Supporting Information

for

Complementarity of solution and solid state mechanochemical reaction conditions demonstrated by 1,2-debromination of tricyclic imides

Petar Štrbac and Davor Marjetić

*Beilstein J. Org. Chem.* 2022, 18, 746–753. doi:10.3762/bjoc.18.75

Details of experimental procedures and characterization data of selected compounds
1. General ............................................................... S1

2. Synthetic details .................................................. S2

3. NMR spectra ........................................................ S8

4. IR spectra ........................................................... S21

5. Table S1 ............................................................. S28

6. References .......................................................... S30

1. General

Chemicals and solvents were purchased from Sigma-Aldrich. Silvergal (dentistry silver copper amalgam, 70% Ag/Cu) was provided by Galenika. Kemika, Sigma Aldrich and VWR Chemicals supplied the solvents, which were used without further purification, unless otherwise stated. THF was dried over sodium/benzophenone.

All NMR spectra were recorded on Bruker Avance 300 MHz and Bruker Avance 600 MHz spectrometers in commercially available deuterated solvents. Chemical shifts (δ) are expressed in ppm according to tetramethylsilane (TMS) as internal standard, and coupling constants (J) are expressed in Hertz (Hz). The following abbreviations were used to denote multiplicity in 1H spectra: s-singlet; d-doublet; dd-doublet of doublets; t-triplet; m-multiplet; brs-broad signal. Infrared spectra (FTIR-ATR) were recorded using a Fourier transform infrared attenuated total reflection PerkinElmer UATR Two Spectrometer (from 400 cm⁻¹ to 4000 cm⁻¹).

Milling reactions were carried out in a Retsch MM400 vibrational mill (frequency 30 Hz), using stainless steel (SS) vials (10 mL) and one 12 mm SS ball.

Thin layer chromatography was performed on silica gel plates (silica gel 60 F254, Merck), whereas for column chromatography silica gel (Silica gel 60, 0.063-0.200 mm, Merck) was used. For each synthesis elution solvents and their ratio are specified.

High resolution mass spectra (HRMS) were recorded on a Waters Micromass Q-TOF micro and 4800 Plus Maldi TOF/TOF Analyser instrument.
2. Synthetic details

Preparation of \( N \)-methyl-2,3-dibromomaleimide (41)
A two-step literature procedure was followed.
Step 1) Preparation of 2,3-dibromomaleimide\(^1\)
Succinimide (17 g, 172 mmol) was heated on an oil bath to 140 °C in a two neck 250 mL round-bottom flask fitted with a magnetic stirrer and reflux condenser. Bromine (26.6 mL) was added dropwise over 2.5 h to the molten succinimide while stirring. The temperature was held at 140–150 °C. Reaction mixture was cooled and 50 mL of water used to transfer the solid content of the flask to a beaker where it was digested for 2 hours at 60 °C with stirring. The solid was filtered off, washed well with water and dried. After drying the product was isolated as colorless solid (26.51 g, 60%).
\(^1\)H NMR (DMSO-\(d_6\)) \( \delta \) 11.65 (s, 1H, NH)

FTIR-ATR \( \nu_{\text{max}}/\text{cm}^{-1} \): 3224, 1722 (C=O), 1581, 1030.

Step 2) Methylation of 2,3-dibromomaleimide\(^2\)
The 2,3-dibromomaleimide (26.0 g, 102 mmol), anhydrous potassium carbonate (16.0 g, 116 mmol) and dimethyl sulfide (10.5 mL, 111 mmol) were refluxed in acetone (130 mL) for two hours. The dark reaction mixture was poured into water (400 mL), left overnight and the product filtered off as buff colored crystals (12.1 g, 44%).
Spectral data are identical to literature.
\(^1\)H NMR (CDCl\(3\)) \( \delta \) 3.13 (s, 3H, CH\(_3\))

FTIR-ATR \( \nu_{\text{max}}/\text{cm}^{-1} \): 2496, 1708 (C=O), 1679, 1385, 995.

Preparation of cycloadduct 10
The literature procedure was followed. A solution of \( N \)-methyl-2,3-dibromomaleimide (4.0 g, 14.9 mmol) in furan (8 mL) was heated at 70 °C over weekend in a sealed high pressure tube. After cooling solvent was removed in vacuum and solid was recrystallized from ethyl acetate to afford pure product as colorless solid (1.69 g, 34%).
Adduct 10 spectral data are identical to literature.\(^3\)
\(^1\)H NMR (CDCl\(3\)) \( \delta \) 6.69 (t, \( J=1.1 \) Hz, 2H, C=CH), 5.34 (t, \( J=1.1 \) Hz, oxa-bridge), 3.09 (s, 3H, NMe)

FTIR-ATR \( \nu_{\text{max}}/\text{cm}^{-1} \): 3095, 1705 (C=O), 1428, 1380, 885.

Preparation of 2,3-dicarboxymethoxy anthracene (36)
The literature procedure was followed. To a solution of 2,3-anthracene dicarboxylic acid (3.72 g, 14 mmol) in methanol (150 mL) conc. sulfuric acid (3.5 mL) was added and stirred at reflux for 5 days. The mixture was then cooled to 0 °C, the solid was filtered, air dried and then
dissolved in mixture of water (80 mL) and CH$_2$Cl$_2$ (120 mL) with stirring. Separated CH$_2$Cl$_2$
layer was washed with 5% NaHCO$_3$ (20 mL), water (2 × 80 mL), dried over MgSO$_4$ and
evaporated under vacuum to afford the pure product as yellow solid (0.850 g, 21%).
Anthracene 36 spectral data are identical to literature.$^4$
$^1$H NMR (CDCl$_3$) δ 8.49 (s, 2H, Ar), 8.43 (s, 2H, Ar), 8.04 (dd, $J$=6.4, 3.2 Hz, 2H, Ar), 7.56
(dd, $J$=6.4, 3.2 Hz, 2H, Ar), 3.98 (s, 6H, Me).
FTIR-ATR $\nu_{\text{max}}$/cm$^{-1}$: 2958, 1712 (C=O), 1294, 1228, 1048.

Adduct 42
A mixture of anthracene (100 mg, 0.56 mmol) and N-methyldibromomaleimide (60 mg, 0.22
mmol) was heated in round bottomed flask attached to glass tube in pyrolysis furnace at 250 °C
for 15 min. After cooling, excess anthracene was removed by sublimation in high vacuo to
afford the product as colourless solid (100 mg, 98%).
$^1$H NMR (CDCl$_3$) δ 7.47 (dd, $J$=5.5, 3.5 Hz, 2H, Ar), 7.31 (dd, $J$=5.5, 3.5 Hz, 2H, Ar), 7.27
(dd, $J$=5.5, 3.5 Hz, 2H, Ar), 7.17 (dd, $J$=5.5, 3.5 Hz, 2H, Ar), 4.95 (s, 2H bridge-[2.2.2]), 2.59
(s, 3H, NMe).
$^{13}$C NMR (CDCl$_3$) δ 171.6 (C=O), 137.6, 137.1, 128.2, 127.5, 126.8, 125.7, 66.1, 54.9, 25.8
(CH$_3$).
FTIR-ATR $\nu_{\text{max}}$/cm$^{-1}$: 2962, 1713 (C=O), 1016, 766.
HRMS-MALDI found: [M+H]$^+$: 445.9382. calculated for C$_{19}$H$_{13}$N$_1$O$_2$Br$_2$ 444.9313, [M+H]$^+$: 445.9391.

Preparation of the Zn/Ag couple

Zinc dust (150 mg) was activated with 10% hydrochloric acid (0.70 mL), washed successively
with acetone (2 × 1 mL) and diethyl ether (1 mL). A suspension of silver acetate (5 mg) in
boiling acetic acid (0.70 mL) was then added, and the mixture stirred for 1 minute. The
supernatant liquid was decanted and the zinc was washed with diethyl ether (4 × 1 mL) and
then with methanol (1 mL).

General ball-milling procedure with Zn/Cu couple

Dibromide 10 (50 mg, 0.15 mmol), diene (5 equiv., excess), zinc dust (75 mg, 1.15 mmol, 7.7
equiv., excess), copper dust (15 mg 0.24 mmol, 1.6 equiv, excess) and THF ($\eta$ = 0.33 or 0.66
µL mg$^{-1}$) were ball milled at 30 Hz for set time. Reaction mixture was then dissolved in a small
volume of dichloromethane, and the solution was filtered through a short plug of Celite. The
products were separated by radial chromatography and details are described for each product.
Adduct 14
Purified by radial chromatography, elution solvent 10% ethyl acetate in petroleum ether. Colorless solid, isolated yield 42%.
$^1$H NMR (CDCl$_3$) $\delta$ 7.31 (dd, $J$=5.4, 3.5 Hz, 2H, Ar), 7.23 (dd, $J$=5.4, 3.5 Hz, 2H, Ar), 7.17 (dd, $J$=5.4, 3.5 Hz, 2H, Ar), 7.04 (dd, $J$=5.4, 3.5 Hz, 2H, Ar), 6.42 (s, 2H, C=CH), 4.80 (s, 2H, bridge-oxa), 4.74 (s, 2H, bridge [2.2.2]), 2.35 (s, 3H, NMe);
$^{13}$C NMR (CDCl$_3$) $\delta$ 176.7 (C=O), 141.2, 139.9, 137.9, 126.9, 126.8, 124.9, 124.4, 81.6 (oxa bridge), 65.5, 48.1 (bridge [2.2.2]), 24.0 (NMe),
FTIR-ATR $\nu$max/cm$^{-1}$: 2198, 1694 (C=O), 1289, 1015.
HRMS-MALDI found: [M+H]$^+$: 356.1290, calculated for C$_{23}$H$_{17}$N$_1$O$_3$ 355.1208, [M+H]$^+$: 356.1287.

Product 15
Spectral data obtained from crude spectra, are in accordance to literature
$^1$H NMR (CDCl$_3$) $\delta$ 6.37 (t, $J$=1.1 Hz, 2H, C=CH), 5.29-5.32 (m, 2H, oxa-bridge), 3.50 (dd, $J$=3.5, 1.6 Hz, 2H, exo-H), 2.79 (s, 3H, NMe).

N-methylphthalimide 16
NMR Spectral data are in accordance to literature
$^1$H NMR (CDCl$_3$) $\delta$ 7.81 (dd, $J$=5.5, 3.0 Hz, 2H, ArH), 7.67 (dd, $J$=5.5, 3.0 Hz, 2H, ArH), 3.15 (s, 3H, NMe).
FTIR-ATR $\nu$max/cm$^{-1}$: 2924, 1706 (C=O), 1431, 1378, 1006.

Product 17
Spectral data obtained from crude spectra, are in accordance to literature
$^1$H NMR (CDCl$_3$) $\delta$ 6.48 (t, $J$=1.1 Hz, 2H, C=CH), 5.25 (t, $J$=1.1 Hz, 2H, oxa-bridge), 2.96 (s, 3H, NMe), 2.84 (s, 2H, endo-H).

Adducts 19 and 20
Purified by preparative TLC, elution solvent dichloromethane / 1% methanol, then polarity increased to 2% to afford a mixture of 19 and 20 as colorless solid (8% yield).
Spectral data obtained from mixture of two isomers are in accordance to literature
Adduct 19: $^1$H NMR (CDCl$_3$) $\delta$ 6.56 (t, $J$=1.1 Hz, 4H, C=CH), 5.21 (t, $J$=1.1 Hz, 4H, oxa bridge), 2.67 (s, $J$=8.7, 3H, CH$_3$)
Adduct 20: $^1$H NMR (CDCl$_3$) $\delta$ 6.52 (t, $J=0.9$ Hz, 2H, =CH), 6.49 (t, $J=0.9$ Hz, 2H, C=CH), 5.12 (t, $J=0.9$ Hz, 2H, oxa bridge), 4.72 (t, $J=0.9$ Hz, 2H, oxa bridge), 2.84 (s, $J=8.7$, 3H, CH$_3$)

Adducts 22 and 23
Purified by preparative TLC, elution solvent dichloromethane – 1% methanol, then the polar solvent was increased to 2%.
Adduct 22 colorless solid, (yield 14%).
$^1$H NMR spectral data are in accordance to literature.
$^1$H NMR (CDCl$_3$) $\delta$ 6.54 (t, $J=0.9$ Hz, 2H, C=CH oxa side), 6.31 (t, $J=1.5$ Hz, 2H, C=CH CH$_2$ side), 5.06 (t, $J=0.7$ Hz, 2H, bridge-oxa), 3.54 (nm, 2H, bridge CH$_2$), 3.06 (td, $J=8.9$, 1.2 Hz, 1H, CH$_2$), 2.69 (s, 3H, NMe), 1.69 (td, $J=8.9$, 1.2 Hz, 1H, CH$_2$).
$^{13}$C NMR (CDCl$_3$) $\delta$ 177.2 (C=O), 140.4, 138.9, 81.5 (oxa-bridge), 79.6, 68.8, 49.5, 46.1, 24.2 (CH$_3$).
FTIR-ATR $\nu$max/cm$^{-1}$: 2954, 1689 (C=O), 1427, 1285, 1018.
HRMS-MALDI found: [M+H]$^+$: 244.0982, calculated for C$_{14}$H$_{13}$N$_1$O$_2$: 243.0895 [M+H]$^+$: 244.0974.
Adduct 23 colorless solid (yield 4.5%).
$^1$H NMR (CDCl$_3$) $\delta$ 6.18 (t, $J=1.3$ Hz, 2H, C=CH), 5.97 (t, $J=1.5$ Hz, 2H, C=CH), 4.34 (s, 2H, bridge-oxa), 3.17 (t, 2H, $J=1.2$ Hz, bridge CH$_2$), 2.88 (brs, 2H, bridge CH$_2$), 2.87 (d, $J=8.4$ Hz, 1H, CH$_2$), 2.81 (s, 3H, NMe), 2.35 (dd, $J=2.5$, 1.4 Hz, 2H, endo), 1.39 (td, $J=10.1$, 1.2 Hz, 1H, CH$_2$), 1.33 (td, $J=8.2$, 1.2 Hz, 1H, CH$_2$), 1.12 (d, $J=8.4$ Hz, 1H, CH$_2$).
FTIR-ATR $\nu$max/cm$^{-1}$: 2963, 1695 (C=O), 1284, 1021.

Adducts 25 and 26
Products were purified by radial chromatography, elution solvent 1% methanol in dichloromethane.
Adduct 25 colorless solid (yield 14 %) $^1$H NMR (CDCl$_3$) $\delta$ 8.15 (dd, $J=8.0$, 1.2 Hz, 4H, Ar), 7.59 (t, $J=7.4$ Hz, 4H, Ar), 7.49 (tt, $J=7.4$, 1.1 Hz, 2H, Ar), 7.12 (dd, $J=5.5$, 3.3 Hz, 2H, Ar), 7.07 (dd, $J=5.5$, 3.3 Hz, 2H, Ar), 6.55 (t, $J=0.7$ Hz, 2H, C=CH), 5.04 (t, $J=0.7$ Hz, 2H, bridge-oxa), 2.33 (s, 3H, NMe).
$^{13}$C NMR (CDCl$_3$) $\delta$ 196.1 (C=O), 139.5, 136.7, 132.5, 129.7, 129.3, 129.2, 127.8, 122.7, 80.6, (oxa-bridge), 76.2 (oxa-bridge), 56.2, 50.1 (CH$_3$).
FTIR-ATR $\nu$max/cm$^{-1}$: 2918, 1693 (C=O), 1289, 635.
HRMS-MALDI found: [M+Na]$^+$ 470.1396, calculated for C$_{29}$H$_{21}$N$_1$O$_4$: 447.1471. [M+H]$^+$: 448.1549, [M+Na]$^+$: 470.1368.
Adduct 26
Obtained from crude spectra:
$^1$H NMR (CDCl$_3$) $\delta$ 8.20-6.94 (m, ArH overlap with impurities), 4.46 (s, 2H, bridge-oxa), 2.64 (s, 2H, endo), 2.31 (s, 3H, NMe).

1,2-dibenzoylbenzene 27

Colorless solid, spectral data are in accordance to literature.

$^1$H NMR (CDCl$_3$) $\delta$ 7.69-7.71 (m, 4H, Ar), 7.61-7.62 (m, 4H, ArH), 7.49-7.53 (m, 2H, ArH), 7.36-7.39 (m, 4H, ArH).

$^{13}$C NMR (CDCl$_3$) $\delta$ 196.1 (C=O), 139.5, 136.7, 132.5, 129.9, 129.3, 129.2, 127.8.

Adduct 33

Purified by preparative TLC, elution solvent dichloromethane. Colorless solid (yield 35%).

$^1$H NMR (CDCl$_3$) $\delta$ 7.62 (dd, $J$=5.7, 3.3 Hz, 2H, Ar), 7.41 (dd, $J$=5.5, 3.3 Hz, 2H, Ar), 7.27 (dd, $J$=5.7, 3.3 Hz, 2H, Ar), 7.17 (dd, $J$=5.5, 3.3 Hz, 2H, Ar), 6.45 (t, $J$=0.9 Hz, 2H, C=CH), 5.12 (t, $J$=0.9 Hz, 2H, bridge-oxa), 4.24 (brs, 2H, OH), 2.37 (s, 3H, NMe).

$^{13}$C NMR (CDCl$_3$) $\delta$ 177.2 (C=O), 141.8, 138.4, 137.9, 127.0, 126.9, 120.3, 79.4 (oxa-bridge), 77.0, 68.4, 24.2 (CH$_3$).

FTIR-ATR $\nu_{\text{max}}$/cm$^{-1}$: 2918, 1660 (C=O), 1447, 1272.

HRMS-MALDI found: 387.0318, calculated for C$_{23}$H$_{17}$N$_1$O$_3$ 387.1107 [M+H]$^+$: 388.1185.

Adduct 35

Purified by preparative TLC, elution solvent dichloromethane. Colorless solid (yield 24%).

$^1$H NMR (CDCl$_3$) $\delta$ 7.05-7.32 (m, 8H, Ar), 6.44 (d, $J$=5.6 Hz, 1H, C=CH), 6.42 (d, $J$=5.6 Hz, 1H, C=CH), 5.09 (s, 1H, bridge-oxa), 4.83 (s, 1H, bridge-oxa), 4.69 (s, 1H, bridge [2.2.2]), 4.37 (brs, 1H, OH), 2.36 (s, 3H, NMe).

$^{13}$C NMR (CDCl$_3$) $\delta$ 177.6 (C=O), 176.3 (C=O), 143.3, 140.4, 139.5, 137.9, 137.8, 137.7, 127.0, 126.96, 126.91, 126.87, 124.5, 123.8, 120.9, 120.7, 81.7 (oxa-bridge), 79.2 (oxa-bridge), 78.4 (q-OH), 66.8 (q), 66.6 (q), 46.9 (bridge [2.2.2]), 24.1 (CH$_3$).

FTIR-ATR $\nu_{\text{max}}$/cm$^{-1}$: 3375, 2918, 1682 (C=O), 1018.

HRMS-MALDI found: [M+H]$^+$: 372.1240, calculated for C$_{23}$H$_{17}$N$_1$O$_4$ 371.1157 [M+H]$^+$: 372.1236.

Adducts 37 and 38
Purified by radial chromatography, elution solvent 1% methanol in dichloromethane. Colorless solid, mixture 1:1.3 (yield 32%). Spectral data were obtained from the mixture of two isomeric adducts.

Adduct 37

$^1$H NMR (CDCl$_3$) δ 7.59 (s, 2H, Ar), 7.30 (dd, $J$=5.5, 3.3 Hz, 2H, Ar), 7.17 (dd, $J$=5.5, 3.3 Hz, 2H, Ar), 6.42 (s, 2H, C=CH), 4.81 (s, 4H, bridge-oxa, bridge [2.2.2]), 3.84 (s, 6H, CO$_2$Me), 2.42 (s, 3H, NMe).

Adduct 38

$^1$H NMR (CDCl$_3$) δ 7.67 (s, 2H, Ar), 7.21 (dd, $J$=5.5, 3.3 Hz, 2H, Ar), 7.06 (dd, $J$=5.5, 3.3 Hz, 2H, Ar), 6.41 (s, 2H, C=CH), 4.83 (s, 2H, bridge-oxa), 4.81 (s, 2H, bridge [2.2.2]), 3.86 (s, 6H, CO$_2$Me), 2.36 (s, 3H, NMe). HRMS-MALDI found: [M+H]$^+$: 472.1404, calculated for C$_{27}$H$_{21}$N$_1$O$_7$: 471.1318 [M+H]$^+$: 472.1396.

Adduct 45

Spectral data obtained from crude spectra:

$^1$H NMR (CDCl$_3$) δ 7.47 (dd, $J$=5.5, 3.5 Hz, 2H, Ar), 7.31 (dd, $J$=5.5, 3.5 Hz, 2H, Ar), 7.27 (dd, $J$=5.5, 3.5 Hz, 2H, Ar), 7.17 (dd, $J$=5.5, 3.5 Hz, 2H, Ar), 4.95 (s, 2H bridge-[2.2.2]), 2.59 (s, 3H, NMe).

Adduct 46

Purified by preparative TLC, elution solvent dichloromethane. Colorless solid (yield 77%).

$^1$H NMR (CDCl$_3$) δ 7.89 (brs, 4H, Ar), 7.47-7.59 (m, 6H, Ar), 7.16 (dd, $J$=5.4, 3.1 Hz, 2H, Ar), 7.03 (brs, 4H, Ar), 6.97 (dd, $J$=5.4, 3.1 Hz, 2H, Ar), 6.90 (dd, $J$=5.1, 3.1 Hz, 2H, Ar), 6.32 (dd, $J$=5.4, 3.1 Hz, 2H, Ar), 4.64 (s, 2H bridge-[2.2.2]), 1.96 (s, 3H, NMe).

$^{13}$C NMR (CDCl$_3$) δ 176.3 (C=O), 139.3, 134.3, 127.6, 127.1, 126.6, 125.7, 124.9, 120.3, 90.2 (oxa bridge), 70.2 (bridge-[2.2.2]), 47.3, 23.8 (CH$_3$).

FTIR-ATR $\nu_{\text{max}}$/cm$^{-1}$: 3023, 1698 (C=O), 1298, 703.

HRMS-MALDI found: 381.1365 [M-anthracene+H]$^+$: calculated for C$_{39}$H$_{27}$N$_1$O$_3$ 557.1991 [M+H]$^+$: 558.2069, [M-anthracene+H$_2$]$^+$: 381.1315.
3. NMR spectra

S1. $^1$H NMR (300 MHz, CDCl$_3$) of 2,3-dibromomaleimide.

S2. $^1$H NMR (300 MHz, CDCl$_3$) of $N$-methyl-dibromomaleimide 41.
S3. $^1$H NMR (300 MHz, CDCl$_3$) of cycloadduct 10.

S4. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of anthracene 35.
S5. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of 42.

S6. APT $^{13}$C NMR (300 MHz, CDCl$_3$) spectrum of 42.
S7. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of anthracene 14.

S8. $^{13}$C NMR (300 MHz, CDCl$_3$) spectrum of anthracene 14.
S9. $^1$H NMR (300 MHz, CDCl$_3$) of methylphthalimide 16.

S10. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of adduct 22.
S11. $^{13}$C NMR (300 MHz, CDCl$_3$) spectrum of adduct 22.

S12. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of adduct 23.
S13. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of adduct 25.

S14. APT $^{13}$C NMR (300 MHz, CDCl$_3$) spectrum of adduct 25.
S15. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of crude adduct 26.

S16. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of 1,2-dibenzoylbenzene 27.
S17. APT $^{13}$C NMR (300 MHz, CDCl$_3$) spectrum of 1,2-dibenzoylbenzene 27.

S18. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of 33.
S19. $^{13}$C NMR (300 MHz, CDCl$_3$) spectrum of 33.

S20. APT $^{13}$C NMR (300 MHz, CDCl$_3$) spectrum of 33.
S21. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of 35.

S22. $^{13}$C NMR (300 MHz, CDCl$_3$) spectrum of 35.
S23. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of adducts 37 (■) and 38 (●).

S24. $^1$H NMR (300 MHz, CDCl$_3$) spectrum of 46.
S25. $^{13}$C NMR (300 MHz, CDCl$_3$) spectrum of 46.
4. IR spectra

**S-IR-1.** IR-ATR spectrum of 2,3-dibromomaleimide.

**S-IR-2.** IR-ATR spectrum of N-methyl-2,3-dibromomaleimide.
S-IR-3. IR-ATR spectrum of cycloadduct 10.

S-IR-4. IR-ATR spectrum of anthracene 36.
S-IR-5. IR-ATR spectrum of \( N \)-methylphthalimide 16.

\[
\text{\emph{NMe}}
\]

S-IR-6. IR-ATR spectrum of 42.
S-IR-47 IR-ATR spectrum of 14.

S-IR-8. IR-ATR spectrum of adduct 22.
S-IR-9. IR-ATR spectrum of adduct 23.

S-IR-10. IR-ATR spectrum of 25.
S-IR-11. IR-ATR spectrum of 33.

S-IR-12. IR-ATR spectrum of 35.
S-IR-13. IR-ATR spectrum of 37 and 38.

S-IR-14. IR-ATR spectrum of 46.
Table S1. Optimization of mechanochemical Zn/Ag debromination of dibromide 10

| Entry | Reducing agent / catalyst | Conditions ² | Time/h | Conversion /% | Yield /% | Ratio 10:14:15:16:17 |
|-------|---------------------------|--------------|-------|---------------|---------|----------------------|
| 1     | Zn/Ag couple              | Ball-mill    | 0.5   | 81            | 2       | 78                   | 1                         | 1:0.11:4.2:0.07 |
| 2     | Zn/Ag couple              | NaCl         | 0.5   | quant         | 8       | 8                    | 81                        | 0.0:1:0.1:1:0.3 |
| 3     | Zn/Ag couple              | LAG THF \(\eta=1\) | 0.5   | quant         | 58      | 4                    | 29                        | 9:0.1:0.07:0.5:0.15 |
| 4     | Zn/Ag couple              | LAG THF \(\eta=1, \text{NaCl}\) | 0.5   | 96            | 33      | 13                   | 42                        | 8:0.1:0.8:0.3:1:0.2 |
| 5     | Zn dust, Ag wire          |              | 0.5   |               |         |                      | NR                       |                          |
| 6     | Zn dust, Ag wire          | LAG THF \(\eta=1\) | 0.5   | 33            | 27      | 3                    | 3                         | 1:0.4:0.05:0.05 |
| 7     | Zn dust, Ag wire          | LAG MeOH \(\eta=1\) | 1     | quant         | 64      | 9                    | 27                        | 0:0.7:0:1:0.3 |
| 8     | Zn dust, Ag wire          | LAG ACN \(\eta=1\) | 1     | 88            | 63      | 13                   | 13                        | 0.2:1:0.2:0.2 |
| 9     | Zn activated, Ag wire     | LAG THF \(\eta=1, \text{NaCl}\) | 0.5   | quant         | 56      | 8                    | 28                        | 8:0:1.05:0.5:0.15 |
| 10    | Zn dust, Silvergal        |              | 0.5   |               |         |                      | NR                       |                          |
| 11    | Zn dust, Silvergal        | LAG THF \(\eta=1\) | 1     | 50            | 40      | 5                    | 5                         | 1:0.8:0.1:0.1 |
| 12    | Zn activated              |              | 0.5   |               |         |                      | NR                       |                          |
| 13    | Zn dust                   |              | 0.5   |               |         |                      | NR                       |                          |
| 14    | Zn dust                   | LAG THF \(\eta=1\) | 0.5   | 12            | 4       | 3                    | 4                         | 1:0.05:0.03:0.05 |
| 15    | Zn dust, Cu dust          | LAG THF \(\eta=1\) | 0.5   | 55            | 50      | 10                   | 5                         | 7:1:0:2:0:1 |
| 16    | Zn dust, Cu dust          | LAG THF \(\eta=1\) | 0.75  | 97            | 64      | 13                   | 19                        | 1:0.05:1:0.2:0:3:0:02 |
| 17    | Zn dust, Cu dust          | LAG THF \(\eta=1, \text{ZnBr}_2\) | 1     | quant         | 67      | 13                   | 20                        | 0:1:0.2:0:3:0 |
| 18    | Zn dust, Cu dust          | LAG THF \(\eta=0.5\) | 1     | 66            | 48      | 6                    | 10                        | 2:0.7:1:0.2:0:13:0:05 |
| 19    | Zn dust, Cu dust          | LAG THF \(\eta=0.5\) | 2     | quant         | 76      | 8                    | 15                        | 0:1:0:11:0.2:0 |

Without anthracene DEBROMINATION
|   | Zn dust, Ag wire | LAG THF $\eta=1$ | 0.5 | 43 | 29 | 11 | 3 | 1:x:0.5:0.2:0.05+unsym prods |
|---|-----------------|-----------------|-----|----|----|----|---|-----------------------------|
|   | Zn dust, Ag wire | LAG THF $\eta=1$ | 1   | 55 | 45 | 5  | 5 | 1:x:1:0.11:0.1+unsym prods  |
|   | Zn dust, Ag wire | LAG MeOH $\eta=1$ | 0.5 | 95.5 | 2 | 75 | 19 | 0.06:x:0.03:1:0.25+unsym prods |

### SOLUTION

|   | Zn/Ag couple | dry THF, Ar | 1 | quant | 86 | 9 | 5 | 0:1:0:1:0.06 |
|---|-------------|-------------|---|--------|----|---|---|----------------|
| 20| Zn dust, Cu dust | dry THF | 1 |        |    |   |   | NR             |
| 21| Zn dust, Cu dust | dry THF, ultrasound | 1.5 |        |    |   |   | NR             |

50 mg dibromide; 132 mg anthracene (5 eq.); 75 mg reducing agent / catalyst; Silvergal = Ag/Cu powder 70% Ag

a) HSVM 30 Hz; LAG THF in $\eta = \mu L mg^{-1}$, b) 32 mg anthracene (1.2 eq.)
5. References

1. Schmidt, E. K. G. Chem. Ber, 1974, 107, 2440-2452; Ciumician, G. L.; Silber, P. Chem. Ber, 1884, 17, 553-559. 2,3-dibromomaleimide
2. Scharf, K. Chem. Ber. 1965, 98, 764-780. N methyl-2,3-dibromomaleimide
3. Warrener, R. N.; Maksimovic, Lj. Tetrahedron Lett. 1994, 35, 2389-2392.
4. Lohier, J.-F.; Wright, K.; Peggion, C.; Formaggio, F.; Toniolo, C.; Wakselman, M.; Mazaleyrat, J.-P. Tetrahedron 2006, 62, 6203-6213. anthracene 2,3-diester
5. Clark, R. D.; Heathcock, C. H. J. Org Chem. 1976, 41, 636-643. Zn/Ag couple preparation
6. Roux, M. V.; Jiménez, P.; Martín-Luengo, M. A.; Dávalos, J. Z.; Sun, Z.; Hosmane, R. S.; Liebman, J. F. J. Org. Chem. 1997, 62, 2732-2737. NMe phthalimide
7. Warrener, R. N.; Elsey, G. M.; Maksimovic, Lj.; Johnston, M. R. Tetrahedron Lett. 1995, 36, 7753-7756. only chemical shift for NMe signal is reported
8. Yang, L.; Wang, J.; Wang, Y.; Li, X.; Liu, W.; Zhang, Z.; Xie, X. J. Org. Chem. 2021, 86, 14311-14320.