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Atom-Economical Thiocyanation-Amination of Alkynes with *N*-Thiocyanato-Dibenzenesulfonimide

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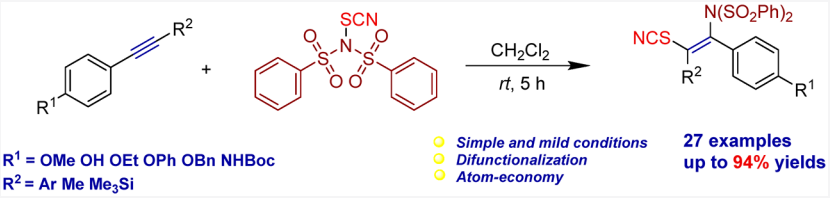
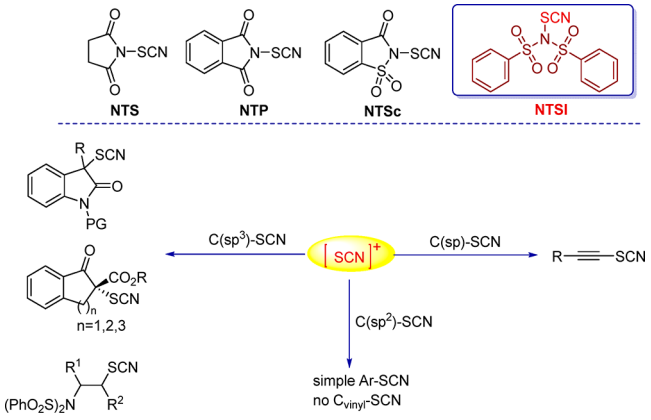


ABSTRACT: A highly regioselective protocol for intermolecular thiocyanation-amination of alkynes by *N*-thiocyano-dibenzenesulfonimide (NTSI) as the SCN and nitrogen sources has been developed. A C−S bond and C−N bond are simultaneously constructed in only one step. The reaction under simple mild conditions features a broad substrate scope, atom economy, high yields (up to 94%), and excellent functional group tolerance.

In recent decades, the method of synthesizing organic thiocyanates has attracted a lot of attention owing to their ubiquitous presence in natural products like alkaloids[1] and huge application in organic synthesis as precursors.[2] Electrophilic thiocyanation has been proven to be an effective and remarkable way to synthesize thiocyanates. Our group have developed some electrophilic thiocyanation reagents[3] with appreciable reactivity which successfully achieved the thiocyanation of ketones, aromatic compounds, and olefins (Scheme 1).[3,4] However, in most of these reactions that have been reported, electrophilic thiocyanation reagents are only used as the source of SCN, while the other part of the reagents is wasted, which is not satisfying to the requirements of atom economy. Although alkenyl thiocyanate has versatile transformation capabilities in synthetic chemistry, the method for constructing a C(sp^2)−SCN bond is still limited comparing with a C(sp^3)−SCN bond. As far as we know, there is only one case of thiocyanation of alkynes,[5] in which the C(sp)−SCN bond is constructed. But the construction of the C(sp^2)−SCN bond has not been achieved by the electrophilic thiocyanation of alkynes. Thus, the electrophilic thiocyanation of alkynes would be an effective complement to the method of constructing alkenyl thiocyanate structures.

Scheme 1. Applications of N-SCN Reagents



At the same time, for the irreplaceable role of amines in medicinal chemistry and agricultural chemistry, regioselective introduction of an amino group is an eternal topic for scholars and engineers,[6] and amination of alkynes is an ideal way to introduce amino groups to organics.[7] Bifunctionalization is a powerful tool to construct various organic compounds, for it can flexibly introduce various functional groups with high atom utilization.[8] Therefore, it will be very fascinating if the bifunctionalization of alkynes can be completed using an electrophilic thiocyanation reagent to simultaneously construct C(sp^2)−SCN and C(sp^2)−N bonds. NTSI reported by us[3c] and the Chen group[4e] recently was chosen to develop the difunctionalization of alkynes because it is an efficient electrophilic thiocyanato reagent reacting with indoles, anilines, and phenols in a high yield. Obviously, control of regioselectivity is still an unignorable challenge, and thiocyanation on benzene rings is also a competitive reaction.

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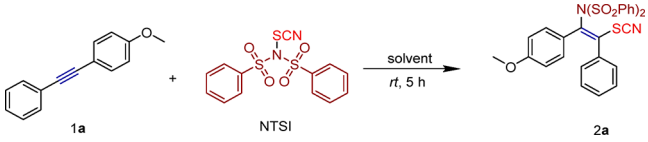
Moreover, the product could be easily converted to 2-aminothiazoles.[9]

As far as we know, the distal end of the triple bond of 1-methoxy-4-(phenylethynyl)benzene has higher electron density,[10] and among the reagents in hand, NTSI has a considerable reactivity, so we embarked upon our investigation of the reaction of 1-methoxy-4-(phenylethynyl)benzene (**1a**) and NTSI. To our delight, the desired difunctional product (**2a**) was facilely obtained in 91% yield at room temperature (Table 1, entry 1). But slightly reduced results were obtained

Table 1. Optimization of the Difunctionalization Reaction Conditions[a]



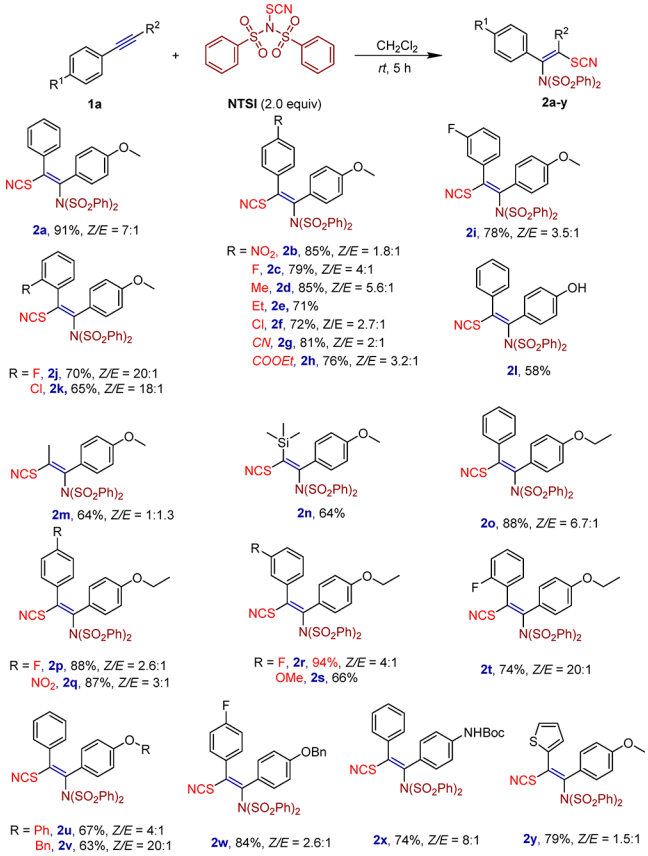
entry	variation from the standard conditions	yield (%)[b]	ratio[c] Z/E
1	none	91	7:1
2	increasing NTSI to 2.5 equiv	78	7:1
3	decreasing NTSI to 1.5 equiv	75	7:1
4	adding $Zn(OTf)_2$ (0.2 equiv)	88	7:1
5	adding $Zn(OTf)_2$ (3 equiv)	85	6:1
6	adding Me_3SiCl (0.2 equiv)	69	7:1
7	adding Me_3SiCl (3 equiv)	32	8:1
8	adding Me_3SiOTf (0.2 equiv)	54	7:1
9	adding Me_3SiOTf (3 equiv)	27	7:1
10	adding TfOH (0.2 equiv)	67	7:1
11	adding TfOH (3 equiv)	25	8:1
12	CH_2ClCH_2Cl instead of CH_2Cl_2	73	6:1
13	THF instead of CH_2Cl_2	23	7:1
14	CH_3CN instead of CH_2Cl_2	44	8:1
15	DMF instead of CH_2Cl_2	trace	
16	DMSO instead of CH_2Cl_2	trace	
17	CH_3OH instead of CH_2Cl_2	trace	
18	0 °C instead of rt	77	8:1

[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **NTSI** (0.2 mmol, 2.0 equiv), solvent (1.0 mL), 5 h, Ar. [b]Isolated yield. [c]Determined by ^1H NMR.

when the loading of NTSI was increased or decreased (Table 1, entries 2 and 3). Considering that the acid (Lewis acid and Bronsted acid) may have an activating effect on the reagent, adding acids (catalytic and excessive amount) was carried out, but giving **2a** in lower yields (Table 1, entries 4−11). Meanwhile, we also screened other solvents such as CH_2ClCH_2Cl, THF, CH_3CN, DMF, DMSO, and CH_3OH (Table 1, entries 12−17), respectively. But we did not get better results. And low temperature resulted in a lower conversion (Table 1, entry 18).

After obtaining the optimal reaction conditions, the applicability of the reaction was tested by enlarging the substrate scope. The reactivity of aryl alkynes is stated in Scheme 2. First, a series of thiocyanation-amination of alkynes with electron-withdrawing or electron-donating substituents at the *para* position of phenol were obtained in good to excellent yields (**2b−k**). *m*-Substituted (**2i**) and *o*-substituted (**2j**, **2k**) alkynes were also got in moderate yields. Moreover, this protocol was proved to be unlimited to diphenylacetylene since substrates like **1m−n** were tested and got an acceptable yield. Encouraged by the above results, we shifted the attention from

Scheme 2. Scope of Substrates[a,b]



[a]Reaction conditions: **1a−x** (0.1 mmol, 1.0 equiv), **NTSI** (0.2 mmol, 2.0 equiv), CH_2Cl_2 (1.0 mL), room temperature, 5 h, Ar. [b]Isolated yield; Z/E ratios were determined by ^1H NMR analysis.

methoxy to hydroxyl (**2l**), ethoxy (**2o−t**), phenoxy (**2u**), benzyloxy (**2v**, **2w**) and NHBoc (**2x**). To our delight, all of them proceeded smoothly with the bifunctionalized products in good to excellent yields, which greatly broadened the application value. Furthermore, a heteroaryl substituent was successfully converted to the corresponding product in 79% yield (**2y**).

Most of products show the good selectivity of configuration from 2:1 to 20:1 according to ^1H NMR. In order to ascertain the dominant configuration of this reaction, the structure of **2v** was confirmed by X-ray crystal structure analysis and proved it to be a *Z*-isomer (Figure 1). It is easy to infer that other

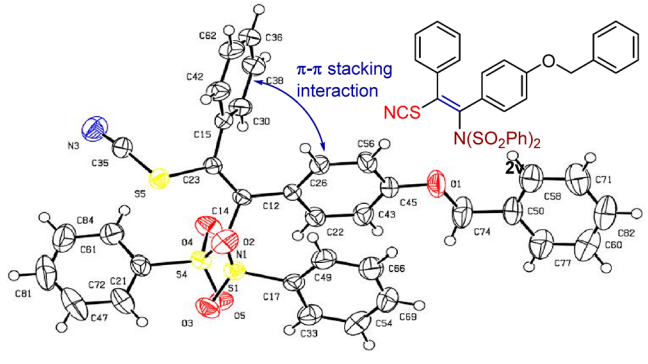


Figure 1. X-ray crystal structure of **2v**.

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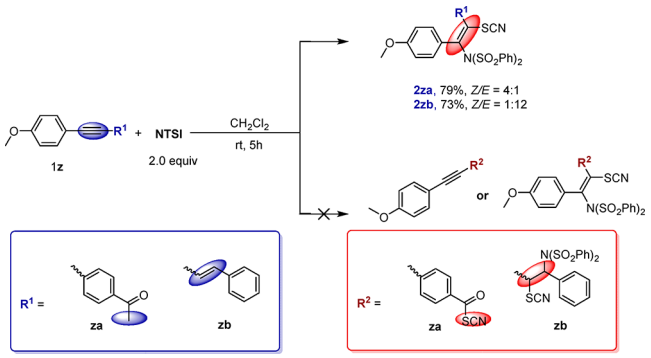
products are also *Z*-selective or a single *Z*-isomer (**2e**, **2l**, **2n**, **2s**) based on the same rule of the chemical shifts of characteristic hydrogen such as the *ortho*-hydrogen of sulfonyl. The X-ray crystallographic study of *E*-**2q**, **2n**, and **2s** was also carried out to further confirm our inference (see Supporting Information). It should be noted that the *o*-substituted alkynes (**2j**, **2k**, **2t**) exhibit significant stereoselectivity (*Z*/*E* = 20:1). Only phenylpropyne (**1m**) shows more preference to the *E*-isomer. On the basis of the crystal structure, the existence of the $\pi-\pi$ stacking interaction between two aromatic rings might greatly enhance *Z*-selectivity while **1n** might be owing to the repulsion between the free radical orbital and C−H σ-bonds of trimethylsilyl.

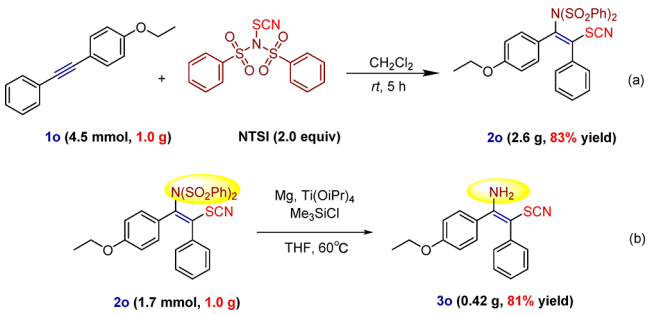
To compare the order of the reactivity of the NTSI reagent toward alkyne, alkene, and α-position of ketone, **1za** bearing alkyne and ketone and **1zb** bearing alkyne and alkene were chosen to react with NTSI. Satisfyingly, only **2z** was obtained in undiminished yield (Scheme 3).

Scheme 3. Function Group Tolerance of NTSI towards Alkyne, Alkene, and Active Protons



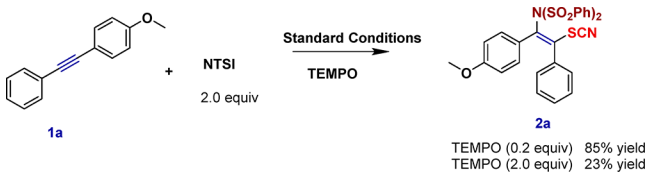
In order to prove the practicality of this reaction, a gram-scale reaction of **1o** was carried out with similar yield and diastereoselectivity (Scheme 4a). Subsequently, the desulfonylation of **1o** was performed, and the amino product (**3o**) was obtained in 81% yield (Scheme 4b), which is an important precursor for the synthesis of thiazole and azirine.[9]

Scheme 4. Gram Scale of Bifunctionalization of Alkyne and Desulfonylation of 2o



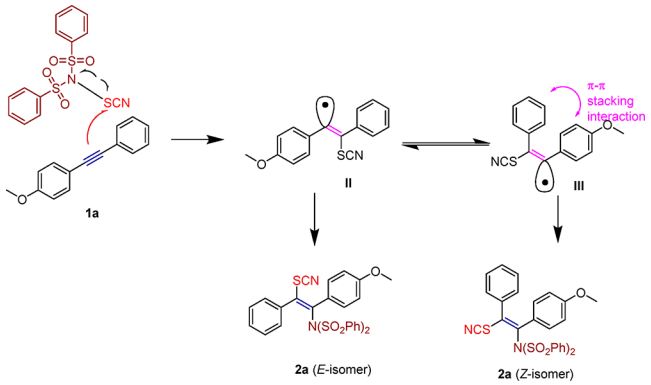
To elucidate the reaction mechanism, the control experiment was carried out (Scheme 5). The transformation was greatly inhibited to 23% yield with 2.0 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), whereas 20 mol % of it gave 85% yield. Further, the trapping experiment was carried out with butylated hydroxytoluene (BHT) under standard reaction conditions, and the free radical adduct ($C_{16}H_{23}NOS$) was detected with HRMS (calcd for $C_{16}H_{24}NOS$ $[M + H]^+$: 278.1573, found: 278.1566). All suggested that this reaction involved a free radical reaction mechanism.

Scheme 5. Control Experiments



On the basis of the above results and other references,[12] the possible Z-selective reaction mechanism is proposed in Scheme 6. The reaction is initiated by alkynes with NTSI to generate ethylenic free radical **II**, and $\pi-\pi$ stacking interaction of the aromatic rings of the substrate facilitates the conversion from **II** to more stable **III**. The intermediates (**II** and **III**) subsequently delivered the desired product with two isomers.

Scheme 6. Proposed Reaction Mechanism



In summary, with simple and mild reaction conditions, we successfully constructed C−S and C−N bonds in one step to generate aminated vinyl thiocyanates by *N*-thiocyanatodibenzenesulfonimide with good yield and great application prospects. As far as we know, this study provides the first example of thiocyanation-amination of alkynes by intermolecular bifunctionalization, which is an important supplement to the limited methods of intermolecular alkyne amination and constructing alkenyl thiocyanate structures.

EXPERIMENTAL SECTION

General Experimental Information. All reactions were carried out under an argon atmosphere, unless otherwise stated. All chemicals were purchased from Acros, Alfa, Aladdin, or InnoChem and used as they come unless otherwise stated. Thin-layer chromatography (TLC) was performed on silica gel F254 TLC glass plates and visualized with UV light. Solvents like petroleum ether (PE) and ethyl acetate (EA) were used directly in column chromatography. THF was dried over sodium (diphenyl ketone) and distilled and stored in Schlenk reservoir; CH_2Cl_2 was distilled over CaH_2 before use. ^1H NMR spectra were recorded on a Bruker Avance400 (400 MHz) spectrometer or Bruker Avance700 (700 MHz) spectrometer, and all signals are reported in ppm with the internal chloroform signal at 7.26 ppm or acetone signal at 2.05 ppm as the standard. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance400 (100 MHz) spectrometer or Bruker Avance700 (175 MHz) spectrometer, and all signals are reported in ppm with the internal chloroform signal at 77.0 ppm or acetone signal at 206.4 and 29.7 ppm as the standard. High resolution mass spectrum (HRMS): AGILENT Q-TOF 6520.

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General Procedure A for Synthesis of 1.[11] The corresponding aryl iodide (1.0 mmol), $Pd(PPh_3)_2Cl_2$ (1−2 mol %), CuI (1 mol %), PPh_3 (1−2 mol %), and phenylacetylene (1.3 equiv) were added to a 250 mL Schlenk flask with a stir bar under Ar. Then THF (80 mL) and Et_3N (80 mL) were added sequentially. The reaction mixture was then stirred at room temperature overnight. Then, 60 mL of water was added and the reaction mixture was extracted with EtOAc (3 × 15 mL), washed with brine, and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using PE and EtOAc as the eluent.

General Procedure B for Synthesis of 2. To a Schlenk tube containing alkynes was added, alkynes (0.1 mmol, 1.0 equiv) was added CH_2Cl_2 (1.0 mL) under an argon atmosphere. Then, NTSI (0.2 mmol, 2.0 equiv) was added. The reaction was stirred at room temperature for 5 h. The reaction mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1, v/v) to afford the pure desired product.

Procedure C for Synthesis of 3o. Under an argon atmosphere, to a mixture of **2o** (1.7 mmol, 1.0 equiv) and Mg powder (17.0 mmol, 10 equiv) in THF (30 mL) were added $Ti(O\text{-}i\text{-}Pr)_4$ (3.4 mmol, 2.0 equiv) and Me_3SiCl (5.1 mmol, 3.0 equiv). The resulting mixture was stirred at 60 °C with a heating mantle. After checking consumption of the substrate by TLC analysis, the mixture was filtered through a pad of Celite. The solvent was removed under reduced pressure by an aspirator; then the reaction mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1, v/v) to afford the pure desired product.

Gram-Scale Reaction. Following the general procedure B, to a glass reaction flask containing **1o** (4.5 mmol, 1.0 equiv) was added CH_2Cl_2 (35 mL) under an argon atmosphere. Then, NTSI (9.0 mmol, 2.0 equiv) was added. The reaction was stirred at room temperature for 5 h. The reaction mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1, v/v) to afford **2o** as a white solid (2.6 g, 83% yield).

*1-Ethoxy-4-((4-fluorophenyl)ethynyl)benzene (**1p**).* **1p** was synthesized following the general procedure A: white solid (202 mg, 84% yield), eluent PE/EtOAc (49:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.46 (m, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.02 (t, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.04 (q, J = 6.8 Hz, 2H), 1.42 (t, J = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.3 (C−F, $^1J_{C-F}$ = 247.4 Hz), 159.1, 133.3 (C−F, $^3J_{C-F}$ = 8.1 Hz), 133.0, 119.8 (C−F, $^4J_{C-F}$ = 3.5 Hz), 115.6 (C−F, $^2J_{C-F}$ = 21.9 Hz), 115.0, 114.6, 89.1, 86.9, 63.5, 14.7 ppm. HRMS (ESI), m/z: calcd for $C_{16}H_{14}FO$ $[M + H]^+$: 241.1023, found: 241.1030.

*1-Ethoxy-4-((4-nitrophenyl)ethynyl)benzene (**1q**).* **1q** was synthesized following the general procedure A: yellow solid (221 mg, 83% yield), eluent PE/EtOAc (49:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.07 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.9, 146.7, 133.4, 132.0, 130.8, 123.6, 114.7, 113.9, 95.3, 86.6, 63.6, 14.7 ppm. HRMS (ESI), m/z: calcd for $C_{16}H_{14}NO_3$ $[M + H]^+$: 268.0968, found: 268.0971.

*1-((4-Ethoxyphenyl)ethynyl)-3-fluorobenzene (**1r**).* **1r** was synthesized following the general procedure A: white solid (199 mg, 83% yield), eluent PE/EtOAc (49:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.8 Hz, 2H), 7.31−7.26 (m, 2H), 7.21−7.18 (m, 1H), 7.03−6.97 (m, 1H), 6.86 (d, J = 8.8 Hz, 2H), 4.05 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5 (C−F, $^1J_{C-F}$ = 244.4 Hz), 159.3, 133.2, 129.8 (C−F, $^3J_{C-F}$ = 8.7 Hz), 127.3 (C−F, $^4J_{C-F}$ = 2.9 Hz), 125.6 (C−F, $^3J_{C-F}$ = 9.5 Hz), 118.2 (C−F, $^2J_{C-F}$ = 22.5 Hz), 115.2 (C−F, $^2J_{C-F}$ = 21.1 Hz), 114.7, 114.6, 90.5, 86.8 (C−F, $^4J_{C-F}$ = 3.2 Hz), 63.6, 14.7 ppm. HRMS (ESI), m/z: calcd for $C_{16}H_{14}FO$ $[M + H]^+$: 241.1023, found: 241.1028.

*1-((4-Ethoxyphenyl)ethynyl)-3-methoxybenzene (**1s**).* **1s** was synthesized following the general procedure A: white solid (199 mg, 79% yield), eluent PE/EtOAc (49:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 9.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.04 (s, 1H), 6.88−6.84 (m, 3H), 4.04 (q, J = 7.2 Hz, 2H), 3.81 (s, J = 7.2 Hz, 3H), 1.42 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.4, 159.1, 133.1, 129.4, 124.7, 124.1, 116.2, 115.1, 114.6,114.6, 89.3, 88.0, 63.5, 55.3, 14.8 ppm. HRMS (ESI), m/z: calcd for $C_{17}H_{17}O_2$ $[M + H]^+$: 253.1223, found: 253.1230.

*1-((4-Ethoxyphenyl)ethynyl)-2-fluorobenzene (**1t**).* **1t** was synthesized following the general procedure A: white solid (204 mg, 85% yield), eluent PE/EtOAc (49:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51−7.46 (m, 3H), 7.30−7.26 (m, 1H), 7.09 (q, J = 8.0 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.05 (q, J = 6.8 Hz, 2H), 1.42 (t, J = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5 (C−F, $^1J_{C-F}$ = 249.4 Hz), 159.3, 133.3, 129.5 (C−F, $^3J_{C-F}$ = 7.9 Hz), 123.9 (C−F, $^4J_{C-F}$ = 3.7 Hz), 115.5 (C−F, $^2J_{C-F}$ = 21 Hz), 114.9, 114.5, 112.3 (C−F, $^2J_{C-F}$ = 15.9 Hz), 94.6 (C−F, $^4J_{C-F}$ = 3.2 Hz), 81.3, 63.6, 14.7 ppm. HRMS (ESI), m/z: calcd for $C_{16}H_{14}FO$ $[M + H]^+$: 241.1023, found: 241.1031.

*1-(Benzyloxy)-4-(phenylethynyl)benzene (**1v**).* **1v** was synthesized following the general procedure A: white solid (253 mg, 89% yield), eluent PE/EtOAc (49:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.6, 1.6 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.43−7.28 (m, 8H), 6.94 (d, J = 8.4 Hz, 2H), 5.08 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.8, 136.7, 133.1, 131.5, 128.6, 128.3, 128.1, 128.0, 127.5, 123.6, 115.7, 115.0, 89.4, 88.2, 70.1 ppm. HRMS (ESI), m/z: calcd for $C_{21}H_{17}O$ $[M + H]^+$: 285.1274, found: 285.1280.

*1-(Benzyloxy)-4-((4-fluorophenyl)ethynyl)benzene (**1w**).* **1w** was synthesized following the general procedure A: white solid (239 mg, 78% yield), eluent PE/EtOAc (49:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.31 (m, 9H), 7.02 (t, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 5.08 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.4 (C−F, $^1J_{C-F}$ = 247.6 Hz), 158.9, 136.6, 133.3 (C−F, $^3J_{C-F}$ = 8.2 Hz), 128.6, 128.1, 127.5, 119.7 (C−F, $^4J_{C-F}$ = 3.5 Hz), 115.6 (C−F, $^2J_{C-F}$ = 21.9 Hz), 115.5, 115.0, 89.0, 87.1, 70.1 ppm. HRMS (ESI), m/z: calcd for $C_{21}H_{16}FO$ $[M + H]^+$: 303.1180, found: 303.1190.

*N-(4-(Phenylethynyl)phenyl)-O-pivaloylhydroxylamine (**1x**).* **1x** was synthesized following the general procedure A: yellow solid (228 mg, 78% yield), eluent PE/EtOAc (20:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52−7.49 (m, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.36−7.30 (m, 5H), 6.52 (s, 1H), 1.52 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.4, 138.5, 132.5, 131.5, 128.3, 128.0, 123.5, 118.1, 117.6, 89.3, 88.6, 80.9, 28.3 ppm. HRMS (ESI), m/z: calcd for $C_{19}H_{20}NO_2$ $[M + H]^+$: 294.1489, found: 294.1497.

*(Z)-N-(1-(4-Methoxyphenyl)-2-phenyl-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2a**).* **2a** was synthesized following the general procedure B: white solid (51 mg, 91% yield, mixture of 7:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 4H), 7.60−7.56 (t, J = 7.6 Hz, 2H), 7.45−7.41 (m, 6H), 7.32−7.31 (m, 3H), 7.08 (d, J = 8.8 Hz, 2H), 6.41 (d, J = 8.8 Hz, 2H), 3.67 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.9, 139.5, 135.5, 135.4, 134.3, 134.1, 133.3, 130.5. 130.0, 129.3, 129.0, 128.8, 127.1, 113.5, 109.4, 55.2 ppm. IR (KBr) 2920, 2848, 2160 (SCN), 1508, 1379, 1259, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{28}H_{22}KN_2O_5S_3$ $[M + K]^+$: 601.0322, found: 601.0316.

*N-(1-(4-Methoxyphenyl)-2-(4-nitrophenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2b**).* **2b** was synthesized following the general procedure B: yellow solid (52 mg, 85% yield, mixture of 1.8:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 7.6 Hz, 4H), 7.63−7.58 (m, 4H), 7.44 (t, J = 7.6 Hz, 4H), 7.07 (d, J = 8.8 Hz, 2H), 6.44 (d, J = 9.2 Hz, 2H), 3.69 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.7, 147.9, 142.1, 139.2, 138.9, 134.4, 133.6, 131.6, 130.9, 129.2, 129.0, 126.1, 124.3, 113.9, 108.8, 55.4 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.63−7.58 (overlap with *Z*, 2H), 7.49 (d, j = 7.6 Hz, 4H), 7.46−7.42 (overlap with *Z*, 2H), 7.20 (t, J = 8.0 Hz, 4H), 6.81 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3, 148.2, 140.3, 139.0, 138.0, 133.7, 133.1, 131.6, 130.1, 128.8, 128.4, 125.9, 123.9, 114.3, 108.5, 55.6 ppm. IR (KBr) 2931, 2843, 2160 (SCN), 1508, 1379, 1346, 1261, 1168, 750

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cm^{-1}. HRMS (ESI), m/z: calcd for $C_{28}H_{21}KN_3O_7S_3$ $[M + K]^+$: 646.0173, found: 646.0167.

*N-(2-(4-Fluorophenyl)-1-(4-methoxyphenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2c**).* **2c** was synthesized following the general procedure B: white solid (46 mg, 79% yield, mixture of 4:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 4H), 7.61−7.57 (overlap with *E*, 2H), 7.49−7.42 (overlap with *E*, 6H), 7.07 (d, J = 8.8 Hz, 2H), 7.01 (t, J = 8.4 Hz, 2H), 6.43 (d, J = 8.8 Hz, 2H), 3.69(s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3 (C−F, $^1J_{C-F}$ = 250.7 Hz), 160.0, 139.4, 135.8, 134.2, 133.3, 133.0, 132.6 (C−F, $^3J_{C-F}$ = 8.6 Hz), 131.4 (C−F, $^4J_{C-F}$ = 3.4 Hz), 129.2, 128.8, 126.9, 116.4 (C−F, $^2J_{C-F}$ = 22 Hz), 113.6, 109.3, 55.3 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.69 (m, 2H), 7.61−7.57 (overlap with *Z*, 2H), 7.49−7.42 (overlap with *Z*, 6H), 7.23 (t, J = 8.0 Hz, 4H), 6.91 (t, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.9, 139.2, 133.5, 133.1, 132.3 (C−F, $^3J_{C-F}$ = 8.6 Hz), 128.3, 116.1 (C−F, $^2J_{C-F}$ = 21.9 Hz), 114.1, 55.5 ppm. IR (KBr) 2922, 2843, 2160 (SCN), 1508, 1379, 1257, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{28}H_{25}FN_3O_5S_3$ $[M + NH_4]^+$: 598.0935, found: 598.0925.

*N-(1-(4-Methoxyphenyl)-2-thiocyanato-2-(m-tolyl)vinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2d**).* **2d** was synthesized following the general procedure B: white solid (49 mg, 85% yield, mixture of 5.6:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 4H), 7.57 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 4H), 7.33 (d, J = 8.0 Hz, 2H), 7.12−7.08 (m, 4H), 6.41 (d, J = 8.8 Hz, 2H), 3.67 (s, 3H), 2.31 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.8, 140.3, 139.5, 134.6, 134.1, 133.2, 132.5, 130.4, 129.8, 129.2, 128.8, 127.4, 113.5, 109.6, 55.2, 21.3 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.62−7.55 (overlap with *Z*, 4H), 7.44−7.41 (overlap with *E*, 6H), 7.17 (t, J = 8.0 Hz, 4H), 7.03 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 2.31 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8, 139.3, 133.1, 132.9, 130.0, 129.7, 128.9, 128.1, 126.8, 114.1, 109.2, 55.5, 21.4 ppm. IR (KBr) 3132, 2922, 2848, 2160 (SCN), 1602, 1508, 1402, 1257, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{29}H_{28}N_3O_5S_3$ $[M + NH_4]^+$: 594.1186, found: 594.1184.

*(Z)-N-(2-(4-Ethylphenyl)-1-(4-methoxyphenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2e**).* **2e** was synthesized following the general procedure B: white solid (41 mg, 71% yield), eluent PE/EtOAc (8:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 4H), 7.58 (t, J = 7.2 Hz, 2H), 7.43 (t, J = 8.0 Hz, 4H), 7.35 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 6.41 (d, J = 8.8 Hz, 2H), 3.68 (s, 3H), 2.62 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.7, 146.4, 139.5, 134.7, 134.6, 134.1, 133.2, 132.6, 130.5, 129.2, 128.8, 128.5, 127.4, 113.4, 109.6, 55.2, 28.7, 14.9 ppm. IR (KBr) 2922, 2850, 2160 (SCN), 1602, 1508, 1379, 1259, 1168, 750 cm^{-1}. HRMS(ESI), m/z: calcd for $C_{30}H_{26}KN_2O_5S_3$ $[M + K]^+$: 629.0635, found: 629.0643.

*N-(2-(2-Chlorophenyl)-1-(4-methoxyphenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2f**).* **2f** was synthesized following the general procedure B: white solid (43 mg, 72% yield, mixture of 2.7:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 4H), 7.58 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 4H), 7.38 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 6.43 (d, J = 8.8 Hz, 2H), 3.69 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1, 139.3, 136.3, 136.0, 134.2, 133.3, 133.0, 132.8, 131.8, 129.4, 129.2, 128.9, 126.8, 113.7, 109.2, 55.3 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H), 7.60−7.56 (overlap with *Z*, 2H), 7.50−7.41 (overlap with *Z*, 6H), 7.23 (t, J = 8.0 Hz, 4H), 7.16 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.0, 139.1, 136.4, 135.4, 133.9, 133.5, 132.4, 132.2, 131.4, 128.8, 128.3, 126.4, 114.1, 108.8, 55.5 ppm. IR (KBr) 2920, 2848, 2158 (SCN), 1602, 1508, 1379, 1257, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{28}H_{21}ClKN_2O_5S_3$ $[M + K]^+$: 634.9933, found: 634.9928.

*N-(2-(4-Cyanophenyl)-1-(4-methoxyphenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2g**).* **2g** was synthesized following the general procedure B: yellow solid (48 mg, 81% yield, mixture of 2:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 4H), 7.62−7.42 (overlap with *E*, 10H), 7.05 (d, J = 8.8 Hz, 2H), 6.44 (d, J = 8.8 Hz, 2H), 3.70 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.6, 139.2, 138.9, 138.4, 134.4, 133.5, 132.8, 131.2, 130.8, 129.2, 128.9, 126.2, 118.0, 114.2, 113.8, 108.8, 55.4 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.62−7.42 (overlap with *Z*, 10H), 7.24 (t, J = 8.4 Hz, 4H), 6.79 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3, 140.2, 138.6, 137.5, 133.8, 133.1, 132.5, 131.2, 130.7, 128.8, 128.4, 125.9, 117.9, 113.7, 113.3, 108.8, 55.5 ppm. IR (KBr) 2924, 2850, 2229, 2160 (SCN), 1602, 1508, 1379, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{29}H_{21}KN_3O_5S_3$ $[M + K]^+$: 626.0275, found: 626.0280.

*Ethyl-4-(2-(4-methoxyphenyl)-2-(N-(phenylsulfonyl)-phenylsulfonamido)-1-thiocyanatovinyl)benzoate (**2h**).* **2h** was synthesized following the general procedure B: white solid (48 mg, 76% yield, mixture of 3.2:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 7.6 Hz, 4H), 7.59 (t, J = 7.6 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.6 Hz, 4H), 7.07 (d, J = 8.8 Hz, 2H), 6.41 (d, J = 8.8 Hz, 2H), 4.36 (q, J = 7.2 Hz, 2H), 3.69 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.7, 160.3, 139.4, 139.1, 137.1, 134.2, 133.4, 132.3, 131.5, 130.5, 130.1, 129.2, 128.9, 126.7, 113.7, 109.0, 61.3, 55.3, 14.3 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.87(d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.61−7.57 (overlap with *Z*, 2H), 7.46−7.40 (overlap with *Z*, 6H), 7.18 (t, J = 7.6 Hz, 4H), 6.79 (d, J = 7.6 Hz, 2H), 4.43 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.6, 161.1, 139.9, 138.3, 136.0, 133.1, 132.8, 131.8, 130.0, 130.0, 128.8, 128.3, 126.3, 114.2, 108.7, 61.2, 55.5, 14.4 ppm. IR (KBr) 2922, 2848, 2160 (SCN), 1716, 1508, 1379, 1259, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{31}H_{26}KN_2O_7S_3$ $[M + K]^+$: 673.0534, found: 673.0536.

*N-(2-(3-Fluorophenyl)-1-(4-methoxyphenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2i**).* **2i** was synthesized following the general procedure B: white solid (45 mg, 78% yield, mixture of 3.5:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 4H), 7.60−7.56 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 4H), 7.34−7.26 (overlap with *E*, 1H), 7.24−7.15 (overlap with *E*, 2H), 7.09 (d, J = 8.8 Hz, 2H), 7.02−6.98 (m, 1H), 6.43 (d, J = 8.8 Hz, 2H), 3.67 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 162.7 (C−F, $^1J_{C-F}$ = 246.9 Hz), 160.2, 139.3, 137.6 (C−F, $^3J_{C-F}$ = 7.9 Hz), 136.8, 134.3, 133.3, 132.4, 130.8 (C−F, $^3J_{C-F}$ = 8.0 Hz), 129.2, 128.9, 126.7, 126.4, 117.4 (C−F, $^2J_{C-F}$ = 22.9 Hz), 117.1 (C−F, $^2J_{C-F}$ = 20.8 Hz), 113.7, 109.1, 55.3 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.56 (overlap with *Z*, 3H), 7.48−7.46 (m, 6H), 7.34−7.26 (overlap with *Z*, 2H), 7.24−7.15 (overlap with *Z*, 4H), 6.91−6.87 (m, 1H), 6.78 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 162.4 (C−F, $^1J_{C-F}$ = 246.6 Hz), 161.0, 139.1, 136.2 (C−F, $^3J_{C-F}$ = 7.9 Hz), 135.7, 133.6, 133.1, 132.0, 130.5 (C−F, $^3J_{C-F}$ = 8.1 Hz), 128.8, 128.3, 125.9, 114.2, 108.7, 55.5 ppm. IR (KBr) 2926, 2850, 2160 (SCN), 1508, 1379, 1259, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{28}H_{25}FN_3O_5S_3$ $[M + NH_4]^+$: 598.0935, found: 598.0925.

*N-(1-(4-Ethoxyphenyl)-2-(2-fluorophenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2j**).* **2j** was synthesized following the general procedure B: white solid (41 mg, 70% yield, mixture of 20:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 4H), 7.60 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 4H), 7.41−7.31 (m, 2H), 7.16 (d, J = 8.8 Hz, 2H), 7.14−7.03 (m, 2H), 6.46 (d, J = 8.8 Hz, 2H), 3.69 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3 (C−F, $^1J_{C-F}$ = 251.5 Hz), 159.7, 139.4, 138.1, 134.2, 132.5, 132.2 (C−F, $^3J_{C-F}$ = 8.3 Hz), 131.9 (C−F, $^4J_{C-F}$ = 1.6 Hz), 129.3, 128.9, 128.4, 127.0, 124.8 (C−F, $^4J_{C-F}$ = 3.6 Hz), 123.5 (C−F, $^2J_{C-F}$ = 13.7 Hz), 116.4 (C−F, $^2J_{C-F}$ = 20.9 Hz), 113.5, 108.9, 55.3 ppm. IR (KBr) 2920, 2838, 2160

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(SCN), 1602, 1508, 1379, 1255, 1168, 752 cm^{-1}. HRMS (ESI), *m/z*: calcd for $C_{28}H_{25}FN_3O_5S_3$ $[M + NH_4]^+$: 598.0935, found: 598.0925.

*N-(2-(2-Chlorophenyl)-1-(4-methoxyphenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2k**).* **2k** was synthesized following the general procedure B: white solid (39 mg, 65% yield, mixture of 18:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.55−7.51 (m, 3H), 7.42−7.35 (m, 4H), 7.30−7.22 (m, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 8.8 Hz, 2H), 3.67 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 139.8, 138.9, 138.1, 134.4, 134.1, 132.2, 132.1, 131.2, 130.4, 129.6, 129.2, 128.9, 128.7, 127.4, 113.5, 108.7, 55.2 ppm. *E*-isomer: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.4, 134.1, 131.9, 126.8 ppm. IR (KBr) 3132, 2922, 2848, 2158 (SCN), 1508, 1398, 1255, 1168, 750 cm^{-1}. HRMS (ESI), *m/z*: calcd for $C_{28}H_{21}ClKN_2O_5S_3$ $[M + K]^+$: 634.9933, found: 634.9937.

*(Z)-N-(1-(4-Hydroxyphenyl)-2-phenyl-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2l**).* **2l** was synthesized following the general procedure B: white solid (31 mg, 58% yield), eluent PE/EtOAc (8:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 4H), 7.59(t, *J* = 7.2 Hz, 2H), 7.44−7.42 (m, 6H), 7.31−7.29 (m, 3H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.32 (d, *J* = 8.8 Hz, 2H), 5.14 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.2, 139.4, 135.5, 135.4, 134.5, 134.2, 133.5, 130.5, 130.0, 129.2, 129.0, 128.9, 127.3, 115.0, 109.4 ppm. IR (KBr) 3392, 3064, 2926, 2160 (SCN), 1510, 1379, 1269, 1168, 750 cm^{-1}. HRMS (ESI), *m/z*: calcd for $C_{27}H_{24}N_3O_5S_3$ $[M + NH_4]^+$: 566.0873, found: 566.0876.

*N-(1-(4-Methoxyphenyl)-2-thiocyanatoprop-1-en-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2m**).* **2m** was synthesized following the general procedure B: white solid (32 mg, 64% yield, mixture of 1:1.3 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 4H), 7.63−7.58 (overlap with *E*, 2H), 7.49−7.42 (overlap with *E*, 4H), 7.36 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.39 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.4, 139.3, 135.0, 134.1, 132.5, 132.3, 129.3, 128.7, 126.5, 113.8, 109.2, 55.3, 22.3 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 4H), 7.63−7.58 (overlap with *Z*, 2H), 7.49−7.42 (overlap with *Z*, 6H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 1.84 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.9, 139.2, 134.8, 134.2, 131.9, 132.4, 128.9, 128.8, 126.4, 114.1, 108.8, 55.3, 21.4 ppm. IR (KBr) 3163, 2920, 2848, 2158 (SCN), 1604, 1508, 1379, 1255, 1168, 750 cm^{-1}. HRMS (ESI), *m/z*: calcd for $C_{23}H_{24}N_3O_5S_3$ $[M + NH_4]^+$: 518.0873, found: 518.0864.

*(Z)-N-(1-(4-Methoxyphenyl)-2-thiocyanato-2-(trimethylsilyl)-vinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2n**).* **2n** was synthesized following the general procedure B: white solid (34 mg, 64% yield), eluent PE/EtOAc (8:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.2 Hz, 4H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 0.12 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8, 148.8, 138.5, 134.1, 133.5, 132.5, 128.5, 128.4, 128.0, 112.8, 110.6, 54.6 ppm. IR (KBr) 2920, 2848, 2150 (SCN), 1604, 1506, 1381, 1257, 1170, 750 cm^{-1}. HRMS (ESI), *m/z*: calcd for $C_{25}H_{30}N_3O_5S_3Si$ $[M + NH_4]^+$: 576.1111, found: 576.1103.

*N-(1-(4-Ethoxyphenyl)-2-phenyl-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2o**).* **2o** was synthesized following the general procedure B: white solid (51 mg, 88% yield, mixture of 6.7:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 4H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.46−7.41 (m, 6H), 7.32−7.28 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.39 (d, *J* = 8.8 Hz, 2H), 3.89 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.3, 139.5, 135.6, 135.5, 134.1, 133.3, 130.5. 129.9, 129.3, 129.0, 128.8, 128.2, 126.9, 113.9, 109.5, 63.4, 14.7 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.75−7.73(m, 2H), 7.60−7.55 (overlap with *Z*, 2H), 7.45−7.41 (overlap with *Z*, 2H), 7.37 (d, *J* = 7.6 Hz, 4H), 7.32−7.28 (overlap with *Z*, 3H), 7.18 (t, *J* = 7.6 Hz, 4H), 6.76 (d, *J* = 8.8 Hz, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 139.1, 133.4, 132.9, 130.2, 130.1, 129.0, 128.9, 126.4, 114.5, 109.1, 63.7, 14.8 ppm. IR (KBr) 3120, 3012, 2160 (SCN), 1508, 1379, 1259, 1168, 750 cm^{-1}. HRMS (ESI), *m/z*: calcd for $C_{29}H_{24}KN_2O_5S_3$ $[M + K]^+$: 615.0479, found: 615.0475.

*N-(1-(4-(Benzyloxy)phenyl)-2-(4-fluorophenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2p**).* **2p** was synthesized following the general procedure B: white solid (54 mg, 88% yield, mixture of 2.6:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 4H,), 7.53 (t, *J* = 7.6 Hz, 2H), 7.47−7.35 (overlap with *E*, 11H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 9.2 Hz, 2H), 3.90 (q, *J* = 6.8 Hz, 2H), 1.36 (t, *J* = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3 (C−F, $^1J_{C-F}$ = 250.6 Hz), 159.1, 139.4, 136.4, 135.8, 134.2, 134.0, 133.3, 132.7, 132.6 (C−F, $^3J_{C-F}$ = 8.6 Hz), 131.4 (C−F, $^4J_{C-F}$ = 3.4 Hz), 129.2, 128.8, 128.2 (C−F, $^4J_{C-F}$ = 2.3 Hz), 127.4, 127.1, 116.4 (C−F, $^2J_{C-F}$ = 22.0 Hz), 114.5, 109.3, 69.8 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.68(m, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.47−7.35 (overlap with *Z*, 11H), 7.18 (t, *J* = 8.0 Hz, 4H), 6.90 (t, *J* = 7.2 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.06 (q, *J* = 6.8 Hz, 2H), 1.46 (t, *J* = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.0, 139.1, 136.5, 134.8, 133.5, 133.0, 132.3 (C−F, $^3J_{C-F}$ = 8.7 Hz), 130.1, 128.8, 128.7, 128.3, 127.5, 126.7, 116.1 (C−F, $^2J_{C-F}$ = 21.8 Hz), 115.0, 70.1 ppm. IR(KBr) 2920, 2842, 2160 (SCN), 1600, 1508, 1379, 1259, 1168, 750 cm^{-1}. HRMS (ESI), *m/z*: calcd for $C_{34}H_{25}KFN_2O_5S_3$ $[M + K]^+$: 695.0541, found: 695.0539.

*N-(1-(4-Ethoxyphenyl)-2-(4-nitrophenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2q**).* **2q** was synthesized following the general procedure B: yellow solid (53 mg, 87% yield, mixture of 3:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 4H), 7.63−7.58 (overlap with *E*, 4H), 7.46−7,42 (overlap with *E*, 4H), 7.05 (d, *J* = 9.2 Hz, 2H), 6.42 (d, *J* = 9.2 Hz, 2H), 3.90 (q, *J* = 6.8 Hz, 2H), 1.35 (t, *J* = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1, 147.9, 142.2, 139.2, 139.0, 134.4, 133.6, 131.6, 130.7, 129.2, 128.9, 126.0, 124.3, 114.4, 108.8, 63.6, 14.6 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.2 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.63−7.58 (overlap with *Z*, 2H), 7.49 (d, *J* = 7.6 Hz, 4H), 7.46−7.42 (overlap with *Z*, 2H), 7.19 (t, *J* = 7.6 Hz, 4H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.07 (q, *J* = 6.8 Hz, 2H), 1.46 (t, *J* = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8, 148.2, 140.3, 139.0, 138.1, 133.7, 133.1, 131.6, 130.1, 128.8, 128.4, 125.7, 123.9, 114.7, 108.4, 63.8, 14.8 ppm. IR(KBr) 2983, 2920, 2850, 2160 (SCN), 1602, 1508, 1379, 1257, 1168, 750 cm^{-1}. HRMS (ESI), *m/z*: calcd for $C_{29}H_{23}KN_3O_7S_3$ $[M + K]^+$: 660.0330, found: 660.0329.

*N-(1-(4-Ethoxyphenyl)-2-(3-fluorophenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2r**).* **2r** was synthesized following the general procedure B: white solid (53 mg, 94% yield, mixture of 4:1 *Z*:*E* isomers), eluent PE/EtOAc (8:1, v/v); *Z*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 4H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.33−7.28 (overlap with *E*, 1H), 7.25−7.21 (overlap with *E*, 1H), 7.17−7.14 (m, 1H), 7.07 (d, *J* = 9.2 Hz, 2H), 7.03−6.98 (m, 1H), 6.41 (d, *J* = 9.2 Hz, 2H), 3.90 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.7 (C−F, $^1J_{C-F}$ = 246.7 Hz), 159.6, 139.4, 137.6 (C−F, $^3J_{C-F}$ = 7.9 Hz), 136.9, 134.2, 133.3, 132.3 (C−F, $^4J_{C-F}$ = 2.4 Hz), 130.7 (C−F, $^3J_{C-F}$ = 8.2 Hz), 129.3, 128.9, 126.5, 126.4 (C−F, $^4J_{C-F}$ = 3.0 Hz), 117.4 (C−F, $^2J_{C-F}$ = 22.9 Hz), 117.0 (C−F, $^2J_{C-F}$ = 21.1 Hz), 114.1, 109.1, 63.5, 14.6 ppm. *E*-isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.57 (overlap with *Z*, 3H), 7.49−7.42 (overlap with *Z*, 6H), 7.33−7.28 (overlap with *Z*, 1H), 7.25−7.21 (overlap with *Z*, 5H), 6.91−6.87 (m, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.4 (C−F, $^1J_{C-F}$ = 246.4 Hz), 160.4, 139.2, 136.2 (C−F, $^3J_{C-F}$ = 8.1 Hz), 135.7, 130.5 (C−F, $^3J_{C-F}$ = 8.4 Hz), 128.8, 128.3, 126.2, 125.9 (C−F, $^4J_{C-F}$ = 2.9 Hz), 117.4, 114.6, 108.7, 63.7, 14.8 ppm. IR (KBr) 3142, 2987, 2922, 2850, 2160 (SCN), 1602, 1508, 1381, 1259, 1168, 750 cm^{-1}. HRMS (ESI), *m/z*: calcd for $C_{29}H_{27}FN_3O_5S_3$ $[M + NH_4]^+$: 612.1091, found: 612.1085.

*(Z)-N-(1-(4-Ethoxyphenyl)-2-(3-methoxyphenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2s**).* **2s** was synthesized following the general procedure B: white solid (40 mg, 66%

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yield), eluent PE/EtOAc (8:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 4H), 7.58 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 4H), 7.21 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 8.8 Hz, 2H), 7.03−7.01 (m, 1H), 6.97−6.96 (m, 1H), 6.85−6.82 (m, 1H), 6.40 (d, J = 8.8 Hz, 2H), 3.89 (q, J = 6.8 Hz, 2H), 3.72 (s, 3H), 1.35 (t, J = 6.8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.8, 159.3, 139.5, 136.7, 135.7, 134.1, 133.9, 133.1, 130.1, 129.3, 128.8, 127.0, 123.0, 116.0, 115.5, 114.0, 109.4, 63.4, 55.4, 14.7 ppm. IR (KBr) 2920, 2848, 2160 (SCN), 1602, 1508, 1379, 1259, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{30}H_{26}KN_2O_6S_3$ $[M + K]^+$: 645.0585, found: 645.0581.

*N-(2-(2-Fluorophenyl)-1-(4-methoxyphenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2t**).* **2t** was synthesized following the general procedure B: white solid (44 mg, 74% yield, mixture of 20:1 Z:E isomers), eluent PE/EtOAc (8:1, v/v); Z-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 4H), 7.59 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 4H), 7.41−7.30 (m, 2H), 7.15 (d, J = 9.2 Hz, 2H), 7.14−7.02 (m, 2H), 6.44 (d, J = 9.2 Hz, 2H), 3.89 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H,) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7 (C−F, $^1J_{C-F}$ = 251.5 Hz), 159.7, 139.4, 138.1, 134.2, 132.5, 132.1 (C−F, $^3J_{C-F}$ = 8.2 Hz), 131.9 (C−F, $^4J_{C-F}$ = 1.3 Hz), 129.3, 128.9, 128.2, 126.7, 124.8 (C−F, $^4J_{C-F}$ = 3.2 Hz), 123.5 (C−F, $^2J_{C-F}$ = 13.8 Hz), 116.5 (C−F, $^2J_{C-F}$ = 21 Hz), 114.0, 108.9, 63.5, 14.6 ppm. IR (KBr) 2920, 2850, 2158 (SCN), 1602, 1508, 1379, 1255, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{29}H_{27}FN_3O_5S_3$ $[M + NH_4]^+$: 612.1091, found: 612.1085.

*N-(1-(4-Phenoxyphenyl)-2-phenyl-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2u**).* **2u** was synthesized following the general procedure B: white solid (42 mg, 67% yield, mixture of 4:1 Z:E isomers), eluent PE/EtOAc (8:1, v/v); Z-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 4H), 7.61 (t, J = 7.6 Hz, 2H), 7.49−7.40 (overlap with E, 7H), 7.36−7.29 (overlap with E, 5H), 7.11 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 7.6 Hz, 2H), 6.48 (d, J = 8.8 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.0, 155.7, 139.5, 135.7, 135.3, 135.0, 134.2, 133.3, 130.5, 130.2, 129.9, 129.3, 129.1, 128.9, 128.3, 124.3, 119.7, 117.3, 109.4 ppm. E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.74 (m, 2H), 7.63−7.59 (overlap with Z, 2H), 7.49−7.40 (overlap with Z, 4H), 7.36−7.29 (overlap with Z, 3H), 7.25−7.12 (m, 5H), 7.15 (d, J = 7.2 Hz, 4H), 7.07 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.2, 155.6, 139.1, 135.0, 134.2, 133.5, 133.5, 133.1, 130.3, 130.1, 130.1, 129.2, 129.0, 128.9, 128.6, 124.5, 120.0, 117.7, 108.8 ppm. IR (KBr) 2922, 2850, 2160 (SCN), 1585, 1504, 1484, 1379, 1274, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{33}H_{28}N_3O_5S_3$ $[M + NH_4]^+$: 642.1186, found: 642.1180.

*N-(1-(4-(Benzyloxy)phenyl)-2-phenyl-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2v**).* **2v** was synthesized following the general procedure B: white solid (40 mg, 63% yield, mixture of 20:1 Z:E isomers), eluent PE/EtOAc (8:1, v/v); Z-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.6 Hz, 4H,), 7.53 (t, J = 7.6 Hz, 2H), 7.45−7.30 (m, 14H), 7.07 (d, J = 8.8 Hz, 2H), 6.47 (d, J = 8.8 Hz, 2H), 4.93 (s, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 139.4, 136.5, 135.4, 134.5, 134.1, 133.3, 132.0, 130.5, 130.0, 129.2, 129.1, 128.8, 128.7, 128.2, 127.4, 127.3, 114.4, 109.4, 69.8 ppm. IR (KBr) 2922, 2850, 2156 (SCN), 1597, 1508, 1458, 1377, 1274, 1166, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{34}H_{26}KN_2O_5S_3$ $[M + K]^+$: 677.0635, found: 677.0626.

*N-(1-(4-(Benzyloxy)phenyl)-2-(4-fluorophenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2w**).* **2w** was synthesized following the general procedure B: white solid (54 mg, 84% yield, mixture of 2.6:1 Z:E isomers), eluent PE/EtOAc (8:1, v/v); Z-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 4H), 7.53 (t, J = 7.6 Hz, 2H), 7.47−7.35 (overlap with E, 11H), 7.05 (d, J = 8.4 Hz, 2H), 7.01 (t, J = 8.4 Hz, 2H), 6.50 (d, J = 9.2 Hz, 2H), 4.95 (s, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.3 (C−F, $^1J_{C-F}$ = 250.6 Hz), 159.1, 139.4, 136.4, 135.8, 134.2, 134.0, 133.3, 132.7, 132.6 (C−F, $^3J_{C-F}$ = 8.6 Hz), 131.4 (C−F, $^4J_{C-F}$ = 3.4 Hz), 129.2, 128.8, 128.2 (C−F, $^4J_{C-F}$ = 2.3 Hz), 127.4, 127.1, 116.4 (C−F, $^2J_{C-F}$ = 22.0 Hz), 114.5, 109.3, 69.8 ppm. E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.68 (m, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.47−7.35 (overlap with Z, 11H), 7.18 (t, J = 8.0 Hz, 4H), 6.90 (t, J = 7.2 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 5.10 (s, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 139.1, 136.5, 134.8, 133.5, 133.0, 132.3 (C−F, $^3J_{C-F}$ = 8.7 Hz), 130.1, 128.8, 128.7, 128.3, 127.5, 126.7, 116.1 (C−F, $^2J_{C-F}$ = 21.8 Hz), 115.0, 70.1 ppm. IR (KBr) 2920, 2842, 2160 (SCN), 1600, 1508, 1379, 1259, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{34}H_{25}KFN_2O_5S_3$ $[M + K]^+$: 695.0541, found: 695.0539.

*N-(2-Phenyl-1-(4-((pivaloyloxy)amino)phenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2x**).* **2x** was synthesized following the general procedure B: white solid (48 mg, 74% yield, mixture of 8:1 Z:E isomers), eluent PE/EtOAc (8:1, v/v); Z-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 4H), 7.58 (t, J = 7.6 Hz, 2H), 7.45−7.41 (m, 6H), 7.31−7.29 (m, 3H), 7.06 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.45 (s, 1H), 1.48 (s, 9H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.2, 139.4, 139.0, 135.3, 135.2, 135.2, 134.2, 132.6, 130.4, 130.1, 129.3, 129.1, 128.9, 128.3, 117.3, 109.3, 81.1, 28.3 ppm. IR (KBr) 2926, 2852, 2160 (SCN), 1730, 1604, 1508, 1379, 1259, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{32}H_{33}N_4O_6S_3$ $[M + NH_4]^+$: 665.1557, found: 665.1556.

*N-(1-(4-Methoxyphenyl)-2-thiocyanato-2-(thiophen-2-yl)vinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2y**).* **2y** was synthesized following the general procedure B: yellow solid (45 mg, 79% yield, mixture of 8:1 Z:E isomers), eluent PE/EtOAc (8:1, v/v); Z-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 4H), 7.59 (t, J = 7.6 Hz, 2H), 7.52−7.40 (overlap with E, 5H), 7.26−7.21 (m, 3H), 6.97−6.95 (m, 1H), 6.50 (d, J = 8.8 Hz, 2H), 3.72 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.3, 139.4, 137.6, 135.5, 134.1, 133.3, 132.1, 130.4, 129.2, 128.9, 127.7, 127.2, 126.1, 114.8, 109.4, 55.3 ppm. E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 4H), 7.63 (t, J = 7.2 Hz, 2H), 7.52−7.40 (overlap with Z, 6H), 7.05−7.03 (m, 1H),6.93 (d, J = 8.8 Hz, 2H), 6.71−6.70 (m, 1H), 6.52−6.47 (m, 1H), 3.84 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.5, 139.4, 138.5, 135.3, 134.4, 132.8, 132.1, 129.4, 129.1, 129.0, 128.2, 127.4, 126.8, 113.7, 109.3, 55.4 ppm. IR (KBr) 2920, 2848, 2160 (SCN), 1602, 1379, 1259, 1168, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{26}H_{20}KN_2O_5S_4$ $[M + K]^+$: 606.9887, found: 606.9882.

*N-(2-(4-Acetylphenyl)-1-(4-methoxyphenyl)-2-thiocyanatovinyl)-N-(phenylsulfonyl)benzenesulfonamide (**2za**).* **2za** was synthesized following the general procedure B: yellow solid (48 mg, 79% yield, mixture of 4:1 Z:E isomers), eluent PE/EtOAc (8:1, v/v); Z-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.6 Hz, 4H), 7.92 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.6 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 8.0 Hz, 4H), 7.10 (d, J = 9.2 Hz, 2H), 6.44 (d, J = 9.2 Hz, 2H), 3.71 (s, 3H), 2.60 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.2, 160.3, 140.1, 139.3, 137.6, 137.3, 134.3, 133.5, 130.8, 130.4, 129.2, 128.9, 128.3, 126.6, 113.7, 109.1, 55.3, 26.7 ppm. E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.79 (m, 4H), 7.63−7.60 (overlap with Z, 2H), 7.49−7.43 (overlap with Z, 6H), 7.19 (t, J = 7.6 Hz, 4H), 6.82 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.60 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.0, 161.1, 139.1, 138.5, 137.8, 136.3, 133.1, 132.6, 131.9, 128.9, 128.7, 126.3, 114.2, 108.7, 55.5, 26.7 ppm. IR (KBr) 2921, 2848, 2158 (SCN), 1685, 1603, 1509, 1379, 1260, 1169, 750 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{30}H_{25}N_2O_6S_3$ $[M + H]^+$: 605.0869, found: 605.0863.

*N-((1E,3E)-1-(4-Methoxyphenyl)-4-phenyl-2-thiocyanatobuta-1,3-dien-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (**2zb**).* **2zb** was synthesized following the general procedure B: yellow solid (43 mg, 73% yield, mixture of 1:12 Z:E isomers), eluent PE/EtOAc (8:1, v/v); E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz, 4H), 7.46 (d, J = 9.2 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.20−7.16 (m, 7H), 7.04 (d, J = 15.6 Hz, 1H), 6.99 (d, J = 6.8 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 15.6 Hz, 1H), 3.77 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1, 139.7, 139.1, 137.9, 135.3, 133.9, 133.2, 129.4, 129.2, 128.8, 128.7, 128.5, 127.7, 127.3, 123.4, 113.9, 109.3, 55.5 ppm. IR (KBr) 2920, 2842, 2157 (SCN), 1653, 1602, 1506, 1379, 1258, 1170, 752 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{30}H_{24}N_2NaO_5S_3$ $[M + Na]^+$: 611.0740, found: 611.0746.

*(Z)-1-(4-Ethoxyphenyl)-2-phenyl-2-thiocyanatoethen-1-amine (**3o**).* **3o** was synthesized following procedure C: white solid (420 mg, 81% yield), eluent PE/EtOAc (4:1, v/v); ^{1}H NMR (700 MHz,

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$(CD_3)_2CO$) δ 7.39 (d, J = 9.1 Hz, 2H), 7.32−7.25 (m, 5H), 6.80 (d, J = 9.1 Hz, 2H), 6.43 (s, 2H), 4.04 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (175 MHz, $(CD_3)_2CO$)) δ 168.8, 158.4, 145.4, 133.6, 130.0, 129.3, 128.6, 128.2, 126.9, 119.0, 113.7, 63.0, 14.2 ppm. IR (KBr) 3433, 3269, 2158 (SCN), 1606, 1531, 1246, 1178, 758 cm^{-1}. HRMS (ESI), m/z: calcd for $C_{17}H_{17}N_2OS$ $[M + H]^+$: 297.1056, found: 297.1047.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02780.

Characterization data, copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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