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Halogen bonded dimers and ribbons from the self-assembly of 3-halobenzophenones

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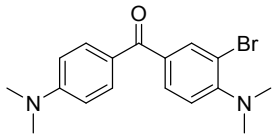
Synthesis

General

Melting points were determined on a BUCHI Melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 or 500 [300.13 MHz (^{1}H), 75.47 MHz (^{13}C) or 500.13 MHz (^{1}H), 125.77 MHz (^{13}C)] spectrometers with TMS as internal reference. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity [s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet)], and coupling constant (*J*, Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift (*δ*, ppm). Unequivocal ^{1}H assignments were made with aid of 2D COSY ($^{1}H/^{1}H$), while ^{13}C assignments were made on the basis of 2D HSQC ($^{1}H/^{13}C$) and HMBC experiments. Elemental analyses were obtained with a Carlo Erba 1108 CHNS analyzer. High resolution mass spectra analysis (HRMS-ESI) were performed on a microTOF (focus) mass spectrometer (Bruker Daltonics, Bremen, Germany). Ions were generated using an Apollo II (ESI) source. Ionization was achieved by electrospray, using a voltage of 4500 V applied to the needle, and a counter voltage between 100 and 150 V applied to the capillary. Silica gel 60 F254 (Merck) was used for TLC, and the spots were detected with UV light (254 nm). Flash column chromatography was carried out on silica gel 60 (Merck).

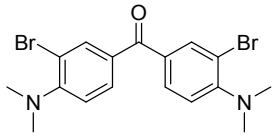
3-Bromo-4,4'-di(dimethylamino)benzophenone ***1***



N-Bromosuccinimide (356 mg, 2.0 mmol, 1 equiv) was slowly added to a solution of Michler's ketone (540 mg, 2.0 mmol, 1 equiv) in dichloromethane (10 mL). After stirring at room temperature for 12 h, water (10 mL) was added, and the aqueous phase was extracted with dichloromethane (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Silica gel flash column chromatography (eluent: dichloromethane) of the residue gave the compound as a pale yellow solid (400 mg, 1.15 mmol, 58% yield). Slow evaporation of a dichloromethane solution of the compound afforded pale yellow crystals suitable for XRD.

Melting point: 111-113ºC. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 ºC): δ 7.97 (d, $^{4}J_{H-H}$ 2.1 Hz, 1H, aromatic C*H*), 7.77 (d, $^{3}J_{H-H}$ 9.0 Hz, 2H, aromatic C*H*), 7.67 (dd, $^{4}J_{H-H}$ 2.1, $^{3}J_{H-H}$ 8.4 Hz, 1H, aromatic C*H*), 7.10 (d, $^{3}J_{H-H}$ 8.4 Hz, 1H, aromatic C*H*), 6.70 (d, $^{3}J_{H-H}$ 9.0 Hz, 2H, aromatic C*H*), 3.08 (s, 6H, CH_3), 2.91 (s, 6H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$, 25ºC): δ 192.6 (*C*=O), 154.1, 153.0, 135.6, 134.0, 132.4, 129.8, 124.7, 119.2, 117.0, 110.6, 43.7, 40.0; ESI^{+}-MS: m/z: 347 $[M]^{+}$ ($C_{17}H_{19}{}^{79}BrON_2$), 349 $[M]^{+}$ ($C_{17}H_{19}{}^{81}BrON_2$). Anal. Calcd for $C_{17}H_{19}BrN_2O$: C, 58.80; H, 5.52; N, 8.07. Found: C, 59.21; H, 5.73; N, 7.76%.

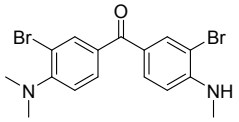
3,3'-Dibromo-4,4'-di(dimethylamino)benzophenone ***2***



N-Bromosuccinimide (266 mg, 1.5 mmol, 2 equiv) was slowly added to a solution of Michler's ketone (200 mg, 0.75 mmol, 1 equiv) in dichloromethane (10 mL). After stirring at room temperature for 12 h, water (10 mL) was added, and the aqueous phase was extracted with dichloromethane (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Silica gel flash column chromatography (eluent: dichloromethane) of the residue gave the compound as a pale yellow solid (264 mg, 0.62 mmol, 83% yield). Slow evaporation of a dichloromethane solution of the compound afforded pale yellow crystals suitable for XRD.

Melting point: 128-130ºC. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 ºC): δ 8.00 (d, $^{4}J_{H-H}$ 2.1 Hz, 2H, aromatic C*H*), 7.68 (dd, $^{4}J_{H-H}$ 2.1, $^{3}J_{H-H}$ 8.4 Hz, 2H, aromatic C*H*), 7.06 (d, $^{3}J_{H-H}$ 8.4 Hz, 2H, aromatic C*H*), 2.93 (s, 12H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$, 25ºC): δ = 191.9 (*C*=O), 155.3, 136.1, 132.0, 130.2, 119.0, 116.8, 43.6; ESI^{+}-MS: m/z: 425 $[M+H]^{+}$ ($C_{17}H_{18}{}^{79}Br_2N_2O$), 427 $[M+H]^{+}$ ($C_{17}H_{18}{}^{79}Br^{81}BrN_2O$), 429 $[M+H]^{+}$ ($C_{17}H_{18}{}^{81}Br_2N_2O$). Anal. Calcd for $C_{17}H_{18}Br_2N_2O$: C, 47.91; H, 4.26; N, 6.57. Found: C, 47.13; H, 4.27; N, 6.21%.

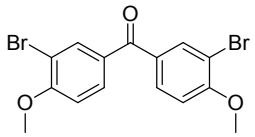
*[3-Bromo-4-(dimethylamino)phenyl][3-bromo-4-(methylamino)phenyl]methanone **3***



Bromine (6 equiv, 6 mmol, 309 µL) was slowly added to Michler's ketone (1 equiv, 1 mmol, 268 mg) in a round bottom flask under nitrogen at room temperature. After stirring at room temperature for 20 min, ethanol (10 mL) was added at 0ºC and the solution was stirred at room temperature for 10 min. Saturated aqueous sodium thiosulfate (10 mL) was added slowly at 0ºC, and the solid that formed was extracted with dichloromethane (3 x 10 mL), the organic phases were dried over sodium sulfate, filtered, and evaporated to dryness. Thin layer chromatography (eluent: hexane/dichloromethane, 1/1) of the residue gave compound **3** as a yellow solid (8 mg, 0.019 mmol, 2 % yield). Slow evaporation of a dichloromethane solution of the compounds afforded pale yellow crystals suitable for XRD.

^{1}H NMR (300.13 MHz, $CDCl_3$, 25 ºC): δ 7.98 (d, $^{4}J_{H\text{-}H}$ 2.0 Hz, 1H, aromatic C*H*), 7.97 (d, $^{4}J_{H\text{-}H}$ 2.0 Hz, 1H, aromatic C*H*), 7.71 (dd, $^{3}J_{H\text{-}H}$ 8.5, $^{4}J_{H\text{-}H}$ 2.0 Hz, 1H, aromatic C*H*), 7.65 (dd, $^{3}J_{H\text{-}H}$ 8.3, $^{4}J_{H\text{-}H}$ 2.0 Hz, 1H, aromatic C*H*), 7.07 (d, $^{3}J_{H\text{-}H}$ 8.3, 1H, aromatic C*H*), 6.62 (d, $^{3}J_{H\text{-}H}$ 8.5, 1H, aromatic C*H*), 2.98 (s, 3H, NHCH_3), 2.91 (s, 6H, N(CH_3)$_2$); The quantity was too low to record a ^{13}C NMR spectrum. ESI$^+$-MS: m/z: 411 $[M+H]^+$ ($C_{16}H_{17}{}^{79}Br_2N_2O$), 413 $[M+H]^+$ ($C_{16}H_{17}{}^{79}Br^{81}BrN_2O$), 415 $[M+H]^+$ ($C_{16}H_{17}{}^{81}Br_2N_2O$). ESI$^+$-HRMS: calculated for ($C_{16}H_{17}{}^{79}Br_2N_2O$): 410.97076, found: 410.96983, calculated for ($C_{16}H_{17}{}^{79}Br^{81}BrN_2O$): 412.96872, found: 412.96732, calculated for ($C_{16}H_{17}{}^{81}Br_2N_2O$): 414.96667, found: 414.96486. Melting point: The quantity was too low.

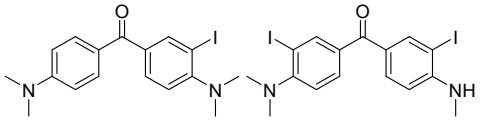
*3,3'-Dibromo-4,4'-dimethoxybenzophenone **5***



4,4'-Dimethoxybenzophenone (commercial by Aldrich) (1 equiv, 1 mmol, 242 mg) was set up in a round bottom flask under nitrogen at room temperature. Bromine (3 equiv, 3 mmol, 155 µL) was added slowly and the red slurry was stirred for 20 min. Ethanol (10 mL) was added slowly at 0ºC, and the resulting solution was stirred at room temperature for 10 min. Saturated aqueous sodium thiosulfate (10 mL) was added slowly at 0ºC, and the solid that formed was collected by filtration, washed with water and ethanol. The product was obtained as a white microcrystalline solid (300mg, 75% yield). Slow evaporation from dichloromethane gave crystals suitable for single crystal XRD.

Melting point: 112-114ºC. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 ºC): δ 8.02 (d, $^{4}J_{H\text{-}H}$ 2.1 Hz, 2H, aromatic C*H*), 7.74 (dd, $^{4}J_{H\text{-}H}$ 2.1, $^{3}J_{H\text{-}H}$ 8.5 Hz, 2H, aromatic C*H*), 6.97 (d, $^{3}J_{H\text{-}H}$ 8.5 Hz, 2H, aromatic C*H*), 3.99 (s, 6H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$, 25ºC): δ = 192.0 (*C*=O), 159.3, 135.3, 131.3, 113.8, 111.9, 111.1, 56.7; ESI$^+$-MS: m/z: 399 $[M+H]^+$ ($C_{15}H_{13}{}^{79}Br_2O_3$), 401 $[M+H]^+$ ($C_{15}H_{13}{}^{79}Br^{81}BrO_3$), 403 $[M+H]^+$ ($C_{15}H_{13}{}^{81}Br_2O_3$). ESI$^+$-HRMS: calculated for ($C_{15}H_{13}{}^{79}Br_2O_3$): 398.92313, found: 398.92246, calculated for ($C_{15}H_{13}{}^{79}Br^{81}BrO_3$): 400.92116, found: 400.91990, calculated for ($C_{15}H_{13}{}^{81}Br_2O_3$): 402.91935, found: 402.91749.

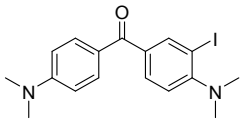
*[4-(Dimethylamino)-3-iodophenyl][4-(dimethylamino)phenyl]methanone **4** and [4-(dimethylamino)-3-iodophenyl][3-iodo-4-(methylamino)phenyl]methanone **6***



A mixture of Michler's ketone (0.9 mmol, 250 mg, 1 equiv), NaOCl (3 mL), wet SiO_2 (50% w/w, 3 g) and iodine (0.9 mmol, 236 mg, 1 equiv) was stirred at room temperature in CH_2Cl_2 for 72 h. The reaction mixture was filtered and washed with 5% aqueous sodium thiosulfate solution (3 x 10 mL). The aqueous phase was extracted with dichloromethane (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Thin layer chromatography (eluent: dichloromethane) of the residue gave the compounds [4-(dimethylamino)-3-iodophenyl][4-(dimethylamino)phenyl]methanone as a brown solid (30 mg, 0.08 mmol, 9% yield) and [4-(dimethylamino)-3-iodophenyl][(3-iodo-4-(methylamino)phenyl]methanone (15 mg, 0.029 mmol, 3%

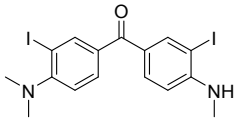
yield). Slow evaporation of a dichloromethane solution of the compounds afforded brown crystals suitable for XRD.

[4-(dimethylamino)-3-iodophenyl][4-(dimethylamino)phenyl]methanone ***4***



^{1}H NMR (300.13 MHz, $CDCl_3$, 25 ºC): δ 8.24 (d, $^{4}J_{H\text{-}H}$ 2.0 Hz, 1H, aromatic C*H*), 7.77 (d, $^{3}J_{H\text{-}H}$ 9.1 Hz, 2H, aromatic C*H*), 7.71 (dd, $^{4}J_{H\text{-}H}$ 2.0, $^{3}J_{H\text{-}H}$ 8.3 Hz, 1H, aromatic C*H*), 7.07 (d, $^{3}J_{H\text{-}H}$ 8.3 Hz, 1H, aromatic C*H*), 6.69 (d, $^{3}J_{H\text{-}H}$ 9.1 Hz, 2H, aromatic C*H*), 3.08 (s, 6H, CH_3), 2.86 (s, 6H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$, 25ºC): δ 192.0 (*C*=O), 161.9, 151.1, 142.9, 140.8, 133.3, 132.4, 132.4, 131.2, 131.0, 131.0, 129.8, 120.7, 44.6, 44.4; ESI^{+}-MS: m/z: 395 $[M+H]^{+}$ ($C_{17}H_{20}IN_2O$). ESI^{+}-HRMS: calculated for ($C_{17}H_{20}IN_2O$): 395.06202, found: 395.06106. Melting point: The quantity was too low.

[4-(dimethylamino)-3-iodophenyl][3-iodo-4-(methylamino)phenyl]methanone ***6***



^{1}H NMR (300.13 MHz, $CDCl_3$, 25 ºC): δ 8.40-8.29 (m, 2H, aromatic C*H*), 8.19 (d, $^{4}J_{H\text{-}H}$ 1.8 Hz, 1H, aromatic C*H*), 8.08 (d, $^{4}J_{H\text{-}H}$ 1.9 Hz, 1H, aromatic C*H*), 7.69 (dd, $^{4}J_{H\text{-}H}$ 1.9, $^{3}J_{H\text{-}H}$ 9.7 Hz, 1H, aromatic C*H*), 6.54 (d, $^{3}J_{H\text{-}H}$ 8.6 Hz, 1H, aromatic C*H*), 3.42 (s, 6H, CH_3), 3.01 (s, 3H, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$, 25ºC): δ 195.2 (*C*=O), 171.4, 156.5, 151.6, 143.7, 142.6, 142.4, 141.7, 133.0, 130.9, 108.3, 44.8, 30.9; ESI^{+}-MS: m/z: 507 $[M+H]^{+}$ ($C_{16}H_{17}I_2N_2O$). ESI^{+}-HRMS: calculated for ($C_{16}H_{17}I_2N_2O$): 506.94302, found: 506.94131. Melting point: The quantity was too low.

NMR spectra

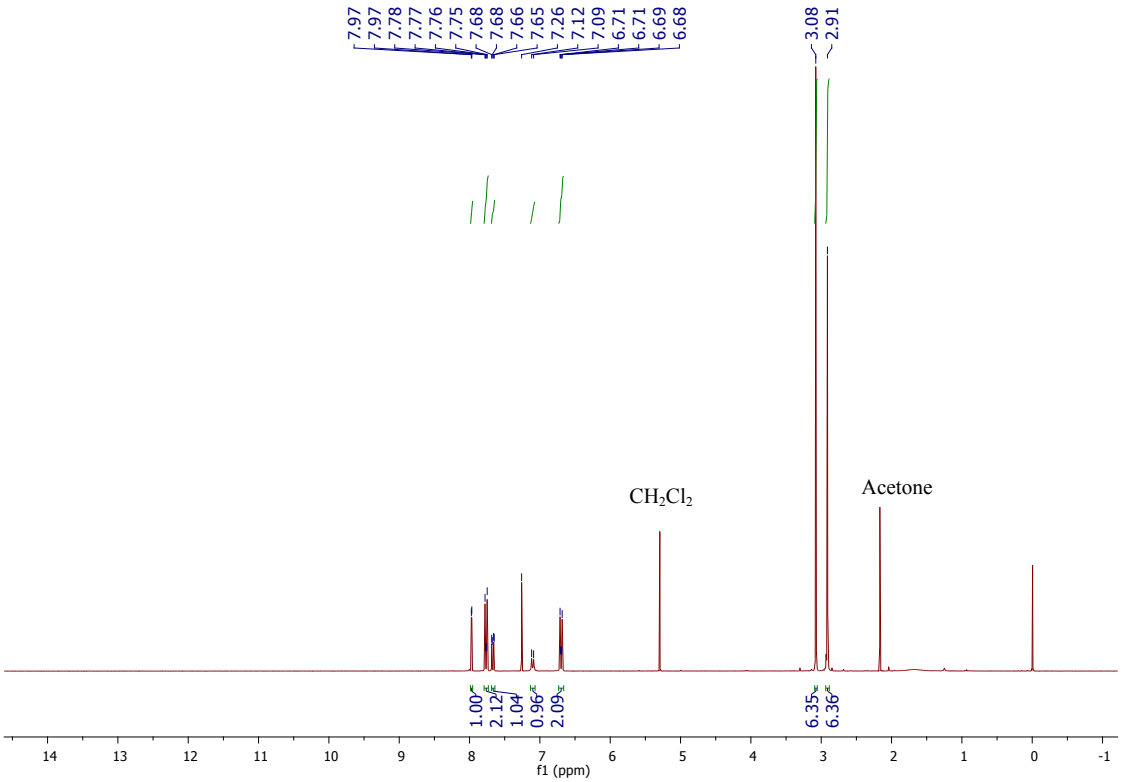


Figure S1. ^{1}H NMR spectrum of 3-bromo-4,4'-di(dimethylamino)benzophenone **1** in $CDCl_3$

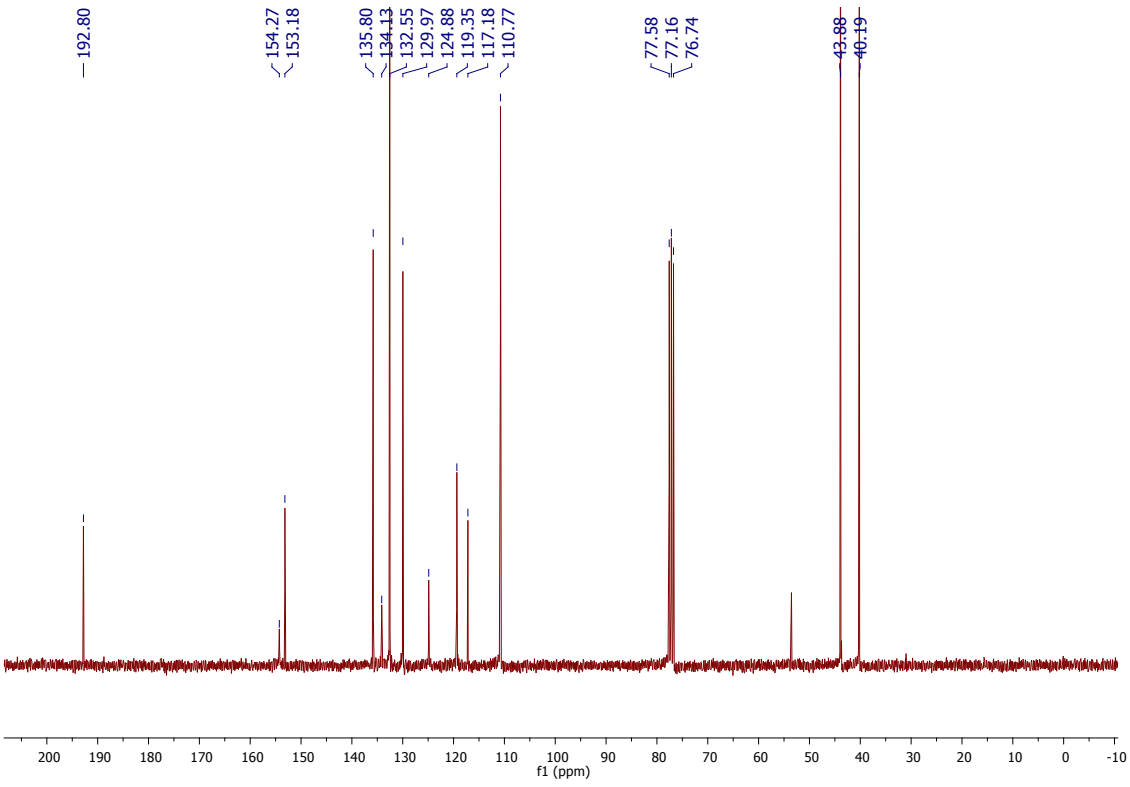


Figure S2. ^{13}C NMR spectrum of 3-bromo-4,4'-di(dimethylamino)benzophenone **1** in $CDCl_3$

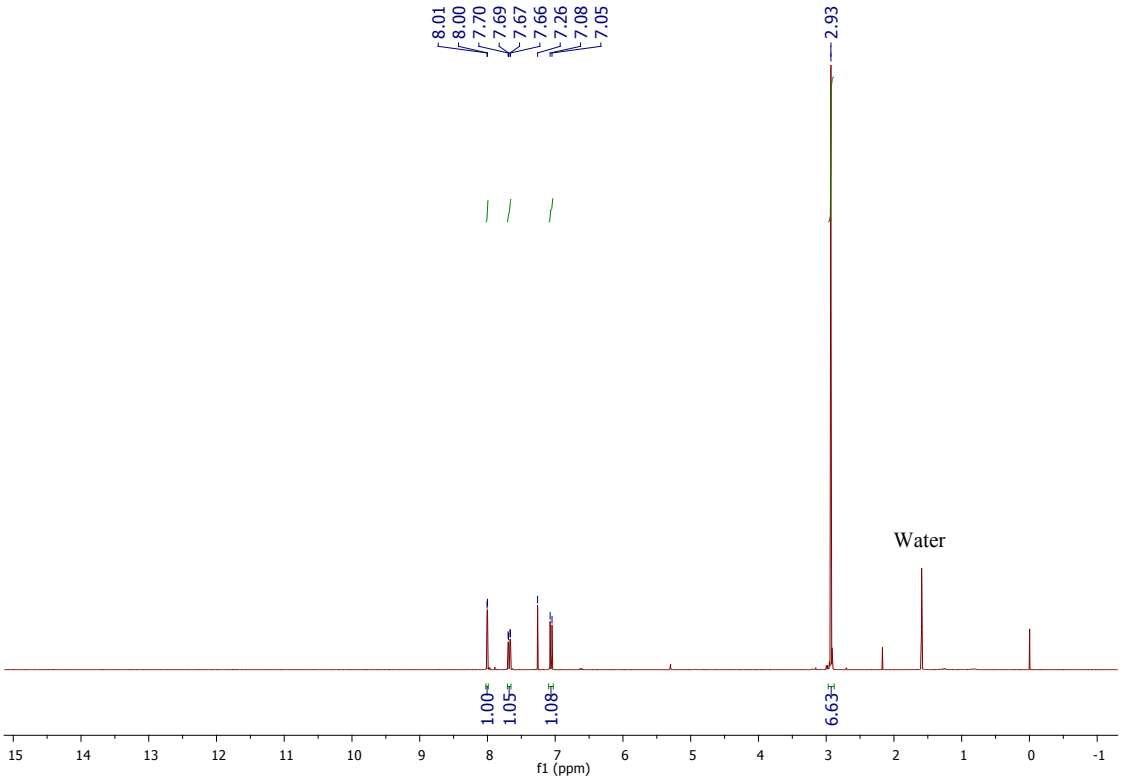


Figure S3. ^{1}H NMR spectrum of 3,3'-dibromo-4,4'-di(dimethylamino)benzophenone **2** in $CDCl_3$

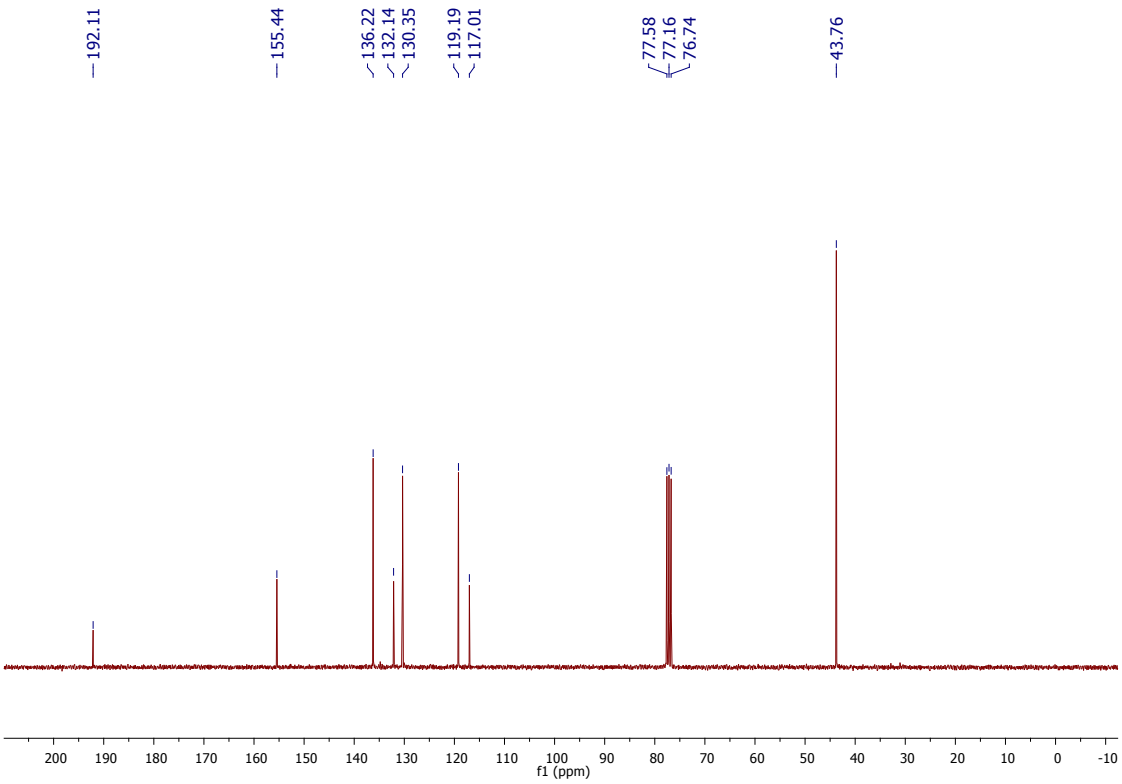


Figure S4. ^{13}C NMR spectrum of 3,3'-dibromo-4,4'-di(dimethylamino)benzophenone **2** in $CDCl_3$

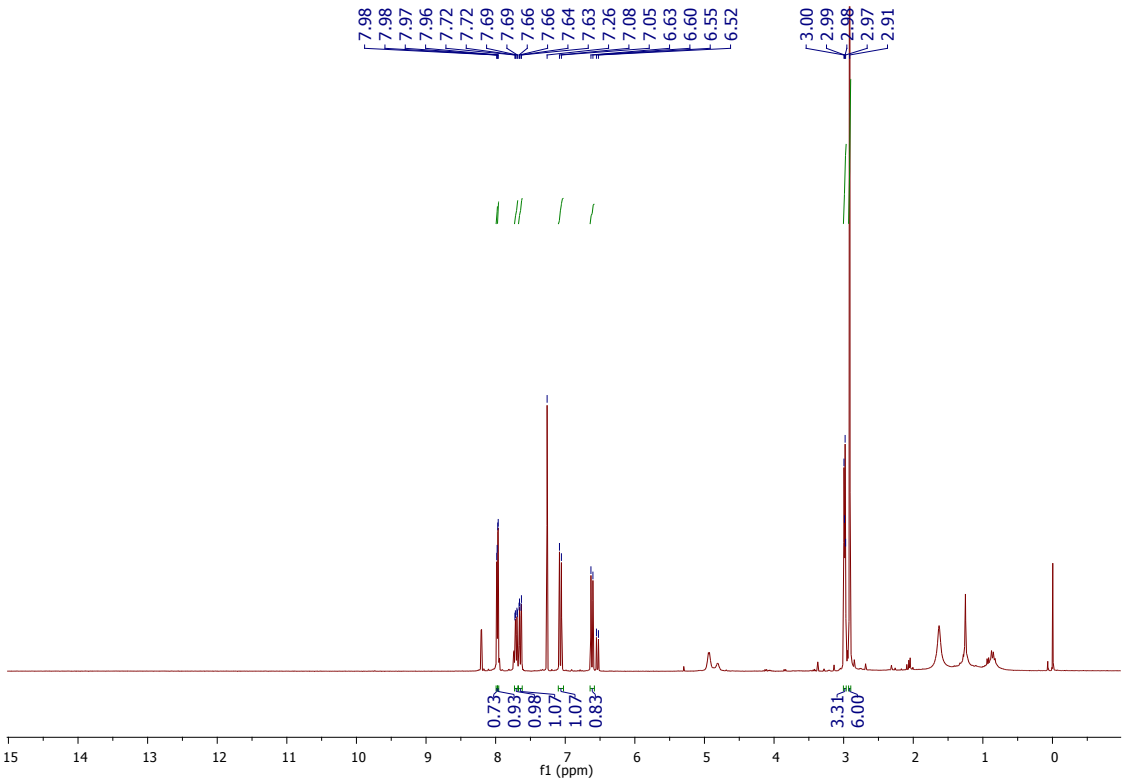


Figure S5. ^{1}H NMR spectrum of [3-bromo-4-(dimethylamino)phenyl][(3-bromo-4-(methylamino)phenyl]methanone **3** in $CDCl_3$

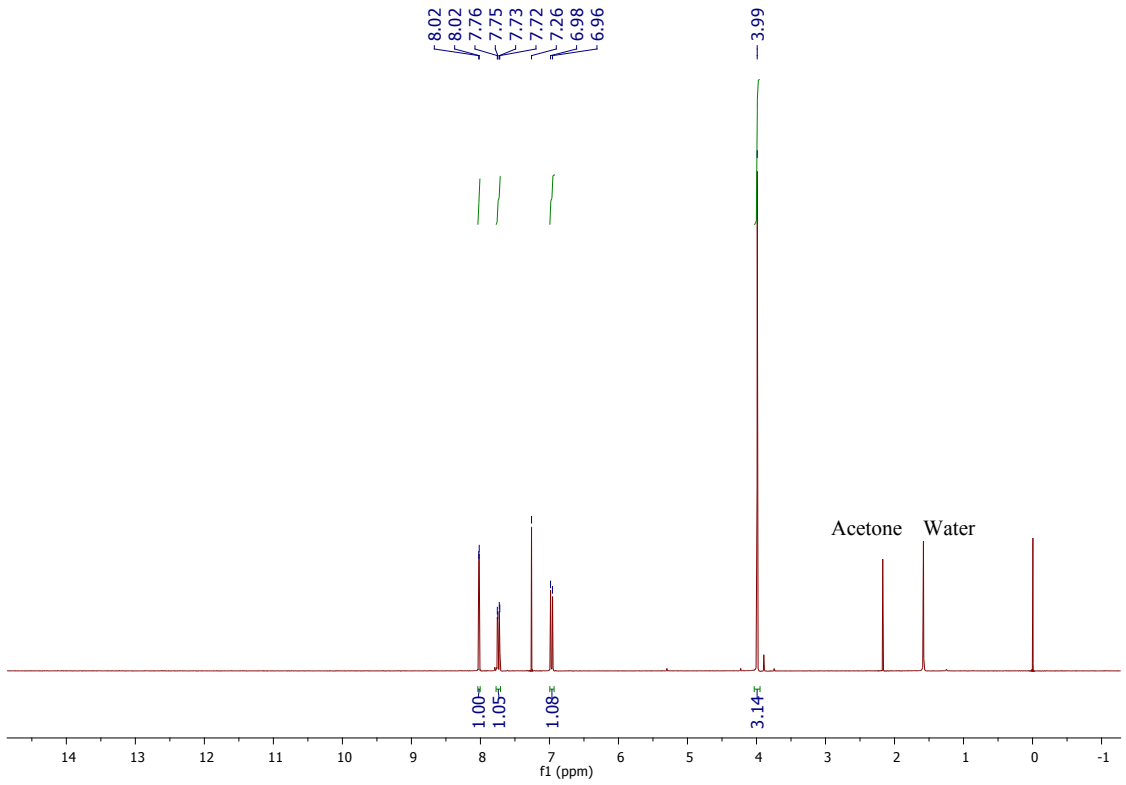


Figure S6. ^{1}H NMR spectrum of 3,3'-dibromo-4,4'-dimethoxybenzophenone **5** in $CDCl_3$

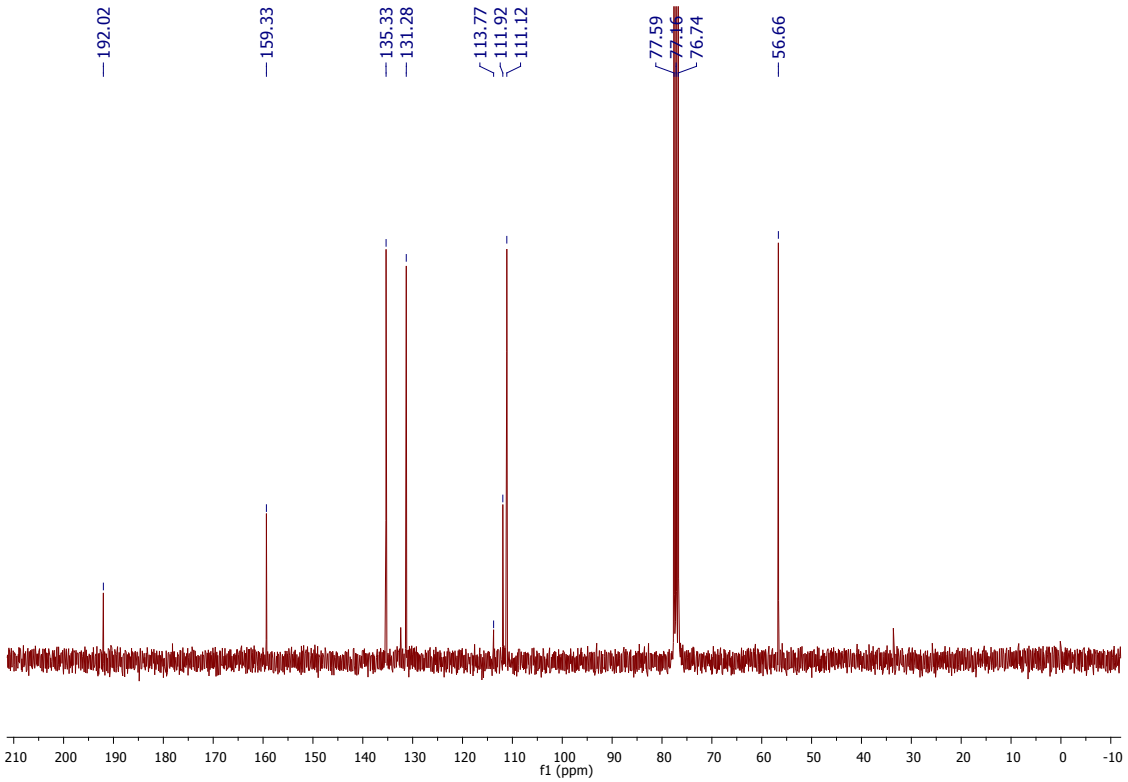


Figure S7. ^{13}C NMR spectrum of 3,3'-dibromo-4,4'-dimethoxybenzophenone **5** in $CDCl_3$

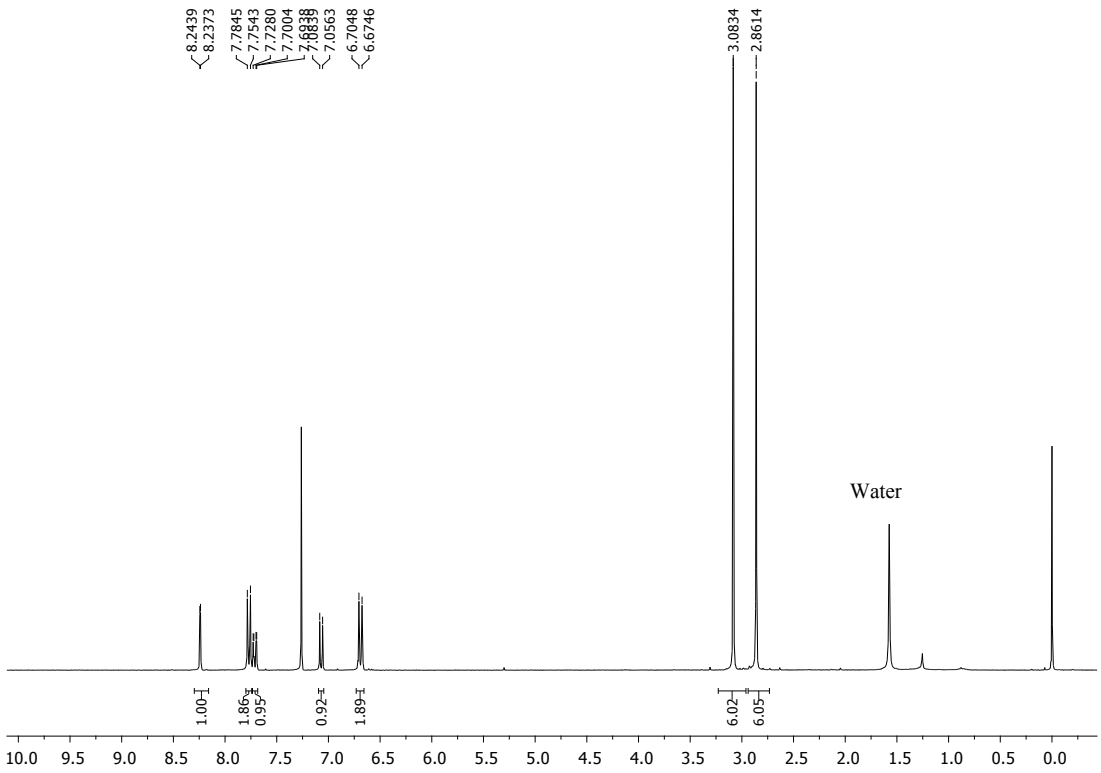


Figure S8. ^{1}H NMR spectrum of [4-(dimethylamino)-3-iodophenyl][4-(dimethylamino)phenyl]methanone **4** in $CDCl_3$

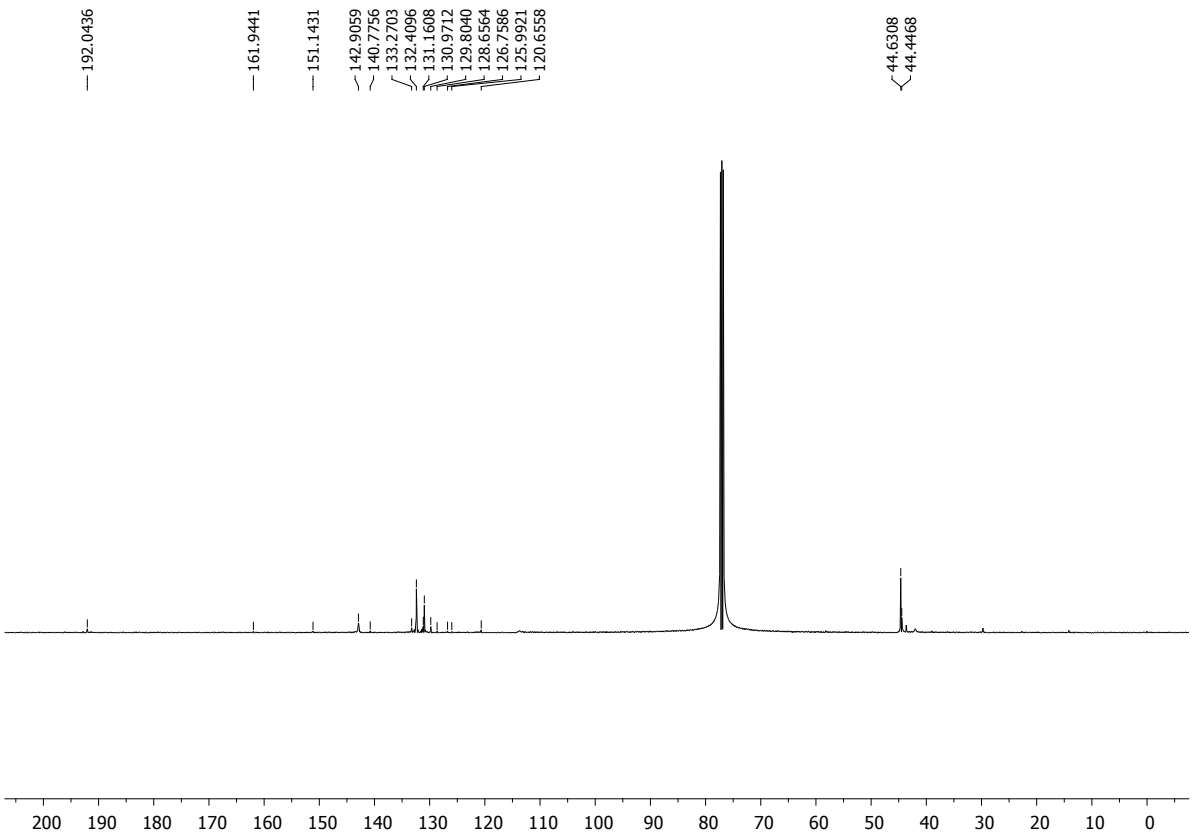


Figure S9. ^{13}C NMR spectrum of [4-(dimethylamino)-3-iodophenyl][4-(dimethylamino)phenyl]methanone **4** in $CDCl_3$

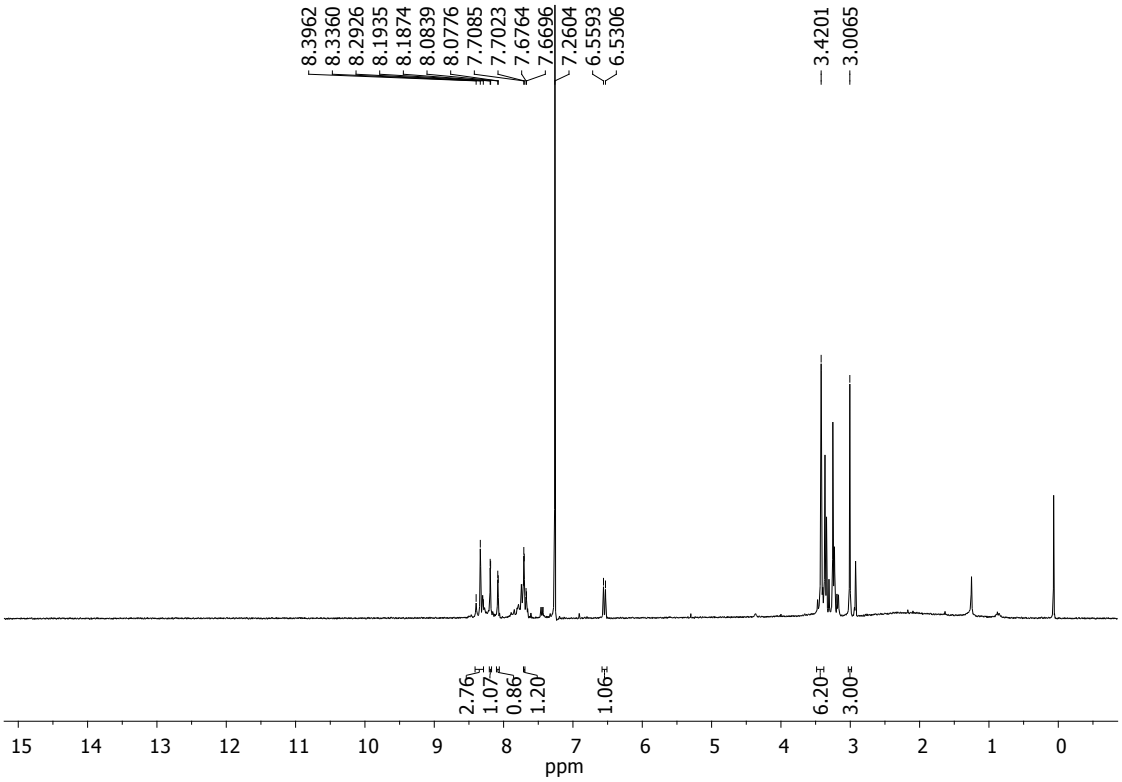


Figure S10. ^{1}H NMR spectrum of [4-(dimethylamino)-3-iodophenyl][3-iodo-4-(methylamino)phenyl]methanone **6** in $CDCl_3$

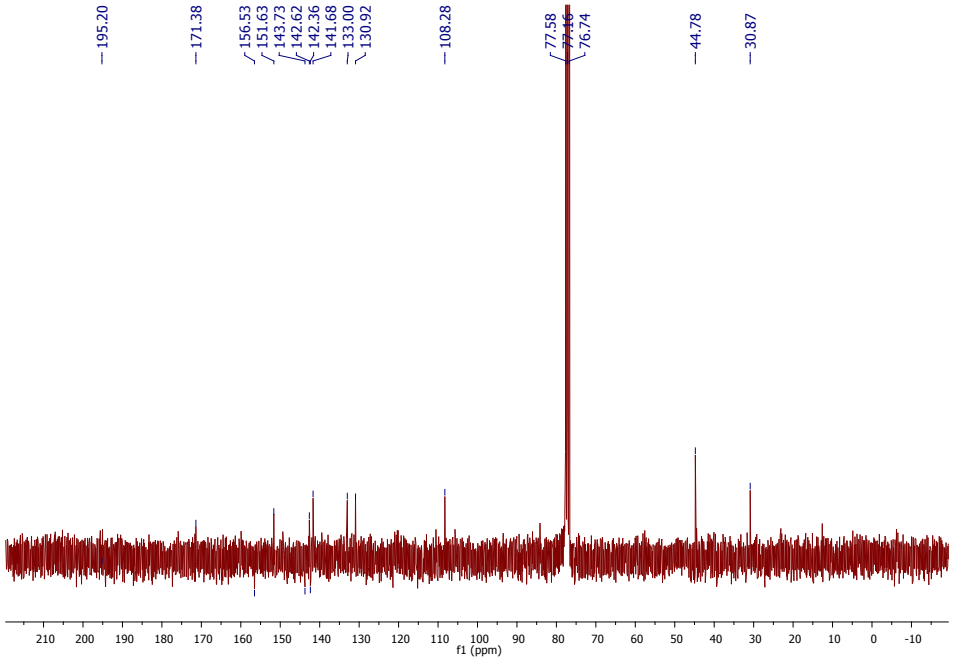


Figure S11. ^{13}C NMR spectrum of [4-(dimethylamino)-3-iodophenyl][3-iodo-4-(methylamino)phenyl)methanone **6** in $CDCl_3$

Crystal structures

Single-crystals were manually selected from the crystallization vial. A suitable single-crystal was mounted on a glass fiber with the help of silicon grease. Data were collected at 180(2) K on a Bruker X8 Kappa APEX II charge-coupled device (CCD) area-detector diffractometer (Mo K_a graphite-monochromated radiation, λ = 0.71073 Å) controlled by the APEX2 software package,[1] and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely using the software interface Cryopad.[2] Images were processed using the software package SAINT+,[3] and data were corrected for absorption by the multi-scan semi-empirical method implemented in SADABS.[4] The structure was solved using the direct methods algorithm implemented in SHELXS-97,[5,6] which allowed the immediate location of the majority of the atoms. All remaining non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least squares refinement cycles on F^2 using SHELXL-97.[5,7] All non-hydrogen atoms were successfully refined using anisotropic displacement parameters.

Hydrogen atoms bound to carbon were located at their idealized positions using appropriate *HFIX* instructions in SHELXL (*43* for the aromatic and vinylic, *23* for the $–CH_2–$ moieties and *13* for the chiral tertiary carbon atoms) and included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacements parameters (U_{iso}) fixed at 1.2 times U_{eq} of the atom to which they are attached.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-906867, CCDC-906868 and CCDC 1531065-1531068. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, U.K. Fax: (+44) 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.

(1) APEX2, *Data Collection Software Version 2.1-RC13, Bruker AXS, Delft, The Netherlands* **2006**.

(2) Cryopad, *Remote monitoring and control, Version 1.451, Oxford Cryosystems, Oxford, United Kingdom* **2006**.

(3) SAINT+, *Data Integration Engine v. 7.23a* © 1997-2005, *Bruker AXS, Madison, Wisconsin, USA*.

(4) G. M. Sheldrick, *SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program* **1998**, *Bruker AXS, Madison, Wisconsin, USA*.

(5) G. M. Sheldrick, *Acta Cryst. A*, **2008**, *64*, 112-122.

(6) G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution, University of Göttingen* **1997**.

(7) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen* **1997**.