Supporting Information

Ru(II)-catalyzed Chemo- and Regioselective Cyclotrimerization of Three Unsymmetrical Alkynes through Boron Temporary Tether. One-pot Four-component Coupling via Cyclotrimerization/Suzuki-Miyaura Coupling

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Experimental Section

General. ¹H and ¹³C NMR spectra were obtained for samples in CDCl₃ solution. Flash chromatography was performed with a silica gel column (Merck Silica gel 60) eluted with mixed solvents [hexane / ethyl acetate]. Elemental analyses were performed by the Microanalytical Center of Kyoto University or Instrumental Analysis Facility of Nagoya University. Melting points were obtained in capillary tubes and are uncorrected. 1,2-Dichloroethane was dried over CaH₂ and distilled. Alkynylboronates¹ and Cp*RuCl(cod)² were prepared according to the literature procedures.

(1) Brown, H. C.; Bhat, N. G.; Srebnik, M. *Tetrahedron Lett.* **1988**, 29, 2631-2634.

(2) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161-1164.

Representative Procedure for One-pot Synthesis of Biaryls: Synthesis of Biphenyl 8a from 1-

Hexynylboronate 2a, propargyl alcohol 3a, 1-Hexyne 4a, and Iodoacetophenone 7a. To a

solution of Cp*RuCl(cod) (**1**) (9.5 mg, 0.025 mmol), 1-hexynylboronate **2a** (105.1 mg, 0.50 mmol),

and 1-hexyne (104.3 mg, 2.0 mmol) in dry degassed 1,2-dichloroethane (1 mL) was added a

solution of propargyl alcohol (30.8 mg, 0.55 mmol) in dry degassed 1,2-dichloroethane (3 mL) within 15 min at room temperature under Ar atmosphere. The solution was stirred at room temperature under Ar atmosphere for 5 h, and then, the solvent was removed under reduced pressure. To the residue were added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (13.0 mg, 0.0125 mmol), PCy_3 (15.9 mg, 0.055 mmol), *p*-iodoacetophenone **7a** (184.5 mg, 0.75 mmol), toluene (3.5 mL), and 2 M aq. K_2CO_3 (1.5 mL), and the reaction mixture was degassed at -78°C under reduced pressure. After heating at 70°C under Ar atmosphere for 3 h, the resultant solution was extracted with AcOEt (3 mL $\times$ 3) and the organic layer was dried with MgSO_4 . The solvent was evaporated and the crude product was purified by silica gel flash column chromatography (hexane-AcOEt 6:1) to give biphenyl **8aaa** (123.4 mg, 73%) as pale yellow oil (Rf 0.2, Hexane-AcOEt 3:1): IR (neat) 3424, 1682, 1604 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25°C): δ 0.75 (t, $J = 7.2$ Hz, 3 H), 0.96 (t, $J = 7.2$ Hz, 3 H), 1.15 (h, $J = 7.5$ Hz, 2 H), 1.32-1.47 (m, 4 H), 1.60-1.70 (m, 2 H), 1.98 (br s, 1 H), 2.29 (t, $J = 8.1$ Hz, 2 H), 2.64 (t, $J = 8.1$ Hz, 2 H), 2.64 (s, 3 H), 4.28 (s, 2 H), 7.06 (d, $J = 1.5$ Hz, 1 H), 7.21 (d, $J = 1.5$ Hz, 1 H), 7.27-7.32 (m, 2 H), 7.97-8.02 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3 , 25°C): δ 13.82, 14.02, 22.50, 22.54, 26.60, 33.00, 33.54, 33.62, 35.51, 63.32, 125.05, 128.04, 128.27, 129.89, 135.53, 136.28, 138.04, 140.35, 142.50, 144.71, 197.69; MS (EI): m/z (%): 338 (100) [M^+], 323 (18) [$\text{M}^+ - \text{CH}_3$], 295 (50) [$\text{M}^+ - \text{COCH}_3$], 277 (70) [$\text{M}^+ - \text{COCH}_3 - \text{H}_2\text{O}$], 265 (25) [$\text{M}^+ - \text{COCH}_3 - \text{CH}_2\text{O}$]; EA calcd (%) for $\text{C}_{23}\text{H}_{30}\text{O}_8$ (338.48): C 81.61, H 8.93; found: C 81.51, H 9.03.

Analytical Data for 8aab: oil (Rf 0.45, Hexane-AcOEt 3.5:1): IR (neat) 3315, 1609 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 0.77 (t, $J = 7.5$ Hz, 3 H), 0.98 (t, $J = 7.5$ Hz, 3 H), 1.18 (h, $J = 7.5$ Hz, 2 H), 1.34-1.49 (m, 4 H), 1.58 (br s, 1 H), 1.62-1.73 (m, 2 H), 2.32 (t, $J = 7.8$ Hz, 2 H), 2.66 (t, $J = 7.8$ Hz, 2 H), 4.33 (s, 2 H), 7.07 (s, 1 H), 7.16-7.22 (m, 3 H), 7.33-7.45 (m, 3 H); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 13.87, 14.10, 22.59, 22.66, 33.06, 33.64, 33.72, 35.58, 63.80, 125.05, 126.83, 128.10, 128.26, 129.48, 137.52, 138.45, 139.15, 140.91, 142.05; MS (EI): m/z (%): 296 (100) [M^+], 278 (11) [$\text{M}^+ - \text{H}_2\text{O}$], 253 (40) [$\text{M}^+ - (\text{CH}_2)_2\text{CH}_3$], 235 (90) [$\text{M}^+ - (\text{CH}_2)_2\text{CH}_3 - \text{H}_2\text{O}$], 220 (35) [$\text{M}^+ - \text{C}_6\text{H}_4$]; EA calcd (%) for $\text{C}_{21}\text{H}_{28}\text{O}$ (296.45): C 85.08, H 9.52; found: C 85.04, H 9.55.

Analytical Data for 8aac: oil (Rf 0.3, Hexane-AcOEt 3:1): IR (neat) 3326, 1607 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 0.80 (t, $J = 7.2$ Hz, 3 H), 0.98 (t, $J = 7.5$ Hz, 3 H), 1.14-1.26 (m, 2 H), 1.36-1.49 (m, 4 H), 1.62-1.75 (m, 3 H), 2.35 (t, $J = 8.0$ Hz, 2 H), 2.66 (t, $J = 7.8$ Hz, 2 H), 3.86 (s, 3 H), 4.34 (s, 2 H), 6.94-6.98 (m, 2 H), 7.06 (d, $J = 1.5$ Hz, 1 H), 7.09-7.14 (m, 2 H), 7.18 (d, $J = 1.5$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 13.91, 14.07, 22.60, 22.63, 33.09, 33.64, 33.71, 35.55, 55.18, 63.79, 113.52, 124.97, 128.17, 130.45, 131.24, 137.13, 138.86, 141.32, 141.86, 158.26; MS (EI): m/z (%): 326 (100) [M^+], 308 (5) [$\text{M}^+ - \text{H}_2\text{O}$], 283 (40) [$\text{M}^+ - (\text{CH}_2)_2\text{CH}_3$], 265 (90) [$\text{M}^+ - (\text{CH}_2)_2\text{CH}_3 - \text{H}_2\text{O}$]; EA calcd (%) for $\text{C}_{22}\text{H}_{30}\text{O}_2$ (326.47): C 80.94, H 9.26; found: C 80.96, H 9.24.

Analytical Data for 8aad: oil (Rf 0.15, Hexane-AcOEt 2:1): IR (neat) 3362 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 0.76 (t, $J = 7.5$ Hz, 3 H), 0.95 (t, $J = 7.5$ Hz, 3 H), 1.17 (h, $J = 7.5$ Hz, 2 H), 1.32-1.46 (m, 4 H), 1.59-1.69 (m, 2 H), 2.47 (t, $J = 7.8$ Hz, 2 H), 2.63 (t, $J = 7.8$ Hz, 2 H), 4.18 (s, 2 H), 4.45 (br s, 1 H), 7.08 (d, $J = 1.8$ Hz, 1 H), 7.14 (d, $J = 1.8$ Hz, 1 H), 7.30 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 1 H), 7.37 (dt, $J = 7.5, 1.0$ Hz, 1 H), 7.77 (dt, $J = 7.5, 1.8$ Hz, 1 H), 8.65 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 13.83, 14.07, 22.55 (2 C), 33.13, 33.56, 33.65, 35.47, 64.56, 121.92, 125.33, 127.41, 129.05, 136.06, 136.91, 139.78, 140.68, 143.26, 148.67, 158.53; MS (EI): m/z (%): 297 (100) [M^+], 279 (49) [$\text{M}^+ - \text{H}_2\text{O}$], 268 (21) [$\text{M}^+ - \text{CH}_2\text{CH}_3$], 250 (96) [$\text{M}^+ - \text{H}_2\text{O} - \text{CH}_2\text{CH}_3$]; EA calcd (%) for $\text{C}_{20}\text{H}_{27}\text{NO}$ (297.43): C 80.76, H 9.15, N 4.71; found: C 80.39,

H 9.29, N, 4.40.

Analytical Data for 8a_{ae}: oil (R_f 0.35, Hexane-AcOEt 3:1): IR (neat) 3330 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 0.83 (t, *J* = 7.5 Hz, 3 H), 0.97 (t, *J* = 7.5 Hz, 3 H), 1.25 (h, *J* = 7.5 Hz, 2 H), 1.36-1.53 (m, 4 H), 1.60-1.71 (m, 2 H), 1.74 (br s, 1 H), 2.43 (t, *J* = 7.8 Hz, 2 H), 2.65 (t, *J* = 7.8 Hz, 2 H), 4.45 (s, 2 H), 6.89 (dd, *J* = 3.3, 1.2 Hz, 1 H), 7.07 (s, 1 H), 7.10 (dd, *J* = 5.1, 3.3 Hz, 1 H), 7.20 (s, 1 H), 7.38 (dd, *J* = 5.1, 1.2 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 13.94, 14.07, 22.60, 22.69, 33.23, 33.63, 34.12, 35.59, 63.74, 125.22, 125.56, 126.84, 127.36, 128.30, 129.19, 139.21, 140.64, 143.27, 143.33; MS (EI): *m/z* (%): 302 (100) [M⁺], 284 (11) [M⁺-H₂O], 269 (20) [M⁺-H₂O-CH₃], 255 (42) [M⁺-H₂O-CH₂CH₃], 241 (30) [M⁺-H₂O-CH₂CH₂CH₃]; EA calcd (%) for C₁₉H₂₆OS (302.48): C 75.45, H 8.66; found: C 75.54, H 8.47.

Analytical Data for 8a_b: oil (R_f 0.3, Hexane-AcOEt 2:1): IR (neat) 3384, 1681, 1604 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 0.74 (t, *J* = 7.5 Hz, 3 H), 1.14 (h, *J* = 7.2 Hz, 2 H), 1.32-1.42 (m, 2 H), 2.02 (br s, 1 H), 2.30 (t, *J* = 7.5 Hz, 2 H), 2.64 (s, 3 H), 3.43 (s, 3 H), 4.28 (s, 2 H), 4.48 (s, 2 H), 7.21 (d, *J* = 1.8 Hz, 1 H), 7.26-7.29 (m, 2 H), 7.35 (d, *J* = 1.8 Hz, 1 H), 7.98-8.01 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 13.82, 22.51, 26.66, 33.00, 33.46, 58.32, 63.20, 74.53, 124.30, 127.48, 128.13, 129.71, 135.73, 137.76, 138.33, 138.46, 140.80, 144.33, 197.66; MS (EI): *m/z* (%): 326 (100) [M⁺], 311 (20) [M⁺-CH₃], 295 (88) [M⁺-OCH₃], 281 (14) [M⁺-CH₂OCH₃], 265 (69) [M⁺-OCH₃-CH₂O]; EA calcd (%) for C₂₁H₂₆O₃ (326.43): C 77.27, H 8.03; found: C 77.11, H 8.19.

Analytical Data for 8a_c: oil (R_f 0.3, Hexane-AcOEt 2:1): IR (neat) 3435, 1681, 1604 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 0.75 (t, *J* = 7.5 Hz, 3 H), 1.15 (h, *J* = 7.2 Hz, 2 H), 1.31-1.41 (m, 2 H), 1.56 (br s, 1 H), 2.09-2.19 (m, 2 H), 2.66 (s, 3 H), 2.29 (t, *J* = 7.8 Hz, 2 H), 3.59 (t, *J* = 6.5 Hz, 2 H), 4.31 (s, 2 H), 7.08 (d, *J* = 1.6 Hz, 1 H), 7.21 (d, *J* = 1.6 Hz, 1 H), 7.28-7.32 (m, 2 H), 7.99-8.04 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 13.85, 22.52, 26.68, 32.70, 33.02, 33.55, 35.99, 44.35, 63.33, 125.14, 128.14, 128.48, 129.84, 135.72, 136.91, 138.36, 140.38, 140.79, 144.45, 197.66; MS (EI): *m/z* (%): 358 (100) [M⁺], 343 (24) [M⁺-CH₃], 297 (58) [MH⁺-CH₂CHCl],

255 (64) [$\text{MH}^+\text{-CH}_2\text{CHCl-CH}_2\text{CHCH}_3$]; EA calcd (%) for $\text{C}_{22}\text{H}_{27}\text{ClO}_2$ (358.90): C 73.62, H 7.58; found: C 73.54, H 7.68.

Analytical Data for 8ada: oil (Rf 0.3, Hexane-AcOEt 1:1): IR (neat) 3448, 1736, 1683, 1604 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 0.75 (t, $J = 7.5$ Hz, 3 H), 1.14 (h, $J = 7.5$ Hz, 2 H), 1.30-1.41 (m, 2 H), 1.65 (br s, 1 H), 2.01 (q, $J = 7.5$ Hz, 2 H), 2.28 (t, $J = 7.8$ Hz, 2 H), 2.38 (t, $J = 7.2$ Hz, 2 H), 2.65 (s, 3 H), 2.69 (t, $J = 7.5$ Hz, 2 H), 3.68 (s, 3 H), 4.29 (s, 2 H), 7.05 (d, $J = 1.8$ Hz, 1 H), 7.20 (d, $J = 1.8$ Hz, 1 H), 7.27-7.32 (m, 2 H), 7.99-8.03 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 13.86, 22.55, 26.48, 26.69, 33.05, 33.57 (2 C), 35.01, 51.58, 63.40, 125.20, 128.13, 128.44, 129.87, 135.70, 136.81, 138.27, 140.70, 141.25, 144.53, 173.76, 197.66; MS (EI): m/z (%): 382 (5) [M^+], 364 (81) [$\text{M}^+\text{-H}_2\text{O}$], 333 (10) [$\text{M}^+\text{-H}_2\text{O-OCH}_3$], 321 (100) [$\text{M}^+\text{-H}_2\text{O-CH}_2\text{CH}_2\text{CH}_3$], 291 (72) [$\text{M}^+\text{-H}_2\text{O-CH}_2\text{CO}_2\text{CH}_3$]; EA calcd (%) for $\text{C}_{24}\text{H}_{30}\text{O}_4$ (382.49): C 75.36, H 7.91; found: C 75.28, H 7.99.

Analytical Data for 8aea: oil (Rf 0.3, Hexane-AcOEt 2:1): IR (neat) 3798, 1682, 1604 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 0.75 (t, $J = 7.5$ Hz, 3 H), 1.15 (h, $J = 7.2$ Hz, 2 H), 1.32-1.42 (m, 2 H), 1.84 (br s, 1 H), 2.28 (t, $J = 7.8$ Hz, 2 H), 2.34 (s, 3 H), 2.64 (s, 3 H), 4.28 (s, 2 H), 7.07 (s, 1 H), 7.20 (s, 1 H), 7.27-7.31 (m, 2 H), 7.98-8.02 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 13.85, 21.30, 22.54, 26.66, 32.97, 33.57, 63.33, 125.83, 128.10, 128.99, 129.92, 135.62, 136.21, 137.54, 138.10, 140.54, 144.61, 197.69; MS (EI): m/z (%): 296 (85) [M^+], 281 (20) [$\text{M}^+\text{-CH}_3$], 254 (22) [$\text{M}^+\text{-CH}_2\text{CO}$], 235 (50) [$\text{M}^+\text{-COCH}_3\text{-H}_2\text{O}$], 220 (25) [$\text{M}^+\text{-COCH}_3\text{-H}_2\text{O-CH}_3$], 205 (100) [$\text{M}^+\text{-COCH}_3\text{-H}_2\text{O-2CH}_3$]; EA calcd (%) for $\text{C}_{20}\text{H}_{24}\text{O}_2$ (296.40): C 81.04, H 8.16; found: C 80.96, H 8.24.

Analytical Data for 8baa: oil (Rf 0.1, Hexane-AcOEt 3:1): IR (neat) 3431, 1683, 1604 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 0.94 (t, $J = 7.5$ Hz, 3 H), 1.39 (h, $J = 7.5$ Hz, 2 H), 1.59-1.70 (m, 2 H), 2.05 (br s, 1 H), 2.63 (s, 3 H), 2.66 (t, $J = 7.8$ Hz, 2 H), 3.20 (s, 3 H), 4.05 (s, 2 H), 4.30 (s, 2 H), 7.28 (s, 1 H), 7.29-7.33 (m, 3 H), 7.96-8.01 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 14.01, 22.52, 26.63, 33.57, 35.49, 58.15, 62.95, 72.34, 127.05, 127.56, 128.01, 129.74, 135.60,

137.78, 136.15, 138.16, 142.86, 143.46, 197.66; MS (EI): m/z (%): 326 (30) [M^+], 308 (22) [$M^+ - H_2O$], 293 (41) [$M^+ - H_2O - CH_3$], 277 (10) [$M^+ - H_2O - OCH_3$], 265 (100) [$M^+ - OCH_3 - CH_2O$]; EA calcd (%) for $C_{21}H_{26}O_3$ (326.43): C 77.27, H 8.03; found: C 77.07, H 8.15.

Analytical Data for 8caa: oil (Rf 0.3, Hexane-AcOEt 2:1): IR (neat) 3429, 1682, 1604 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.96 (t, $J = 7.5$ Hz, 3 H), 1.40 (h, $J = 7.2$ Hz, 2 H), 1.60-1.70 (m, 2 H), 1.73 (br s, 1 H), 1.77-1.86 (m, 2 H), 2.47 (t, $J = 7.8$ Hz, 2 H), 2.64 (s, 3 H), 2.64 (t, $J = 7.2$ Hz, 2 H), 3.35 (t, $J = 6.6$ Hz, 2 H), 4.29 (s, 2 H), 7.07 (d, $J = 1.2$ Hz, 1 H), 7.24 (d, $J = 1.2$ Hz, 1 H), 7.28-7.32 (m, 2 H), 7.99-8.03 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 14.05, 22.56, 26.69, 30.53, 33.65, 33.80, 35.50, 44.30, 63.35, 125.71, 128.26, 128.49, 129.83, 135.81, 136.55, 138.33 (2 C), 142.88, 144.21, 197.59; MS (EI): m/z (%): 358 (100) [M^+], 343 (31) [$M^+ - CH_3$], 315 (69) [$M^+ - CH_2CH_2CH_3$], 297 (45) [$M^+ - H_2O - CH_2CH_2CH_3$]; EA calcd (%) for $C_{22}H_{27}ClO_2$ (358.90): C 73.62, H 7.58; found: C 73.52, H 7.71.

Analytical Data for 9: oil (Rf 0.4, Hexane-AcOEt 3.5:1): IR (neat) 3329, 1604 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.94 (t, $J = 7.2$ Hz, 6 H), 1.37 (h, $J = 7.2$ Hz, 4 H), 1.55-1.65 (m, 2 H), 1.72 (br s, 1 H), 2.59 (t, $J = 7.8$ Hz, 2 H), 4.64 (s, 2 H), 6.94 (s, 1 H), 7.00 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 14.05, 22.54, 33.76, 35.65, 65.52, 124.29, 127.85, 140.54, 143.05; MS (EI): m/z (%): 220 (69) [M^+], 203 (3) [$M^+ - OH$], 191 (12) [$M^+ - CHO$], 177 (68) [$M^+ - CH_2CH_2CH_3$], 160 (100) [$M^+ - OH - CH_2CH_2CH_3$]; EA calcd (%) for $C_{15}H_{24}O$ (220.35): C 81.76, H 10.98; found: C 81.90, H 11.26.

X-ray Crystallographic Analysis for 2,4-Dinitrophenylhydrazone of 8i.

Single crystals of 2,4-Dinitrophenylhydrazone of **8i** suitable for X-ray analysis were obtained by recrystallization from AcOEt/hexane. A crystal of the dimension $0.1 \times 0.2 \times 0.7$ mm was mounted on a quartz fiber, and diffraction data were collected in θ range of 1.17- 29.19° at 173 K on a Bruker SMART APEX CCD diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda =$

0.71073 Å). The absorption correction was made using SADABS. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2 by using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. Final refinement details are compiled in Tables S1.

Table 1. Crystal data and structure refinement for 2,4-Dinitrophenylhydrazone of 8i.

Empirical formula	$C_{52}H_{56}N_8O_{10}$	
Formula weight	959.10	
Temperature	173(2) K	
Wavelength	0.71073	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 9.7951(9)$	$\alpha = 101.362(2)^\circ$
	$b = 15.3104(13)$	$\beta = 104.892(2)^\circ$
	$c = 18.4426(17)$	$\gamma = 92.428(2)^\circ$
Volume	$2607.8(4) \text{ \AA}^3$	
Z	2	
Density (calculated)	2.443 Mg/m^3	
Absorption coefficient	0.172 mm^{-1}	
F(000)	2040	
Theta range for data collection	1.17 to 29.19°	
Index ranges	$-13 \leq h \leq 13$, $-20 \leq k \leq 12$, $-24 \leq l \leq 23$	
Reflections collected	20331	
Independent reflections	13683 [$R(\text{int}) = 0.0369$]	
Completeness to $\theta = 29.19^\circ$	96.8 %	
Absorption correction	Empirical (SADABS)	
Max. and min. transmission	1.000000 and 0.628986	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13683 / 0 / 639	
Goodness-of-fit on F^2	0.889	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1098$, $wR2 = 0.3099$	
R indices (all data)	$R1 = 0.2405$, $wR2 = 0.3758$	
Largest diff. peak and hole	1.564 and $-0.503 \text{ e. \AA}^{-3}$

FigureS1. ORTEP diagrams for 2,4-dinitrophenylhydrazone of 8i, showing the two crystallographically unique molecules in the unit cell.