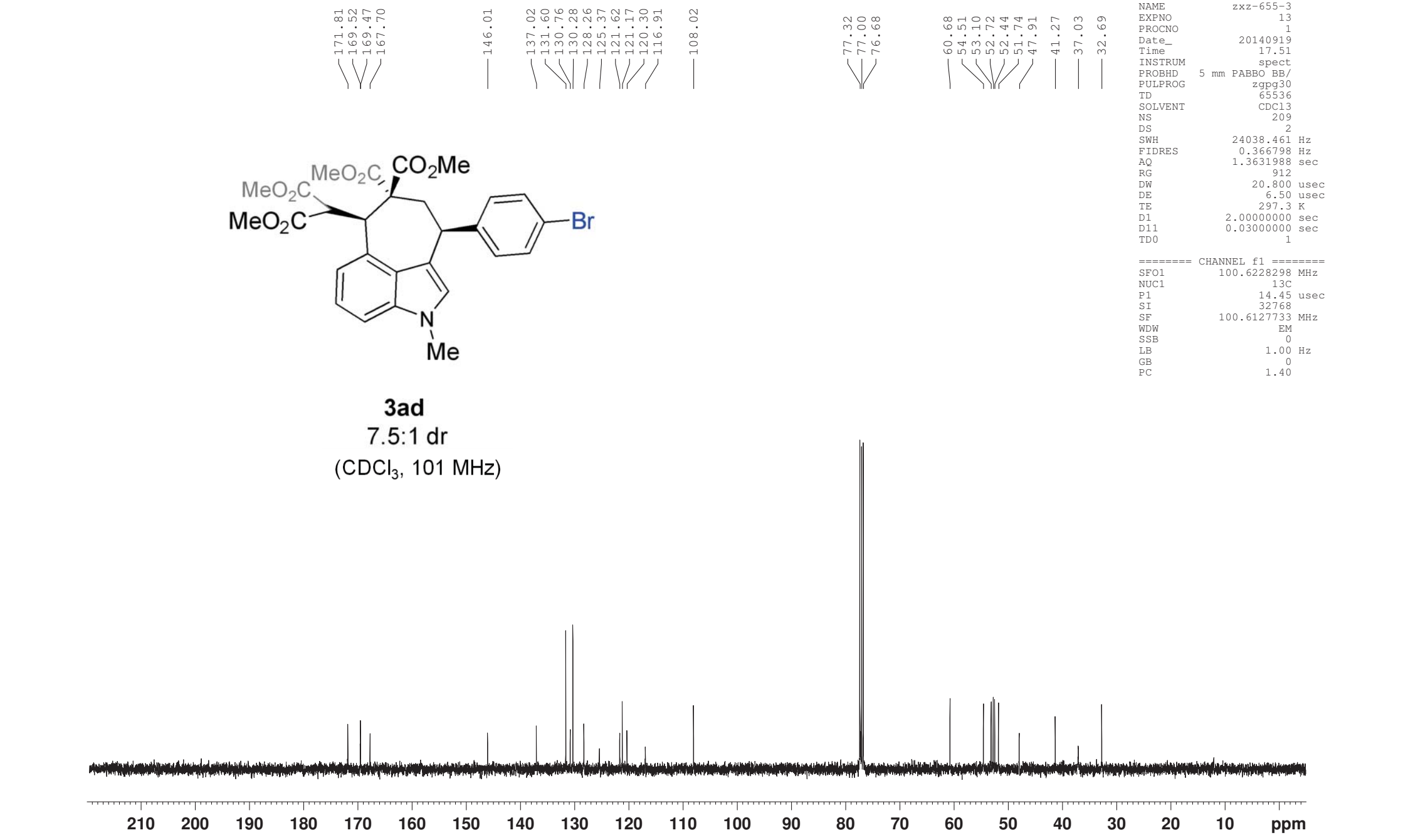
3ad

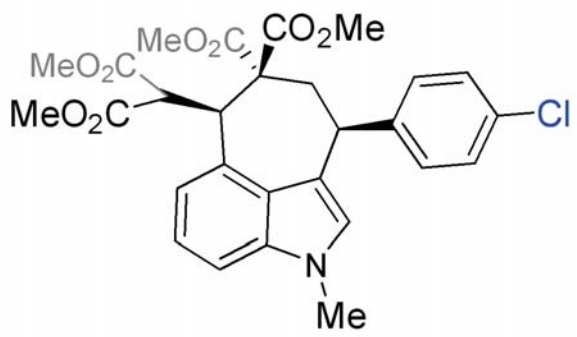
7.5:1 dr

($CDCl_3$, 400 MHz)

```
NAME            zxz-655-3
EXPNO                  12
PROCNO                  1
Date_            20140919
Time                17.46
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      4
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894966 sec
RG                    144
DW                 62.400 usec
DE                  6.50 usec
TE                 296.6 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 11.60 usec
SI                  65536
SF           400.1300115 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




171.81
169.52
169.47
167.70
146.01
137.02
131.60
130.76
130.28
128.26
125.37
121.62
121.17
120.30
116.91
108.02
77.32
77.00
76.68
60.68
54.51
53.10
52.72
52.44
51.74
47.91
41.27
37.03
32.69
NAME zxz-655-3
EXPNO 13
PROCNO 1
Date_ 20140919
Time 17.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 209
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 912
DW 20.800 usec
DE 6.50 usec
TE 297.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127733 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MeO2C
MeO2C
MeO2C
CO2Me
Br
N
Me
3ad
7.5:1 dr
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

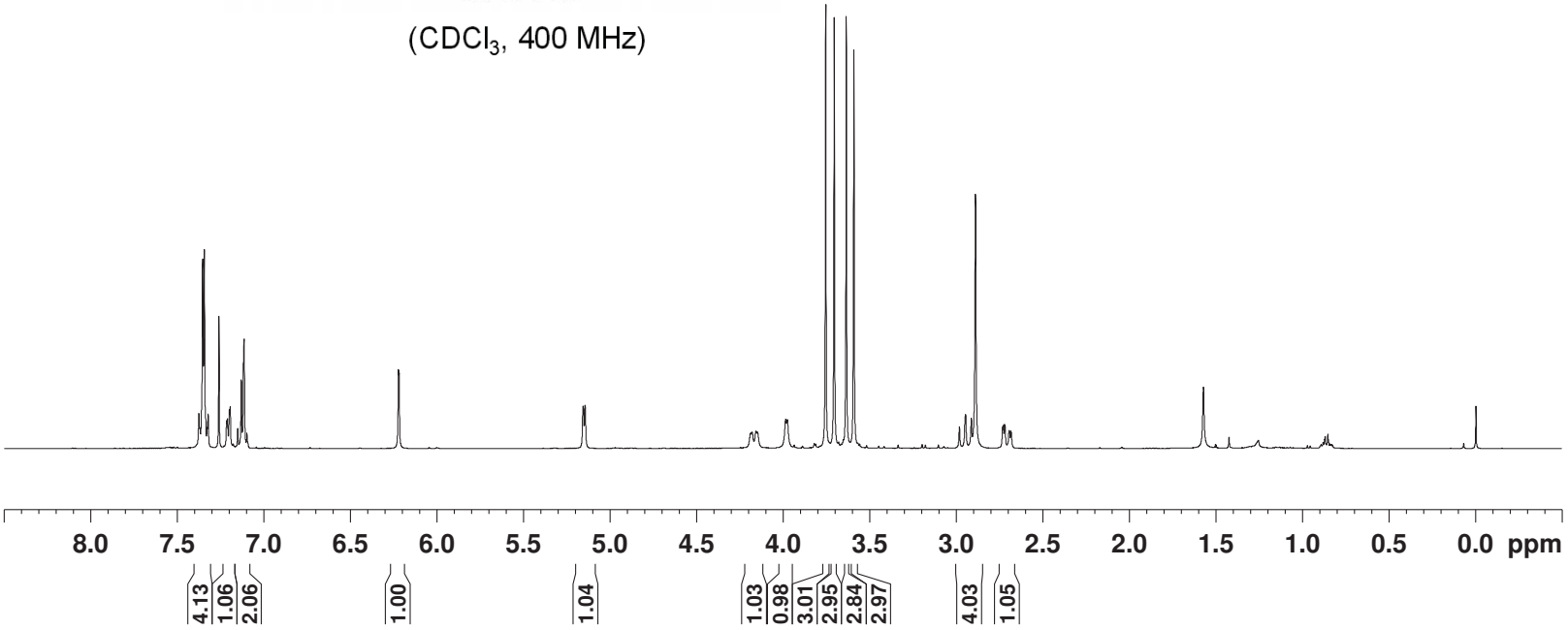


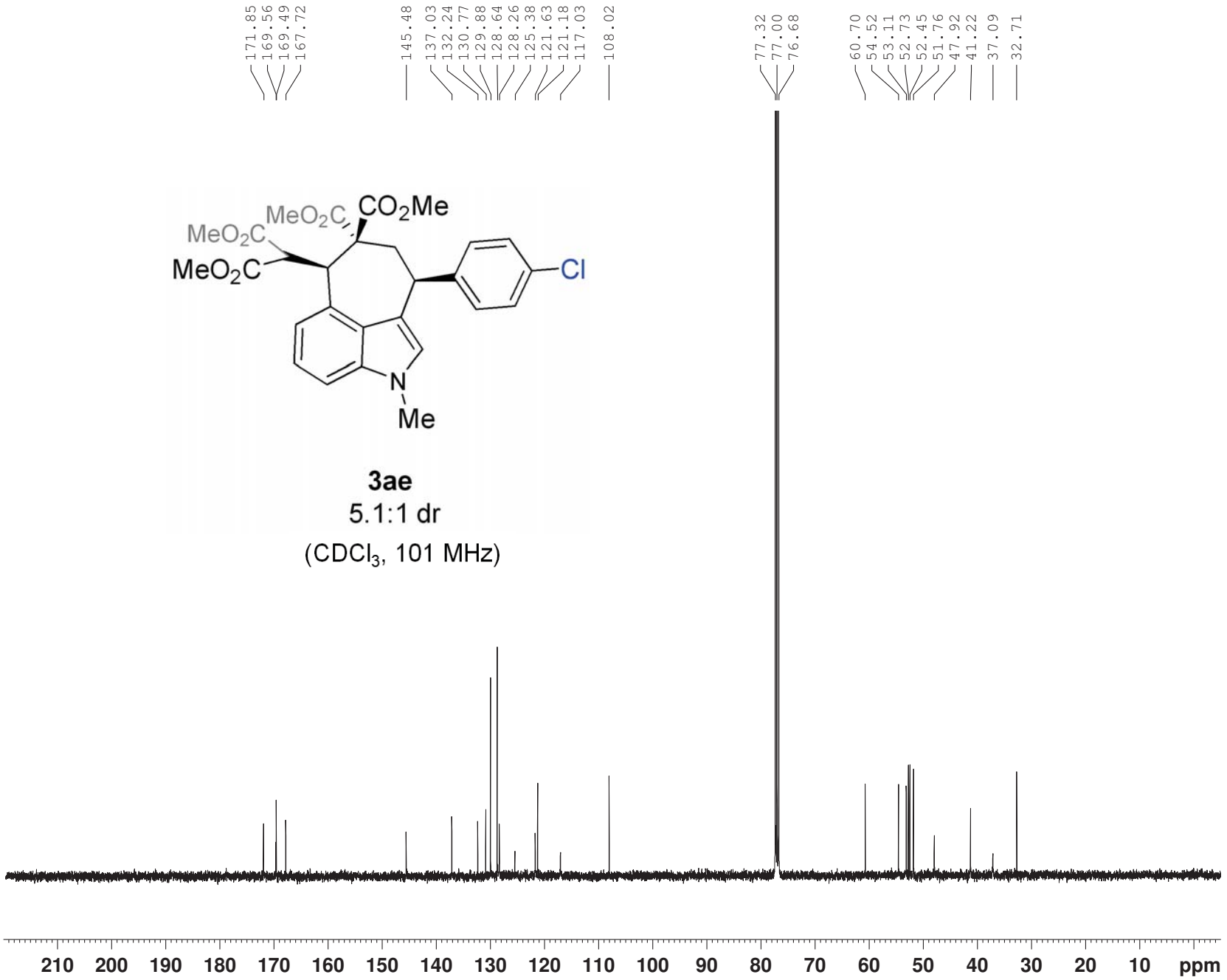
3ae

5.1:1 dr

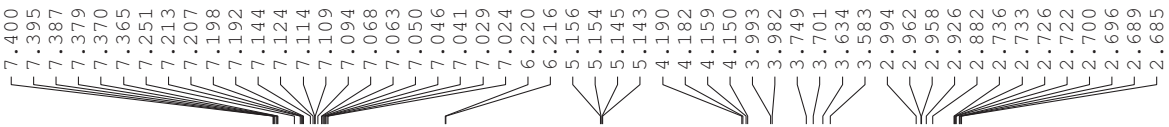
($CDCl_3$, 400 MHz)

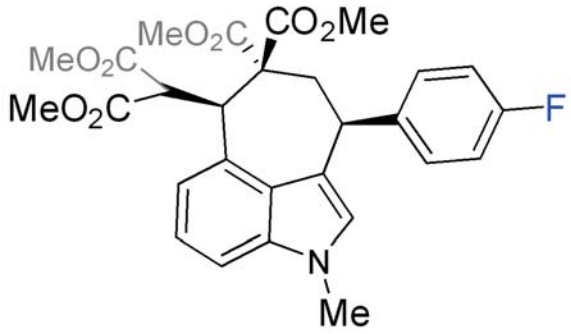
```
NAME      zxz-655-2-20140929
EXPNO               10
PROCNO               1
Date_         20140929
Time             12.23
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES           0.122266 Hz
AQ            4.0894966 sec
RG                 203
DW               62.400 usec
DE                6.50 usec
TE               295.1 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                1H
P1                11.60 usec
SI                65536
SF          400.1300104 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```





NAME	zxz-655-2-20140929
EXPNO	11
PROCNO	1
Date_	20140929
Time	12.52
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	500
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	296.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.45 usec
SI	32768
SF	100.6127714 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



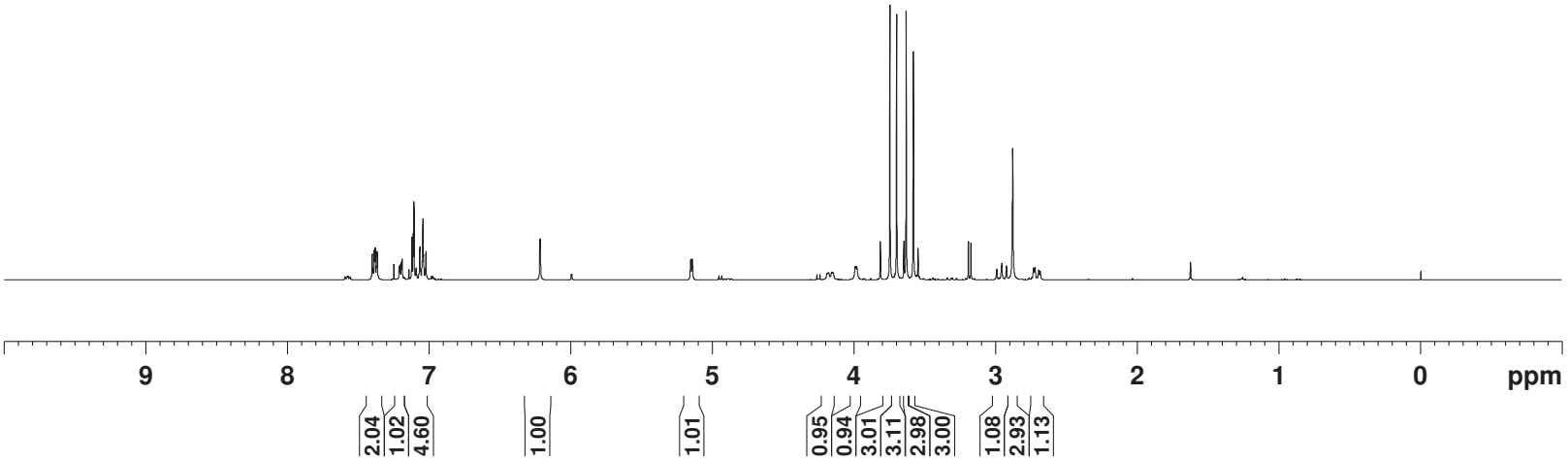


3af

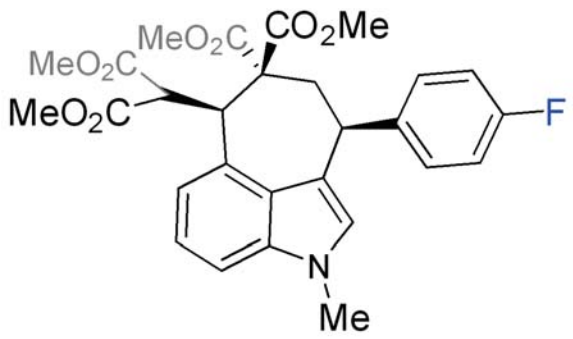
6.8:1 dr

($CDCl_3$, 400 MHz)

```
NAME      zxz-20180505-5-chun
EXPNO                  10
PROCNO                  1
Date_            20180521
Time                17.54
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       2
DS                       2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894966 sec
RG                    80.6
DW                 62.400 usec
DE                  6.50 usec
TE                 295.4 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                   65536
SF           400.1300130 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



171.85
169.54
169.44
167.68
162.80
160.37
142.67
142.64
137.00
130.74
129.88
129.80
128.23
125.32
121.53
121.07
117.30
115.28
115.07
107.96
77.32
77.00
76.68
60.65
54.46
53.04
52.67
52.37
51.69
47.85
41.02
37.25
32.63

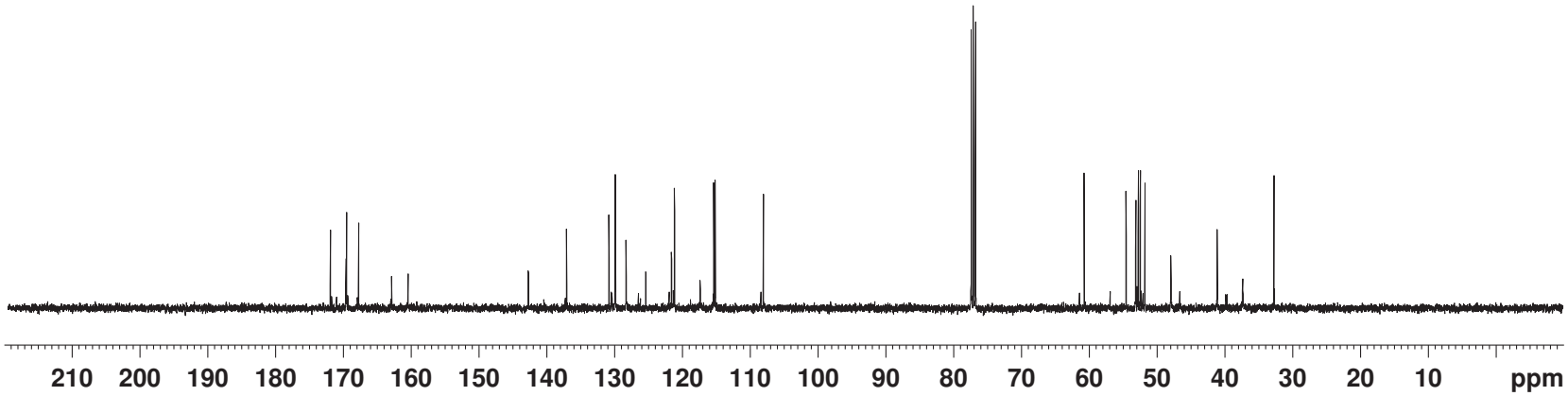


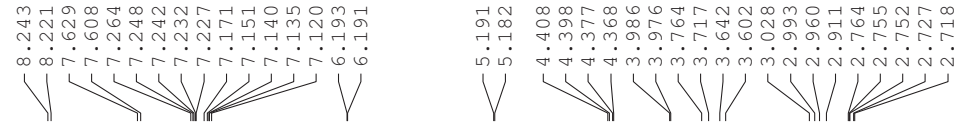
3af

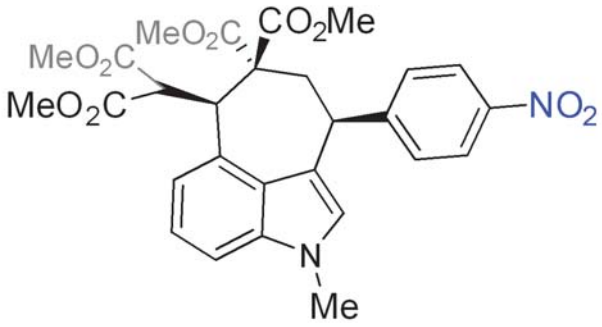
6.8:1 dr

($CDCl_3$, 101 MHz)

```
NAME        zxz-20180505-5-chun
EXPNO                    11
PROCNO                    1
Date_              20180521
Time                  18.00
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      100
DS                        2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                    6.50 usec
TE                   296.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                   14.70 usec
SI                    32768
SF             100.6127780 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                    1.40
```





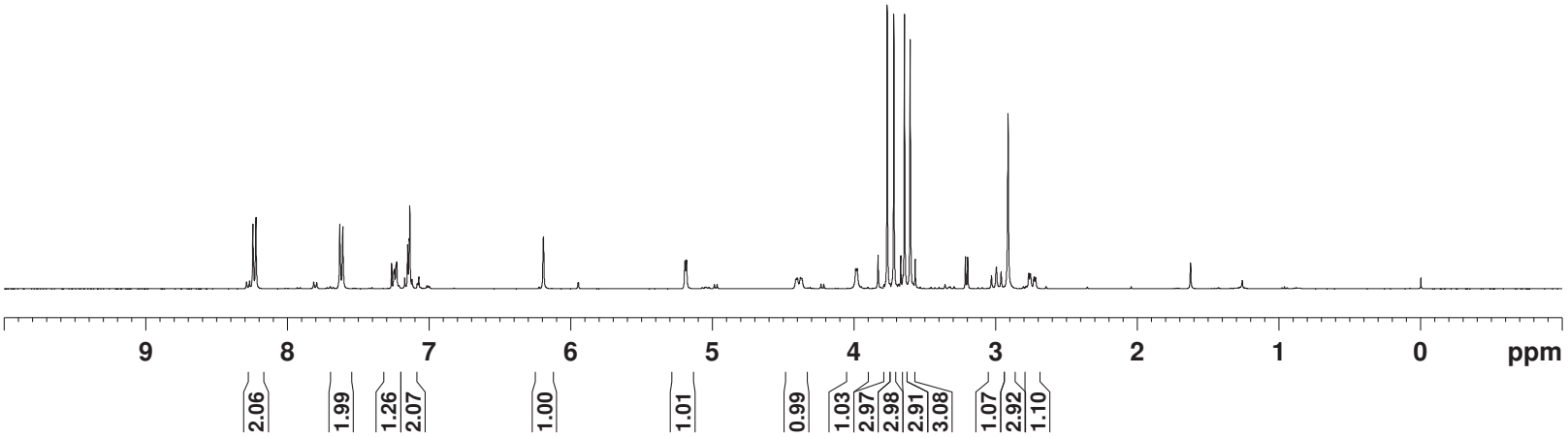


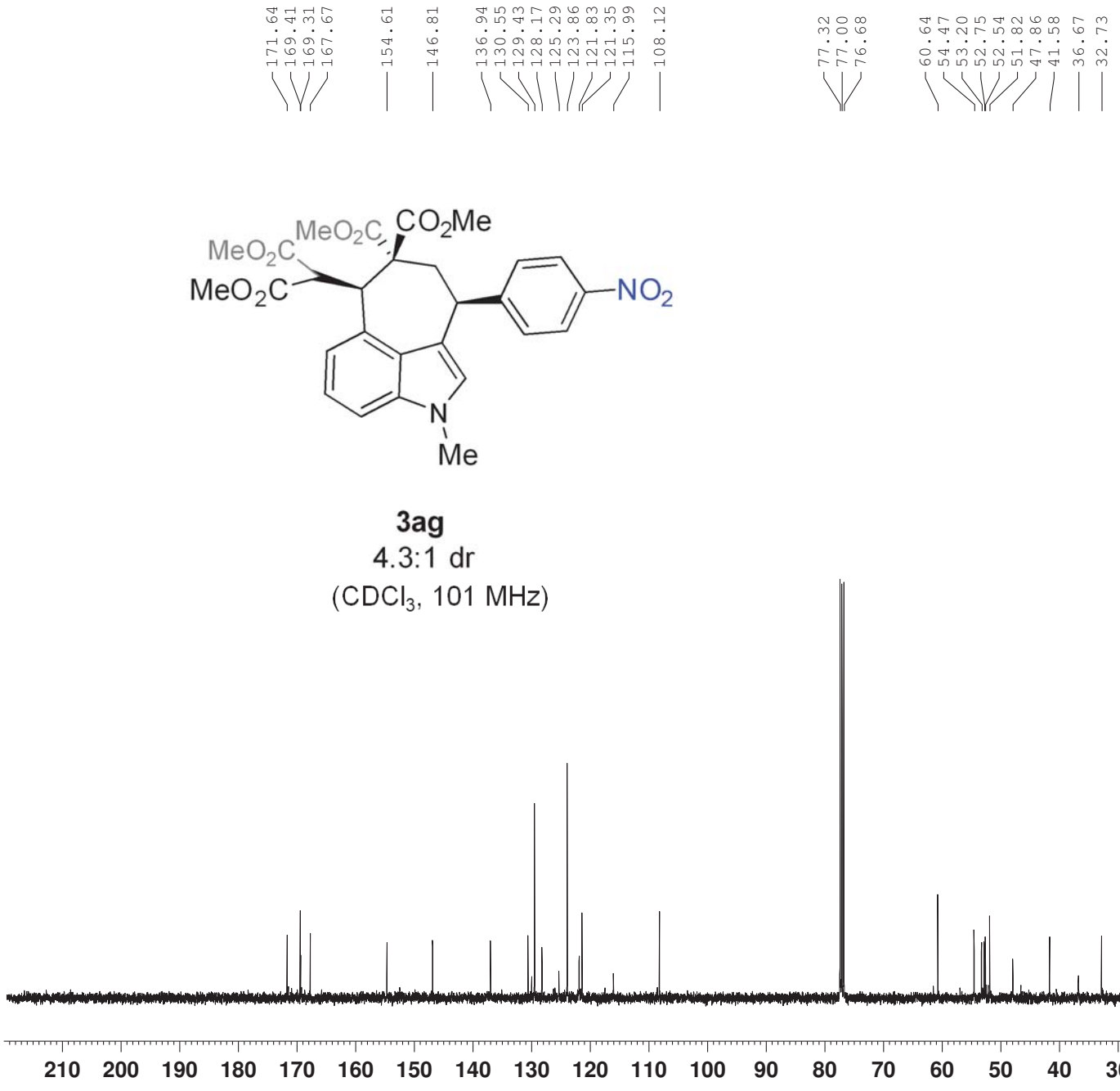
3ag

4.3:1 dr

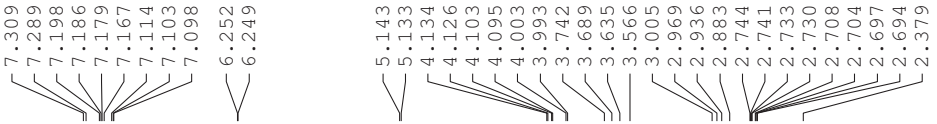
($CDCl_3$, 400 MHz)

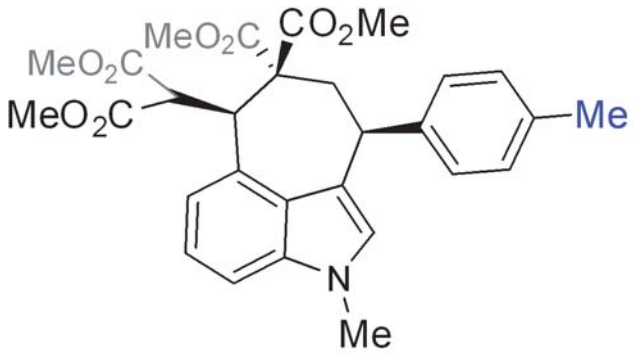
```
NAME      zxz-20180505-12-chun
EXPNO                   10
PROCNO                   1
Date_             20180522
Time                  3.35
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        2
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894966 sec
RG                      203
DW                   62.400 usec
DE                    6.50 usec
TE                   295.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           400.1324710 MHz
NUC1                    1H
P1                   12.40 usec
SI                    65536
SF             400.1300080 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```






```
NAME        zxz-20180505-12-chun
EXPNO                        11
PROCNO                        1
Date_                  20180522
Time                       3.42
INSTRUM                   spect
PROBHD     5 mm PABBO BB/
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          100
DS                            2
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         2050
DW                       20.800 usec
DE                        6.50 usec
TE                       295.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1              100.6228298 MHz
NUC1                       13C
P1                       15.50 usec
SI                        32768
SF                100.6127755 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



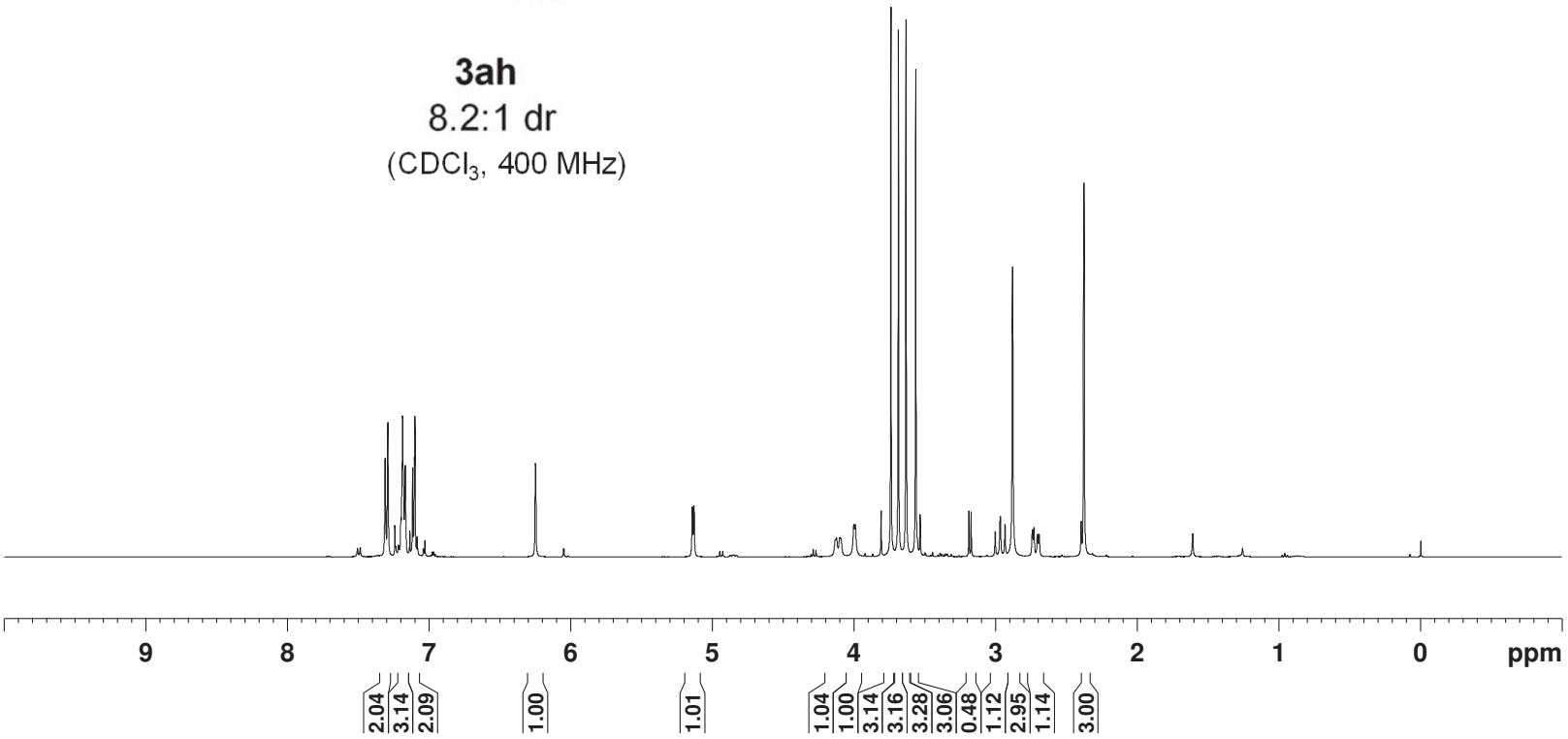


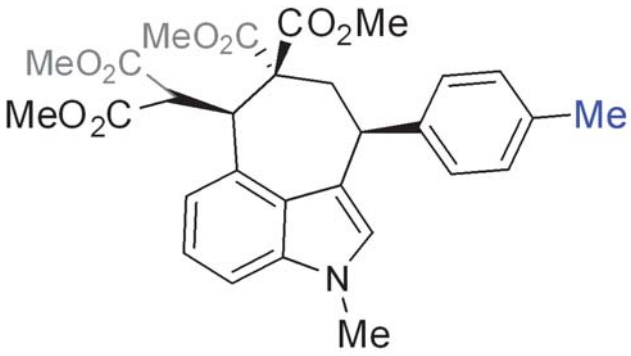
3ah

8.2:1 dr

($CDCl_3$, 400 MHz)

```
NAME        zxz-20180505-2-20180521
EXPNO                    12
PROCNO                    1
Date_              20180521
Time                  17.33
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        2
DS                        2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                       80.6
DW                    62.400 usec
DE                     6.50 usec
TE                    295.0 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                      1H
P1                    10.92 usec
SI                    65536
SF               400.1300173 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



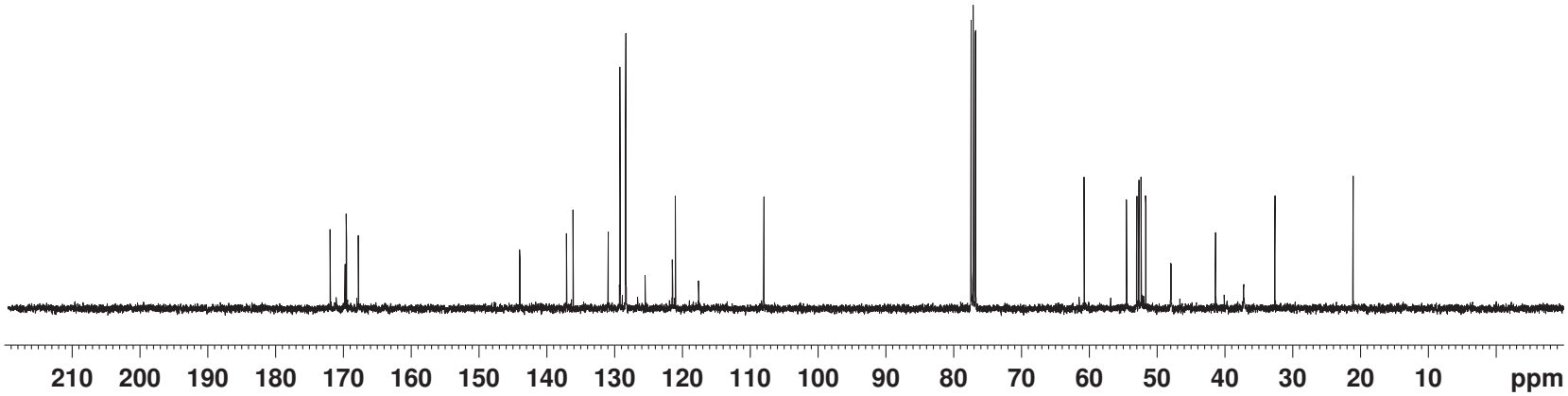


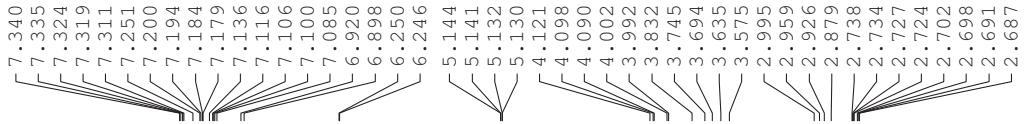
3ah

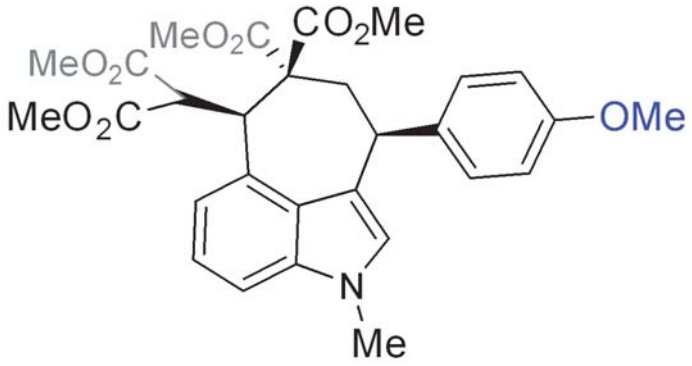
8.2:1 dr

($CDCl_3$, 101 MHz)

```
NAME        zxz-20180505-2-20180521
EXPNO                 13
PROCNO                 1
Date_           20180521
Time               17.39
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  100
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE                295.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1               13C
P1               14.70 usec
SI                32768
SF          100.6127788 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



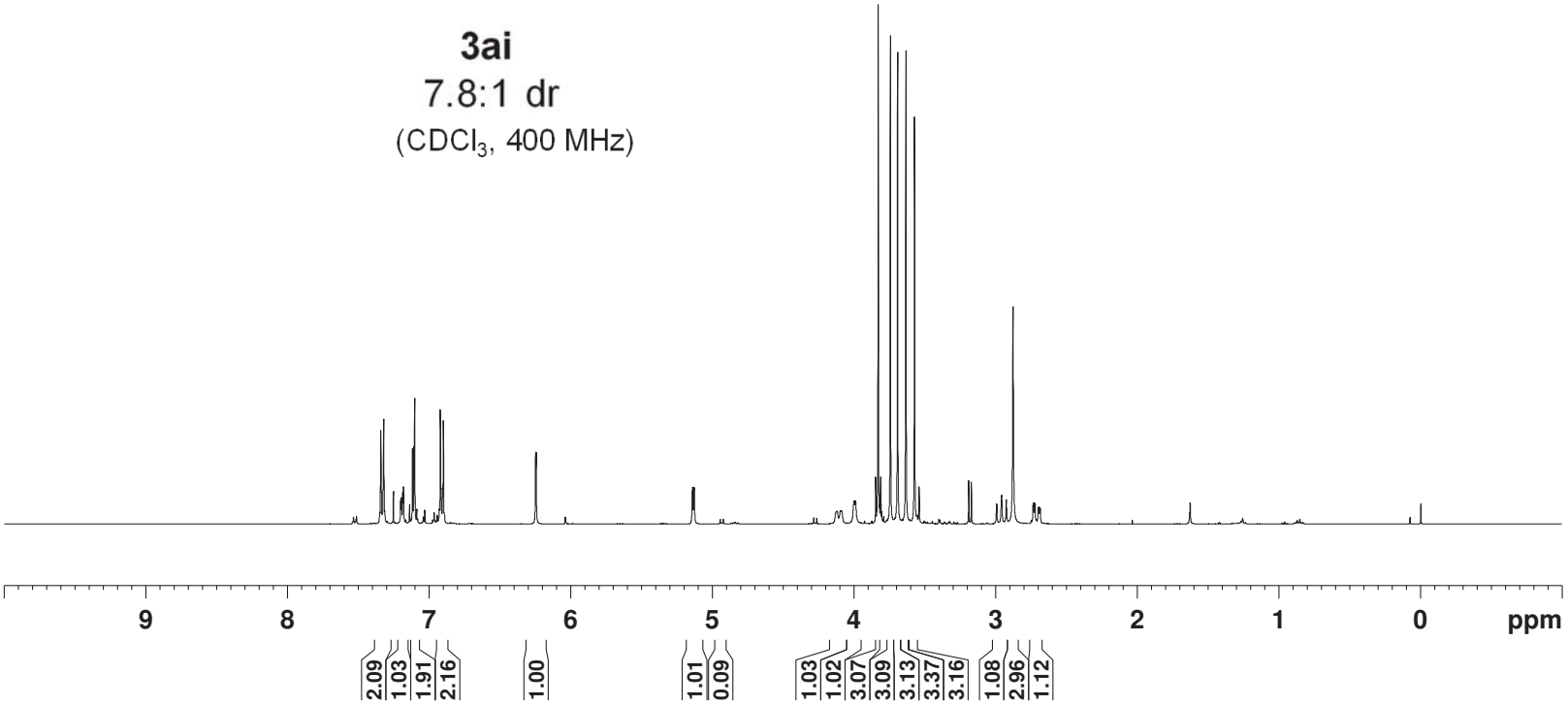




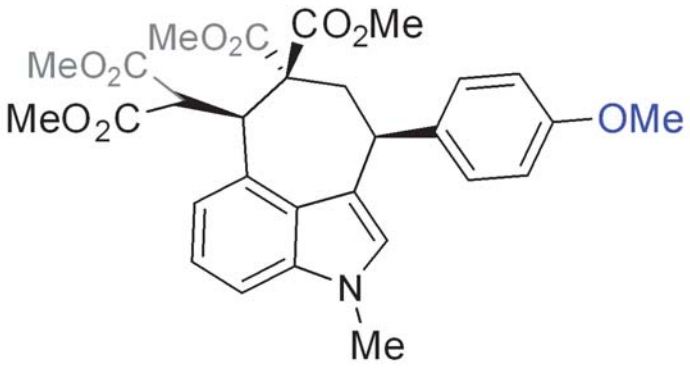
3ai

7.8:1 dr

($CDCl_3$, 400 MHz)




```
NAME      zxz-20180505-3-chun
EXPNO                  10
PROCNO                  1
Date_            20180521
Time                17.44
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       2
DS                       2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894966 sec
RG                    90.5
DW                 62.400 usec
DE                  6.50 usec
TE                 295.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                    1H
P1                  10.92 usec
SI                   65536
SF            400.1300132 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

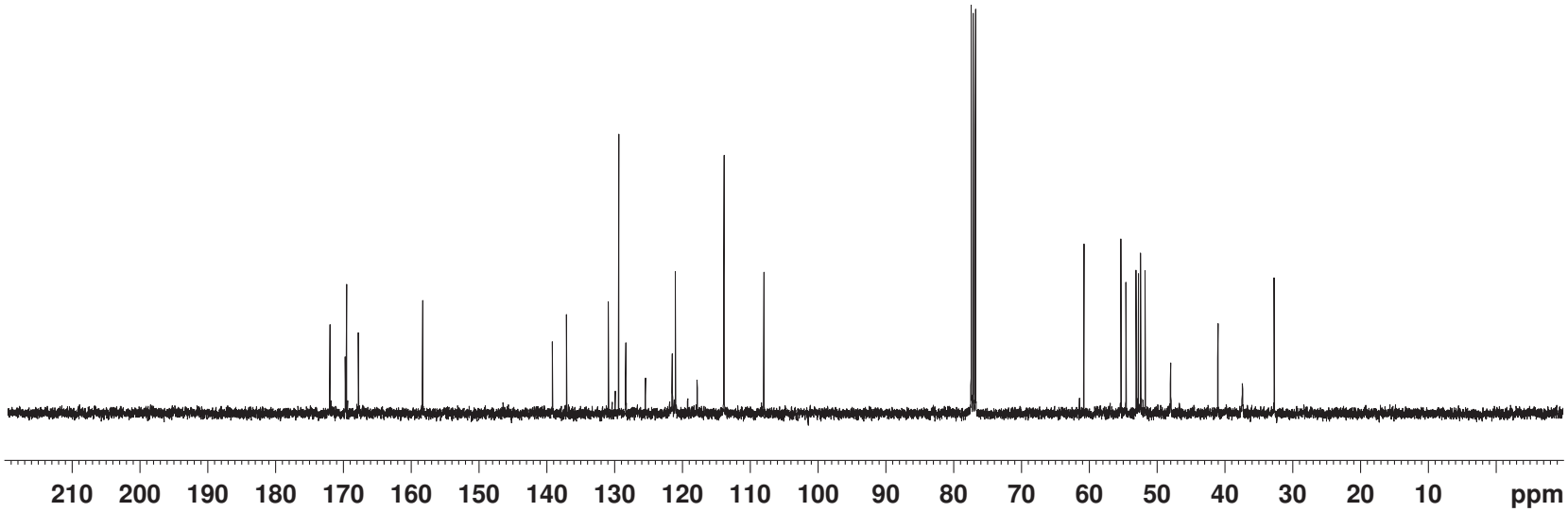


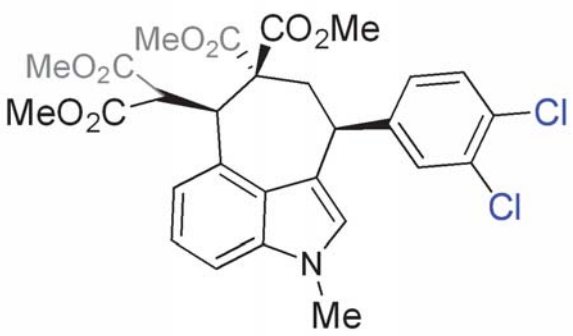
3ai

7.8:1 dr

($CDCl_3$, 101 MHz)

```
NAME        zxz-20180505-3-chun
EXPNO                        11
PROCNO                        1
Date_                  20180521
Time                      17.50
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         100
DS                           2
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         2050
DW                       20.800 usec
DE                        6.50 usec
TE                       296.2 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228298 MHz
NUC1                       13C
P1                       14.70 usec
SI                         32768
SF                 100.6127775 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

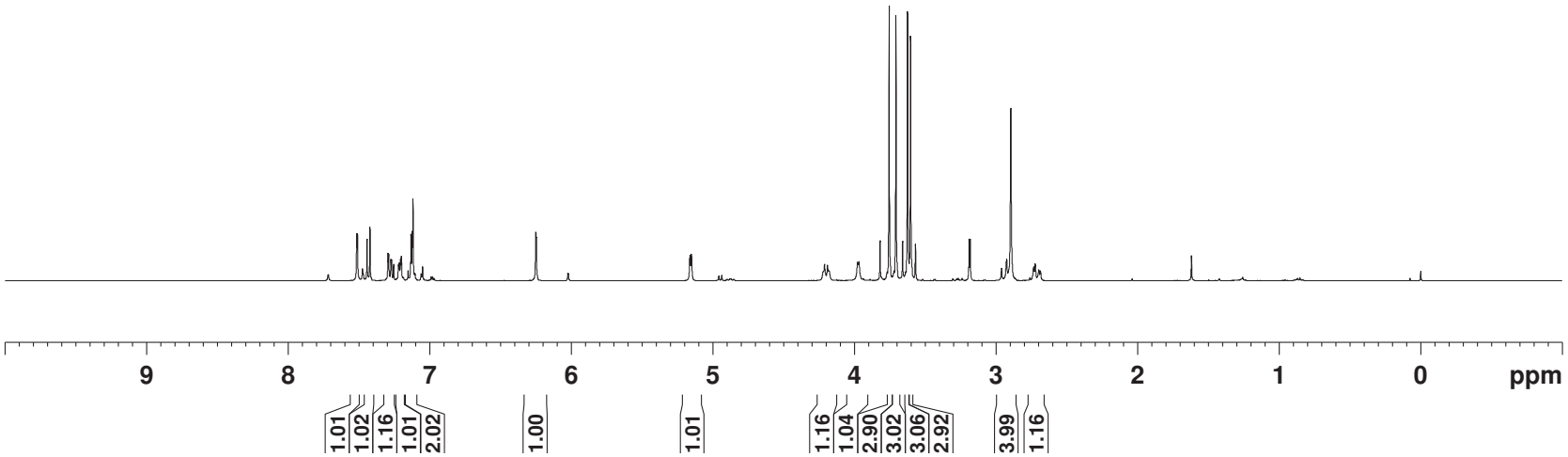


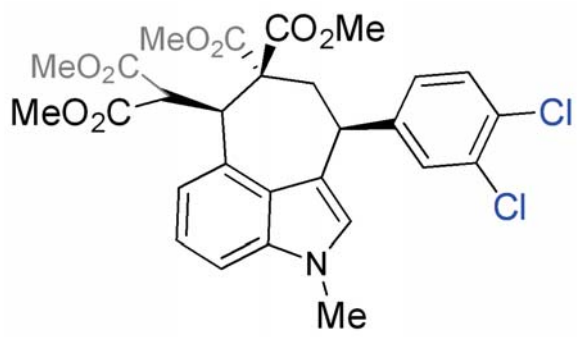


3aj
6.1:1 dr

($CDCl_3$, 101 MHz)

```
NAME        zxz-20180505-10-chun
EXPNO                         10
PROCNO                         1
Date_                   20180522
Time                        3.16
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                     zg30
TD                         65536
SOLVENT                    CDCl3
NS                             2
DS                             2
SWH                     8012.820 Hz
FIDRES                  0.122266 Hz
AQ                      4.0894966 sec
RG                           161
DW                        62.400 usec
DE                         6.50 usec
TE                        294.9 K
D1                    1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                        12.40 usec
SI                         65536
SF                  400.1300109 MHz
WDW                           EM
SSB                            0
LB                         0.30 Hz
GB                             0
PC                          1.00
```





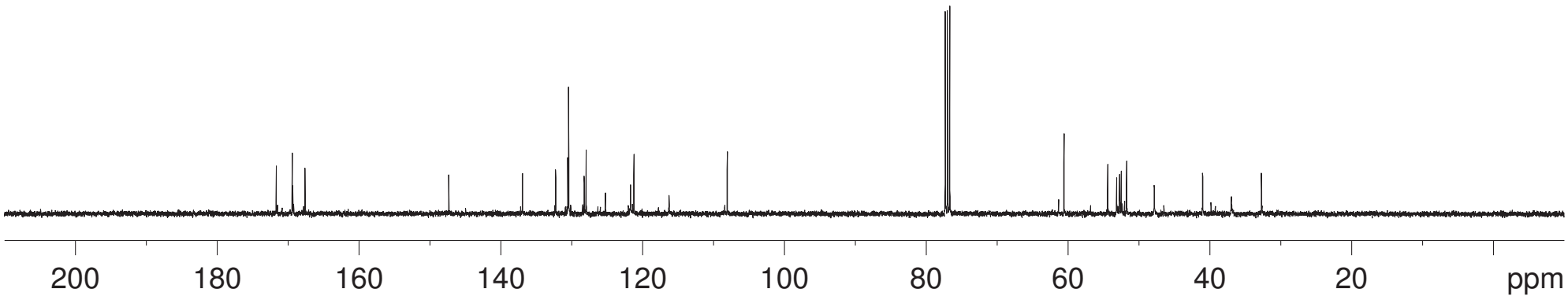
3aj

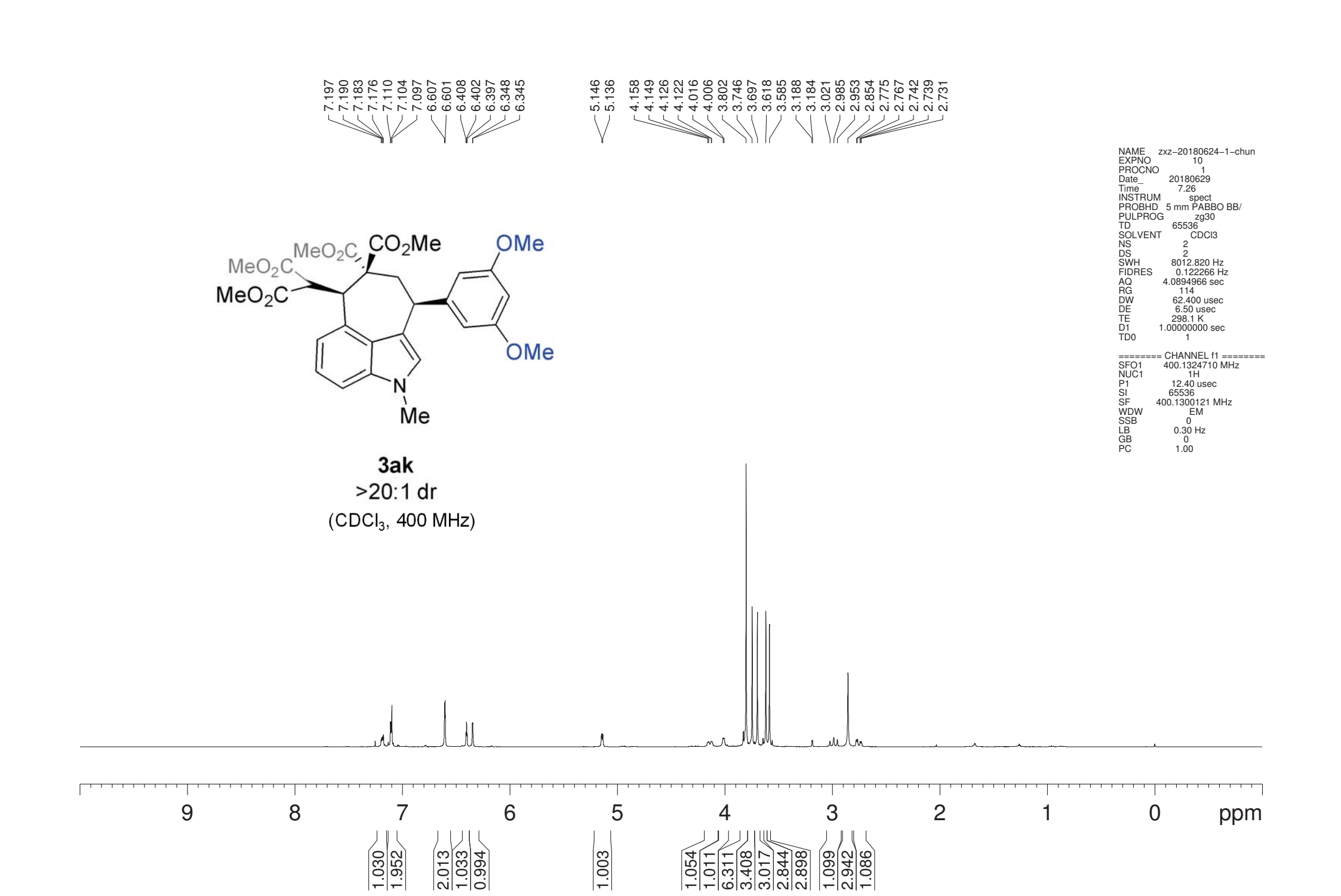
6.1:1 dr

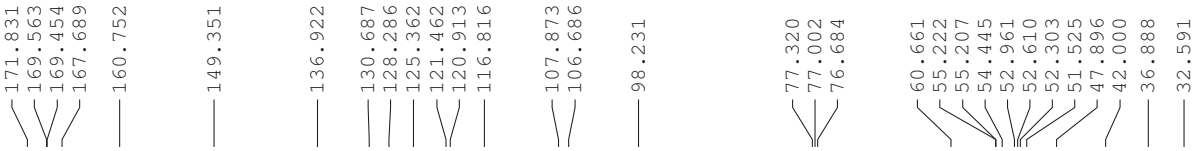
($CDCl_3$, 101 MHz)

171.685
169.432
169.346
167.629
147.346
136.945
132.259
130.561
130.445
130.401
128.231
127.964
125.232
121.707
121.228
116.265
108.061
77.315
76.998
76.679
60.559
54.390
53.126
52.710
52.474
51.725
47.822
41.002
36.935
32.706

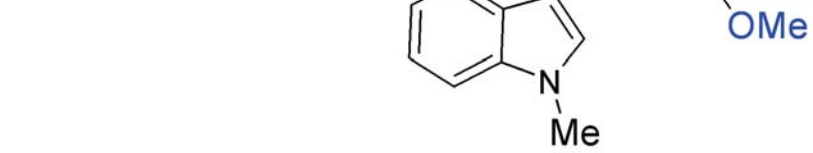
```
NAME     zxz-20180505-10-chun
EXPNO          12
PROCNO          1
Date_       20180522
Time          3.22
INSTRUM       spect
PROBHD   5 mm PABBO BB/
PULPROG       zgpg30
TD             65536
SOLVENT        CDCl3
NS               100
DS                 2
SWH        24038.461 Hz
FIDRES       0.366798 Hz
AQ         1.3631988 sec
RG              2050
DW             20.800 usec
DE              6.50 usec
TE             295.7 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0             1

======== CHANNEL f1 ========
SFO1       100.6228298 MHz
NUC1             13C
P1              15.50 usec
SI              32768
SF         100.6127773 MHz
WDW              EM
SSB               0
LB              1.00 Hz
GB                0
PC              1.40
```




7.197
7.190
7.183
7.176
7.110
7.104
7.097
6.607
6.601
6.408
6.402
6.397
6.348
6.345
5.146
5.136
4.158
4.149
4.126
4.122
4.016
4.006
3.802
3.746
3.697
3.618
3.585
3.188
3.184
3.021
2.985
2.953
2.854
2.775
2.767
2.742
2.739
2.731
NAME zxz–20180624–1–chun
EXPNO 10
PROCNO 1
Date_ 20180629
Time 7.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 114
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.40 usec
SI 65536
SF 400.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
MeO2C
MeO2C
MeO2C
CO2Me
OMe
OMe
N
Me
3ak
>20:1 dr
(CDCl3, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.030
1.952
2.013
1.033
0.994
1.003
1.054
1.011
6.311
3.408
3.017
2.844
2.898
1.099
2.942
1.086



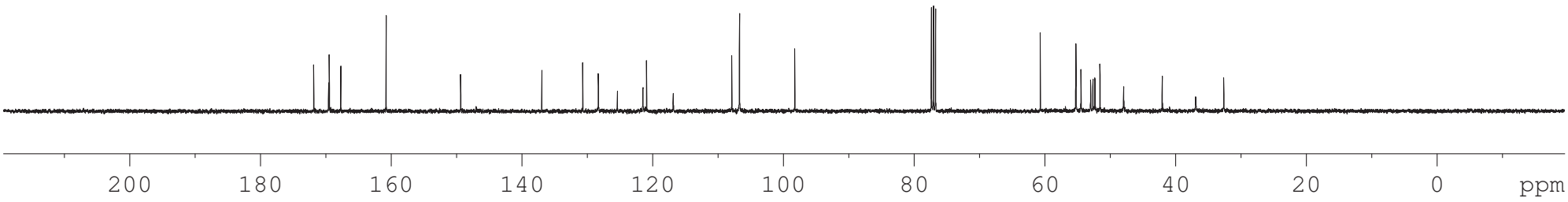

```
NAME        zxz-20180624-1-chun
EXPNO                       11
PROCNO                       1
Date_                 20180629
Time                      7.32
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         100
DS                           2
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         2050
DW                       20.800 usec
DE                        6.50 usec
TE                       298.8 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1            100.6228298 MHz
NUC1                     13C
P1                     15.50 usec
SI                       32768
SF               100.6127795 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

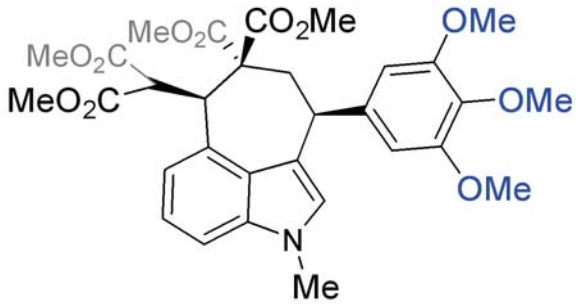


3ak

>20:1 dr

($CDCl_3$, 101 MHz)



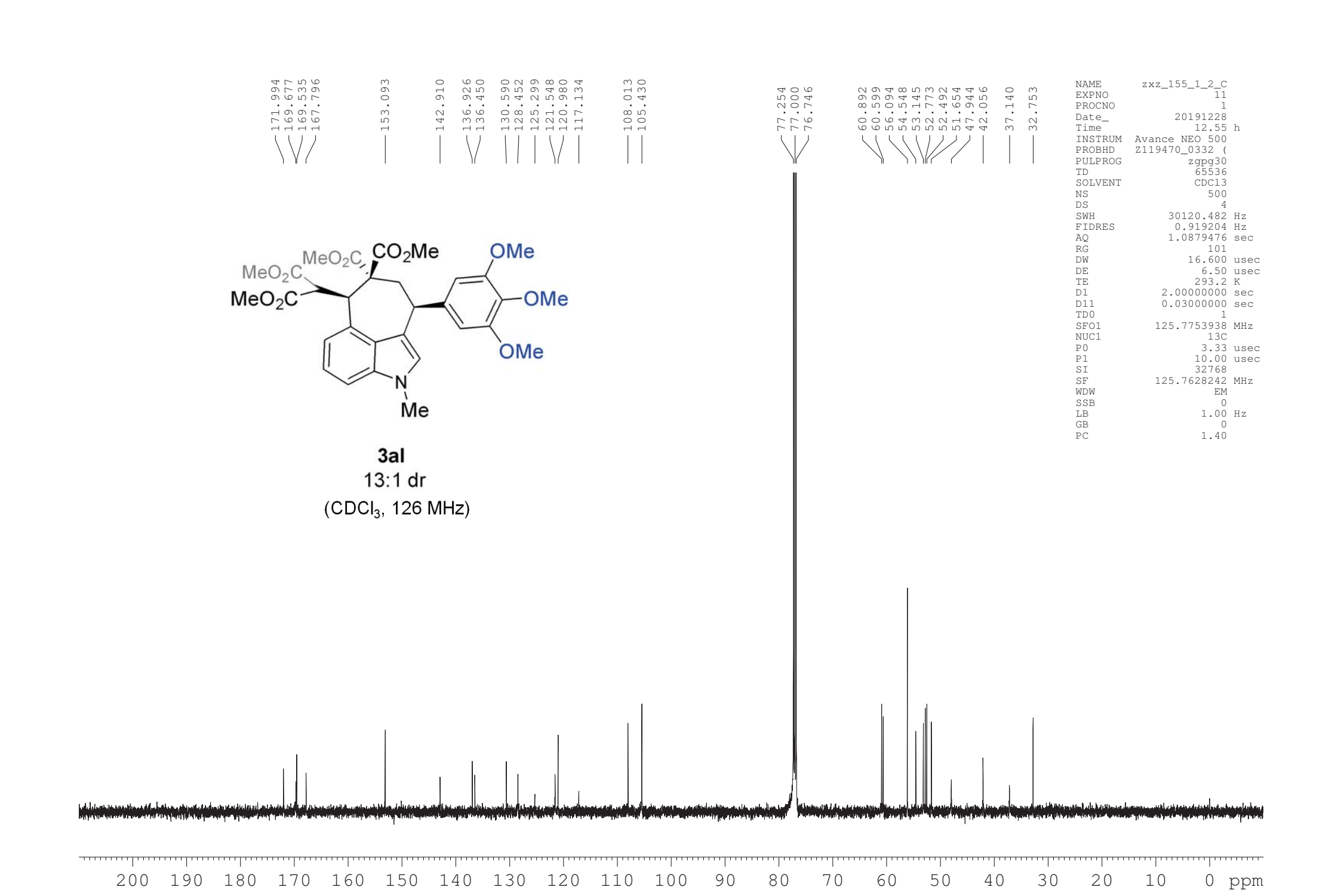


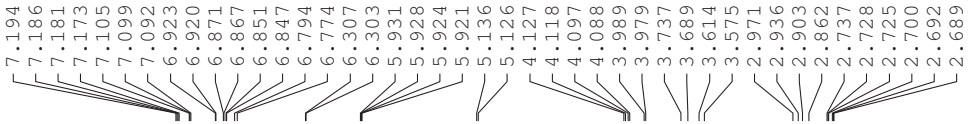
3al

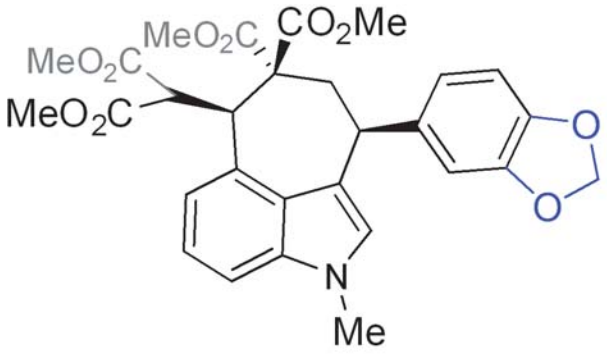
13:1 dr

($CDCl_3$, 500 MHz)

NAME zxz_155_1_2_H
EXPNO 21
PROCNO 1
Date_ 20200104
Time 15.41 h
INSTRUM Avance NEO 500
PROBHD Z119470_0332 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2768500 sec
RG 100
DW 50.000 usec
DE 10.79 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
SFO1 500.1530884 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
SI 65536
SF 500.1500097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


171.994
169.677
169.535
167.796
153.093
142.910
136.926
136.450
130.590
128.452
125.299
121.548
120.980
117.134
108.013
105.430
77.254
77.000
76.746
60.892
60.599
56.094
54.548
53.145
52.773
52.492
51.654
47.944
42.056
37.140
32.753
NAME zxz_155_1_2_C
EXPNO 11
PROCNO 1
Date_ 20191228
Time 12.55 h
INSTRUM Avance NEO 500
PROBHD Z119470_0332 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 4
SWH 30120.482 Hz
FIDRES 0.919204 Hz
AQ 1.0879476 sec
RG 101
DW 16.600 usec
DE 6.50 usec
TE 293.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7753938 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
SI 32768
SF 125.7628242 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MeO2C
MeO2C
MeO2C
CO2Me
OMe
OMe
OMe
N
Me
3aI
13:1 dr
(CDCl3, 126 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



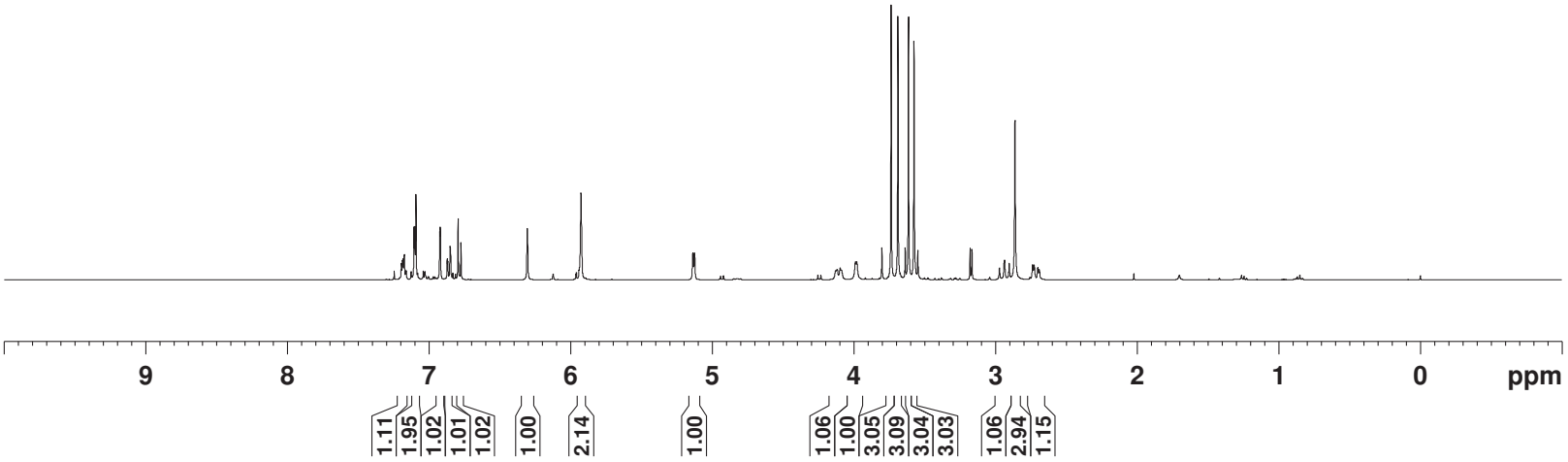


3am

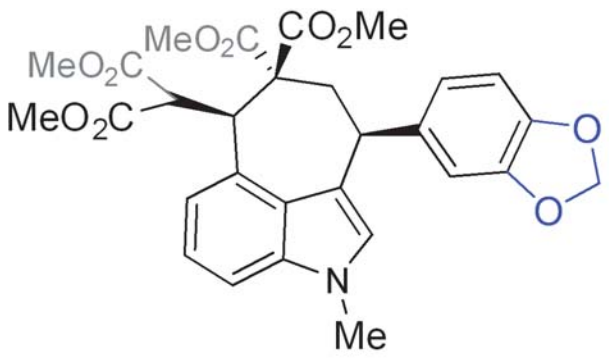
8.8:1 dr

($CDCl_3$, 400 MHz)

```
NAME      zxz-20180505-4-chun
EXPNO                  21
PROCNO                  1
Date_           20180520
Time               16.54
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     2
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                    32
DW                62.400 usec
DE                 6.50 usec
TE                298.7 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                10.92 usec
SI                 65536
SF           400.1300147 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```



171.76
169.45
169.36
167.57
147.55
146.06
140.81
136.91
130.68
128.22
125.24
121.37
121.22
120.88
117.23
108.68
107.82
100.73
60.55
54.36
52.89
52.53
52.22
51.52
47.77
41.40
37.28
32.51

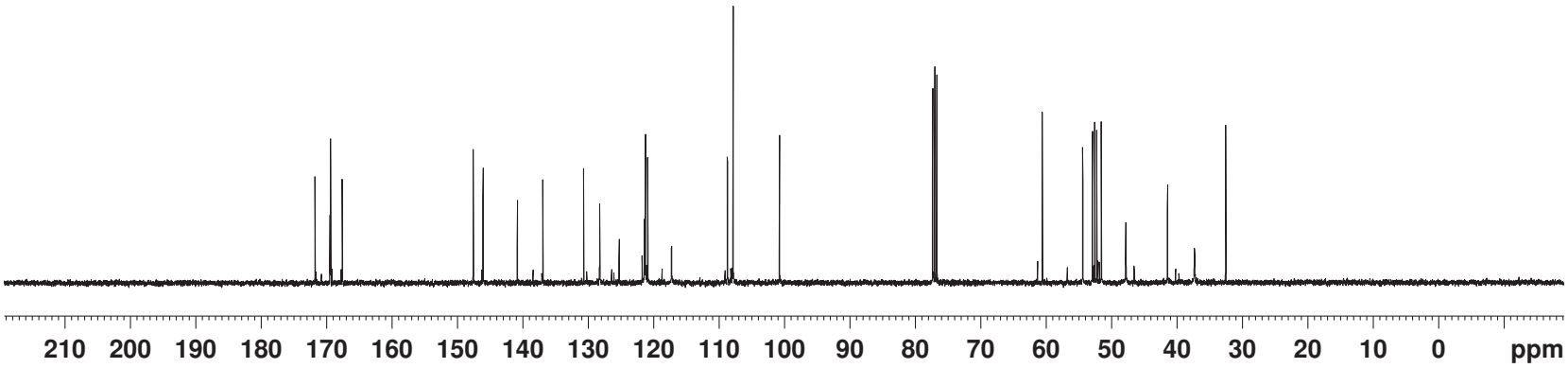


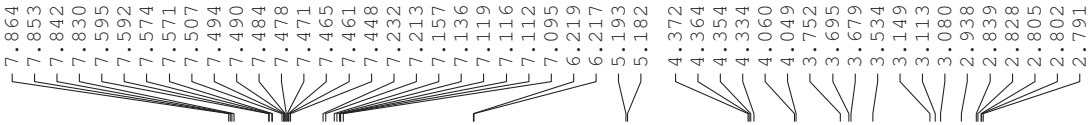
3am

8.8:1 dr

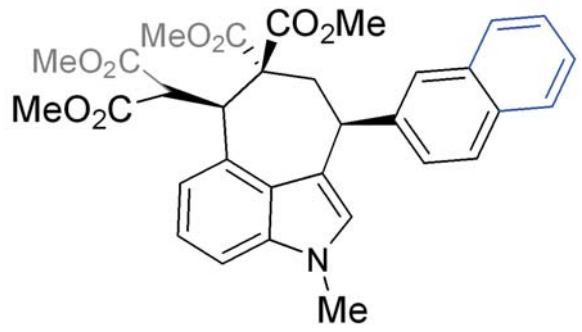
($CDCl_3$, 101 MHz)

```
NAME        zxz-20180505-4-chun
EXPNO                       22
PROCNO                       1
Date_                 20180520
Time                     17.00
INSTRUM                  spect
PROBHD     5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         100
DS                           2
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                        2050
DW                      20.800 usec
DE                       6.50 usec
TE                      299.5 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228298 MHz
NUC1                       13C
P1                      14.70 usec
SI                       32768
SF                 100.6127876 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```





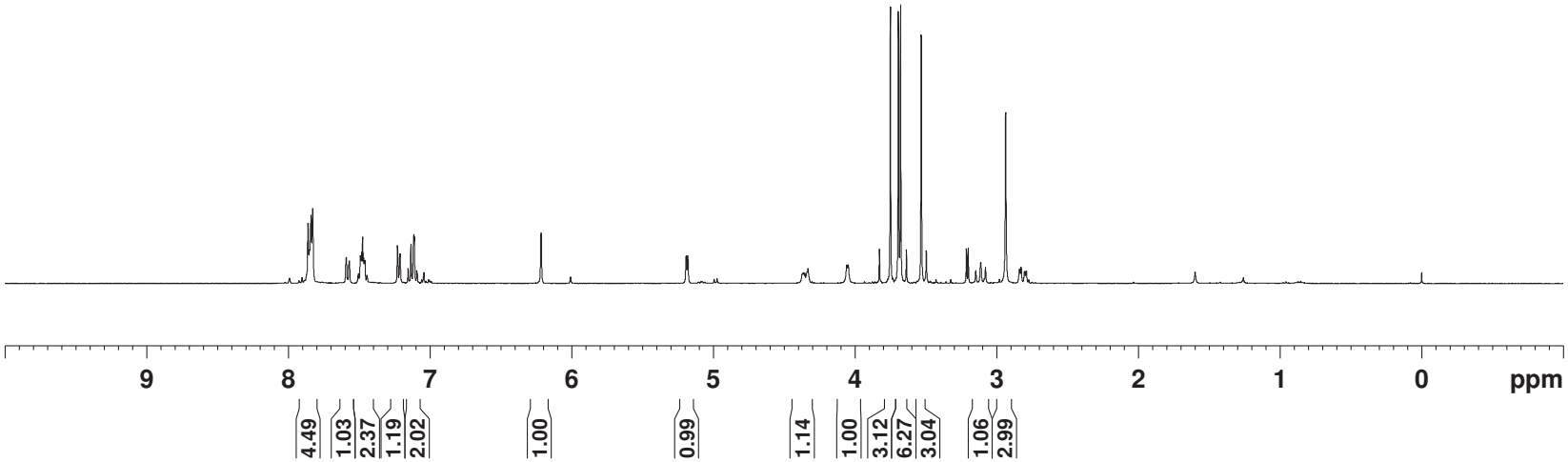

```
NAME      zxz-20180505-11-chun
EXPNO                   10
PROCNO                   1
Date_             20180522
Time                  3.25
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       2
DS                       2
SWH               8012.820 Hz
FIDRES               0.122266 Hz
AQ                4.0894966 sec
RG                     144
DW                  62.400 usec
DE                   6.50 usec
TE                  295.0 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                  12.40 usec
SI                   65536
SF            400.1300207 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



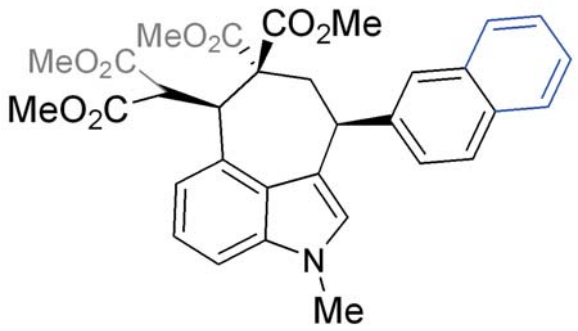
3an

6.3:1 dr

($CDCl_3$, 400 MHz)



171.86
169.67
169.50
167.74
144.09
137.04
133.47
132.53
130.85
128.52
128.29
127.65
127.62
126.92
126.63
125.95
125.46
121.50
121.05
117.22
107.97
77.32
77.00
76.68
60.81
54.54
53.03
52.68
52.43
51.73
47.98
41.90
36.90
32.61

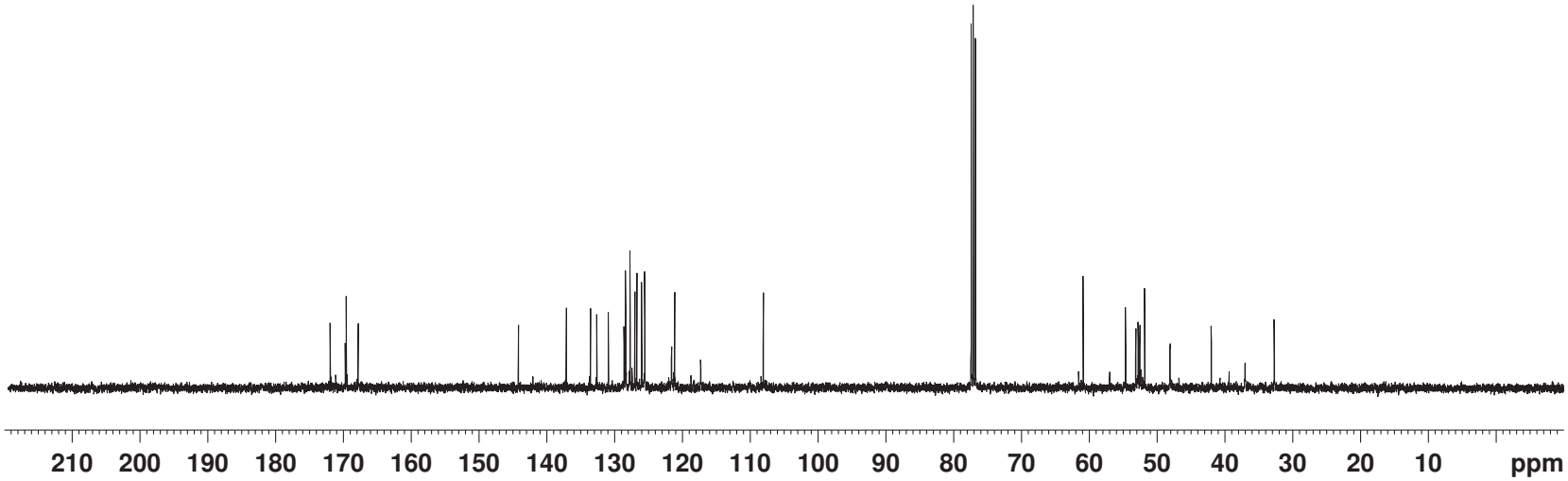


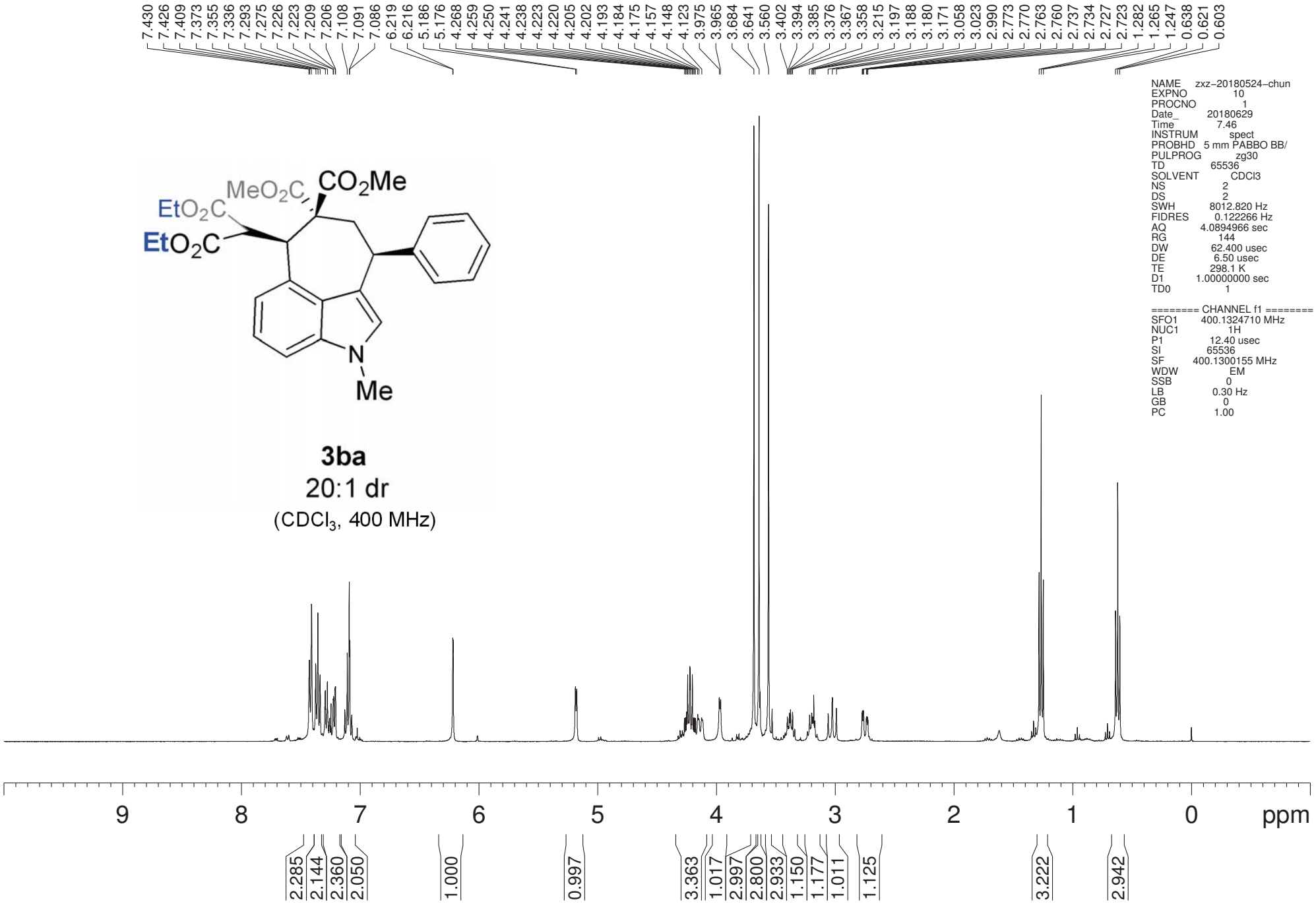
3an

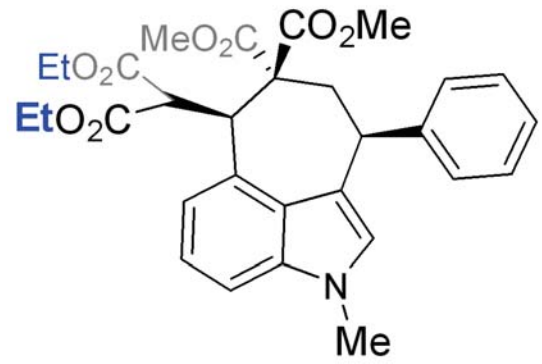
6.3:1 dr

($CDCl_3$, 101 MHz)

```
NAME        zxz-20180505-11-chun
EXPNO                         11
PROCNO                         1
Date_                   20180522
Time                        3.32
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                   zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                           100
DS                             2
SWH                    24038.461 Hz
FIDRES                  0.366798 Hz
AQ                     1.3631988 sec
RG                          2050
DW                        20.800 usec
DE                         6.50 usec
TE                        295.7 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                100.6228298 MHz
NUC1                        13C
P1                        15.50 usec
SI                         32768
SF                 100.6127788 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```




7.430 7.426 7.409 7.373 7.355 7.336 7.293 7.275 7.226 7.223 7.209 7.206 7.108 7.091 7.086 6.219 6.216 5.186 5.176 4.268 4.259 4.250 4.241 4.238 4.223 4.220 4.205 4.202 4.193 4.184 4.175 4.157 4.148 4.123 3.975 3.965 3.684 3.641 3.560 3.402 3.394 3.385 3.376 3.367 3.358 3.215 3.197 3.188 3.180 3.171 3.058 3.023 2.990 2.773 2.770 2.763 2.760 2.737 2.734 2.727 2.723 1.282 1.265 1.247 0.638 0.621 0.603
NAME zxz–20180524–chun
EXPNO 10
PROCNO 1
Date_ 20180629
Time 7.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 144
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 12.40 usec
SI 65536
SF 400.1300155 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
MeO2C
CO2Me
EtO2C
EtO2C
N
Me
3ba
20:1 dr
(CDCl3, 400 MHz)
9 8 7 6 5 4 3 2 1 0 ppm
2.285 2.144 2.360 2.050 1.000 0.997 3.363 1.017 2.997 2.800 2.933 1.150 1.177 1.011 1.125 3.222 2.942



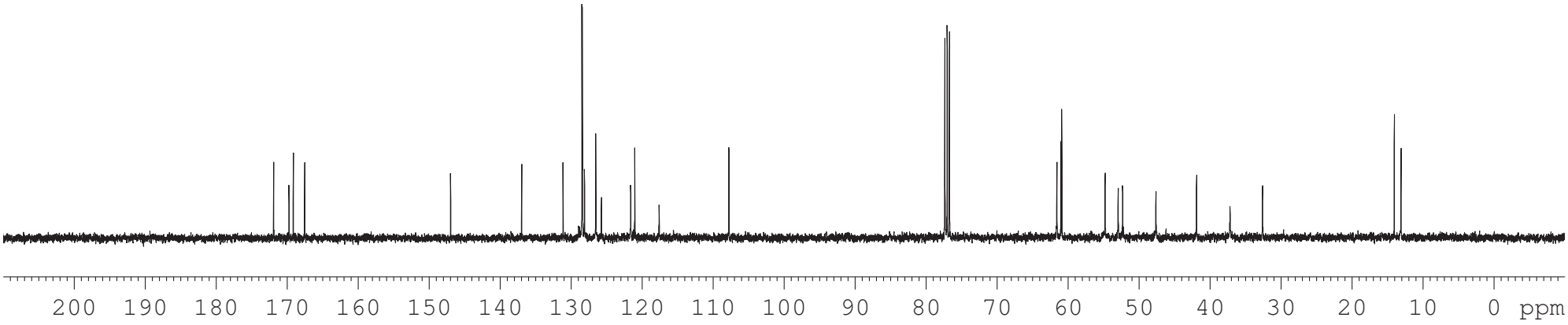
3ba

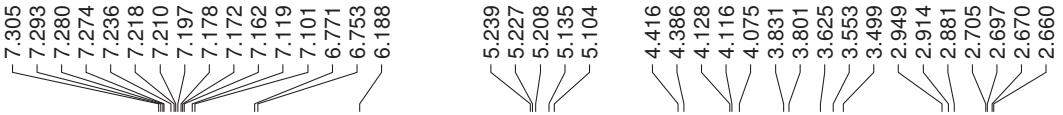
20:1 dr

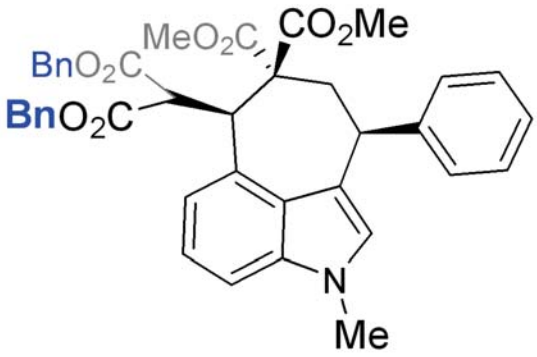
($CDCl_3$, 101 MHz)

171.888
169.731
169.131
167.523
146.961
136.955
131.135
128.455
128.403
128.103
126.515
125.714
121.598
121.028
117.591
107.751
77.317
76.999
76.681
61.540
60.969
60.849
54.750
52.909
52.275
47.580
41.859
37.156
32.566
14.004
13.044

```
NAME      zxz-20180524-chun
EXPNO                    11
PROCNO                    1
Date_              20180629
Time                   7.52
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     100
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                   6.50 usec
TE                  298.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                    13C
P1                   15.50 usec
SI                    32768
SF            100.6127773 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```





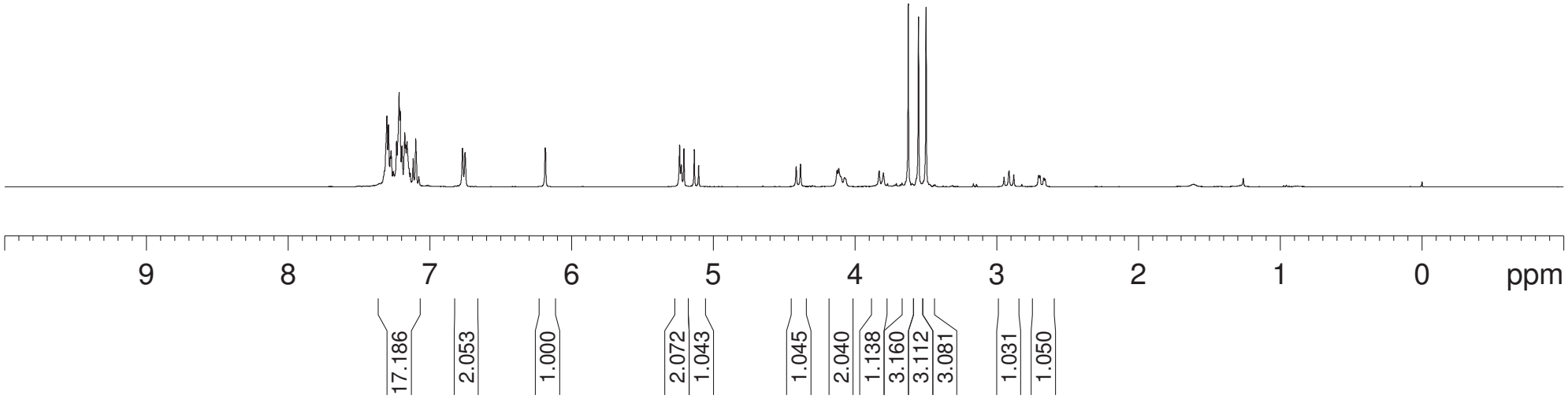


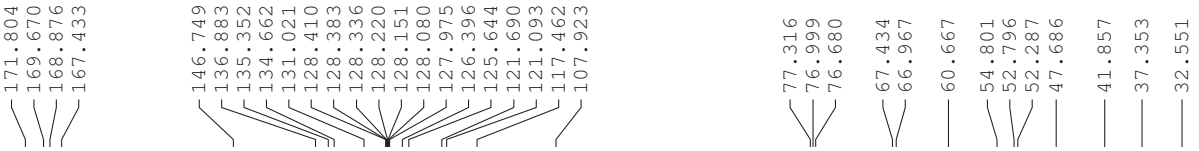
3ca

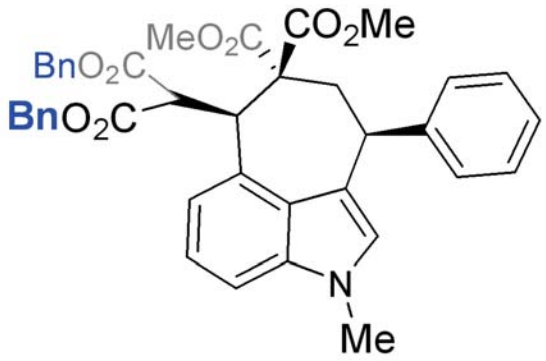
>20:1 dr

($CDCl_3$, 400 MHz)

```
NAME     zxz-20180622-1-chun
EXPNO            10
PROCNO            1
Date_         20180628
Time             8.42
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG         zg30
TD             65536
SOLVENT         CDCl3
NS                2
DS                2
SWH          8012.820 Hz
FIDRES       0.122266 Hz
AQ           4.0894966 sec
RG              128
DW             62.400 usec
DE              6.50 usec
TE              297.4 K
D1          1.00000000 sec
TD0               1

======== CHANNEL f1 ========
SFO1       400.1324710 MHz
NUC1              1H
P1               12.40 usec
SI             65536
SF         400.1300297 MHz
WDW               EM
SSB               0
LB             0.30 Hz
GB                0
PC             1.00
```





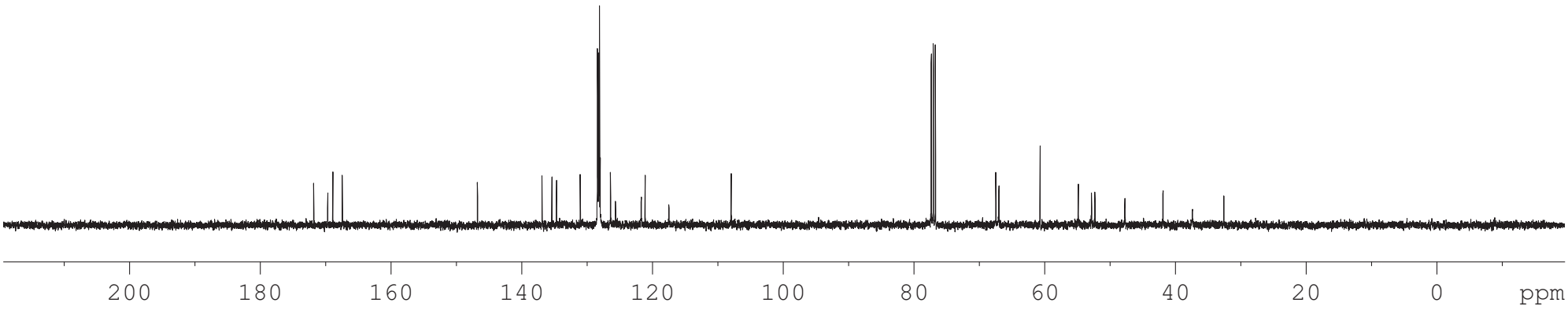


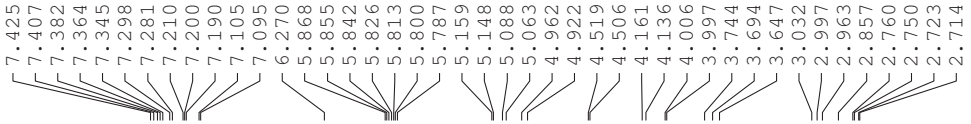
3ca

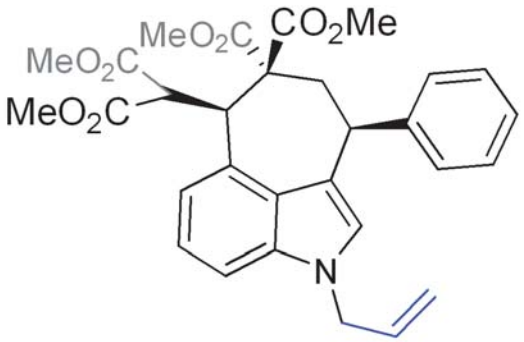
>20:1 dr

($CDCl_3$, 101 MHz)

```
NAME        zxz-20180622-1-chun
EXPNO                    11
PROCNO                    1
Date_               20180628
Time                    8.44
INSTRUM                 spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          29
DS                           2
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                        2050
DW                      20.800 usec
DE                       6.50 usec
TE                      298.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228298 MHz
NUC1                       13C
P1                       15.50 usec
SI                       32768
SF                 100.6127824 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```





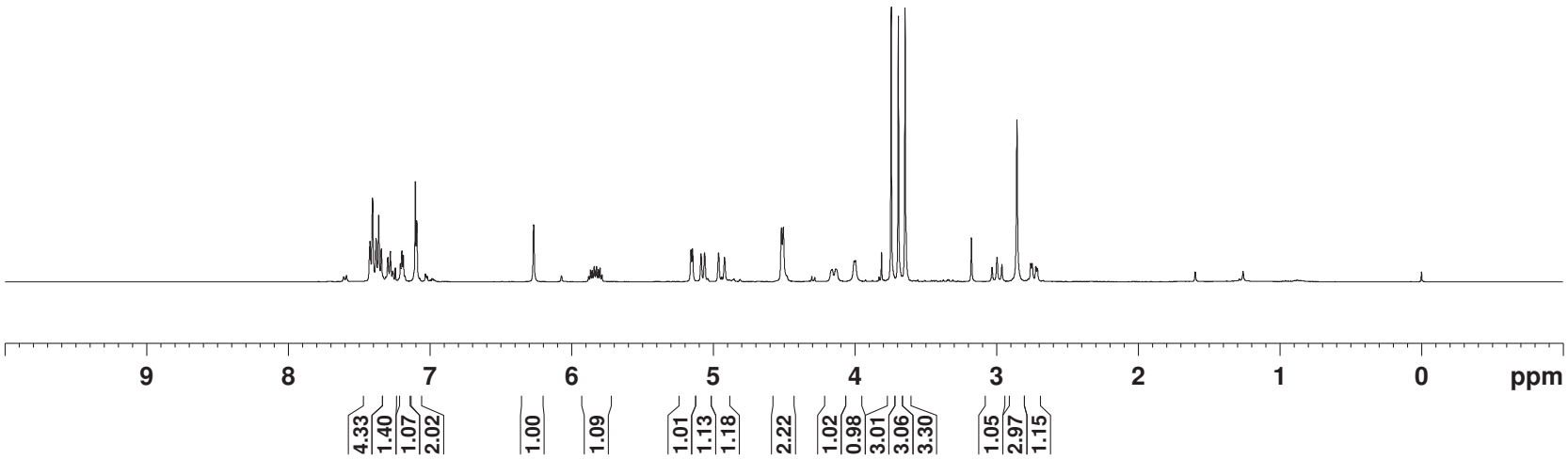


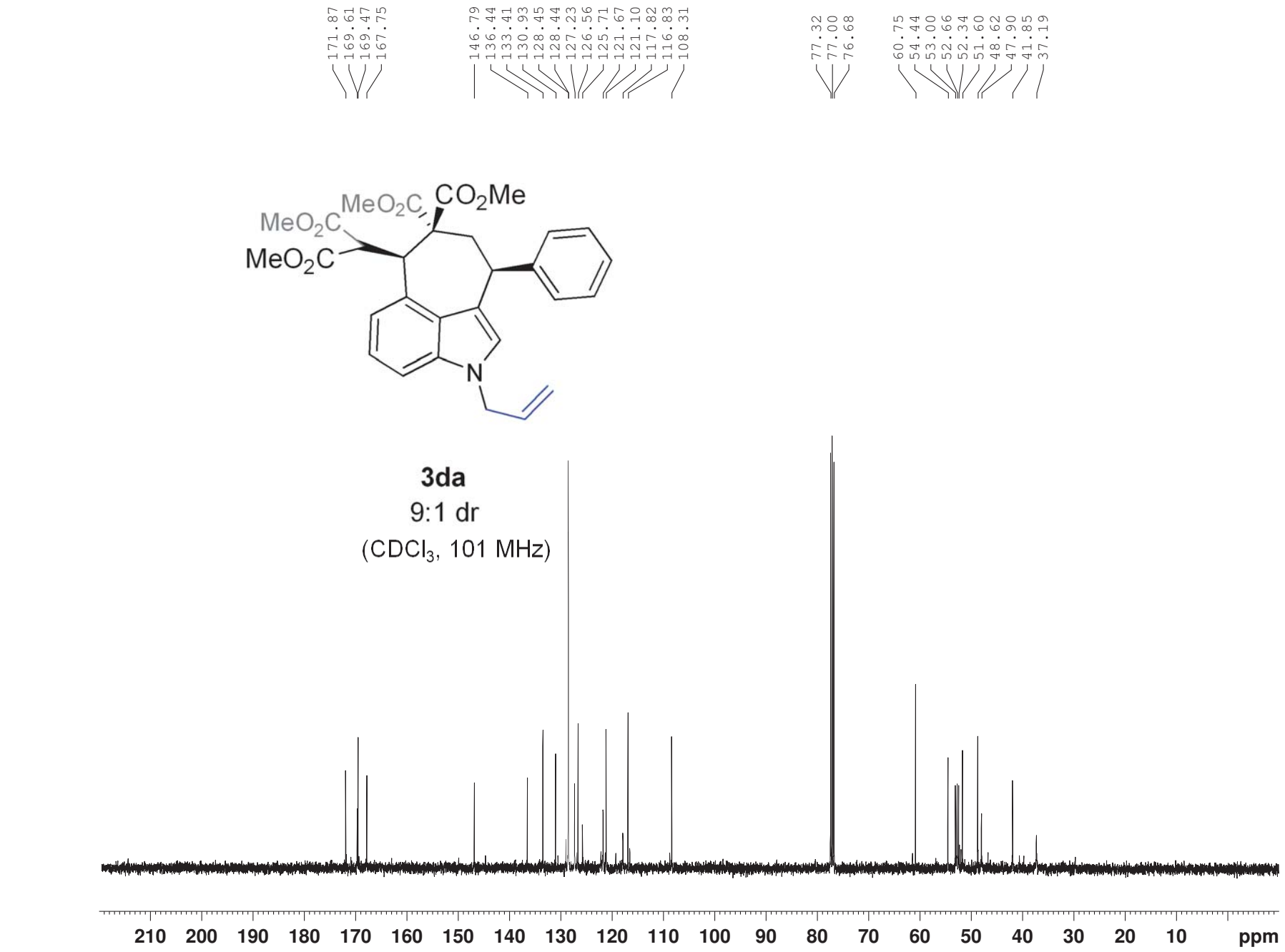
3da

9:1 dr

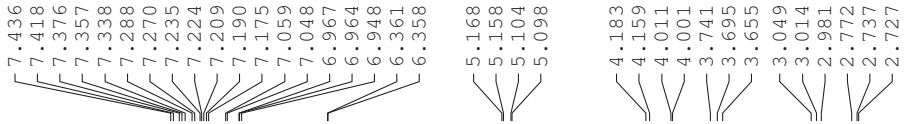
($CDCl_3$, 400 MHz)

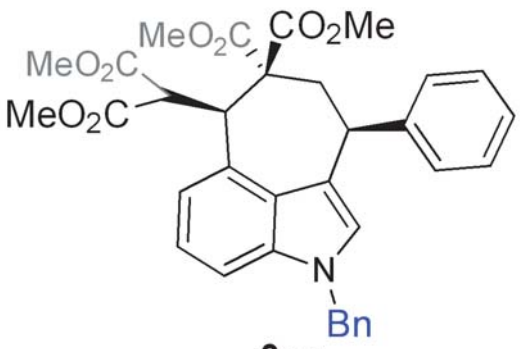
```
NAME        zxz-20180519-1-chun
EXPNO                        10
PROCNO                        1
Date_                  20180523
Time                       0.17
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                            2
DS                            2
SWH                    8012.820 Hz
FIDRES                 0.122266 Hz
AQ                     4.0894966 sec
RG                          144
DW                       62.400 usec
DE                        6.50 usec
TE                       295.2 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                       12.40 usec
SI                        65536
SF                  400.1300148 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```





NAME	zxz-20180519-1-chun
EXPNO	11
PROCNO	1
Date_	20180523
Time	0.23
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	100
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	296.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	15.50 usec
SI	32768
SF	100.6127780 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



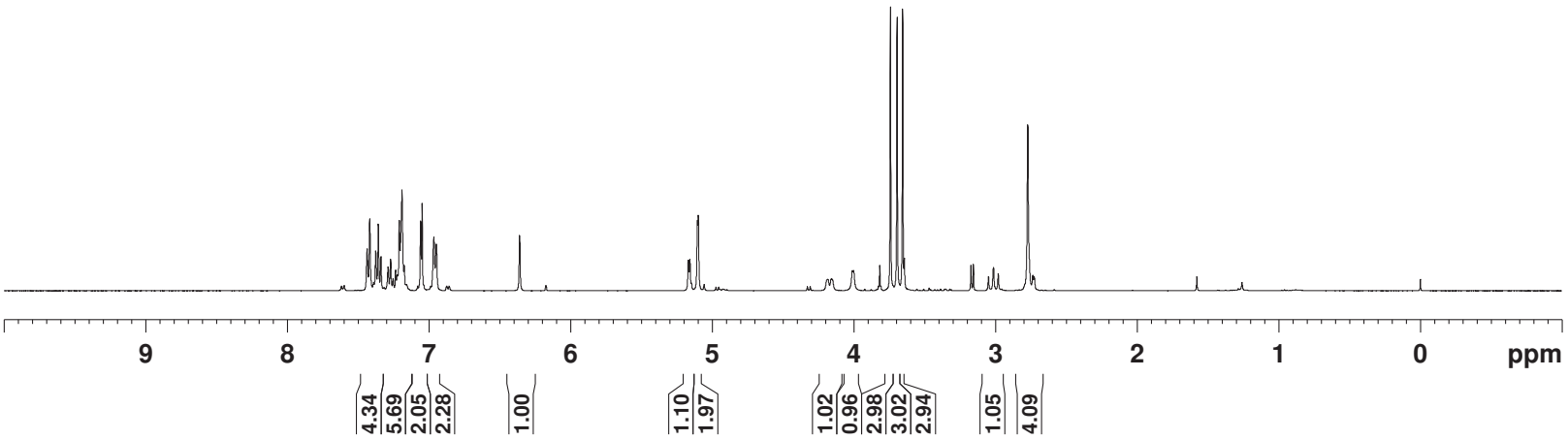


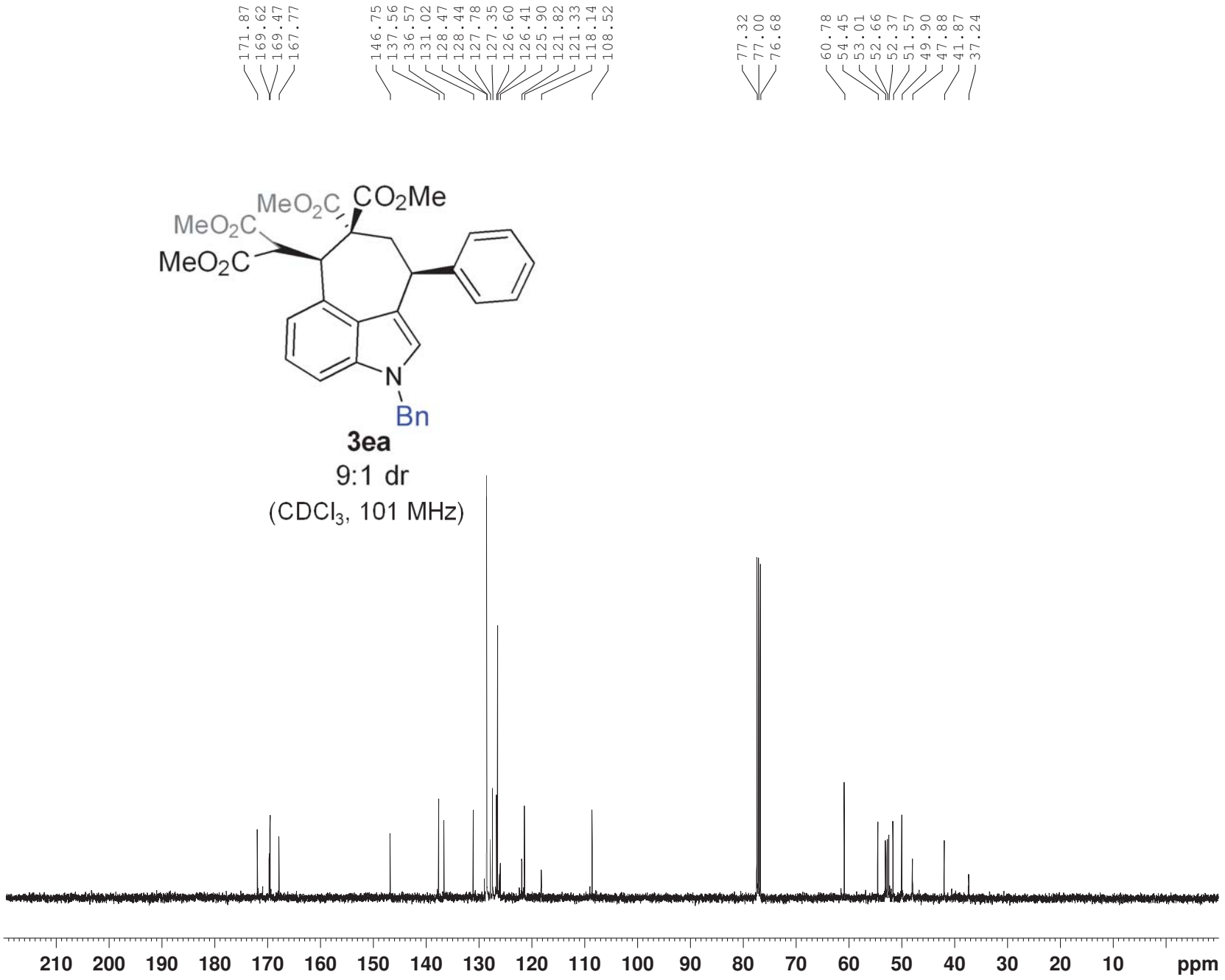
3ea

9:1 dr

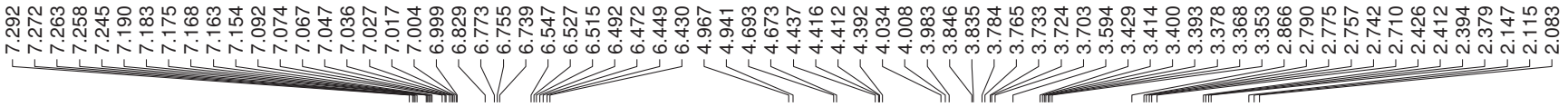
($CDCl_3$, 400 MHz)

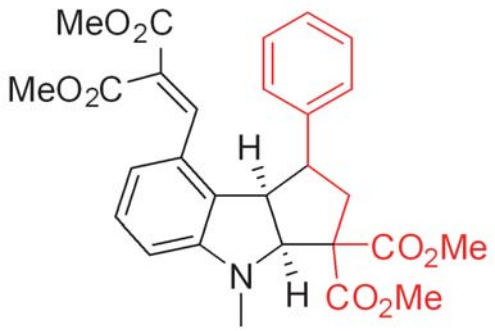
```
NAME        zxz-20180519-2-chun
EXPNO                        10
PROCNO                        1
Date_                  20180523
Time                       0.27
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                            2
DS                            2
SWH                    8012.820 Hz
FIDRES                 0.122266 Hz
AQ                     4.0894966 sec
RG                          144
DW                       62.400 usec
DE                        6.50 usec
TE                       295.3 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                400.1324710 MHz
NUC1                        1H
P1                       12.40 usec
SI                        65536
SF                  400.1300191 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```





NAME	zxz-20180519-2-chun
EXPNO	11
PROCNO	1
Date_	20180523
Time	0.34
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	100
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	296.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	15.50 usec
SI	32768
SF	100.6127785 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



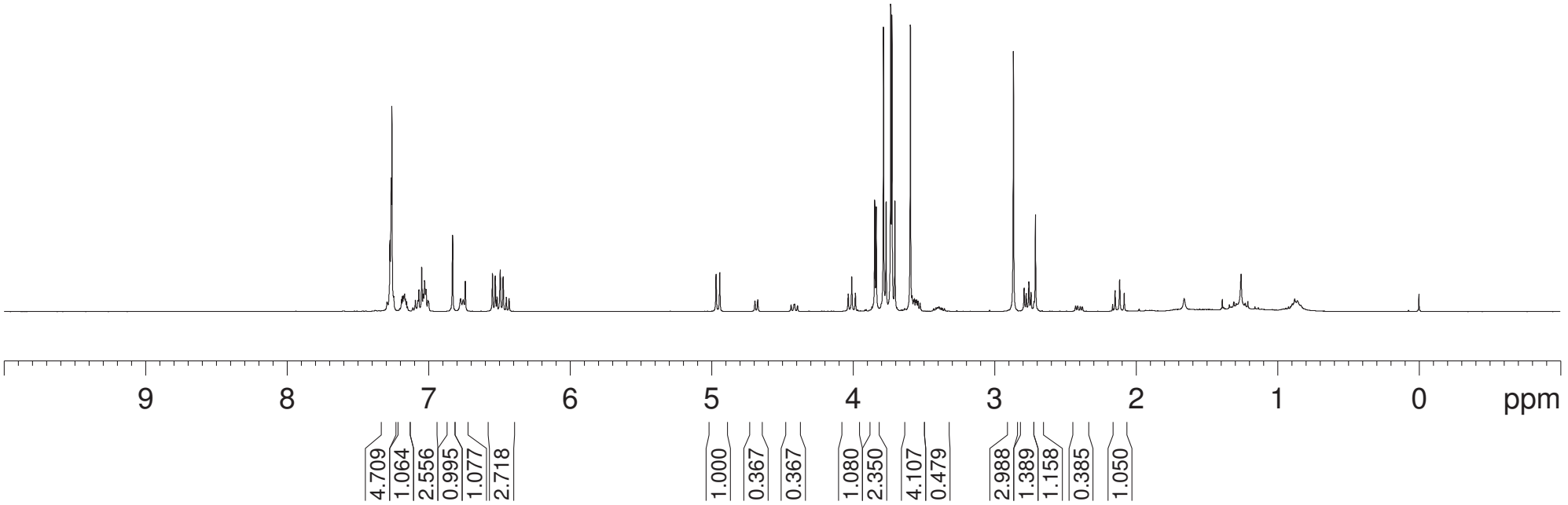


4aa

5:1 dr

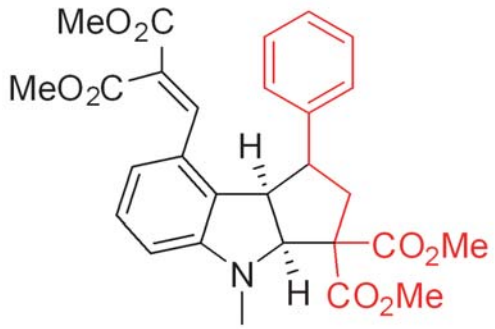
($CDCl_3$, 400 MHz)

```
NAME     zxz-692-1-20141007
EXPNO            10
PROCNO            1
Date_         20141007
Time              3.55
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                8
DS                2
SWH          8012.820 Hz
FIDRES       0.122266 Hz
AQ           4.0894966 sec
RG              101
DW           62.400 usec
DE            6.50 usec
TE            296.9 K
D1           1.00000000 sec
TD0               1

======== CHANNEL f1 ========
SFO1       400.1324710 MHz
NUC1              1H
P1            14.10 usec
SI             65536
SF         400.1300085 MHz
WDW               EM
SSB               0
LB            0.30 Hz
GB                0
PC            1.00
```



171.991
171.480
169.962
169.176
166.961
166.836
164.218
163.905
155.307
153.114
141.027
140.981
139.855
138.215
131.707
130.370
129.935
129.600
129.345
128.697
128.655
128.542
128.126
127.796
127.127
126.741
125.065
123.722
117.234
116.749
110.156
109.951

77.761
77.605
77.316
76.999
76.680
65.871
64.438
54.333
53.653
52.939
52.755
52.422
52.334
52.255
52.218
52.113
51.969
49.616
48.125
44.488
38.541
38.398
37.591

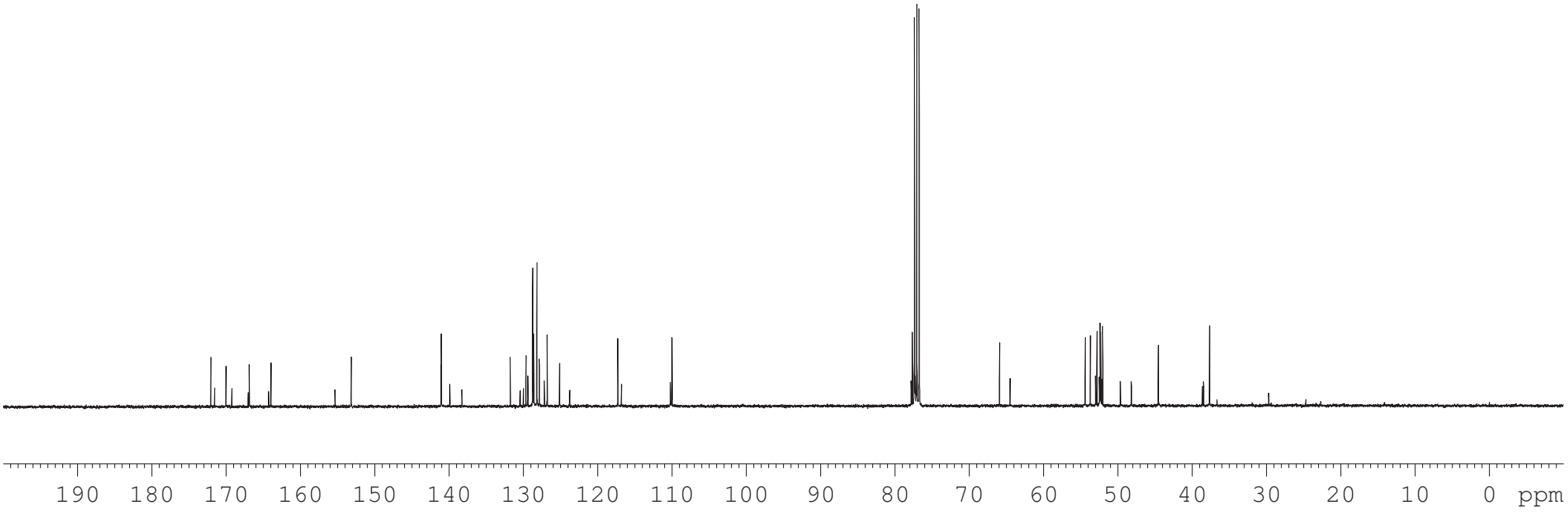


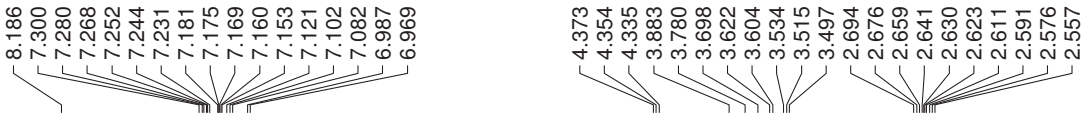
4aa

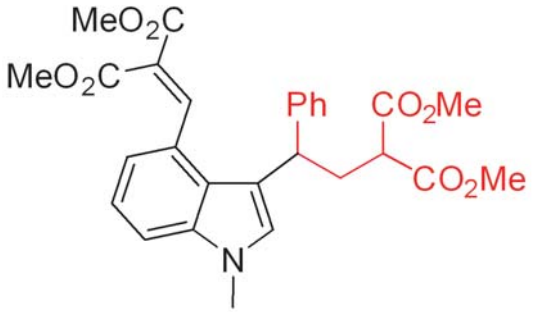
5:1 dr

($CDCl_3$, 101 MHz)

```
NAME        zxz-692-1-20141007
EXPNO                   11
PROCNO                   1
Date_              20141007
Time                   5.06
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1200
DS                        2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                      645
DW                   20.800 usec
DE                    6.50 usec
TE                   298.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                   12.00 usec
SI                    32768
SF             100.6127736 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



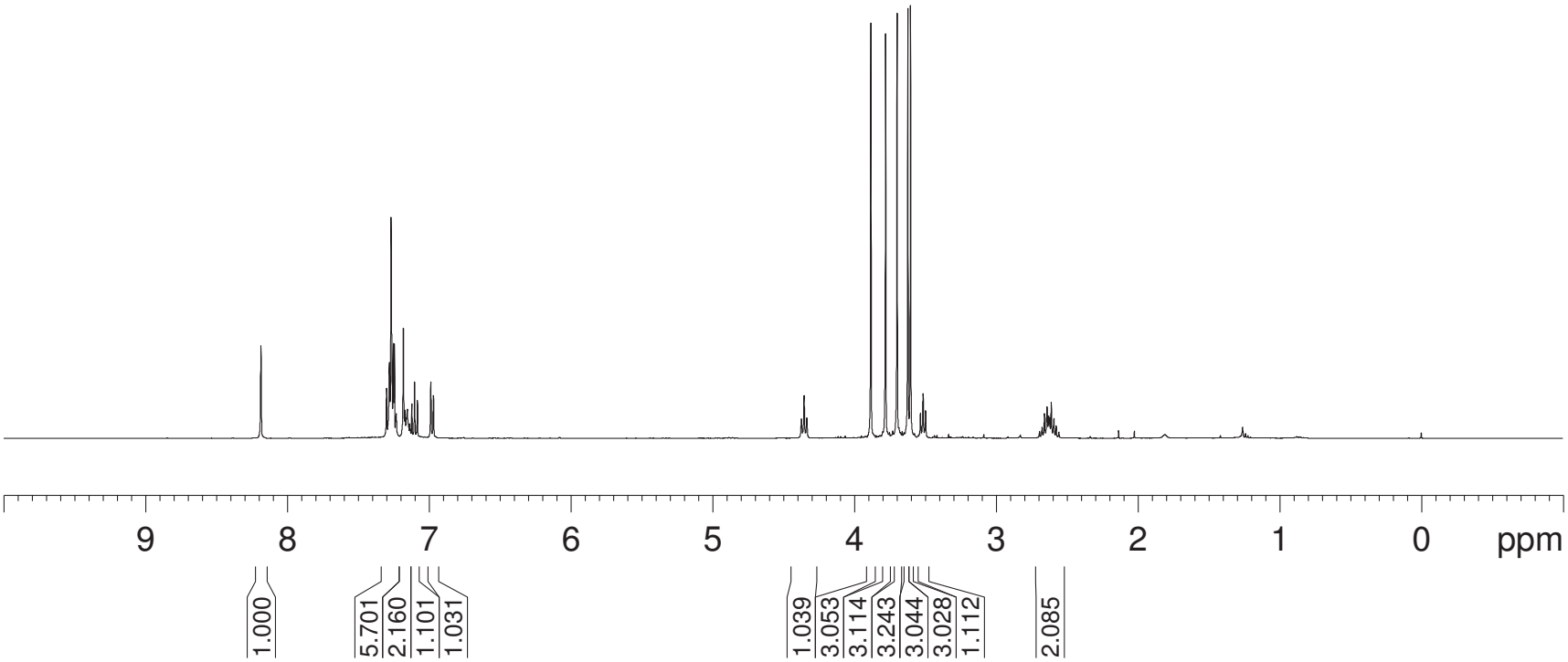


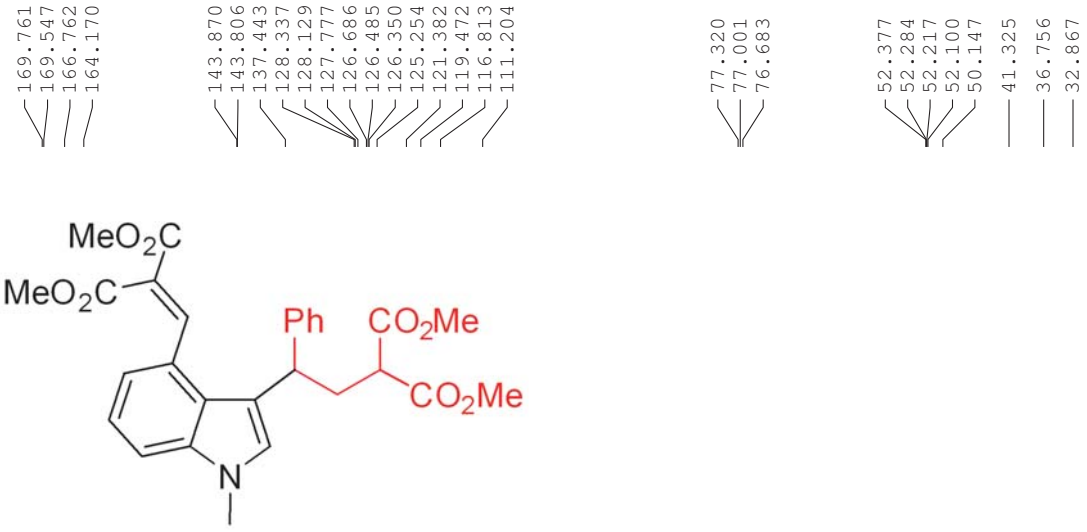


5aa

($CDCl_3$, 400 MHz)

```
NAME        zxz-638-fc
EXPNO            10
PROCNO            1
Date_        20140903
Time             9.04
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                4
DS                2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894966 sec
RG               32
DW               62.400 usec
DE               6.50 usec
TE               296.8 K
D1            1.00000000 sec
TD0               1

======== CHANNEL f1 ========
SFO1       400.1324710 MHz
NUC1              1H
P1               14.10 usec
SI              65536
SF         400.1300154 MHz
WDW               EM
SSB               0
LB             0.30 Hz
GB                0
PC             1.00
```

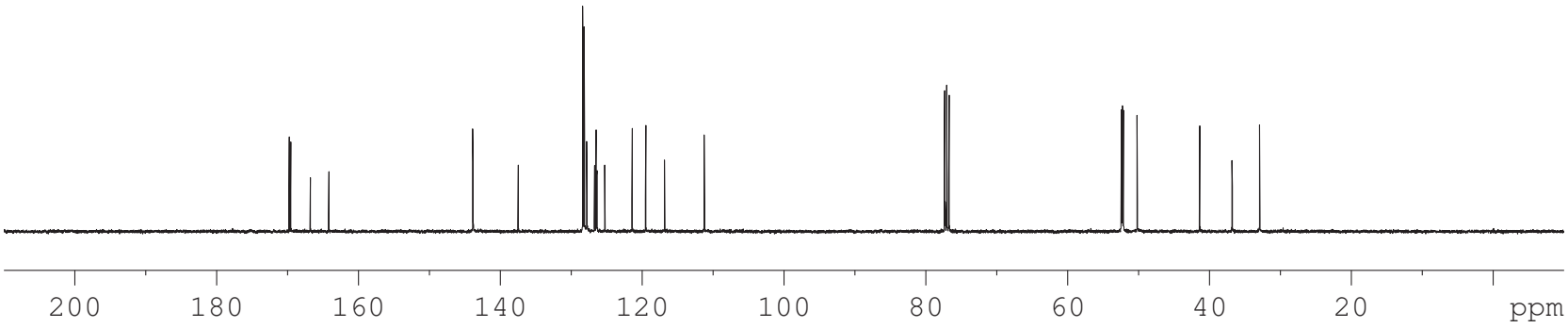


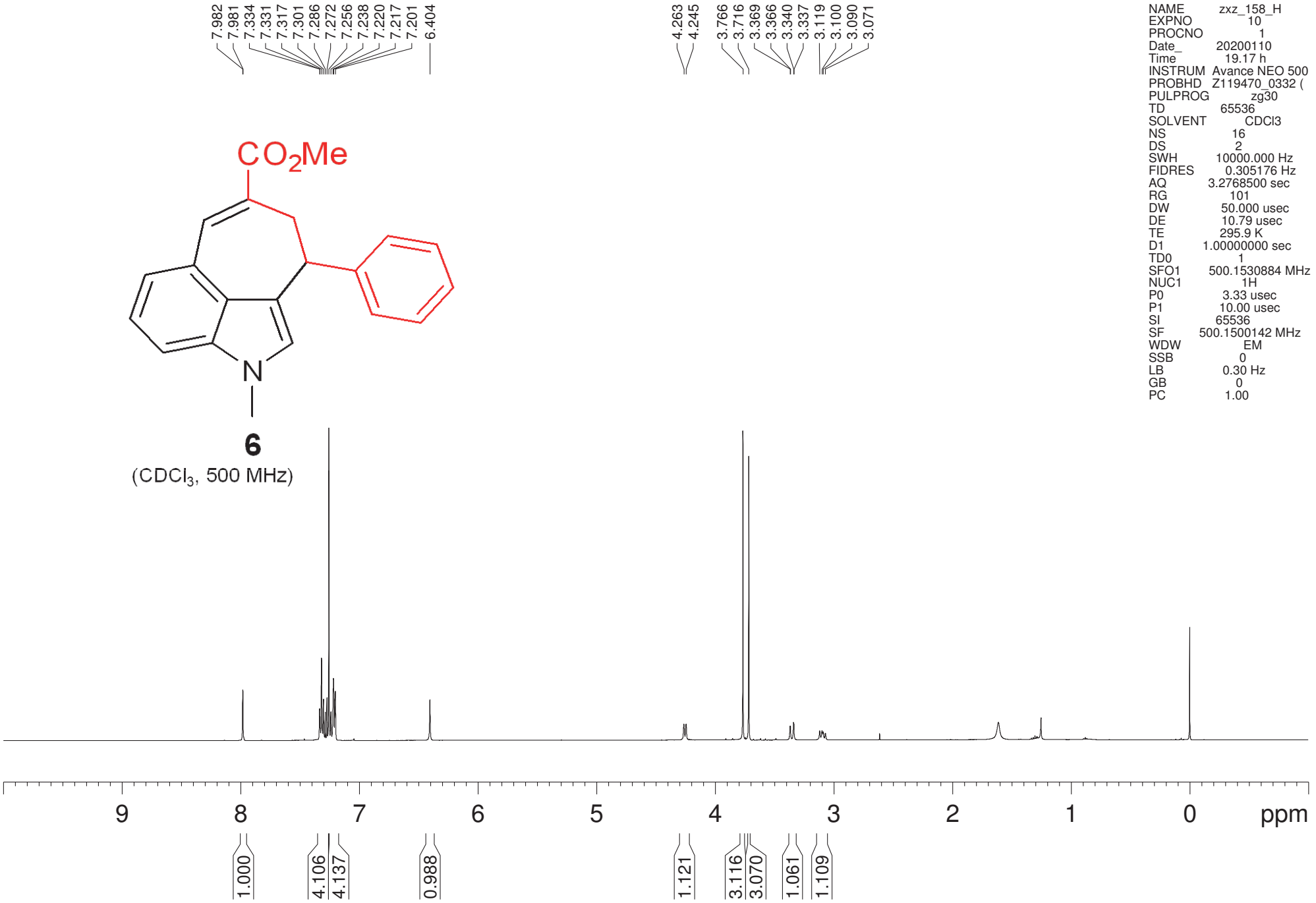


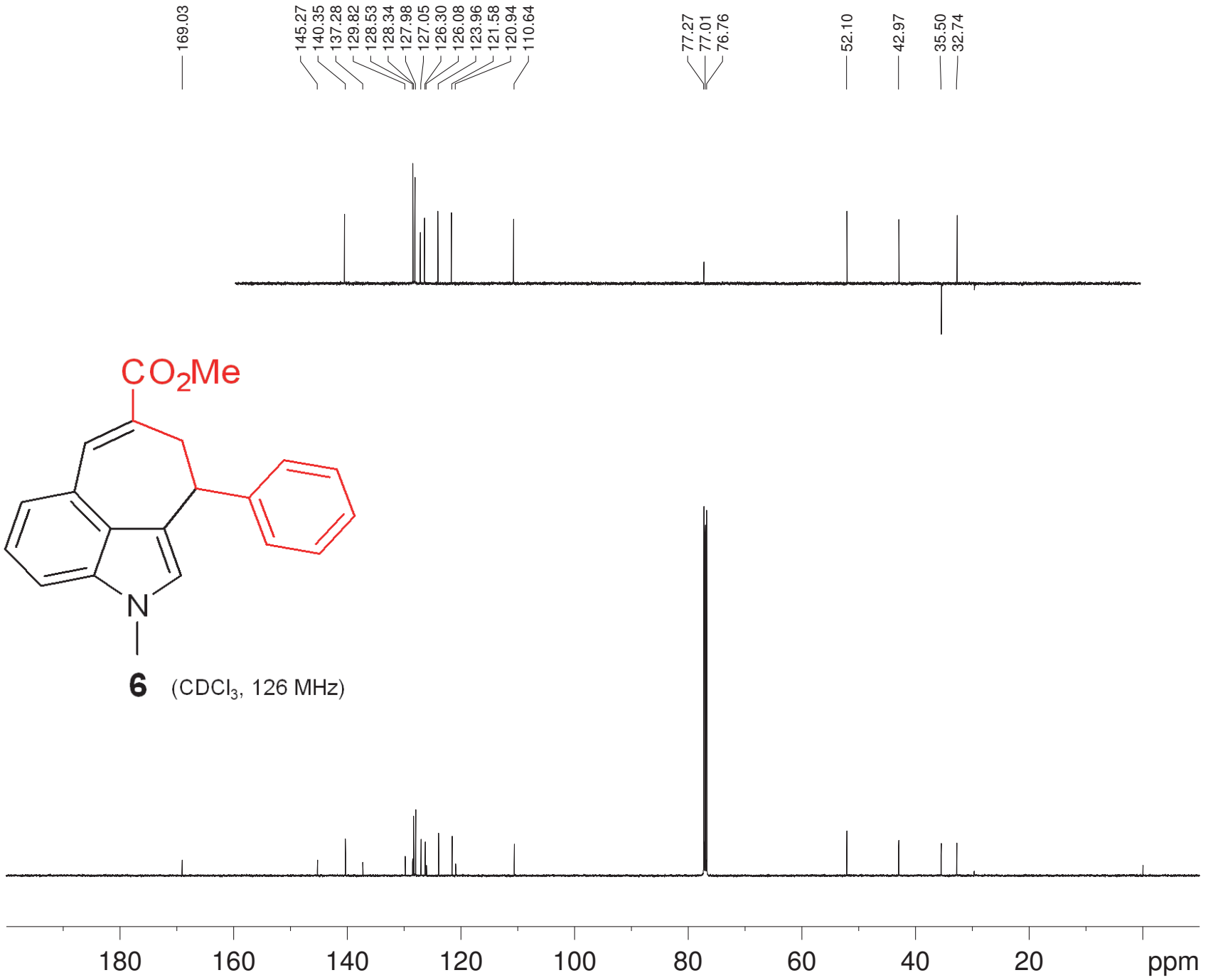
5aa

($CDCl_3$, 101 MHz)

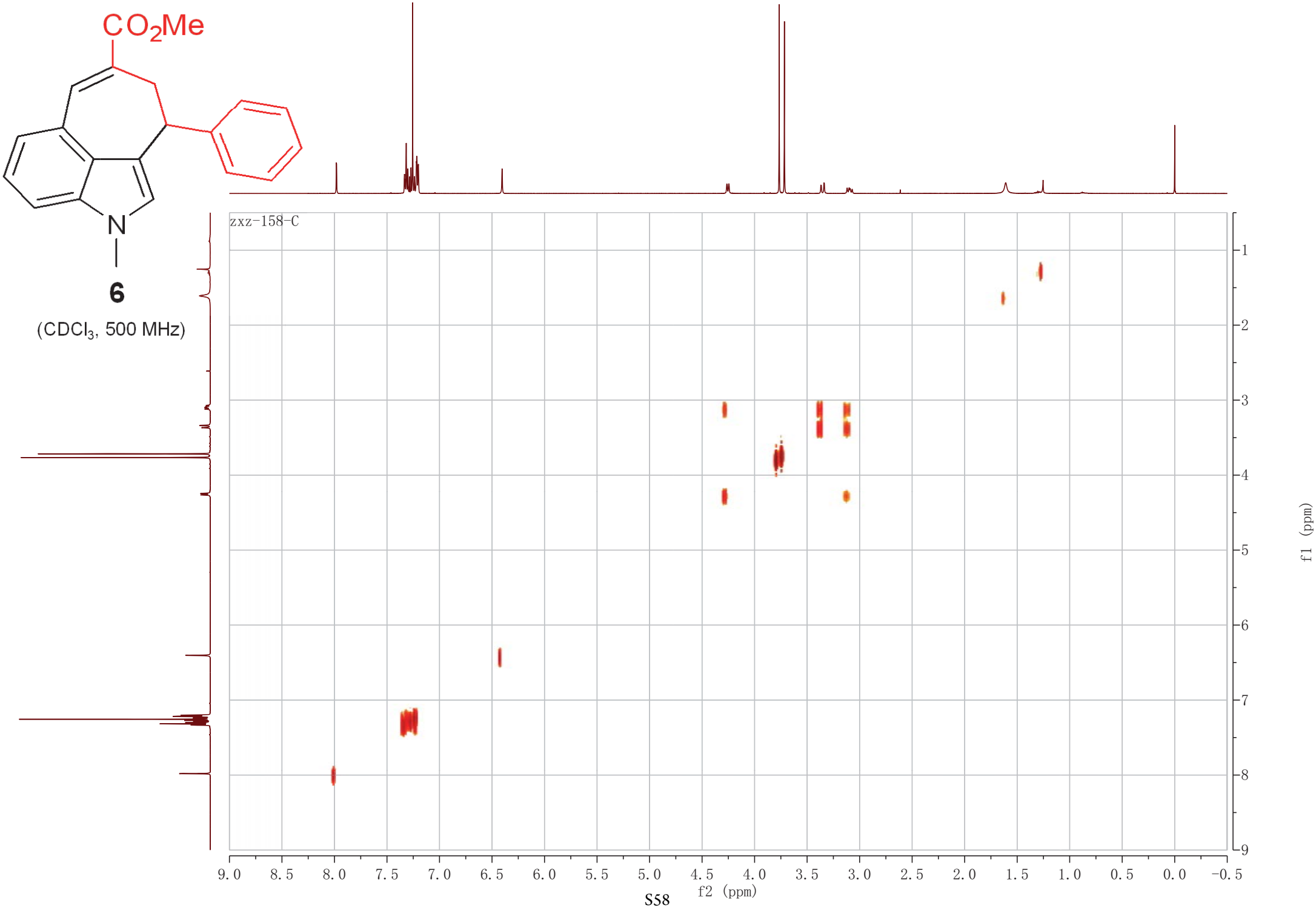
```
NAME          zxz-638-fc
EXPNO                 12
PROCNO                 1
Date_           20140903
Time                9.17
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 1620
DW                20.800 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                12.00 usec
SI                32768
SF          100.6127839 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

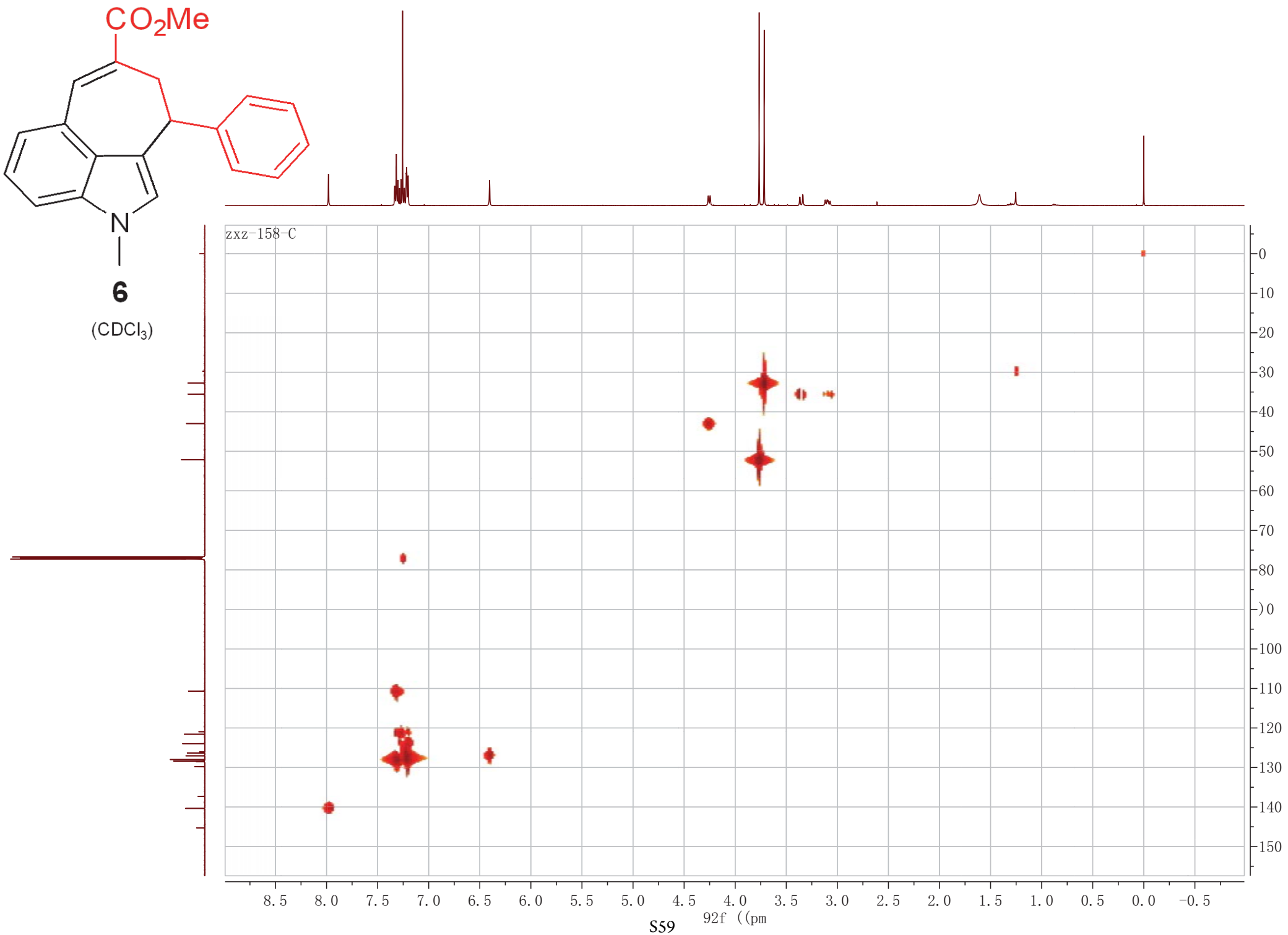



7.982
7.981
7.334
7.331
7.317
7.301
7.286
7.272
7.256
7.238
7.220
7.217
7.201
6.404
4.263
4.245
3.766
3.716
3.369
3.366
3.340
3.337
3.119
3.100
3.090
3.071
NAME zxz_158_H
EXPNO 10
PROCNO 1
Date_ 20200110
Time 19.17 h
INSTRUM Avance NEO 500
PROBHD Z119470_0332 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2768500 sec
RG 101
DW 50.000 usec
DE 10.79 usec
TE 295.9 K
D1 1.00000000 sec
TD0 1
SFO1 500.1530884 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
SI 65536
SF 500.1500142 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
CO2Me
N
6
(CDCl3, 500 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.000
4.106
4.137
0.988
1.121
3.116
3.070
1.061
1.109



NAME	zxz-158-C
EXPNO	11
PROCNO	1
Date_	20200111
Time	0.48 h
INSTRUM	Avance NEO 500
PROBHD	Z119470_0332 (
PULPROG	deptsp135
TD	65536
SOLVENT	CDCl3
NS	500
DS	8
SWH	20000.000 Hz
FIDRES	0.610352 Hz
AQ	1.6384500 sec
RG	101
DW	25.000 usec
DE	6.50 usec
TE	296.5 K
CNST2	145.0000000
D1	2.00000000 sec
D2	0.00344828 sec
D12	0.00002000 sec
TD0	1
SFO1	125.7728786 MHz
NUC1	13C
P1	10.00 usec
P13	2000.00 usec
SI	32768
SF	125.7628175 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40


CO2Me
N
6
(CDCl3, 500 MHz)
zxz-158-C
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 -0.5
f2 (ppm)
1 2 3 4 5 6 7 8 9
f1 (ppm)


CO2Me
N
6
(CDCl3)
zxz-158-C
0
10
20
30
40
50
60
70
80
)0
100
110
120
130
140
150
91f ((pm
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
-0.5
92f ((pm