Supporting Information for

CuCl-Mediated tandem CO insertion and annulation of 1,4-dilithio-1,3-dienes: formation of multiply substituted cyclopentadienones and/or their head-to-head dimers

Qian Luo, Chao Wang, Wen-Xiong Zhang and Zhenfeng Xi*

Contents

1. Experimental details and characterization data for all new compounds.

General Methods. All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Diethyl ether was refluxed and distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. 1,4-Dihalo-1,3-butadiene compounds are prepared by the reported ways. [1] *t*-BuLi was obtained from Acros Organics. ^{1}H NMR, and ^{13}C NMR spectra were recorded on a JEOL-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75.4 MHz for ^{13}C) in $CDCl_3$ at room temperature using Me_4Si as an internal standard, unless otherwise noted. IR spectra were obtained on a Thermo Nicolet AVATAR 330 FT-IR spectrophotometer. HRMS were recorded on a ZAB-HS instrument.

A typical procedure for syntheses of cyclopentadienones 2a–c and/or their head-to-head dimers 3a–c: To a 10 mL solution of 1,4-diiodo-1,3-diene compound (1.0 mmol) in Et_2O at –78 °C was added *t*-BuLi (4.0 mmol, 1.5 mol/L in pentane). After this reaction mixture was stirred at –78 °C for 1 h, CuCl (2.0 mmol) was added and kept at –78 °C for 0.5 h. Then CO was bubbled into the vessel for 5 min, followed by addition of ^{t}BuOO^{t}Bu (2.0 mmol) to this reaction mixture. After 1 h of stirring at 0 °C, the reaction mixture was quenched with water and extracted with Et_2O. The extraction was washed with brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo and the residue was purified by column chromatograph using silica gel (hexane: Et_2O = 20:1) to afford the final products **2a–c** and **3a–c.**

2a: red oil (25 mg, 10%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.2 Hz, 6H, CH_3), 0.99 (t, *J* = 7.2 Hz, 6H, CH_3), 1.33–1.54 (m, 8H, CH_2), 2.04 (t, *J* = 7.5 Hz, 4H, CH_2), 2.23 (t, *J* = 7.5 Hz, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.23 (2 CH_3),

14.43 (2 CH_3), 22.52 (2 CH_2), 22.85 (2 CH_2), 24.91 (2 CH_2), 28.30 (2 CH_2), 125.78 (2 quat. C), 154.95 (2 quat. C), 204.94 (1 ketone C=O). IR (neat): ν (C=O) = 1716 cm^{-1}. HRMS (IE): calcd. for $C_{17}H_{28}O$: 248.2140, found 248.2145. The NMR data are identical with the literature. [2]

2b: red oil (33 mg, 11%); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87–1.00 (m, 12H, CH_3), 1.23–1.44 (m, 16H, CH_2), 2.05 (t, J = 7.2 Hz, 4H, CH_2), 2.24 (t, J = 7.2 Hz, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.03 (2 CH_3), 14.12 (2 CH_3), 23.15 (2 CH_2), 23.21 (2 CH_2), 23.27 (2 CH_2), 26.61 (2 CH_2), 31.64 (2 CH_2), 32.27 (2 CH_2), 126.27 (2 quat. C), 154.57 (2 quat. C), 203.89 (1 ketone C=O). IR (neat): ν (C=O) = 1714 cm^{-1}. HRMS (IE): calcd. for $C_{21}H_{36}O$: 304.2766, found 304.2757. The NMR data are identical with the literature. [2]

2c: orange oil (23 mg, 12%); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.5 Hz, 6H, CH_3), 1.11 (t, J = 7.5 Hz, 6H, CH_3), 2.10 (q, J = 7.5 Hz, 4H, CH_2), 2.29 (q, J = 7.5 Hz, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.79 (2 CH_3), 14.45 (2 CH_3), 15.88 (2 CH_2), 19.07 (2 CH_2), 126.68 (2 quat. C), 155.85 (2 quat. C), 204.62 (1 ketone C=O). IR (neat): ν (C=O) = 1682 cm^{-1}. HRMS (IE): calcd. for $C_{13}H_{20}O$: 192.1514, found 192.1516.

3a: Colorless solid (151 mg, 61%); m. p. 82.1~83.4 ^oC; ^1H NMR (300 MHz, $CDCl_3$,): δ = 0.74 (t, J = 7.2 Hz, 6H, CH_3), 0.82 (t, J = 7.2 Hz, 6H, CH_3), 0.97 (t, J = 7.2 Hz, 6H, CH_3), 1.09 (t, J = 7.2 Hz, 6H, CH_3), 1.36–1.73 (m, 24H, CH_2), 2.18–2.41 (m, 8H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.70 (2 CH_3), 15.05 (2 CH_3), 15.40 (2 CH_3), 15.66 (2 CH_3), 17.56 (2 CH_2), 19.22 (2 CH_2), 21.49 (2 CH_2), 21.72 (2 CH_2), 26.56 (2 CH_2), 32.49 (2 CH_2), 32.92 (2 CH_2), 33.30 (2 CH_2), 53.83 (2 quat. C), 60.85 (2 quat. C), 144.84 (2 quat. C), 173.41 (2 quat. C), 209.36 (2 ketone C=O). IR (neat): ν (C=O) = 1692 cm^{-1}. HRMS (EI): calcd. for $C_{34}H_{56}O_2$: 496.4280, found 496.4277.

3b: Colorless solid (128 mg, 42%); m. p. 65.6~67.0 ^oC; ^1H NMR (300 MHz, $CDCl_3$):

δ = 0.82 (t, *J* = 7.2 Hz, 6H, CH_3), 0.83 (t, *J* = 7.2 Hz, 6H, CH_3), 0.94 (t, *J* = 6.9 Hz, 6H, CH_3), 1.00 (t, *J* = 7.2 Hz, 6H, CH_3), 1.11–1.64 (m, 40H, CH_2), 2.20–2.38 (m, 8H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.85 (2 CH_3), 13,87 (2 CH_3), 13.91 (4 CH_3), 23.29 (2 CH_2), 23.83 (2 CH_2), 24.16 (6 CH_2), 26.30 (2 CH_2), 28.01 (2 CH_2), 29.95 (2 CH_2), 30.21 (2 CH_2), 30.31 (2 CH_2), 30.46 (2 CH_2), 30.73 (2 CH_2), 53.73 (2 quat. C), 60.77 (2 quat. C), 144.90 (2 quat. C), 173.44 (2 quat. C), 209.27 (2 ketone C=O). IR (neat): *ν* (C=O) = 1694 cm^{-1}. HRMS (EI): calcd. for $C_{42}H_{72}O_2$: 608.5532, found 608.5525.

3c: Colorless solid (92 mg, 48%); m. p. 92.3~93.5 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.62 (t, *J* = 7.2 Hz, 6H, CH_3), 1.08 (t, *J* = 7.5 Hz, 6H, CH_3), 1.11 (t, *J* = 7.5 Hz, 6H, CH_3), 1.28 (t, *J* = 7.5 Hz, 6H, CH_3), 1.43–1.85 (m, 8H, CH_2), 2.26–2.54 (m, 8H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.36 (2 CH_3), 10.92 (2 CH_3), 12.74 (4 CH_3), 17.31 (2 CH_2), 21.91 (2 CH_2), 23.13 (2 CH_2), 23.32 (2 CH_2), 53.80 (2 quat. C), 61.19 (2 quat. C), 146.33 (2 quat. C), 173.90 (2 quat. C), 209.45 (2 ketone C=O). IR (neat): *ν* (C=O) = 1681 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{40}O_2$: 384.3028, found 384.3019.

3d: Obtained as colorless solid (135 mg, 55%) in a manner analogous to that described for the synthesis of **3a**. It was noted that only trace amount of cyclopentadienone was observed in this process. M. p. 117.1~118.5 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (t, *J* = 7.2 Hz, 6H, CH_3), 0.91 (t, *J* = 7.2 Hz, 6H, CH_3), 1.12–1.37 (m, 20H, CH_2), 1.71–1.92 (m, 8H, CH_2), 2.08–2.91 (m, 12H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.87 (2 CH_3), 13.90 (2 CH_3), 22.70 (2 CH_2), 22.77 (2 CH_2), 23.53 (2 CH_2), 24.09 (2 CH_2), 26.65 (2 CH_2), 27.62 (2 CH_2), 27.99 (2 CH_2), 28.35 (2 CH_2), 29.13 (2 CH_2), 31.11 (2 CH_2), 54.49 (2 quat. C), 54.57 (2 quat. C), 141.90 (2 quat. C), 174.79 (2 quat. C), 208.19 (2 ketone C=O). IR (neat): *ν* (C=O) = 1692 cm^{-1}. HRMS (IE): calcd. for $C_{34}H_{52}O_2$: 492.3967, found 492.3968.

A typical procedure for syntheses of cyclopentadienones 2d–h: To a 10 mL solution of 1,4-diiodo-1,3-diene compound (1.0 mmol) in Et_2O at –78 °C was added

t-BuLi (4.0 mmol, 1.5 mol/L in pentane). After this reaction mixture was stirred at –78 °C for 1 h, CuCl (2.0 mmol) was added and kept at –78 °C for 0.5 h. Then CO was bubbled into the vessel for 5 min, followed by addition of ^{t}BuOO^{t}Bu (2.0 mmol) to this reaction mixture. After 1 h of stirring at 0 °C, the reaction mixture was quenched with water and extracted with Et_2O. The extraction was washed with brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo and the residue was purified by column chromatograph using silica gel (hexane: Et_2O = 20:1) to afford exclusively the final products **2d**–**h.**

2d: red solid (269 mg, 70%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.90–6.94 (m, 4H, CH), 7.15–7.19 (m, 4H, CH), 7.23–7.26 (m, 12H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 125.30 (2 quat. C), 127.45 (2 CH), 127.98 (4 CH), 128.03 (4 CH), 128.50 (2 CH), 129.33 (4 CH), 130.14 (4 CH), 130.73 (2 quat. C), 133.05 (2 quat. C), 154.47 (2 quat. C), 200.24 (1 ketone C=O). IR (neat): *ν* (C=O) = 1702 cm^{-1}. HRMS (IE): calcd. for $C_{29}H_{20}O$: 384.1514, found 384.1522. The NMR data are identical with the literature. [3]

2e: orange oil (236 mg, 70%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.40 (s, 18H, TMS), 0.92 (t, *J* = 6.6 Hz, 6H, CH_3), 1.33–1.48 (m, 8H, CH_2), 2.40 (t, *J* = 7.2 Hz, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.06 (6 CH_3) 13.86 (2 CH_3), 23.18 (2 CH_2), 28.05 (2 CH_2), 32.87 (2 CH_2), 128.21 (2 quat. C), 172.85 (2 quat. C), 211.12 (1 ketone C=O). IR (neat): *ν* (C=O) = 1700 cm^{-1}. HRMS (IE): calcd. for $C_{19}H_{36}OSi_2$: 336.2305, found 336.2317. The NMR data are identical with the literature. [2]

2f: red oil (145 mg, 50%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 7.5 Hz, 3H, CH_3), 1.10 (t, *J* = 7.5 Hz, 3H, CH_3), 2.24–2.39 (m, 4H, CH_2), 7.15–7.39 (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.09 (1 CH_3), 14.45 (1 CH_3), 16.22 (1 CH_2), 19.59 (1 CH_2), 124.79 (1 quat. C), 126.95 (1 CH), 127.35 (1 quat. C), 127.86 (2 CH), 128.17 (2 CH), 128.22 (2 CH), 128.63 (2 CH), 129.65 (1 CH), 131.00 (1 quat. C), 134.52 (1 quat. C), 154.05 (1 quat. C), 157.48 (1 quat. C), 202.56 (1 ketone C=O). IR (neat): *ν* (C=O) = 1711 cm^{-1}. HRMS (IE): calcd. for $C_{21}H_{20}O$: 288.1514, found

288.1512.

2g: red oil (234 mg, 68%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.57 (t, *J* = 6.9 Hz, 3H, CH_3), 0.75 (t, *J* = 6.9 Hz, 3H, CH_3), 0.80–1.53 (m, 8H, CH_2), 2.12 (t, *J* = 6.9 Hz, 2H, CH_2), 2.42 (t, *J* = 6.9 Hz, 2H, CH_2), 7.22–7.43 (m, 10H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.39 (1 CH_3), 13.75 (1 CH_3), 22.41 (1 CH_2), 22.66 (1 CH_2), 22.84 (1 CH_2), 26.69 (1 CH_2), 29.90 (1 CH_2), 31.62 (1 CH_2), 125.00 (1 quat. C), 127.05 (1 CH), 127.85 (2 CH), 128.07 (1 CH), 128.17 (2 CH), 128.35 (2 CH), 129.30 (2 CH), 131.72 (1 quat. C), 134.17 (1 quat. C), 153.47 (1 quat. C), 158.28 (2 quat. C), 202.53 (1 ketone C=O). IR (neat): *ν* (C=O) = 1690 cm^{-1}. HRMS (IE): calcd. for $C_{25}H_{28}O$: 344.2140, found 344.2145. The NMR data are identical with the literature. [2]

2h: green oil (109 mg, 45%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.2 Hz, 3H, CH_3), 0.90 (t, *J* = 7.2 Hz, 3H, CH_3), 1.23–1.55 (m, 8H, CH_2), 2.17 (t, *J* = 7.5 Hz, 2H, CH_2) 2.45 (t, *J* = 7.5 Hz, 2H, CH_2) 6.93–7.29 (m, 4H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.88 (2 CH_3), 22.58 (1 CH_2), 22.75 (1 CH_2), 22.99 (1 CH_2), 25.97 (1 CH_2), 29.94 (1 CH_2), 31.42 (1 CH_2), 118.90 (1 CH), 121.59 (1 CH), 127.79 (1 CH), 131.11 (1 quat. C), 133.08 (1 CH), 134.75 (1 quat. C), 145.64 (1 quat. C), 157.71 (1 quat. C), 198.50 (1 ketone C=O). IR (neat): *ν* (C=O) = 1718 cm^{-1}. HRMS (IE): calcd. for $C_{17}H_{22}O$: 242.1671, found 242.1679. The NMR data are identical with the literature. [2]

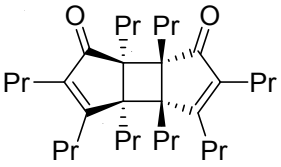
References:

1) Representative methods for the preparation of 1,4-dihalo-1,3-diene derivatives, see: (*a*) E. Negishi; F. E. Cederbaum and T. Takahashi, *Tetrahedron Lett*., 1986, **27**, 2829–2832; (*b*) S. L. Buchwald and R. B. Nielsen, *J. Am. Chem. Soc*., 1989, **111**, 2870–2874; (*c*) C. Xi, S. Huo, T. H. Afifi, R. Hara and T. Takahashi, *Tetrahedron Lett*., 1997, **38**, 4099–4102; (*d*) S. Yamaguchi, R. Jin, K. Tamao, and F. Sato, *J. Org. Chem*., 1998, **63**, 10060–10062; (*e*) Z. Xi, Z. Song, G. Liu, X. Liu and T. Takahashi, *J. Org. Chem*., 2006, **71**, 3154–3158.

2) Z. Xi and Q. Song, *J. Org. Chem.*, 2000, **65**, 9157–9159.

3) P. A. Wender, T. J. Paxton and T. J. Williams, *J. Am. Chem. Soc*., 2006, **128**, 14814–14815.

2. **Copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds.**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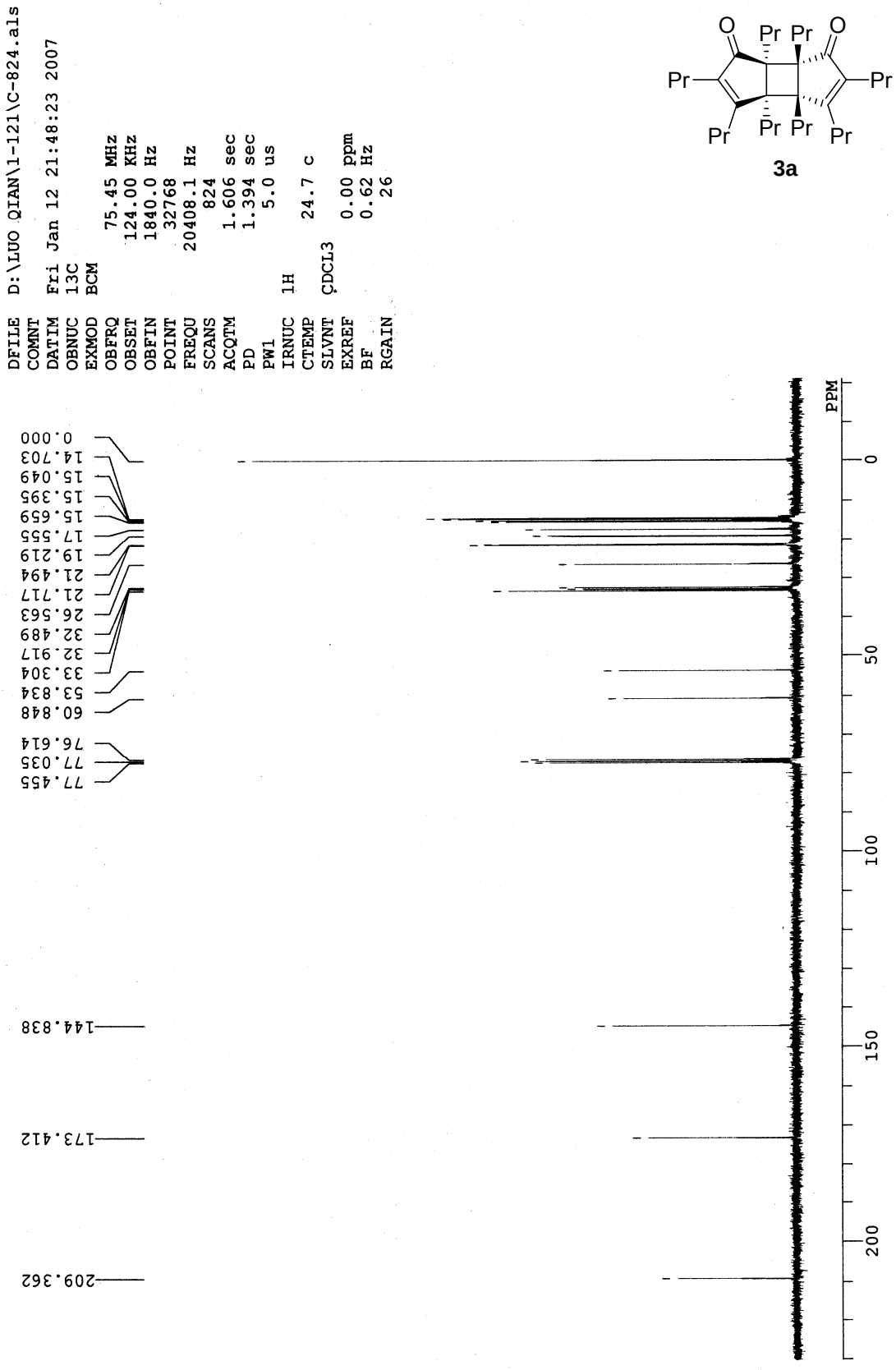
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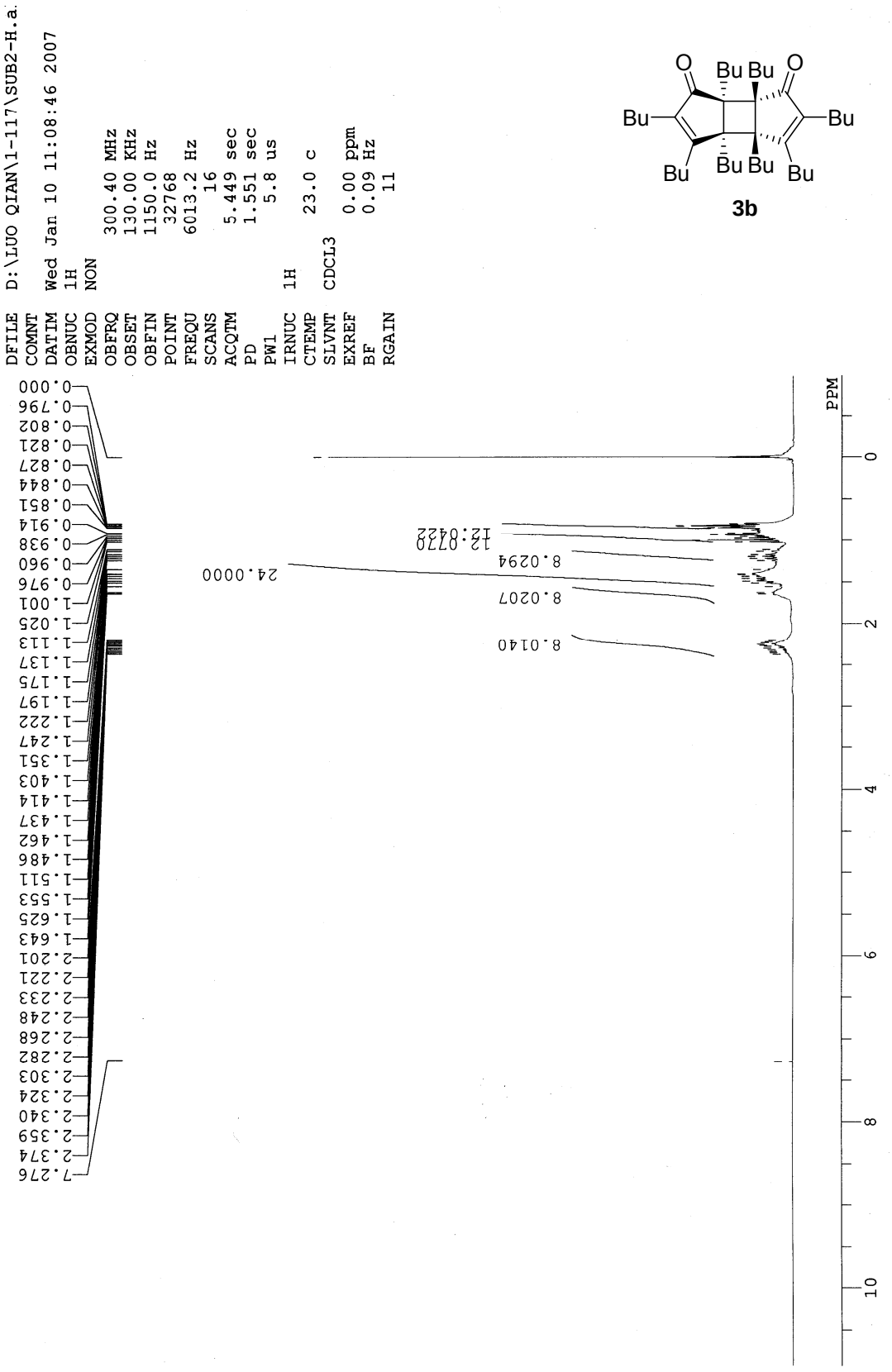
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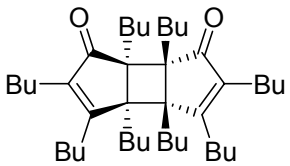
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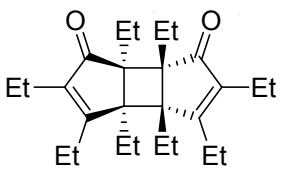
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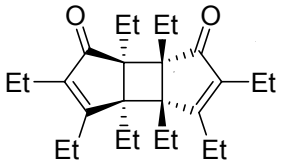
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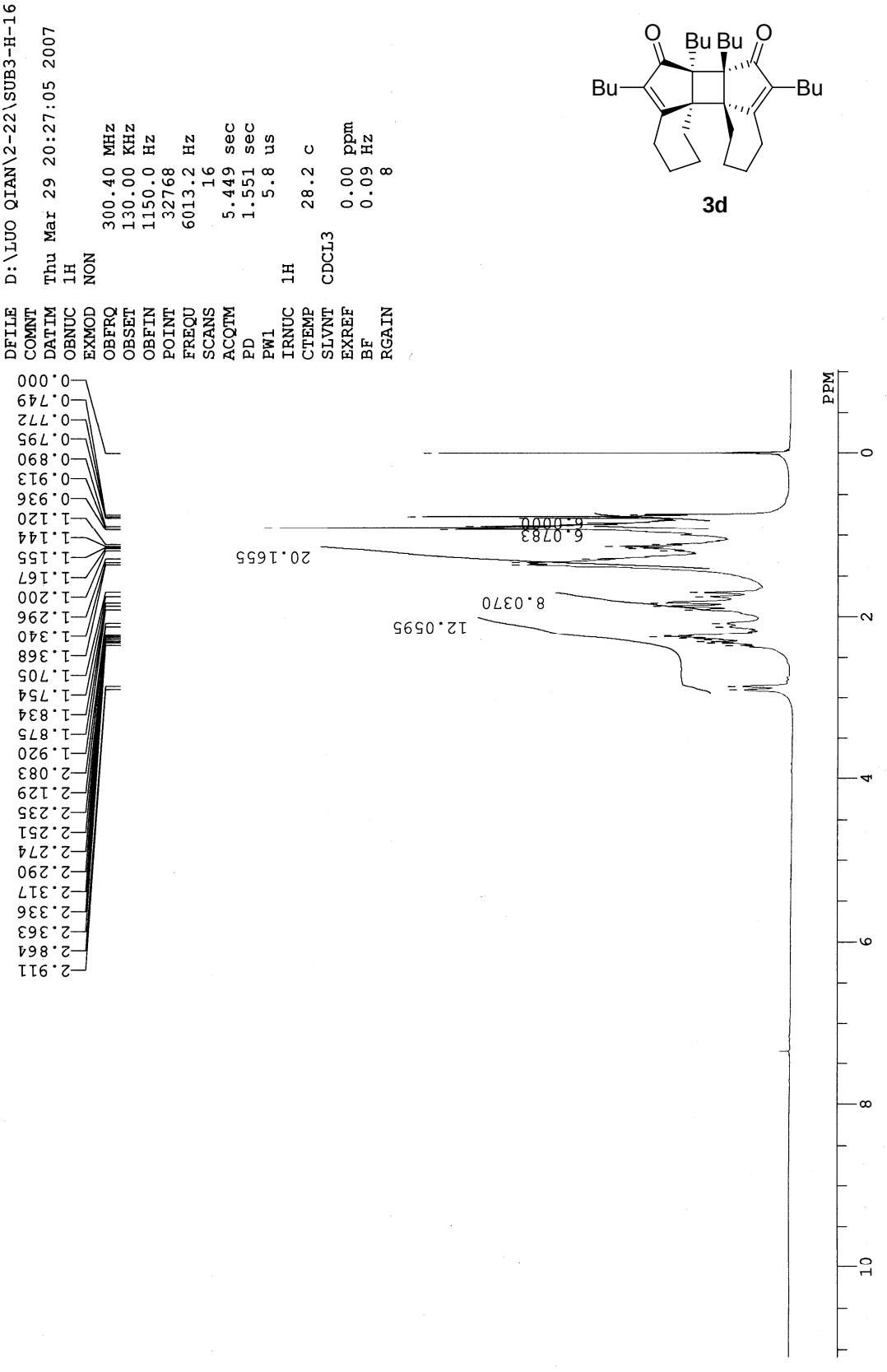
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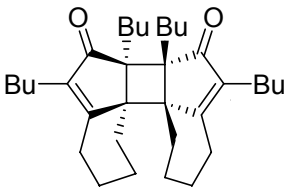
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 28.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 8
0.000
0.749
0.772
0.795
0.890
0.913
0.936
1.120
1.144
1.155
1.167
1.200
1.296
1.340
1.368
1.705
1.754
1.834
1.875
1.920
2.083
2.129
2.235
2.251
2.274
2.290
2.317
2.336
2.363
2.864
2.911
20.1655
12.0595
8.0370
6.0783
6.0000
PPM
0
2
4
6
8
10
O
Bu
Bu
O
Bu
Bu

3d


O
Bu
Bu
O
Bu
Bu

3d

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OBSET 124.00 KHz
OBFTN 1840.0 Hz
POINT 32768
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SCANS 1280
ACQTM 1.606 sec
PD 1.394 sec
PW1 5.0 us
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 26
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13.904
22.697
22.772
23.530
24.090
26.645
27.618
27.989
28.351
29.126
31.112
54.485
54.568
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PPM
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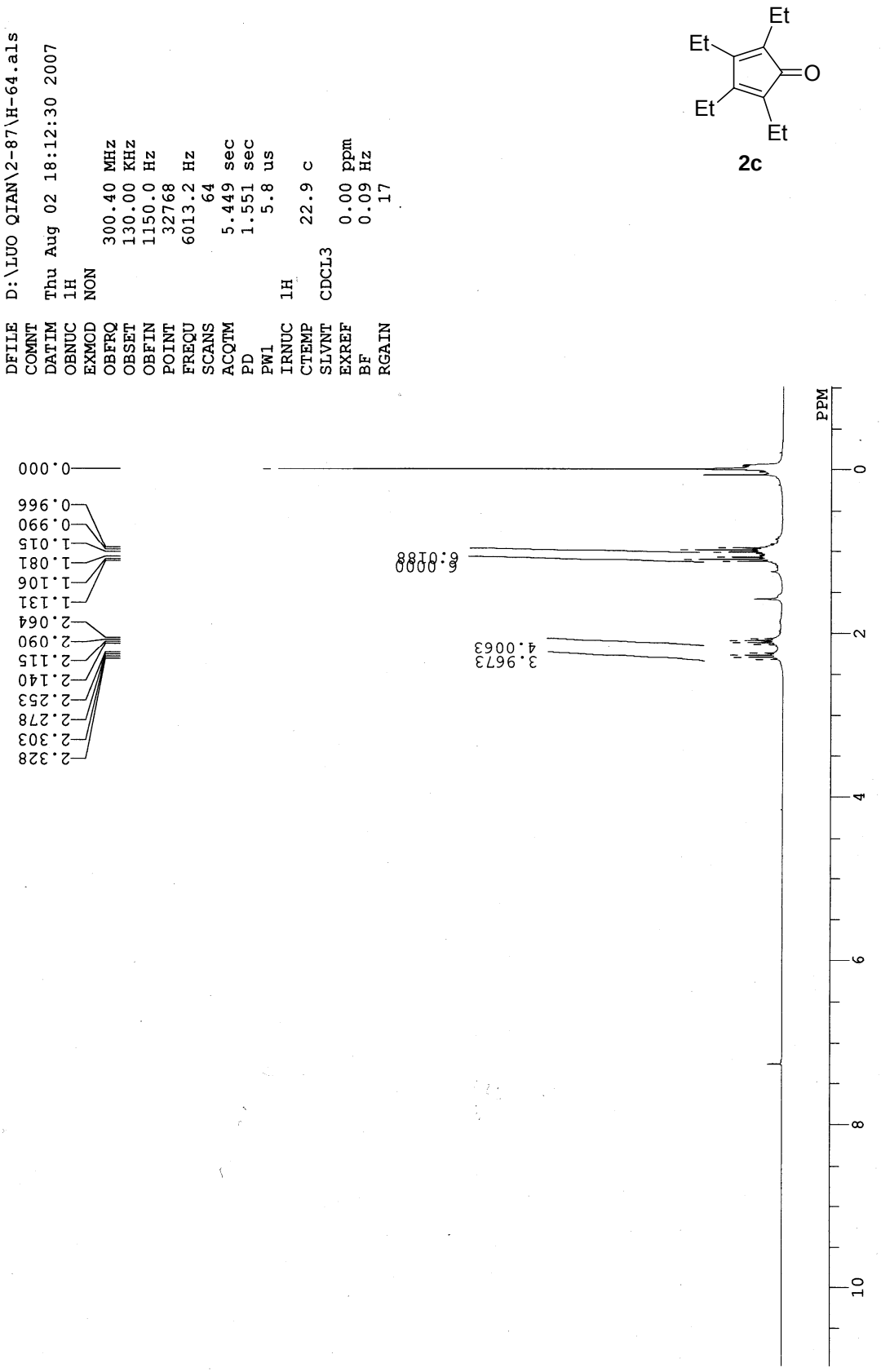
50
100
150
200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OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 64
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 17
0.000
0.966
0.990
1.015
1.081
1.106
1.131
2.064
2.090
2.115
2.140
2.253
2.278
2.303
2.328
6.0000
6.0188
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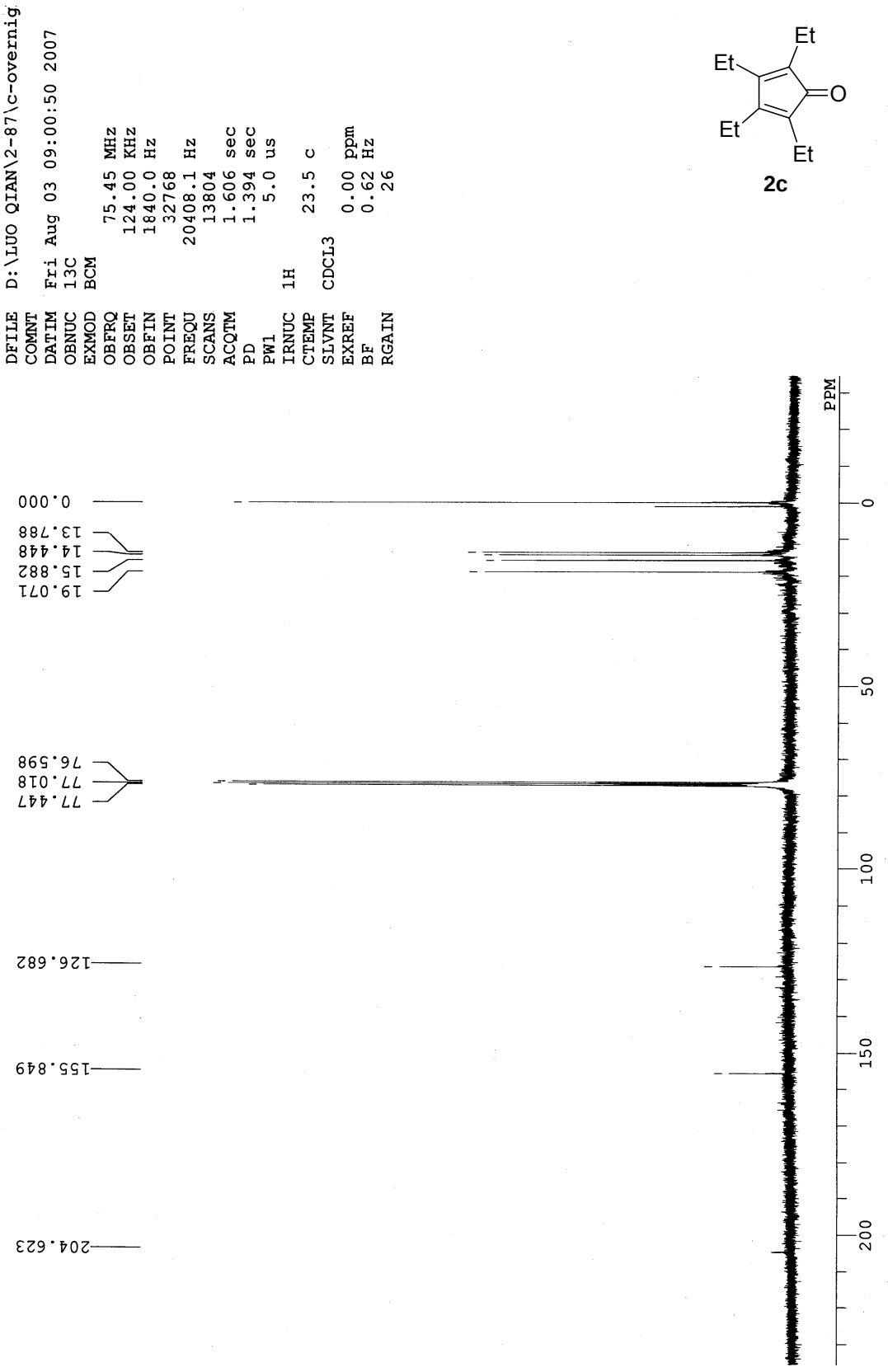
4.0063
PPM
0
2
4
6
8
10

Et
Et
O
Et
Et

2c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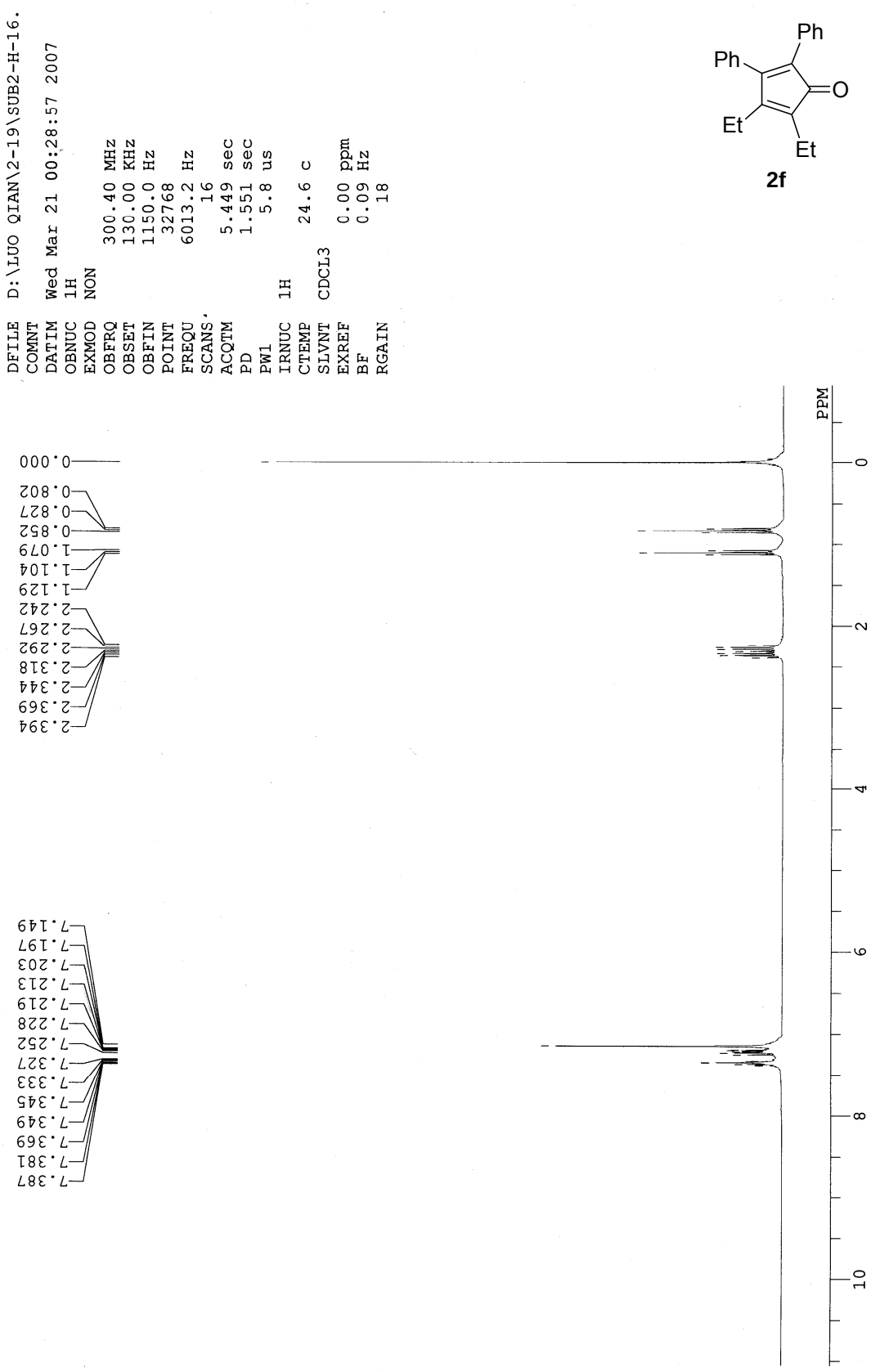
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 13804
ACQTM 1.606 sec
PD 1.394 sec
PW1 5.0 us
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 26
0.000
13.788
14.448
15.882
19.071
76.598
77.018
77.447
126.682
155.849
204.623
PPM
0
50
100
150
200
Et
Et
Et
Et
O
2c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EXMOD NON
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OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.09 Hz
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0.852
1.079
1.104
1.129
2.242
2.267
2.292
2.318
2.344
2.369
2.394
7.149
7.197
7.203
7.213
7.219
7.228
7.252
7.327
7.333
7.345
7.349
7.369
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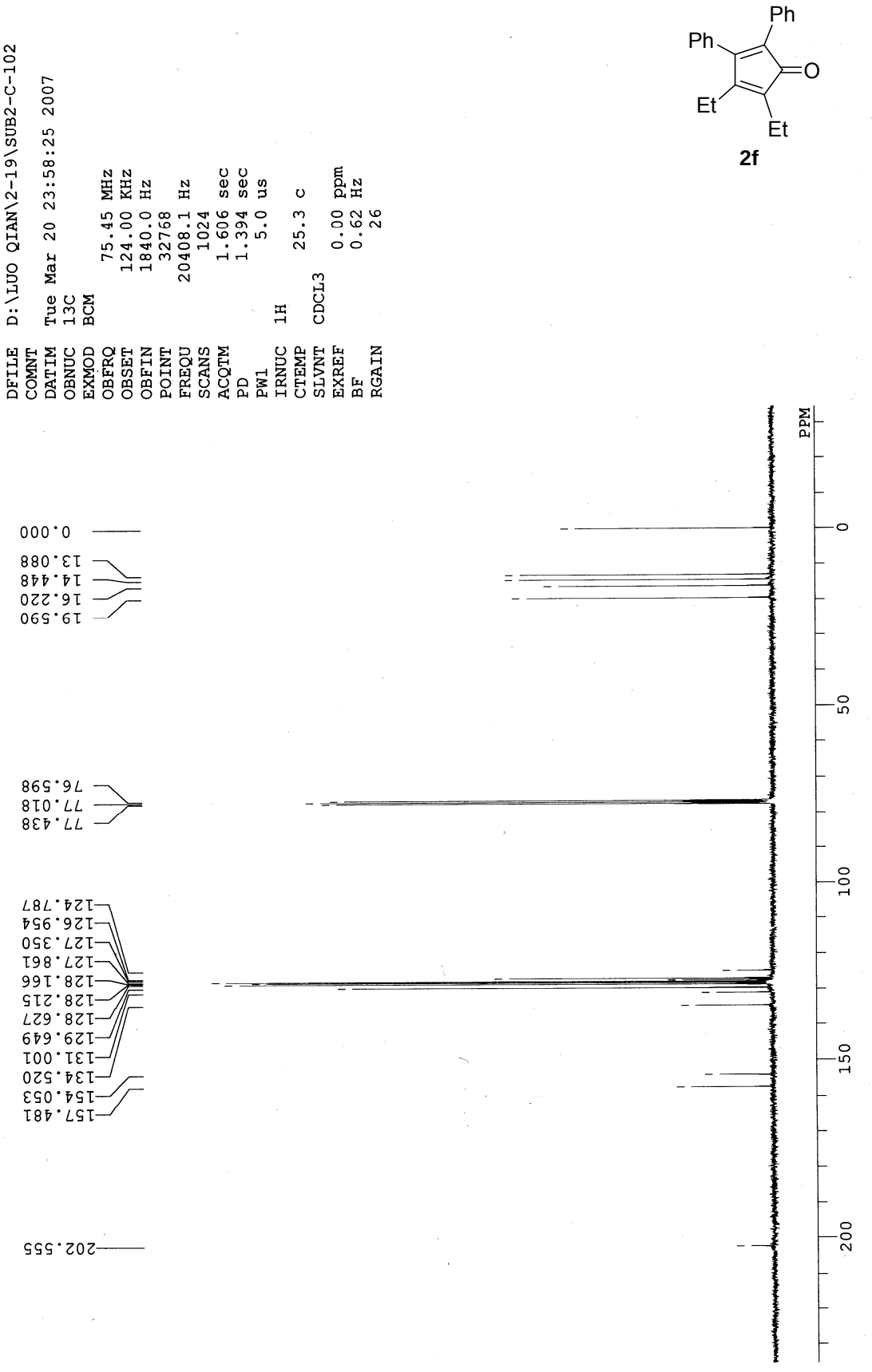
7.387
PPM
0
2
4
6
8
10

Ph
Ph
O
Et
Et

2f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O
Et
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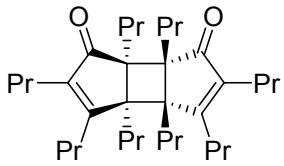
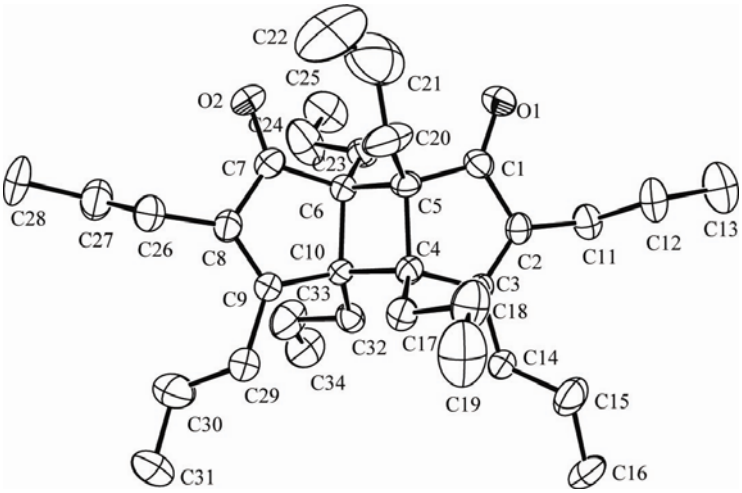
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 1024
ACQTM 1.606 sec
PD 1.394 sec
PW1 5.0 us
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 26
0.000
13.088
14.448
16.220
19.590
76.598
77.018
77.438
124.787
126.954
127.350
127.861
128.166
128.215
128.627
129.649
131.001
134.520
154.053
157.481
202.555
PPM
0
50
100
150
200

3. X-ray crystallographic studies of 3a and 3d: Crystals for X-ray analyses of **3a** and **3d** were obtained as described in the preparations. The crystals were sealed in thin-walled glass capillaries. Data collections were performed at 20 °C on a Rigaku RAXIS RAPID IP, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. These structures were solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-668730 (**3a**) and CCDC-668731. Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



3a

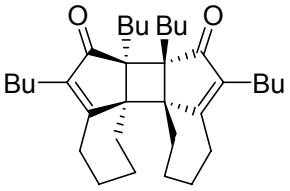


EFig. 1 ORTEP drawing of **3a** with 30% thermal ellipsoids.

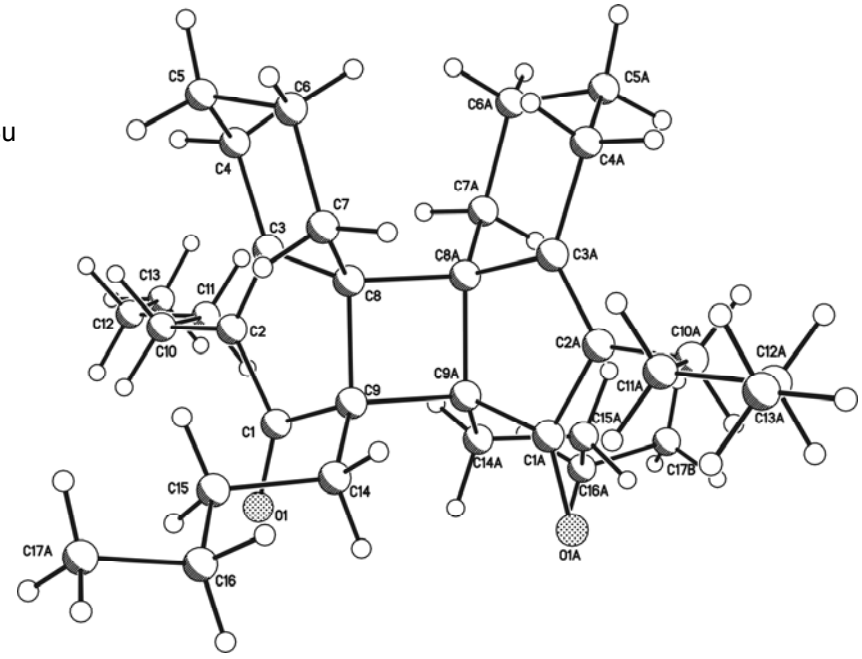
Table 1. Crystal data and structure refinement for **3a**.

Identification code	**3a**
CCDC number	668730
Empirical formula	$C_{34}H_{56}O_2$

Formula weight	496.79
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic,Aba2
Unit cell dimensions	a = 19.655(4) Å alpha = 90 °. b = 20.326(4) Å beta = 90 °. c = 16.036(3) Å gamma = 90 °.
Volume	6407(2) $Å^3$
Refls. No. for cell measurement	11916
Theta range for cell measurement	1.92 to 25.02 °.
Z, Calculated density	8,1.030 Mg/m^3
Absorption coefficient	0.061 mm^{-1}
F(000)	2208
Crystal shape / Crystal colour	block / colourless
Crystal size	0.45 x 0.20 x 0.18 mm
Theta range for data collection	1.92 to 25.02 °.
Limiting indices	$-23 \leqslant h \leqslant 23$, $-24 \leqslant k \leqslant 24$, $-19 \leqslant l \leqslant 19$
Reflections collected / unique	11916 / 2929 [$R_{(int)}$ = 0.0506]
Reflections with I>2sigma(I)	1209
Completeness to theta = 25.02 °	99.6 %
Decay correction (%)	0
Absorption correction	Empirical
Max. and min. transmission	0.989 and 0.973
Method for primary solution	direct
Method for secondary solution	difmap
Hydrogen addition / treatment	geom / constr
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2929 / 2 / 334
Goodness-of-fit on F^2	0.985
Final R indices [I>2sigma(I)]	R_1 = 0.0527, wR_2 = 0.1108
R indices (all data)	R_1 = 0.1280, wR_2 = 0.1210
Absolute structure parameter	-1(3)
Extinction coefficient	0.0044(2)
Largest diff. peak and hole	0.398 and -0.167 $e.A^{-3}$
Max. and mean shift/sigma	0.000 and 0.000
Measurement device	Rigaku RAXIS RAPID IP
Measurement method	\W
Program for data collection	Rapid-AUTO (Rigaku,2000)
Program for cell refinement	Rapid-AUTO
Program for data reduction	CrystalStructure (Rigaku/MSC,2000)
Program for structure solution	SHELXS-97,(Sheldrick,1997)
Program for structure refinement	SHELXL-97,(Sheldrick,1997)
Program for molecular graphics	Siemens SHELXTL V4.2,(Sheldrick,1990)
Program for publication material	SHELXL-97,(Sheldrick,1997)



3d



EFig. 2 ORTEP drawing of **3d** with 30% thermal ellipsoids (A = 1–x, y, 1/2–Z).

Table 5. Crystal data and structure refinement for **3d**.

Identification code	**3d**
CCDC number	668731
Empirical formula	$C_{34}H_{52}O$
Formula weight	492.76
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 22.715(5) Å alpha = 90 °. b = 8.6051(17) Å beta = 109.25(3) °. c = 16.731(3) Å gamma = 90 °.
Volume	3087.4(11) A^3
Refls. No. for cell measurement	7422
Theta range for cell measurement	2.55 to 25.03 °.
Z, Calculated density	4, 1.060 Mg/m^3
Absorption coefficient	0.063 mm^{-1}
F(000)	1088
Crystal shape / Crystal colour	block / colourless
Crystal size	0.35 x 0.30 x 0.12 mm
Theta range for data collection	2.55 to 25.03 °.
Limiting indices	0≤h≤26, 0≤k≤10, -19≤1≤18
Reflections collected / unique	7422 / 2700 [$R_{(int)}$ = 0.0461]
Reflections with I>2sigma(I)	923
Completeness to theta = 25.03 °	98.7 %

Decay correction (%)	0
Absorption correction	Empirical
Max. and min. transmission	0.992 and 0.978
Method for primary solution	direct
Method for secondary solution	difmap
Hydrogen addition / treatment	geom / constr
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2700 / 7 / 174
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R_1 = 0.0685, wR_2 = 0.1558
R indices (all data)	R_1 = 0.1758, wR_2 = 0.1757
Extinction coefficient	0.0024(4)
Largest diff. peak and hole	0.296 and -0.168 e.A^{-3}
Max. and mean shift/sigma	0.000 and 0.000
Measurement device	Rigaku RAXIS RAPID IP
Measurement method	\W
Program for data collection	Rapid-AUTO (Rigaku,2000)
Program for cell refinement	Rapid-AUTO
Program for data reduction	CrystalStructure (Rigaku/MSC,2000)
Program for structure solution	SHELXS-97,(Sheldrick,1997)
Program for structure refinement	SHELXL-97,(Sheldrick,1997)
Program for molecular graphics	Siemens SHELXTL V4.2,(Sheldrick,1990)
Program for publication material	SHELXL-97,(Sheldrick,1997)