Cycloaddition Cascades of Strained Cyclic Alkynes and Oxadiazinones

Melissa Ramirez,† Evan R. Darzi,† Joyann S. Donaldson, K. N. Houk,* and Neil K. Garg*

Department of Chemistry and Biochemistry, University of California

Los Angeles, California 90095, United States

Supporting Information – Table of Contents

Part I: Experimental Section.....S2
Materials and Methods.....S2
Experimental Procedures.....S3
A. Comparison of Reactivities: Benzyne vs. Cyclohexyne.....S3
B. One Pot Reaction.....S4
C. Synthesis of *N*-Boc Piperidyne Precursor.....S5
D. Synthesis of Pyrone Intermediates.....S6
E. Synthesis of Tricyclic Products.....S9
F. Synthesis of Pentacene and Tetracene Precursors.....S15
G. Aryne Addition to PAH Scaffold.....S17
NMR Spectra.....S19
^{1}H NMR Spectra.....S19
^{13}C NMR Spectra.....S42
Crystallographic Information.....S63

Part II: Computational Section.....S65
A. Complete Citation for Gaussian 16.....S65
B. HOMO and LUMO Energies.....S65
C. Transition State Structures and D/IAS Analysis.....S66
DA1.....S66
r-DA1.....S69
DA2.....S74
D. Substituent Effects on DA1 and DA2.....S75
E. Free Energy Profiles.....S78
F. Cartesian Coordinates and Energies of Optimized Structures.....81

References.....S106

Part I: Experimental Section

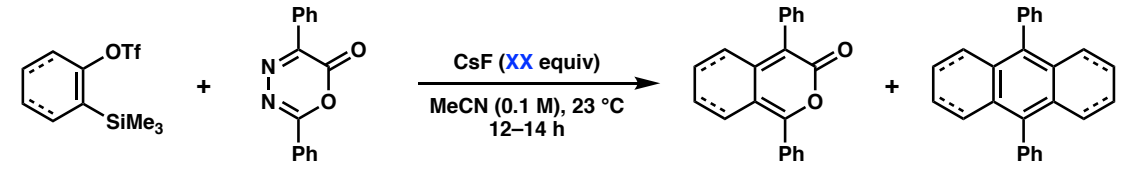
Materials and methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (passed through activated alumina columns). All commercially available reagents were used as received unless otherwise specified. Cesium fluoride (CsF), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (**20**), 2*H*-pyran-2-one (**49**), Garg 4,5-indolyne precursor (**60**), and benzyl 4-(trifluoromethylsulfonyloxy)-3-(trimethylsilyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (**61**) were obtained from Sigma–Aldrich. The Sigma–Aldrich product numbers are as follows: 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**20**): 470430; ; 2*H*-pyran-2-one (**49**): 463159; Garg 4,5-indolyne precursor (**60**): 795569; benzyl 4-(trifluoromethylsulfonyloxy)-3-(trimethylsilyl)-5,6-dihydropyridine-1(2*H*)-carboxylate (**61**): 803928. The TCI product number for 1-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate (precursor to **59**) is T2465. The Combi-Blocks product number for 3-bromo-4-oxo-piperidine-1-carboxylic acid tert-butyl ester (**52**) is ST-3851. Oxadiazinones **2**,[7] **43**,[7] **44**,[7] **45**,[7] and **46**[7] and silyl triflates **21**,[1] **47**,[2] and **62**[3] are known compounds and were prepared following literature procedures. The ^{1}H-NMR spectral data matched those reported in the literature. Unless stated otherwise, reactions were performed at room temperature (approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV, anisaldehyde, and potassium permanganate staining. Silicycle silica gel 60 (particle size 0.040–0.063 mm) was used for flash column chromatography. Compound **54** was purified using Yamazen Smart Flash AKROS with ELS detector and Universal columns and compounds **55** and **56** were purified using a Teledyne ISCO CombiFlash® NextGen™ instrument using RediSep Rf high-performance silica gold columns (24 g, catalog No. 692203346, 12 g, catalog No. 692203345). ^{1}H NMR spectra were recorded on Bruker spectrometers (at 100, 125, 400, and 500 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectra are reported in terms of chemical shift (at 125 MHz). High-resolution mass spectra were obtained on Thermo Scientific™ Exactive Mass Spectrometers with DART ID-CUBE. X-ray structures shown in Figure 9 of the manuscript were created using CYLview. IR spectra were obtained on a Perkin-Elmer UATR Two FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-}

[1]). Uncorrected melting points were measured using a Digimelt MPA160 melting point apparatus. DART-MS spectra were collected on a Thermo Exactive Plus MSD (Thermo Scientific) equipped with an ID-CUBE ion source and a Vapur Interface (IonSense Inc.). Both the source and MSD were controlled by Excalibur software v. 3.0. The analyte was spotted onto OpenSpot sampling cards (IonSense Inc.) using CH_2Cl_2 as the solvent. Ionization was accomplished using UHP He (Airgas Inc.) plasma with no additional ionization agents. The mass calibration was carried out using Pierce LTQ Velos ESI (+) and (–) Ion calibration solutions (Thermo Fisher Scientific).

Experimental Procedures

A. Comparison of Reactivities: Benzyne vs. Cyclohexyne

General Procedure A for Comparison of the Reactivities of Benzyne vs. Cyclohexyne (Reaction of Silyl Triflate 29 and Oxadiazinone 2 is used as an example, Figure S1, Entry 6). To a stirred solution of silyl triflate **21** (22.5 mg, 0.0744 mmol, 1.0 equiv) and oxadiazinone **2** (37.5 mg, 0.15 mmol, 2.0 equiv) in MeCN (1.5 mL, 0.1 M) was added CsF (56.5 mg, 0.372 mmol, 5.0 equiv). The reaction was purged with nitrogen for ten minutes before being sealed with a Teflon cap and left to stir at 23 °C. After 14 h, the reaction mixture was filtered through celite (monster pipette, 4 cm tall) with EtOAc (10 mL) as the eluent and then concentrated under reduced pressure. 75% yield of pyrone **29** and 4% yield of tricycle **35** were obtained as determined using ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an external standard. See pages S7 and S10 for the tabulated ^{1}H NMR data of pyrone **29** and tricycle **35**, respectively). Spectral data for tricycle **35**[4] match those previously reported. Purification of the crude material via flash chromatography (Isco 4g gold, 0 → 100% EtOAc) afforded pyrone **29** (75% yield) as a yellow solid. Pyrone **29**: R_f 0.32, (9:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, CD_3Cl): 7.62–7.59 (m, 2H), 7.48–7.42 (m, 5H), 7.38–7.34 (m, 1H), 7.30–7.27 (m, 2H), 2.68–2.65 (t, 2H), 2.53–2.49 (t, 2H), 1.68–1.64 (m, 4H). The spectral data matched those previously reported in the literature.[4]



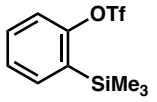
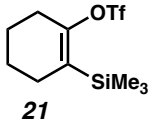
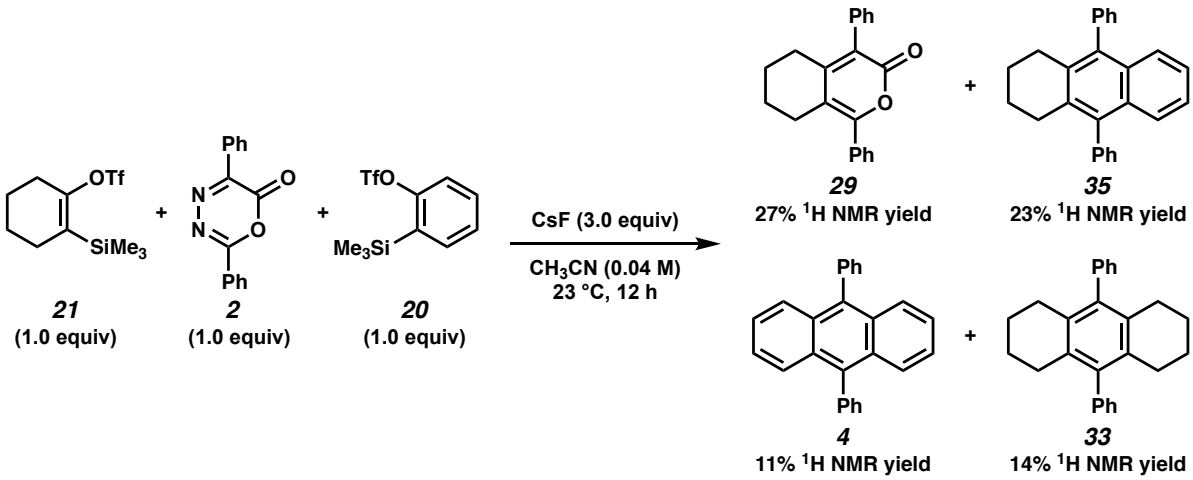
Entry	Strained Alkyne Precursor	Equivs of Silyl Triflate	Equivs of CsF	Yield of 16	Yield of 18
1	 20	2	10	0%	33%
2		1	5	0%	28%
3		0.5	2.5	0%	33%
4	 21	2	10	4%	25%
5		1	5	34%	20%
6		0.5	2.5	75%	4%

Figure S1. Comparison of the reactivities of benzyne (derived from **20**) and cyclohexyne (derived from **21**) with oxadiazinone **2**. Yields determined using ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an external standard.

B. One Pot Reaction

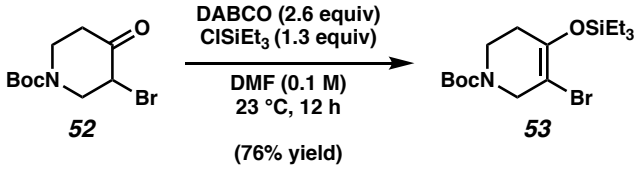
Procedure for One Pot Reaction of Silyl Triflates



To a stirred solution of silyl triflate **21** (25.0 mg, 0.0827 mmol, 1.0 equiv), oxadiazinone **2** (20.7 mg, 0.0827 mmol, 1.0 equiv), and silyl triflate **20** (24.7 mg, 0.0827 mmol, 1.0 equiv), in MeCN (2.1 mL, 0.04 M) was added CsF (37.7 mg, 0.248 mmol, 3.0 equiv). The reaction was purged with

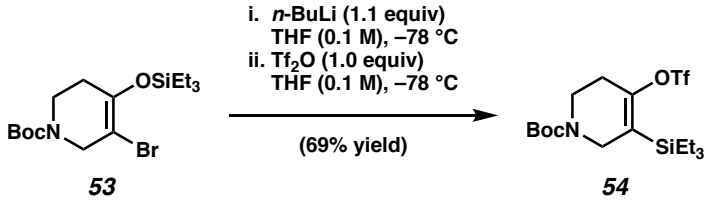
nitrogen for ten minutes before being sealed with a Teflon cap and left to stir at 23 °C. After 12 h, the reaction mixture was filtered through celite (monster pipette, 4 cm tall) with EtOAc (10 mL) as the eluent and then concentrated under reduced pressure. Yields of pyrone **29**, tricycle **35**, 9,10-diphenylanthracene (**4**), and tricycle **33** were determined using ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an external standard. See pages S7, S11, and S10 for the tabulated ^{1}H NMR data of pyrone **29**, tricycle **33**, and tricycle **35**, respectively. Spectral data for pyrone **29**, tricycles **35**,[4] and **33**,[4] and 1,9-diphenylanthracene (**4**)[5] match those previously reported.

C. Synthesis of *N*-Boc Piperidyne Precursor



Bromo silyl enol ether 53. A heterogenous solution of known bromoketone **52** (900 mg, 3.24 mmol, 1.0 equiv) in DMF (11.0 mL, 0.1 M) was sonicated until all solids dissolved. To the solution was added $SiEt_3Cl$ (780 mg, 5.18 mmol, 1.3 equiv) dropwise at 23 °C. Next, DABCO (835 mg, 7.44 mmol, 2.30 equiv) was added to the reaction. The resulting mixture was allowed to stir at 23 °C. After 12 h, the reaction mixture was quenched with sat. $NaHCO_3$ (1 mL) and water (4 mL) and extracted with Et_2O (3 x 4 mL). The combined organic layers were washed with water (1 x 15 mL) and brine (1 x 15 mL), dried with sodium sulfate, filtered, and concentrated under reduced pressure to provide the crude reaction mixture. Purification of the crude material via flash chromatography (100:1 hexanes:EtOAc → 40:1 hexanes:EtOAc) afforded silyl enol ether **53** (76% isolated yield) as a clear oil. Bromo silyl enol ether **53**: R_f 0.67 (5:1 hexanes:EtOAc); ^{1}H-NMR (600 MHz, $CDCl_3$): δ 4.07 (br s, 2H), 3.57 (br s, 2H), 2.28 (br s, 2H), 1.46 (s, 9H), 1.00 (t, J = 7.9, 9H), 0.71 (q, J = 7.9, 6H). The spectral data matched those previously reported in the literature.[6]

*Note: Bromo silyl enol ether **53** was obtained as a mixture of rotamers. These data represent empirically observed chemical shifts from the ^{1}H NMR spectrum.*



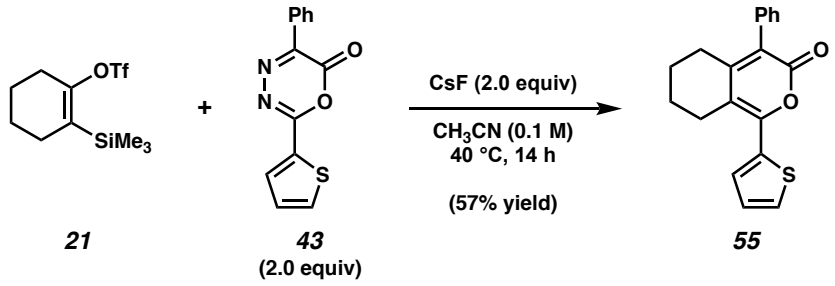
53 ***54***

Silyl triflate 54. A solution of silyl enol ether **53** (470 mg, 1.20 mmol, 1.0 equiv) in THF (12.0 mL) was cooled to –78 °C. To the solution was added *n*-BuLi (0.575 mL, 1.32 mmol, 1.10 equiv, 2.29 M) dropwise at –78 °C over 30 min. The resulting mixture was stirred at –78 °C for 1.5 h. Next, Tf_2O (0.202 mL, 0.100 mmol, 1.00 equiv) was added dropwise at –78 °C over 20 minutes. After stirring for 12 h at –78 °C, the reaction was quenched with sat. $NaHCO_3$ (1 mL) and allowed to warm to room temperature. After 1 h, the reaction was diluted with water (15 mL) and extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with water (15 mL) and brine (15 mL), dried with sodium sulfate, and concentrated under reduced pressure to provide the crude reaction mixture. Purification of the crude material via flash chromatography (Yamazen, 8g SiO_2, 9:1 hexanes:EtOAc) afforded silyl triflate **54** (69% isolated yield) as a clear oil. Silyl triflate **54**: R_f 0.44 (9:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.01 (br s, 2H), 3.57 (m, 2H), 2.53 (m, 2H), 1.46 (s, 9H), 0.97–0.94 (t, J = 7.7, 9H), 0.77–0.72 (q, J = 7.9, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): 154.3, 124.2, 122.1, 119.6, 117.1, 114.5, 80.5, 45.7, 45.3, 40.9, 40.2, 28.4, 7.36, 6.77, 6.74, 5.60, 5.10, 2.83; IR (film): 2957, 2884, 1699, 1413, 1264 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{17}H_{30}F_3NO_5SSi^+$, 446.16388; found 446.16418.

*Note: Silyl triflate **54** was obtained as a mixture of rotamers. These data represent empirically observed chemical shifts from the ^{1}H and ^{13}C NMR spectrum.*

D. Synthesis of Pyrone Intermediates

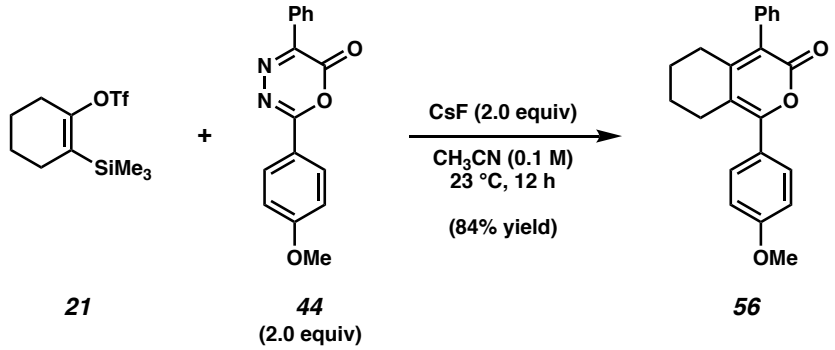
General Procedure B (Preparation of pyrone 55 is used as an example).



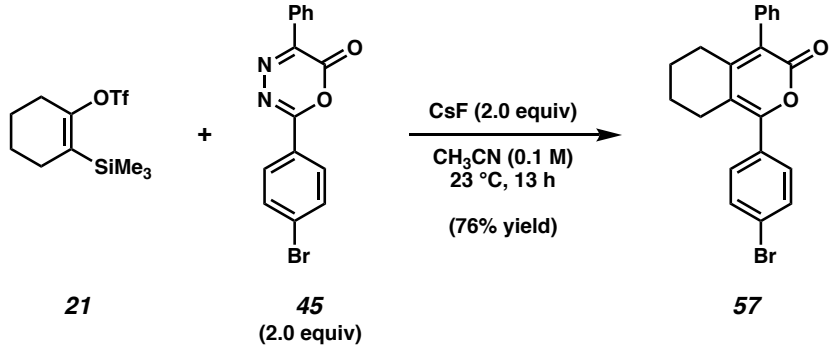
21 ***43*** (2.0 equiv) ***55***

Pyrone 55. To a stirred solution of silyl triflate **21** (45.4 mg, 0.150 mmol, 1.0 equiv) and oxadiazinone **43** (76.9 mg, 0.300 mmol, 2.0 equiv) in MeCN (1.5 mL, 0.1 M) was added CsF (45.6 mg, 0.300 mmol, 2.0 equiv). The reaction was purged with nitrogen for ten minutes before being sealed with a Teflon cap and left to stir at 40 °C. After 14 h, the reaction mixture was filtered through celite (monster pipette, 4 cm tall) with EtOAc (10 mL) as the eluent and then concentrated under reduced pressure. Purification of the crude material via flash chromatography (Isco 4g gold, 0 → 100% EtOAc) afforded pyrone **55** (57% yield, average of two experiments) as a yellow solid. Pyrone **55**: mp 100–104 °C , R_f 0.33 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.66–7.64 (dd, *J* = 3.9, 1.1, 1H), δ 7.53–7.52 (dd, *J* = 5.1, 1.2, 1H), δ 7.45–7.41 (m, 2H), δ 7.37–7.33 (m, 1H), δ 7.27–7.26 (m, 1H), δ 7.25–7.24 (m, 1H), δ 7.27–7.26 (m, 1H), δ 2.83–2.80 (t, *J* = 6.6, 2H), δ 2.50–2.46 (t, *J* = 6.5, 2H), δ 1.82–1.76 (m, 2H), δ1.67–1.61 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 161.3, 153.8, 150.6, 135.0, 134.6, 129.9, 129.4, 129.0, 128.7, 128.1, 127.6, 124.0, 113.0, 29.5, 26.0, 22.4, 21.7; IR (film): 3623, 3546, 1702, 1524, 1443 cm $^{-1}$; HRMS–APCI (*m/z*) $[M + H]^+$ calcd for $C_{19}H_{17}O_2S^+$, 309.0944; found, 309.0916.

Any modification of the conditions shown in the representative procedure above are specified in the corresponding reaction scheme.

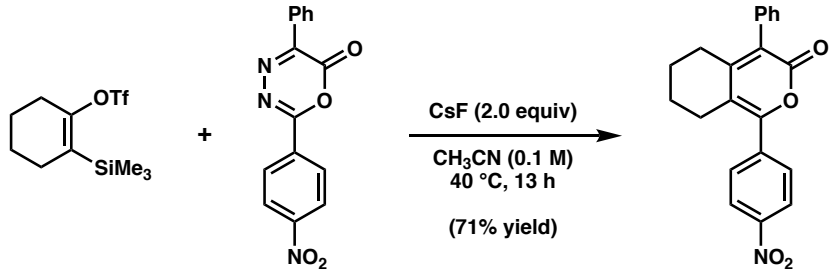


Pyrone 56. Followed General Procedure B using silyl triflate **21** (45 mg, 150 μmol, 1.0 equiv) afforded, after purification via flash chromatography (Isco 4g gold, 0 → 100% EtOAc), pyrone **56** (84% yield, average of two experiments) as a light yellow solid. Pyrone **56**: mp 146–150 °C, R_f 0.24 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.59–7.55 (m, 2H), δ 7.45–7.41 (m, 2H), δ 7.37–7.33 (m, 1H), δ 7.29–7.25 (m, 2H), δ 6.98–6.94 (d, J = 8.9 2H), δ 3.86 (s, 3H), δ 2.68–2.65 (m, 2H), δ 2.51–2.47 (m, 2H), δ 1.67–1.64 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): 158.6, 140.3, 137.7, 137.5, 134.1, 133.7, 132.3, 131.6, 131.36, 131.33, 130.3, 128.6, 127.0, 126.2, 126.1, 124.7, 114.0, 55.4, 29.6, 29.5, 23.2, 23.1; IR (film): 1700, 1607, 1507, 1264, 1177 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{22}H_{21}O_3^+$, 333.1485; found 333.1456.



Pyrone 57. Followed General Procedure B using silyl triflate **21** (45 mg, 149 μmol, 1.0 equiv) afforded, after purification via flash chromatography (2:1 hexanes:EtOAc), pyrone **57** (76% yield, average of two experiments) as a light yellow solid. Pyrone **57**: mp 155–157 °C, R_f 0.72 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.60–7.58 (m, 2H), δ 7.50–7.42 (m, 4H), δ 7.38–7.34 (m, 1H), δ 7.28–7.26 (m, 2H), δ 2.65–2.62 (m, 2H), δ 2.52–2.49 (m, 2H), δ 1.68–1.64 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): 161.0, 154.1, 153.9, 134.3, 131.6, 131.5, 130.6, 129.7, 128.7,

128.1, 124.6, 124.2, 114.7, 28.5, 25.5, 22.0, 21.4; IR (film): 3058, 2939, 2864, 2246, 1698 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{21}H_{18}BrO_2^+$, 381.0452; found 381.0485.

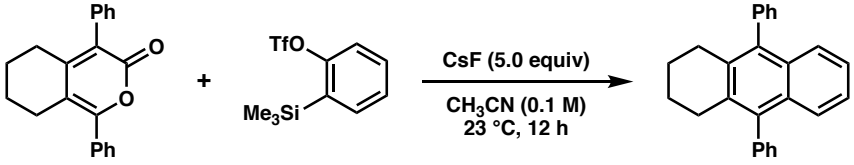


21 ***46*** (2.0 equiv) ***58***

Pyrone 58. Followed General Procedure B using silyl triflate **21** (45 mg, 149 μmol, 1.0 equiv) afforded, after purification via flash chromatography (2:1 hexanes:EtOAc), pyrone **58** (71% yield, average of two experiments) as a yellow foam. Pyrone **58**: R_f 0.26 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.33–8.31 (d, 2H), δ 7.82–7.80 (m, 2H), δ 7.47–7.44 (m, 2H), δ 7.40–7.37 (m, 1H), 7.29–7.27 (m, 2H), δ 2.69–2.67 (t, J = 6.6, 2H), δ 2.55–2.53 (t, J = 6.7, 2H), δ 1.70–1.69 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): 161.5, 153.6, 152.4, 148.1, 138.5, 133.9, 130.1, 129.6, 128.7, 128.3, 125.7, 123.6, 116.2, 28.5, 25.5, 21.8, 21.3; IR (film): 3063, 2939, 2865, 1705, 1520 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{21}H_{18}NO_4^+$, 348.1230; found 348.1200.

E. Synthesis of Tricyclic Products

General Procedure C (Preparation of cycloadduct 35 is used as an example).

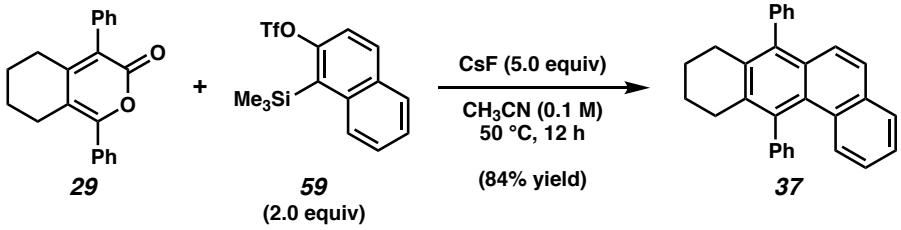


29 ***20*** (2.0 equiv) ***35***

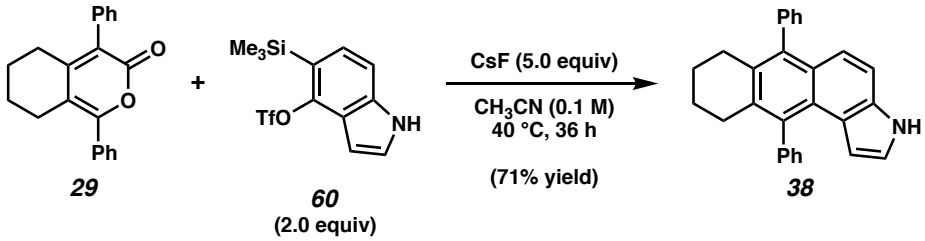
Cycloadduct 35. To a stirred solution of pyrone **29** (30 mg, 99.2 μmol, 1.0 equiv) and silyl triflate **20** (59.2 mg, 0.20 mmol, 2.0 equiv) in MeCN (1.0 mL, 0.1 M) was added CsF (75 mg, 0.50 mmol, 5.0 equiv). The reaction was purged with nitrogen for ten minutes before being sealed with a Teflon cap and left to stir at 23 °C. After 12 h, the reaction mixture was filtered through celite (monster pipette, 4 cm tall) with EtOAc (10 mL) as the eluent and then concentrated under reduced pressure.

Purification of the crude material via flash chromatography (100:1 hexanes:Et_2O) afforded cycloadduct **35** (86% yield, average of two experiments) as a white solid. Cycloadduct **35**: mp > 260 °C, R_f 0.59 (20:1 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.53 (t, J = 7.5, 4H), 7.46–7.43 (m, 2H), 7.35–7.31 (m, 6H), 7.24–7.22 (q, J = 3.3, 2H), 2.63 (s, 4H), 1.71 (s, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): 140.3, 137.8, 133.7, 131.3, 130.3, 128.6, 127.0, 126.1, 124.7, 29.5, 23.1. The spectral data matched those previously reported in the literature.[4]

Any modification of the conditions shown in the representative procedure above are specified in the following scheme

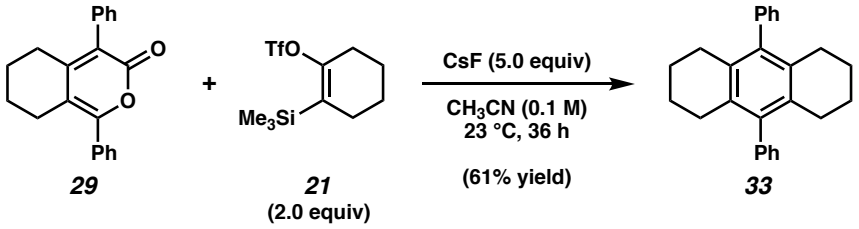


Cycloadduct 37. Followed General Procedure C using pyrone **29** (50 mg, 0.165 mmol, 1.0 equiv) afforded, after purification via flash chromatography (100:1 hexanes:Et_2O), cycloadduct **37** (84% yield, average of two experiments) as a white solid. Cycloadduct **37**: mp 189–193 °C, R_f 0.47 (20:1 hexanes:Et_2O); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.71–7.69 (dd, J = 8.0, 1.4, 1H), 7.56–7.52 (m, 4H), 7.35–7.29 (m, 6H), 7.01–6.98 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): 144.1, 140.8, 139.1, 138.5, 135.4, 134.3, 133.1, 130.7, 130.3, 130.2, 129.9, 129.4, 128.6, 128.24, 128.23, 127.1, 127.0, 126.9, 126.3, 125.35, 125.33, 124.8, 30.1, 29.7, 23.3, 22.8; IR (film): 3055, 3025, 2931, 2856, 1441 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{30}H_{24}^+$, 385.19508; found 385.19522.

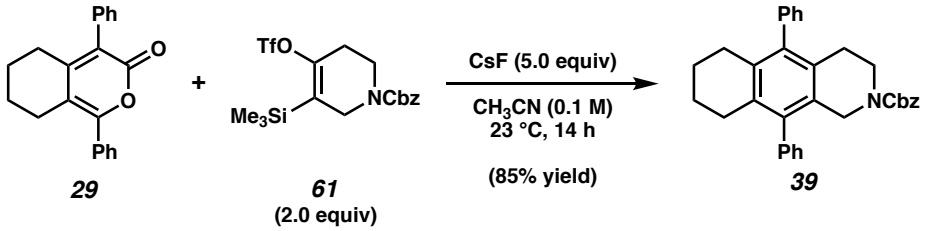


Cycloadduct 38. Followed General Procedure C using pyrone **29** (40 mg, 0.132 mmol, 1.0 equiv) afforded, after purification via flash chromatography (100% hexanes → 5:1 hexanes:Et_2O),

cycloadduct **38** (71% yield, average of two experiments) as a light yellow solid. Cycloadduct **38**: mp >260 °C, R_f 0.60 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, CD_3Cl): δ 8.22 (s, 1H), 7.58–7.51 (m, 5H), 7.46–7.43 (m, 1H), 7.40–7.39 (d, *J* = 7.0, 2H), 7.34–7.33 (d, *J* = 7.0, 2H), 7.28–7.27 (d, *J* = 9.2, 1H), 7.14–7.12 (d, *J* = 9.2, 1H), 6.84–6.83 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): 143.3, 141.6, 138.8, 136.8, 133.8, 132.8, 130.7, 130.4, 130.2, 129.2, 128.5, 127.4, 127.1, 126.7, 125.7, 121.9, 121.7, 120.5, 111.9, 105.7, 29.5, 23.4, 23.3; IR (film): 2991, 1421, 1264, 895, 731 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{28}H_{23}N^+$, 374.19033; found 374.19000.



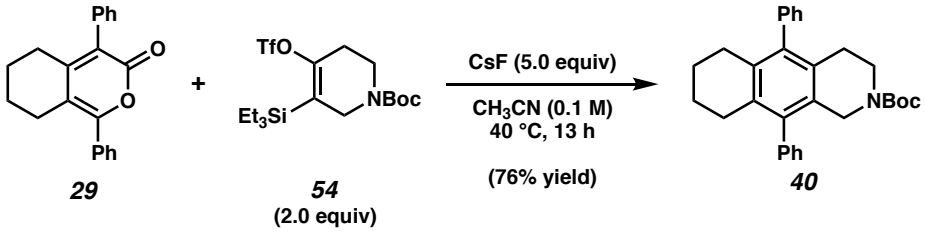
Cycloadduct 33. Followed General Procedure C using pyrone **29** (40 mg, 0.132 mmol, 1.0 equiv) afforded, after purification via flash chromatography (100:1 hexanes:CH_2Cl_2), cycloadduct **33** (61% yield, average of two experiments) as a white solid. Cycloadduct **33**: R_f 0.32, (9:1 hexanes:EtOAc); ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62–7.59 (m, 2H), 7.48–7.42 (m, 5H), 7.38–7.34 (m, 1 H), 7.30–7.27 (m, 2H), 2.68–2.65 (m, 2H), 2.53–2.49 (m, 2H), 1.68–1.64 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): 162.2, 155.4, 154.0, 134.5, 132.7, 129.8, 129.7, 129.1, 128.7, 128.3, 128.0, 124.2, 114.3, 28.5, 25.4, 22.1, 21.5. The spectral data matched those previously reported in the literature.[4]



Cycloadduct 39. Followed General Procedure C using pyrone **29** (40 mg, 0.132 mmol, 1.0 equiv) afforded, after purification via flash chromatography (100% hexanes → 9:1 hexanes:EtOAc), cycloadduct **39** (85% yield, average of two experiments) as a yellow foam. Cycloadduct **39**: R_f 0.60 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.45–7.42 (m, 4H), 7.36–7.29 (m, 6H),

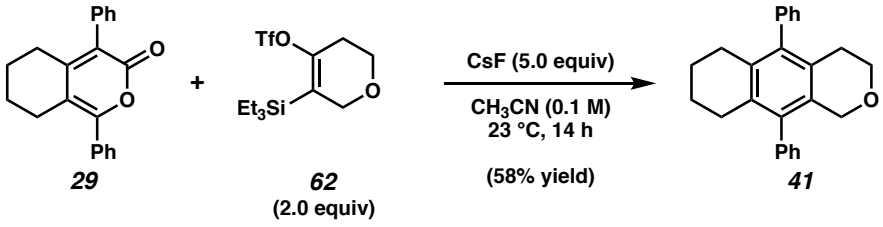
7.19–7.16 (m, 5H), 5.05 (s, 1H), 4.23 (s, 2H), 3.53–3.51 (t, J = 6.0, 2 H), 2.46–2.43 (m, 2H), 2.36 (s, 4H), 1.60 (s, 4H). Spectral data matched those previously reported for tricycle **39**.[7]

*Note: Cycloadduct **39** was obtained as a mixture of rotamers. This data represent empirically observed chemical shifts from the ^{1}H NMR spectra.*



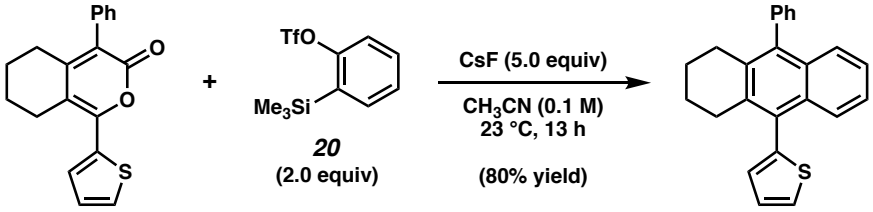
Cycloadduct 40. Followed General Procedure C using pyrone **29** (40 mg, 0.132 mmol, 1.0 equiv) afforded, after purification via flash chromatography (100% PhH), cycloadduct **40** (76% yield, average of two experiments) as a white foam. Cycloadduct **40**: R_f 0.86 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.45 (t, 4H), 7.36–7.34 (m, 2H), 7.20–7.17 (m, 4H), 4.14 (s, 1H), 3.46 (t, J = 7.4, 2H), 2.37–2.44 (m, 6H), 1.61 (s, 3H), 1.36 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): 154.6, 140.6, 139.5, 133.2, 129.2, 128.9, 128.6, 127.0, 126.7, 79.3, 44.9, 41.7, 40.8, 28.9, 28.6, 28.4, 23.06, 23.03; IR (film): 2971, 2930, 1738, 1697, 1365, 1216, 1168, 702 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{30}H_{33}NO_2^+$, 440.2584; found 440.2585.

*Note: Cycloadduct **40** was obtained as a mixture of rotamers. These data represent empirically observed chemical shifts from the ^{1}H NMR and ^{13}C NMR spectra.*



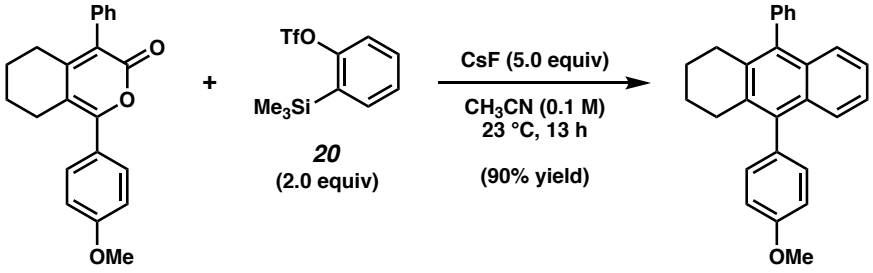
Cycloadduct 41. Followed General Procedure C using pyrone **29** (40 mg, 0.132 mmol, 1.0 equiv) afforded, after purification via flash chromatography (100% PhH), cycloadduct **41** (58% yield, average of two experiments) as a white foam. Cycloadduct **41**: mp >260 °C, R_f 0.75 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.46–7.42 (m, 4H), 7.37–7.34 (m, 2H), 7.21–

7.17 (m, 4H), 4.35 (s, 2H), 3.78 (t, *J* = 5.7, 2H), 2.41 (t, *J* = 5.7, 2H), 2.37–2.34 (m, 4H), 1.63–1.60 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): 140.9, 140.4, 139.2, 137.9, 133.5, 133.0, 130.0, 129.0, 128.8, 128.7, 127.1, 126.8, 67.6, 65.4, 28.9, 28.5, 27.8; IR (film): 3058, 2931, 2857, 1441, 1119 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{25}H_{24}O^+$, 341.1899; found 341.1894.



55 ***63***

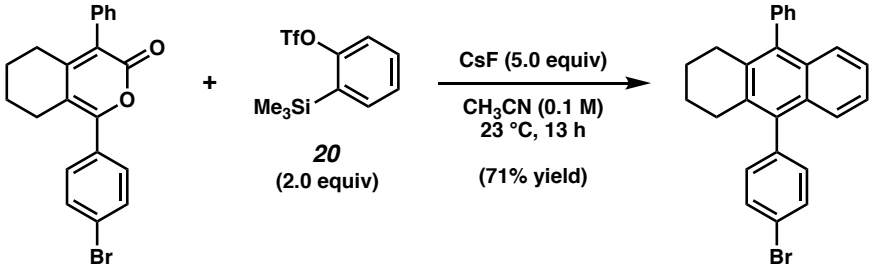
Cycloadduct 63. Followed General Procedure C using pyrone **55** (20 mg, 64.9 μmol, 1.0 equiv) afforded, after purification via flash chromatography (4:1 hexanes:EtOAc), cycloadduct **63** (80% yield, average of two experiments) as a light yellow solid. Cycloadduct **63**: mp 196–198 °C, R_f 0.66 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.55–7.50 (m, 4H), δ 7.46–7.43 (m, 1H), δ 7.33–7.28 (m, 4H), δ 7.24–7.22 (m, 2H), δ 2.79–2.76 (m, 2H), δ 2.62–2.59 (m, 2H), δ 1.75–1.72 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): 140.5, 140.0, 139.1, 136.6, 133.7, 132.6, 131.2, 130.1, 129.8, 128.6, 127.9, 127.3, 127.1, 126.1, 126.0, 125.8, 125.1, 124.9, 29.4, 29.3, 23.1, 23.0; IR (film): 2936, 1426, 1264, 895, 731 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{24}H_{20}S^+$, 341.13585; found 341.13387.



56 ***64***

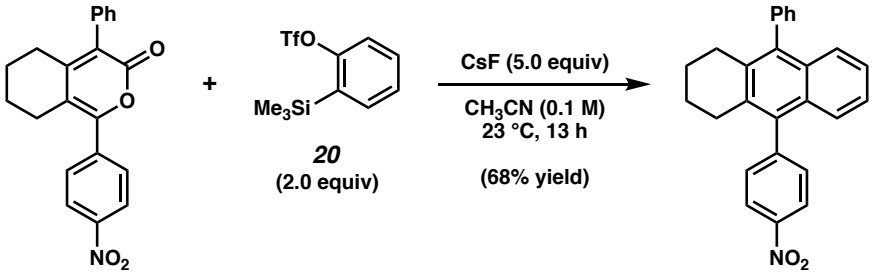
Cycloadduct 64. Followed General Procedure C using pyrone **56** (20 mg, 60.0 μmol, 1.0 equiv) afforded, after purification via flash chromatography (100% hexanes → 24:1 hexanes:EtOAc), cycloadduct **64** (90% yield, average of two experiments) as a white solid. Cycloadduct **64**: mp 200–204 °C, R_f 0.68 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54–7.50 (m, 2H), δ 7.46–7.41 (m, 1H), δ 7.40–7.37 (m, 1H), δ 7.34–7.29 (m, 3H), δ 7.23–7.21 (m, 4H), δ 7.08–7.04

(m, 2H), δ 3.91 (s, 3H), δ 2.64–2.61 (m, 4H), δ 1.72–1.69 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): 158.6, 140.3, 137.7, 137.5, 134.1, 133.7, 132.3, 131.6, 131.4, 131.3, 130.3, 128.6, 127.0, 126.2. 126.1, 124.7, 114.0, 55.4, 29.6, 29.5, 23.2, 23.1; IR (film): 2933, 1610, 1516, 1264, 1243 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{27}H_{24}O^+$, 365.18999; found 365.18820.



57 ***65***

Cycloadduct 65. Followed General Procedure C using pyrone **57** (20 mg, 54.3 μmol, 1.0 equiv) afforded, after purification via flash chromatography (Biotage 10g SiO_2, 7% → 58% EtOAc in hexanes, cycloadduct **65** (71% yield, average of two experiments) as a white solid. Cycloadduct **65**: mp 196–199 °C, R_f 0.72 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.66–7.65 (d, J = 8.2, 2H), δ 7.53–7.50 (m, 2H), δ 7.46–7.43 (m, 1H), δ 7.36–7.29 (m, 4H), δ 7.25–7.23 (m, 2H), δ 7.20–7.18 (d, J = 8.2, 2H), δ 2.61–2.60 (m, 4H), δ 1.71 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): 140.0, 139.1, 138.0, 136.3, 133.6, 132.0, 131.7, 131.1, 130.9, 130.1, 128.5, 126.9, 126.1, 125.6, 124.8, 124.7, 121.1, 29.4, 29.3, 22.9; IR (film): 1411, 1265, 862, 730, 701 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{26}H_{21}Br^+$, 413.08994; found 413.08276.

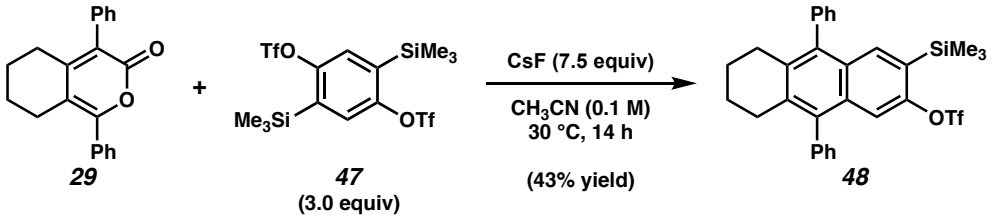


58 ***66***

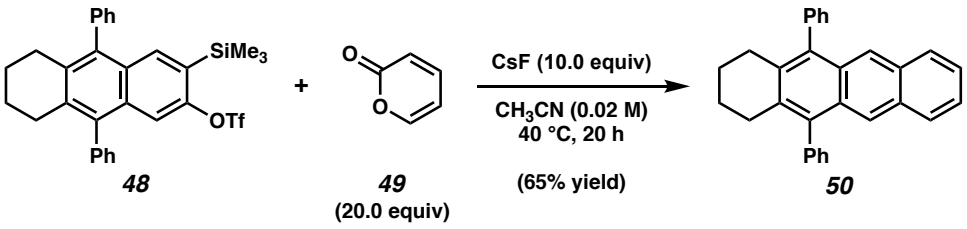
Cycloadduct 66. Followed General Procedure C using pyrone **58** (15 mg, 44.0 μmol, 1.0 equiv) afforded, after purification via flash chromatography (2:1 hexanes:EtOAc), cycloadduct **66** (68% yield, average of two experiments) as a light yellow solid. Cycloadduct **66**: mp 258–260 °C, R_f

0.35 (5:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.41–8.39 (d, J = 8.9, 2H), δ 7.55–7.50 (m, 4H), δ 7.47–7.44 (m, 1H), δ 7.37–7.34 (m, 1H), δ 7.30–7.24 (m, 4H), δ 7.19–7.17 (m, 1H), δ 2.63–2.61 (m, 2H), δ 2.56–2.55 (m, 2H), δ 1.73–1.70 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): 140.5, 140.0, 139.1, 136.6, 133.7, 132.6, 131.2, 130.1, 129.8, 128.6, 127.9, 127.3, 127.1, 126.1, 126.0, 125.8, 125.1, 124.9, 29.4, 29.3, 23.1, 23.0; IR (film): 1391, 1264, 862, 731, 704 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{26}H_{21}NO_2^+$, 380.16451; found 380.16464.

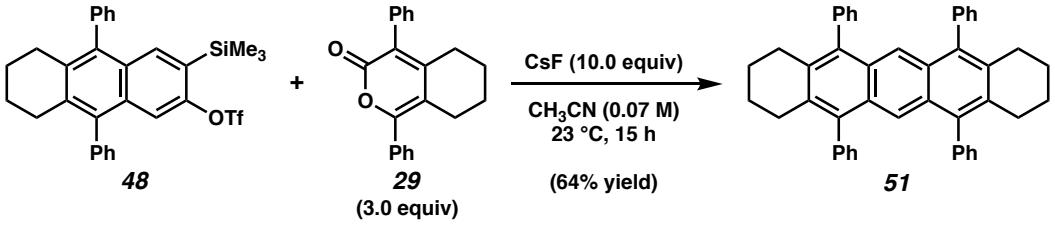
F. Synthesis of Pentacene and Tetracene Precursors



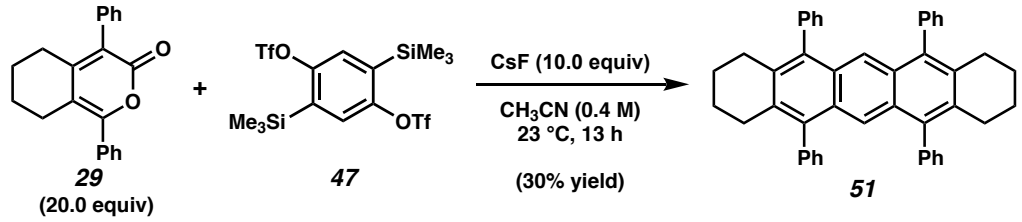
Silyl Triflate 48. To a stirred solution of pyrone **29** (15 mg, 50.0 mmol, 1.0 equiv) and silyl triflate **47** (77.2 mg, 0.15 mmol, 3.0 equiv) in MeCN (0.5 mL, 0.1 M) was added CsF (56.5 mg, 0.37 mmol, 7.5 equiv). The reaction was purged with nitrogen for ten minutes before being sealed with a Teflon cap and left to stir at 30 °C. After 14 h, the reaction mixture was filtered through celite (monster pipette, 4 cm tall) with CH_2Cl_2 (10 mL) as the eluent and then concentrated under reduced pressure. Purification of the crude material via flash chromatography (20:1 hexanes:PhH) afforded cycloadduct **48** (43% yield) as a light yellow solid. Cycloadduct **48**: mp 141–144 °C, R_f 0.24 (20:1 hexanes:PhH); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54–7.51 (m, 4H), δ 7.50 (s, 1H), δ 7.47–7.44 (m, 2H), δ 2.66–2.64 (m, 4H), δ 1.73–1.70 (m, 4H), δ 0.19 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): 152.2, 139.3, 138.8, 138.0, 137.8, 136.1, 135.9, 135.0, 132.3, 130.1, 130.0, 129.7, 128.7, 128.6, 127.5, 127.4, 119.8, 117.2, 115.4, 115.3, 29.5, 29.4, 22.9, 22.8, –0.7; IR (film): 1391, 1264, 842, 732, 703 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{30}H_{29}F_3O_3SSi^+$, 555.1631; found 555.1596.



Tetracene Precursor 50. To a stirred solution of silyl triflate **48** (130 mg, 0.230 mmol, 1.0 equiv) and pyrone **49** (75 mg, 4.69 mmol, 20.0 equiv) in degassed MeCN (11.7 mL, 0.02 M) was added CsF (356 mg, 2.34 mmol, 10.0 equiv). The reaction was purged with nitrogen for ten minutes before being sealed with a Teflon cap and left to stir at 40 °C. After 20 h, the reaction mixture was filtered through celite (fritted funnel, 3 cm tall) with CH_2Cl_2 (50 mL) as the eluent and then concentrated under reduced pressure. Purification of the crude material via flash chromatography (100:1 hexanes:PhH → 10:1 hexanes:PhH) afforded tetracene precursor **50** (65% yield) as a light yellow solid. Tetracene precursor **50**: mp 199–202 °C, R_f 0.32 (100% hexanes); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 2H), δ 7.75–7.73 (dd, J = 3.2, 6.3, 2H), δ 7.60–7.57 (m, 4H), δ 7.53–7.49 (m, 2H), δ 7.40–7.37 (m, 4H), δ 7.30–7.28 (m, 2H), δ 2.68–2.67 (m, 4H), δ 1.75–1.72 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): 140.4, 137.1, 133.6, 130.8, 130.6, 130.5, 128.7, 128.3, 127.1, 124.9, 124.7, 29.5, 23.1; IR (film): 1264, 732, 703 cm^{-1}; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{30}H_{24}^+$, 385.19508; found 385.19197.

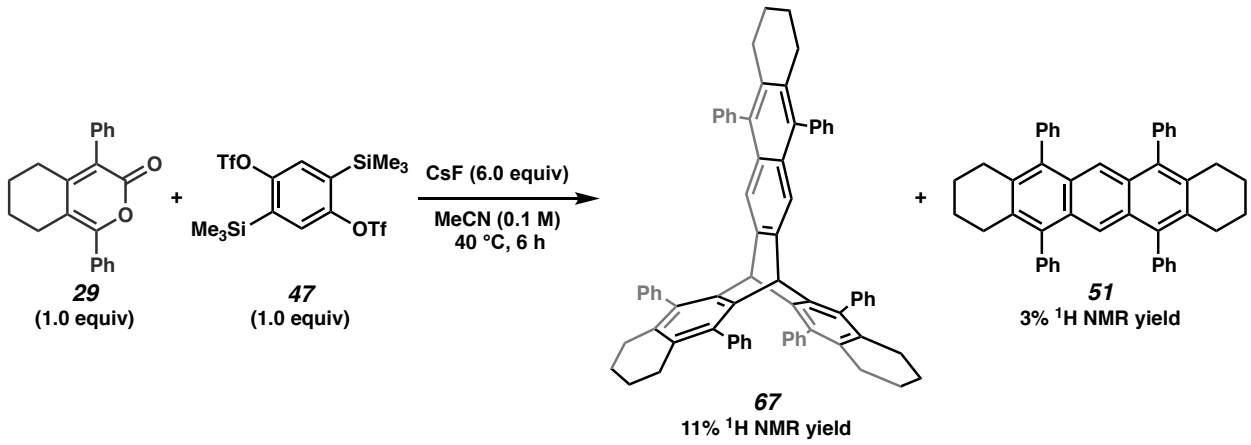


Pentacene Precursor 51. To a stirred solution of silyl triflate **48** (10 mg, 0.0180 mmol, 1.0 equiv) and pyrone **29** (16.4 mg, 0.0541 mmol, 3.0 equiv) in degassed MeCN (0.258 mL) was added CsF (27.4 mg, 0.0180 mmol, 10.0 equiv). The reaction was purged with nitrogen for ten minutes before being sealed with a Teflon cap and left to stir at 23 °C. After 15 h, the reaction mixture was filtered through celite (monster pipette, 4 cm tall) with CH_2Cl_2 (10 mL) as the eluent and then concentrated under reduced pressure. Purification of the crude material via flash chromatography (10:1 hexanes:PhH → 5:1 hexanes:PhH) afforded pentacene precursor **51** (64% yield) as a yellow solid. Pentacene precursor **51**: mp >260 °C, R_f 0.12 (100% hexanes); ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.30–7.26 (m, 14H), δ 7.12–7.11 (m, 8H), δ 2.63 (m, 8H), δ 1.68 (m, 8H); ^{13}C-NMR (500 MHz, CD_2Cl_2): 140.1, 137.2, 133.2, 130.4, 130.0, 128.4, 126.8, 123.4, 29.5, 23.3; IR (film): 2988, 1424, 1264, 731, 703 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{46}H_{38}^+$, 591.30463; found 591.30200.



Pentacene Precursor 51. To a stirred solution of pyrone **29** (233 mg, 0.771 mmol, 20.0 equiv) and silyl triflate **47** (20.0 mg, 0.0386 mmol, 1.0 equiv) in degassed MeCN (1.10 mL) was added CsF (58.6 mg, 0.386 mmol, 10.0 equiv). The reaction was purged with nitrogen for ten minutes before being sealed with a Teflon cap and left to stir at 23 °C. After 13 h, the reaction mixture was filtered through celite (monster pipette, 4 cm tall) with CH_2Cl_2 (10 mL) as the eluent and then concentrated under reduced pressure. Purification of the crude material via flash chromatography (10:1 hexanes:PhH → 5:1 hexanes:PhH) afforded pentacene precursor **51** (30% yield) as a yellow solid. Spectral data for pentacene precursor **51** matched those previously reported (see page S16).

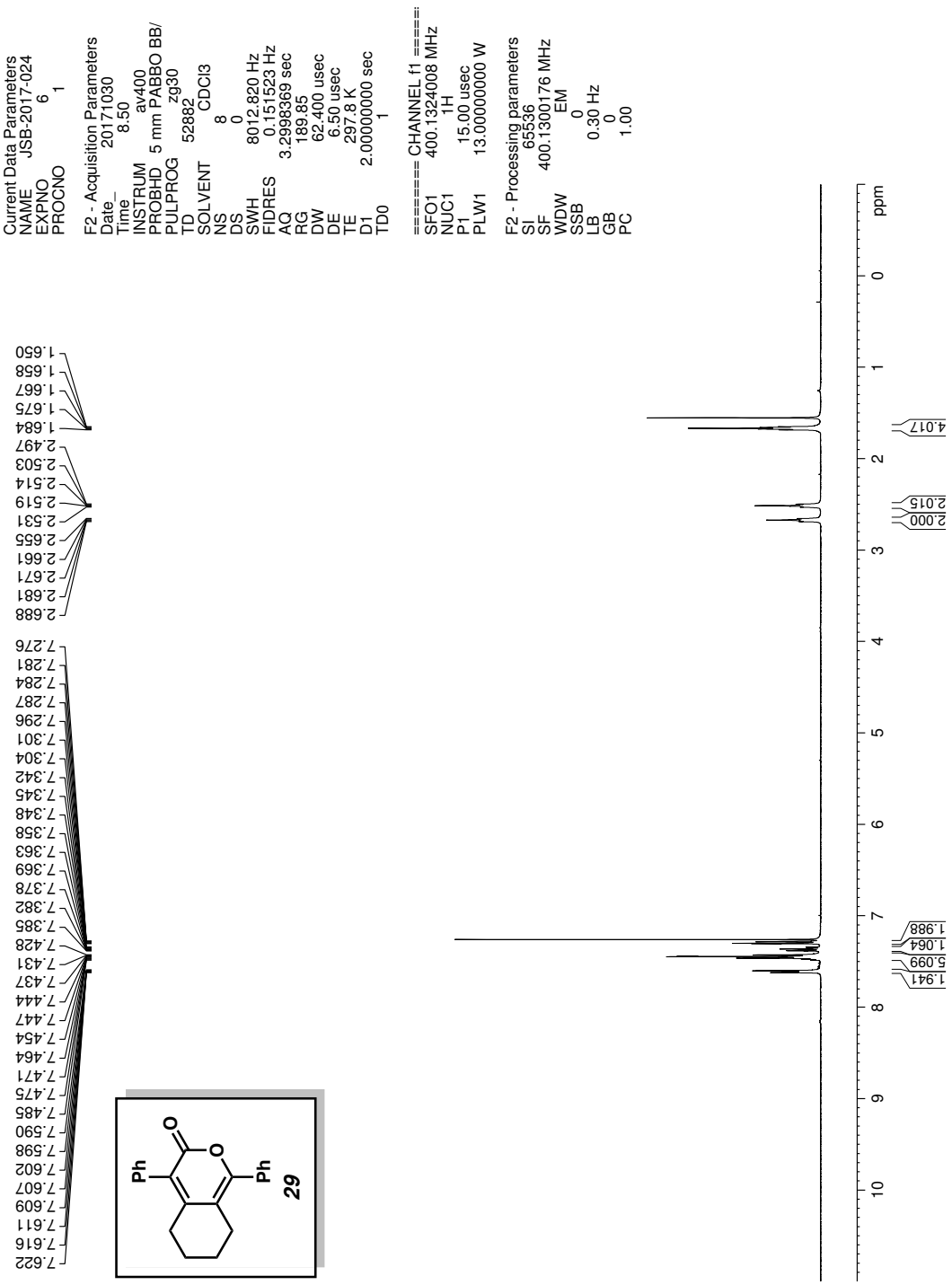
G. Aryne Addition to PAH Scaffold

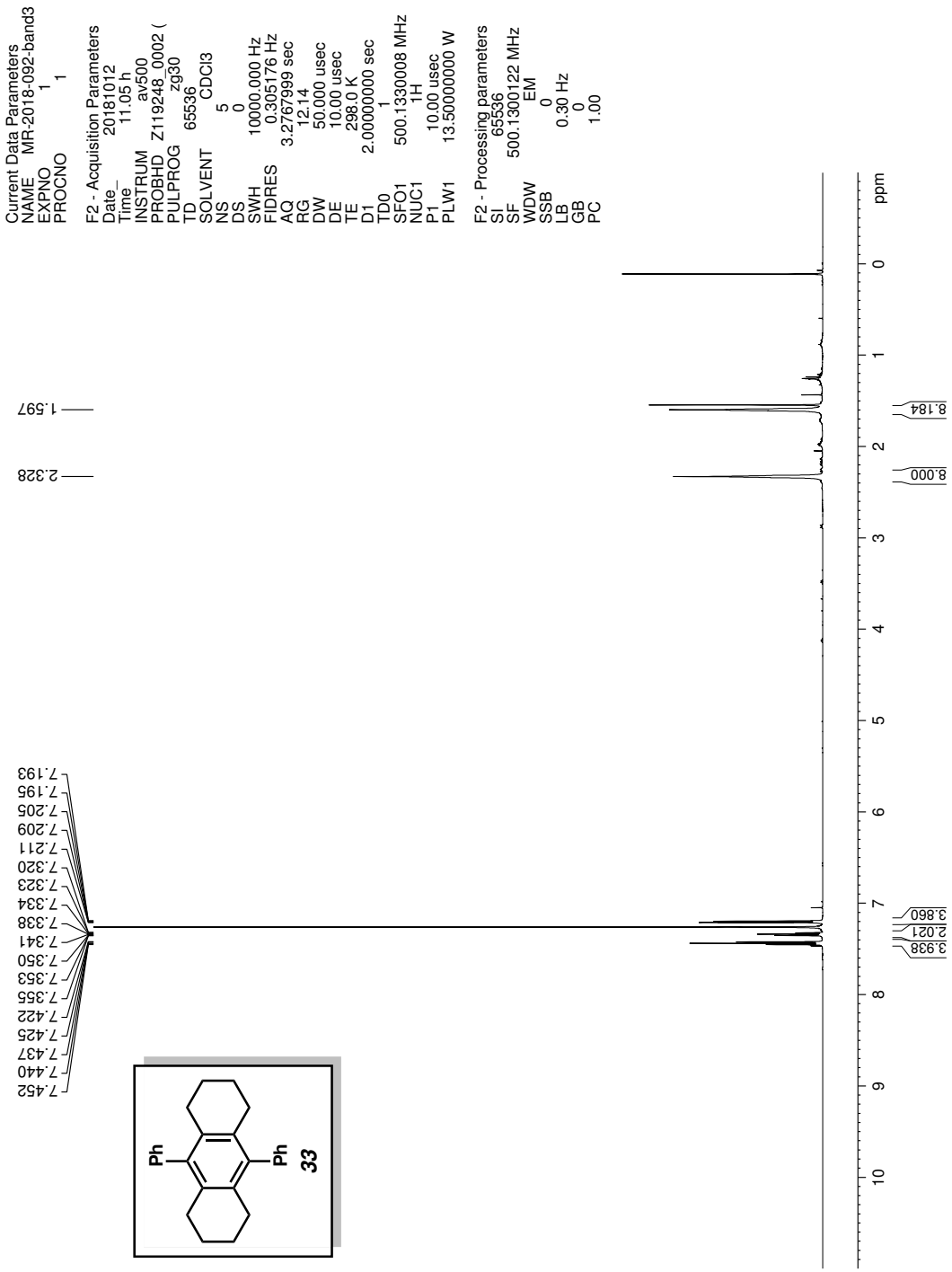


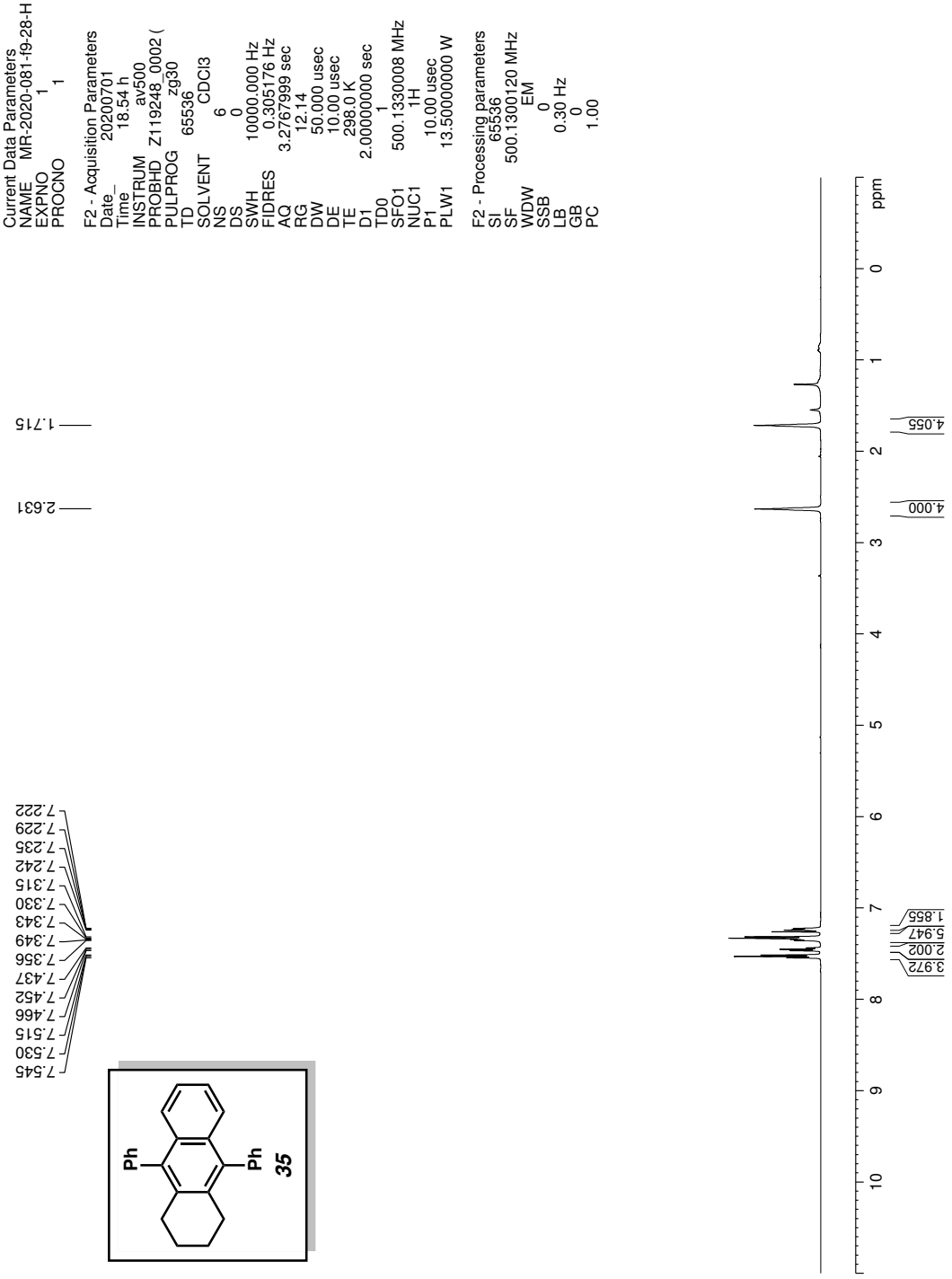
Triptycene derivative 67. To a stirred solution of pyrone **29** (8.8 mg, 0.029 mmol, 1.0 equiv) and silyl triflate **47** (15.0 mg, 0.029 mmol, 1.0 equiv) in degassed MeCN (0.300 mL) was added CsF (26.4 mg, 0.174 mmol, 6.0 equiv). The reaction was purged with nitrogen for ten minutes before being sealed with a Teflon cap and left to stir at 40 °C. After 6 h, the reaction mixture was filtered through celite (monster pipette, 4 cm tall) with CH_2Cl_2 (10 mL) as the eluent and then concentrated under reduced pressure. Yields of triptycene derivative **67** and pentacene precursor **51** were determined using ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an external standard. Spectral

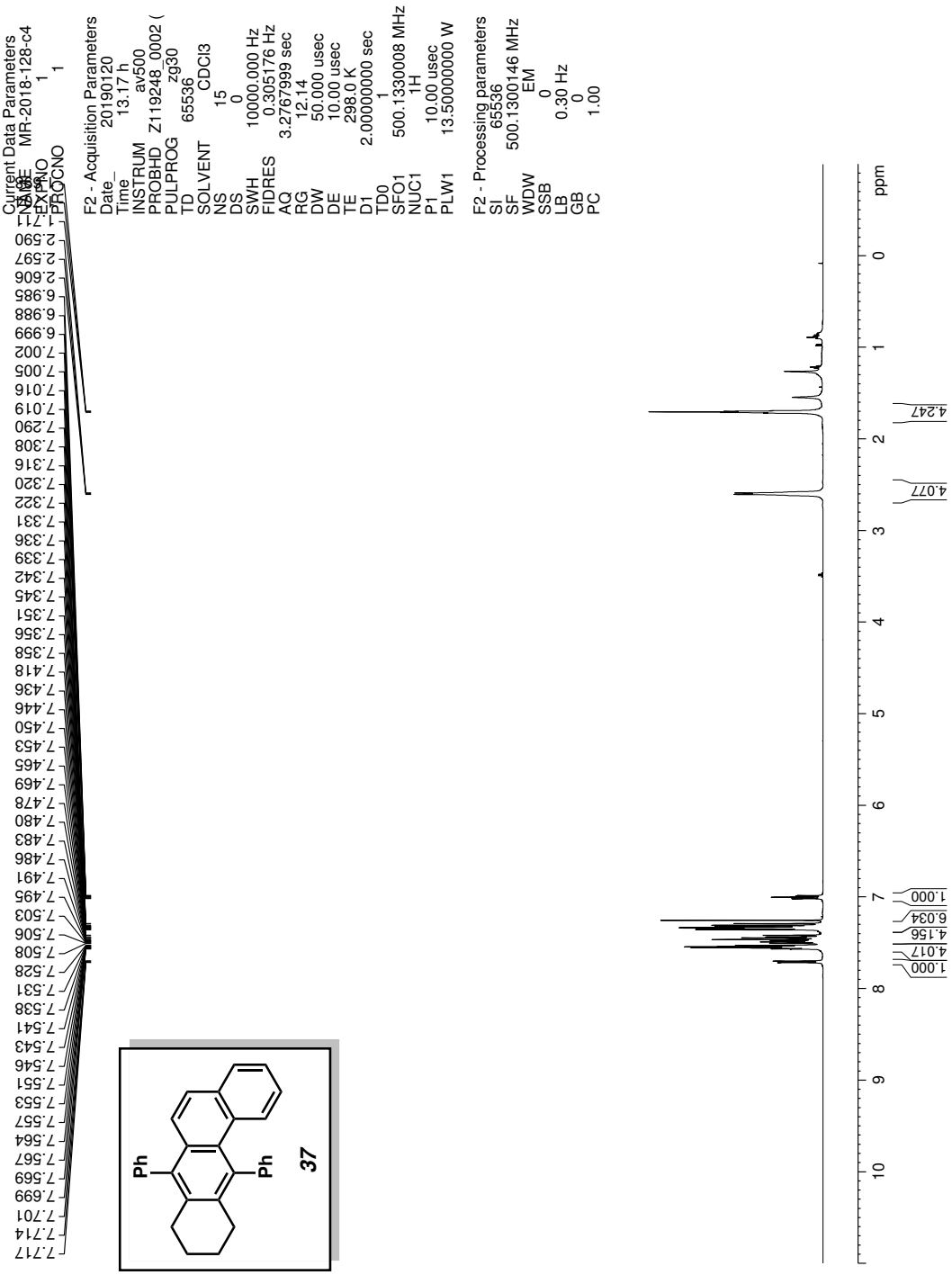
data for pentacene precursor **51** matched those previously reported (see page S16). Triptycene derivative **67**: mp >260 °C, R_f 0.20 (100% hexanes); ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.56–7.53 (m, 4H), δ 7.51–7.48 (m, 2H), δ 7.10–7.07 (td, *J* = 1.2, 7.4, 4H), δ 7.24–7.20 (m, 8H), δ 7.19–7.16 (tt, *J* =1.3, 7.4, 4H), δ 6.98–6.96 (dt, *J* =1.3, 7.3, 4H), δ 6.79 (s, 2H), δ 6.77 (m, 4H), δ 4.77 (s, 2H), δ 2.56 (m, 4H), δ 2.40–2.34 (m, 4H), δ 2.18–2.12 (m, 4H), δ 1.68–1.66 (m, 4H), δ 1.26 (br s, 8H); ^{13}C-NMR (125 MHz, CD_2Cl_2): 142.1, 140.8, 140.3, 139.2, 137.9, 136.9, 133.3, 132.2, 130.5, 129.9, 129.7, 129.6, 128.7, 128.6, 127.8, 127.2, 126.8, 119.6, 30.0, 29.6, 29.2, 23.3; IR (film): 3053, 2988, 1736, 1419, 1264 cm $^{-1}$; HRMS-APCI (m/z) $[M + H]^+$ calcd for $C_{72}H_{58}^+$, 921.44658; found 921.44299.

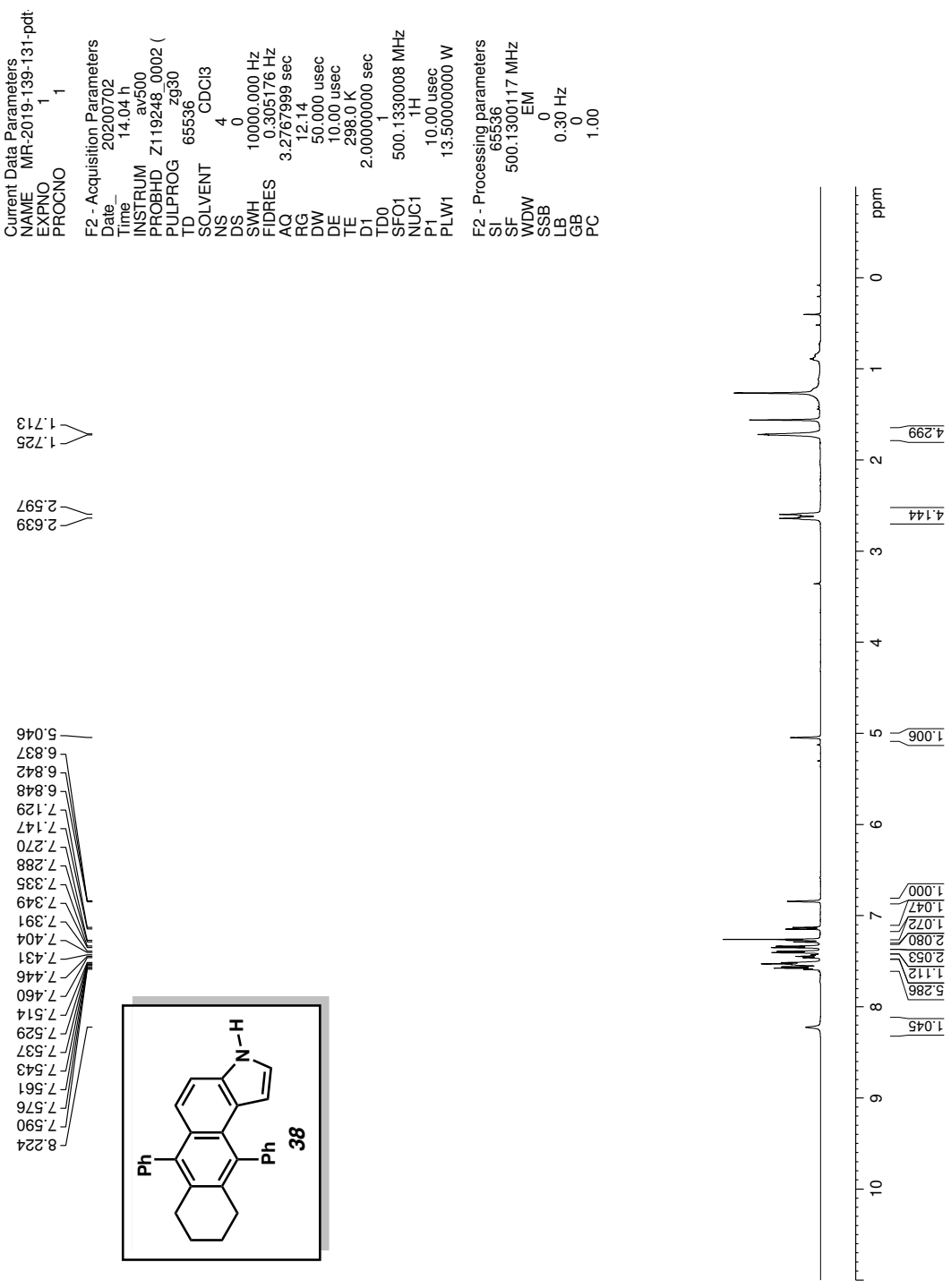
^{1}H NMR

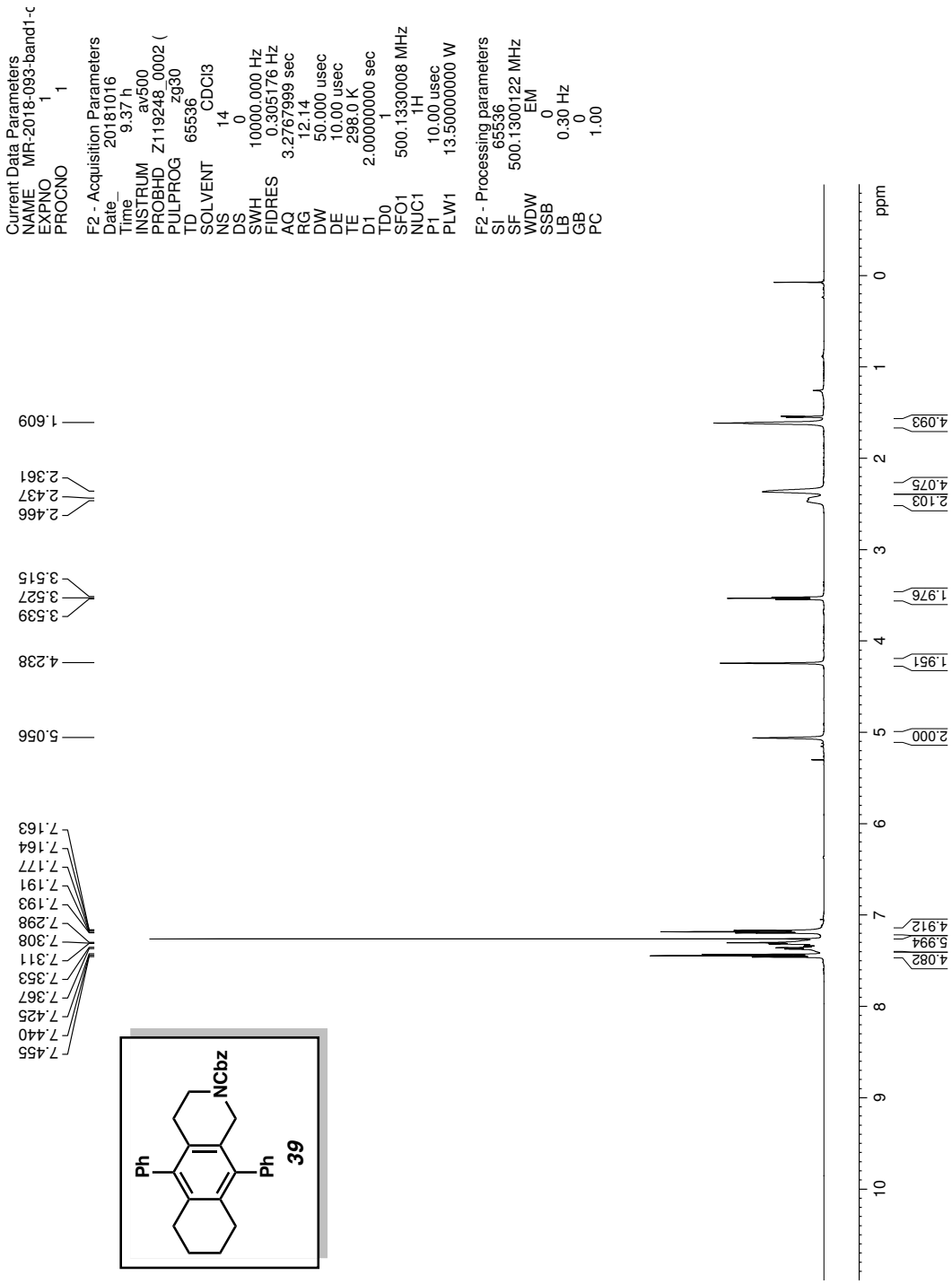

Current Data Parameters
NAME JSB-2017-024
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171030
Time_ 8.50
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 189.85
DW 62.400 usec
DE 6.50 usec
TE 297.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ======
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.650
1.658
1.667
1.675
1.684
2.497
2.503
2.514
2.519
2.531
2.655
2.661
2.671
2.681
2.688
7.276
7.281
7.284
7.287
7.296
7.301
7.304
7.342
7.345
7.348
7.358
7.363
7.369
7.378
7.382
7.385
7.428
7.431
7.437
7.444
7.447
7.454
7.464
7.471
7.475
7.485
7.590
7.598
7.602
7.607
7.609
7.611
7.616
7.622
Ph
O
O
Ph
29
4.017
2.000
2.015
1.941
5.099
1.064
1.988
ppm

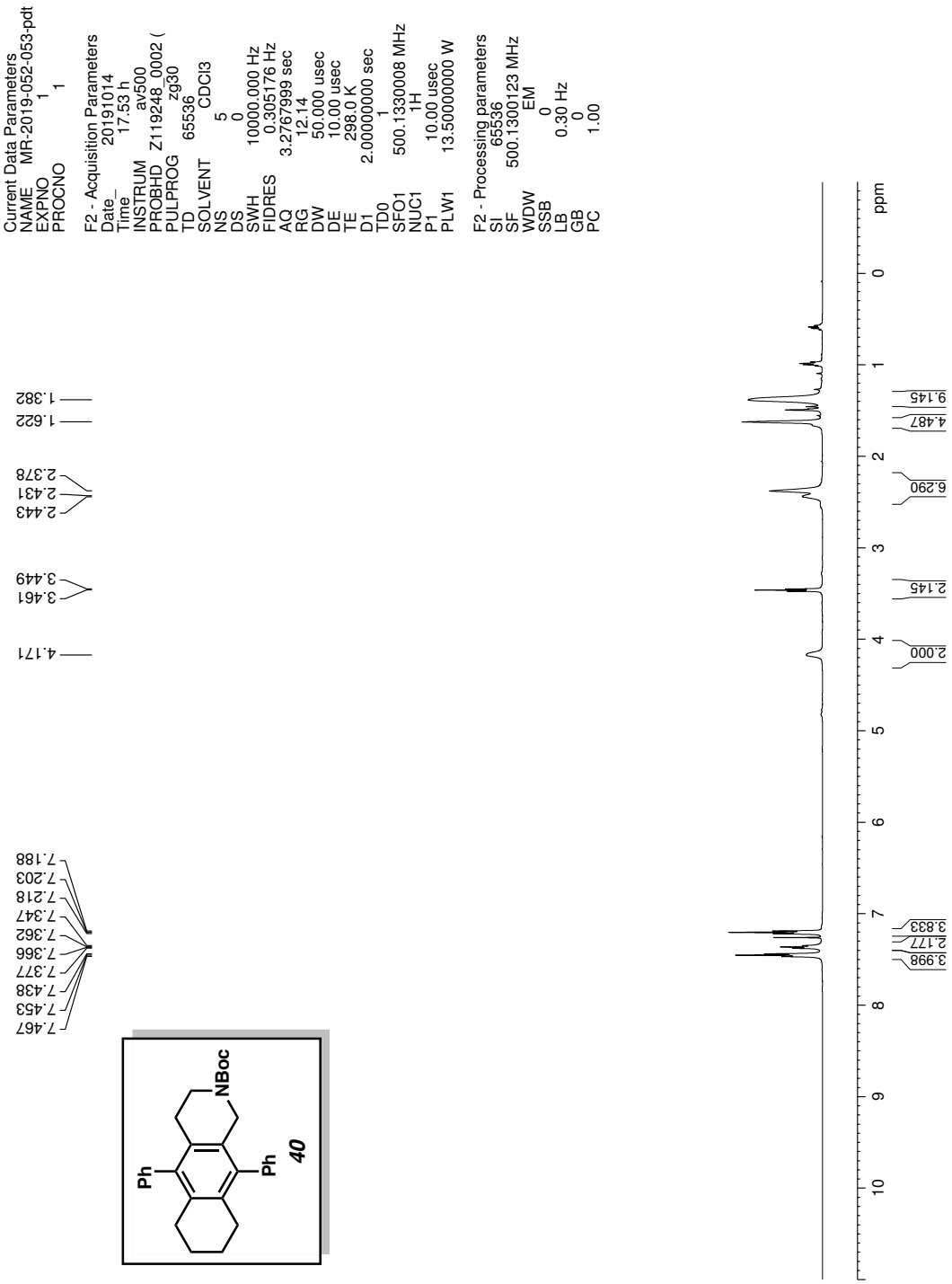

Current Data Parameters
NAME MR-2018-092-band3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181012
Time_ 11.05 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.597
2.328
7.193
7.195
7.205
7.209
7.211
7.320
7.323
7.334
7.338
7.341
7.350
7.353
7.355
7.422
7.425
7.437
7.440
7.452
8.184
8.000
3.860
2.021
3.938
ppm
Ph
Ph
33

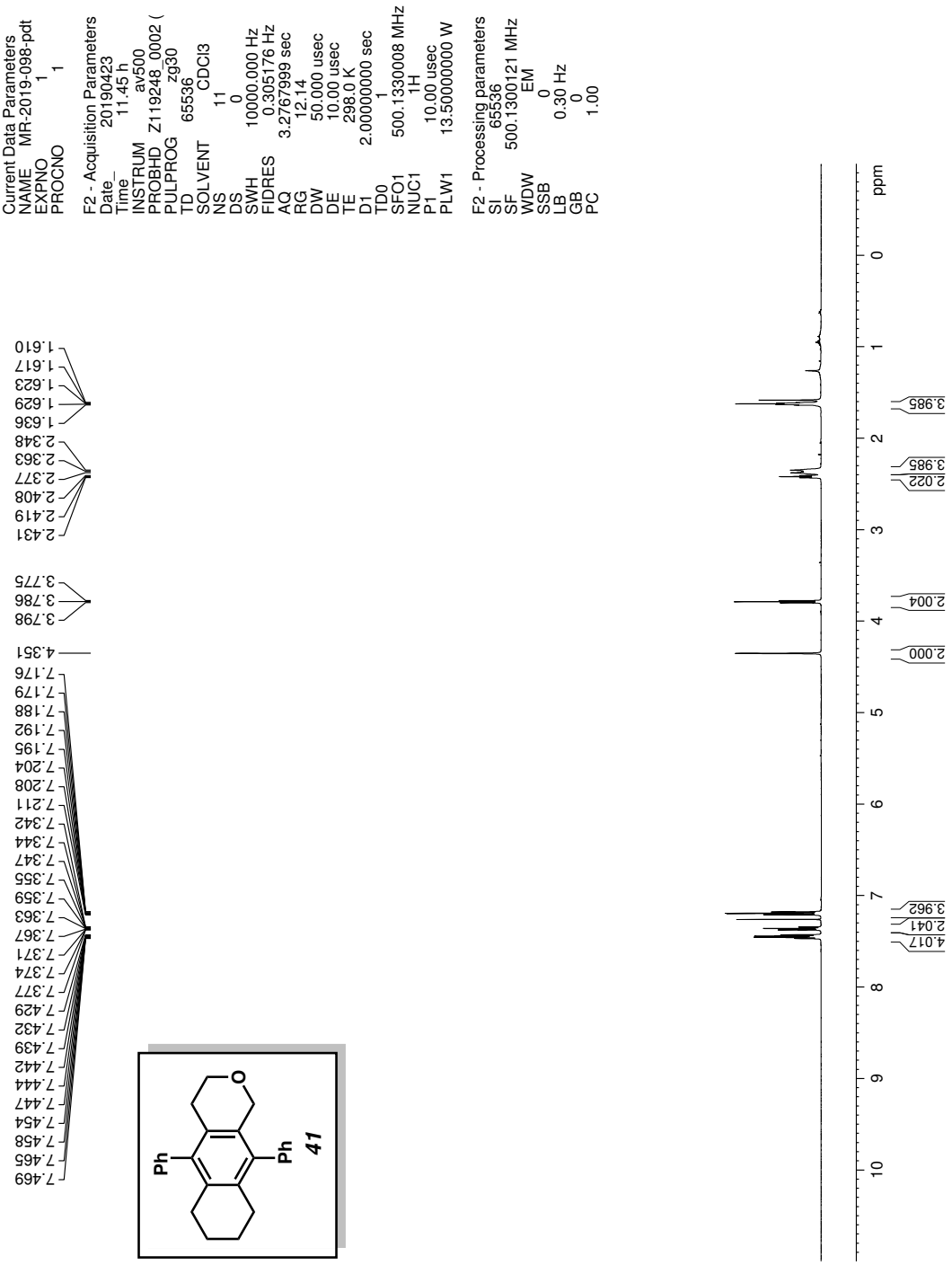

Current Data Parameters
NAME MR-2020-081-f9-28-H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200701
Time_ 18.54 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 6
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.715
2.631
7.222
7.229
7.235
7.242
7.315
7.330
7.343
7.349
7.356
7.437
7.452
7.466
7.515
7.530
7.545
Ph
Ph
35
4.055
4.000
3.972
2.002
5.947
1.855
ppm

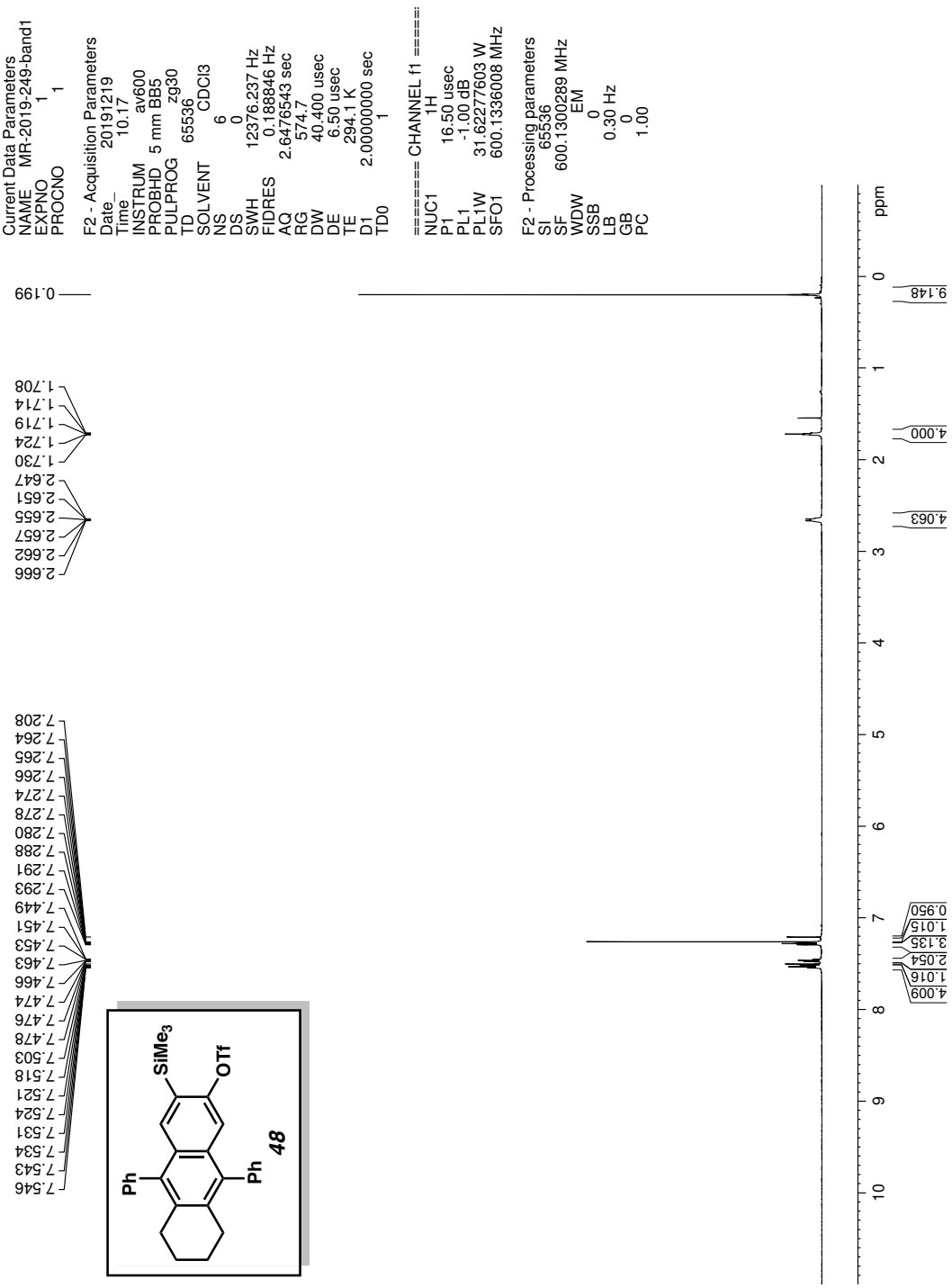

Current Data Parameters
NAME MR-2018-128-c4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190120
Time 13.17 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 15
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
Ph
37
4.247
4.077
1.000
4.017
4.156
6.034
1.000
ppm

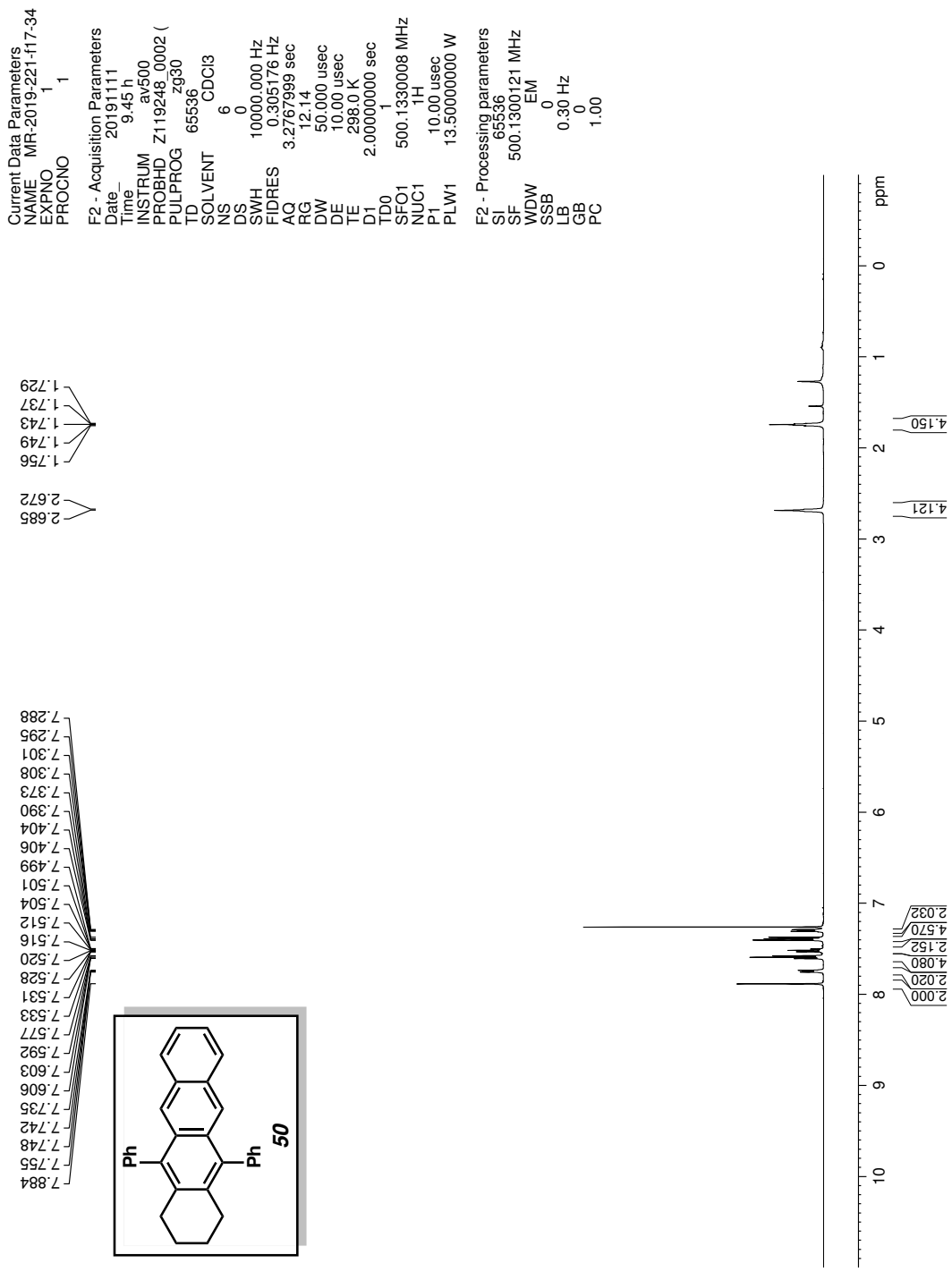

Current Data Parameters
NAME MR-2019-139-131-pdt
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200702
Time_ 14.04 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300117 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.713
1.725
2.597
2.639
5.046
6.837
6.842
6.848
7.129
7.147
7.270
7.288
7.335
7.349
7.391
7.404
7.431
7.446
7.460
7.514
7.529
7.537
7.543
7.561
7.576
7.590
8.224
Ph
Ph
N–H
38
4.299
4.144
1.006
1.000
1.047
1.072
2.080
2.053
1.112
5.286
1.045
ppm

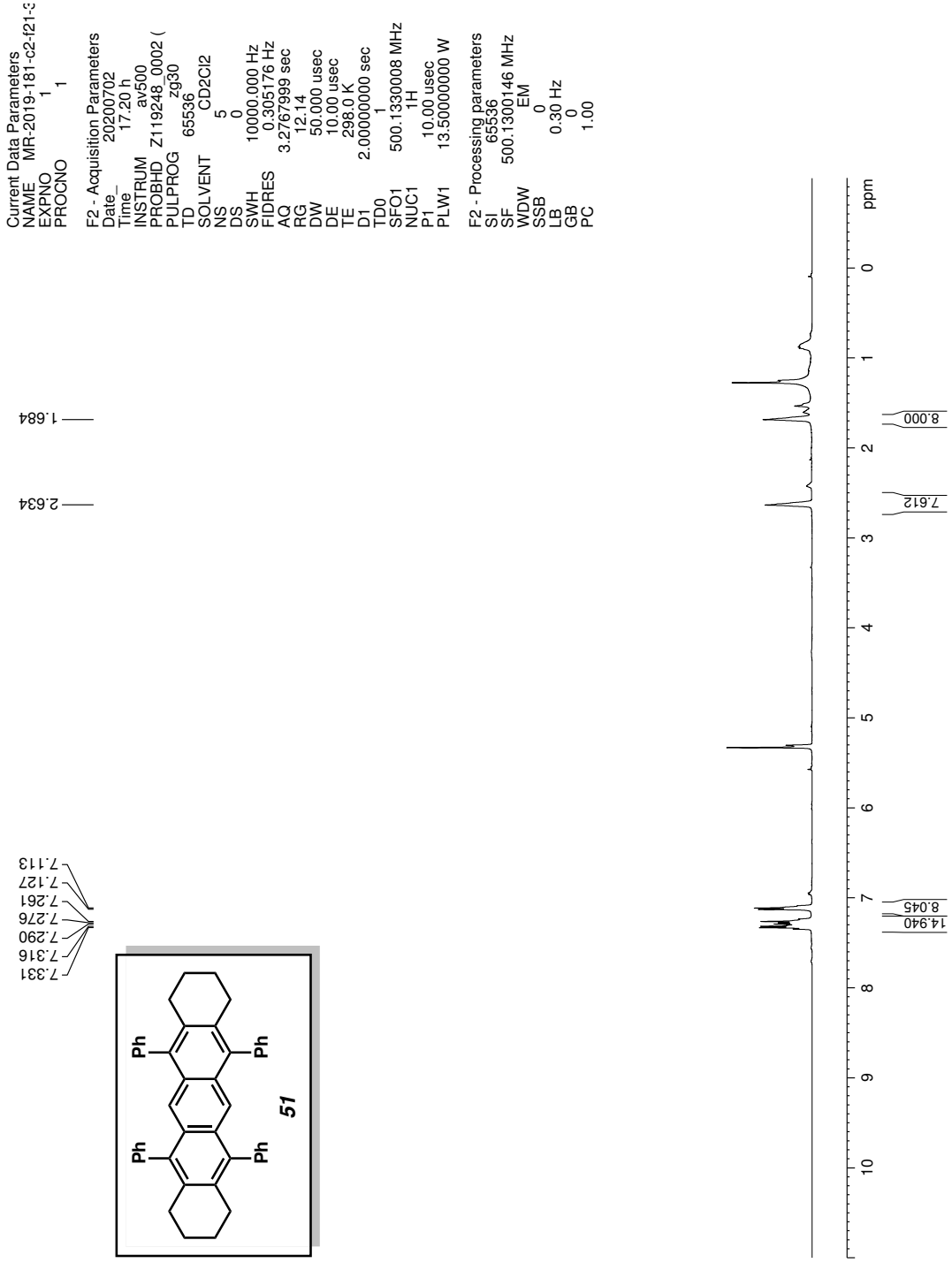

Current Data Parameters
NAME MR-2018-093-band1-c
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181016
Time 9.37 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 14
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.609
2.361
2.437
2.466
3.515
3.527
3.539
4.238
5.056
7.163
7.164
7.177
7.191
7.193
7.298
7.308
7.311
7.353
7.367
7.425
7.440
7.455
4.093
2.103
4.075
1.976
1.951
2.000
4.082
5.994
4.912
ppm
NCbz
Ph
Ph
39

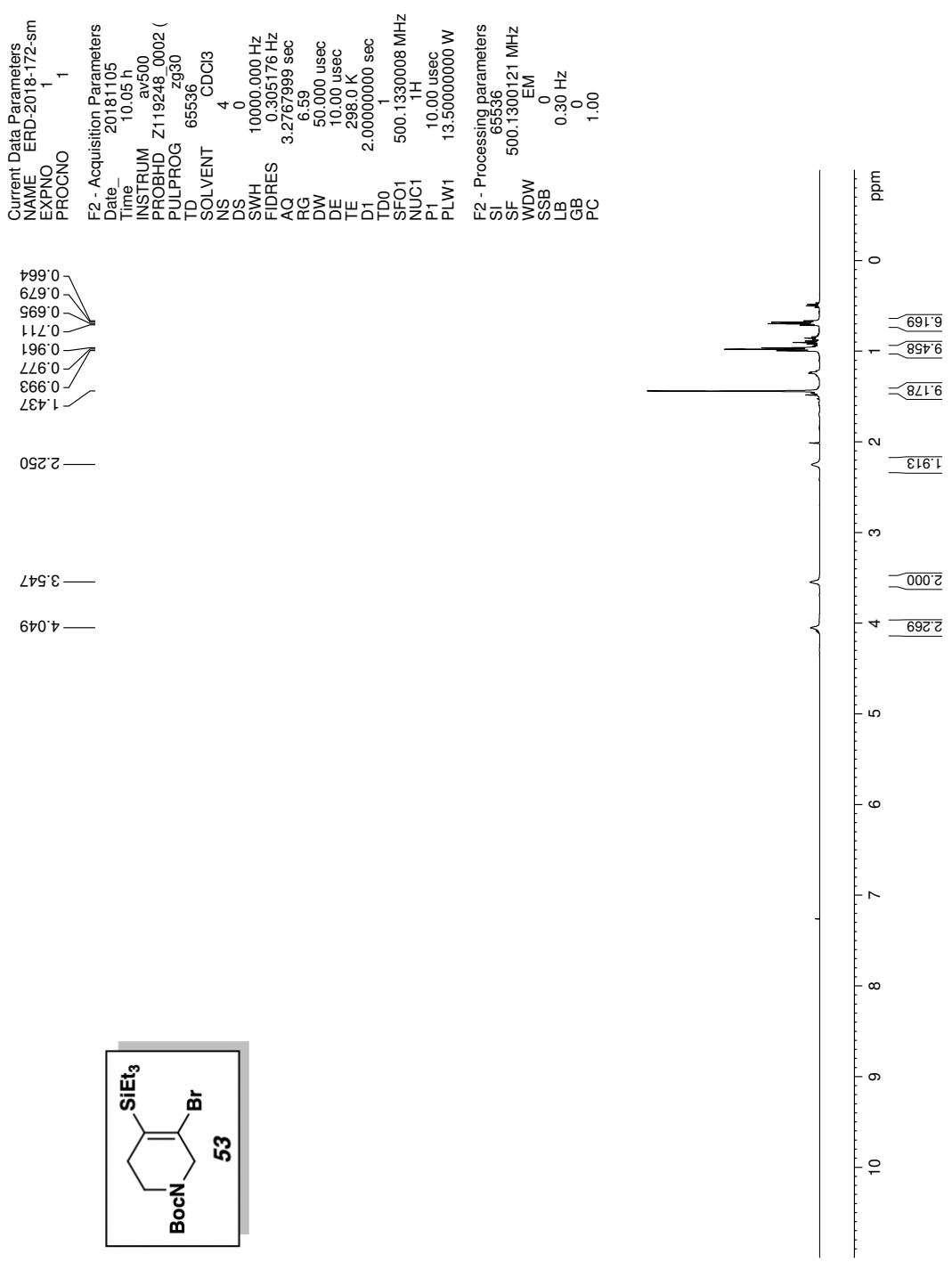

Current Data Parameters
NAME MR-2019-052-053-pdt
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191014
Time 17.53 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.467
7.453
7.438
7.377
7.366
7.362
7.347
7.218
7.203
7.188
4.171
3.461
3.449
2.443
2.431
2.378
1.622
1.382
NBoc
Ph
Ph
40
3.998
2.177
3.833
2.000
2.145
6.290
4.487
9.145
ppm

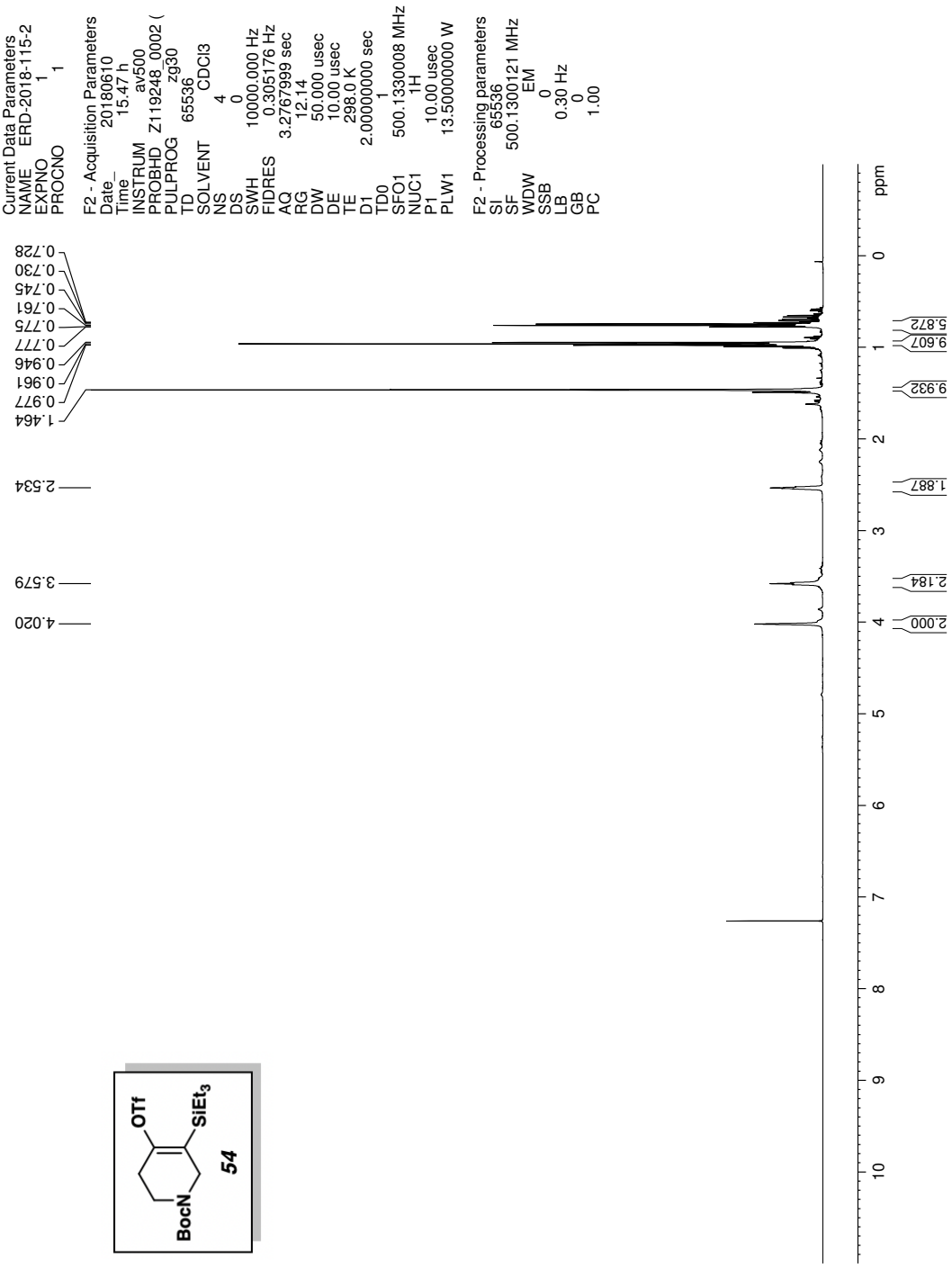

Current Data Parameters
NAME MR-2019-098-pdt
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190423
Time 11.45 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 11
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.610
1.617
1.623
1.629
1.636
2.348
2.363
2.377
2.408
2.419
2.431
3.775
3.786
3.798
4.351
7.176
7.179
7.188
7.192
7.195
7.204
7.208
7.211
7.342
7.344
7.347
7.355
7.359
7.363
7.367
7.371
7.374
7.377
7.429
7.432
7.439
7.442
7.444
7.447
7.454
7.458
7.465
7.469
Ph
Ph
41
3.985
3.985
2.022
2.004
2.000
3.962
2.041
4.017
ppm

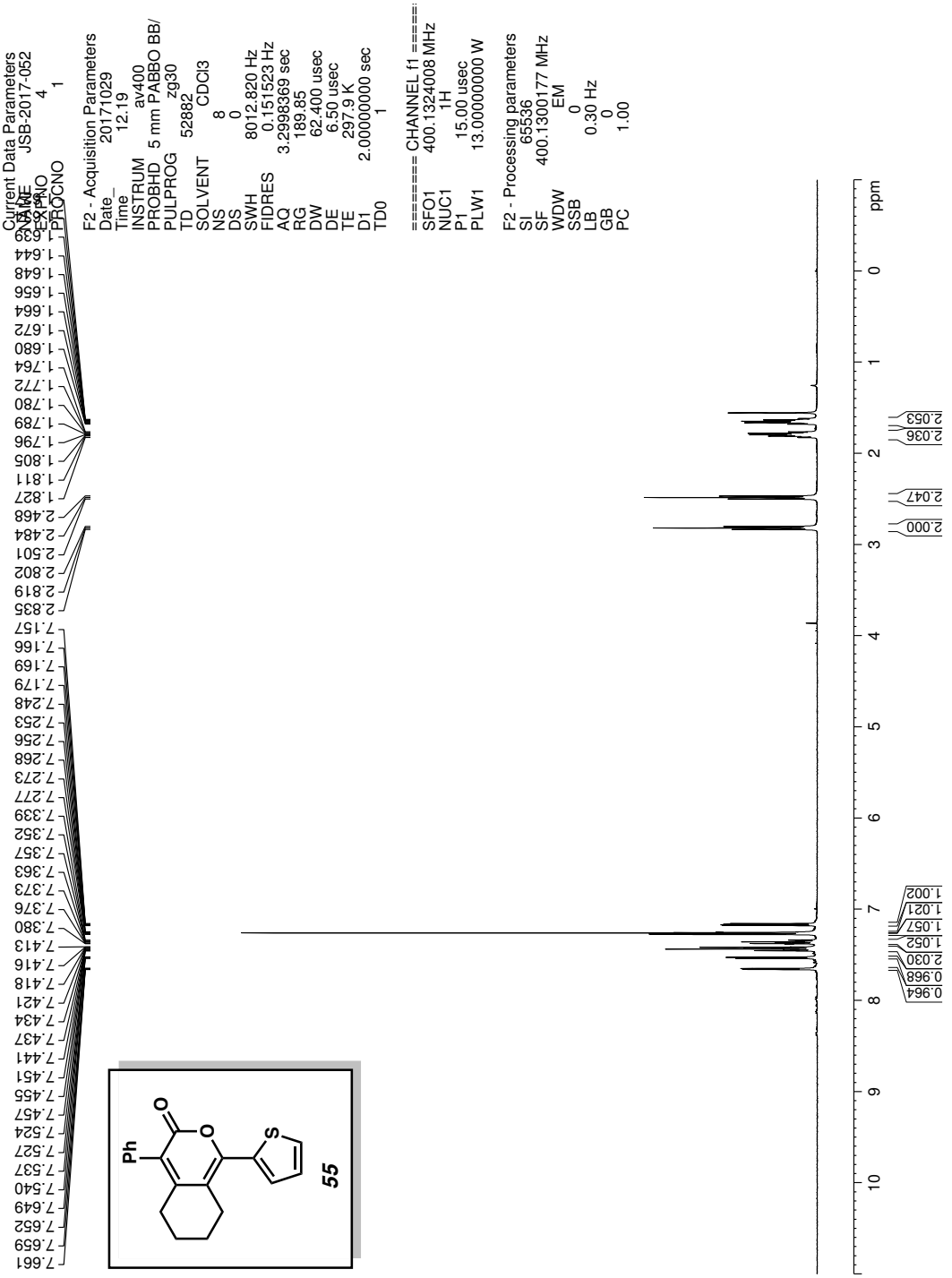

Current Data Parameters
NAME MR-2019-249-band1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191219
Time 10.17
INSTRUM av600
PROBHD 5 mm BB5
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 6
DS 0
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 574.7
DW 40.400 usec
DE 6.50 usec
TE 294.1 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 16.50 usec
PL1 -1.00 dB
PL1W 31.62277603 W
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300289 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.199
1.708
1.714
1.719
1.724
1.730
2.647
2.651
2.655
2.657
2.662
2.666
7.208
7.264
7.265
7.266
7.274
7.278
7.280
7.288
7.291
7.293
7.449
7.451
7.453
7.463
7.466
7.474
7.476
7.478
7.503
7.518
7.521
7.524
7.531
7.534
7.543
7.546
SiMe3
OTf
Ph
Ph
48
9.148
4.000
4.063
4.009
1.016
2.054
3.135
1.015
0.950
ppm

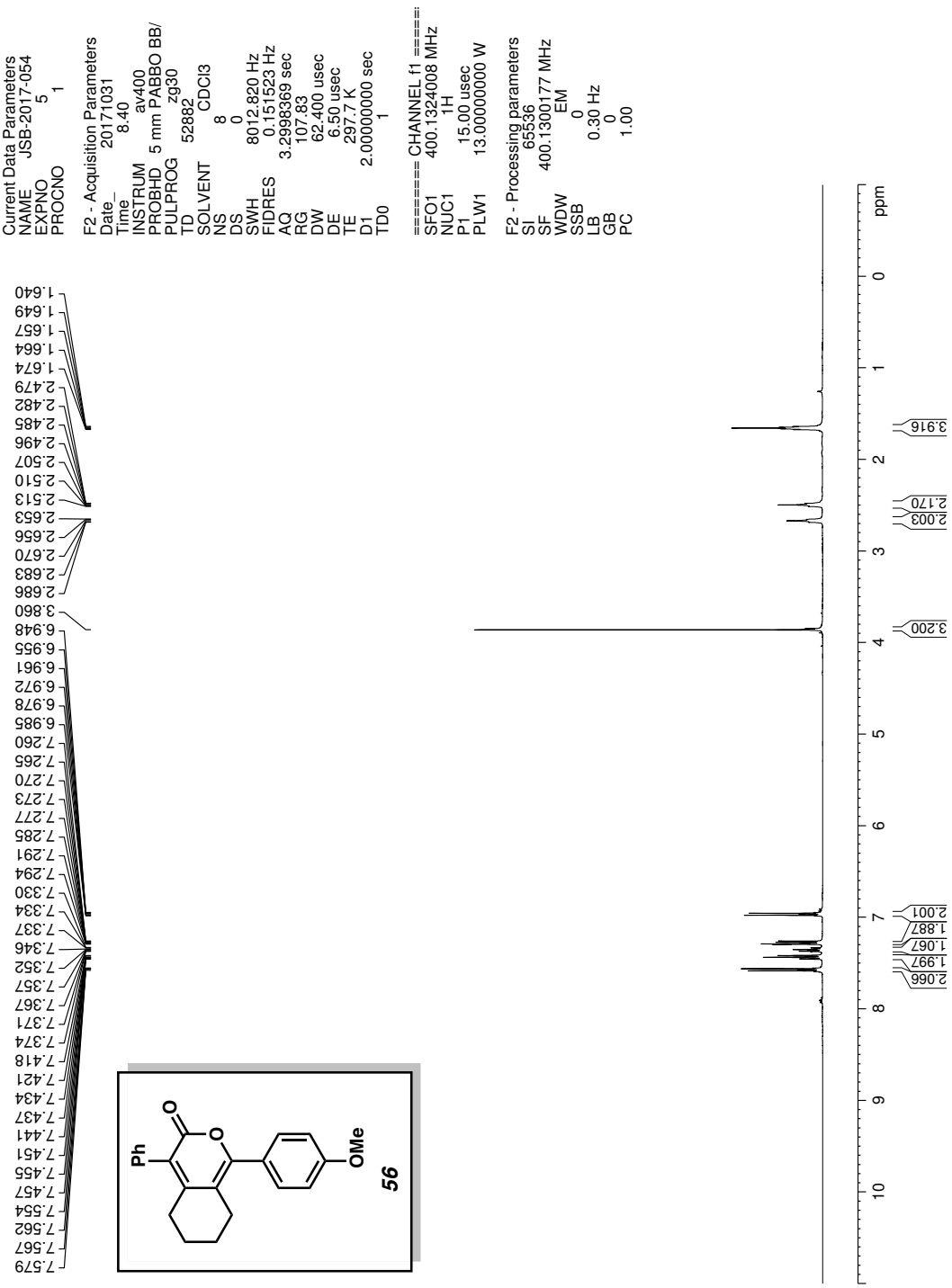

Current Data Parameters
NAME MR-2019-221-f17-34
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191111
Time 9.45 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 6
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.884
7.755
7.748
7.742
7.735
7.606
7.603
7.592
7.577
7.533
7.531
7.528
7.520
7.516
7.512
7.504
7.501
7.499
7.406
7.404
7.390
7.373
7.308
7.301
7.295
7.288
2.685
2.672
1.756
1.749
1.743
1.737
1.729
Ph
Ph
50
ppm
2.000
2.020
4.080
2.152
4.570
2.032
4.150
4.121

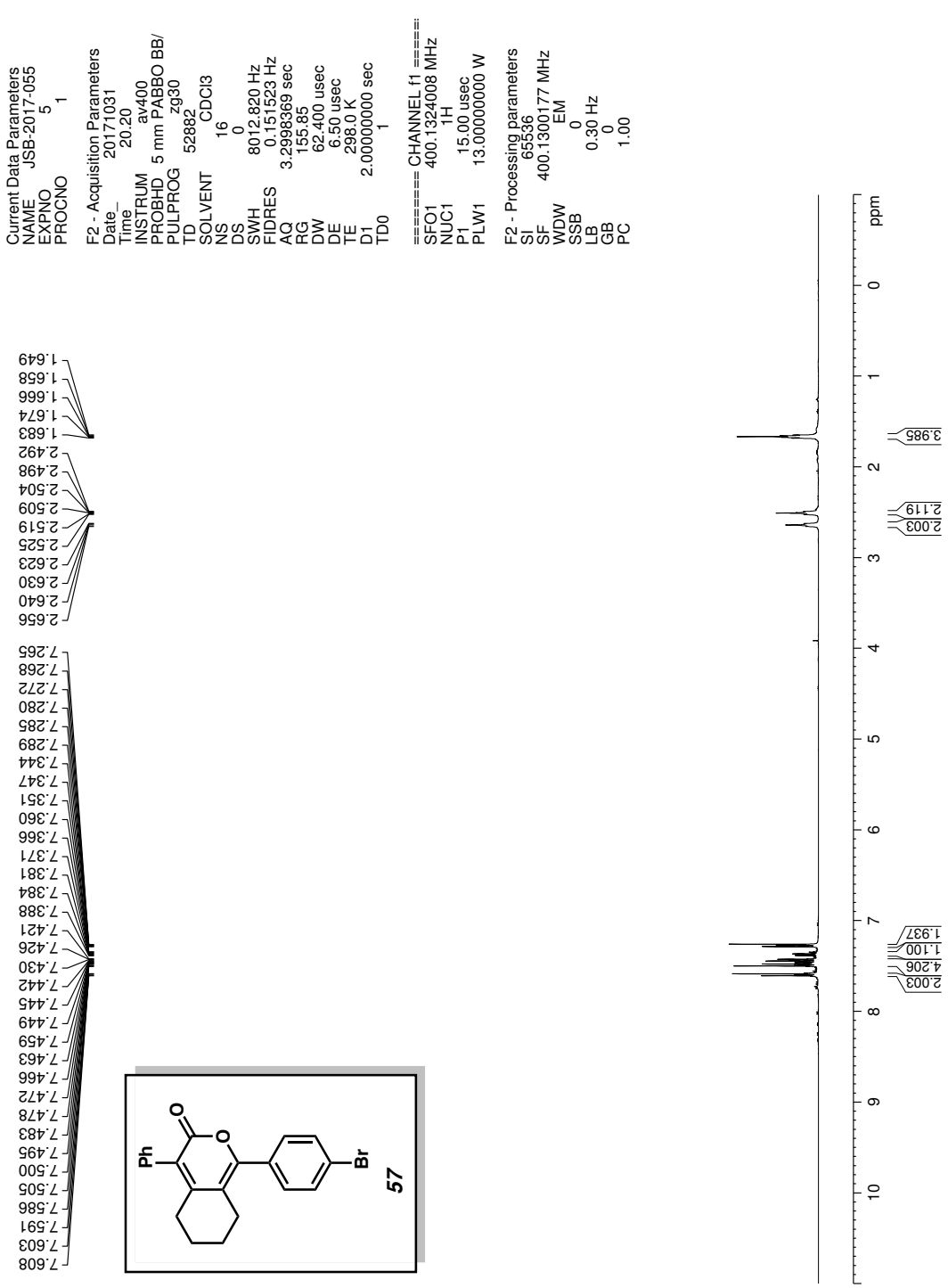

Current Data Parameters
NAME MR-2019-181-c2-f21-s
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200702
Time 17.20 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 5
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.684
2.634
7.113
7.127
7.261
7.276
7.290
7.316
7.331
Ph
Ph
Ph
Ph
51
8.000
7.612
14.940
8.045
ppm

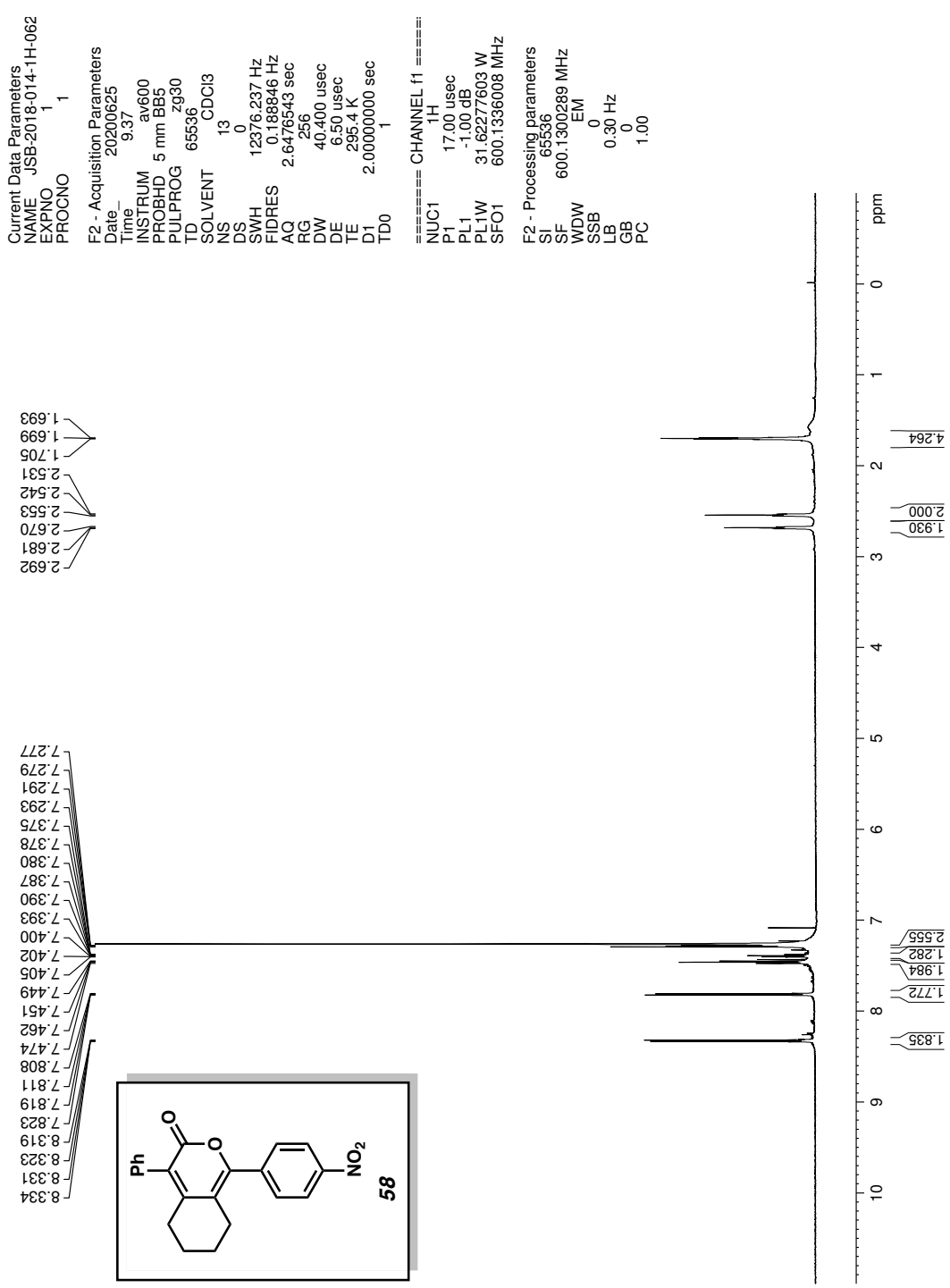

Current Data Parameters
NAME ERD-2018-172-sm
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181105
Time_ 10.05 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 6.59
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.664
0.679
0.695
0.711
0.961
0.977
0.993
1.437
2.250
3.547
4.049
SiEt3
Br
BocN
53
6.169
9.458
9.178
1.913
2.000
2.269
ppm

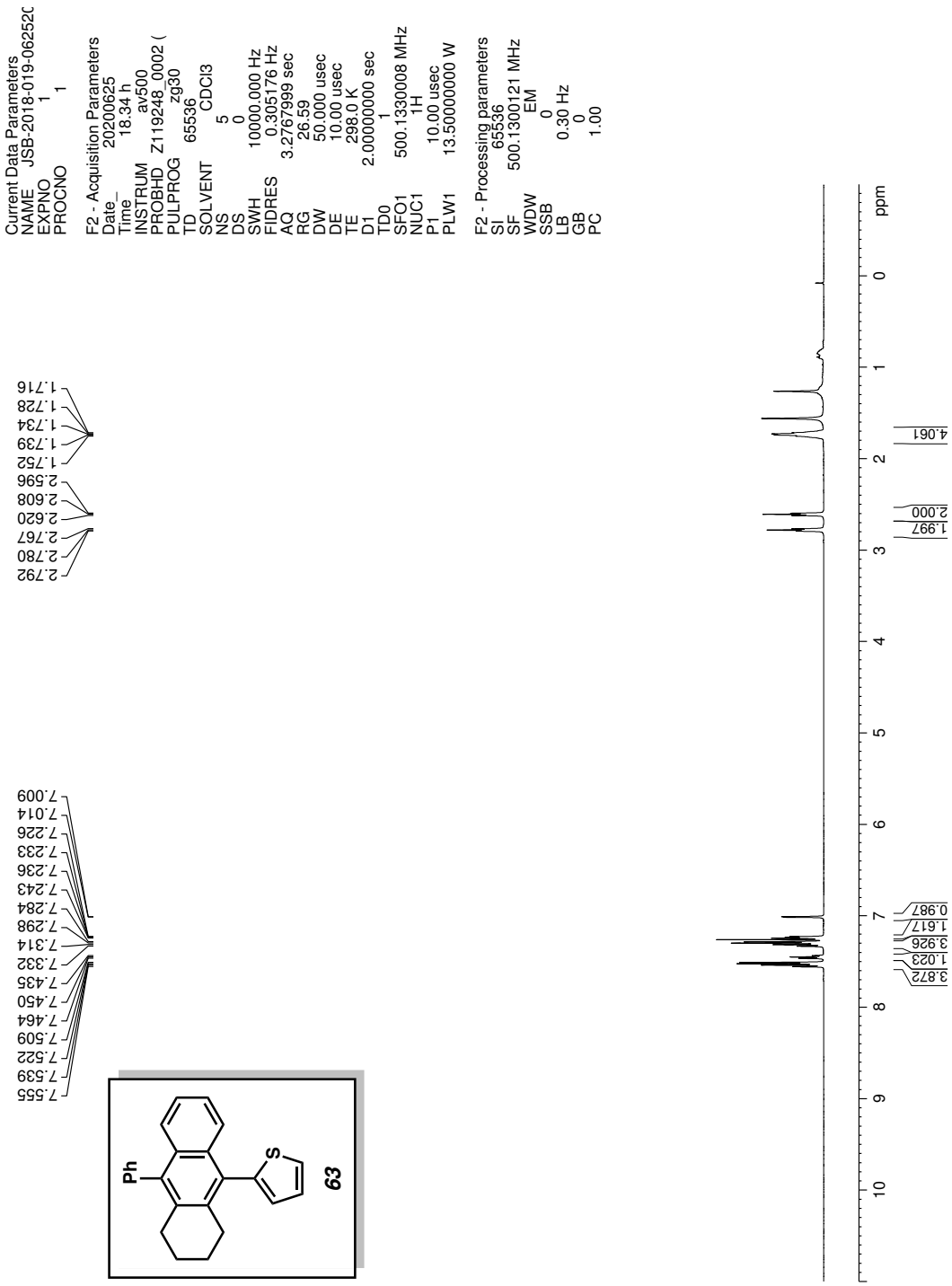

Current Data Parameters
NAME ERD-2018-115-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180610
Time 15.47 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.728
0.730
0.745
0.761
0.775
0.777
0.946
0.961
0.977
1.464
2.534
3.579
4.020
5.872
9.607
9.932
1.887
2.184
2.000
ppm
OTf
SiEt3
BocN
54

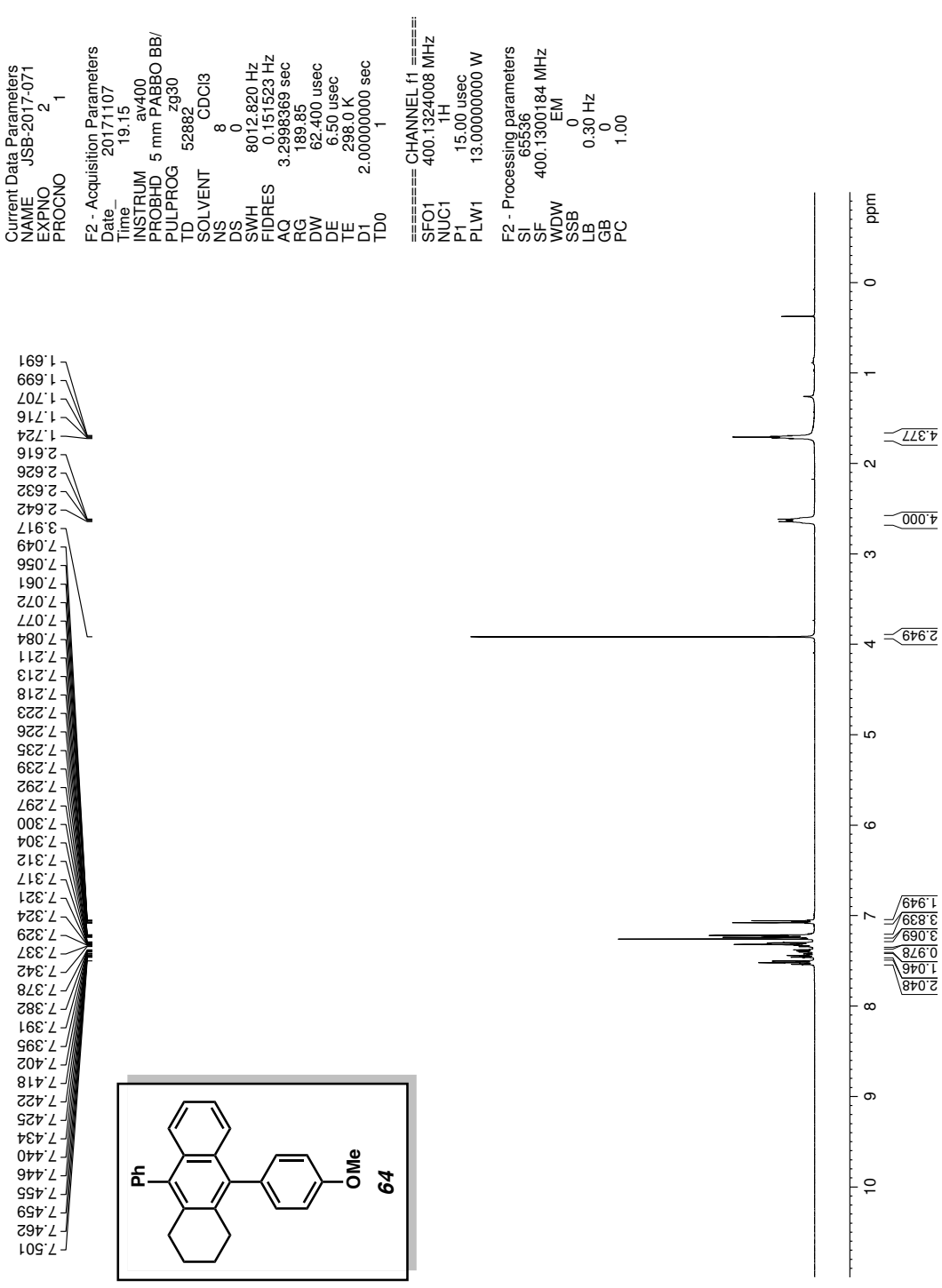

Current Data Parameters
NAME JSB-2017-052
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171029
Time_ 12.19
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 189.85
DW 62.400 usec
DE 6.50 usec
TE 297.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1300177 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
O
O
S
55
ppm

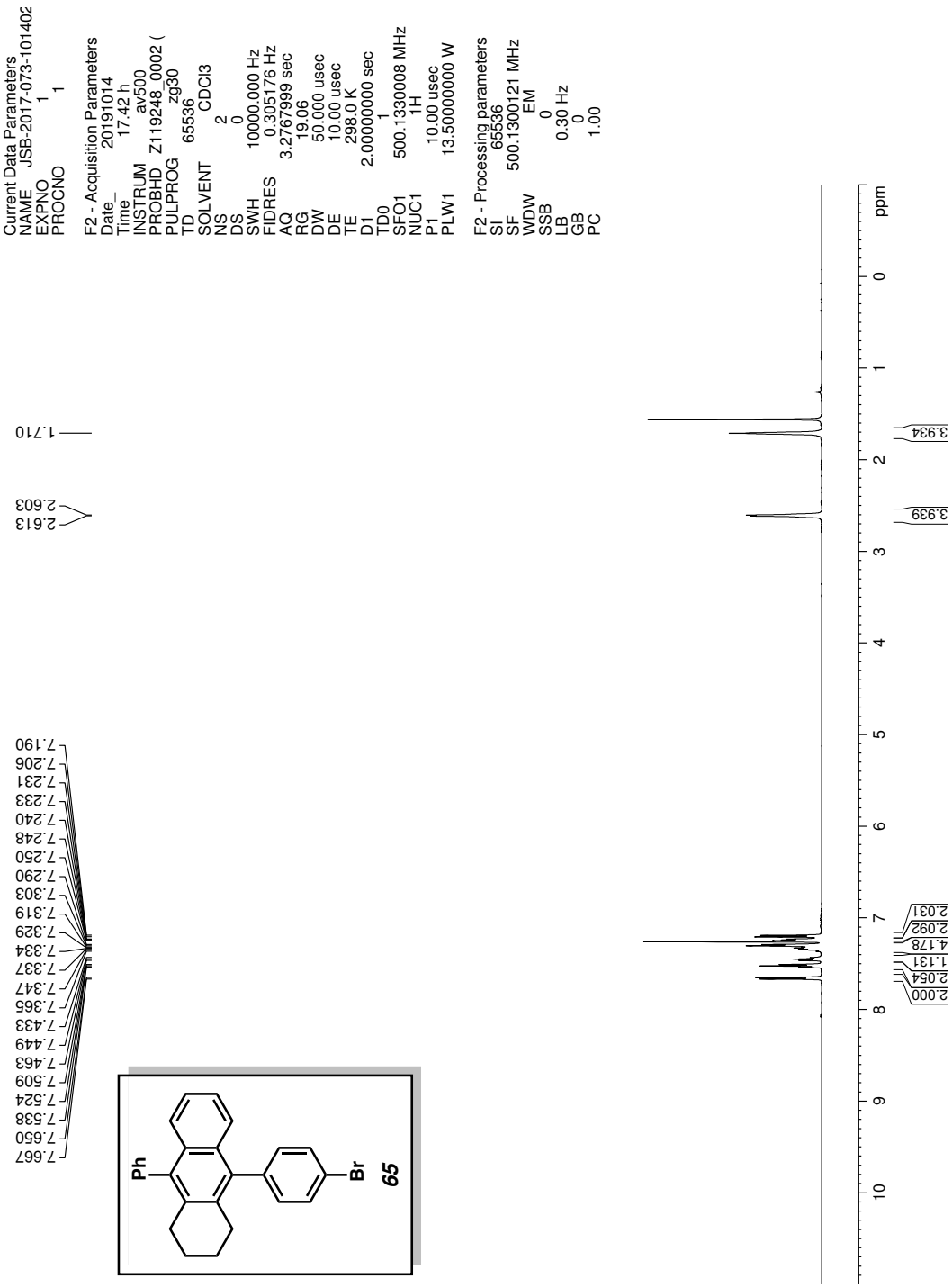

Current Data Parameters
NAME JSB-2017-054
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171031
Time 8.40
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 107.83
DW 62.400 usec
DE 6.50 usec
TE 297.7 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ======
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1300177 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
O
O
OMe
56
3.916
2.003
2.170
3.200
2.066
1.997
1.067
1.887
2.001
ppm

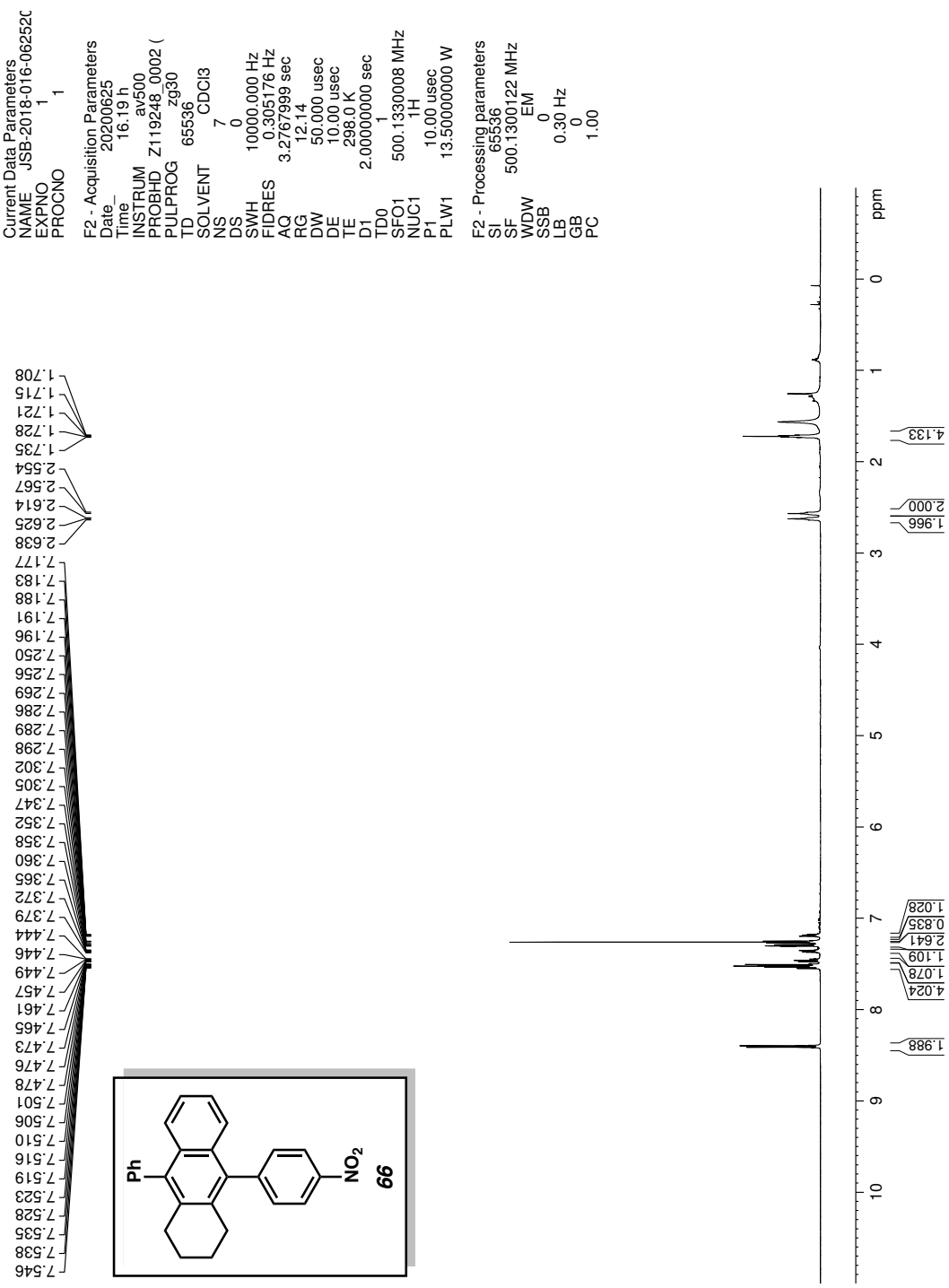

Current Data Parameters
NAME JSB-2017-055
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171031
Time 20.20
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ======
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1300177 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.608
7.603
7.591
7.586
7.505
7.500
7.495
7.483
7.478
7.472
7.466
7.463
7.459
7.449
7.445
7.442
7.430
7.426
7.421
7.388
7.384
7.381
7.371
7.366
7.360
7.351
7.347
7.344
7.289
7.285
7.280
7.272
7.268
7.265
2.656
2.640
2.630
2.623
2.525
2.519
2.509
2.504
2.498
2.492
1.683
1.674
1.666
1.658
1.649
Ph
O
O
Br
57
3.985
2.119
2.003
2.003
4.206
1.100
1.937
ppm

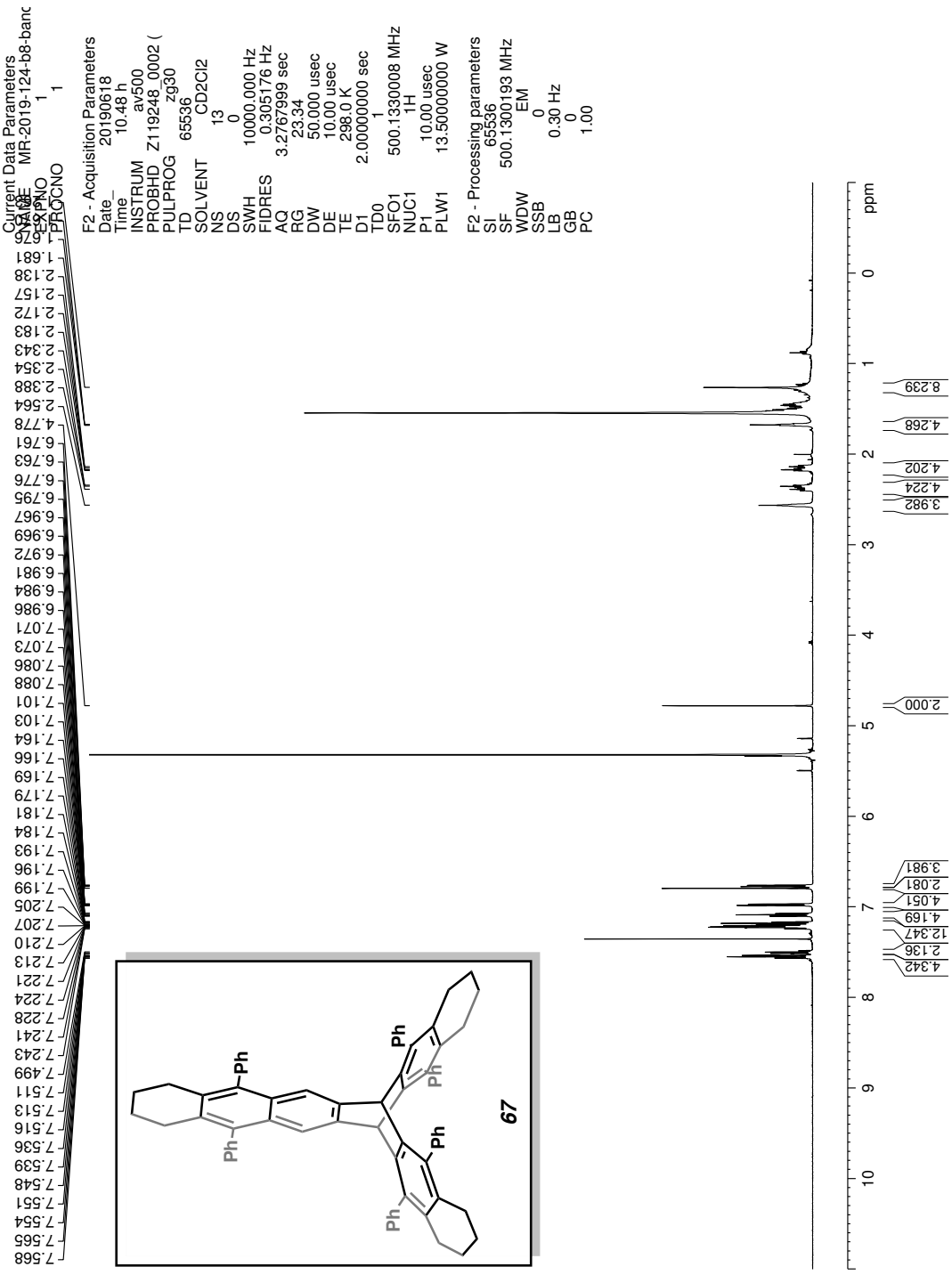

Current Data Parameters
NAME JSB-2018-014-1H-062
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200625
Time_ 9.37
INSTRUM av600
PROBHD 5 mm BB5
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 13
DS 0
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 256
DW 40.400 usec
DE 6.50 usec
TE 295.4 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 17.00 usec
PL1 -1.00 dB
PL1W 31.62277603 W
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300289 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.334
8.331
8.323
8.319
7.823
7.819
7.811
7.808
7.474
7.462
7.451
7.449
7.405
7.402
7.400
7.393
7.390
7.387
7.380
7.378
7.375
7.293
7.291
7.279
7.277
2.692
2.681
2.670
2.553
2.542
2.531
1.705
1.699
1.693
Ph
O
O
NO2
58
4.264
2.000
1.930
2.555
1.282
1.984
1.772
1.835
ppm


Current Data Parameters
NAME JSB-2018-019-06252(
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200625
Time 18.34 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 26.59
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.555
7.539
7.522
7.509
7.464
7.450
7.435
7.332
7.314
7.298
7.284
7.243
7.236
7.233
7.226
7.014
7.009
2.792
2.780
2.767
2.620
2.608
2.596
1.752
1.739
1.734
1.728
1.716
Ph
S
63
ppm
3.872
1.023
3.926
1.617
0.987
4.061
2.000
1.997

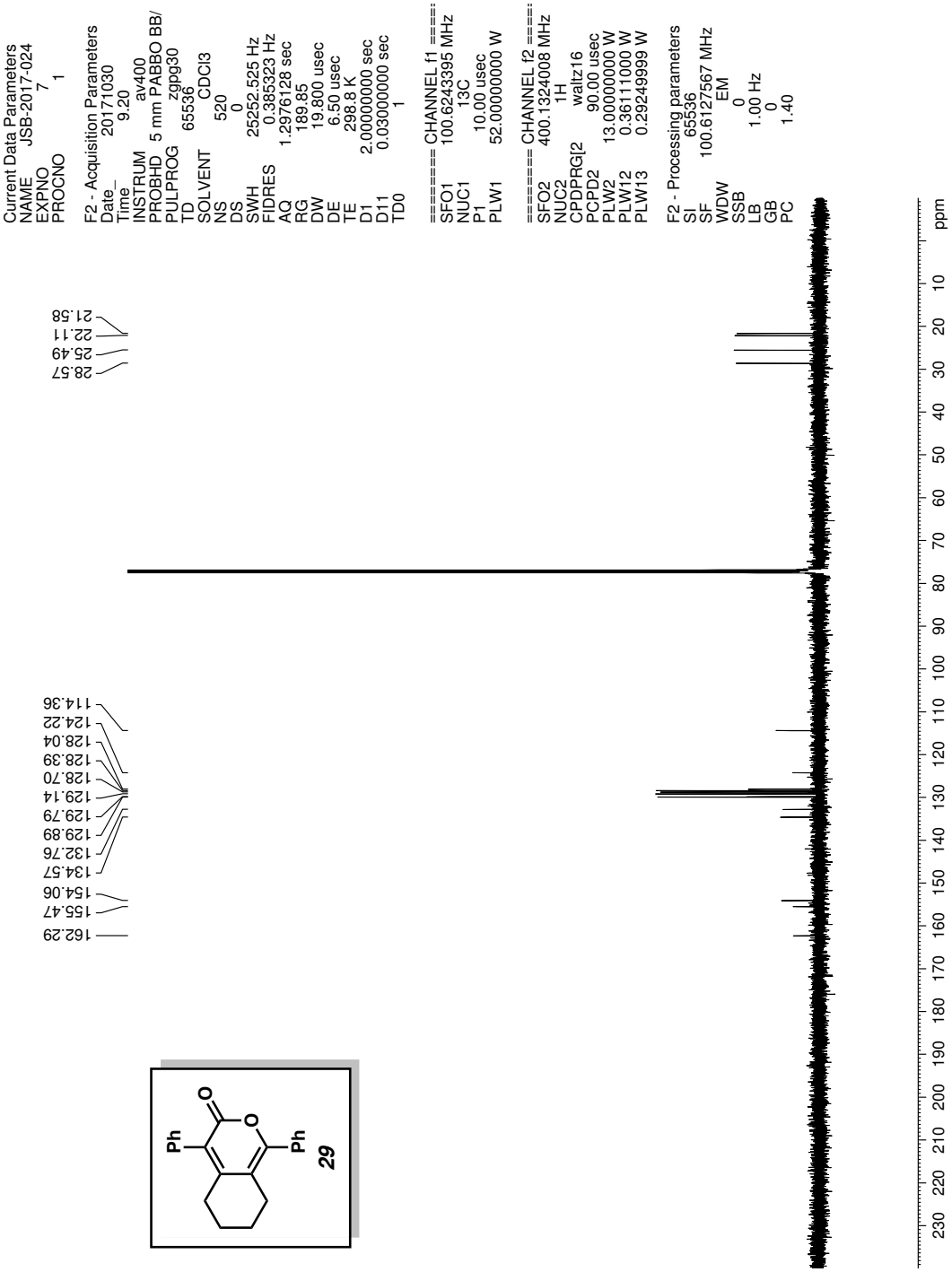

Current Data Parameters
NAME JSB-2017-071
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171107
Time 19.15
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 189.85
DW 62.400 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ======
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1300184 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
OMe
64
ppm
4.377
4.000
2.949
1.949
3.839
3.069
0.978
1.046
2.048

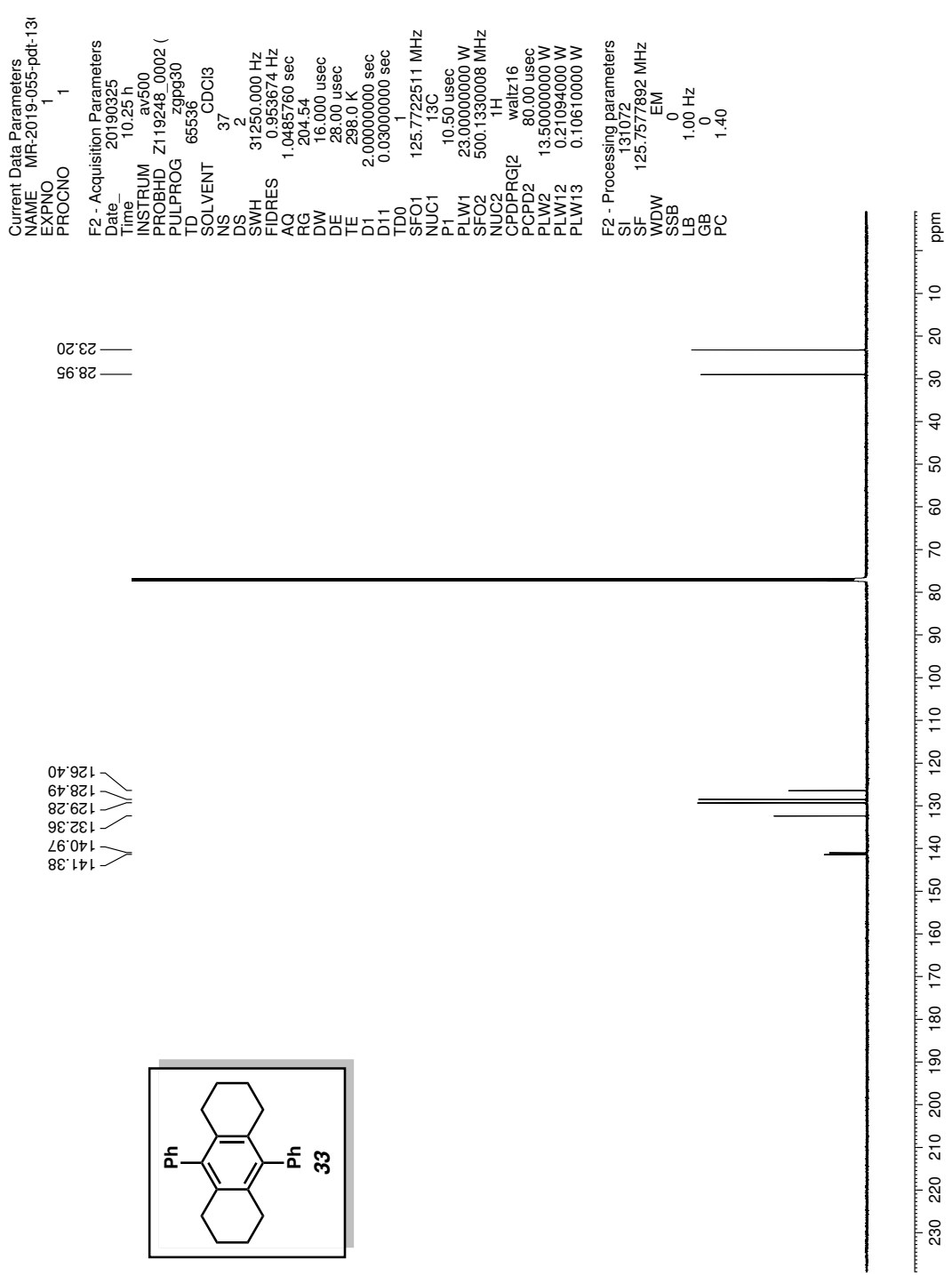

Current Data Parameters
NAME JSB-2017-073-101402
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191014
Time 17.42 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 19.06
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.710
2.603
2.613
7.190
7.206
7.231
7.233
7.240
7.248
7.250
7.290
7.303
7.319
7.329
7.334
7.337
7.347
7.365
7.433
7.449
7.463
7.509
7.524
7.538
7.650
7.667
Ph
Br
65
3.934
3.939
2.000
2.054
1.131
4.178
2.092
2.031
ppm

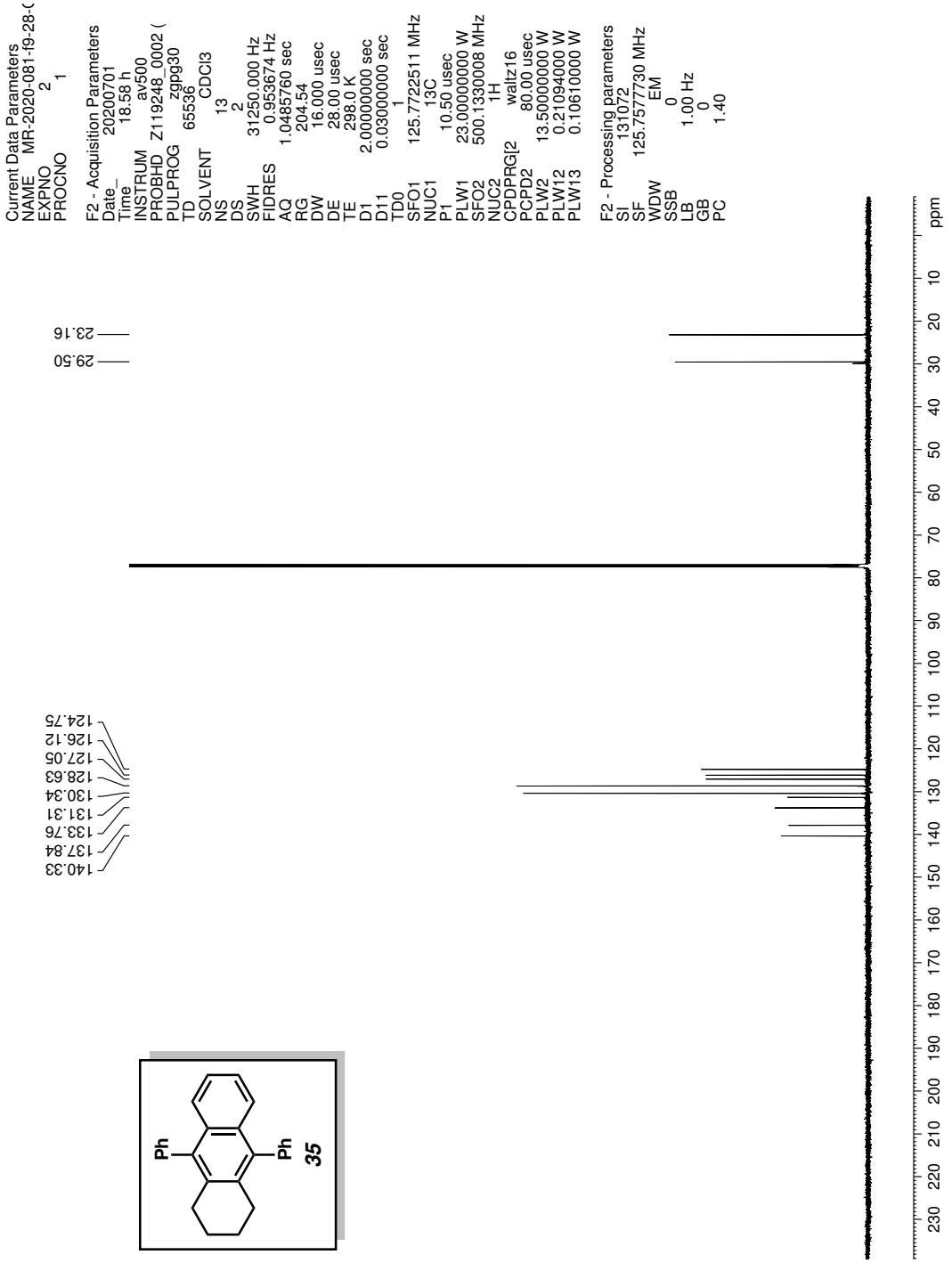

Current Data Parameters
NAME JSB-2018-016-06252C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200625
Time 16.19 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 7
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.27677999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
NO2
66
ppm
4.133
2.000
1.966
1.028
0.835
2.641
1.109
1.078
4.024
1.988

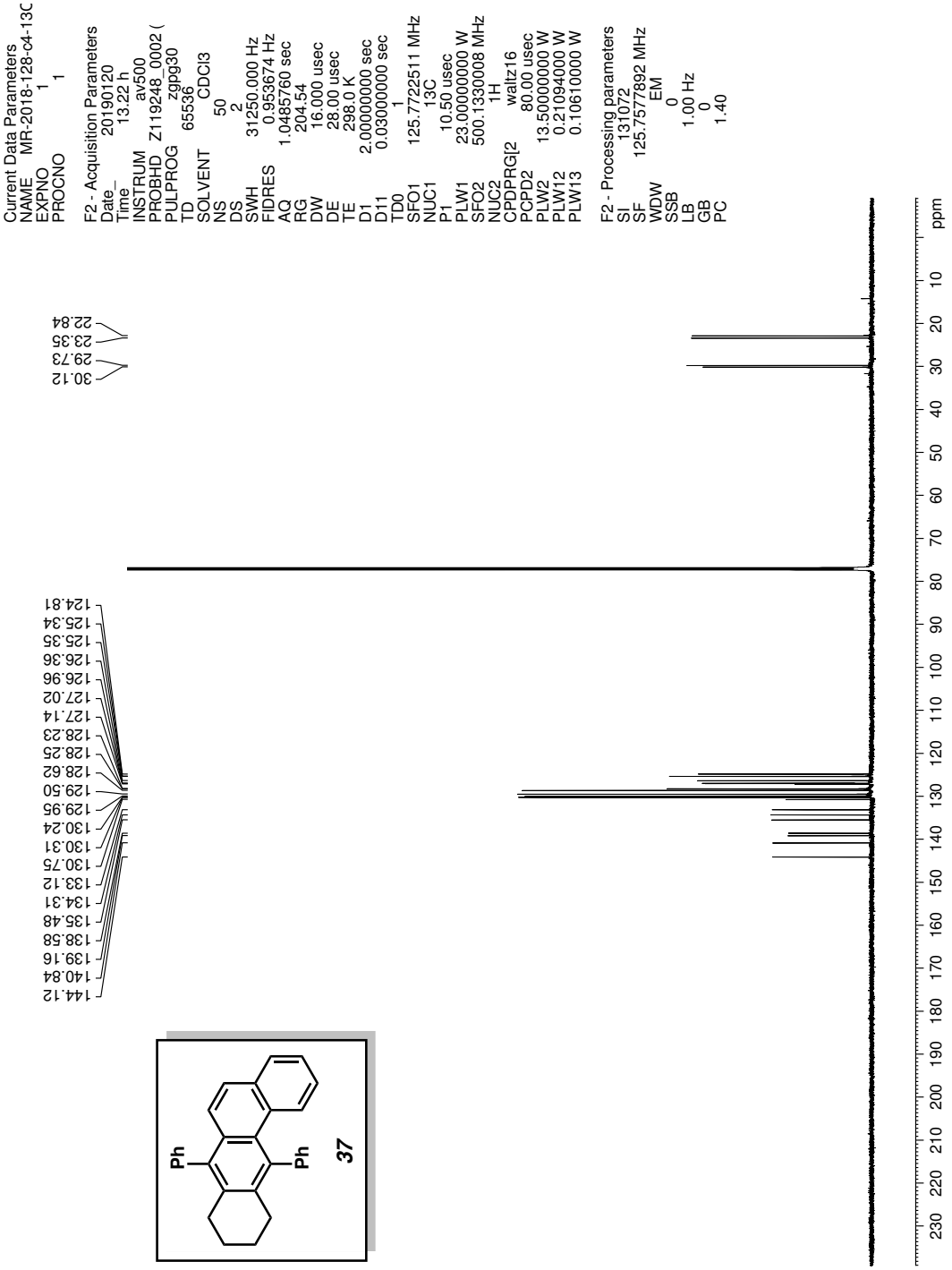

Current Data Parameters
NAME MR-2019-124-b8-banc
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190618
Time 10.48 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 13
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 23.34
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300193 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm
8.239
4.268
4.202
4.224
3.982
2.000
3.981
2.081
4.051
4.169
12.347
2.136
4.342
Ph
Ph
Ph
Ph
Ph
67

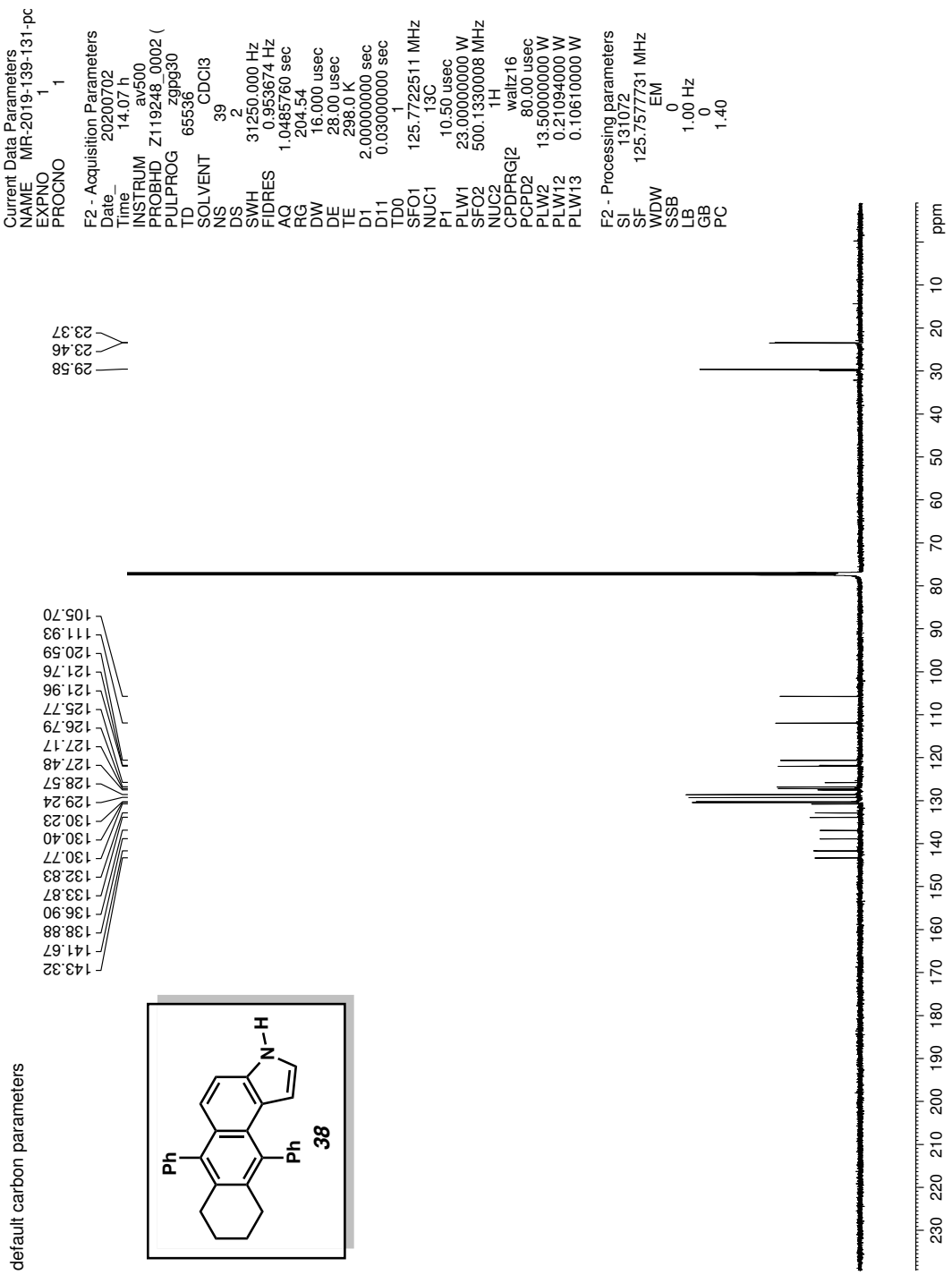
^{13}C NMR

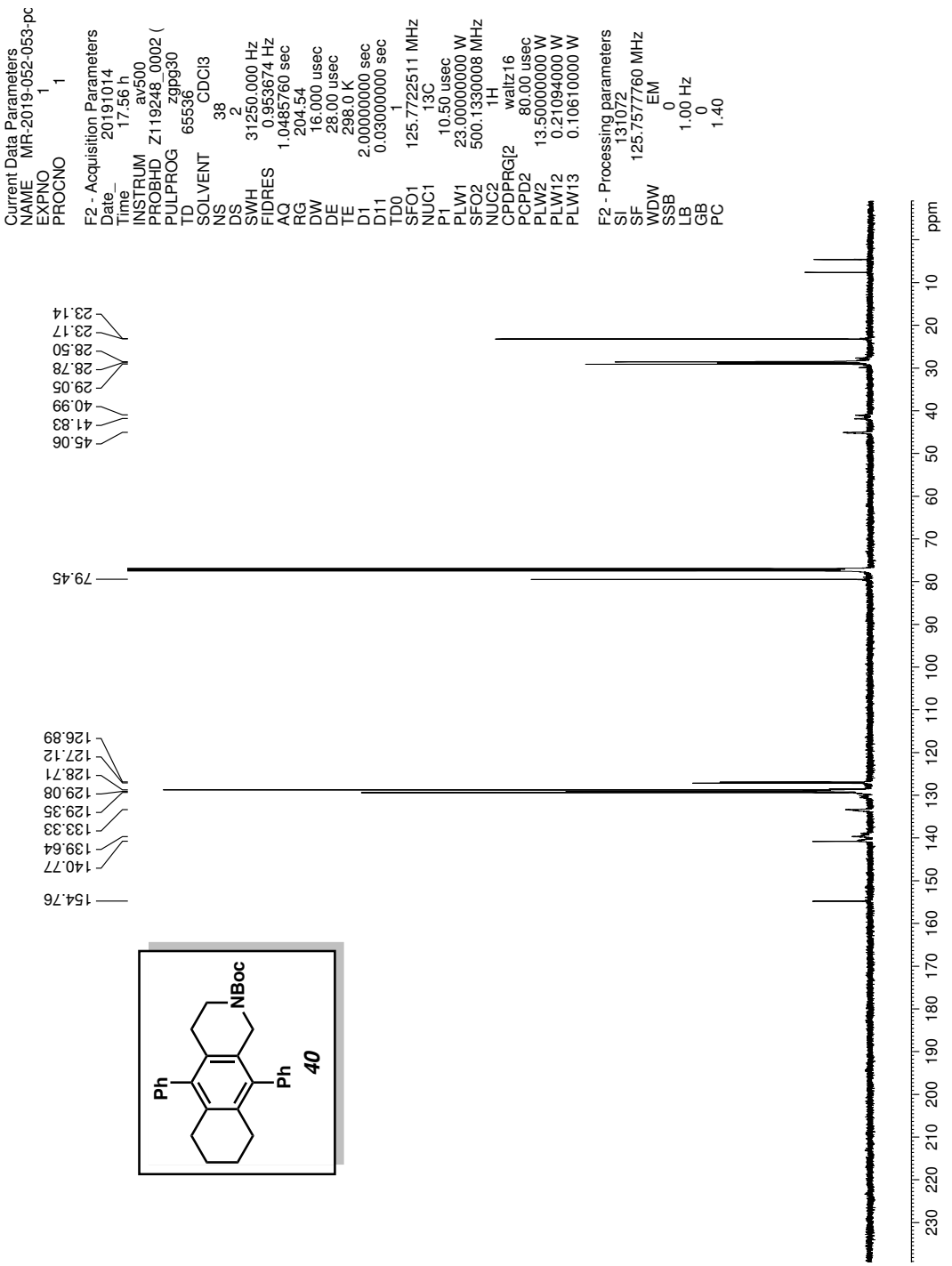

Current Data Parameters
NAME JSB-2017-024
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171030
Time 9.20
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 520
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 189.85
DW 19.800 usec
DE 6.50 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 =====
SFO1 100.6243395 MHz
NUC1 13C
P1 10.00 usec
PLW1 52.00000000 W
======== CHANNEL f2 =====
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W
PLW13 0.29249999 W
F2 - Processing parameters
SI 65536
SF 100.6127567 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
21.58
22.11
25.49
28.57
114.36
124.22
128.04
128.39
128.70
129.14
129.79
129.89
132.76
134.57
154.06
155.47
162.29
O
O
Ph
Ph
29
ppm

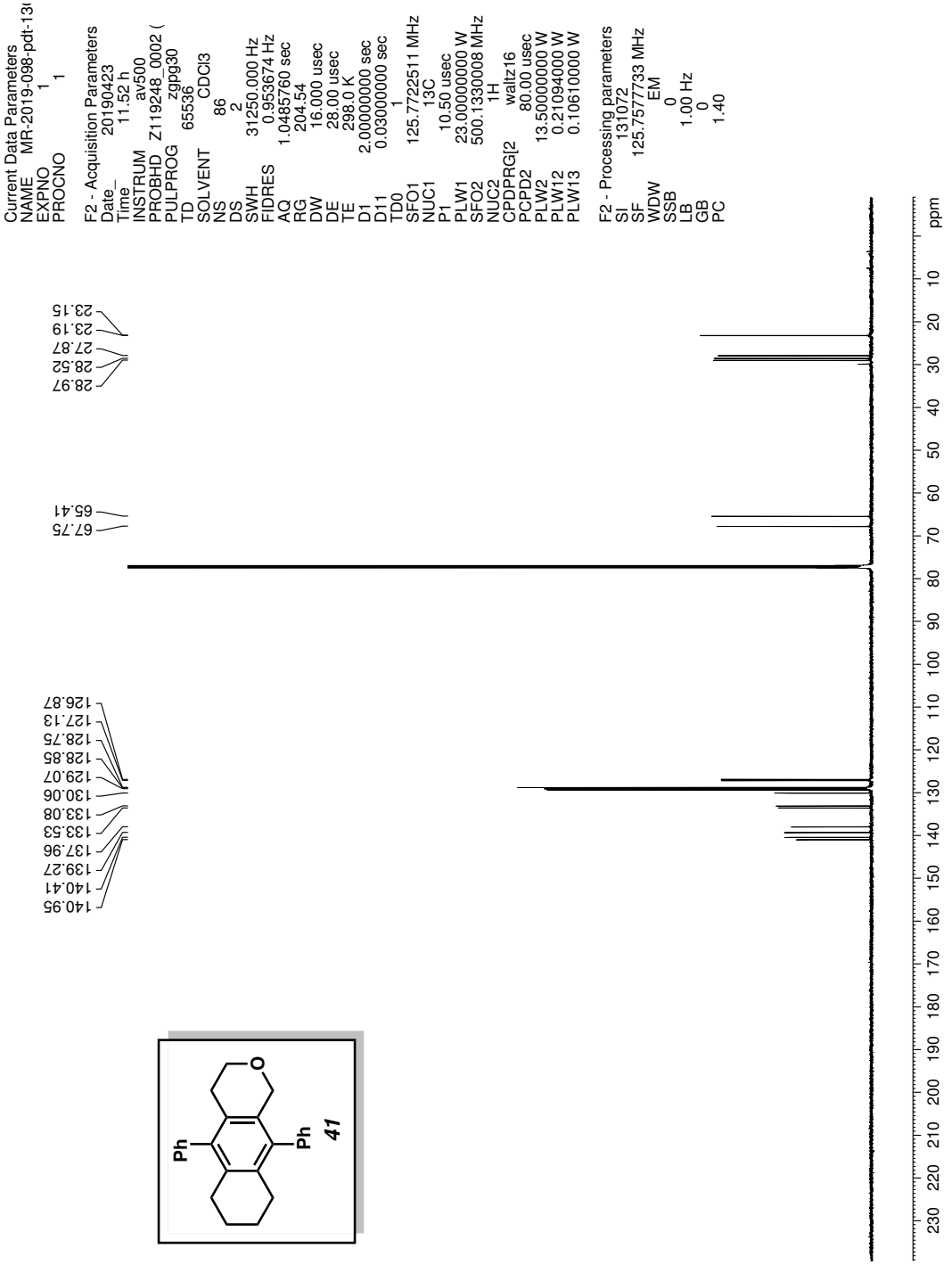

Current Data Parameters
NAME MR-2019-055-pdt-13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190325
Time_ 10.25 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 37
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
23.20
28.95
126.40
128.49
129.28
132.36
140.97
141.38
Ph
Ph
33
ppm

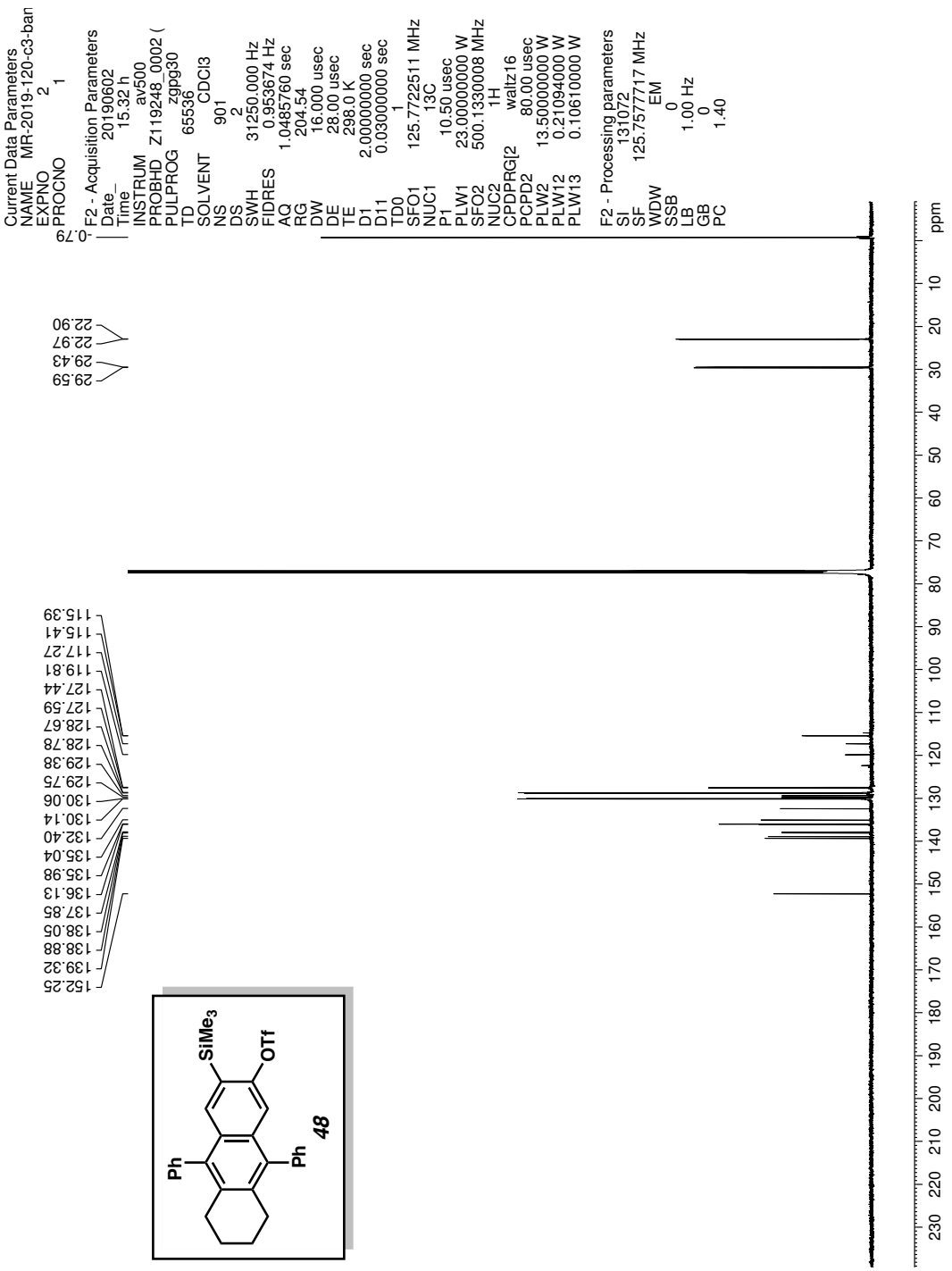

Current Data Parameters
NAME MR-2020-081-f9-28-C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200701
Time 18.58 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 13
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577730 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
23.16
29.50
124.75
126.12
127.05
128.63
130.34
131.31
133.76
137.84
140.33
Ph
Ph
35
ppm

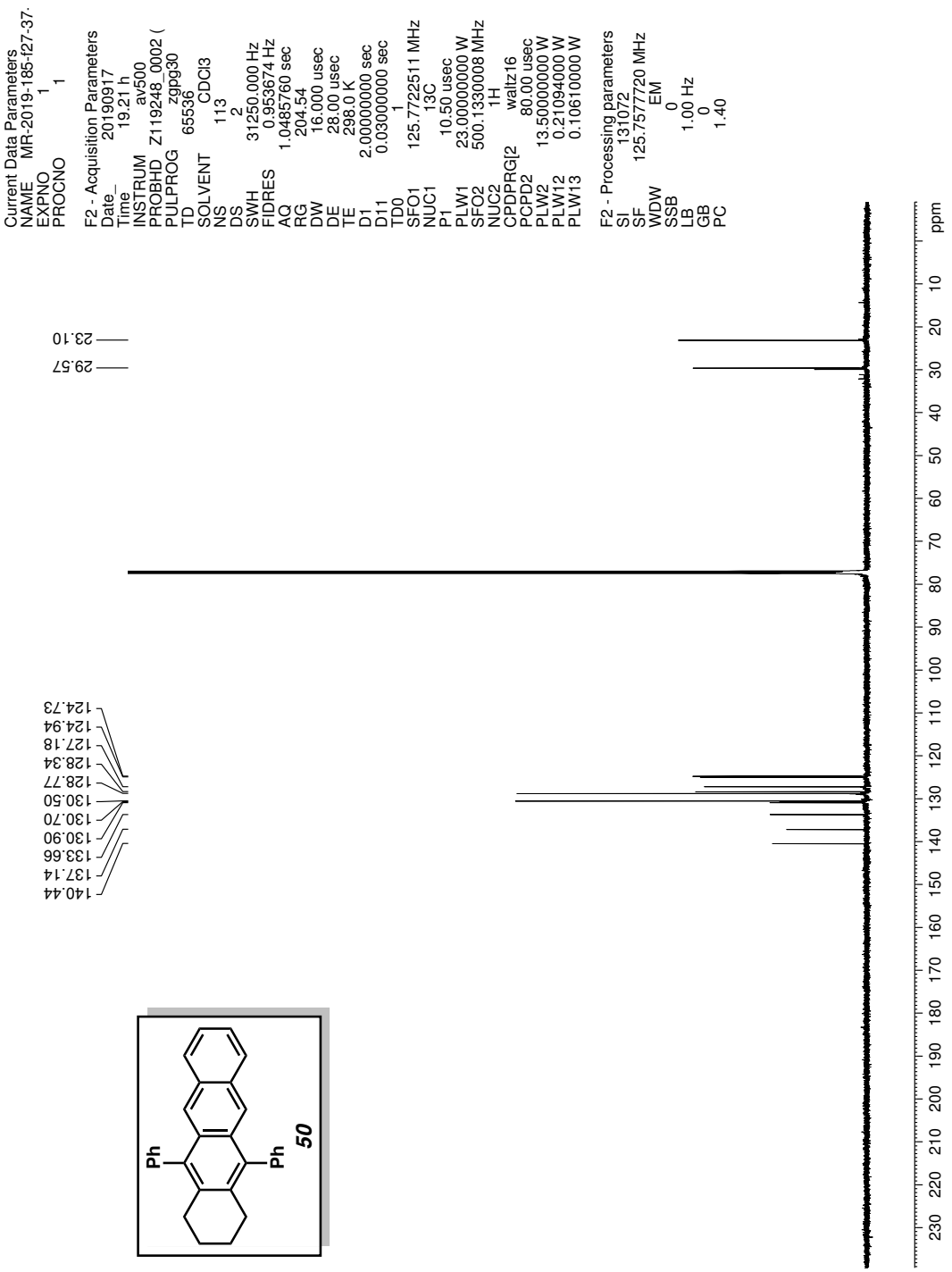

Current Data Parameters
NAME MR-2018-128-c4-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190120
Time_ 13.22 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 50
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
30.12
29.73
23.35
22.84
144.12
140.84
139.16
138.58
135.48
134.31
133.12
130.75
130.31
130.24
129.95
129.50
128.62
128.25
128.23
127.14
127.02
126.96
126.36
125.35
125.34
124.81
Ph
Ph
37
ppm

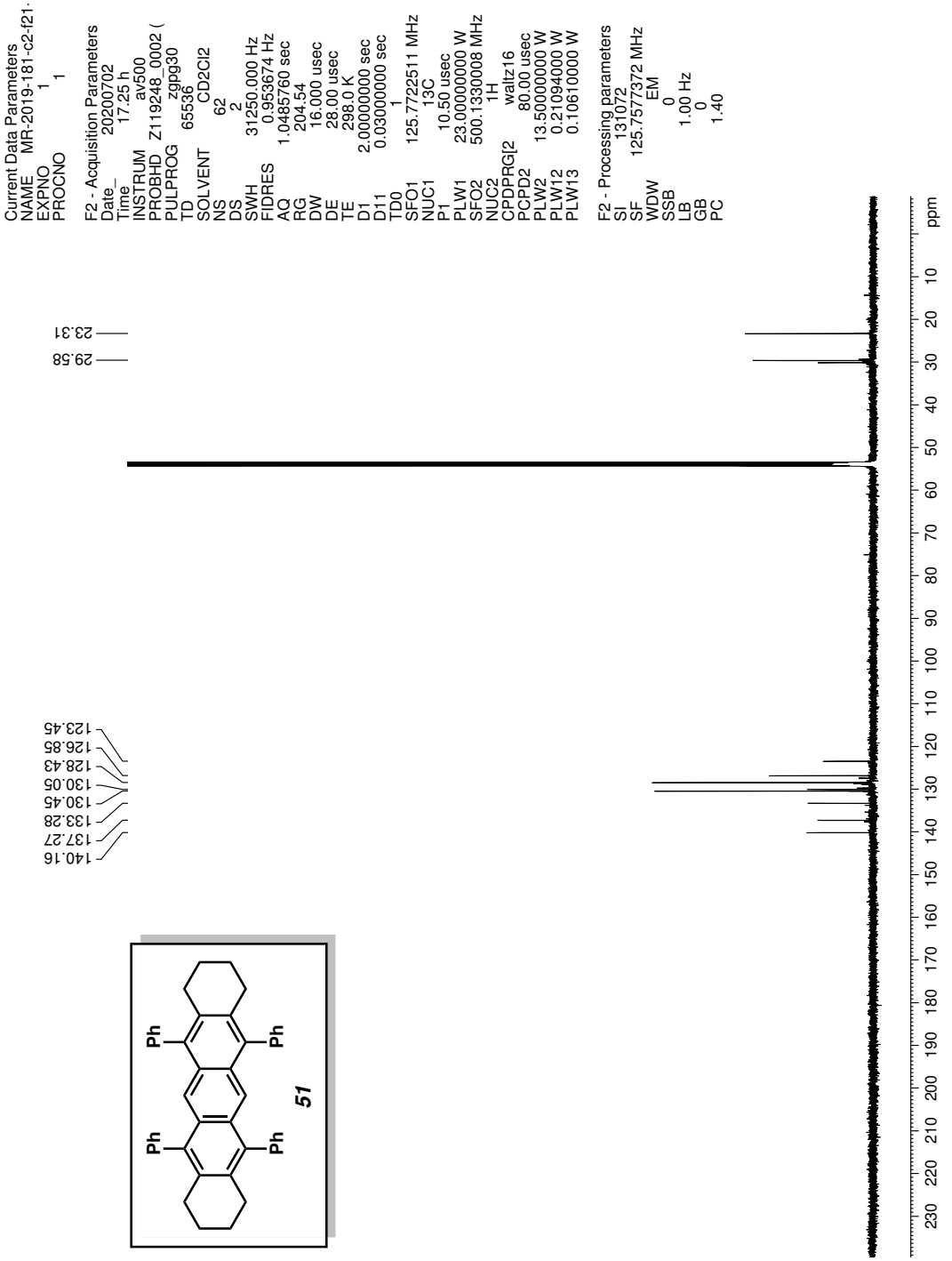

Current Data Parameters
NAME MR-2019-139-131-pc
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200702
Time_ 14.07 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 39
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577731 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
default carbon parameters
29.58
23.46
23.37
143.32
141.67
138.88
136.90
133.87
132.83
130.77
130.40
130.23
129.24
128.57
127.48
127.17
126.79
125.77
121.96
121.76
120.59
111.93
105.70
Ph
Ph
N–H
38
ppm

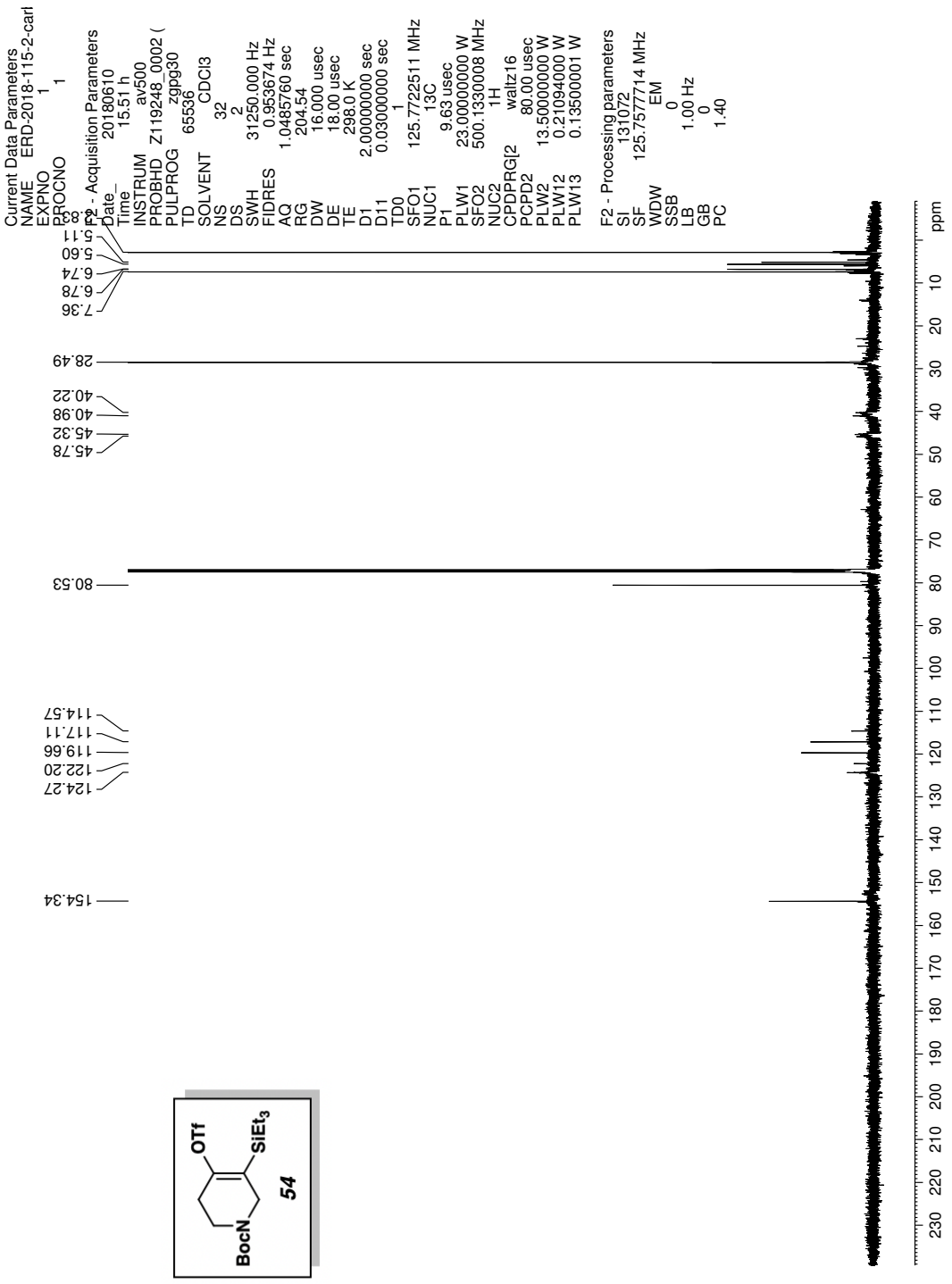

Current Data Parameters
NAME MR-2019-052-053-pc
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191014
Time 17.56 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 38
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577760 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
23.14
23.17
28.50
28.78
29.05
40.99
41.83
45.06
79.45
126.89
127.12
128.71
129.08
129.35
133.33
139.64
140.77
154.76
NBoc
Ph
Ph
40
ppm

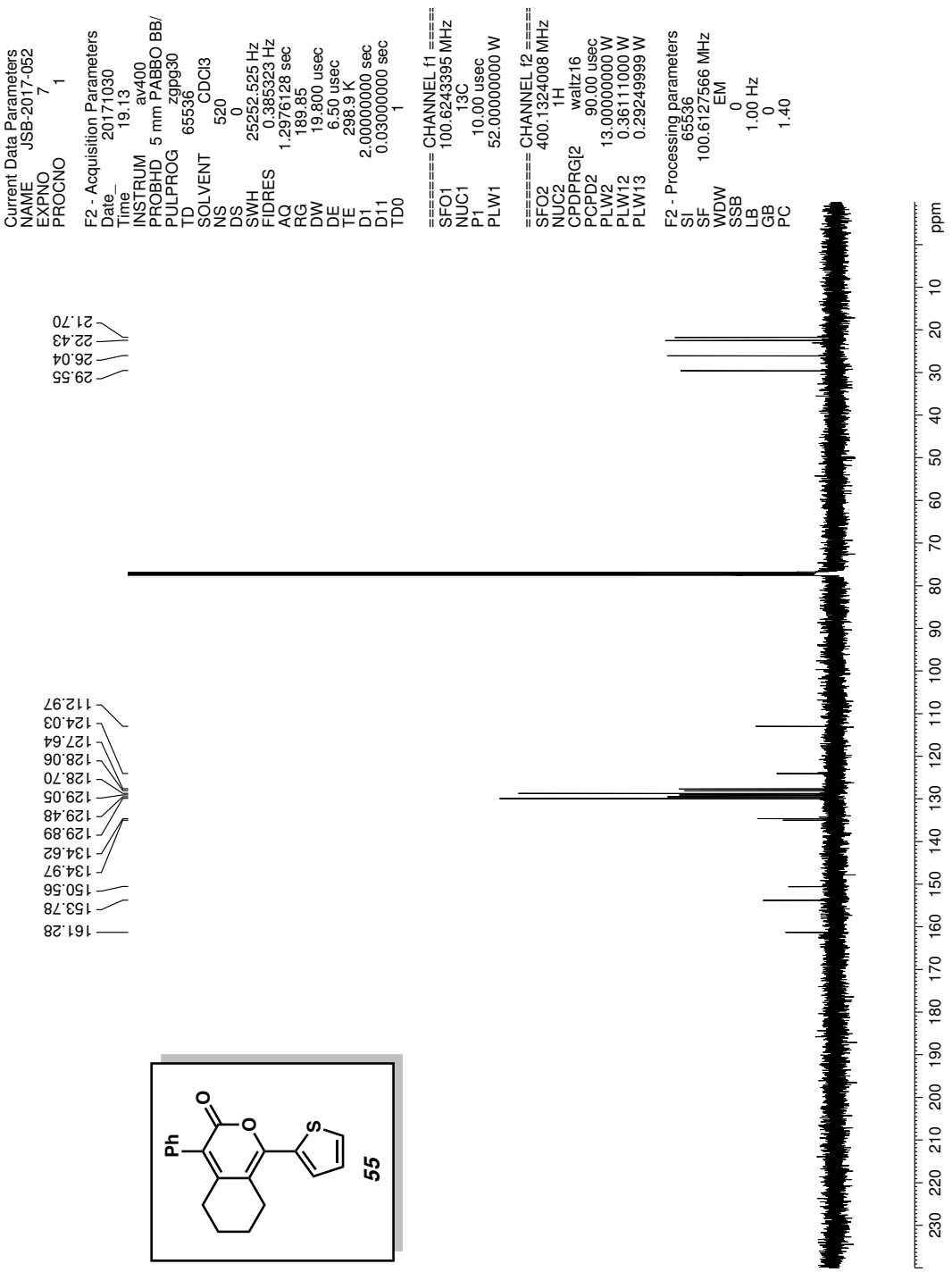

Current Data Parameters
NAME MR-2019-098-pdt-13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190423
Time 11.52 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 86
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577733 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
23.15
23.19
27.87
28.52
28.97
65.41
67.75
126.87
127.13
128.75
128.85
129.07
130.06
133.08
133.53
137.96
139.27
140.41
140.95
Ph
Ph
O
41
ppm

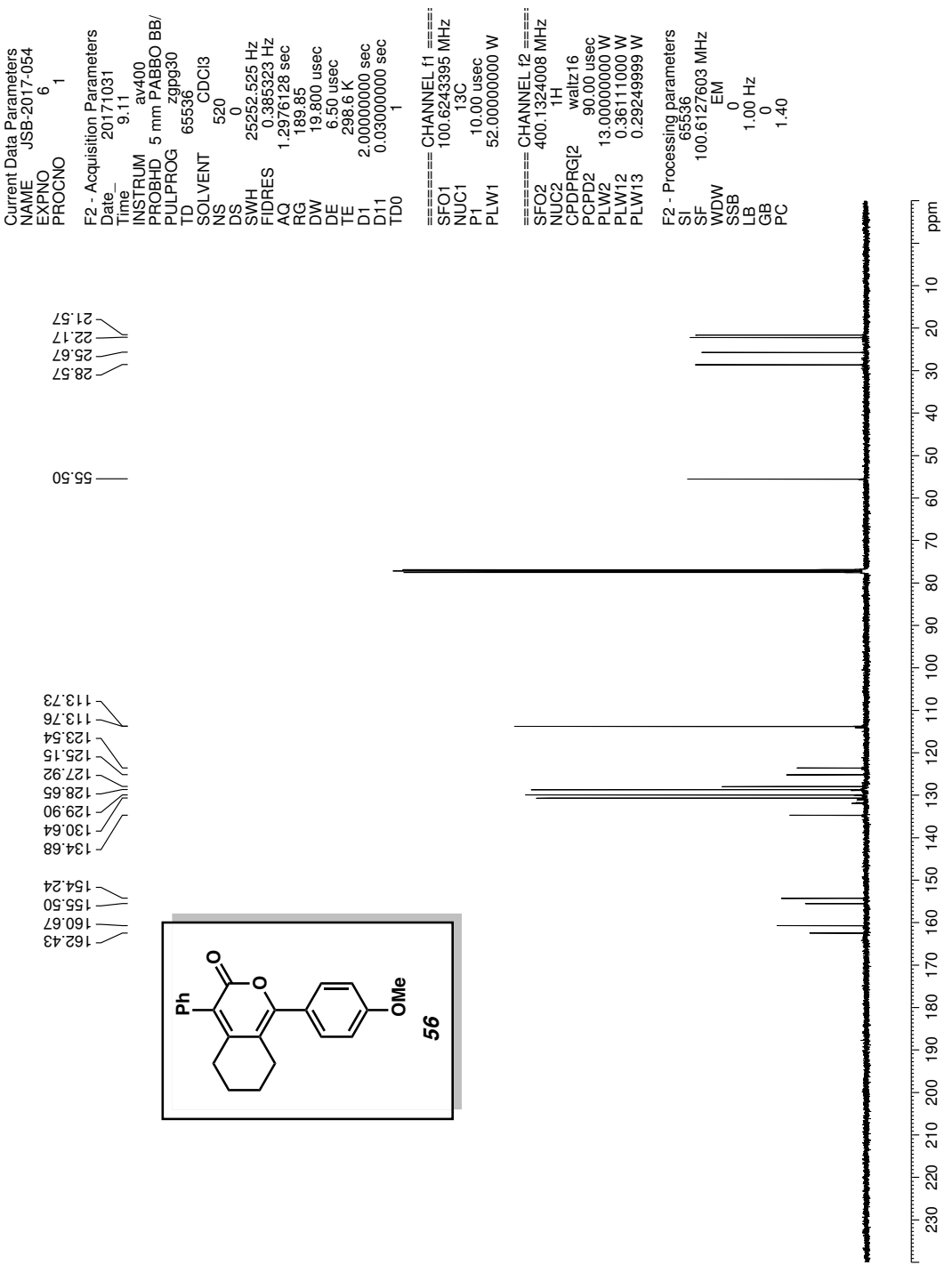

Current Data Parameters
NAME MR-2019-120-c3-ban
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190602
Time 15.32 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 901
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577717 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
-0.79
29.59
29.43
22.97
22.90
115.39
115.41
117.27
119.81
127.44
127.59
128.67
128.78
129.38
129.75
130.06
130.14
132.40
135.04
135.98
136.13
137.85
138.05
138.88
139.32
152.25
SiMe3
OTf
Ph
Ph
48
ppm

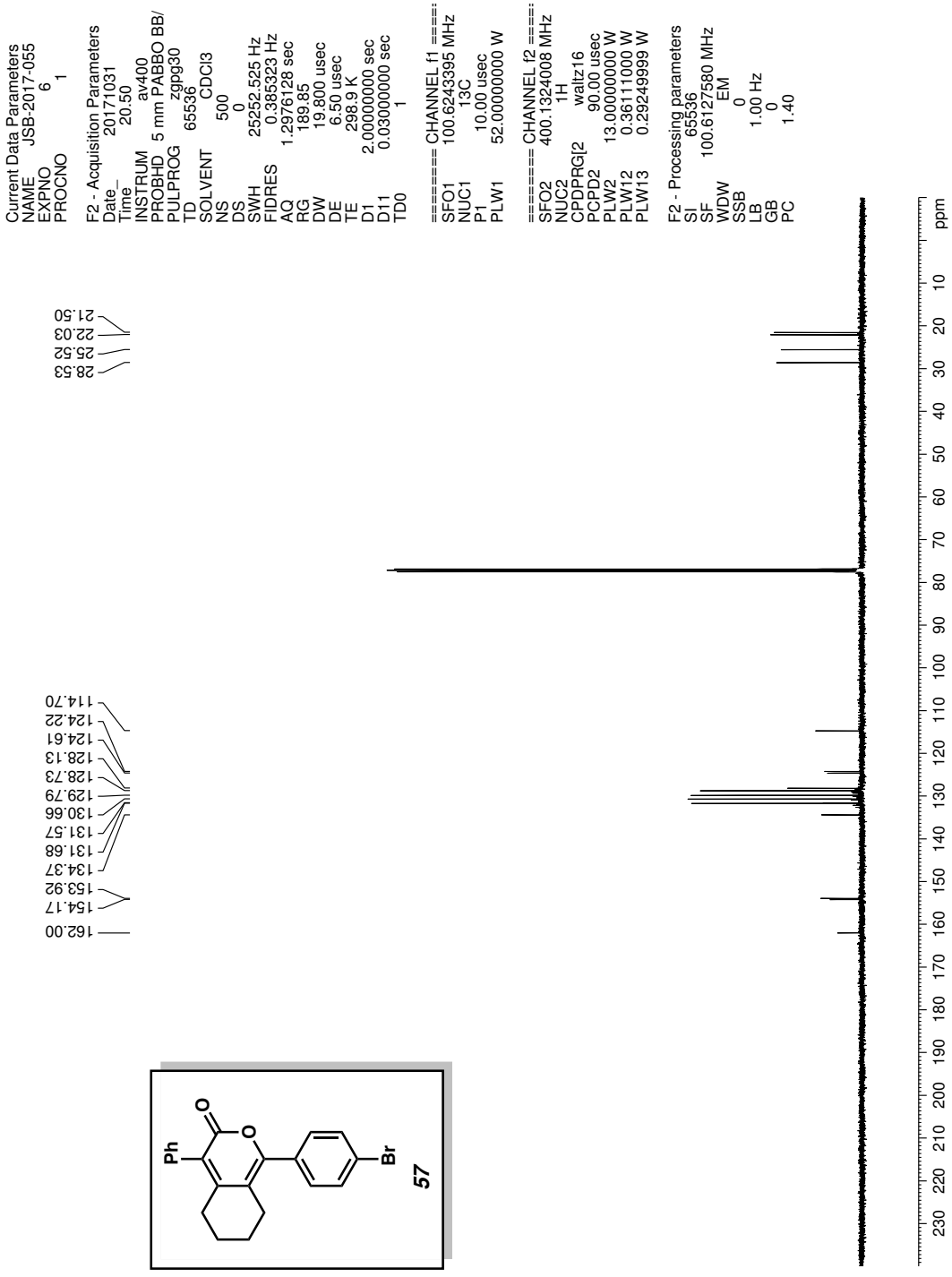

Current Data Parameters
NAME MR-2019-185-f27-37-
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190917
Time 19.21 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 113
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577720 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
23.10
29.57
124.73
124.94
127.18
128.34
128.77
130.50
130.70
130.90
133.66
137.14
140.44
Ph
Ph
50
ppm

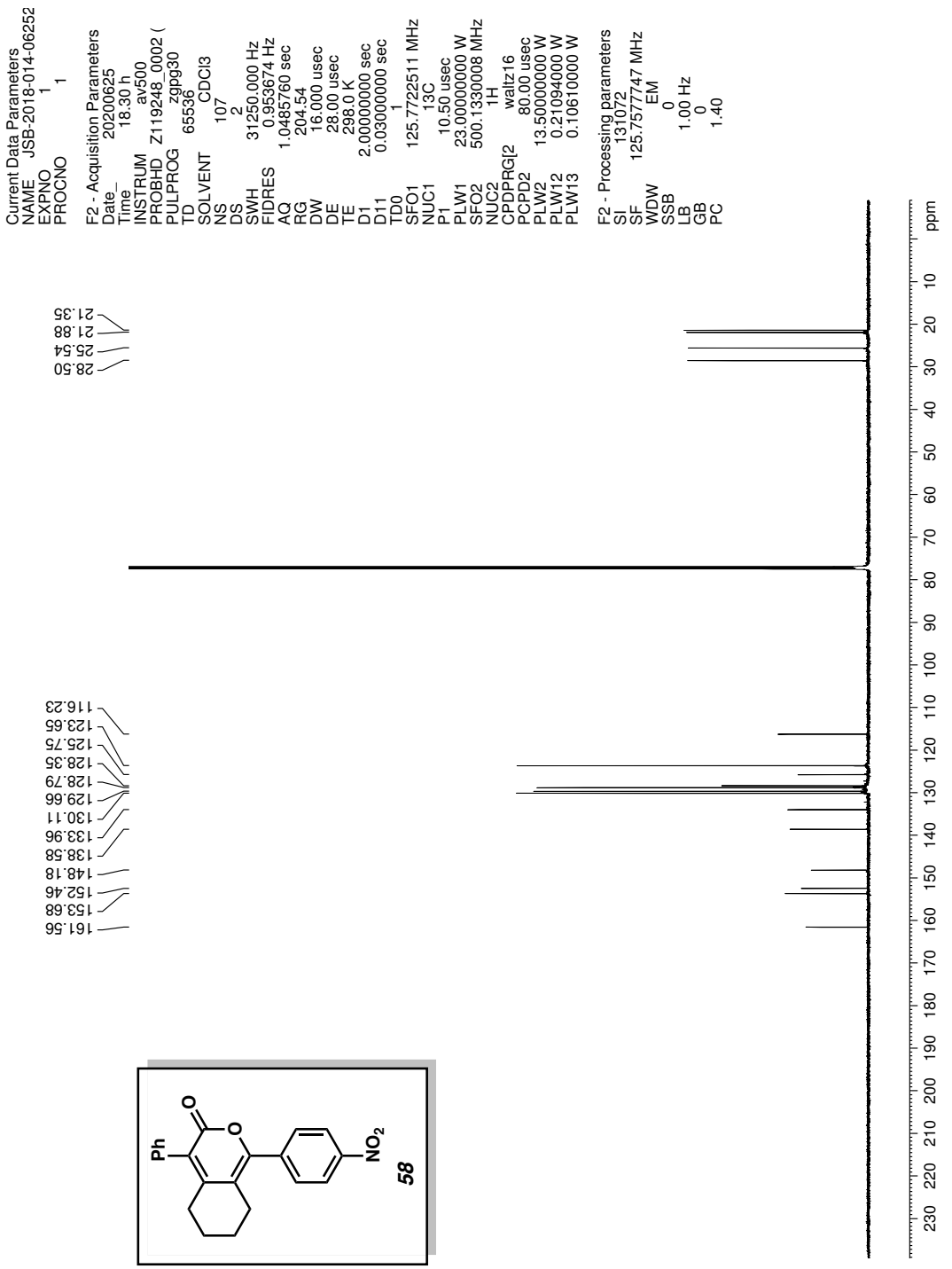

Current Data Parameters
NAME MR-2019-181-c2-f21-
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200702
Time 17.25 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CD2Cl2
NS 62
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577372 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
23.31
29.58
123.45
126.85
128.43
130.05
130.45
133.28
137.27
140.16
Ph
Ph
Ph
Ph
51
ppm

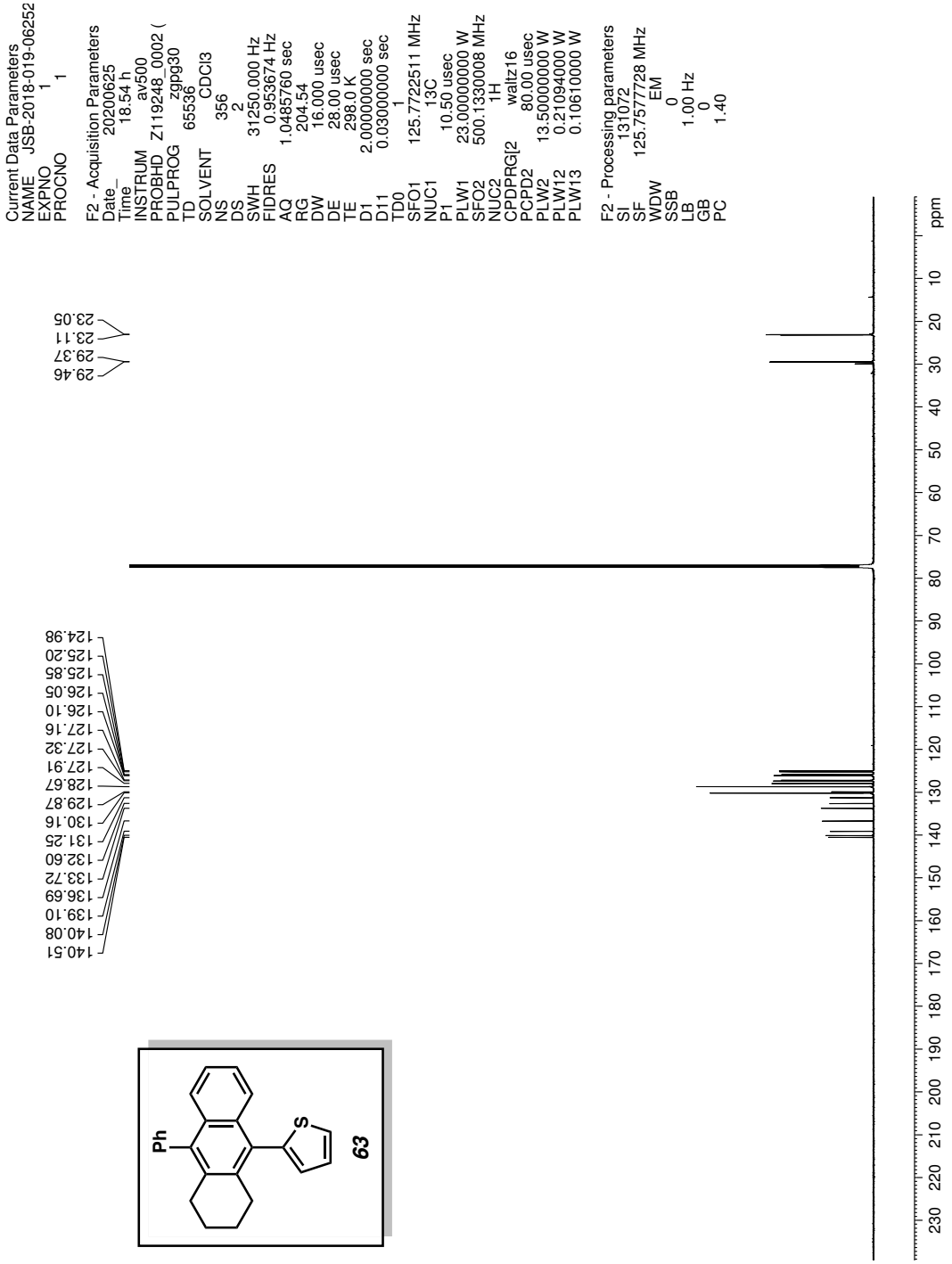

Current Data Parameters
NAME ERD-2018-115-2-carl
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180610
Time 15.51 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.13500001 W
F2 - Processing parameters
SI 131072
SF 125.7577714 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
7.36
6.78
6.74
5.60
5.11
28.49
40.22
40.98
45.32
45.78
80.53
114.57
117.11
119.66
122.20
124.27
154.34
ppm
OTf
SiEt3
BocN
54

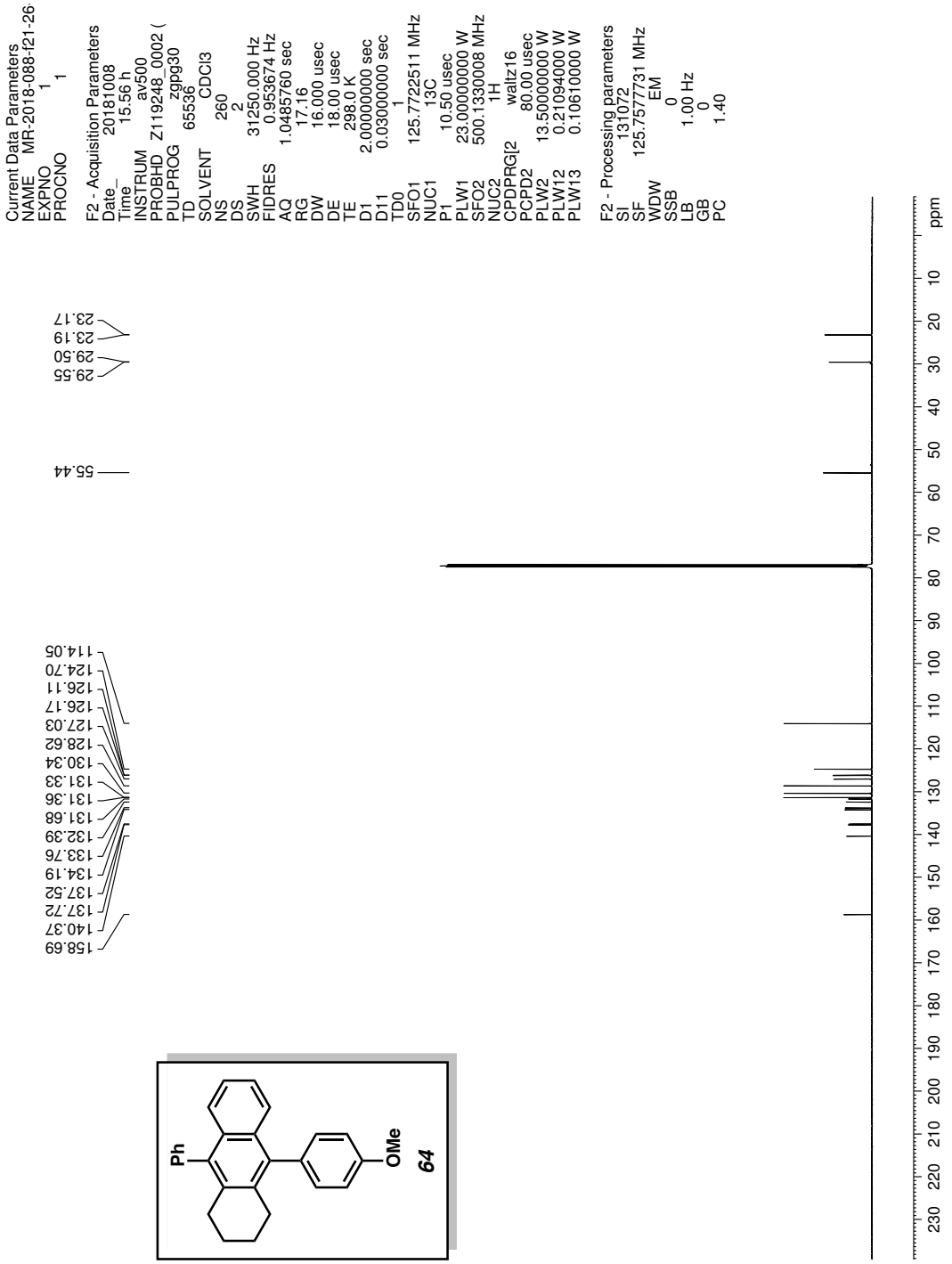

Current Data Parameters
NAME JSB-2017-052
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171030
Time 19.13
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 520
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 189.85
DW 19.800 usec
DE 6.50 usec
TE 298.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 =====
SFO1 100.6243395 MHz
NUC1 13C
P1 10.00 usec
PLW1 52.00000000 W
======== CHANNEL f2 =====
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W
PLW13 0.29249999 W
F2 - Processing parameters
SI 65536
SF 100.6127566 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
161.28
153.78
150.56
134.97
134.62
129.89
129.48
129.05
128.70
128.06
127.64
124.03
112.97
29.55
26.04
22.43
21.70
Ph
O
O
S
55
ppm

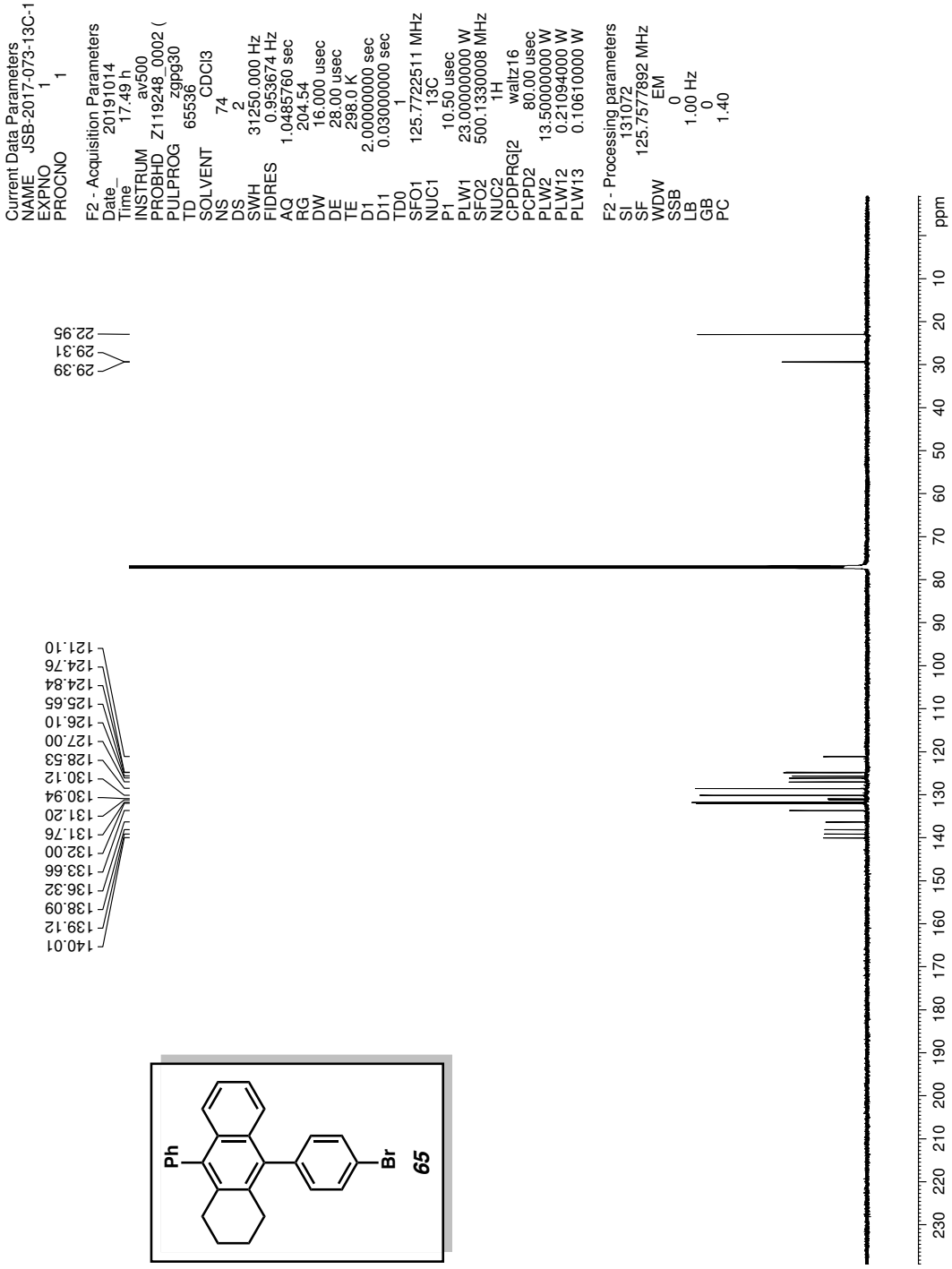

Current Data Parameters
NAME JSB-2017-054
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171031
Time 9.11
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 520
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 189.85
DW 19.800 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6243395 MHz
NUC1 13C
P1 10.00 usec
PLW1 52.00000000 W
======== CHANNEL f2 ========
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W
PLW13 0.29249999 W
F2 - Processing parameters
SI 65536
SF 100.6127603 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
21.57
22.17
25.67
28.57
55.50
113.73
113.76
123.54
125.15
127.92
128.65
129.90
130.64
134.68
154.24
155.50
160.67
162.43
Ph
O
O
OMe
56
ppm

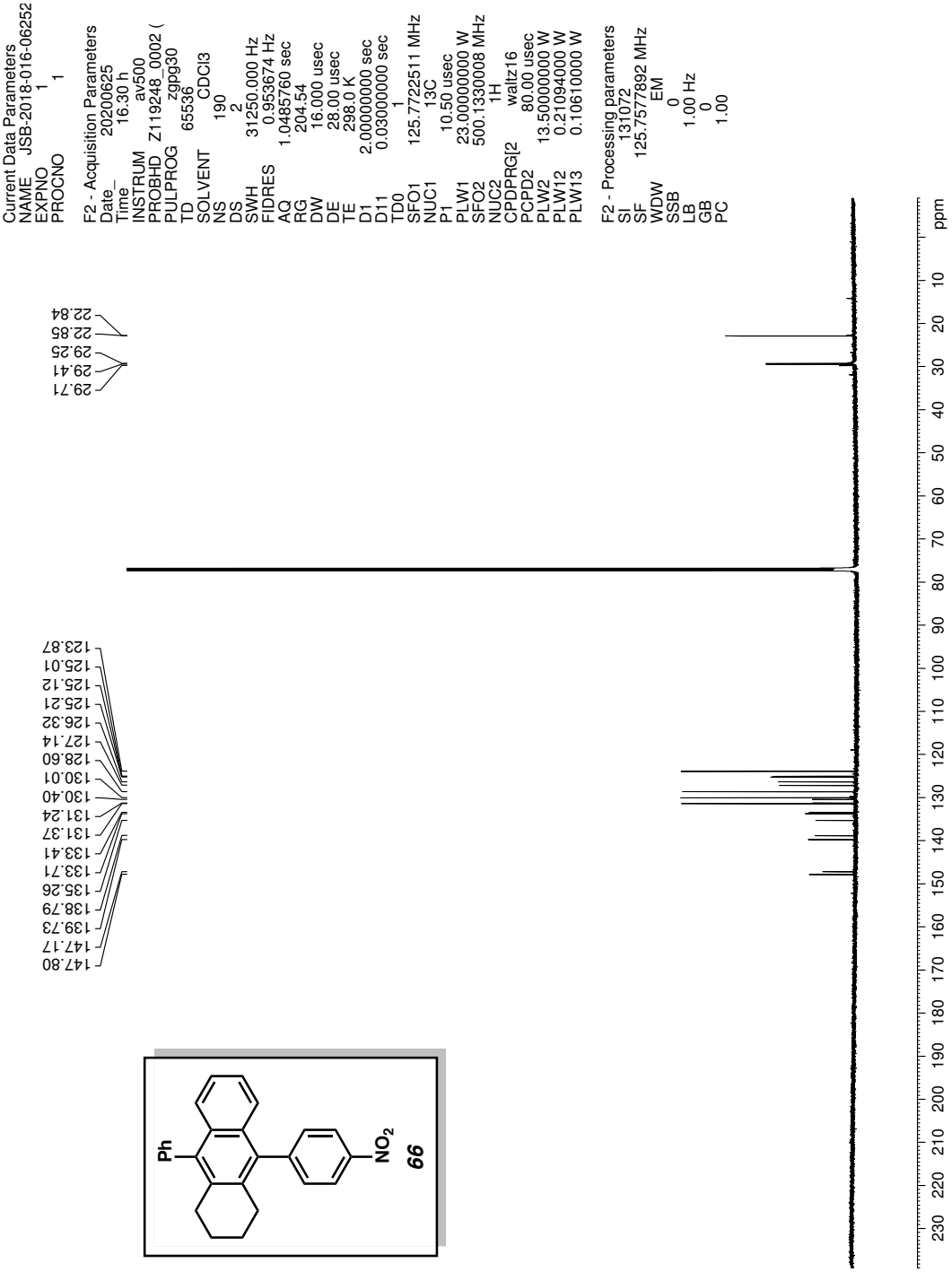

Current Data Parameters
NAME JSB-2017-055
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171031
Time_ 20.50
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976128 sec
RG 189.85
DW 19.800 usec
DE 6.50 usec
TE 298.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6243395 MHz
NUC1 13C
P1 10.00 usec
PLW1 52.00000000 W
======== CHANNEL f2 ========
SFO2 400.1324008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.36111000 W
PLW13 0.29249999 W
F2 - Processing parameters
SI 65536
SF 100.6127580 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
162.00
154.17
153.92
134.37
131.68
131.57
130.66
129.79
128.73
128.13
124.61
124.22
114.70
28.53
25.52
22.03
21.50
Ph
O
O
Br
57
ppm

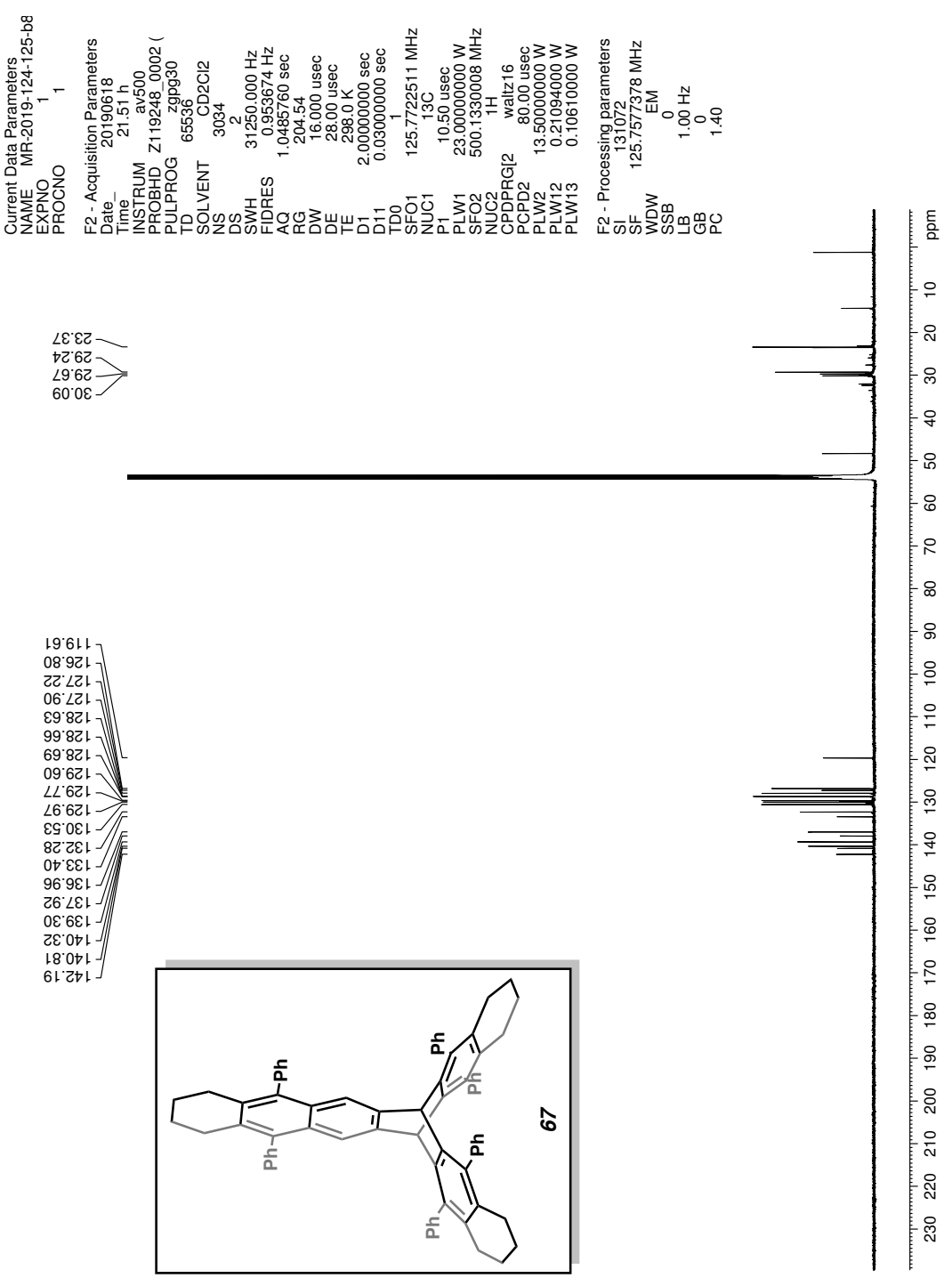

Current Data Parameters
NAME JSB-2018-014-06252
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200625
Time 18.30 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 107
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577747 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
28.50
25.54
21.88
21.35
161.56
153.68
152.46
148.18
138.58
133.96
130.11
129.66
128.79
128.35
125.75
123.65
116.23
Ph
O
O
NO2
58
ppm


Current Data Parameters
NAME JSB-2018-019-06252
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200625
Time_ 18.54 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 356
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577728 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
29.46
29.37
23.11
23.05
140.51
140.08
139.10
136.69
133.72
132.60
131.25
130.16
129.87
128.67
127.91
127.32
127.16
126.10
126.05
125.85
125.20
124.98
Ph
S
63
ppm


Current Data Parameters
NAME MR-2018-088-f21-26
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181008
Time 15.56 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 260
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 17.16
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577731 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
158.69
140.37
137.72
137.52
134.19
133.76
132.39
131.68
131.36
131.33
130.34
128.62
127.03
126.17
126.11
124.70
114.05
55.44
29.55
29.50
23.19
23.17
Ph
OMe
64
ppm


Current Data Parameters
NAME JSB-2017-073-13C-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191014
Time 17.49 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 74
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
22.95
29.31
29.39
121.10
124.76
124.84
125.65
126.10
127.00
128.53
130.12
130.94
131.20
131.76
132.00
133.66
136.32
138.09
139.12
140.01
Ph
Br
65
ppm


Current Data Parameters
NAME JSB-2018-016-06252
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200625
Time 16.30 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 190
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
22.84
22.85
29.25
29.41
29.71
123.87
125.01
125.12
125.21
126.32
127.14
128.60
130.01
130.40
131.24
131.37
133.41
133.71
135.26
138.79
139.73
147.17
147.80
Ph
NO2
66
ppm


Current Data Parameters
NAME MR-2019-124-125-b8
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190618
Time 21.51 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CD2Cl2
NS 3034
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577378 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
30.09
29.67
29.24
23.37
142.19
140.81
140.32
139.30
137.92
136.96
133.40
132.28
130.53
129.97
129.77
129.60
128.69
128.66
128.63
127.90
127.22
126.80
119.61
Ph
Ph
Ph
Ph
Ph
67
ppm

Crystallographic Information

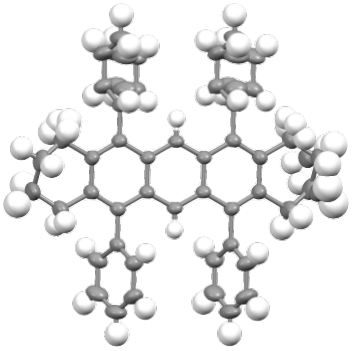


Figure S2. ORTEP representation of X-ray crystallographic structure **51** (CCDC Registry #2070892).

Table S1. Crystal data and structure refinement for **51**.

Identification code	cu_garg1906_a	
Empirical formula	C46 H38	
Formula weight	590.76	
Temperature	298(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.3930(2) Å	a= 90°.
	b = 8.5510(2) Å	b= 92.6530(10)°.
	c = 17.3991(3) Å	g = 90°.
Volume	1693.23(6) $Å^3$	
Z	2	
Density (calculated)	1.159 Mg/m^3	
Absorption coefficient	0.491 mm^{-1}	
F(000)	628	
Crystal size	.2 x .2 x .2 mm^3	
Theta range for data collection	3.884 to 70.070°.	
Index ranges	-13<=h<=13, -10<=k<=10, -20<=l<=21	

Reflections collected	32926
Independent reflections	3184 [R(int) = 0.0392]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.75 and 0.70
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3184 / 279 / 302
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0521, wR2 = 0.1505
R indices (all data)	R1 = 0.0664, wR2 = 0.1657
Extinction coefficient	n/a
Largest diff. peak and hole	0.165 and -0.171 e.Å^{-3}

Part II: Computational Section

All calculations were carried out with Gaussian 16. Geometry optimizations were performed with M06-2X functional[8] and the 6-31G(d) basis set. Frequency analysis was conducted at the same level of theory as for geometry optimizations to verify the stationary points to be minima or first-order saddle points. Free energy corrections were calculated both with and without Truhlar's quasiharmonic oscillator approximation.[9] Single-point energy calculations were performed with the same functional using a larger 6-311+G(d,p) basis set and the SMD solvent model[10] for acetonitrile to obtain more accurate energetics. HOMO and LUMO energies were computed using M06-2X/6-311+G(d,p). Optimized structures are presented using CYLview.[11]

A. Complete Citation for Gaussian 16

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16, Rev. A.03*, Wallingford, CT, 2016.

B. HOMO and LUMO Energies

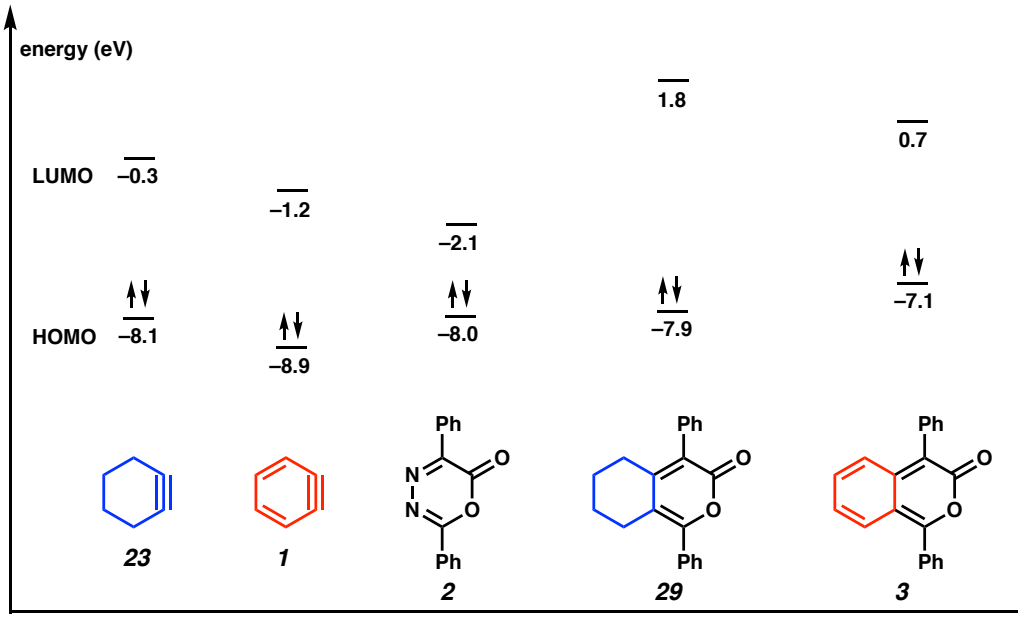
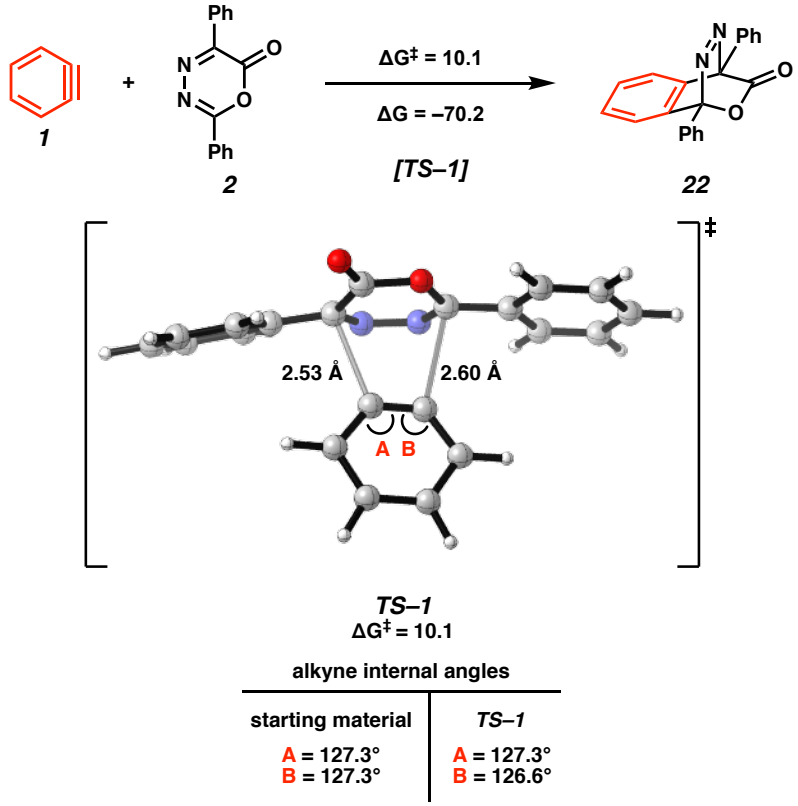


Figure S3. HOMO and LUMO energies of cyclohexyne (**23**), benzyne (**1**), oxadiazinone **2**, and pyrones **29** and **3**. Energies calculated with M06-2X/6-311+G(d,p) and in units of kcal mol^{-1}.

C. Transition State Structures and D/IAS Analysis

DA1



TS–1
ΔG‡ = 10.1

alkyne internal angles

starting material	*TS–1*
A = 127.3°	A = 127.3°
B = 127.3°	B = 126.6°

Figure S4. Transition states structure for DA1 of benzyne (**1**) and oxadiazinone **2** and alkyne internal angles in the starting material and **TS–1**. Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN) and are provided in kcal mol^{-1}. The alkyne internal angles in starting material **1** and **TS–1** differ by a small degree (0°–0.7°), demonstrating that benzyne (**1**) is predistorted for DA1. Predistortion of benzyne (**1**) results in a lower energy barrier for cycloaddition when compared to $\Delta G^{‡}$ for DA1 of cyclohexyne (**23**) and oxadiazinone **2** (see Figure S5).

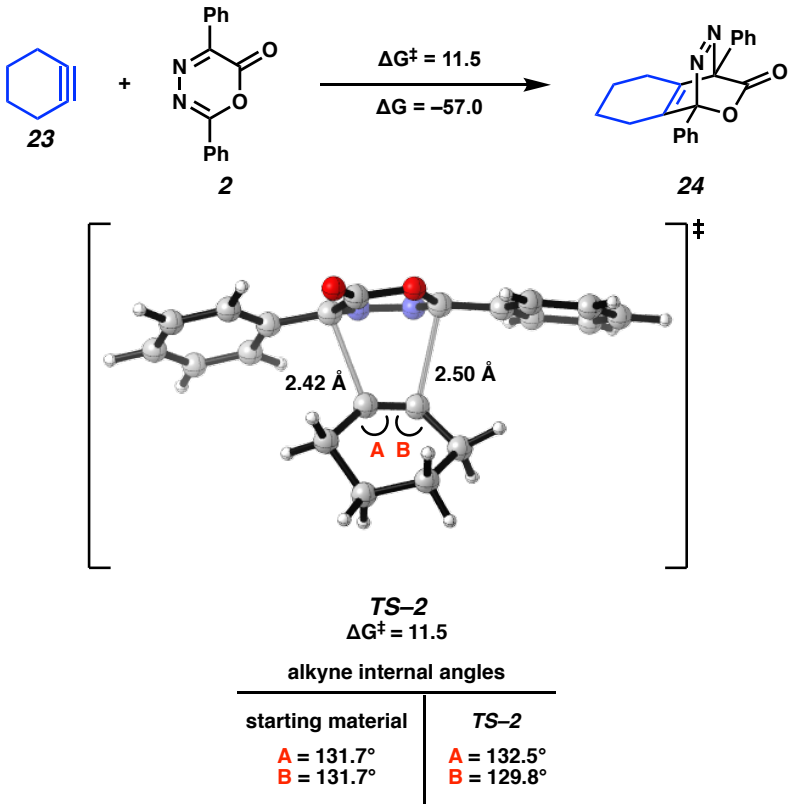


Figure S5. Transition state structure for DA1 of cyclohexyne (**23**) and oxadiazinone **2** and alkyne internal angles in the starting material and **TS–1**. Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN) and are provided in kcal mol^{-1}. The alkyne internal angles in starting material **23** and **TS–2** differ by 0.8° to 1.9°, demonstrating that cyclohexyne (**23**) is less predistorted than benzyne (**1**) (see Figure S4) for DA1. Less predistortion of cyclohexyne (**23**) results in a higher energy barrier for cycloaddition when compared to $\Delta G^{\ddagger}$ for DA1 of benzyne (**1**) and oxadiazinone **2** (see Figure S4). We hypothesize that the more stabilizing $\Delta E_{int}^{\ddagger}$ in **TS–2** than in **TS–1** results from the presence of (1) attractive, non-covalent interactions between the sp^3-hybdridized protons of cyclohexyne (**23**) with aromatic protons on oxadiazinone **2** and (2) a more reactive, higher energy HOMO for the dienophile component in **TS–2**. The computed energy of the HOMO of cyclohexyne (**23**) is –8.1 eV while that of benzyne (**1**) is –8.9 eV.

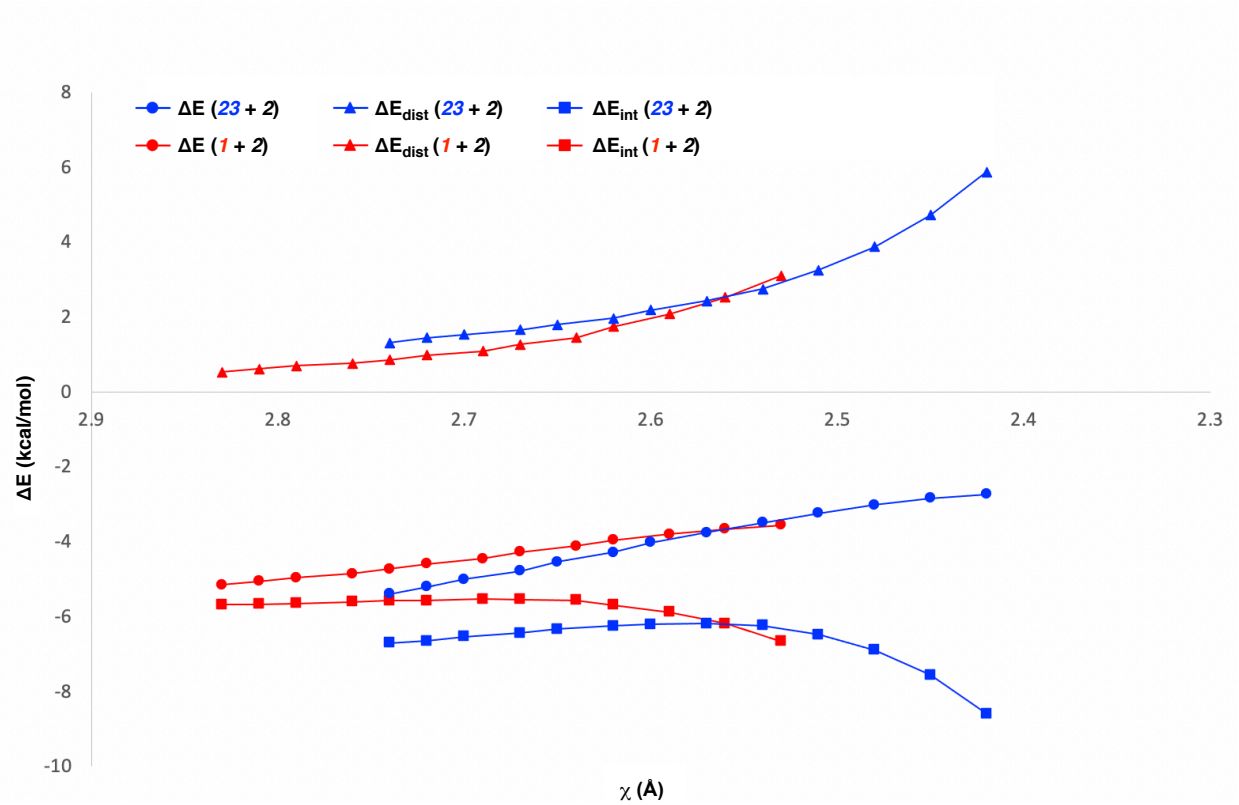


Figure S6. D/IAS analysis along the reaction coordinate for DA1 of benzyne (**1**) and cyclohexyne (**23**) with oxadiazinone **2**. The x-axis corresponds to the length of the forming bond α to the carbonyl of oxadiazinone **2** and represents reaction progression. Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN) and are provided in kcal mol^{-1}. These results demonstrate that ΔE_{dist} is lower along the reaction pathway for DA1 of benzyne (**1**) with oxadiazinone **2** and results in a lower $\Delta E^{\ddagger}$ for cycloaddition. DA1 of cyclohexyne (**23**) with oxadiazinone **2** involves more stabilizing ΔE_{int} along the reaction coordinate, but this effect does not outcompete ΔE_{dist}, which is unfavorable.

r-DA1

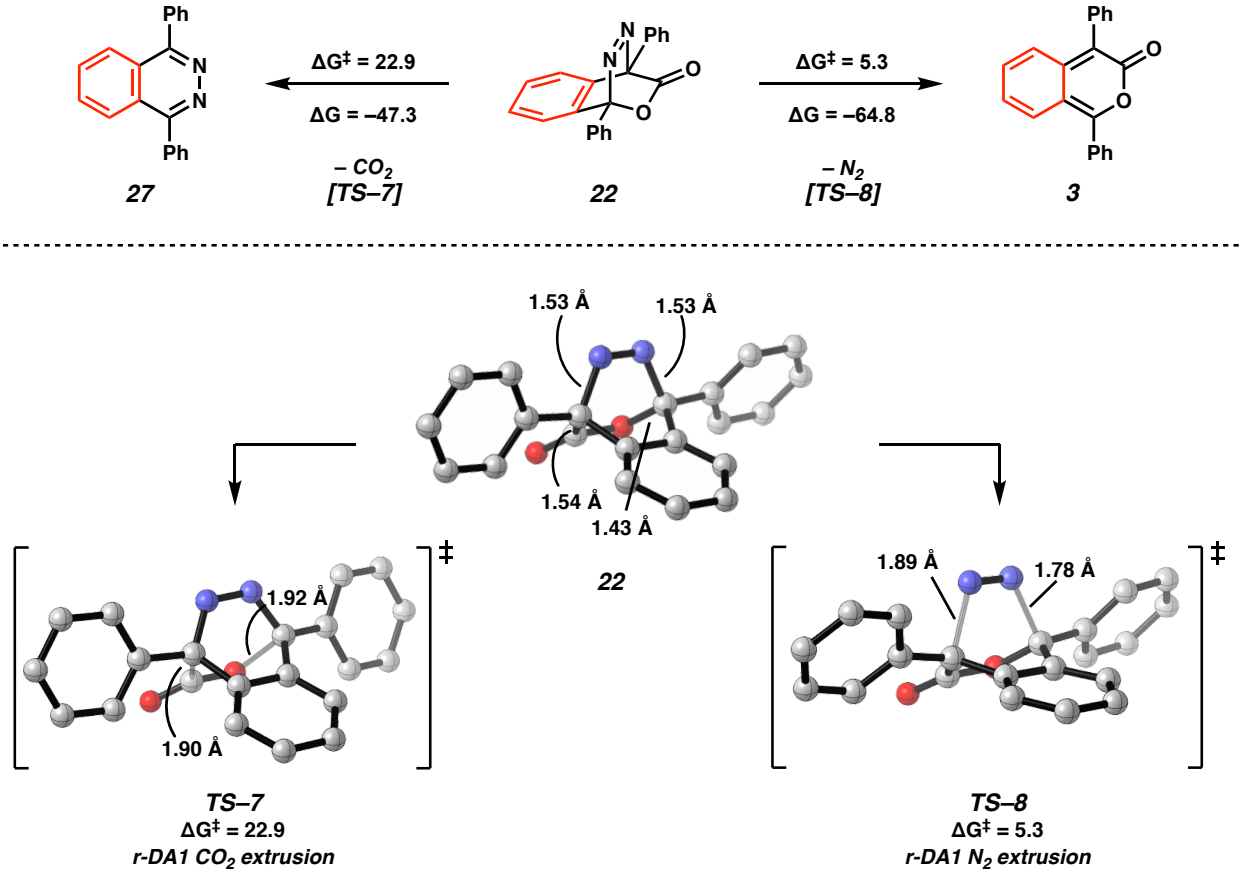


Figure S7. Transition state structures for r-DA1 from [2.2.2] bicycle **22**. Protons hidden for clarity. **TS–7** involves CO_2 extrusion and **TS–8** involves N_2 extrusion. Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN) and are provided in kcal mol^{-1}. Bond lengths are labelled to show that the change in C–N bond lengths that is required to arrive at **TS–8** for N_2 release is smaller than the change in C–O and C–C bond lengths needed to arrive at **TS–7** for CO_2 extrusion.

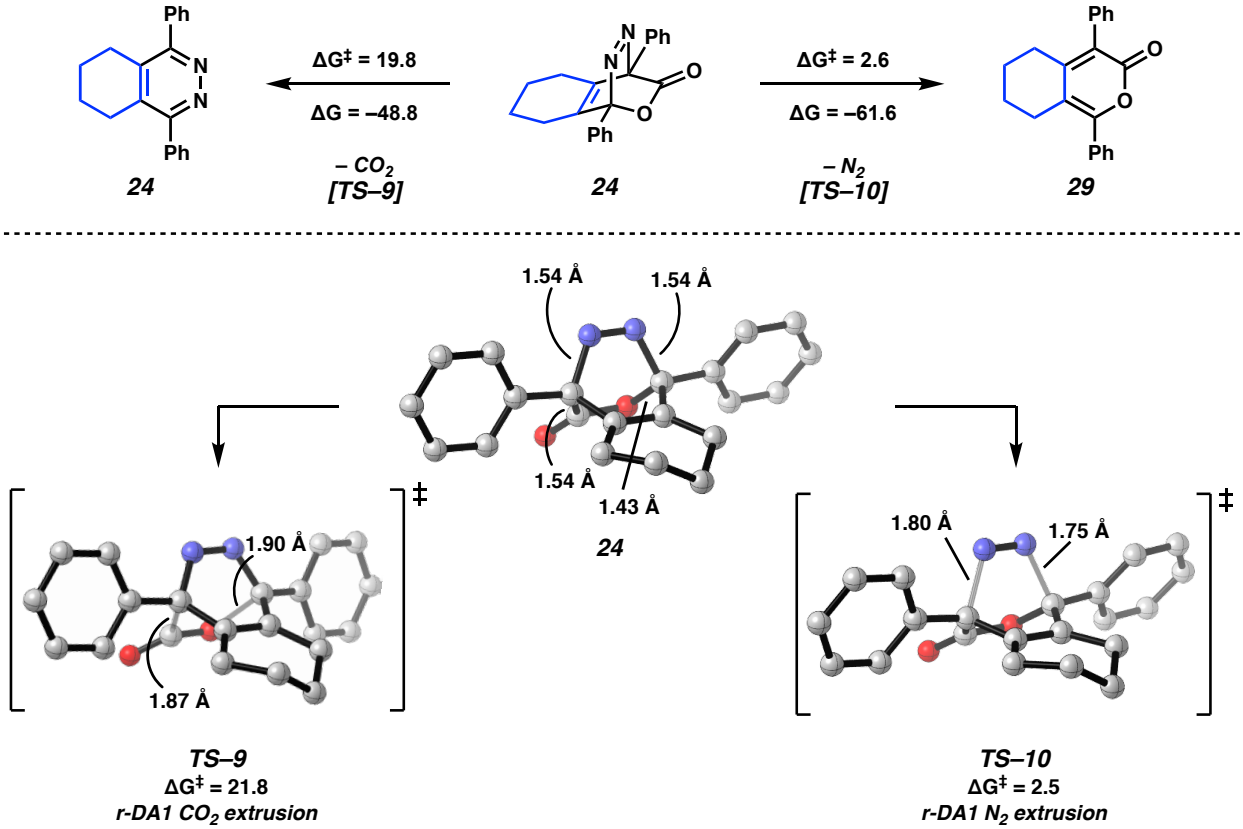


Figure S8. Transition state structures for r-DA1 from [2.2.2] bicycle **24**. **TS–9** involves CO_2 extrusion and **TS–10** involves N_2 extrusion. Protons hidden for clarity. Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN) and are provided in kcal mol^{-1}. Bond lengths are labelled to show that the change in C–N bond lengths that is required to arrive at **TS–10** for N_2 release is smaller than the change in C–O and C–C bond lengths needed to arrive at **TS–9** for CO_2 extrusion.

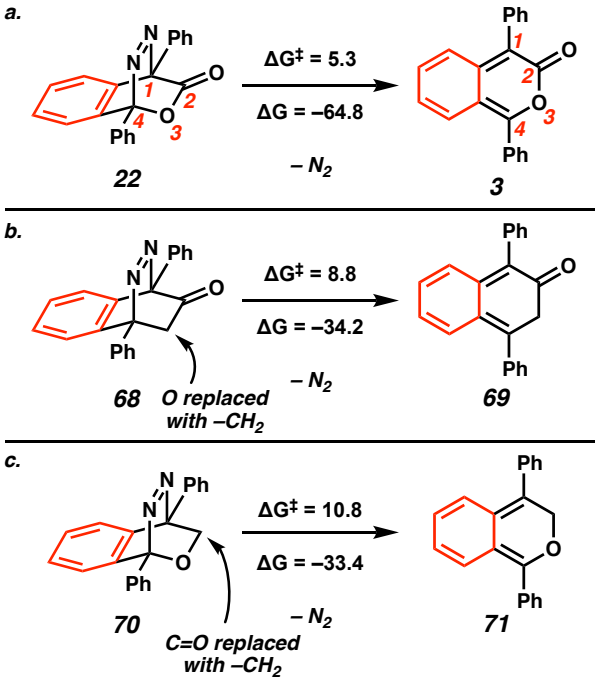


Figure S9. Energetics of r-DA1 N_2 extrusion from bicycles **22**, **68**, and **70**. Comparison of $\Delta G^{\ddagger}$ and ΔG for r-DA1 from bicycle **22** versus bicycle **68** demonstrates that replacement of O3 with a CH_2 group increases $\Delta G^{\ddagger}$ from 5.3 kcal mol^{-1} to 8.8 kcal mol^{-1} and decreases exergonicity from –64.8 kcal mol^{-1} to –34.2 kcal mol^{-1}. These results provide support for the presence of a stabilizing hyperconjugative interaction between the lone pair of O3 and the C4–N σ* orbital in r-DA1 of bicycle **22**, which lowers $\Delta G^{\ddagger}$. An analogous comparison of $\Delta G^{\ddagger}$ and ΔG for r-DA1 from bicycle **22** versus bicycle **70** suggests that there is additional hyperconjugation between the C2=O π orbital and the adjacent C1–N σ* orbital in r-DA1 of intermediate **22** that is also stabilizing. Replacing C2=O with a CH_2 group increases $\Delta G^{\ddagger}$ from 5.3 kcal mol^{-1} to 10.8 kcal mol^{-1} and decreases exergonicity from –64.8 kcal mol^{-1} to –33.4 kcal mol^{-1}.

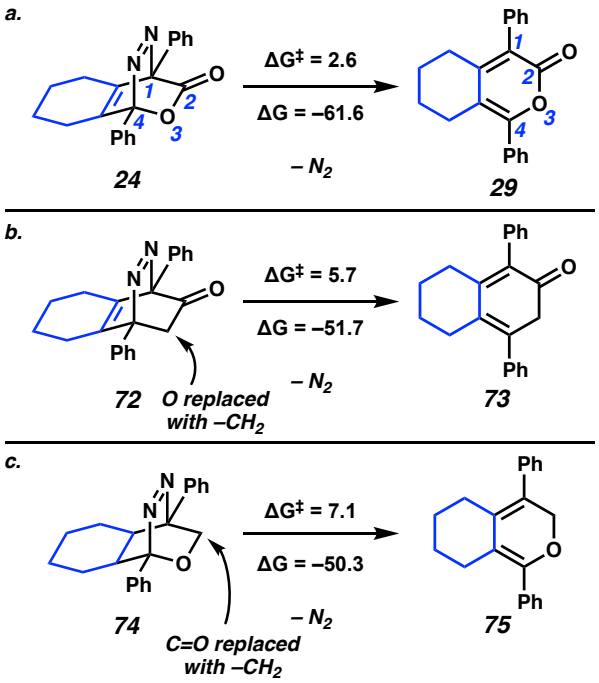
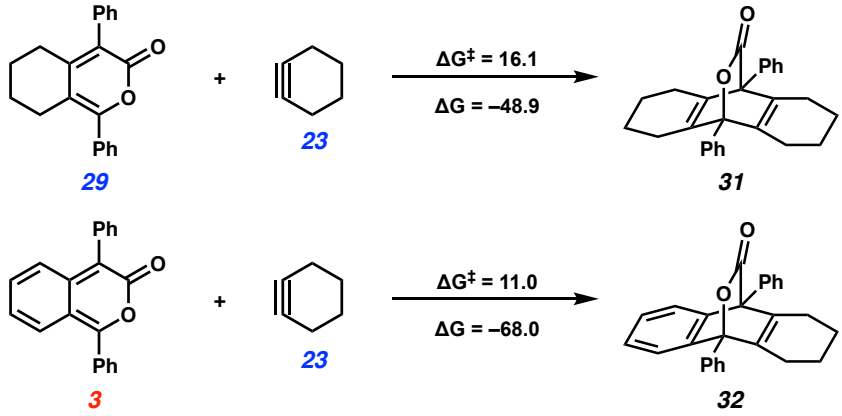


Figure S10. Energetics of r-DA1 N_2 extrusion from bicycles **24**, **72**, and **74**. Comparison of $\Delta G^{‡}$ and ΔG for r-DA1 from bicycle **24** versus bicycle **72** demonstrates that replacement of O3 with a CH_2 group increases $\Delta G^{‡}$ from 2.6 kcal mol^{-1} to 5.7 kcal mol^{-1} and decreases exergonicity from –61.6 kcal mol^{-1} to –51.7 kcal mol^{-1}. These results provide support for the presence of a stabilizing hyperconjugative interaction between the lone pair of O3 and the C4–N σ* orbital in r-DA1 of bicycle **24**, which lowers $\Delta G^{‡}$. An analogous comparison of $\Delta G^{‡}$ and ΔG for r-DA1 from bicycle **24** versus bicycle **74** suggests that there is additional hyperconjugation between the C2=O π orbital and the adjacent C1–N σ* orbital in r-DA1 of intermediate **24** that is also stabilizing. Replacing C2=O with a CH_2 group increases $\Delta G^{‡}$ from 2.6 kcal mol^{-1} to 7.1 kcal mol^{-1} and decreases exergonicity from –61.6 kcal mol^{-1} to –50.3 kcal mol^{-1}.

DA2



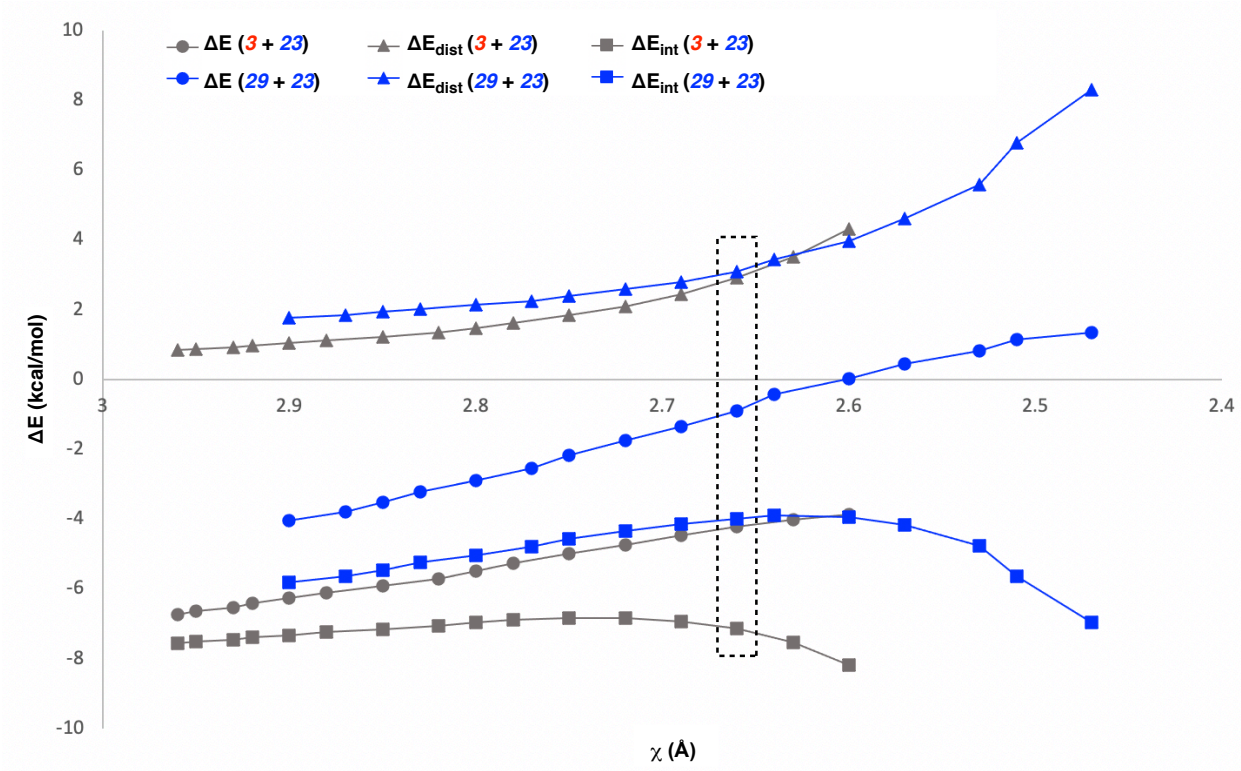


Figure S11. D/IAS results for DA2 of alkylpyrone **29** with cyclohexyne (**23**) and benzopyrone **2** with cyclohexyne (**23**) along the reaction coordinate. The x-axis corresponds to the length of the forming bond α to the carbonyl of the pyrone bridgehead and represents reaction progression. Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN) and are provided in kcal mol^{-1}. These results reveal that ΔE_{int} is significantly more stabilizing in DA2 of alkylpyrone **29** with cyclohexyne (**23**) and results in a lower $\Delta E^{‡}$ for cycloaddition. The same conclusion cannot be reached if ΔE_{int} is only analyzed at the corresponding DA2 transition states. The points inside the

dashed box are ΔE, ΔE_{int}, and ΔE_{dist} values at analogous geometries for the three reactions. These analogous geometries and energy values are shown in Figure 4e of the manuscript.

D. Substituent Effects on DA1 and DA2

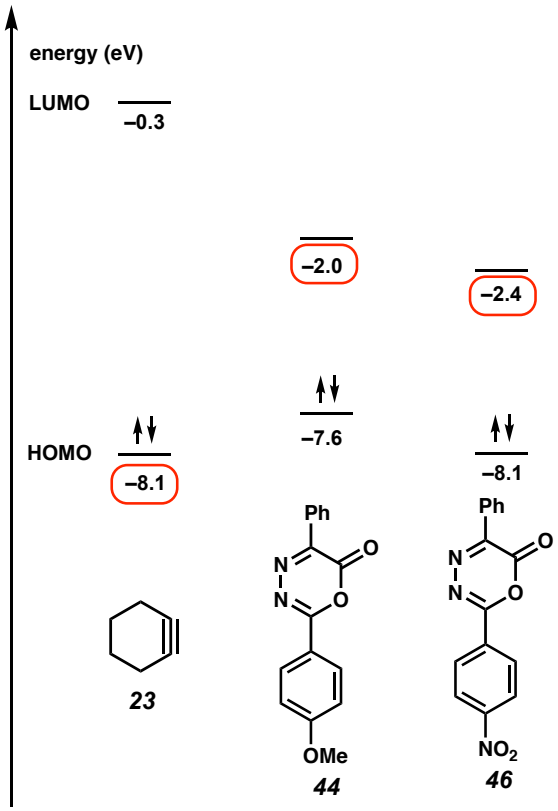


Figure S12. MO Energies of cyclohexyne (**23**), methoxy-substituted oxadiazinone **44**, and nitro-substituted oxadiazinone **46**. Energies were calculated with M06-2X/6-311+G(d,p). These results demonstrate that DA1 reaction of cyclohexyne (**23**) with oxadiazinones **44** and **46** are inverse electron-demand DA reactions involving the HOMO of cyclohexyne (**23**) and the LUMO of oxadiazinone **44** or **46**. The LUMO of nitro-substituted oxadiazinone **46** is lower lying than the LUMO of methoxy-substituted oxadiazinone **44**. Therefore, DA1 of cyclohexyne (**23**) and **46** should occur more readily. Experimental results show that DA1 of cyclohexyne (**23**) and **46** is lower yielding than DA1 of **23** and **44** (Figure 7, entries 2 and 4), which is attributed to difficulty with purification of the corresponding pyrone product (i.e., pyrone **58**).

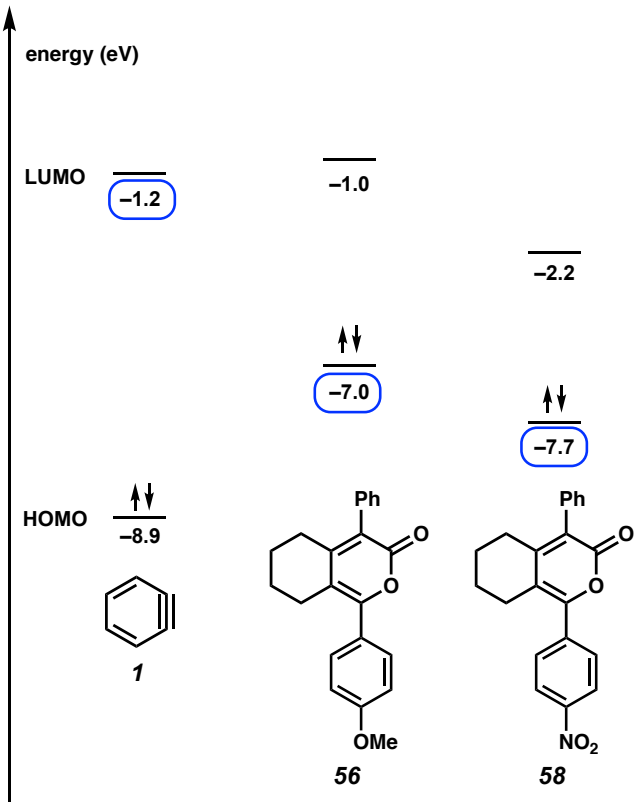
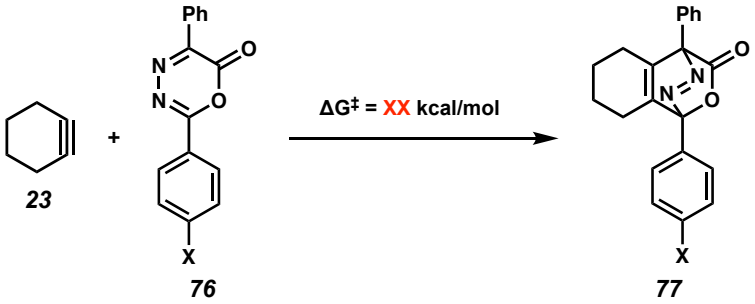


Figure S13. MO Energies of benzyne (**1**), methoxy-substituted pyrone **56**, and nitro-substituted pyrone **58**. Energies were calculated with M06-2X/6-311+G(d,p). These results demonstrate that DA2 reaction of benzyne (**1**) with pyrones **56** and **58** are inverse electron-demand DA cycloadditions involving the LUMO of benzyne (**1**) and the HOMO of pyrone **56** or **58**. The HOMO of methoxy-substituted pyrone **56** is higher-lying than the HOMO of pyrone **58**. In experiments, DA2 of benzyne (**1**) and methoxy-containing pyrone **56** is higher-yielding than DA2 of benzyne (**1**) and nitro-containing pyrone **58** (Figure 7, entries 2 and 4). This can be explained by the higher-lying HOMO of pyrone **56**, which is more reactive because of the electron-donating effect of the methoxy substituent.



oxadiazinone	substituent	ΔG‡
44	OMe	12.2
46	NO_2	11.0

Figure S14. Gibbs free energy barrier ($\Delta G^{\ddagger}$) for DA1 of cyclohexyne (**23**) with *p*-substituted oxadiazinone **76**. Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN). DA1 cycloaddition of cyclohexyne (**23**) and methoxy-containing oxadiazinone **44** has $\Delta G^{\ddagger}$ of 12.2 kcal mol^{-1} while DA1 reaction of cyclohexyne (**23**) and nitro-substituted oxadiazinone **46** has $\Delta G^{\ddagger}$ of 11.0 kcal mol^{-1}. These results provide further support for the stabilizing effect of an electron-withdrawing group on the oxadiazinone fragment in the corresponding TS for DA1 of cyclohexyne (**23**) and oxadiazinone **46**. Experimental results show that DA1 of **23** and **46** is lower yielding than DA1 of **23** and **44** (Figure 7, entries 2 and 4), which is attributed to difficulty with the purification of the corresponding pyrone product (i.e., pyrone **58**).

E. Free Energy Profiles

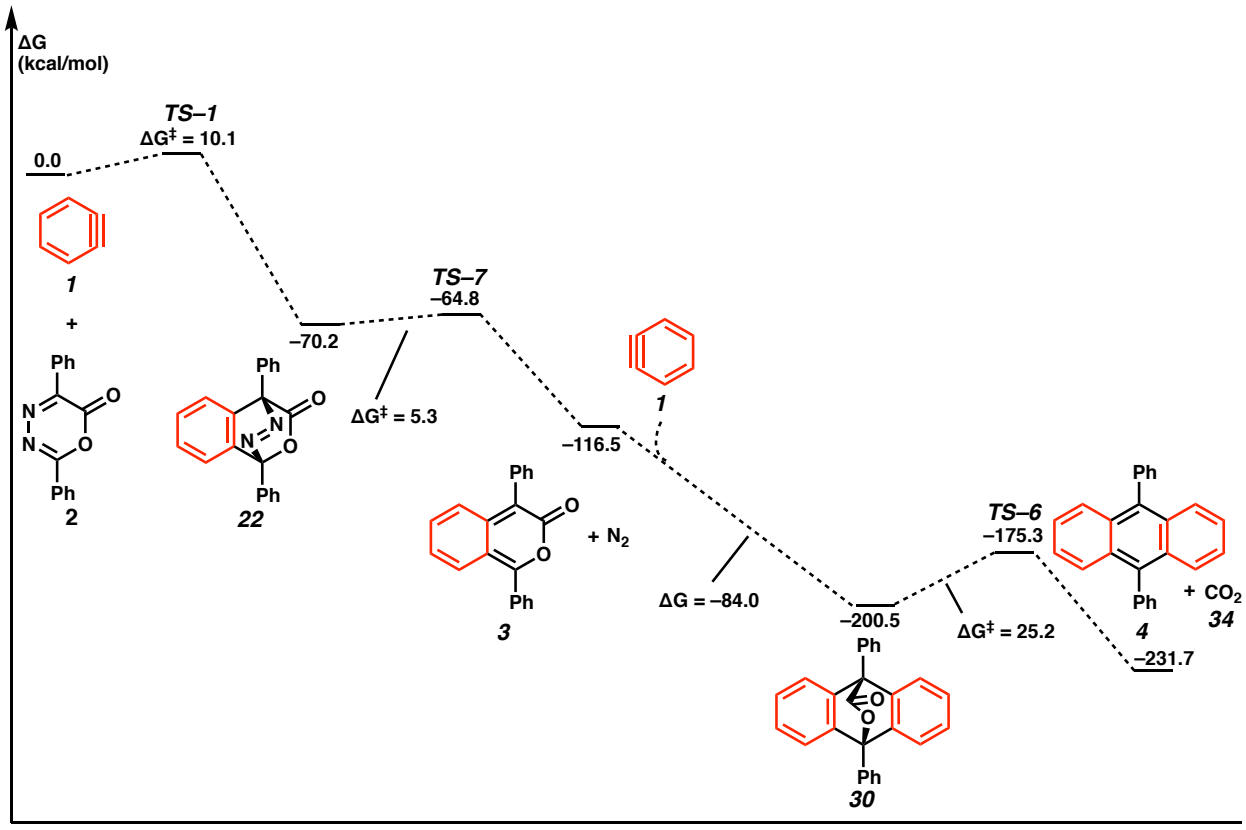


Figure S12. Free energy profile for the cycloaddition cascade of benzyne (**1**) and oxadiazinone **2** resulting in 9,10-diphenylanthracene (**4**). Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN) and are in units of kcal mol^{-1}.

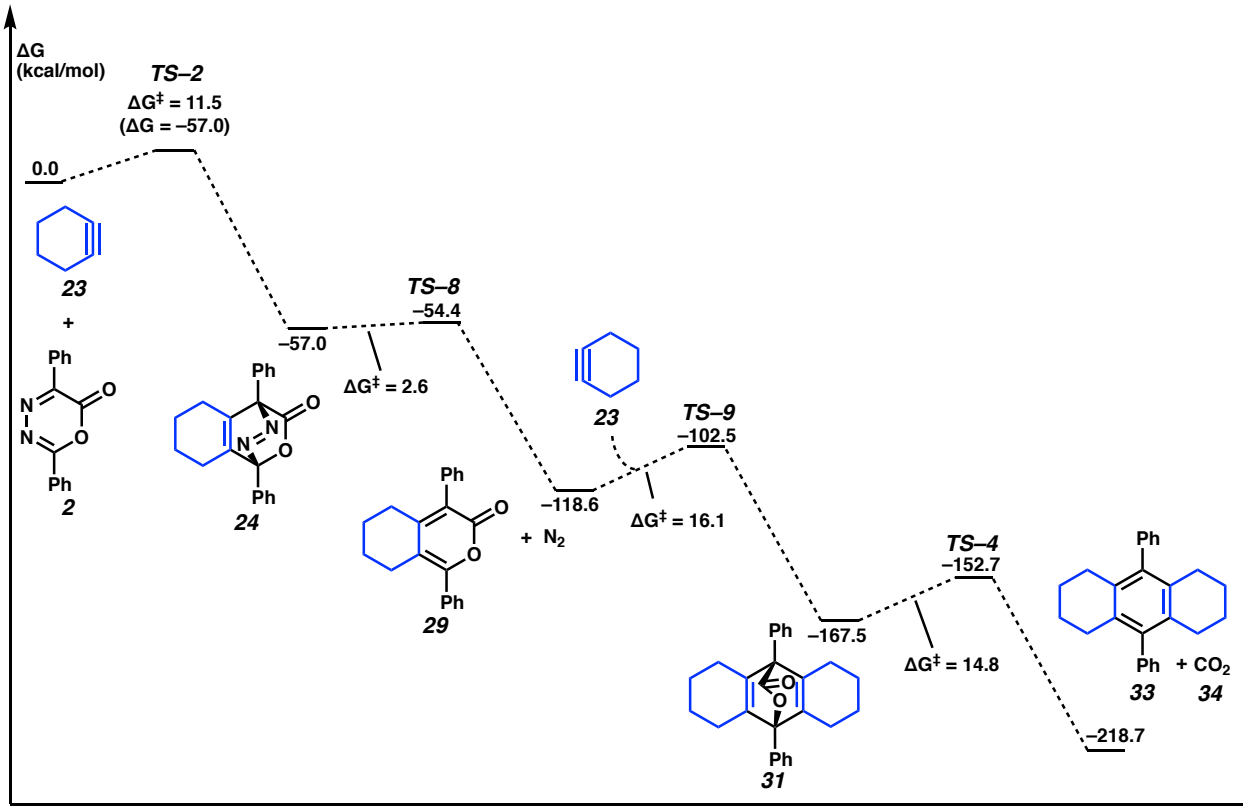


Figure S13. Free energy profile for the cycloaddition cascade of cyclohexyne (**23**) and oxadiazinone **2** resulting in tricyclic product **33**. Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN) and are in units of kcal mol^{-1}.

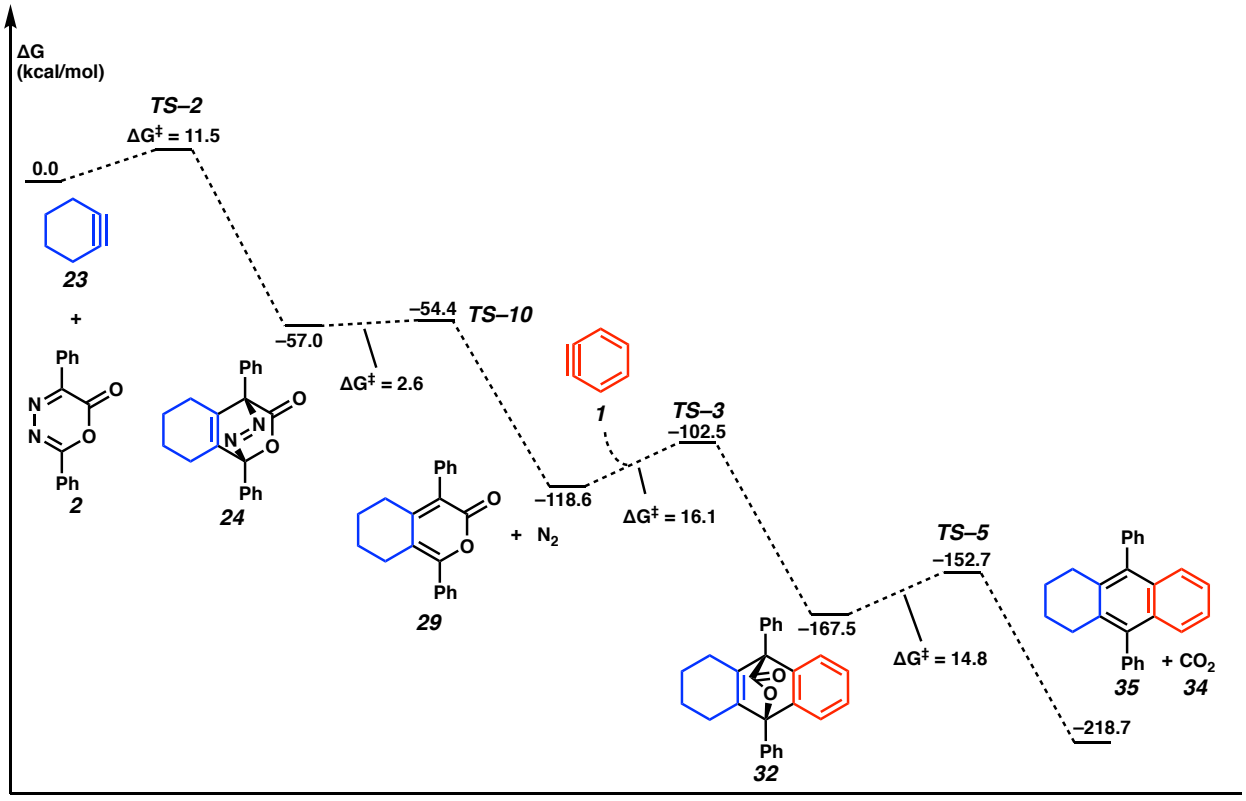


Figure S14. Free energy profile for the cycloaddition cascade of cyclohexyne (**23**), oxadiazinone **2**, and benzyne (**1**) resulting in tricyclic product **35**. Energies were calculated with M06-2X/6-311+G(d,p)/SMD(MeCN) and are in units of kcal mol^{-1}.

F. Cartesian Coordinates and Energies of Optimized Structures

benzyne (**1**)

C	0.70253200	1.05306600	0.00000200
C	1.46049800	-0.13262800	0.00000000
C	0.62259500	-1.23253100	-0.00000100
C	-0.62259500	-1.23253100	-0.00000100
C	-1.46049800	-0.13262800	-0.00000200
C	-0.70253200	1.05306600	0.00000100
H	1.22589500	2.00550700	0.00000400
H	2.54456900	-0.13295000	0.00000100
H	-2.54456900	-0.13295000	-0.00000200
H	-1.22589500	2.00550700	0.00000300

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -230.875821994 Hartrees
Zero-point correction = 0.076226 Hartrees
Thermal correction to enthalpy = 0.081603 Hartrees
Thermal correction to Gibbs free energy = 0.048891 Hartrees
Quasiharmonic free energy correction = 0.048891 Hartrees

oxadiazinone **2**

C	-1.38974300	-0.15847100	-0.00010600
C	1.28291800	-0.07603600	-0.00010600
C	0.54870000	1.21593200	0.00018200
N	0.64174600	-1.20400900	-0.00036600
N	-0.72309100	-1.25925300	-0.00033400
O	0.98663900	2.32987400	0.00049200
O	-0.82068800	1.06589300	0.00010900
C	2.76587400	-0.12454500	-0.00004500
C	3.38172600	-1.38690500	0.00044900
C	3.57134100	1.02232500	-0.00049700
C	4.76317600	-1.49803300	0.00048700
H	2.75708000	-2.27232200	0.00079000
C	4.95863500	0.90008200	-0.00045700
H	3.12188300	2.00550500	-0.00087600
C	5.55974200	-0.35283200	0.00003400
H	5.22193500	-2.48196900	0.00089500
H	5.56945800	1.79737300	-0.00080200
H	6.64197800	-0.44049300	0.00007500
C	-2.85996800	-0.13923500	-0.00005400
C	-3.55686900	1.07239900	0.00017100
C	-3.55561400	-1.35359200	-0.00022000
C	-4.94726000	1.06564200	0.00022800
H	-3.01054400	2.00913700	0.00030100

C	-4.94335400	-1.35002500	-0.00015700
H	-2.99266900	-2.28045900	-0.00039200
C	-5.64045000	-0.14200100	0.00006600
H	-5.48972800	2.00549300	0.00040400
H	-5.48458700	-2.29063000	-0.00028200
H	-6.72611900	-0.14317400	0.00011600

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -837.439699212 Hartrees
Zero-point correction = 0.221302 Hartrees
Thermal correction to enthalpy = 0.235590 Hartrees
Thermal correction to Gibbs free energy = 0.179907 Hartrees
Quasiharmonic free energy correction = 0.048891 Hartrees

benzopyrone **3**

C	-0.74591900	3.38061100	-0.58879500
C	-1.45030300	2.23157300	-0.45389900
C	-0.77570300	0.97677000	-0.23239000
C	0.67709900	0.93219200	-0.20722500
C	1.37004100	2.19134900	-0.36194800
C	0.68906500	3.35183600	-0.53420400
H	-1.25565700	4.31990800	-0.77422600
H	-2.52968400	2.23254500	-0.55418500
C	-1.45456800	-0.21114600	-0.06978900
C	1.34465000	-0.27611300	-0.07775500
H	2.45333500	2.18495100	-0.38014500
H	1.23829900	4.27860200	-0.67157000
C	0.59649600	-1.51443600	-0.11107600
O	1.00830400	-2.64442000	-0.17385200
O	-0.79784000	-1.36980700	-0.03501900
C	2.81350000	-0.39377400	0.07812000
C	3.48724500	0.36110700	1.04679800
C	3.55188500	-1.28124100	-0.71452400
C	4.86509700	0.25347300	1.20290100
H	2.91665400	1.02433400	1.69199000
C	4.92922300	-1.38668600	-0.55839800
H	3.03652400	-1.89223600	-1.44681900
C	5.59120400	-0.61917500	0.39679400
H	5.36904900	0.84231000	1.96336300
H	5.48862200	-2.07535300	-1.18426000
H	6.66644100	-0.70784500	0.51912000
C	-2.90999200	-0.39915500	0.07467800
C	-3.51571800	-1.50511500	-0.53507600
C	-3.68555700	0.46572500	0.85627300
C	-4.88131000	-1.71698400	-0.39721000
H	-2.90548400	-2.18951500	-1.11524100

C	-5.05129700	0.24522000	0.99591700
H	-3.20968200	1.28878000	1.38024800
C	-5.65243500	-0.84035000	0.36381300
H	-5.34529500	-2.57028500	-0.88138800
H	-5.64415900	0.91405600	1.61164600
H	-6.71889400	-1.01051300	0.47442000

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -958.99066 Hartrees
Zero-point correction = 0.292770 Hartrees
Thermal correction to enthalpy = 0.310714 Hartrees
Thermal correction to Gibbs free energy = 0.247176 Hartrees
Quasiharmonic free energy correction = 0.24953984 Hartrees

9,10-diphenylanthracene (**4**)

C	-0.71207100	3.65431600	-0.00024100
C	-1.40179400	2.47835300	-0.00017100
C	-0.71883700	1.21882100	-0.00005500
C	0.71883500	1.21882300	-0.00005200
C	1.40179100	2.47835500	-0.00011800
C	0.71206600	3.65431800	-0.00020500
C	-1.41858600	0.00000000	0.00000000
C	1.41858500	0.00000200	-0.00000100
C	0.71883700	-1.21882100	0.00005100
C	-0.71883500	-1.21882200	0.00005300
C	-1.40179100	-2.47835300	0.00016900
H	-2.48696800	-2.47997700	0.00021400
C	-0.71206600	-3.65431600	0.00023900
C	0.71207100	-3.65431500	0.00020300
C	1.40179400	-2.47835100	0.00011700
H	-1.24902000	4.59792300	-0.00033900
H	-2.48697200	2.47997500	-0.00021600
H	2.48696800	2.47997900	-0.00010400
H	1.24901300	4.59792600	-0.00025900
H	-1.24901300	-4.59792400	0.00033700
H	1.24902000	-4.59792200	0.00025700
H	2.48697200	-2.47997400	0.00010400
C	2.91180100	0.00000100	0.00000000
C	3.62091500	0.00006000	1.20416700
C	3.62091600	-0.00005800	-1.20416600
C	5.01327500	0.00006000	1.20454800
H	3.07122100	0.00010800	2.14152300
C	5.01327600	-0.00006000	-1.20454600
H	3.07122300	-0.00010500	-2.14152300
C	5.71205300	-0.00000100	0.00000100
H	5.55249300	0.00010900	2.14706300

H	5.55249500	-0.00010900	-2.14706100
H	6.79771000	-0.00000100	0.00000200
C	-2.91180100	-0.00000100	0.00000000
C	-3.62091500	0.00074100	1.20416700
C	-3.62091600	-0.00074400	-1.20416600
C	-5.01327500	0.00073300	1.20454800
H	-3.07122100	0.00132500	2.14152200
C	-5.01327600	-0.00073700	-1.20454500
H	-3.07122200	-0.00132900	-2.14152100
C	-5.71205300	-0.00000200	0.00000200
H	-5.55249300	0.00131000	2.14706300
H	-5.55249500	-0.00131400	-2.14705900
H	-6.79771000	-0.00000200	0.00000200

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1001.4824 Hartrees
Zero-point correction = 0.358831 Hartrees
Thermal correction to enthalpy = 0.378196 Hartrees
Thermal correction to Gibbs free energy = 0.310140 Hartrees
Quasiharmonic free energy correction = 0.31483747 Hartrees

bicycle **22**

C	-0.74764600	3.39363600	-0.30399000
C	-1.46210900	2.20368700	-0.16939000
C	-0.74965600	1.01727100	-0.07870000
C	0.64336500	1.00553100	-0.09989800
C	1.35824200	2.18911600	-0.22481800
C	0.64654800	3.38416800	-0.33150700
H	-1.28154300	4.33473600	-0.38843800
H	-2.54763100	2.19620900	-0.14358900
C	-1.29843400	-0.37748300	0.07666800
C	1.21020500	-0.39084600	0.08511700
H	2.44353000	2.17871500	-0.23289000
H	1.18747100	4.32004700	-0.43051900
C	0.58181000	-1.23174700	-1.03590100
N	0.54727400	-0.94821900	1.34723000
N	-0.67613400	-0.91656100	1.36355500
O	1.15483900	-1.87083400	-1.86773800
O	-0.77099300	-1.19234900	-0.97353000
C	2.70984000	-0.47539700	0.17832000
C	3.33850900	-0.65158300	1.41111800
C	3.48542000	-0.29549000	-0.97072300
C	4.72884900	-0.65835700	1.49122000
H	2.73876400	-0.79227800	2.30300700
C	4.87341700	-0.30031700	-0.88491300
H	3.00111400	-0.16338500	-1.93279500

C	5.49899000	-0.48336400	0.34626800
H	5.20842300	-0.80105200	2.45465400
H	5.46637100	-0.16570500	-1.78429500
H	6.58272800	-0.49000200	0.41110000
C	-2.79153400	-0.50751100	0.11380800
C	-3.50959900	-0.84641500	-1.03180800
C	-3.46199800	-0.21618200	1.30206600
C	-4.89980700	-0.90137200	-0.98244600
H	-2.97864700	-1.07562700	-1.94951300
C	-4.85145300	-0.26852600	1.34410700
H	-2.89155700	0.03612700	2.19100700
C	-5.57169400	-0.61230800	0.20228700
H	-5.45840800	-1.17253000	-1.87272100
H	-5.37114000	-0.04770600	2.27109300
H	-6.65582500	-0.65769600	0.23722600

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1068.45679806 Hartrees
Zero-point correction = 0.303704 Hartrees
Thermal correction to enthalpy = 0.322551 Hartrees
Thermal correction to Gibbs free energy = 0.257021 Hartrees
Quasiharmonic free energy correction = 0.26011665 Hartrees

cyclohexyne (**23**)

C	-0.71395600	1.04349400	-0.29188600
C	-1.58881400	-0.19118700	0.11820200
C	-0.60708600	-1.29405400	0.02726700
C	0.60707900	-1.29405000	-0.02726700
C	1.58881500	-0.19119400	-0.11820200
C	0.71396000	1.04349200	0.29188600
H	-1.96758800	-0.08926900	1.14100700
H	-2.45307500	-0.28283900	-0.54602100
H	-0.64968800	1.06008000	-1.38650500
H	-1.22643400	1.96254000	0.01584900
H	2.45307300	-0.28285000	0.54602400
H	1.96759200	-0.08927600	-1.14100600
H	0.64969200	1.06007800	1.38650500
H	1.22644200	1.96253500	-0.01585000

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -233.2943 Hartrees
Zero-point correction = 0.123404 Hartrees
Thermal correction to enthalpy = 0.129874 Hartrees
Thermal correction to Gibbs free energy = 0.094946 Hartrees
Quasiharmonic free energy correction = 0.094946 Hartrees

bicycle **24**

C	-0.72109500	3.34018300	-0.65747600
C	-1.56993200	2.16436100	-0.16542600
C	-0.72311600	0.92715000	-0.07381000
C	0.61404200	0.91777100	-0.09274300
C	1.46387900	2.15456800	-0.18704400
C	0.61532400	3.40196800	0.08606900
H	-1.27372500	4.27629600	-0.53224200
H	-2.41827500	1.98606900	-0.83644500
C	-1.28528700	-0.46331800	0.07980000
C	1.20063200	-0.47421800	0.08287900
H	2.29561500	2.08343400	0.52279900
H	0.42196900	3.47381200	1.16409700
C	0.57804300	-1.31725700	-1.03884900
N	0.55166500	-1.07386700	1.34215000
N	-0.66751700	-1.03767400	1.36678000
O	1.15665300	-1.94129900	-1.87998000
O	-0.77149200	-1.29741500	-0.96406700
C	2.70170900	-0.54623100	0.16903200
C	3.33681400	-0.70986900	1.40077300
C	3.47326300	-0.36400400	-0.98198600
C	4.72736300	-0.69849700	1.47804500
H	2.74156200	-0.85649400	2.29500200
C	4.86133700	-0.35279200	-0.89999000
H	2.98582100	-0.24844700	-1.94463100
C	5.49264500	-0.52034100	0.33026400
H	5.21080500	-0.83117700	2.44104800
H	5.45032900	-0.21759200	-1.80192600
H	6.57654900	-0.51357200	0.39228700
C	-2.77932000	-0.58031500	0.12254500
C	-3.50757100	-0.91109600	-1.01917900
C	-3.44160100	-0.28381000	1.31381700
C	-4.89828100	-0.94787600	-0.96386800
H	-2.98328500	-1.14850100	-1.93884300
C	-4.83127100	-0.31875200	1.36282100
H	-2.86440000	-0.04501600	2.20254900
C	-5.56131800	-0.65081400	0.22388300
H	-5.46423400	-1.21225100	-1.85160600
H	-5.34388500	-0.09439100	2.29294800
H	-6.64576000	-0.68230300	0.26366200
H	1.92369400	2.21265500	-1.18326500
H	1.17454100	4.29799700	-0.19988900
H	-0.52989200	3.21929300	-1.73138100
H	-2.00528500	2.38981700	0.81835900

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1070.8538 Hartrees

Zero-point correction = 0.350358 Hartrees
Thermal correction to enthalpy = 0.370318 Hartrees
Thermal correction to Gibbs free energy = 0.302783 Hartrees
Quasiharmonic free energy correction = 0.30567612 Hartrees

alkylpyrone **29**

C	-0.65035300	3.27617200	-0.90996500
C	-1.50658400	2.23854600	-0.18886300
C	-0.77958100	0.91839200	-0.02023800
C	0.67207000	0.86983100	-0.01516400
C	1.47556700	2.14239500	-0.22838700
C	0.66661100	3.43600600	-0.16125800
H	-1.19225500	4.22573700	-0.96157700
H	-2.44911600	2.07347600	-0.71952500
C	-1.44998400	-0.26144400	0.08122400
C	1.32409100	-0.32770600	0.08206300
H	2.31074100	2.17748300	0.47403900
H	0.45215100	3.69224200	0.88459200
C	0.57354400	-1.57893500	0.09627700
O	1.02448600	-2.69512400	0.07129000
O	-0.80036700	-1.44722700	0.13335200
C	2.80501200	-0.46826100	0.09763100
C	3.56523200	0.04492000	1.15220800
C	3.45659100	-1.14358200	-0.93857200
C	4.95020700	-0.08931600	1.15959900
H	3.06086200	0.53874600	1.97910900
C	4.84114900	-1.27543900	-0.93401500
H	2.86847800	-1.57637500	-1.74217900
C	5.59180000	-0.74535800	0.11231900
H	5.52677900	0.31116400	1.98800900
H	5.33478100	-1.79975200	-1.74649600
H	6.67220700	-0.85253700	0.11709200
C	-2.91415400	-0.47226700	0.09962800
C	-3.44646300	-1.58592700	-0.56297100
C	-3.77740200	0.38313500	0.79171400
C	-4.81646000	-1.81487100	-0.56185700
H	-2.77515300	-2.26837200	-1.07364100
C	-5.14830900	0.14663000	0.79687300
H	-3.37419500	1.21775000	1.35493600
C	-5.67197800	-0.94716100	0.11406200
H	-5.21782400	-2.67670700	-1.08583900
H	-5.80580500	0.81300400	1.34646000
H	-6.74207700	-1.12990200	0.11737600
H	1.93597200	2.05544400	-1.22279800
H	1.26454000	4.25487500	-0.57327500

H	-0.45633100	2.95431600	-1.94163300
H	-1.77033600	2.65365300	0.79437700

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -961.41256 Hartrees
Zero-point correction = 0.339887 Hartrees
Thermal correction to enthalpy = 0.358971 Hartrees
Thermal correction to Gibbs free energy = 0.292458 Hartrees
Quasiharmonic free energy correction = 0.29575728 Hartrees

bicyclic lactone **30**

C	-0.70080200	3.40096700	-1.45113300
C	-1.42176500	2.30895600	-0.96632700
C	-0.73643400	1.23379000	-0.41923900
C	0.66006900	1.24326000	-0.33895800
C	1.37298000	2.34677500	-0.78970300
C	0.68553800	3.42022800	-1.35854300
C	-1.34261700	0.00000000	0.24321200
C	1.25740000	-0.00002600	0.34931500
C	0.66005200	-1.24330200	-0.33895900
C	-0.73645300	-1.23381200	-0.41922100
C	-1.42180500	-2.30897100	-0.96629600
H	-2.50615000	-2.31079900	-0.99987700
C	-0.70086400	-3.40099700	-1.45110000
C	0.68547600	-3.42028200	-1.35851900
C	1.37294100	-2.34683600	-0.78969400
H	-1.22909600	4.24461900	-1.88411500
H	-2.50610900	2.31080300	-0.99991300
H	2.45331000	2.37788500	-0.69903900
H	1.24229500	4.27970900	-1.71900100
H	-1.22917600	-4.24464400	-1.88407100
H	1.24221500	-4.27977700	-1.71897100
H	2.45327000	-2.37796900	-0.69903100
C	2.77669600	-0.00002400	0.35476700
C	3.57969700	-0.00006600	1.49610900
C	3.40317400	0.00004600	-0.90163800
C	4.97066100	-0.00004800	1.37631800
H	3.12493600	-0.00011400	2.47649700
C	4.78647300	0.00006400	-1.01802800
H	2.78869300	0.00008700	-1.79941800
C	5.57982100	0.00001500	0.12860300
H	5.57738800	-0.00008500	2.27677100
H	5.24425900	0.00011700	-2.00266000
H	6.66234600	0.00002800	0.04510300
C	-2.84866900	0.00001400	0.33383500
C	-3.50656200	0.00003700	1.56188300

C	-3.59975500	0.00000100	-0.84694200
C	-4.89952900	0.00004700	1.60681500
H	-2.92686200	0.00004500	2.47699400
C	-4.98938800	0.00001200	-0.79858800
H	-3.08867000	-0.00001800	-1.80741800
C	-5.64356800	0.00003500	0.43183300
H	-5.40270600	0.00006500	2.56887800
H	-5.56079200	0.00000200	-1.72164700
H	-6.72841900	0.00004400	0.47185600
C	0.53452200	-0.00004800	1.71938500
O	-0.81324800	0.00001600	1.59841400
O	1.02893800	0.00011100	2.81207900

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1190.0319 Hartrees
Zero-point correction = 0.376354 Hartrees
Thermal correction to enthalpy = 0.397868 Hartrees
Thermal correction to Gibbs free energy = 0.327406 Hartrees
Quasiharmonic free energy correction = 0.33002912 Hartrees

bicyclic lactone **31**

C	0.63728200	3.74873500	-0.74788700
C	1.49045500	2.48047600	-0.81247500
C	0.68488100	1.27863600	-0.38866100
C	-0.64913000	1.26105300	-0.32075300
C	-1.51564500	2.43904700	-0.68199000
C	-0.71544200	3.51737900	-1.41674300
H	1.16835600	4.58045300	-1.22176800
H	2.36954900	2.57704500	-0.16620500
C	1.30810900	0.02500800	0.23260500
C	-1.23722500	-0.01344400	0.32799800
H	-2.36583400	2.12298100	-1.29371500
H	-0.55065000	3.19973400	-2.45490000
C	-0.53698400	-0.03798900	1.71108500
O	-1.05470500	-0.09736200	2.79474600
O	0.80656600	-0.00266400	1.60584000
C	-2.75621800	-0.02664100	0.31281100
C	-3.36711400	-0.15232200	-0.94408700
C	-3.57551000	0.11528600	1.43391100
C	-4.74828700	-0.15209700	-1.08199700
H	-2.73898300	-0.23870300	-1.82918000
C	-4.96464800	0.11483200	1.29458100
H	-3.13283000	0.21670100	2.41495300
C	-5.55705900	-0.02071400	0.04569900
H	-5.19289400	-0.25245200	-2.06755900
H	-5.58394400	0.22135800	2.18036300

H	-6.63829300	-0.02136100	-0.05307300
C	2.81717400	0.02453100	0.30725000
C	3.49372100	-0.10392600	1.51893500
C	3.55471800	0.13973500	-0.87557200
C	4.88761100	-0.11667000	1.54436000
H	2.92733000	-0.18979400	2.43856600
C	4.94416500	0.12607900	-0.84861800
H	3.03378900	0.24503100	-1.82496900
C	5.61614000	-0.00293000	0.36552900
H	5.40271200	-0.21643300	2.49496500
H	5.50197400	0.21722200	-1.77563300
H	6.70142300	-0.01320300	0.38962900
H	-1.95549600	2.84566100	0.24069100
H	-1.29666300	4.44419500	-1.45442800
H	0.47830300	4.02055100	0.30343500
H	1.87866700	2.34679000	-1.83211100
C	0.71445700	-1.22221000	-0.43301800
C	1.56036600	-2.35240300	-0.95103000
C	-0.61604400	-1.26843900	-0.32894500
C	0.69438300	-3.45710500	-1.56059800
H	2.16462700	-2.74823200	-0.12168100
H	2.28298500	-1.98916100	-1.69011200
C	-1.42547100	-2.50984600	-0.61138500
C	-0.51903200	-3.74060200	-0.67736800
H	1.29523200	-4.36071100	-1.70428400
H	0.34659800	-3.14043200	-2.55269200
H	-2.18785400	-2.62746300	0.16742900
H	-1.97876200	-2.40665000	-1.55412200
H	-1.08400000	-4.59902800	-1.05462700
H	-0.17815500	-3.99463600	0.33451400

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1194.8156 Hartrees
Zero-point correction = 0.469826 Hartrees
Thermal correction to enthalpy = 0.493604 Hartrees
Thermal correction to Gibbs free energy = 0.418365 Hartrees
Quasiharmonic free energy correction = 0.42146089 Hartrees

bicyclic lactone **32**

C	-0.65181600	3.30160200	-1.67304000
C	-1.53528200	2.24786900	-1.00169900
C	-0.70907000	1.12647600	-0.43276900
C	0.62336200	1.15743500	-0.33268200
C	1.45398000	2.36628400	-0.68303300
C	0.57222200	3.60906300	-0.81350000
H	-1.23633200	4.20733900	-1.86256900

H	-2.26830000	1.86281700	-1.71830700
C	-1.32723100	-0.10534300	0.24111800
C	1.24626800	-0.08496900	0.34907900
H	2.22215100	2.51059100	0.08533100
H	0.24320300	3.92670300	0.18413000
C	0.53421000	-0.07262600	1.72261000
O	1.03604500	-0.02983400	2.81275400
O	-0.81068600	-0.10924600	1.60442800
C	2.76495500	-0.06055000	0.33970400
C	3.37718600	-0.06220600	-0.92296900
C	3.58025000	-0.03184200	1.47198700
C	4.75837200	-0.03141300	-1.05602400
H	2.75169900	-0.09924200	-1.81284200
C	4.96945600	-0.00064600	1.33606500
H	3.13504300	-0.03246800	2.45710100
C	5.56427700	0.00110000	0.08130100
H	5.20531800	-0.03424300	-2.04565700
H	5.58648700	0.02133500	2.22928800
H	6.64548000	0.02567200	-0.01478700
C	-2.83523700	-0.08347300	0.33254100
C	-3.48724300	0.05657900	1.55686700
C	-3.59681900	-0.18047300	-0.83714700
C	-4.87919100	0.09794400	1.60840400
H	-2.90274300	0.12807000	2.46610500
C	-4.98561500	-0.13936100	-0.78311800
H	-3.09715900	-0.29816400	-1.79606600
C	-5.63188700	0.00091900	0.44314800
H	-5.37405100	0.20645000	2.56866000
H	-5.56229300	-0.21719300	-1.69970200
H	-6.71608800	0.03317600	0.48759100
H	2.00106100	2.19473200	-1.61974500
H	1.15173600	4.43290000	-1.24193700
H	-0.31628400	2.92479900	-2.64804600
H	-2.12668500	2.69716300	-0.19069600
C	0.66953200	-1.34909000	-0.31203200
C	-0.72560200	-1.35243800	-0.39935300
C	1.39446900	-2.45872700	-0.72582900
C	-1.40030200	-2.45033400	-0.91247800
C	0.71870500	-3.55336500	-1.26870200
H	2.47471300	-2.47749200	-0.62899700
C	-0.66733800	-3.54921900	-1.36453100
H	-2.48448800	-2.46778700	-0.94310600
H	1.28415900	-4.41723600	-1.60420600
H	-1.18718500	-4.41047800	-1.77250400

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1192.4247 Hartrees

Zero-point correction = 0.423221 Hartrees
Thermal correction to enthalpy = 0.445841 Hartrees
Thermal correction to Gibbs free energy = 0.373099 Hartrees
Quasiharmonic free energy correction = 0.37586229 Hartrees

tricyclic product **33**

C	0.64160700	3.64897000	-0.71651500
C	1.48794700	2.49014600	-0.20001900
C	0.69811100	1.20408800	-0.02267800
C	-0.70249500	1.20793900	-0.00792100
C	-1.48997200	2.50302100	-0.12359400
C	-0.63952100	3.74975400	0.10275000
C	1.39477200	-0.01236000	0.12128000
C	-1.40169500	-0.00944500	0.11524300
C	-0.70699200	-1.21250200	0.25077600
C	0.69707200	-1.21258200	0.26487500
C	1.35419300	-2.55931400	0.44301300
H	2.44112400	-2.49035300	0.36408100
C	0.80560700	-3.57976100	-0.57184000
C	-0.73631000	-3.52029400	-0.69353400
C	-1.37083600	-2.56585200	0.33400400
H	0.38277400	3.47932200	-1.77030200
H	2.33417800	2.30350300	-0.87010800
H	-1.94543100	2.56023400	-1.12240900
H	-1.21463400	4.64276400	-0.16282200
H	1.26159000	-3.38025600	-1.54731500
H	-1.01617300	-3.16821500	-1.69180300
H	-2.44703800	-2.49024700	0.16277100
C	2.88973200	-0.01075200	0.11125000
C	3.59291200	-0.44338800	-1.01743700
C	3.61130200	0.42655600	1.22524500
C	4.98497000	-0.43867000	-1.03259100
H	3.03534300	-0.78424300	-1.88656700
C	5.00335700	0.43221900	1.21271500
H	3.07006000	0.75810400	2.10788500
C	5.69370600	0.00053300	0.08297600
H	5.51700400	-0.77636500	-1.91714200
H	5.55011600	0.77104800	2.08779400
H	6.77935100	0.00508200	0.07227100
C	-2.89638500	-0.00912200	0.09778700
C	-3.62527400	-0.21246900	1.27317100
C	-3.59263000	0.18635200	-1.09838300
C	-5.01760500	-0.21827300	1.25408600
H	-3.08955000	-0.36918500	2.20598500
C	-4.98448200	0.17927200	-1.12054100

H	-3.03204300	0.33796500	-2.01747500
C	-5.70080700	-0.02186400	0.05667300
H	-5.56881700	-0.37809300	2.17606400
H	-5.50980700	0.32870000	-2.05918100
H	-6.78638600	-0.02762300	0.04064400
H	-1.23961800	-2.98267800	1.34302000
H	-1.17139400	-4.51813100	-0.57988400
H	1.13084400	-4.58206100	-0.27532600
H	1.13578200	-2.92111300	1.45772200
H	-2.33017000	2.47723200	0.57916600
H	1.21848600	4.57850800	-0.67192300
H	1.93377600	2.77614300	0.76341600
H	-0.38108100	3.83673800	1.16669300

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1006.299 Hartrees
Zero-point correction = 0.453960 Hartrees
Thermal correction to enthalpy = 0.476172 Hartrees
Thermal correction to Gibbs free energy = 0.402166 Hartrees
Quasiharmonic free energy correction = 0.4072234 Hartrees

carbon dioxide (**34**)

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16290100
O	0.00000000	0.00000000	-1.16290100

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -188.57523 Hartrees
Zero-point correction = 0.011960 Hartrees
Thermal correction to enthalpy = 0.015523 Hartrees
Thermal correction to Gibbs free energy = -0.008737 Hartrees

dinitrogen

N	0.00000000	0.00000000	0.54938200
N	0.00000000	0.00000000	-0.54938200

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -109.51676 Hartrees
Zero-point correction = 0.005767 Hartrees
Thermal correction to enthalpy = 0.009072 Hartrees
Thermal correction to Gibbs free energy = -0.012671 Hartrees

tricyclic product **35**

C	0.64304000	3.64477500	-0.40821200
C	1.49082200	2.43557200	-0.02442900
C	0.71450800	1.12813700	-0.00696400
C	-0.71453400	1.12813000	0.00660400

C	-1.49081800	2.43558100	0.02420500
C	-0.64303200	3.64466000	0.40836500
C	1.40575600	-0.07030700	0.00244000
C	-1.40577300	-0.07032700	-0.00275500
C	-0.71123200	-1.31642500	-0.00758400
C	0.71124000	-1.31641300	0.00725900
C	1.39656800	-2.56300200	0.03216000
C	0.70677100	-3.74735100	0.02001100
C	-0.70671100	-3.74735900	-0.02048700
C	-1.39652800	-2.56303100	-0.03258100
H	0.39289500	3.60431200	-1.47686600
H	2.34843400	2.33580400	-0.69792600
H	-1.91811700	2.60878800	-0.97369200
H	-1.21768700	4.56265800	0.24755700
H	1.24637800	-4.68935000	0.04040700
H	-1.24630200	-4.68936700	-0.04096200
C	2.89986100	-0.07185600	0.00675100
C	3.61442400	-0.36689200	-1.15842500
C	3.60753000	0.22056300	1.17575200
C	5.00666000	-0.36361200	-1.15590300
H	3.06727400	-0.60191900	-2.06765800
C	4.99967800	0.22326800	1.18042900
H	3.05601300	0.44155900	2.08593600
C	5.70239600	-0.06739000	0.01379600
H	5.54869500	-0.59352100	-2.06832500
H	5.53620300	0.45017900	2.09685800
H	6.78809900	-0.06538900	0.01653200
C	-2.89987500	-0.07191600	-0.00680200
C	-3.61415400	-0.36745600	1.15841600
C	-3.60783600	0.22101100	-1.17550900
C	-5.00639200	-0.36413100	1.15625500
H	-3.06678100	-0.60288400	2.06741100
C	-4.99997900	0.22375400	-1.17982900
H	-3.05653200	0.44236800	-2.08573300
C	-5.70241200	-0.06737600	-0.01313400
H	-5.54820200	-0.59439500	2.06872100
H	-5.53674200	0.45107500	-2.09601600
H	-6.78811600	-0.06533100	-0.01560400
H	-2.48116300	-2.56455500	-0.06485000
H	2.48120500	-2.56449800	0.06436300
H	-2.34853100	2.33570800	0.69755500
H	1.21771100	4.56271600	-0.24712900
H	1.91829300	2.60853000	0.97343600
H	-0.39289500	3.60386200	1.47701000

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1003.8963 Hartrees

Zero-point correction = 0.406593 Hartrees
Thermal correction to enthalpy = 0.427726 Hartrees
Thermal correction to Gibbs free energy = 0.356116 Hartrees
Quasiharmonic free energy correction = 0.36087543 Hartrees

TS–1

C	0.66177300	3.81309800	-0.17619500
C	1.46703900	2.67038000	-0.32504900
C	0.71123900	1.52024700	-0.19748900
C	-0.52091300	1.45664100	0.04208300
C	-1.39597600	2.51282700	0.21046400
C	-0.71784100	3.73729300	0.08146000
H	1.12289600	4.79268400	-0.26943600
H	2.53301000	2.72198800	-0.51921600
C	-1.27007700	-0.95218200	-0.08409000
H	-2.45984700	2.44075100	0.41153900
H	-1.28221800	4.66040700	0.18157300
C	-0.57193500	-1.07866400	1.22010300
N	-0.62899100	-1.16324300	-1.21070900
N	0.71034400	-1.13441900	-1.24068300
O	-1.05017100	-1.19264000	2.31171300
O	0.79783900	-1.13620900	1.09405600
C	-2.74513600	-0.82646000	-0.13612400
C	-3.40964500	-1.15580700	-1.32505800
C	-3.48340400	-0.33663800	0.94873800
C	-4.78639700	-1.00974400	-1.42138400
H	-2.82908500	-1.52134600	-2.16452700
C	-4.86293500	-0.18455800	0.84009100
H	-2.98200600	-0.08113500	1.87403500
C	-5.51841400	-0.52260200	-0.33960400
H	-5.29135800	-1.27493400	-2.34505800
H	-5.42575600	0.19566300	1.68705300
H	-6.59533000	-0.40768000	-0.41756500
C	2.82945600	-0.85544900	-0.09877000
C	3.51684100	-0.79075300	1.11595100
C	3.52545500	-0.76729300	-1.30945300
C	4.89989800	-0.64465100	1.11619500
H	2.96795500	-0.85435100	2.04908300
C	4.90593500	-0.62120200	-1.29865000
H	2.96896000	-0.81496100	-2.23917000
C	5.59507100	-0.56075100	-0.08743100
H	5.43481100	-0.59581800	2.05923300
H	5.44725200	-0.55499100	-2.23704300
H	6.67474000	-0.44664000	-0.08308100
C	1.36415900	-0.99460200	-0.12142800

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1068.3213 Hartrees
Zero-point correction = 0.298025 Hartrees
Thermal correction to enthalpy = 0.318530 Hartrees
Thermal correction to Gibbs free energy = 0.246690 Hartrees
Quasiharmonic free energy correction = 0.25267384 Hartrees

TS–2

C	0.85285300	3.47779600	0.16469300
C	1.63397800	2.36355700	-0.60698200
C	0.67166800	1.23614100	-0.60495600
C	-0.53610900	1.23270000	-0.37583900
C	-1.47221500	2.28889300	0.06175700
C	-0.63988700	3.58665300	-0.20806800
H	1.33863100	4.44417600	-0.01217600
H	2.58274100	2.13476000	-0.10934700
C	1.32923700	-1.09518300	0.00340500
C	-1.28519400	-1.02562000	0.04902900
H	-2.41939700	2.30593800	-0.48566400
H	-0.72448100	3.82584800	-1.27493600
C	-0.57863700	-0.78804000	1.33028800
N	-0.66231400	-1.59116900	-0.97003500
N	0.66872400	-1.56031900	-1.02507200
O	-1.04325800	-0.51591600	2.40291500
O	0.78083000	-0.96475100	1.23277500
C	-2.75565400	-0.86586300	-0.05943400
C	-3.30266400	-0.76603600	-1.34738800
C	-3.60518000	-0.78891800	1.05061700
C	-4.66941600	-0.60198900	-1.52141900
H	-2.63442000	-0.81593300	-2.20062000
C	-4.97628600	-0.62666200	0.86651700
H	-3.19821400	-0.85784000	2.05060900
C	-5.51274300	-0.53145100	-0.41290700
H	-5.07872700	-0.52271500	-2.52388900
H	-5.62653200	-0.57589500	1.73442200
H	-6.58194800	-0.39901500	-0.54882200
C	2.79295100	-0.93877100	-0.02527300
C	3.47803600	-0.49324900	1.10850100
C	3.48807800	-1.19941600	-1.21058200
C	4.85687600	-0.31444500	1.05443500
H	2.92934600	-0.29049700	2.02205600
C	4.86401200	-1.02023900	-1.25425100
H	2.93372200	-1.53760600	-2.07927700
C	5.55069600	-0.57738200	-0.12371000
H	5.38944400	0.02889600	1.93577200

H	5.40433200	-1.22672900	-2.17262300
H	6.62668500	-0.43774500	-0.16223200
H	-1.70443600	2.16429300	1.12634800
H	-1.08942700	4.41799200	0.34627100
H	0.93608400	3.26443500	1.23715600
H	1.86475300	2.66853000	-1.63343200

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1070.7386 Hartrees
Zero-point correction = 0.345467 Hartrees
Thermal correction to enthalpy = 0.366875 Hartrees
Thermal correction to Gibbs free energy = 0.293906 Hartrees
Quasiharmonic free energy correction = 0.29962022 Hartrees

TS–3

C	-0.64139400	-3.30409100	-1.94573700
C	-1.46062400	-2.12080500	-1.43648000
C	-0.71586400	-1.32916500	-0.37976000
C	0.71208500	-1.31626800	-0.34253400
C	1.51100600	-2.22001100	-1.26497500
C	0.71344300	-2.80164400	-2.43000100
H	-1.18609600	-3.80609600	-2.75139300
H	-2.42448000	-2.45409200	-1.03997100
C	-1.38369200	-0.54698100	0.53532000
C	1.36277300	-0.47583200	0.54136200
H	2.39751400	-1.70008600	-1.62996300
H	0.55606600	-2.03092700	-3.19568100
C	0.62763700	0.08555000	1.67778900
O	1.09494900	0.58101900	2.67062600
O	-0.74349900	-0.01147900	1.59651200
C	2.83902700	-0.29138000	0.56739400
C	3.50206900	0.26155000	-0.53438600
C	3.58643800	-0.65316700	1.69238700
C	4.88269200	0.43160100	-0.52167900
H	2.91956000	0.56995800	-1.39942800
C	4.96802500	-0.48710100	1.70287200
H	3.07743700	-1.05062500	2.56365600
C	5.62014800	0.05322200	0.59766100
H	5.38076800	0.86509900	-1.38360000
H	5.53583300	-0.77467200	2.58233900
H	6.69748700	0.18675000	0.61133000
C	-2.84892800	-0.37197800	0.65834100
C	-3.43322300	-0.37630000	1.93000300
C	-3.65877900	-0.16795000	-0.46429600
C	-4.80658000	-0.21226500	2.07012600
H	-2.80218500	-0.50486100	2.80271000

C	-5.03132600	0.00150900	-0.31952800
H	-3.20536900	-0.10950500	-1.44859300
C	-5.60960800	-0.02699900	0.94730900
H	-5.25009500	-0.22431000	3.06069500
H	-5.64819700	0.16642100	-1.19736900
H	-6.68118900	0.10517500	1.05952100
H	1.88863800	-3.04428100	-0.64234800
H	1.29155200	-3.60443800	-2.89805100
H	-0.49992600	-4.03761200	-1.14136200
H	-1.68132800	-1.47161700	-2.29536600
C	-0.78405200	1.60418600	-0.82893400
C	-1.60032300	2.58057000	-1.37670500
C	0.44331500	1.74416400	-0.58085300
C	-0.89161600	3.76142700	-1.65577000
H	-2.66565500	2.48827300	-1.56744200
C	1.22947200	2.85971900	-0.79521500
C	0.47763800	3.89693300	-1.37416500
H	-1.42217300	4.60291700	-2.09336700
H	2.28182600	2.96216400	-0.55094000
H	0.96986100	4.83910600	-1.59975400

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1192.2932 Hartrees
Zero-point correction = 0.417366 Hartrees
Thermal correction to enthalpy = 0.441645 Hartrees
Thermal correction to Gibbs free energy = 0.363015 Hartrees
Quasiharmonic free energy correction = 0.36822571 Hartrees

TS–4

C	0.52462600	3.81109000	-0.34235100
C	1.42164600	2.59956700	-0.59238300
C	0.66687000	1.30195100	-0.40496100
C	-0.68332700	1.22998200	-0.30070900
C	-1.56952700	2.43949400	-0.46268400
C	-0.81464000	3.63054200	-1.05054500
H	1.02835200	4.72288100	-0.67830000
H	2.28188800	2.61484400	0.08515700
C	1.35690700	0.06580400	-0.07942900
C	-1.24768000	-0.06108500	0.16032400
H	-2.43187300	2.17966400	-1.08669200
H	-0.63630100	3.45850500	-2.12019000
C	-0.52968500	-0.21673800	1.77677400
O	-1.31282500	-0.51600000	2.64956400
O	0.70963100	-0.03415800	1.77791900
C	-2.76273000	-0.08713900	0.12613700
C	-3.36862100	-0.38921000	-1.10105500

C	-3.58083000	0.30892900	1.18711500
C	-4.74852000	-0.33343500	-1.26015400
H	-2.74157900	-0.65071600	-1.95070800
C	-4.96477600	0.36389300	1.02802000
H	-3.13836600	0.55789600	2.14208800
C	-5.55539400	0.03930400	-0.18797400
H	-5.19131700	-0.57282500	-2.22242400
H	-5.58255500	0.66619300	1.86833000
H	-6.63404100	0.08417000	-0.30402100
C	2.84420700	0.10253500	0.08741300
C	3.47815300	-0.10536400	1.31253400
C	3.61609600	0.32076500	-1.05947700
C	4.86977400	-0.08452800	1.38378500
H	2.88034700	-0.27667900	2.19892900
C	5.00435500	0.33611300	-0.98207900
H	3.12271900	0.47651200	-2.01653000
C	5.63547700	0.13482000	0.24325600
H	5.35536400	-0.24245000	2.34193700
H	5.59122400	0.50705500	-1.87940100
H	6.71911300	0.14876300	0.30675900
H	-1.98953200	2.70241500	0.51897700
H	-1.42934900	4.53238500	-0.96908700
H	0.34975000	3.91496700	0.73623500
H	1.83699100	2.65069900	-1.60892400
C	0.77460500	-1.19414100	-0.51565800
C	1.65256100	-2.38267300	-0.82386800
C	-0.57186500	-1.27654100	-0.36666500
C	0.82855700	-3.59851800	-1.24450800
H	2.24414900	-2.62248500	0.07110500
H	2.38193900	-2.12358400	-1.60039100
C	-1.30765000	-2.59553400	-0.40648600
C	-0.35290600	-3.78339400	-0.29456300
H	1.46570000	-4.48815600	-1.25922200
H	0.45115400	-3.45499200	-2.26568600
H	-2.04489400	-2.60340200	0.40458900
H	-1.88603200	-2.67237800	-1.33653400
H	-0.89066100	-4.71188600	-0.51026800
H	0.01927500	-3.85507000	0.73555800

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1194.7888 Hartrees
Zero-point correction = 0.466863 Hartrees
Thermal correction to enthalpy = 0.490974 Hartrees
Thermal correction to Gibbs free energy = 0.414777 Hartrees
Quasiharmonic free energy correction = 0.4182318 Hartrees

TS–5

C	0.96472500	-3.50532400	-1.08847500
C	1.58963500	-2.29943500	-0.84951200
C	0.82272300	-1.17061700	-0.49922800
C	-0.57837700	-1.26850000	-0.35990300
C	-1.18444000	-2.52368600	-0.53531200
C	-0.42400600	-3.61444500	-0.91666600
C	1.42073200	0.09496800	-0.14554300
C	-1.27490900	-0.07662200	0.17060600
C	-0.71622600	1.21394600	-0.28821700
C	0.68654500	1.30975200	-0.40350800
C	1.29976500	2.55494300	-0.64424500
H	2.38120100	2.62844600	-0.66496500
C	0.52086700	3.67280100	-0.85885800
C	-0.87671700	3.57279000	-0.78785100
C	-1.48871400	2.37051000	-0.48287800
H	1.54633300	-4.37223200	-1.38375600
H	2.66709800	-2.20618200	-0.93904400
H	-2.25066500	-2.63177800	-0.37231000
H	-0.90977600	-4.57286000	-1.07369300
H	0.98845100	4.62919700	-1.06867300
H	-1.48759400	4.45387200	-0.96068000
H	-2.56836700	2.31358900	-0.40053000
C	-2.78733900	-0.10999800	0.12760900
C	-3.60319600	0.31329400	1.18025100
C	-3.39384700	-0.43102200	-1.09493100
C	-4.98667100	0.37493800	1.01939700
H	-3.15848400	0.58597800	2.12740000
C	-4.77359900	-0.36983500	-1.25436100
H	-2.76944400	-0.72235700	-1.93614900
C	-5.57855700	0.02959900	-0.19048200
H	-5.60273800	0.69909000	1.85274400
H	-5.21719700	-0.62520600	-2.21214000
H	-6.65684200	0.07945100	-0.30830300
C	2.89584600	0.13394100	0.04770200
C	3.47548300	-0.25688100	1.25661000
C	3.71232000	0.48685300	-1.03313900
C	4.86173400	-0.26494100	1.38466800
H	2.83421100	-0.53751500	2.08357400
C	5.09716700	0.46305800	-0.89973800
H	3.25946200	0.76478100	-1.98159200
C	5.67421400	0.09297900	0.31226300
H	5.30761400	-0.55967600	2.32962900
H	5.72254500	0.73318900	-1.74484900
H	6.75446800	0.07866100	0.41839700

C	-0.55670300	-0.21469600	1.84525700
O	0.66561900	-0.00367600	1.83794700
O	-1.36949600	-0.52240800	2.68278300

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1192.3902 Hartrees
Zero-point correction = 0.419918 Hartrees
Thermal correction to enthalpy = 0.443031 Hartrees
Thermal correction to Gibbs free energy = 0.368475 Hartrees
Quasiharmonic free energy correction = 0.37229192 Hartrees

TS–6

C	0.96472500	-3.50532400	-1.08847500
C	1.58963500	-2.29943500	-0.84951200
C	0.82272300	-1.17061700	-0.49922800
C	-0.57837700	-1.26850000	-0.35990300
C	-1.18444000	-2.52368600	-0.53531200
C	-0.42400600	-3.61444500	-0.91666600
C	1.42073200	0.09496800	-0.14554300
C	-1.27490900	-0.07662200	0.17060600
C	-0.71622600	1.21394600	-0.28821700
C	0.68654500	1.30975200	-0.40350800
C	1.29976500	2.55494300	-0.64424500
H	2.38120100	2.62844600	-0.66496500
C	0.52086700	3.67280100	-0.85885800
C	-0.87671700	3.57279000	-0.78785100
C	-1.48871400	2.37051000	-0.48287800
H	1.54633300	-4.37223200	-1.38375600
H	2.66709800	-2.20618200	-0.93904400
H	-2.25066500	-2.63177800	-0.37231000
H	-0.90977600	-4.57286000	-1.07369300
H	0.98845100	4.62919700	-1.06867300
H	-1.48759400	4.45387200	-0.96068000
H	-2.56836700	2.31358900	-0.40053000
C	-2.78733900	-0.10999800	0.12760900
C	-3.60319600	0.31329400	1.18025100
C	-3.39384700	-0.43102200	-1.09493100
C	-4.98667100	0.37493800	1.01939700
H	-3.15848400	0.58597800	2.12740000
C	-4.77359900	-0.36983500	-1.25436100
H	-2.76944400	-0.72235700	-1.93614900
C	-5.57855700	0.02959900	-0.19048200
H	-5.60273800	0.69909000	1.85274400
H	-5.21719700	-0.62520600	-2.21214000
H	-6.65684200	0.07945100	-0.30830300
C	2.89584600	0.13394100	0.04770200

C	3.47548300	-0.25688100	1.25661000
C	3.71232000	0.48685300	-1.03313900
C	4.86173400	-0.26494100	1.38466800
H	2.83421100	-0.53751500	2.08357400
C	5.09716700	0.46305800	-0.89973800
H	3.25946200	0.76478100	-1.98159200
C	5.67421400	0.09297900	0.31226300
H	5.30761400	-0.55967600	2.32962900
H	5.72254500	0.73318900	-1.74484900
H	6.75446800	0.07866100	0.41839700
C	-0.55670300	-0.21469600	1.84525700
O	0.66561900	-0.00367600	1.83794700
O	-1.36949600	-0.52240800	2.68278300

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1189.9879 Hartrees
Zero-point correction = 0.372884 Hartrees
Thermal correction to enthalpy = 0.394986 Hartrees
Thermal correction to Gibbs free energy = 0.322992 Hartrees
Quasiharmonic free energy correction = 0.32613004 Hartrees

TS–7

C	-0.69264300	3.35772600	-0.82041000
C	-1.41604000	2.21056800	-0.55489300
C	-0.73400000	0.99918100	-0.37189300
C	0.67048000	0.95169000	-0.41793000
C	1.39275000	2.13274700	-0.66228700
C	0.71042700	3.31529600	-0.87467700
H	-1.21093200	4.29445800	-0.99776300
H	-2.50056200	2.23032900	-0.51614500
C	-1.34745200	-0.28090200	-0.02583900
C	1.26877800	-0.34582500	-0.10308400
H	2.47668300	2.09990100	-0.69824500
H	1.26575700	4.22289100	-1.08969000
C	0.56671800	-1.46725300	-0.77834400
N	0.49721300	-0.66393700	1.58786500
N	-0.66377300	-0.56118600	1.59315900
O	1.03971800	-2.43466300	-1.31040500
O	-0.79917400	-1.35350400	-0.70532200
C	2.73964100	-0.42847500	0.10929100
C	3.28358100	0.26969100	1.19455400
C	3.59293200	-1.12872000	-0.74811700
C	4.65387600	0.26639300	1.42339500
H	2.61925500	0.80993300	1.86404200
C	4.96638400	-1.12544700	-0.51659600
H	3.18098700	-1.67804400	-1.58515100

C	5.50012800	-0.43302600	0.56557000
H	5.06057400	0.80583500	2.27327700
H	5.62075700	-1.67276800	-1.18811800
H	6.57132000	-0.43890400	0.74264000
C	-2.82152900	-0.41575900	0.11118800
C	-3.54195700	-1.26748200	-0.72627600
C	-3.48422200	0.32330800	1.09418500
C	-4.92329700	-1.36498000	-0.58778100
H	-3.01758900	-1.84797000	-1.47737300
C	-4.86423500	0.22313200	1.22668200
H	-2.91044000	0.95960300	1.76314400
C	-5.58577700	-0.62012800	0.38380100
H	-5.48308400	-2.02697200	-1.24092500
H	-5.37529300	0.79385500	1.99550800
H	-6.66313000	-0.70135500	0.49021700

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1068.4452 Hartrees
Zero-point correction = 0.300931 Hartrees
Thermal correction to enthalpy = 0.320013 Hartrees
Thermal correction to Gibbs free energy = 0.254457 Hartrees
Quasiharmonic free energy correction = 0.25701985 Hartrees

TS–8

C	-0.68445000	3.30803000	-0.96964700
C	-1.53473200	2.18641700	-0.37250500
C	-0.72258500	0.92073400	-0.25562800
C	0.63597900	0.89406600	-0.27479000
C	1.48067600	2.13639800	-0.42151000
C	0.65218100	3.40987100	-0.23523700
H	-1.22959700	4.25532500	-0.91582100
H	-2.42403600	1.99851300	-0.98458900
C	-1.32580200	-0.37867900	0.01311000
C	1.23699100	-0.41537700	-0.00816600
H	2.30925100	2.10452500	0.29318300
H	0.45908000	3.56299500	0.83460600
C	0.57376300	-1.48719800	-0.81937900
N	0.50404500	-0.88227600	1.56679000
N	-0.66653800	-0.80660900	1.57784600
O	1.10084700	-2.35840500	-1.45505400
O	-0.78384600	-1.41708800	-0.74962200
C	2.72279300	-0.50590100	0.14063300
C	3.31849700	-0.21042000	1.36975200
C	3.53325300	-0.79986700	-0.95933200
C	4.70370500	-0.21654800	1.49975400
H	2.69214900	0.01585800	2.22698000

C	4.91856500	-0.80283000	-0.82550500
H	3.07665600	-1.04030300	-1.91262100
C	5.50718800	-0.51323700	0.40207600
H	5.15481300	0.00793800	2.46147000
H	5.53831300	-1.03768700	-1.68535000
H	6.58807600	-0.52018500	0.50416200
C	-2.80653700	-0.51172300	0.11060300
C	-3.53207000	-1.17985500	-0.87543800
C	-3.47112700	0.06889700	1.19230000
C	-4.91903800	-1.25477500	-0.78204200
H	-3.00717900	-1.64215800	-1.70453200
C	-4.85636000	-0.00741200	1.28067100
H	-2.89728900	0.55957200	1.97392900
C	-5.58263000	-0.66816400	0.29205000
H	-5.48069100	-1.77644200	-1.55059500
H	-5.36816200	0.44123000	2.12624300
H	-6.66411900	-0.73103100	0.36321600
H	1.94687400	2.12675700	-1.41687900
H	1.22368800	4.27569000	-0.58361500
H	-0.50079800	3.09905700	-2.03131600
H	-1.90513500	2.49191500	0.61586000

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1070.8472 Hartrees
Zero-point correction = 0.348105 Hartrees
Thermal correction to enthalpy = 0.368254 Hartrees
Thermal correction to Gibbs free energy = 0.300230 Hartrees
Quasiharmonic free energy correction = 0.30322944 Hartrees

TS–9

C	-0.57659000	-3.90971500	-0.89874600
C	-1.40034600	-2.62712300	-0.81680300
C	-0.67205900	-1.53969000	-0.05333100
C	0.74228000	-1.50621300	-0.00184200
C	1.56536100	-2.66015000	-0.54420200
C	0.79632400	-3.59034400	-1.47933400
H	-1.10308400	-4.64473700	-1.51598100
H	-2.37522600	-2.81752900	-0.35704700
C	-1.35022800	-0.47715500	0.52205600
C	1.36572900	-0.37722400	0.52029900
H	2.46872500	-2.28785000	-1.03002300
H	0.66731200	-3.10981400	-2.45799600
C	0.62152900	0.49930200	1.42855100
O	1.08385400	1.34263500	2.15991600
O	-0.73500000	0.30310200	1.45086300
C	2.83750200	-0.16114900	0.46361700

C	3.47614700	0.00064800	-0.77137300
C	3.60452200	-0.10379000	1.63097700
C	4.85181200	0.19014000	-0.84262800
H	2.87385100	-0.01063100	-1.67735800
C	4.98206300	0.08297300	1.55990400
H	3.11374300	-0.19245900	2.59431100
C	5.60978600	0.22727300	0.32566800
H	5.33021000	0.31703700	-1.80908500
H	5.56583000	0.12167900	2.47455500
H	6.68382600	0.37810600	0.27428000
C	-2.81913300	-0.29052300	0.56591600
C	-3.42763200	0.11793300	1.75826300
C	-3.61153300	-0.47165000	-0.57356400
C	-4.80435000	0.30707300	1.81498600
H	-2.81283200	0.28751900	2.63549100
C	-4.98675400	-0.27904300	-0.51363400
H	-3.14067800	-0.72738500	-1.51737900
C	-5.58870300	0.10462900	0.68262100
H	-5.26466100	0.61736900	2.74800200
H	-5.58747500	-0.41697100	-1.40747600
H	-6.66274000	0.25622200	0.72810600
H	1.91383900	-3.23606200	0.32584400
H	1.37841100	-4.50262400	-1.64491300
H	-0.46290700	-4.34630000	0.10204900
H	-1.59819200	-2.28728100	-1.84355300
C	-0.74666500	1.16843700	-1.17304600
C	-1.78403600	2.20607700	-1.42086100
C	0.46825300	1.33278800	-1.02585600
C	-0.97273300	3.48891700	-1.77213900
H	-2.37393800	2.34814400	-0.50558700
H	-2.49131100	1.95972000	-2.22007000
C	1.32651100	2.53938300	-1.01753000
C	0.27830300	3.68910000	-0.89640300
H	-1.62651100	4.36393300	-1.67835500
H	-0.66594900	3.42704600	-2.82394300
H	2.02385400	2.56539100	-0.17322100
H	1.91241400	2.61947600	-1.94052900
H	0.75558300	4.64206500	-1.15205800
H	-0.02508100	3.74462700	0.15631100

Electronic energy (M06-2X/6-311+G(d,p)/SMD(MeCN)) = -1194.7051 Hartrees
Zero-point correction = 0.464217 Hartrees
Thermal correction to enthalpy = 0.489378 Hartrees
Thermal correction to Gibbs free energy = 0.409835 Hartrees
Quasiharmonic free energy correction = 0.41457021 Hartrees

References

[1] A.S. Devlin, J. Du Bois, *Chem. Sci*. **2013**, *4*, 1059–1063.

[2] N. Pavliček, B. Schuler, S. Collazos, N. Moll, D. Pérez, E. Guitián, G. Meyer, D. Peña, L. Gross, *Nature Chemistry* **2015**, *7*, 623–628.

[3] T. K. Shah, J. M. Medina, N. K. Garg, *J. Am. Chem. Soc*. **2016**, *138*, 4948–4954.

[4] T. Meguro, S. Chen, K. Kanemoto, S. Yoshida, T. Hosoya, *Chem. Lett.* **2019**, *48*, 582–585.

[5] B. Han, P. Ma, X. Cong, H. Chen, X. Zeng, *J. Am. Chem. Soc.* **2019**, *141*, 9018–9026.

[6] M. M. Yamano, A. V. Kelleghan, Q. Shao, M. Giroud, B. J. Simmons, B. Li, S. Chen, K. N. Houk, N. K. Garg, *Nature* **2020**, *586*, 242–247.

[7] E. R. Darzi, J. S. Barber, N. K. Garg, *Angew. Chem., Int. Ed*. **2019**, *58*, 9419–9424.; *Angew. Chem.* **2019**, *131*, 9519–9524.

[8] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.

[9] R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2011**, *115*, 14556.

[10] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

[11] C. Y. Legault, CYLView, 1.0b; Université de Sherbrooke: Quebec, Montreal, Canada, http://www.cylview.org (2009).