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Catalytic 1,2-Dicyanation of Alkynes by Palladium(II) under Aerobic Conditions

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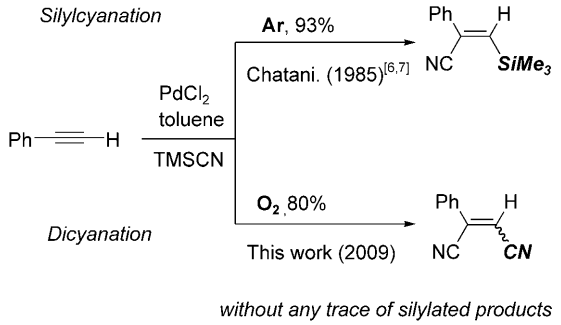
Abstract: A stereoselective 1,2-dicyanation of various alkynes in the presence of trimethylsilyl cyanide (TMSCN) by palladium(II) catalysis under aerobic conditions is investigated. This reaction includes two cyanation pathways, *syn*- and *anti*-cyanopalladation to alkynes that are activated by Pd(II). High *syn*-selectivity was observed in the reaction using terminal alkynes that have bulky substituents at a propargyl position and aliphatic internal alkynes. Furthermore, a dramatic acceleration was observed with substrates having an *N*-arenesulfonyl functionality at a propargyl position, this indicates that both sulfoxide and carbon-carbon triple bond act as Lewis bases to Pd(II).

Keywords: alkynes; cyanation; oxygen; palladium

Introduction

A cyano group is one of the most important functionalities in organic synthesis because it has been considered to be an equivalent to carbonyl, carboxyl, amino and hydroxymethyl groups and its introduction, particularly to carbon-carbon multiple bonds, has been one of the major topics in synthetic organic chemistry.[1] Palladium[2] and nickel[3] chemistry have been mainly focused to achieve such transformations. Very recently, we reported a catalytic 1,2-dicyanation of various alkynes using TMSCN with Pd(II) under an oxygen atmosphere (1 atm),[4] and this protocol can be recognized as a unique cyanation of alkynes.[5] As shown in Scheme 1, treatment of phenylacetylene and TMSCN with $PdCl_2$ under an oxygen atmosphere proceeded *via* 1,2-dicyanation effectively. Although Chatani and co-workers have reported the palladium-catalyzed silylcyanation of terminal alkynes under argon,[6] our protocol enables the realization of the 1,2-dicyanation under an oxygen atmosphere (Scheme 1). This novel catalytic cyanation did not give any trace of silylated products and these interesting results were sufficient to prompt us to examine the mechanistic perspective and origin of stereoselectivity. In this article, we report on the catalytic 1,2-dicyanation in detail (scope, limitation and perspective) with *syn*- and *anti*-cyanopalladation as key catalytic processes.

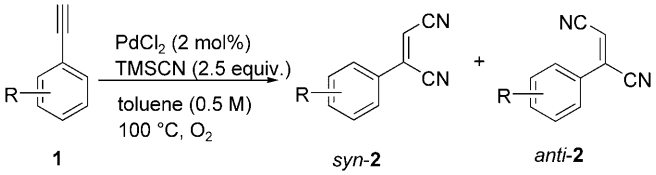


Scheme 1. Pd-catalyzed cyanation of phenylacetylene with TMSCN.

Results and Discussion

In the beginning, we investigated the scope of substrates in the 1,2-dicyanation using aromatic alkynes. After a survey of the reaction conditions, we realized that the best result was obtained under following conditions: $PdCl_2$ (2 mol%) with TMSCN (2.5 equiv.) in toluene (0.5 M) under oxygen (1 atm) at 100 °C. The results of several aromatic alkynes are shown in Table 1. The reactions effectively proceeded to give the corresponding 1,2-dicyano adducts (**2a**–**e**) with a range of 50–82% yields. In particular, the aryl–Br

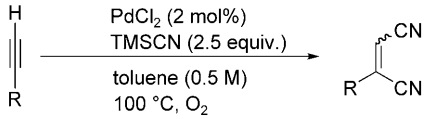
Table 1. 1,2-Dicyanation of aromatic alkynes.



1 *syn*-**2** *anti*-**2**

Entry	R	Time [h]	Yield [%]	*syn/anti*
1	**1a**: H	14	**2a**: 80	2.5:1
2	**1b**: 4-CF_3	17	**2b**: 50	3:1
3	**1c**: 4-MeO	17	**2c**: 81	3:1
4	**1d**: 2-MeO	15	**2d**: 74	2:1
5	**1e**: 4-Br	17	**2e**: 82	3:1

Table 2. 1,2-Dicyanation of aliphatic alkynes.



1 **2**

Entry	R	Time [h]	Yield [%]	*syn/anti*
1	**1f**: $AcO(CH_2)_3$	15	**2f**: 80	2:1
2	**1g**: $BnO(CH_2)_3$	14	**2g**: 72	1:1
3	**1h**: $TBDPSO(CH_2)_3$	14	**2h**: 77	1.5:1
4	**1i**: $TBSO(CH_2)_3$	14	**2i**: 50	2:1
5	**1j**: $XCO(CH_2)_2$[a]	14	**2j**: 72	1:1
6	**1k**: $PhN(Ts)CH_2$	16	**2k**: 78	1:1
7	**1m**: *n*-Hex	16	**2m**: 79	1:1
8	**1n**: *c*-Hex	16	**2n**: 51	3:1

[a] X = 4-morpholinyl.

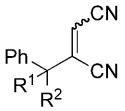
bond was inert during the reaction (entry 5), this indicates Pd(0) species would not be concerned in a catalytic cycle.[7] As given in Table 1, the stereoselectivity observed with up to 3:1 of *syn*/*anti*-adducts was not influenced by the electronic or steric effects of the aromatic rings. On the other hand, the chemical yields were found to be dependent on substituents. The reaction of **1b** which has an electron-withdrawing group (CF_3) gave **2b** in 50% yield which is lower than with H and an MeO group (entries 1–3). These results suggest the electron density of C≡C triple bond is important to be activated by Pd(II) for the efficient dicyanation.

Further modification to use other metal catalysts (Ni and Pt), cyanating agents [*n*-Bu_3SnCN, $Me_2(OH)CN$], ligands (phosphines, phosphites, COD, isonitrile and pyridine derivatives) and additives (Ag and Cu salts and TMSOTf) all failed to improve the chemical yield or stereoselectivity. The reaction of **1a** with a stoichiometric amount of $Pd(CN)_2$ under argon did not furnish the 1,2-dicyanation at all. Finally, careful investigations revealed that there is no interconversion between *syn*- and *anti*-adducts under the reaction conditions. For example, the treatment of *syn*-**2a** under the optimized conditions gave no products and was recovered quantitatively.

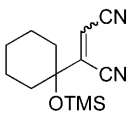
In the case of aliphatic terminal alkynes, the reaction also proceeded with wide tolerance of functionalities, including acetate, ethers and amides, to give **2f–k** in moderate to good yields (Table 2, entries 1–6). Based on the results that **1n** gave slightly better *syn*-selectivity than **1m** (entry 7 *vs.* 8), the stereoselectivity could be influenced by substituents at the propargyl position.

Next, we examined the reaction of substrates bearing a tetrasubstituted carbon at a propargyl position in the presence of 5 mol% of catalyst (Figure 1). As expected, **2o** was obtained from the corresponding alkyne with high *syn*-selectivity. Other *syn*-products including an alkyl ether (**2p**) and a fully carbon-substituted stereogenic center (**2q**) were obtained in the respective yields of 53 and 63% with high selectivity. Tetrasubstitution was essential for high *syn*-selectivity regardless of substitution pattern (alkyl, aryl, alkoxy, siloxy and cycloalkyl) (**2r–t**) and tritylacetylene gave *syn*-**2u**, exclusively.

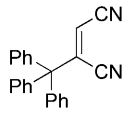
Because the molecular oxygen is essential for this catalytic cyanation, we examined the PdO_2 as a promoter in the absence of oxygen (Table 3). A Pd complex, $(PPh_3)_2PdO_2$ was prepared according to the re-



2o: R^1 = Me, R^2 = OTMS, 77% (11:1)
2p: R^1 = Et, R^2= OMe, 53% (11:1)
2q: R^1 = Me, R^2= *n*-Pr, 63% (15:1)
2r: R^1 = Et, R^2= OTMS, 86% (13:1)
2s: R^1 = Ph, R^2= OTMS, 79% (12:1)



2t: 52% (25:1)

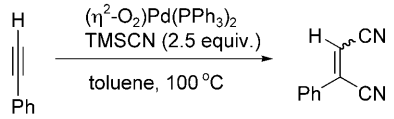


2u: 72% (syn only)

Ten mol% of $PdCl_2$ was used.

Figure 1. Products, yields and *syn/anti* ratios in the 1,2-dicyanation of terminal alkynes bearing a tetrasubstituted carbon at the propargyl position.

Table 3. Reaction of **1a** with palladium oxide.



1a **2a**

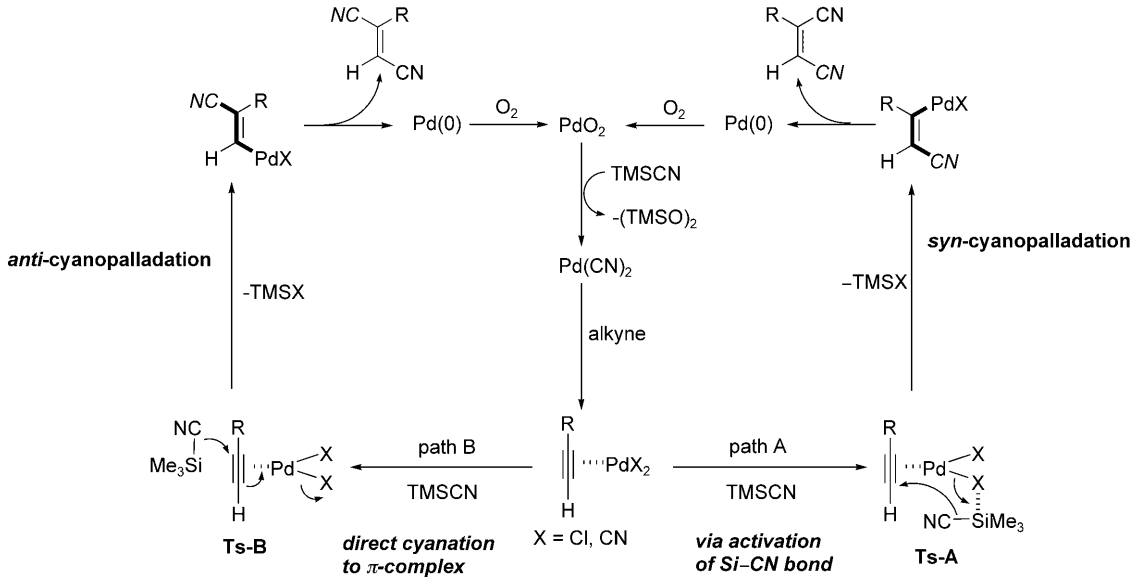
Entry	Pd complex	Conditions	Results
1	50 mol%	Ar, 17h	36% (*syn/anti* = 5/1)
2	2 mol%	O_2, 12 h	72% (*syn/anti* = 3/1)

ported procedure[8] and employed in the 1,2-dicyanation reaction under argon atmosphere. Although no re-oxidation process of the Pd(0) species was present under these conditions, the above complex (50 mol%) proceeded the reaction to give 36% of **2a** (entry 1). This complex also catalyzed the reaction under the standard conditions to give a similar result as in Table 1 (entry 2). These results suggest that PdO_2, generated by the oxidation of Pd(0), is proposed to be one of the important species in a catalytic cycle.

Based on above results, we herein propose new palladium-catalyzed cyanation pathways including nucleophilic attack of C≡N to C≡C triple bond (Scheme 2). The reaction is triggered by activation of terminal alkynes by Pd(II) and the resulting π-complex reacts with external TMSCN. According to the facts that 1) the selectivity observed in **2** was quite dependent on the structure of the substrates and 2) **1o–u** gave higher *syn*-selectictivity, we herein propose different cyanation pathways. Path A shows a cyanation at the terminal carbon *via* activation of carbon-silicon bond, that is, X on a Pd complex acts as a Lewis base. An Si–CN bond can be activated to promote nucleophilic attack giving ***syn*-cyanopalladation**. On the other hand, direct cyanation into an internal carbon can be proposed to explain the formation of *anti*-adducts.[9] This cyanation is occurred at the more substituted carbon (path B: ***anti*-cyanopalladation)** and could be prevented by bulky substituents at the propargyl position due to steric effects. As mentioned above, these cyanopalladations could be triggered by *nucleophilic* cyanation by the *external* CN source, because a CN group on Pd(II) acts as a pseudohalide and is not feasible to be transferred to alkynes directly.[1] The resulting cyanoalkenyl-palladium cyanides give the products by reductive elimination together with Pd(0), which is quickly converted to $Pd(CN)_2$, probably *via* PdO_2. Based on this proposal, bulkier substituents would prevent the initial cyanation to the internal carbon (path B) and seem to be reasonable to explain the high *syn*-selectivity shown in Figure 1.

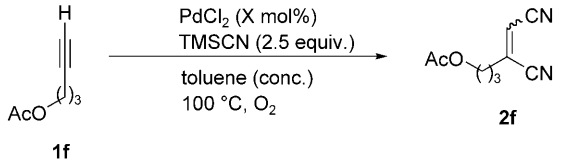
An additional study on concentration effects[9] would also support the above plausible cyanation pathways. As shown in Table 4, the stereoselectivity of **2f** was strongly influenced by the concentration of the substrate and the *syn*-adduct was predominant under highly diluted conditions (entries 1–6) or lower catalyst loading (entries 7–9) when **1f** was used as a substrate. These results suggest that the formation of the *syn*-adduct is preferred because the activation of both TMSCN and alkyne by Pd(II) (**Ts-A**) seems to be more feasible than direct cyanation to π-complex (**Ts-B**) under high dilution conditions.

Having succeeded in the development of Pd-catalyzed 1,2-dicyantion using terminal alkynes, we next focused on internal alkynes (Table 5). Because no reaction was observed under the above conditions



Scheme 2. Plausible catalytic cycle for the 1,2-dicyanation of terminal alkynes.

Table 4. Concentration effect on the catalytic 1,2-dicyanation of **1f**.



Entry	X	Conc. (M)	Time [h]	Yield [%][a]	*syn/anti*
1	2	2.0	14	71	0.8:1
2	2	1.0	13	73	0.9:1
3[b]	2	0.5	15	80	2.0:1
4	2	0.25	13	58	2.4:1
5	2	0.1	14	55	4.2:1
6	2	0.05	14	27	14:1
7	10	0.5	16	84	0.6:1
8	5	0.5	16	80	0.7:1
9	1	0.5	16	17	2.5:1

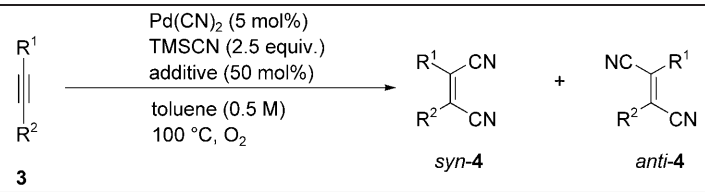
[a] Based on isolated *syn*-adduct.
[b] The result of Table 2 (entry 1).

(entry 1), we surveyed the additives that could generate highly reactive palladium species. In the reaction of **3a**, the combination of $Pd(CN)_2$ with TMSOTf,[10] which would afford a cationic Pd complex or $Pd(OTf)_2$, was found to be the most effective after careful screening of a combination of Pd sources and additives, giving the desired adduct *syn*-**4a**, exclusively (entry 2). The Lewis acidity of the additive was also important. For example, TMSOMs did not promote the reaction at all (entry 3). Although **3b** also gave *syn*-**4b** in 45% (entry 4), the substrates having longer alkyl chain such as **3c** and **3d** were ineffective (entries 5 and 6). It should be noted that ethyl and methyl groups can be critically discriminated, and the former completely prevented the reaction. In the case of aromatic alkynes, the length of the alkyl chain was not significant. For example, both **3e** and **3f** were converted to the corresponding dicyano adducts in respective yields of 36 and 26% (entries 7 and 8). Even though their yields and selectivity are lower, it should be noted that *anti*-adducts were obtained when a phenyl group is introduced to the alkynes. These results show that the cyanation is dependent on both steric and electronic factors and nucleophilic cyanation could occur at an *sp*-carbon connected to a phenyl group. Conjugated enyne (**3g**) was found to be inert, affording no reaction under similar conditions (entry 9).

The above results indicate that the cyanation could occur when the stronger Lewis acidic Pd(II) complex activates the internal alkynes. Such a hypothesis prompted us to continue the survey of the Lewis basic functionalities, and the *N*-sulfonyl group was found to be most effective, as shown in Table 6.

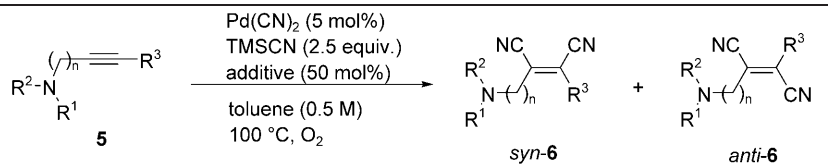
Internal alkyne **5a** is less reactive in the absence of additive (entry 1). The addition of TMSOTf accelerated the reaction to completion within 3 h and the stereoselectivity was assigned by NMR to be *syn*/*anti* = 4:5 (entry 2). Substrate **5b** gave the *syn*-adduct exclusively with a longer reaction time (entry 3) and the *N*-acetyl derivative **5c** resulted in no reaction (entry 4). *N*-Benzyl derivative **5d** required a longer reaction time to afford 60% of **6d** with lower selectivity (entry 5). Aromatic alkyne **5e** was transformed to **6e** within 3 h and the *anti*-adduct was predominantly obtained (entry 6). This is analogous to the above results of **3e** and **3f** in that aromatic alkynes promote both *syn*- and *anti*-dicyanation. As described in entry 7, an

Table 5. Catalytic 1,2-dicyanation of internal alkynes **3**.



Entry	Substrate	Additive	Time [h]	Yield [%]	*syn/anti*
1	**3a**: R^1 = Me, R^2 = *n*-Pen	none	24	**4a**: 0 (NR)	
2	**3a**: R^1 = Me, R^2 = *n*-Pen	TMSOTf	19	**4a**: 67	*syn* only
3	**3a**: R^1 = Me, R^2 = *n*-Pen	TMSOMs	24	**4a**: 0 (NR)	
4	**3b**: R^1 = Me, R^2 = $PivO(CH_2)_2$	TMSOTf	14	**4b**: 45	*syn* only
5	**3c**: R^1 = R^2 = *n*-Bu	TMSOTf	23	**4c**: 0 (NR)	
6	**3d**: R^1 = Et, R^2 = *n*-Pr	TMSOTf	48	**4d**: 0 (NR)	
7	**3e**: R^1 = Me, R^2 = Ph	TMSOTf	21	**4e**: 36	3:1
8	**3f**: R^1 = *n*-Bu, R^2 = Ph	TMSOTf	21	**4f**: 26	2:1
9	**3g**: R^1 = *n*-Bu, R^2 = (*E*)-CHCHPh	TMSOTf	22	**4g**: 0 (NR)	

Table 6. Catalytic 1,2-dicyanation of **5**.



Entry	Substrate	n	R^1	R^2	R^3	Additive	Time [h]	Yield [%]	*syn/anti*
1	**5a**	1	Ts	Ph	Me	none	3	**6a**: <12	
2	**5a**	1	Ts	Ph	Me	TMSOTf	3	**6a**: 80	4:5
3	**5b**	2	Ts	Ph	Me	TMSOTf	21	**6b**: 19	*syn* only
4	**5c**	1	Ac	Ph	Me	TMSOTf	3	**6c**: 0	
5	**5d**	1	Ts	Bn	Me	TMSOTf	20	**6d**: 60	2:1
6	**5e**	1	Ts	Ph	Ph	TMSOTf	3	**6e**: 80	1:4
7	**5f**	1	Ts	Ph	Et	TMSOTf	3	**6f**: 0 (NR)	
8	**5g**	1	Ts	4-$MeOC_6H_4$	Ph	TMSOTf	16	**6g**: 0 (NR)	
9	**5h**	1	Ts	4-$CF_3C_6H_4$	Ph	TMSOTf	3	**6h**: 62	1:8

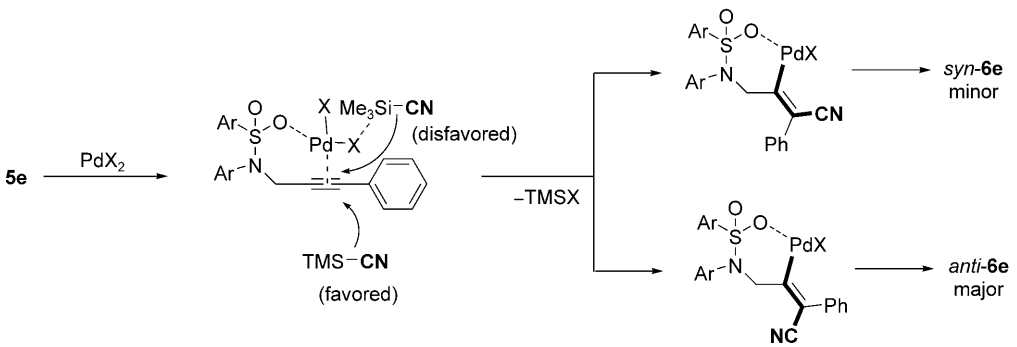
ethyl group exhibited a similar tendency to prevent the reaction.

Next we investigated the electronic effect of R^2 on the stereoselectivity. When a methoxy group was introduced, the Lewis acidity of Pd(II) could be decreased and the reaction was prevented (entry 8). On the other hand, an electron-withdrawing group such as CF_3 promoted the reaction with better *anti*-selectivity (entry 9). The stereochemistry of all the *syn*-adducts was confirmed by NOE observations between allylic methylene and methyl or aromatic protons.

These results suggest that a propargyl *N*-sulfonyl group and a C≡C triple bond act as a bidentate template, as shown in Scheme 3. The steric bulk of R^3 is important to achieve higher *anti*-selectivity (entry 2 *vs.* 6). Because of the steric effect of a phenyl group and X, *anti*- rather than *syn*-attack of TMSCN would proceed predominantly (Scheme 3).

Conclusions

We have demonstrated a palladium-catalyzed 1,2-dicyanation of various alkynes including *syn*- and *anti*-cyanopalladation. The stereoselectivity was found to be dependent on the structure of the substrates. For example, high *syn*-selectivity was achieved when terminal alkynes having a tetrasubstituted carbon at a propargyl position (**2o**–**u**) and aliphatic internal alkynes (**3a, b**) were used. Aromatic internal alkynes were converted to both *syn*- and *anti*-adducts *via* nucleophilic cyanation. Furthermore, the internal alkynes having an *N*-tosylamino group at a propargyl position were transformed to the corresponding dicyano adducts. These observations give us a new perspective on a palladium-catalyzed dicyanation of alkynes, and further applications are currently underway.



Scheme 3. Plausible reaction pathways from **5e**.

Experimental Section

All the analytical and spectral data of **2a**, **2f**, **2k–o**, **2q–u**, **4a,b** and **4e** that have been previously reported[4,11] are excluded in following section.

General Remarks

All reactions were performed with dry solvents and reagents were purified by the usual methods. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm Merck silica gel plates (60F–254). Column chromatography was performed with silica gel (Fuji Silysia, PSQ-60B). IR spectra were recorded on a JASCO FT/IR-230 Fourier transform spectrophotometer. NMR spectra were recorded on JEOL-JMN-Alpha-400 and/or JEOL-JMN-ECP-600 spectrometers, operating at 400 and 600 MHz for ^{1}H NMR and 100 and 150 MHz for ^{13}C NMR with calibration using residual undeuterated solvent as an internal reference. Mass spectra were measured by a JEOL JMS-AX 500 (for LR- and HR-MS) and a JEOL JMS-HX 110 (for HR-MS), respectively.

Typical Procedure for Pd-Catalyzed 1,2-Dicyanation of Terminal Alkynes

To a solution of alkyne (1.0 mmol) in toluene (2.0 mL) were added palladium chloride (3.5 mg, 0.02 mmol, 2 mol%) and TMSCN (0.34 mL, 2.5 mmol) at room temperature. The mixture was stirred for 14–17 h at 100 °C under oxygen. After monitoring the reaction by TLC, the following direct column chromatography (hexane-AcOEt) gave the desired 1,2-dicyano adducts.

2-[4-(Trifluoromethyl)phenyl]maleonitrile (*syn*-2b): mp 127–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45 (s, 1H), 7.80 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 100.1, 113.7, 114.2, 121.8 (J = 203.3 Hz), 126.7 (J = 3.1 Hz), 127.2, 132.1, 133.0, 134.3 (J = 25.3 Hz); IR (ATR): ν = 3050, 2224, 1415, 1320, 1067 cm^{-1}; LR-MS (EI): m/z = 222 (M^+), 203 (M^+−F), 195 (M^+−HCN), 153; HR-MS (EI): m/z = 222.0414, calcd. for $C_{11}H_5F_3N_2$: 222.0405 (M^+).

2-[4-(Trifluoromethyl)phenyl]fumaronitrile (*anti*-2b): mp 46–47 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.28 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.1, 114.0, 115.7, 123.1 (J = 203.6 Hz), 126.5 (J = 3.2 Hz), 128.7, 131.8, 132.9, 134.2 (J = 25.3 Hz); IR (ATR): ν = 3050, 2224, 1415, 1320, 1067 cm^{-1}; LR-MS (EI): m/z = 222 (M^+), 203 (M^+−F), 195 (M^+−HCN), 153; HR-MS (EI): m/z = 222.0404, calcd. for $C_{11}H_5F_3N_2$: 222.0405 (M^+).

2-(4-Methoxyphenyl)maleonitrile (*syn*-2c): mp 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3H), 6.20 (s, 1H), 6.98 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 103.9, 114.3, 115. 2, 122.4, 128.6, 132.6, 133.1, 163.4; IR (ATR): ν = 3074, 2212, 1599, 1507, 1176 cm^{-1}; LR-MS (FAB): m/z = 185 (M^++H), 184 (M^+), 154, 136; HR-MS (FAB): m/z = 185.0718, calcd. for $C_{11}H_8N_2O$ (M^++H): 185.0715.

2-(4-Methoxyphenyl)fumaronitrile (*anti*-2c): mp 48–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 3H), 5.96 (s, 1H), 7.00–7.10 (m, 2H), 7.47–7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 111.7, 114.1, 116.0, 119.2, 121.0, 130.0. 131.1, 133.6, 156.9; IR (ATR): ν = 3036, 2212, 1602, 1510, 1259 cm^{-1}; LR-MS (EI): m/z = 184 (M^+), 169 (M^+−Me), 154, 84; HR-MS (FAB): m/z = 185.0717, calcd. for $C_{11}H_8N_2O$ (M^++H): 185.0715.

2-(2-Methoxyphenyl)maleonitrile (*syn*-2d): mp 130–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.96 (s, 3H), 6.99 (s, 1H), 7.03 (d, J = 8.4 Hz, 1H), 7.07–7.12 (m, 1H), 7.46–7.52 (m, 1H), 7.69 (dd, J = 8.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8, 111.0, 111.9, 114.7, 115.6, 118.5, 121.2, 130.4, 131.2, 133.6, 158.6; IR (ATR): ν = 3115, 2212, 1551, 1259 cm^{-1}; LR-MS (FAB): m/z = 185 (M^++H), 154, 136; HR-MS (FAB): m/z = 185.0716, calcd. for $C_{11}H_8N_2O$ (M^++H): 185.0715.

2-(2-Methoxyphenyl)fumaronitrile (*anti*-2d): mp 95–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 3H), 6.17 (s, 1H), 7.01 (d, J = 8.4 Hz, 1H), 7.04–7.10 (m, 1H), 7.47–7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 111.7,111.8, 114.1, 116.0, 119.2, 121.0, 130.0, 131.1, 133.6, 156.9; IR (ATR): ν = 3052, 2221, 1598, 1488, 1255 cm^{-1}; LR-MS (EI): m/z = 184 (M^+), 156, 135; HR-MS (EI): m/z = 184.0644, calcd. for $C_{11}H_8N_2O$ (M^+): 184.0636.

2-(4-Bromophenyl)maleonitrile (*syn*-2e): mp 185–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.38 (s, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.8,113.8, 114.5, 127.96, 128.00, 128.8, 132.4, 133.0; IR (ATR): ν = 3677, 2220, 1581, 1489, 1323 cm^{-1}; LR-MS (EI): m/z = 232, 234 (M^+), 153(M^+−Br), 126; HR-MS (EI): m/z = 231.9634, calcd. for $C_{10}H_5{}^{79}BrN_2$ (M^+): 231.9636.

2-(4-Bromophenyl)fumaronitrile (*anti*-2e): mp 95–100 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.17 (s, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.9,114.4, 115.8, 127.7, 128.6, 129.5, 131.9, 132.7; IR (ATR): ν = 3031, 2217, 1488, 1255 cm^{-1}; LR-MS (EI): m/z = 232, 234 (M^+), 183, 185, 153(M^+−Br), 126; HR-MS (EI): m/z = 231.9644, calcd. for $C_{10}H_5{}^{79}BrN_2$ (M^+): 231.9636.

2-[3-(Benzyloxy)propyl]maleonitrile (*syn*-2g): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88–1.95 (m, 2H), 2.55 (dt, J = 7.2, 1.6 Hz, 2H), 3.45 (t, J = 5.6 Hz, 2H), 4.49 (s, 2H), 5.77 (t, J = 1.6 Hz, 1H), 7.29–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.2, 32.0. 67.4, 73.0, 112.0, 113.7, 114.7, 127.7, 127.8, 128.4, 135.8, 137.8; IR (ATR): ν = 3060, 2861, 2229, 1717, 1454, 1101 cm^{-1}; LR-MS (EI): m/z = 226 (M^+), 116, 107, 91; HR-MS (FAB): m/z = 227.1171, calcd. for $C_{14}H_{15}N_2O$ (M^++H): 227.1184.

2-[3-(Benzyloxy)propyl]fumaronitrile (*anti*-2g): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94–2.01 (m, 2H), 2.74 (dt, J = 7.6, 1.2 Hz, 2H), 3.54 (t, J = 5.6 Hz, 2H), 4.52 (s, 2H), 5.94 (t, J = 1.2 Hz, 1H), 7.27–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.5, 30.8. 68.1, 73.1, 112.2, 113.3, 116.0, 127.6, 127.7, 128.4, 136.6, 137.8; IR (ATR): ν = 3060, 2862, 2231, 1454, 1100 cm^{-1}; LR-MS (EI): m/z = 226 (M^+), 107, 91; HR-MS (FAB): m/z = 276.0739, calcd. for $C_{14}H_{15}N_2OK$ (M^++K): 265.0743.

2-[3-(*tert*-Butyldiphenylsilyloxy)propyl]maleonitrile (*syn*-2h): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 9H), 1.79–1.89 (m, 2H), 2.55 (t, J = 6.8 Hz, 2H), 3.69 (t, J = 5.6 Hz, 2H), 5.71 (s, 1H), 7.37–7.48 (m, 6H), 7.60–7.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 26.7, 29.7, 31.7, 61.6, 111.8, 113.7, 114.7, 127.7, 129.8, 133.1, 135.4, 136.0; IR

(ATR): ν = 3071, 2931, 2230, 1428, 1108 cm^{-1}; LR-MS (EI): *m/z* = 374 (M^+), 359 (M^+−Me), 317 (M^+−*t*-Bu), 208, 197, 183, 77; HR-MS (FAB): *m/z* = 375.1880, calcd. for $C_{23}H_{27}N_2OSi$ (M^++H): 375.1893.

2-[3-(*tert*-Butyldiphenylsilyloxy)propyl]fumaronitrile (*anti*-2h): mp 59–62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (s, 9H), 1.84–1.92 (m, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 3.72 (t, *J* = 5.6 Hz, 2H), 5.94 (s, 1H), 7.36–7.47 (m, 6H), 7.65–7.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 26.7, 30.2, 30.6, 62.2, 112.1, 113.3, 116.0, 127.1, 129.8, 133.2, 135.5, 136.8; IR (ATR): ν = 3071, 2931, 2231, 1428, 1106 cm^{-1}; LR-MS (EI): *m/z* = 374 (M^+), 317 (M^+−*t*-Bu), 208, 199, 183, 77; HR-MS (EI): *m/z* = 374.1826, calcd. for $C_{23}H_{26}N_2OSi$ (M^+): 374.1814.

2-[3-(*tert*-Butyldimethylsilyloxy)propyl]maleonitrile (*syn*-2i): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 6H), 0.90 (s, 9H), 1.89 (tt, *J* = 7.2, 6.0 Hz, 2H), 2.72 (dt, *J* = 7.2, 1.2 Hz, 2H), 3.70 (t, *J* = 6.0 Hz, 2H), 5.95 (t, *J* = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.5, 18.2, 25.9, 30.4, 30.7. 61.4, 112.0, 113.3, 116.1, 137.2; IR (ATR): ν = 3061, 2232, 1609, 1104 cm^{-1}; LR-MS (FAB): *m/z* = 251 (M^++H), 235 (M^+−Me), 193 (M^+−*t*-Bu), 73; HR-MS (FAB): *m/z* = 251.1566, calcd. for $C_{12}H_{21}N_2OSi$ (M^++H): 251.1580.

2-[2-(*tert*-Butyldimethylsilyloxy)propyl]fumaronitrile (*anti*-2i): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 6H), 0.90 (s, 9H), 1.83 (tt, *J* = 6.8, 5.6 Hz, 2H), 2.55 (dt, *J* = 6.8, 1.6 Hz, 2H), 3.65 (t, *J* = 5.6 Hz, 2H), 5.90 (t, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.4, 18.2, 25.9, 30.0, 32.1. 60.9, 111.7, 113.8, 128.6, 136.4; IR (ATR): ν = 3062, 2858, 2231, 1609, 1110 cm^{-1}; LR-MS (FAB): *m/z* = 251 (M^++H), 235 (M^+−Me), 193 (M^+−*t*-Bu), 73; HR-MS (FAB): *m/z* = 251.1598, calcd. for $C_{12}H_{21}N_2OSi$ (M^++H): 251.1580.

2-[3-(4-Morpholino)-3-oxopropyl]maleonitrile (*syn*-2j): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.65 (t, *J* = 6.8 Hz, 2H), 2.81 (t, *J* = 6.8 Hz, 2H), 3.46 (t, *J* = 4.8 Hz, 2H), 3.61 (t, *J* = 4.8 Hz, 2H), 3.66–3.73 (m, 4H), 6.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5, 29.9, 42.1, 45.6, 66.3, 66.7, 113.0, 113.3, 115.8, 135.6, 167.9; IR (ATR): ν = 2918, 2228, 1645, 1444, 1115 cm^{-1}; LR-MS (EI): *m/z* = 219 (M^+), 133, 127, 86; HRMS (FAB): *m/z* = 220.1076, calcd. for $C_{12}H_{14}N_3O_2$ (M^++H): 220.1086.

2-[3-(4-Morpholino)-3-oxopropyl]fumaronitrile (*anti*-2j): mp 70–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.70 (t, *J* = 6.8 Hz, 2H), 2.95 (t, *J* = 6.8 Hz, 2H), 3.47 (t, *J* = 4.8 Hz, 2H), 3.63 (t, *J* = 4.8 Hz, 2H), 3.66–3.73 (m, 4H), 6.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.8, 30.0, 42.1, 45.6, 66.3, 66.7, 113.5, 114.7, 115.3, 134.7, 168.0; IR (ATR): ν = 2918, 2228, 1645, 1444, 1115 cm^{-1}; LR-MS (EI): *m/z* = 219 (M^+), 127, 86; HR-MS (FAB): *m/z* = 220.1094, calcd. for $C_{12}H_{14}N_3O_2$ (M^++H): 220.1086.

2-(1-Methoxy-1-phenylpropyl)maleonitrile (*syn*-2p): mp 97–100 °C: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.2 Hz, 3H), 2.29 (dq, *J* = 14.6, 7.2 Hz, 1H), 2.38 (dq, *J* = 14.6, 7.2 Hz, 1H), 3.05 (s, 3H), 6.53 (s, 1H), 7.34–7.39 (m, 3H), 7.41–7.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.7, 24.1, 50.6, 82.0, 111.0, 113.5, 114.1, 126.9, 129.0, 129.05, 129.14, 137.3, 140.7; IR (ATR): ν = 3074, 2987, 2231, 1447, 1067 cm^{-1}; LR-MS (EI): *m/z* = 226 (M^+), 196 (M^+−2Me), 165 (M^+−OMe−Me), 149 (M^+−Ph), 105, 77; HR-MS (EI): *m/z* = 226.1105, calcd. for $C_{14}H_{14}N_2O$ (M^+): 226.1106.

2-(1-Methoxy-1-phenylpropyl)fumaronitrile (*anti*-2p): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.2 Hz, 3H), 2.32 (dq, *J* = 14.8, 7.2 Hz, 1H), 2.44 (dq, *J* = 14.8, 7.2 Hz, 1H), 3.13 (s, 3H), 6.07 (s, 1H), 7.35–7.45 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.8, 24.9, 50.3, 83.3, 111.2, 113.5, 115.6, 126.9, 129.1, 129.2, 138.1, 140.4; IR (ATR): ν = 2942, 2234, 1447, 1065 cm^{-1}; LR-MS (EI): *m/z* = 226 (M^+), 197 (M^+−Et), 165 (M^+−OMe−Me), 149 (M^+−Ph), 105; HR-MS (EI): *m/z* = 226.1117, calcd. for $C_{14}H_{14}N_2O$ (M^+): 226.1106 .

2-Butyl-3-phenylmaleonitrile (*syn*-4f): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.6 Hz, 3H), 1.30–1.39 (m, 2H), 1.61–1.70 (m, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 7.27–7.39 (m, 2H), 7.47–7.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 22.0, 29.9, 30.9, 116.2, 116.4, 127.3, 128.6, 129.2, 129.8, 130.4, 130.8; IR (ATR): ν = 2960, 2221, 1445, 1021 cm^{-1}; LR-MS (EI): *m/z* = 210 (M^+), 168, 154, 141; HR-MS (EI): *m/z* = 210.1150, calcd. for $C_{14}H_{14}N_2$ (M^+): 210.1157.

2-Butyl-3-phenylfumaronitrile (*anti*-4f): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.6 Hz, 3H), 1.52–1.61 (m, 2H), 1.71–1.80 (m, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 7.27–7.39 (m, 2H), 7.47–7.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 21.9, 30.0, 35.3, 115.5, 116.4, 127.2, 128.2, 128.6, 129.1, 130.9, 131.3; IR (ATR): ν = 2960, 2872, 2224, 1446 cm^{-1}; LR-MS (EI): *m/z* = 210 (M^+), 168, 154, 141; HR-MS (EI): *m/z* = 210.1154, calcd. for $C_{14}H_{14}N_2$ (M^+): 210.1157.

(*Z*)-*N*-(2,3-Dicyanobut-2-enyl)-4-methyl-*N*-phenylbenzenesulfonamide (*syn*-6a): mp 59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 3H), 2.45 (s, 3H), 4.45 (s, 2H), 7.07–7.10 (m, 2H), 7.25–7.30 (m, 3H), 7.34–7.38 (m, 3H), 7.50 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 17.5, 21.7, 49.3, 115.3, 116.4, 125.1, 127.4, 127.9, 128.9, 129.2, 129.7, 129.9, 134.2, 138.4, 144.8; IR (ATR): ν = 2225, 1596, 1491, 1346, 1161, 1088 cm^{-1}; LR-MS (EI): *m/z* = 351 (M^+), 247, 196, 155, 91; HR-MS (EI): *m/z* = 351.1051, calcd. for $C_{19}H_{17}N_3O_2S$ (M^+): 351.1041.

(*E*)-*N*-(2,3-Dicyanobut-2-enyl)-4-methyl-*N*-phenylbenzenesulfonamide (*anti*-6a): mp 63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3H), 2.45 (s, 3H), 4.57 (s, 2H), 7.08–7.12 (m, 2H), 7.20–7.42 (m, 6H), 7.50–7.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0, 21.5, 52.1, 113.8, 115.0, 125.9, 126.0, 127.8, 128.6, 128.8, 129.3, 129.6, 133.8, 138.3, 144.4; IR (ATR): ν = 2232, 1596, 1488, 1326, 1154, 1088 cm^{-1}; LR-MS (EI): *m/z*: 351 (M^+), 247, 196, 155, 91, 58; HR-MS (EI): *m/z* = 351.1043, calcd. for $C_{19}H_{17}N_3O_2S$ (M^+): 351.1041.

(*Z*)-*N*-(3,4-Dicyanopent-3-enyl)-4-methyl-*N*-phenylbenzenesulfonamide (*syn*-6b): mp 148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 3H), 2.43 (s, 3H), 2.68 (t, *J* = 6.8 Hz, 2H), 3.78 (d, *J* = 6.8 Hz, 2H), 7.01–7.05 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.32–7.36 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.5, 21.7, 31.1, 48.5, 115.7, 116.6, 125.8, 126.1, 127.8, 128.5, 128.7, 129.5, 129.7, 134.2, 139.1, 144.2; IR (ATR): ν = 2927, 2222, 1594, 1341, 1159 cm^{-1}; LR-MS (EI): *m/z* = 365 (M^+), 260, 155, 91; HR-MS (EI): *m/z* = 365.1199, calcd. for $C_{20}H_{19}N_3O_2S$ (M^+): 365.1198.

(*Z*)-*N*-Benzyl-*N*-(2,3-dicyanobut-2-enyl)-4-methylbenzenesulfonamide (*syn*-6d): mp 157–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (s, 3H), 2.48 (s, 3H), 3.97 (s, 2H), 4.45 (s, 2H), 7.25–7.46 (m, 7H), 7.77 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2, 21.6, 44.7, 52.8, 115.2, 115.9, 124.9, 126.4, 127.4, 128.7, 128.8, 129.0, 130.1, 134.2, 135.4, 144.6; IR (ATR): ν = 2926, 2225, 1329, 1158, 1102 cm^{-1}; LR-MS (EI): *m/z* = 365 (M^+), 260, 252, 210, 155,

104, 91; HR-MS (EI): $m/z = 365.1194$, calcd. for $C_{20}H_{19}N_3O_2S$ (M^+): 365.1198.

(*E*)-*N*-Benzyl-*N*-(2,3-dicyanobut-2-enyl)-4-methylbenzenesulfonamide (*anti*-6d): mp 71–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.95$ (s, 3H), 2.48 (s, 3H), 4.11 (s, 2H), 4.49 (s, 2H), 7.29–7.41 (m, 7H), 7.80 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.8$, 21.5, 49.3, 53.9, 113.8, 115.0, 124.7, 127.0, 127.1, 127.6, 128.6, 128.9, 129.0, 130.1, 134.4, 144.5; IR (ATR): $\nu = 3268$, 2918, 2236, 1598, 1329, 1154 cm^{-1}; LR-MS (EI): $m/z = 365$ (M^+), 253, 210, 185, 106, 91; HR-MS (EI): $m/z = 365.1198$, calcd. for $C_{20}H_{19}N_3O_2S$ (M^+): 365.1198.

(*Z*)-*N*-(2,3-Dicyano-3-phenylallyl)-4-methyl-*N*-phenylbenzenesulfonamide (*syn*-6e): mp 97 °C; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 2.39$ (s, 3H), 4.50 (s, 2H), 6.95 (d, $J = 8.0$ Hz, 2H), 7.14–7.20 (m, 4H), 7.25–7.34 (m, 5H), 7.40–7.85 (m, 2H), 7.51–7.55 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 21.6, 49.8, 115.4, 115.6, 125.6, 128.0, 128.4, 128.9, 129.0, 129.1, 129.4, 129.6, 129.7, 131.5, 134.1, 138.6, 144.6; IR (ATR): $\nu = 3060$, 2362, 1593, 1355, 1159 cm^{-1}; LR-MS (EI): $m/z = 413$ (M^+), 363, 258, 167, 111, 91; HR-MS (EI): $m/z =$ 413.1187, calcd. for $C_{24}H_{19}N_3O_2S$ (M^+): 413.1198.

(*E*)-*N*-(2,3-Dicyano-3-phenylallyl)-4-methyl-*N*-phenylbenzenesulfonamide (*anti*-6e): mp 58 °C; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 2.46$ (s, 3H), 4.78 (s, 2H), 7.15–7.55 (m, 14H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 21.4$, 53.5, 114.6, 115.0, 121.2, 122.6, 127.0, 128.1, 128.7, 128.8, 128.9, 129.3, 129.6, 131.8, 133.8, 138.4, 144.4; IR (ATR): $\nu = 3059$, 2361, 1594, 1491, 1354, 1159 cm^{-1}; LR-MS (EI): $m/z = 413$ (M^+), 258, 182, 155, 91; HR-MS (EI): $m/z = 413.1183$, calcd. for $C_{24}H_{19}N_3O_2S$ (M^+): 413.1198.

(*Z*)-*N*-(2,3-Dicyano-3-phenylallyl)-*N*-(4-trifluoromethylphenyl)-4-methylbenzenesulfonamide (*syn*-6h): mp 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H), 4.53 (s, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.21–7.35 (m, 6H), 7.45–7.59 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.6$, 49.3, 115.2 ($J = 39.6$ Hz), 122.1, 124.7, 126.6 ($J = 13.2$ Hz), 127.8, 128.8, 129.0, 129.4, 129.8, 129.9, 130.6, 130.9, 131.3, 131.6, 133.5, 141.9, 144.9; IR (ATR): $\nu = 2922$, 2224, 1323, 1160, 1067 cm^{-1}; LR-MS (EI): $m/z = 481$ (M^+), 326, 315, 155, 91; HR-MS (EI): $m/z = 481.1066$, calcd. for $C_{25}H_{18}F_3N_3O_2S$ (M^+): 481.1072.

(*E*)-*N*-(2,3-Dicyano-3-phenylallyl)-*N*-(4-trifluoromethylphenyl)-4-methylbenzenesulfonamide (*anti*-6h): mp 149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.47$ (s, 3H), 4.78 (s, 2H), 7.26–7.34 (m, 3H), 7.48–7.55 (m, 6H), 7.65–7.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.4$, 53.3, 114.8 ($J =$ 118.8 Hz), 119.4, 122.1, 126.5 ($J = 13.2$ Hz), 127.1, 127.7, 127.8, 128.2, 129.0, 129.2, 129.67, 129.74, 129.8, 129.9, 132.1, 133.4, 142.1, 145.0; IR (ATR): $\nu = 3069$, 2233, 1614, 1322, 1160, 1046 cm^{-1}; LR-MS (EI): $m/z = 481$ (M^+), 315, 298, 250, 155, 91; HR-MS (EI): $m/z = 480.1025$, calcd. for $C_{25}H_{17}F_3N_3O_2S$ ($M^+ - H$): 480.0993.

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