Stereoselective Synthesis of Alkynyl Vinyl Chalcogenides via Horner–Wittig Reaction

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Abstract: New (diphenylphosphoryl)methyl phenylethynyl sulfides, selenides, or tellurides were prepared by the reaction of (diphenylphosphoryl)methyl *p*-toluenesulfonate with alkynethiols, -selenols, or -tellurols at room temperature. The (diphenylphosphoryl)methyl phenylethynyl sulfides, selenides, or tellurides reacted with aldehydes and cyclic ketones to give the corresponding alkynyl vinyl sulfides, selenides, or tellurides, with preferential *E*-stereochemistry, in a Horner–Wittig-type reaction.

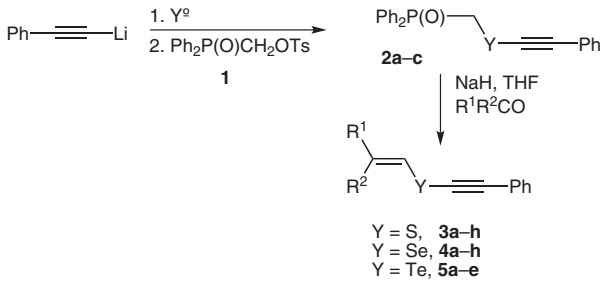
Key words: Wittig reaction, alkynyl vinyl chalcogenides, vinyl chalcogenides, chalcogenium, olefination

Organochalcogenium compounds have become the key component of a variety of versatile and useful reagents for organic synthesis. The multiple applications of organochalcogenium chemistry have been well described in a number of review articles[1] and books.[2] Functionalized alkynyl[3] and alkenyl[4] chalcogenides have a great potential in organic synthesis, since they are valuable intermediates for the selective preparation of several organic compounds. Furthermore, methods for the synthesis of chalcogeno-substituted acetylenes have also been described in recent years,[3,5] although in a reduced number compared to their vinylic counterparts. The most common approach to alkynyl chalcogenides employs the reaction of a metal alkynide with elemental chalcogenium followed by reaction with an alkyl halide or an appropriate electrophilic reagent.[5a]

Among the many applications of vinyl selenides, divinyl selenides, and vinyl sulfides, the cross-coupling reaction with Grignard reagents catalyzed by nickel[6] and palladium[7] to give the corresponding cross-coupled products, has been described. On the other hand, palladium-[4a,8] and nickel-catalyzed[6a,9] cross–coupling reactions and tellurium–metal exchange reactions[10] demonstrate the usefulness of vinyl tellurides.

Except for alkynyl vinyl sulfides, alkynyl vinyl chalcogenides constitute a nearly unexplored class of unsaturated chalcogenides.[11–13] Their preparation include multistep sequences employing aldehydes or 2-chloroethyl thiocyanate[13] and the reaction of lithium acetylides with β-chlorovinyl sulfenamides.[11] The sulfur derivatives, as the corresponding sulfoxides and sulfones, were converted into sulfur, selenium, or nitrogen heterocycles by reaction with sodium sulfide, sodium selenide, or methylamine.[14] Alkynyl vinyl sulfides were also claimed to have pesticide and bactericide activity.[15]

In light of the above comments and from our continuous interest in the development of new vinyl chalcogenides based on Horner–Wittig reaction,[16] we became interested in the development of practical stereoselective synthetic methods for alkynyl vinyl chalcogenides. For instance, we have recently described a detailed study of the synthesis of symmetrical and unsymmetrical divinyl sulfides, selenides, and tellurides from chalcogenyl phosphonates and phosphine oxides, by reaction with arylaldehydes and cyclic ketones.[17] Thus, as a continuation of this study, we planned the preparation of alkynyl vinyl sulfides, selenides, and tellurides by a similar route, starting from (diphenylphosphoryl)methyl phenylethynyl chalcogenides **2a–c**. The alkynylphosphine oxides **2a–c** were prepared in 68–89% isolated yield by the reaction of phenylacetylene with butyllithium at 0 °C, followed by addition of elemental sulfur, selenium, or tellurium to the lithium acetylide and (diphenylphosphoryl)methyl *p*-toluenesulfonate (**1**) (Scheme 1). The compounds **2a–c** can be easily purified by column chromatography and are quite stable compounds. The Horner–Wittig reaction of **2a–c** was subsequently performed, initially by reaction of the sulfur derivative **2a** with benzaldehyde in tetrahydrofuran at 0 °C and using sodium hydride as the base; the corresponding product **3a** was obtained in 70% yield after one hour of reaction (TLC monitoring). Next, a detailed study was performed with aldehydes and ketones and the reaction was showed to be effective also with selenium and tellurium derivatives. The corresponding alkynyl vinyl chalcogenides **3–5** were isolated in good yields (Table 1), the only exception was the reaction of tellurium derivative **2c** with isobutyraldehyde (entry 21).



Scheme 1

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Table 1 Alkynyl Vinyl Chalcogenides Prepared

Entry	R^1	R^2	Y	Compound	Ratio[a] *E*/*Z*	Time (min)	Yield (%)
1	Ph	H	S	**3a**	11:1	60	70
2	4-$MeOC_6H_4$	H	S	**3b**	12:1	80	78
3	4-MeC_6H_4	H	S	**3c**	11:1	70	77
4	4-ClC_6H_4	H	S	**3d**	9:1	60	72
5	*i*-Pr	H	S	**3e**	1:2	40	62
6	Pr	H	S	**3f**	2:1	40	60
7	$(CH_2)_2CH(t\text{-Bu})(CH_2)_2$		S	**3g**	–	80	65[b]
8	Ph	Ph	S	**3h**	–	140	59[b]
9	Ph	H	Se	**4a**	9:1	60	80
10	4-$MeOC_6H_4$	H	Se	**4b**	16:1	80	83
11	4-MeC_6H_4	H	Se	**4c**	12:1	70	81
12	4-ClC_6H_4	H	Se	**4d**	9:1	60	83
13	*i*-Pr	H	Se	**4e**	1:2.5	40	77
14	Pr	H	Se	**4f**	1:2	40	76
15	$(CH_2)_2CH(t\text{-Bu})(CH_2)_2$		Se	**4g**	–	80	70[b]
16	Ph	Ph	Se	**4h**	–	140	64[b]
17	Ph	H	Te	**5a**	9:1	80	58
18	4-$MeOC_6H_4$	H	Te	**5b**	12:1	100	64
19	4-MeC_6H_4	H	Te	**5c**	11:1	90	60
20	4-ClC_6H_4	H	Te	**5d**	9:1	70	60
21	*i*-Pr	H	Te	**5e**	1:2	40	26

[a] Determined by GC and ^{1}H NMR.
[b] HMPA was used as a co-solvent (1 mL/mmol).

Concerning stereochemistry of the reaction, a very high preference for the *E*-isomer could be detected by GC and ^{1}H NMR from the reactions with aromatic aldehydes. This result could be expected from the known behavior of the Horner–Wittig reaction of the diphenylphosphoryl group in stabilized ylides.[18] However, aliphatic aldehydes furnished lower yields with a small preference for the *Z*-isomer, based on the coupling constant values for the vinylic hydrogen.

When the reaction was performed with 4-*tert*-butylcyclohexanone and benzophenone, good yields of the corresponding trisubstituted alkynyl vinyl chalcogenides were obtained with **2a** and **2b** (Table 1, entries 7, 8, 15, and 16). A small amount of hexamethylphosphoramide as a co-solvent and heating to 60 °C was necessary for these reactions. However, similar reactions employing **3c** were unsuccessful.

In summary, we described a highly convenient method for the preparation of alkynyl vinyl chalcogenides through the reaction of (diphenylphosphoryl)methyl phenylethynyl chalcogenides with ketones and aromatic and aliphatic aldehydes by a Horner–Wittig route.

The product ratios were analyzed by gas chromatography using a Shimadzu 14A gas chromatograph, capillary column, equipped with an FID. IR data were collected on a Bruker FT Tensor 27 spectrophotometer. NMR spectroscopy was performed on Bruker 200 MHz and 400 MHz spectrometers, with TMS and $CDCl_3$ as internal standards. Melting points were obtained on a Microquimica MQAPF-301 melting point apparatus. Mass spectrometry was carried out on a Shimadzu QP2010 Plus instrument. Elemental analyses were obtained from Central Analitica, Instituto de Química, Universidade de São Paulo. All new compounds were adequately characterized; detailed data for representative compounds are given below.

(Diphenylphosphoryl)methyl Phenylethynyl Chalcogenides 2a–c; General Procedure

A soln of BuLi (11 mmol) was added to a soln of phenylacetylene (1.12 g, 11 mmol) in THF (15 mL), under an argon atmosphere, at 0 °C. The mixture was stirred at 0 °C for 20 min , then S, Se, or Te

(11 mmol) was added and the mixture was further stirred at r.t. until consumption of the chalcogen. Then, a soln of (diphenylphosphoryl) methyl *p*-toluenesulfonate (**1**, 3.86 g, 10 mmol) in THF (20 mL) was added at 0 °C and the mixture was stirred at r.t. for 2 h (3.5 h for the sulfur derivative). H_2O (50 mL) was added, the mixture was extracted with EtOAc (3 × 50 mL), and the combined organic layers were washed with brine (50 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 7:3).

(Diphenylphosphoryl)methyl Phenylethynyl Sulfide (2a)
Mp 105–107 °C.

IR (KBr): 1183 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.65 (d, J_{P-H} = 8.0 Hz, 2 H), 7.24–7.26 (m, 5 H), 7.49–7.56 (m, 6 H), 7.78–7.88 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.1 (d, J_{P-C} = 66.7 Hz), 78.0 (d, J_{P-C} = 6.1 Hz), 93.2, 122.5, 128.0, 128.3, 128.5 (d, J_{P-C} = 12.2 Hz), 131.1 (d, J_{P-C} = 9.9 Hz), 131.5, 132.2 (d, J_{P-C} = 3.0 Hz).

MS (EI): *m*/*z* (%) = 348 (53, M^+).

Anal. Calcd for $C_{21}H_{17}OPS$: C, 72.40; H, 4.92. Found: C, 71.57; H, 4.97.

(Diphenylphosphoryl)methyl Phenylethynyl Selenide (2b)
Mp 131–132 °C.

IR (KBr): 1188 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.66 (d, J_{P-H} = 6.9 Hz, 2 H), 7.26–7.28 (m, 5 H), 7.44–7.55 (m, 6 H), 7.77–7.88 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.8 (d, J_{P-C} = 67.0 Hz), 69.8 (d, J_{P-C} = 6.3 Hz), 99.6, 122.8, 128.0, 128.3, 128.5 (d, J_{P-C} = 12.0 Hz), 131.0 (d, J_{P-C} = 9.9 Hz), 131.3 (d, J_{P-C} = 103.1 Hz), 131.5, 132.1 (d, J_{P-C} = 2.8 Hz).

MS (EI): *m*/*z* (%) = 396 (20, M^+).

Anal. Calcd for $C_{21}H_{17}OPSe$: C, 63.81; H, 4.33. Found: C, 63.53; H, 4.13.

(Diphenylphosphoryl)methyl Phenylethynyl Telluride (2c)
Mp 139–142 °C.

IR (KBr): 1178 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.76 (d, J_{P-H} = 7.3 Hz, 2 H), 7.25–7.33 (m, 5 H), 7.42–7.52 (m, 6 H), 7.70–7.86 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.87 (d, J_{P-C} = 67.5 Hz), 45.8 (d, J_{P-C} = 6.1 Hz), 112.0, 123.0, 128.1, 128.5, 128.6 (d, J_{P-C} = 11.5 Hz), 130.9 (d, J_{P-C} = 9.9 Hz), 131.8, 132.0 (d, J_{P-C} = 102.7 Hz), 132.1 (d, J_{P-C} = 3.1 Hz).

MS (EI): *m*/*z* (%) = 354 (17).

Anal. Calcd for $C_{21}H_{17}OPTe$: C, 56.82; H, 3.86. Found: C, 57.11; H, 3.67.

Alkynyl Phenylethynyl Chalcogenides 3a–h, 4a–h, and 5a–e; General Procedure
To a soln of (diphenylphosphoryl)methyl phenylethynyl chalcogenide **2** (1 mmol) in THF (10 mL) was added 95% NaH (51 mg, 2 mmol) at 0 °C. After 20 min, the appropriate carbonyl compound (1.5 mmol) was added at 0 °C and the reaction was stirred at r.t. [ketones: at 60 °C and with HMPA (1 mL)] for the time indicated in Table 1. Sat. aq NH_4Cl was added and the mixture was extracted with EtOAc (3 × 20 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes).

Phenylethynyl Styryl Sulfide (3a)
Mp 36–39 °C; ratio *E*/*Z* 11:1.

IR (KBr): 1603, 2166 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.57 (d, *J* = 15.0 Hz, 1 H), 6.86 (d, *J* = 15.0 Hz, 1 H), 7.18–7.36 (m, 8 H), 7.47–7.53 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 74.5, 98.7, 118.6, 122.7, 126.0, 127.6, 128.4, 128.7, 129.6, 131.6, 135.9.

MS (EI): *m*/*z* (%) = 236 (58, M^+).

Anal. Calcd for $C_{16}H_{12}S$: C, 81.31; H, 5.12. Found: C, 81.17; H, 5.03.

4-Methylstyryl Phenylethynyl Sulfide (3c)
Mp 64–66 °C; ratio *E*/*Z* 11:1.

IR (KBr): 1595, 2172 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 6.47 (d, *J* = 15.0 Hz, 1 H), 6.81 (d, *J* = 15.0 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.29–7.31 (m, 3 H), 7.46–7.49 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 74.9, 98.3, 117.4, 122.8, 125.9, 128.3, 128.5, 129.3, 129.8, 131.6, 133.2, 137.5.

MS (EI): *m*/*z* (%) = 250 (68, M^+), 249 (29), 235 (36), 234 (73), 205 (25), 202 (38), 121 (100), 115 (35), 91 (21), 89 (41), 65 (26), 63 (24).

Anal. Calcd for $C_{17}H_{14}S$: C, 81.56; H, 5.64. Found: C, 81.13; H, 5.41.

4-Chlorostyryl Phenylethynyl Sulfide (3d)
Mp 64–67 °C; ratio *E*/*Z* 9:1.

IR (KBr): 1603, 2161 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.53 (d, *J* = 15.0 Hz, 1 H), 6.78 (d, *J* = 15.0 Hz, 1 H), 7.22 (d, *J* = 8.7 Hz, 2 H), 7.26 (d, *J* = 8.7 Hz, 2 H), 7.31–7.34 (m, 3 H), 7.48–7.50 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 74.2, 99.0, 119.6, 122.6, 127.2, 128.1, 128.4, 128.8, 128.8, 131.7, 133.2, 134.5.

MS (EI): *m*/*z* (%) = 270 (37, M^+), 235 (30), 234 (82), 225 (17), 202 (36), 121 (100), 117 (19), 102 (20), 101 (29), 89 (37), 75 (28), 63 (17), 51 (20).

Anal. Calcd for $C_{16}H_{11}ClS$: C, 70.97; H, 4.09. Found: C, 70.71; H, 3.95.

Pent-1-enyl Phenylethynyl Sulfide (3f)
Oil; ratio *E*/*Z* 2:1.

IR (KBr): 1593, 2165 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ (*E* form) = 0.92 (t, *J* = 7.3 Hz, 3 H), 1.44 (sext, *J* = 7.3 Hz, 2 H), 2.13 (dq, *J* = 7.3, 1.2 Hz, 2 H), 5.87 (dt, *J* = 14.7, 1.2 Hz, 1 H), 5.99 (dt, *J* = 14.7, 6.8 Hz, 1 H), 7.28–7.31 (m, 3 H), 7.40–7.47 (m, 2 H); δ (*Z* form) = 0.94 (t, *J* = 7.3 Hz, 3 H), 1.45 (sext, *J* = 7.3 Hz, 2 H), 2.12 (dq, *J* = 7.3, 1.4 Hz, 2 H), 5.75 (dt, *J* = 9.0, 7.3 Hz, 1 H), 6.12 (dt, *J* = 9.0, 1.4 Hz, 1 H), 7.28–7.31 (m, 3 H), 7.40–7.47 (m, 2 H),

^{13}C NMR (100 MHz, $CDCl_3$): δ (*E* + *Z* form) = 13.5, 13.6, 21.9, 22.1, 30.6, 34.7, 76.1, 77.7, 92.9, 96.7, 117.3, 121.8, 123.0, 123.1, 128.2, 128.2, 128.3, 128.3, 131.4, 131.5, 132.7, 132.9.

MS (EI): *m*/*z* (%) = 202 (54, M^+).

Anal. Calcd for $C_{13}H_{14}S$: C, 77.18; H, 6.97. Found: C, 77.98; H, 6.73.

2,2-Diphenylvinyl Phenylethynyl Sulfide (3h)
Mp 51–52 °C.

IR (KBr): 1591, 2171 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.77 (s, 1 H), 7.19–7.45 (m, 15 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 77.8, 93.8, 121.9, 123.8, 127.0, 127.6, 128.1, 128.3, 128.3, 128.3, 128.5, 129.5, 131.5, 137.9, 140.4, 141.9.

MS (EI): *m*/*z* (%) = 312 (57, M^+).

Anal. Calcd for $C_{22}H_{16}S$: C, 84.57; H, 5.16. Found: C, 84.43, H, 5.05.

Phenylethynyl Styryl Selenide (4a)
Mp 55–56 °C; ratio *E*/*Z* 9:1.

IR (KBr): 1600, 2162 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89 (d, *J* = 15.4 Hz, 1 H), 7.01 (d, *J* = 15.4 Hz, 1 H), 7.21–7.35 (m, 8 H), 7.48–7.50 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.8, 103.5, 115.1, 123.0, 126.1, 127.7, 128.3, 128.5, 128.6, 131.6, 133.6, 136.5.

MS (EI): *m*/*z* (%) = 284 (15, M^+), 283 (7), 282 (12), 204 (100), 203 (84), 202 (69), 169 (26), 102 (39), 101 (45), 89 (33), 77 (49), 51 (34).

Anal. Calcd for $C_{16}H_{12}Se$: C, 67.85; H, 4.27. Found: C, 67.61; H, 4.27.

4-Methoxystyryl Phenylethynyl Selenide (4b)
Mp 107–108 °C; ratio *E*/*Z* 16:1.

IR (KBr): 1600, 2162 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3 H), 6.74 (d, *J* = 15.3 Hz, 1 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 6.96 (d, *J* = 15.3 Hz, 1 H), 7.26 (d, *J* = 8.7 Hz, 2 H), 7.30–7.32 (m, 3 H), 7.47–7.49 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 68.3, 102.9, 112.0, 114.1, 123.1, 127.4, 128.3, 128.4, 129.4, 131.6, 133.7, 159.4.

MS (EI): *m*/*z* (%) = 314 (17, M^+).

Anal. Calcd for $C_{17}H_{14}OSe$: C, 65.18; H, 4.50. Found: C, 65.16; H, 4.48.

4-Methylstyryl Phenylethynyl Selenide (4c)
Mp 62–63 °C; ratio *E*/*Z* 12:1.

IR (KBr): 1595, 2152 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 6.83 (d, *J* = 15.3 Hz, 1 H), 6.98 (d, *J* = 15.3 Hz, 1 H), 7.11 (d, *J* = 8.1 Hz, 2 H), 7.22 (d, *J* = 8.1 Hz, 2 H), 7.30–7.32 (m, 3 H), 7.47–7.49 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 68.1, 103.2, 113.7, 123.1, 126.1, 128.3, 128.5, 129.3, 129.3, 131.6, 133.7, 137.7.

MS (EI): *m*/*z* (%) = 298 (14, M^+).

Anal. Calcd for $C_{17}H_{14}Se$: C, 68.69; H, 4.75. Found: C, 68.62; H, 4.70.

4-Chlorostyryl Phenylethynyl Selenide (4d)
Mp 94–96 °C; ratio *E*/*Z* 9:1.

IR (KBr): 1600, 2162 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.88 (d, *J* = 15.3 Hz, 1 H), 6.95 (d, *J* = 15.3 Hz, 1 H), 7.24 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 7.32–7.34 (m, 3 H), 7.48–7.51 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.4, 103.9, 116.0, 122.9, 127.3, 128.4, 128.7, 128.8, 131.7, 132.0, 133.4, 135.0.

MS (EI): *m*/*z* (%) = 318 (9, M^+), 238 (66), 203 (53), 202 (100), 169 (27), 102 (52), 101 (75), 89 (42), 75 (44), 51 (32).

Anal. Calcd for $C_{16}H_{11}ClSe$: C, 60.49; H, 3.49. Found: C, 60.50; H, 3.48.

2,2-Diphenylvinyl Phenylethynyl Selenide (4h)
Mp 80–82 °C.

IR (KBr): 1591, 2156 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.11 (s, 1 H), 7.22–7.34 (m, 6 H), 7.37–7.48 (m, 9 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.6, 99.6, 119.6, 123.1, 127.0, 127.6, 128.3, 128.8, 128.9, 131.6, 139.1, 140.3, 143.9.

MS (EI): *m*/*z* (%) = 360 (2, M^+).

Anal. Calcd for $C_{22}H_{16}Se$: C, 73.54; H, 4.49. Found: C, 73.32; H, 4.40.

4-Methoxystyryl Phenylethynyl Telluride (5b)
Mp 119–121 °C; ratio *E*/*Z* 12:1.

IR (KBr): 1602, 2151 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 7.09 (d, *J* = 16.7 Hz, 1 H), 7.21 (d, *J* = 16.7 Hz, 1 H), 7.30–7.35 (m, 5 H), 7.45–7.50 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 46.0, 55.2, 94.8, 113.7, 113.9, 123.3, 127.5, 128.2, 128.5, 130.7, 131.8, 142.2, 159.5.

MS (EI): *m*/*z* (%) = 364 (8, M^+), 267 (18), 266 (100).

Anal. Calcd for $C_{17}H_{14}OTe$: C, 56.42; H, 3.90. Found: C, 56.09; H, 3.76.

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