# Revised

# Supporting Information

## Radical Additions of TEMPO to Ketenes: Correlation of Free Radical and Nucleophilic Reactivity

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Experimental procedures, X-ray structural information, kinetic data, NMR and IR spectra

33 pages

## Experimental

Reactions were conducted in dried glassware under an atmosphere of $N_2$ or Ar. Chromatography was carried out on silica gel. Mesitylene was dried over Na and distilled, and TEMPO was sublimed at 80 °C and 0.5 torr. Triethylamine was dried by distillation from $CaH_2$, and argon was bubbled through dehyrochlorination solutions for 1 h at the beginning of these reactions.

**Reaction of phenylketene (8a) from Wolff rearrangement with TEMPO**. A solution of diazoacetophenone (**9a**, 21.4 mg, 0.15 mmol) and TEMPO (58.6 mg, 0.38 mmol) in 1 mL toluene was refluxed for 48 h. Chromatography (10% EtOAc/hexanes) gave the bis(TEMPO) adduct **10a** (28.7 mg, 45%) as a white solid which was recrystallized from MeOH/$H_2O$, mp 90-92 °C; IR ($CDCl_3$) 1772 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.41 (s, 3, $CH_3$), 0.63 (s, 3, $CH_3$), 0.80 (s, 3, $CH_3$), 1.02 (s, 3, $CH_3$), 1.06 (s, 3, $CH_3$), 1.12 (s, 3, $CH_3$), 1.24 (s, 3, $CH_3$), 1.27 (s, 3, $CH_3$), 1.24-1.62 (m, 12, $CH_2$), 5.23 (s, 1, CHO), 7.20-7.50 (m, 5, Ph); $^{13}C$ NMR ($CDCl_3$) $\delta$ 16.84, 17.02, 19.90, 20.09, 20.13, 20.52, 30.73, 31.85, 33.30, 34.07, 39.10, 39.30, 40.22, 59.48, 59.82, 60.30, 60.41, 87.59, 127.47, 127.80, 128.12, 139.32, 170.84; CIMS (isobutane) *m/z* 431 ($MH^+$, 0.2), 276 (5), 156 ($TEMPO^+$, 100), 142 (46), 126 (23); EIMS *m/z* 430 ($M^+$, 0.2), 156 ($TEMPO^+$, 100).

**Reaction of phenylketene (8a) from phenylacetyl chloride with TEMPO**. A solution of TEMPO (0.70 g, 4.48 mmol), phenylacetyl chloride (0.100 mL, 0.117 g, 0.756 mmol), and $Et_3N$ (0.90 mmol) in 1.7 mL THF under argon was stirred 22 h at room temperature, and then 5 mL of $CH_2Cl_2$ and 5 mL $NaHCO_3$ solution were added. The layers were separated and the aqueous phase was extracted 3 times with $CH_2Cl_2$, and the combined organic layers were dried over $MgSO_4$ and evaporated, and the residue was recrystallized from pentane and then chromatographed (2.5% EtOAc/benzene) to give **10a** as a gum.

**Reaction of *E*-Phenylvinylketene 8b with TEMPO**. Diazoketone **9b** (30 mg, 0.32 mmol) and TEMPO (80 mg, 0.45 mmol) in 1 mL toluene was photolyzed 3 h with 300 nm light. The solvent was evaporated and the residue chromatographed (40% EtOAc/hexane) giving **10b** as an unseparated 3/1 *E*/*Z* mixture with $^1$H NMR ($CDCl_3$) δ for both stereoisomers 0.8 to 1.8 (TEMPO), and 7.3 (m, Ph), and others assigned to *E*–**10b**: δ 5.25 (1, d, *J* = 6.9 Hz, CHOT), δ 6.02 (1, d, *J* = 16.2 Hz, $CHCO_2$), 7.15 (1, dd, *J* = 15.7, 7.2 Hz, CCH=C) and *Z*–**10b**: δ 4.95 (1, d, *J* = 8.4 Hz, CHOT), 6.3 (1, dd, *J* = 16.0, 8.6 Hz, CCH=C), and 6.70 (1, d, *J* = 15.8 Hz, $CHCO_2T$). IR ($CDCl_3$) 1734 cm$^{-1}$. $^1$H NMR assignments for *E*–**10b** are in accord with those for *E*–$ArCHOHCH=CHCO_2H$: (a) Bourguignon, J.-J.; Schoenfelder, A.; Schmitt, M.; Wermuth, C.-G.; Hechler, V.; Charlier, B.; Maitre, M. *J. Med. Chem*. **1988**, *31*, 893-897; (b) Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc. Perkin Trans. 1* **1990**, 159-162.

**Reaction of Phenylvinylketene 8b from 4-Phenyl-3-butenoyl Chloride with TEMPO**. A solution of TEMPO (200 mg, 1.28 mmol), $Et_3N$ (51 mg, 5.0 mmol), and *E*-$PhCH=CHCH_2COCl$ (69.3 mg, 0.381 mmol) in 10 mL degassed $CH_2Cl_2$ under argon was stirred 2 h over 500 mg 4A molecular sieves at room temperature. The solution was poured into $NaHCO_3$, extracted with $CH_2Cl_2$, and the organic extract was dried, concentrated, and chromatographed with a silica column (5% EtOAc, 2% $Et_3N$/benzene) to give **10b** (48.1 mg, 0.105 mmol, 28%) as a 2/1 *E*/*Z* mixture with $^1$H NMR signals corresponding to those from the Wolff-rearrangement procedure, and $^{13}$C NMR ($CDCl_3$) δ 15.6, 15.7, 15.8, 18.9, 19.0, 19.2, 19.3, 19.4, 30.4, 30.6, 30.7, 32.2, 32.5, 33.4, 33.6, 37.7, 37.9, 38.0, 39.0, 58.3, 58.6, 58.8, 59.1, 59.3, 85.5 (*Z* CHO), 86.1 (*E* CHO), 117.7 (*E*

*C* C=O), 125.2, 125.8, 126.0, 126.3, 126.6, 127.1, 127.3, 132.4, 135.2, 139.3, 147.9 (*E* CHOT), 165.1 (*E* $CO_2$), 169.1 (*Z* $CO_2$). The NMR assignments were confirmed by 2D spectra (pp S-18 to S-24). The signal for *Z* (*C* C=O) is in the δ 126-127 cluster.

**Reaction of Phenylalkynylketene (8c) with TEMPO**. A solution of diazoketone **9c** (56.4 mg, 0.331 mmol) and TEMPO (146.8 mg, 0.940 mmol) in 4 mL toluene was photolyzed for 3.5 h with 350 nm light. The solvent was evaporated and the product chromatographed (25% EtOAc/hexanes) to give **10c** (43.4 mg, 0.0955 mmol, 29%). $^1$H NMR ($CCl_4$) δ 1.15 (s, 9, 3 $CH_3$), 1.18 (s, 6, 2 $CH_3$), 1.28 (s, 3, $CH_3$), 1.29 (s, 3 $CH_3$), 1.32 (s, 3, $CH_3$), 1.2-1.8 (m, 12, $CH_2$), 6.43 (s, 1, CHO), 7.3-7.6 (m, 5, Ph); $^{13}$C NMR ($CDCl_3$) δ ($CDCl_3$) 16.36, 19.87, 19.95, 20.02, 20.20, 31.40, 31.79, 32.92, 38.47, 38.61, 38.87, 59.36, 59.62, 59.69, 99.09, 124.84, 127.81, 127.88, 130.64, 141.42, 164.11, 213.02; IR ($CDCl_3$) 1947, 1722 cm$^{-1}$; EIMS *m*/*z* 455 ($M^+$, 3), 298 (90), 174 (80), 156 (100).

**Reaction of *t*-Butylketene (8d) with TEMPO**. To a solution of TEMPO (0.475 g, 3.04 mmol) in 3 mL THF was added freshly distilled $Et_3N$ (0.233 mL, 0.169 g, 1.67 mmol) and *t*-Bu$CH_2$COCl (0.211 mL, 0.204 g, 1.52 mmol), and the solution was stirred 24 h at room temperature. To the product was added 10 mL of $CH_2Cl_2$ and 10 mL of 10% $NaHCO_3$ solution, and the layers were separated. The aqueous layer was extracted 3 times with 10 mL protons of $CH_2Cl_2$, and the combined organic layers were dried over $MgSO_4$ and the solvent evaporated. Chromatography (10% EtOAc in hexanes) and then recrystallization from pentane gave **10d**: (97.3 mg, 0.237 mmol, 16%), mp 81-83 °C. $^1$H NMR ($CDCl_3$) δ 1.090 (s, 9H, *t*-Bu), 1.094 (s, 6, 2 $CH_3$), 1.12 (s, 3, $CH_3$), 1.13 (s, $CH_3$), 1.21 (s, 6, 2 $CH_3$), 1.36 (s, 3, $CH_3$), 1.364 (s, 3, $CH_3$), 1.24-1.72 (m, 12, 6 $CH_2$), 4.33 (s, 1, CHO); $^{13}$C NMR ($CDCl_3$) δ 16.96, 17.28, 20.65, 20.76, 20.92, 21.10, 26.60 (3 $CH_3$), 32.81, 32.95, 33.36, 35.07, 35.46, 39.68, 39.76, 40.07, 40.92, 59.79, 60.06, 60.48, 61.75, 87.55, 170.65; IR ($CH_2Cl_2$) 1773 $cm^{-1}$, CIMS *m*/*z* 411 ($MH^+$), 254, 156, 140, 126, 69; HRCIMS *m*/*z* calcd for $C_{24}H_{47}N_2O_3$ 411.3587, found 411.3576.

**Reaction of Phenoxyketene (8e) with TEMPO**. A solution of TEMPO (0.84 g, 5.38 mmol), $Et_3N$ (2.15 mmol) and phenoxyacetyl chloride (0.309 g, 1.81 mmol) in 9.0 mL $CH_2Cl_2$ was stirred 60 h with 0.86 g of 4A molecular sieves at room temperature. The mixture was filtered through Celite and 10 mL of $CH_2Cl_2$ and 10 mL of $NaHCO_3$ solution were added, and the layers were separated. The aqueous layer was extracted 3 times with 10 mL aliquots of $CH_2Cl_2$ and the combined organic layers were dried with $MgSO_4$ and the solvent was evaporated to give a viscous liquid which was chromatographed (7% EtOAc/hexane) and rechromatographed (3% EtOAc/benzene) to give **10e** as a gum (470 mg, 1.054 mmol, 58%); IR ($CH_2Cl_2$) 1779 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.96 (s, 3, $CH_3$), 1.01 (s, 3, $CH_3$), 1.07 (s, 3, $CH_3$), 1.14 (s, 3, $CH_3$), 1.16 (s, 3, $CH_3$), 1.23 (s, 3, $CH_3$), 1.24 (s, 3, 1 $CH_3$), 1.27 (s, 3, $CH_3$), 1.31-1.67 (m, 12, 6 $CH_2$), 5.84 (s, 1, CHO), 6.96-7.29 (m, 5, Ph). $^{13}C$ NMR ($CDCl_3$) δ 16.71, 16.88, 19.93, 20.24, 20.36, 31.40, 31.51, 32.56, 33.27, 38.94, 38.97, 39.84, 40.12, 59.68, 60.13, 60.16, 61.07, 103.22, 116.89, 121.90, 129.22, 156.55, 166.07. EIMS *m*/*z* 447 ($M^+$, 0.5), 290 ($M^+$ -OT, 12), 156 ($TEMPO^+$), 140 ($T^+$, 100). HREIMS *m*/*z* calcd $C_{26}H_{43}N_2O_4$ 447.3223, found 447.3203.

**Reaction of tetramethyleneketene (12) with TEMPO**. A mixture of 2-diazocyclohexanone (20 mg, 0.16 mmol) and TEMPO (63 mg, 0.40 mmol) in 1.5 mL $CDCl_3$ was photolyzed 12 h with 300 nm light. The solvent was evaporated and the product chromatographed (10% EtOAc, hexanes) giving **14** (23 mg, 0.056 mmol, 35%) which was recrystallized from pentane, mp 105-107 °C: $^1H$ NMR ($CDCl_3$) δ 1.02 (s, 6, 2

$CH_3$), 1.10 (s, 6, 2 $CH_3$),1.15 (s, 6, 2 $CH_3$), 1.21 (s, 6, 2 $CH_3$), 1.2-1.8 (m, 12, $CH_2$), 1.8 (m, 4, β-$CH_2$ of $C_4H_8$), 2.0-2.2 (m, 2, α-CH of cyclopentyl *trans* to $CO_2T$), 2.4-2.6 (m, 2, α-CH of cyclopentyl *cis* to $CO_2T$); IR ($CDCl_3$) 1753 $cm^{-1}$; $^{13}C$ NMR ($CDCl_3$) δ 16.91 ($CH_2$), 17.06 ($CH_2$), 20.61 (2 $CH_3$), 20.93 (2 $CH_3$), 26.70 (2 $CH_2$), 32.23 (2 $CH_3$), 33.45 (2 $CH_3$), 37.43 (2 $CH_2$), 39.40 (2 $CH_2$), 40.84 (2 $CH_2$), 59.74 (2 C), 60.32 (2 C), 91.91 (CO), 175.68 ($CO_2$); EIMS *m*/*z* 408 ($M^+$, 0.2) 236 (23), 156 (69), 142 (66), 95 (93), 69 (100); CIMS *m*/*z* 409 ($MH^+$, 0.3), 156 (100), 142 (68), 69 (19); HREIMS *m*/*z* calcd for $C_{24}H_{45}N_2O_3$ ($MH^+$) 409.3430 found 409.3415.

**Reaction of ketene 13 with TEMPO**. A solution of 2-diazo-1-indanone (0.158 g, 1.00 mmol) and TEMPO (0.312 g, 2.00 mmol) in 1.5 mL $CDCl_3$ was irradiated for 48 h with 300 nm light. The solvent was evaporated and the residue chromatographed (5% EtOAc in hexanes) to give **15** as an oil (0.119 g, 27%) which was crystallized from pentane to give a solid, mp 101-103 °C. $^1H$ NMR ($CDCl_3$) δ 0.72 (s, 3, $CH_3$), 0.82 (s, 3, $CH_3$) 0.97 (s, 6, 2 $CH_3$), 1.00 (s, 3, $CH_3$), 1.04 (s, 3, $CH_3$), 1.16 (s, 3, $CH_3$), 1.22 (s, 3, $CH_3$); 1.2-1.7 (m, 12, 6 $CH_2$), 3.62 (d, 2, *J* = 14 Hz, CH), 4.30 (d, 2, *J* = 14 Hz, CH), 7.l-7.3 (m, 4, Ar). $^{13}C$ NMR ($CDCl_3$) δ 16.72, 17.00, 19.85, 20.35, 20.39, 20.47, 31.70 (2 C), 31.92, 33.46, 39.02 (2 C), 40.14, 40.18, 40.26, 58.90, 59.93, 60.08 (2 C), 87.08, 122.51 (2 C), 126.46, 129.03, 142.83, 146.58, 170.81. IR ($CDCl_3$) 1759 $cm^{-1}$. EIMS *m*/*z* 443 ($MH^+$), 156 (74), 142 (29), 126 (58), 83 (100), 69 (98). HRFABMS *m*/*z* calcd for $C_{27}H_{43}N_2O_3$ ($MH^+$) 443.3274, found 443.3247.

**Direct observation of ketenes generated by Wolff rearrangement**

Photolysis of $1.0\times10^{-4}$ M diazoacetophenone (**9a**) in isooctane purged with argon with 350 nm light for 5 min resulted in the disappearance of the UV spectrum of **9a** and the formation of a new spectrum due to **8a** , $\lambda_{max}$ 248.5 nm, and $\varepsilon = 1.2\times10^4$, assuming complete conversion to **8a** (eq 4). Similar photolysis of **9a** ($8.5\times10^{-4}$ M in isooctane) showed another band at 378.0 nm, $\varepsilon = 47$, which may be ascribed to the $n\rightarrow\pi^*$ transition of **8a**. Photolysis of **9a** ($8.5\times10^{-4}$ M in isooctane) for 5 min with 300 and 350 nm light results in complete disappearance of the IR bands of **9a** at 2108 and 1639 $cm^{-1}$, and formation of a new band at 2117 $cm^{-1}$ for **8a** (lit[7d] 2118 $cm^{-1}$ in $CH_3CN$). These absorption bands were fairly long-lived, but upon standing overnight at 5 °C the IR band at 2117 $cm^{-1}$ disappeared and was replaced by one at 1713 $cm^{-1}$, assigned as due to $PhCH_2CO_2H$ (an authentic sample gave 1716 $cm^{-1}$ in isooctane).

Previously photolysis of the alkenyl and alkynyl substituted diazoketones **9b** and **9c** was utilized to form the alkenylketene **8b** and the alkynylketene **8c**,[7d,9a] respectively, whose kinetics of hydration were measured when the ketene was generated by laser flash photolysis (LFP) with fast UV detection.[9a] Similarly these ketenes generated by LFP were also detected by time resolved infrared (TRIR), and their kinetics of amination were measured.[7d] Previous attempts[9c] to detect the ketene **8c** by conventional IR were unsuccessful, and when the reaction was monitored in this way only the products of further photolysis of the ketene were observed (1- and 3-phenylpropyne, phenylallene).[9c] Upon photolysis of the diazoketones **9b** and **9c** in isooctane in an IR cell using 300 and 350 nm lamps the disappearance of the IR absorptions due to **9b** and **9c** and the growth of absorptions due to **8b** (2116.5 $cm^{-1}$, lit[7d] 2116 $cm^{-1}$) and **8c** (2130.9

$cm^{-1}$, lit[7d] 2131.9 $cm^{-1}$) are observed, so that after irradiation for 1 min the absorptions due to **9b** and **9c** have decreased by 90%, and the bands due to **8b** and **8c**, respectively, have grown with equal intensity. Three min after ceasing photolysis the bands due to **8b** had disappeared.

Photolysis of **9b** and **9c** in isooctane led to almost complete disppearance of the absorption due to the diazoketones and the appearance of new strong maxima at 223 and 305 nm for **8b**, and 269 and 284 nm due to **8c**, and bands at 237 and 248 nm due to 1-phenylpropyne. The observed UV absorption of **8c** agreed well with the spectrum previously observed in $H_2O$.[13c]

**Ketene detection and kinetics**

Kinetics of the reaction of the ketenes **8a-c**, and tetramethylene ketene **12** with TEMPO were measured by injecting 20 μL of (3.6 to 8.5)×$10^{-4}$ M of **8a-c** and 0.0115 M **12** in isooctane prepared as above into 1.2 mL of a TEMPO solution in isooctane, and observing the decrease in absorption at 249 nm (**8a**), 287 nm (**8b**), 267 nm (**8c**), and 390 nm (**12**). Good first order plots with stable infinity values were observed, and the derived rate constants are reported in Table 1.

The kinetics of **1** were measured by injecting 30 μL of 0.0215 M **1** in isooctane into 2 mL TEMPO solution in isooctane which had been degassed with a stream of Ar and monitoring the decrease in absorption at 404 nm. For **7** kinetics were measured by injecting 12 μL of 0.662 M **7** into 1.2 mL TEMPO solution in mesitylene and measuring the decrease in absorption at 385 nm. All rate constants (Table 1) are averages of at least two runs.

**Table 3**. Rates of Ketene Reactions with TEMPO

| ($Ph_2C{=}C{=}O$) (**1**) | | ($(Me_3SiC{=}C{=}O)_2$) (**7**) | | |
|---|---|---|---|---|
| [TEMPO](M) | $k_{obs}$ ($s^{-1}\times 10$)[2a] | T(°C) | [TEMPO](M) | $k_{obs}$ ($s^{-1}\times 10^{-3}$)[e] |
| 0.1227 | 4.47 | 86.9[b] | 0.502 | 4.91 |
| 0.1002 | 3.65 | | 0.287 | 2.82 |
| 0.0998 | 3.55 | | 0.0721 | 0.752 |
| 0.0768 | 2.53 | 73.8[c] | 0.502 | 2.50 |
| 0.0601 | 2.24 | | 0.360 | 1.81 |
| 0.0519 | 1.88 | | 0.287 | 1.47 |
| 0.0401 | 1.39 | | 0.216 | 1.04 |
| 0.0200 | 0.729 | | 0.144 | 0.0688 |
| 0.00802 | 0.318 | | 0.0721 | 0.0363 |
| | | 58.8[d] | 0.502 | 0.883 |
| | | | 0.360 | 0.626 |
| | | | 0.144 | 0.259 |

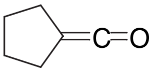
PhCH=C=O (**8a**)

| [TEMPO]($M\times 10^4$) | $k_{obs}$ ($s^{-1}\times 10^{-3}$)[f] |
|---|---|
| 10.62 | 1.44 |
| 8.50 | 1.18 |
| 6.37 | 0.913 |
| 4.25 | 0.647 |
| 2.12 | 0.365 |

**Table 3** (cont'd)

*E*-PhCH=CHCH=C=O (**8b**)

| [TEMPO] ($M \times 10^4$) | $k_{obs}$ ($s^{-1} \times 10^2$)[h] |
|---|---|
| 10.86 | 2.07 |
| 8.68 | 1.62 |
| 6.52 | 1.26 |
| 4.34 | 0.896 |
| 2.17 | 0.441 |


(**12**)

| [TEMPO] (M) | $k_{obs}$ ($s^{-1} \times 10^2$)[i] |
|---|---|
| 0.460 | 1.47 |
| 0.391 | 1.30 |
| 0.326 | 1.04 |
| 0.1833 | 0.646 |
| 0.0916 | 0.378 |

PhC≡CCH=C=O (**8c**)

| [TEMPO]($M\times10^4$) | $k_{obs}$($s^{-1}\times10^{-2}$)[g] |
|---|---|
| 10.62 | 3.84 |
| 8.50 | 3.58 |
| 6.37 | 2.40 |
| 4.25 | 1.52 |
| 2.12 | 0.882 |

[a] 25 °C, in isooctane, $k_{obs} = (0.357\pm0.006)\ M^{-1}\ s^{-1}$ [TEMPO] $+ (2.6\pm43.2) \times 10^{-5}\ s^{-1}$

[b] $k_{obs} = (9.68\pm0.12) \times 10^{-3}\ M^{-1}\ s^{-1}$ [TEMPO] $+ (5.18\pm4.2) \times 10^{-5}\ s^{-1}$

[c] $k_{obs} = (5.04\pm0.07) \times 10^{-3}\ M^{-1}\ s^{-1}$ [TEMPO] $- (1.70\pm2.0) \times 10^{-5}\ s^{-1}$

[d] $k_{obs} = (1.75\pm0.04) \times 10^{-3}\ M^{-1}\ s^{-1}$ [TEMPO] $+ (0.21\pm1.71) \times 10^{-5}\ s^{-1}$

[e] $k_2^{calc} = 1.50 \times 10^{-4}\ M^{-1}\ s^{-1}$ (25.0 °C), $\Delta H^{\ddagger} = 13.8$ kcal/mol, $\Delta S^{\ddagger} = -29.6$ cal $K^{-1}\ M^{-1}$

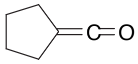
[f] 25°C in isooctane, $k_{obs} = (1.26\pm0.02)\ M^{-1}\ s^{-1}$ [TEMPO] $+ (1.07\pm0.13) \times 10^{-4}\ s^{-1}$.

[g] $k_{obs} = (37.4\pm1.9)\ M^{-1}\ s^{-1}$ [TEMPO] $+ (2.30\pm12.2) \times 10^{-4}\ s^{-1}$

[h] $k_{obs} = (18.4\pm0.4)\ M^{-1}\ s^{-1}$ [TEMPO] $+ (6.20\pm2.71) \times 10^{-4}\ s^{-1}$

[i] $k_{obs} = (2.98\pm0.11) \times 10^{-2}\ M^{-1}\ s^{-1}$ [TEMPO] $+ (1.01\pm0.33) \times 10^{-3}\ s^{-1}$

**Table 4**. Comparative Reactivity of Ketenes with TEMPO and with $H_2O$ at 25 °C

| | $k_2$ (TEMPO) ($M^{-1}$ $s^{-1}$) | log $k$(TEMPO) | $k(H_2O)$ ($s^{-1}$) | log $k(H_2O$ |
|---|---|---|---|---|
| $Ph_2C{=}C{=}O$ | 0.357 | –0.447 | 275[a] | 2.439 |
| $(Me_3SiC{=}C{=}O)_2$ | $1.50 \times 10^{-4}$ | –3.824 | 0.307[b] | –0.513 |
| PhCH=C=O | 1.26 | 0.100 | $4.77 \times 10^{3}$[a] | 3.678 |
| *E*–PhCH=CHCH=C=O | 18.4 | 1.265 | $5.76 \times 10^{3}$[c] | 3.760 |
| PhC≡CCH=C=O | 37.2 | 1.570 | $7.16 \times 10^{4}$[c] | 4.855 |
|  | $2.98 \times 10^{-2}$ | –1.553 | 136[d] | 2.134 |

[a]Ref. 4c [b]Ref. 2c [c]Ref. 9a [d]Ref. 13c