

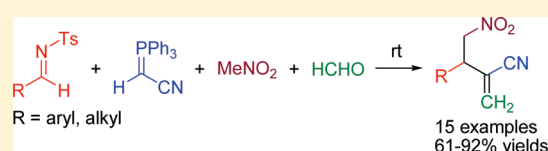
# Four-Component Reaction of *N*-Sulfonylimines, (Cyanomethylene)triphenylphosphorane, Nitromethane, and Formaldehyde for the Synthesis of 3-Substituted 2-Methylene-4-nitrobutanenitriles

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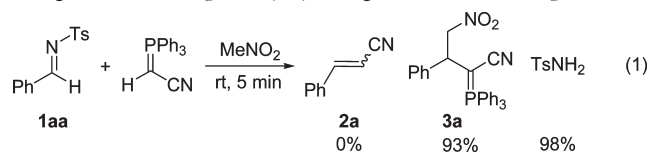
**S** Supporting Information

**ABSTRACT:** An efficient four-component synthesis of 3-substituted 2-methylene-4-nitrobutanenitriles has been developed from *N*-sulfonylimines, (cyanomethylene)triphenylphosphorane, nitromethane, and formaldehyde in the absence of catalysts and additives at room temperature.



Multicomponent reactions are very powerful for the construction of complex organic molecules by transforming in a one-pot manner three or more starting materials into a single product that incorporates portions of all the reactants and exhibit much higher efficiency relative to the sequential synthesis of the same targets by conventional bimolecular reactions.<sup>1</sup> Owing to their intrinsic step-economy, multicomponent reactions are greener than multistep bimolecular reactions through the minimization of the amount of solvents and reagents needed for the reactions and purifications. Hence, there is an increasing demand for the development of multicomponent reactions, especially those with four or more components.<sup>2,3</sup>

In the course of exploring the synthetic utility of carbon–nitrogen bond cleavage,<sup>4,5</sup> we developed a new stereoselective alkene synthesis through the olefination reaction of *N*-sulfonylimines with phosphonium ylides.<sup>5</sup> To our surprise, treatment of *N*-benzylidene-*p*-toluenesulfonamide (**1aa**) with (cyanomethylene)triphenylphosphorane in nitromethane at room temperature did not at all result in the formation of  $\alpha,\beta$ -unsaturated nitrile **2a** (eq 1). Instead, phosphonium ylide **3a** was obtained in 93% yield after crystallization from ethyl acetate/petroleum ether (5:1), and another product was identified as *p*-toluenesulfonamide. This result is in sharp contrast to the corresponding imine olefination reaction between these two reactants occurred in many other solvents such as toluene, chloroform, ethyl acetate, tetrahydrofuran, acetonitrile, *N,N*-dimethylformamide, dimethyl sulfoxide, and methanol.<sup>5c</sup> It is clear that the solvent of nitromethane changes the reaction pathway by acting as a carbon nucleophile.<sup>6</sup>



The efficient three-component synthesis of phosphonium ylide **3a** prompted us to develop a new four-component reaction

according to the following reaction pathway (Scheme 1). Initial addition of (cyanomethylene)triphenylphosphorane to *N*-sulfonylimine **1** results in the formation of betaine **4**, which undergoes rapid proton transfer to give phosphonium ylide **5**.<sup>5c,7</sup> Elimination of the sulfonamide group from phosphonium ylide **5** results in the formation of vinylphosphonium salt **6**. Nitromethane is sufficiently acidic to be deprotonated by the resulting sulfonamide anion and subsequently undergoes Michael addition to vinylphosphonium salt **6** to give phosphonium ylide **3**. Assuming that phosphonium ylide **3** could undergo the Wittig reaction with formaldehyde, we envisioned a four-component reaction of *N*-sulfonylimines, (cyanomethylene)triphenylphosphorane, nitromethane, and formaldehyde leading to 3-substituted 2-methylene-4-nitrobutanenitriles **7**, Rauhut–Carrier-type products that have not been accessed so far by the corresponding reaction of nitroalkenes with acryl nitrile.<sup>8,9</sup>

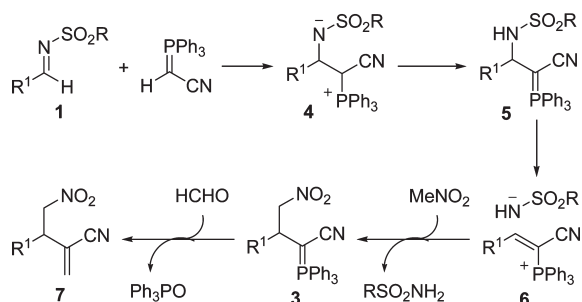
In continuation of our exploration of new multicomponent reactions,<sup>2d,10</sup> we carried out the following experiments to test our hypothesis. The mixture of *N*-sulfonylimine **1aa** and (cyanomethylene)triphenylphosphorane in nitromethane was stirred at room temperature for 5 min, after which time formalin was added. The resulting mixture was stirred for 8 h, and 2-methylene-4-nitro-3-phenylbutanenitrile (**7a**) was obtained in 92% yield (Table 1, entry 1). Encouraged by this result, we evaluated a number of *N*-sulfonyl groups on the imine nitrogen atom in the four-component reaction (Table 1, entries 2–6). In general, the employment of an arenesulfonyl group led to a better yield than that of an alkanesulfonyl group. Nevertheless, the yield was not improved further.<sup>11</sup>

A broad range of aromatic, heteroaromatic, and aliphatic *N*-(*p*-toluenesulfonyl)imines smoothly reacted with (cyanomethylene)triphenylphosphorane, nitromethane, and formaldehyde at room

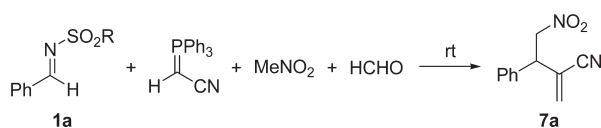
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**Scheme 1.** Proposed Four-Component Reaction of *N*-Sulfonylimines, (Cyanomethylene)triphenylphosphorane, Nitromethane, and Formaldehyde



**Table 1.** Survey of the *N*-Sulfonyl Groups<sup>a</sup>



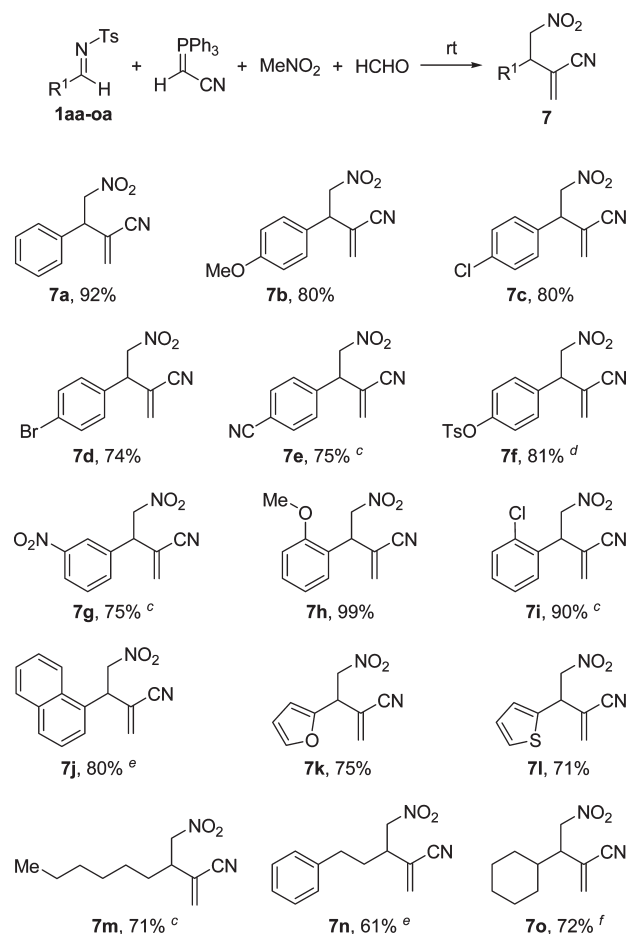
entry	imine	R	yield <sup>b</sup> (%)
1	1aa	4-MeC <sub>6</sub> H <sub>4</sub>	92
2	1ab	4-MeOC <sub>6</sub> H <sub>4</sub>	90
3	1ac	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	82
4	1ad	2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	88
5	1ae	1-naphthyl	90
6	1af	Me	72

<sup>a</sup> Reaction conditions: *N*-sulfonylimine **1a** (0.30 mmol), (cyanomethylene)triphenylphosphorane (0.36 mmol), nitromethane (0.30 mL), rt, 5 min; then formaldehyde (0.60 mmol), rt, 8 h. <sup>b</sup> Isolated yield.

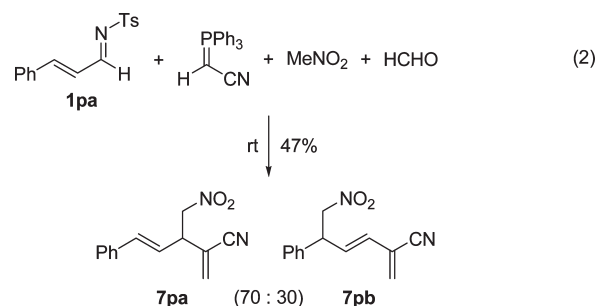
temperature to give structurally diverse 3-substituted 2-methylene-4-nitrobutanenitriles **7** in good to excellent yields (Scheme 2). These Rauhut–Currier-type products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and HRMS spectroscopic analyses, and the structure of product **7f** was further confirmed by single-crystal X-ray analysis (see the Supporting Information). As demonstrated by the results summarized in Scheme 2, both electron-withdrawing and electron-donating groups were successfully introduced into the products by employing the *N*-sulfonylimines bearing such groups on the aromatic rings. Attempts to extend this four-component reaction to an ester-, an amide-, or a ketone-stabilized phosphonium ylide were unsuccessful. Moreover, no desired product was obtained from the four-component reaction when nitromethane and formaldehyde were replaced with nitroethane and benzaldehyde, respectively.

The four-component reaction with an  $\alpha,\beta$ -unsaturated *N*-(*p*-toluenesulfonyl)imine was found to give a mixture of two regioisomeric products in moderate yields. For example, the reaction of *N*-sulfonylimine **1pa**, (cyanomethylene)triphenylphosphorane, nitromethane, and formaldehyde proceeded at room temperature to afford an inseparable 70:30 mixture of regioisomers **7pa** and **7pb** (eq 2). Moreover, the regioselectivity was not enhanced by performing the reaction at lower temperature.<sup>12</sup>

**Scheme 2.** Four-Component Reaction of *N*-Sulfonylimines, (Cyanomethylene)triphenylphosphorane, Nitromethane, and Formaldehyde<sup>a,b</sup>



<sup>a</sup> Reaction conditions: *N*-sulfonylimine **1aa-oa** (0.30 mmol), (cyanomethylene)triphenylphosphorane (0.36 mmol), nitromethane (0.30 mL), rt, 5 min; then formaldehyde (37% by mass in water, 0.60 mmol), rt, 6–30 h. <sup>b</sup> Isolated yields are shown. <sup>c</sup> The corresponding mixture was stirred for 30 min before the addition of formaldehyde. <sup>d</sup> The structure was confirmed by single-crystal X-ray analysis. <sup>e</sup> 0.90 mmol of formaldehyde was used. <sup>f</sup> 1.8 mmol of formaldehyde was used.



In summary, we have developed an unprecedented four-component synthesis of Rauhut–Currier-type products from readily accessible starting materials through carbon–nitrogen bond cleavage. In the absence of catalysts and additives, the four-component reaction of *N*-sulfonylimines, (cyanomethylene)triphenylphosphorane, nitromethane, and formaldehyde proceeds

smoothly at room temperature to afford structurally diverse 3-substituted 2-methylene-4-nitrobutanenitriles in good to excellent yields. This study not only adds a useful entry to increasingly demanding multicomponent reactions but also significantly extends the synthetic utility of carbon–nitrogen bond cleavage.

## EXPERIMENTAL SECTION

**General Information.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using tetramethylsilane as an internal reference.  $^{31}\text{P}$  NMR spectra were recorded using 85% phosphoric acid as an external reference. Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) were expressed in ppm and Hz, respectively. Melting points were uncorrected. *N*-Sulfonylimines and (cyanomethylene)triphenylphosphorane were prepared according to known procedures.<sup>5</sup>

**Three-Component Synthesis of Phosphonium Ylide 3a.** A mixture of *N*-sulfonylimine **1aa** (259 mg, 1.0 mmol) and (cyanomethylene)triphenylphosphorane (361 mg, 1.2 mmol) in nitromethane (1.0 mL) was stirred under nitrogen at room temperature for 5 min and concentrated. The residue was crystallized from ethyl acetate/petroleum ether (5:1), and the resulting solid was collected by filtration and dried in vacuum to give phosphonium ylide **3a** (420 mg, 93%) as a yellow solid: mp 172–175 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63–7.46 (m, 15H), 7.26–7.14 (m, 5H), 4.99 (dd,  $J = 12.0, 9.6$  Hz, 1H), 4.64–4.58 (m, 1H), 3.50–3.42 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7 (d,  $J = 1.3$  Hz), 133.8, 133.7, 133.0 (d,  $J = 2.8$  Hz), 129.2 (d,  $J = 12.1$  Hz), 128.8, 128.5 (d,  $J = 14.8$  Hz), 127.2, 126.9, 125.2 (d,  $J = 90.6$  Hz), 80.4 (d,  $J = 7.7$  Hz), 41.7 (d,  $J = 12.7$  Hz), 12.9 (d,  $J = 140.2$  Hz); IR (film)  $\nu$  2925, 2130, 1599, 1587, 1550, 1482, 1453, 1379  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR (127 MHz,  $\text{CDCl}_3$ )  $\delta$  25.9; HRMS (EI) calcd for  $\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$  (M) 450.1497, found 450.1502. Anal. Calcd for  $\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$ : C, 74.66; H, 5.15; N, 6.22. Found: C, 74.94; H, 5.13; N, 6.21.

**General Procedure for the Four-Component Reaction of *N*-Sulfonylimines, (Cyanomethylene)triphenylphosphorane, Nitromethane, and Formaldehyde.** To nitromethane (0.30 mL) under nitrogen were added *N*-sulfonylimine **1aa–oa** (0.30 mmol) and (cyanomethylene)triphenylphosphorane (109 mg, 0.36 mmol). The mixture was stirred at room temperature for 5 min (or 30 min as specified in Scheme 2). To the resulting mixture was added formalin (37%, 0.045 mL, 0.60 mmol, or another amount as specified in Scheme 2). The mixture was stirred at room temperature for 8 h (for **7c** and **7l**, 6 h; for **7f**, 10 h; for **7j**, 15 h; for **7n**, 18 h; for **7m**, 24 h; for **7o**, 30 h). The mixture was purified directly by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (8:1 to 3:1), to give compound **7**.

**2-Methylene-4-nitro-3-phenylbutanenitrile (7a):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45–7.35 (m, 3H), 7.30–7.25 (m, 2H), 6.06 (s, 1H), 5.93 (s, 1H), 4.96 (dd,  $J = 13.2, 9.0$  Hz, 1H), 4.79 (dd,  $J = 13.2, 6.6$  Hz, 1H), 4.47–4.39 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  134.7, 133.0, 129.7, 129.1, 127.6, 122.3, 116.7, 76.8, 48.1; IR (film)  $\nu$  3023, 2925, 2228, 1622, 1602, 1559, 1499, 1455, 1377  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2$  (M) 202.0742, found 202.0738.

**3-(4-Methoxyphenyl)-2-methylene-4-nitrobutanenitrile (7b):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22–7.16 (m, 2H), 6.95–6.88 (m, 2H), 6.02 (s, 1H), 5.89 (s, 1H), 4.92 (dd,  $J = 13.2, 9.0$  Hz, 1H), 4.74 (dd,  $J = 13.2, 6.9$  Hz, 1H), 4.41–4.33 (m, 1H), 3.80 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0, 132.4, 128.7, 126.4, 122.5, 116.8, 114.9, 76.9, 55.4, 47.3; IR (film)  $\nu$  3022, 2963, 2938, 2841, 2228, 1612, 1585, 1560, 1515, 1465, 1377  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$  (M) 232.0848, found 232.0860.

**3-(4-Chlorophenyl)-2-methylene-4-nitrobutanenitrile (7c):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45–7.38 (m, 2H), 7.30–7.21 (m, 2H), 6.09 (s, 1H), 5.95 (d,  $J = 0.6$  Hz, 1H), 4.95 (dd,  $J = 13.2, 8.7$  Hz, 1H), 4.78 (dd,  $J = 13.2, 6.9$  Hz, 1H), 4.48–4.40 (m, 1H);

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  135.2, 133.2, 129.9, 129.0, 121.9, 116.5, 76.5, 47.4; IR (film)  $\nu$  3055, 2987, 2227, 1620, 1561, 1494, 1376  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{11}\text{H}_9\text{N}_2\text{O}_2\text{Cl}$  (M) 236.0353, found 236.0360.

**3-(4-Bromophenyl)-2-methylene-4-nitrobutanenitrile (7d):** yellowish oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58–7.52 (m, 2H), 7.20–7.13 (m, 2H), 6.07 (s, 1H), 5.93 (d,  $J = 0.8$  Hz, 1H), 4.92 (dd,  $J = 13.2, 8.8$  Hz, 1H), 4.76 (dd,  $J = 13.2, 7.2$  Hz, 1H), 4.44–4.37 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  133.7, 133.2, 132.8, 129.2, 123.3, 121.7, 116.4, 76.4, 47.4; IR (film):  $\nu$  3023, 2921, 2226, 1621, 1590, 1557, 1490, 1434, 1377  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{11}\text{H}_9\text{N}_2\text{O}_2\text{Br}$  (M) 279.9847, found 279.9871.

**3-(4-Cyanophenyl)-2-methylene-4-nitrobutanenitrile (7e):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.4$  Hz, 2H), 7.44 (d,  $J = 8.4$  Hz, 2H), 6.13 (s, 1H), 6.00 (s, 1H), 4.97 (dd,  $J = 13.2, 8.4$  Hz, 1H), 4.82 (dd,  $J = 13.2, 6.9$  Hz, 1H), 4.55–4.47 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.9, 134.0, 133.3, 128.5, 120.9, 118.0, 116.2, 113.1, 76.0, 47.6; IR (film)  $\nu$  3023, 2925, 2256, 2232, 1611, 1561, 1508, 1376  $\text{cm}^{-1}$ ; HRMS (APCI) calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_3\text{O}_2$  (M + H)<sup>+</sup> 228.0773, found 228.0763.

**2-Methylene-4-nitro-3-(4-tosyloxyphenyl)butanenitrile (7f):** white solid; mp 98–100 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71–7.67 (m, 2H), 7.34–7.30 (m, 2H), 7.24–7.20 (m, 2H), 7.07–7.02 (m, 2H), 6.07 (s, 1H), 5.92 (d,  $J = 0.8$  Hz, 1H), 4.90 (dd,  $J = 13.2, 8.8$  Hz, 1H), 4.74 (dd,  $J = 13.2, 6.8$  Hz, 1H), 4.44–4.38 (m, 1H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  149.9, 145.9, 133.7, 133.3, 132.1, 130.0, 129.0, 128.5, 123.5, 121.7, 116.4, 76.5, 47.3, 21.7; IR (film)  $\nu$  3025, 2924, 2226, 1621, 1598, 1557, 1504, 1435, 1376  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_5\text{S}$  (M) 372.0780, found 372.0803.

**2-Methylene-4-nitro-3-(3-nitrophenyl)butanenitrile (7g):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30–8.24 (m, 1H), 8.17 (s, 1H), 7.71–7.61 (m, 2H), 6.16 (s, 1H), 6.04 (s, 1H), 5.01 (dd,  $J = 13.5, 8.4$  Hz, 1H), 4.87 (dd,  $J = 13.5, 7.2$  Hz, 1H), 4.64–4.56 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  148.8, 136.8, 134.1, 133.7, 130.8, 124.1, 122.8, 121.0, 116.2, 76.0, 47.3; IR (film)  $\nu$  3022, 2925, 2228, 1621, 1562, 1535, 1375, 1352  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}_4$  (M + H)<sup>+</sup> 248.0671, found 248.0667.

**3-(2-Methoxyphenyl)-2-methylene-4-nitrobutanenitrile (7h):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38–7.28 (m, 1H), 7.22–7.15 (m, 1H), 7.01–6.89 (m, 2H), 6.04 (s, 1H), 5.91 (s, 1H), 4.94 (dd,  $J = 14.4, 10.8$  Hz, 1H), 4.85–4.75 (m, 2H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 132.8, 130.1, 128.2, 123.1, 121.6, 121.2, 117.1, 111.4, 75.8, 55.5, 42.1; IR (film)  $\nu$  3022, 2943, 2842, 2226, 1621, 1601, 1589, 1557, 1494, 1438, 1377  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$  (M) 232.0848, found 232.0872.

**3-(2-Chlorophenyl)-2-methylene-4-nitrobutanenitrile (7i):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50–7.44 (m, 1H), 7.38–7.28 (m, 3H), 6.12 (s, 1H), 6.03 (d,  $J = 0.3$  Hz, 1H), 5.08–4.90 (m, 2H), 4.82 (dd,  $J = 13.2, 6.3$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  134.2, 132.2, 130.8, 130.2, 128.0, 127.9, 120.5, 116.5, 75.6, 44.0; IR (film)  $\nu$  3062, 2923, 2226, 1621, 1593, 1557, 1476, 1435, 1376  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{11}\text{H}_9\text{N}_2\text{O}_2\text{Cl}$  (M) 236.0353, found 236.0365.

**2-Methylene-3-(1-naphthyl)-4-nitrobutanenitrile (7j):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 8.4$  Hz, 1H), 7.96–7.85 (m, 2H), 7.66–7.40 (m, 4H), 6.13 (s, 1H), 6.02 (s, 1H), 5.34 (dd,  $J = 9.0, 5.7$  Hz, 1H), 5.07 (dd,  $J = 13.5, 9.3$  Hz, 1H), 4.91 (dd,  $J = 13.5, 5.7$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  134.3, 133.5, 130.7, 130.2, 129.8, 129.6, 127.5, 126.5, 125.5, 124.8, 121.9, 116.8, 76.5, 42.9; IR (film):  $\nu$  3055, 2920, 2225, 1620, 1598, 1557, 1512, 1435, 1376  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2$  (M) 252.0899, found 252.0916.

**3-(2-Furyl)-2-methylene-4-nitrobutanenitrile (7k):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 1.2$  Hz, 1H), 6.40–6.37 (m, 1H), 6.33 (d,  $J = 3.3$  Hz, 1H), 6.12 (s, 1H), 5.98 (s, 1H), 4.94–4.79 (m, 2H), 4.60–4.52 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  147.4, 143.6, 134.5, 119.7, 116.2, 111.0, 108.9, 75.0, 42.4; IR (film)  $\nu$

3059, 2924, 2228, 1622, 1565, 1556, 1504, 1433, 1376  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_9\text{H}_8\text{N}_2\text{O}_3$  (M) 192.0535, found 192.0550.

**2-Methylene-4-nitro-3-(2-thienyl)butanenitrile (7l):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.30 (m, 1H), 7.05–7.00 (m, 2H), 6.08 (s, 1H), 5.99 (s, 1H), 4.93 (dd,  $J = 13.2, 9.0$  Hz, 1H), 4.82 (dd,  $J = 13.2, 6.3$  Hz, 1H), 4.71 (dd,  $J = 9.0, 6.3$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  136.5, 133.5, 127.8, 126.4, 121.9, 116.2, 77.0, 43.6; IR (film)  $\nu$  3022, 2229, 1622, 1561, 1432, 1377  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_9\text{H}_8\text{N}_2\text{O}_2\text{S}$  (M) 208.0306, found 208.0331.

**2-Methylene-3-(nitromethyl)nonanenitrile (7m):** yellowish oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.02 (s, 1H), 5.88 (d,  $J = 0.4$  Hz, 1H), 4.52–4.42 (m, 2H), 3.15–3.07 (m, 1H), 1.64–1.50 (m, 2H), 1.40–1.25 (m, 8H), 0.89 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  134.0, 122.1, 116.0, 77.8, 43.9, 31.5, 30.1, 28.8, 26.6, 22.6, 14.1; IR (film)  $\nu$  2930, 2225, 1623, 1556, 1463, 1434, 1379  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{19}\text{N}_2\text{O}_2$  (M + H) $^+$  211.1447, found 211.1436.

**2-Methylene-3-(nitromethyl)-5-phenylpentanenitrile (7n):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28–7.05 (m, 5H), 6.00 (s, 1H), 5.80 (s, 1H), 4.48–4.32 (m, 2H), 3.10–3.00 (m, 1H), 2.75–2.62 (m, 1H), 2.56–2.43 (m, 1H), 1.92–1.74 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.7, 134.8, 128.9, 128.4, 126.7, 121.7, 115.9, 77.7, 43.2, 32.7, 31.6; IR (film)  $\nu$  3026, 2928, 2225, 1621, 1604, 1557, 1497, 1455, 1379  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2$  (M) 230.1055, found 230.1051.

**3-Cyclohexyl-2-methylene-4-nitrobutanenitrile (7o):** yellowish oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.02 (s, 1H), 5.81 (s, 1H), 4.65 (dd,  $J = 12.6, 4.5$  Hz, 1H), 4.50 (dd,  $J = 12.6, 11.1$  Hz, 1H), 2.94–2.82 (m, 1H), 1.84–1.50 (m, 6H), 1.36–0.96 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  134.5, 121.6, 116.5, 76.4, 49.7, 38.1, 30.8, 30.4, 29.8, 26.0, 25.9; IR (film)  $\nu$  3022, 2931, 2855, 2225, 1622, 1555, 1450, 1379  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2$  (M) 208.1212, found 208.1221.

**Four-Component Reaction of  $\alpha,\beta$ -Unsaturated *N*-Sulfonylimine 1pa, (Cyanomethylene)triphenylphosphorane, Nitromethane, and Formaldehyde.** To nitromethane (0.30 mL) under nitrogen were added *N*-sulfonylimine **1pa** (85.5 mg, 0.30 mmol), and (cyanomethylene)triphenylphosphorane (109 mg, 0.36 mmol). The mixture was stirred at room temperature for 30 min. To the resulting mixture was added formalin (37%, 0.045 mL, 0.60 mmol). The mixture was stirred at room temperature for 36 h and purified directly by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (5:1), to give an inseparable 70:30 mixture of regioisomers **7pa** and **7pb** (32.0 mg, 47%) as a yellowish oil. Major isomer **7pa**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.20 (m, 5H), 6.65 (d,  $J = 16.0$  Hz, 1H), 6.07 (dd,  $J = 16.0, 8.0$  Hz, 1H), 6.08 (s, 1H), 5.98 (d,  $J = 1.2$  Hz, 1H), 4.72 (dd,  $J = 12.8, 8.4$  Hz, 1H), 4.63 (dd,  $J = 12.8, 6.8$  Hz, 1H), 4.03–3.96 (m, 1H). Minor isomer **7pb**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.20 (m, 5H), 6.32 (dd,  $J = 15.6, 8.0$  Hz, 1H), 6.13 (d,  $J = 15.6$  Hz, 1H), 5.92 (s, 1H), 5.82 (s, 1H), 4.69 (d,  $J = 7.2$  Hz, 2H), 4.36–4.29 (m, 1H); HRMS (EI) calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$  (M) 228.0899, found 228.0924.

## ASSOCIATED CONTENT

**Supporting Information.** Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for products and crystal data of compound **7f**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) Product **7a** was obtained in 20% yield when *N*-sulfonylimine **1aa** was replaced with PhCH=NPMP (PMP = 4-methoxyphenyl) in the four-component reaction. The mixture of PhCH=NPMP and (cyano-methylene)triphenylphosphorane in nitromethane was stirred at room temperature for 1.5 h before the addition of formaldehyde.

(12) A 63:37 mixture of regioisomers **7pa** and **7pb** was obtained in 51% yield from the four-component reaction carried out at 0 °C.